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THE CURRENT STATUS OF THE TREATMENT OF CORRODED METAL ARTIFACTS

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Definitions and Limitations

First of all, the title: It would be good, of course, if you could define all of these words for yourselves, so that you would really know what they mean. I will try to short-circuit that, for the sake of saving time--The Current Status of the Treatment of Corroded Metal Artifacts, by which we mean the present-day standing of methods of dealing with artifacts. Those artifacts, of course, are products of human skill--fabrications of particular materials.

We are concerned now with metal materials: lustrous, malleable, electrical conductors. Some of you may be smiling at the thought that your ancient objects satisfy that description! There will be some restrictions on my subject matter, quite obviously, partly because what we are supposed to be having here is a dialogue. Dialogue, as you know, means conversation across or through, from one person to another. And the dialogue is supposed to be among three groups. Museum conservators are one (museums, according to my dictionary, are places, buildings, for the storing and the exhibition of objects). Conservators are people whose skill keeps things together. (Sometimes we do not quite succeed!)

Another terminal in this dialogue is the archaeologist. Are there any archaeologists in the house? ... Did someone put up his hand? Good! We have one archaeologist. The burden upon you is grave. This is very disappointing: we ought to have many archaeologists here. Archaeologists are defined as the scholars of prehistory but, nowadays of course we have to add the historic archaeologists, who are scholars also of written-down history. They study fabrications also in words, whereas the earlier archaeologists study fabrications solely in materials. Maybe the historic archaeologists by comparing the two may discern the truth.

Then we have the corrosion scientists, whom we all learned about yesterday. They know all about the techniques but they may not know the constraints that operate within a museum, so I hope to say a little about that also, because some of the things that we *CAN* do we *MAY NOT* do.

Another restriction upon my talk concerns the age of the artifacts. If they are to be archaeological then they must be of some antiquity and I think in North America that means, say, something over 100 years old. So it is not so very limiting after all, but even at that antiquity the lustrous metal objects are probably no longer very lustrous, not when they are first seen. They are crusted over and often penetrated by alteration products--the corrosion products that have formed upon the metal. Often they are very poor electrical conductors also, which affect some of the things we should like to do with them.

The third constraint upon what I want to say is that while we are all experts here, our expertise is in various and different disciplines. Our hosts from the Bureau are experts in their own right: that is why they are here. And the rest of us, by the late John Gettens's definition, are experts because we are visitors--experts are people from a long way away.

Now just a little more clarification before I get into the technicalities that really interest you. Within the museum also there is a dialogue, or there should be. The dialogue

in the museum starts with the archaeologist or the curator of the archaeological objects or with a curator of some other objects from the collections. He is one terminal in the dialogue. And he should be, I think, responsible for the collection even though he is primarily a historian by definition. It would be lovely if some of those historians were here to find out the real nature of their things. The archaeologist has in the museum to talk to the conservator and also, if there is one, to the scientist who can help him with his analyses. So, similar to ours here, we have another triangle within the museum. Now, I would like to put drawings on the board to illustrate all these concepts and I would like to draw a triangle showing archaeologist-or-curator, conservator, and scientist at all three vertices. But then I wondered, "How should I link them together?" Should the links between them be in compression--a great headache all the time from all their interactions--or should they be in tension--another kind of interaction among the parties. But I think perhaps we ought to draw them just as struts, being mutually supportive. I was hoping that many archaeologists would be here today to discover how they could be supported by conservators and scientists. However, that is not to be.

The Archaeologist's Need

Now the archaeologist or the curator is really the person responsible for our problems: he caused the transfer of the object from the ground, in this case (fig. 1) a bronze mirror lying in the ground at Holcombe in Devon, England; or, he is responsible for transferring things from underwater (fig. 2)--(here is something that Lars Barkmann will tell us more about probably, later in the day); or, he is responsible for transferring something

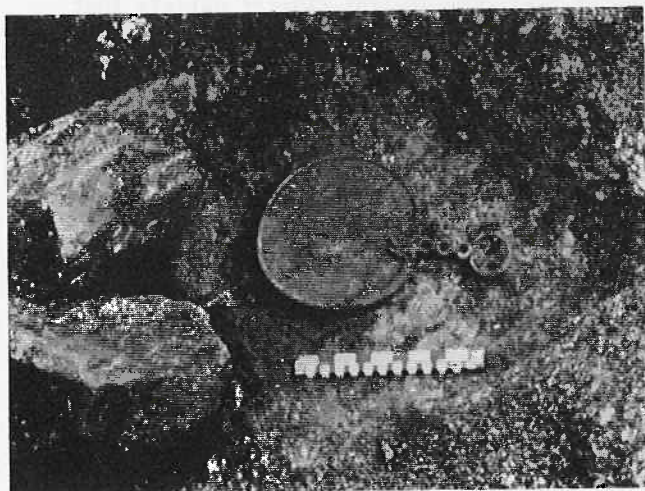


Figure 1. Bronze mirror taken from the ground at Holcombe in Devon, England, dates from the first century A.D.

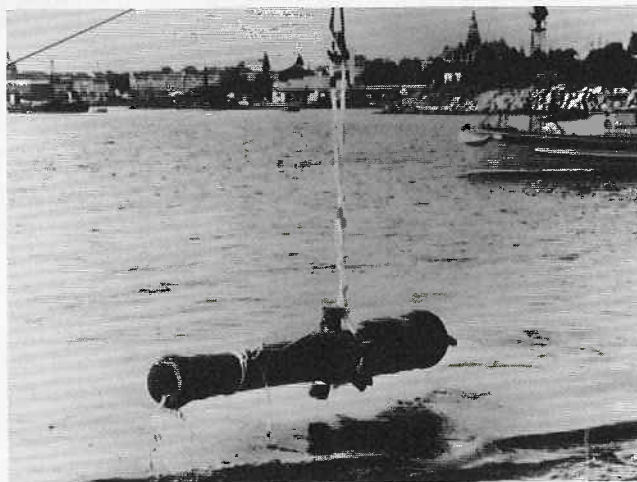


Figure 2. Cannon is transferred from its underwater environment.

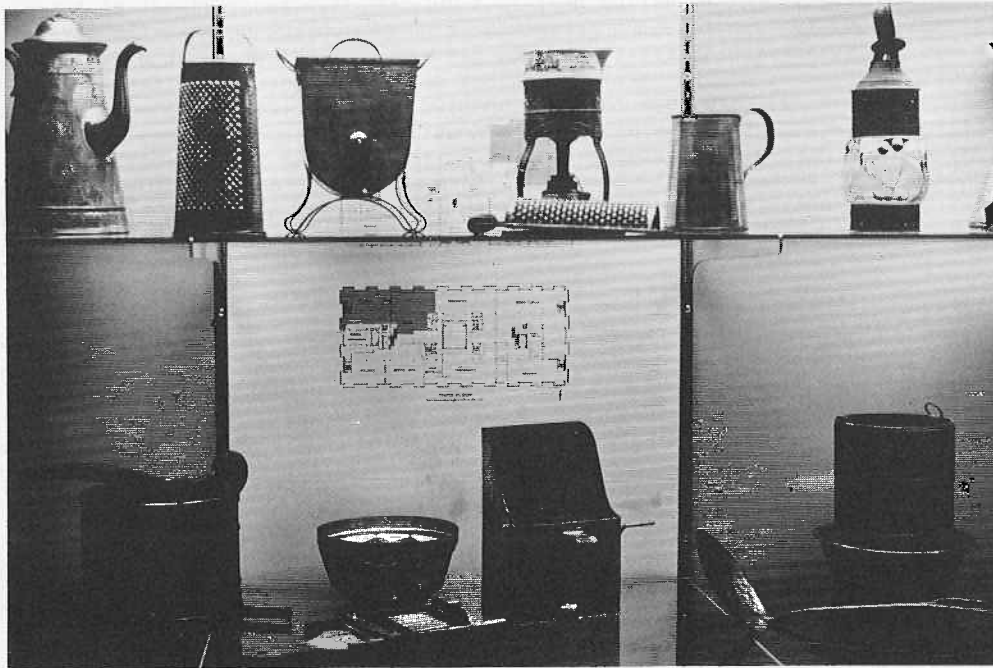


Figure 3. Household utensils displayed.



Figure 4. Chinese bronze from Freer Collection.

from grandmother's attic, or from somebody's sale room. So, he transfers things from one corrosive environment into another one, namely, the museum, or his display cases. Sometimes he wants to display these things in a social context (fig. 3), so that the kind of

appearance they have--you will realise that in a museum, display is almost always visual and appearance is of fundamental importance--the kind of appearance that the curator (and, of course his assistant display-artists) wants differs from object to object, from case to case. Sometimes examples of the very same object may be required in different conditions. Here for example (fig. 3), are some things assembled, partly cleaned but most of them looking soiled, rather as they may have appeared while in use. On the other hand, the curator may wish to have his object regarded as an art-thing in its own right. Here is a Chinese bronze from the Freer Collection (fig. 4) beautiful as an art form, not only because of its form but also because of the corrosion products that have accumulated on its surface and have given it its particular color.

The Conservator's Work for the Archaeologist

Thus the conservator has to be able to take an object, perhaps an excavated one, to free it from soil and then, in that condition perhaps, to stabilise it so that it will not change further at all, realizing that once an object enters the museum it has to be kept indefinitely. Ideally, it should assume some displayable form and then be left in that form, unchanging. So how do we keep a thing which is in an environment that is necessarily corrosive--almost all environments are corrosive to some degree--how do you keep it in that particular form? That is one of the problems that a conservator may face.

On the other hand he may be required to take an object and not only clean it from loose soil but to go further to get it into some specific condition and then, again, to stabilise it so that it stays like that forever. This is not, of course, entirely an object-related technical problem because part of the environment of the object in a museum is people--all sorts and all kinds--with all the associations of people like clothing, dust, dirt and odors and this, that and the other. But I will not talk about this aspect specifically today.

Why then does the curator choose to have an object in a particular condition? Essentially, the curator is intending to study his objects. The older curator studied his objects entirely visually. Here is an Isis (fig. 5) with the child Horus--an ancient



Figure 5. An ancient Egyptian Isis with the child Horus as received in museum.



Figure 6. The same Isis with the child Horus after being cleaned by the conservator.

Egyptian piece shown in the condition as it was received in the museum--just freed from surface dirt. You will notice that somebody--I regret, a curator--has taken a penknife to its leg, just to see what he could find. He has cracked off the corrosion crust. We hope he preserved it in a test tube for scientists to study later!

The function of the conservator may be to clean that object up in order to reveal its shape. He may get it into this condition (fig. 6). When it is "clean" you can see all the decoration, for example, around the eyes. You can also see--a great delight to the curator--this, an inscription on its base. I cannot read the hieroglyphic but I am told that it reads, "Dedicated by Hor, the son of Hor." It is dated from between 600 and 700 B.C. Made of bronze, it is about 7 inches high.

Another reason for conditioning an object then, for keeping it on display or on the storage shelves--is for a more penetrating kind of study--such as the more modern curator indulges in--a scientific one. He may be interested in corrosion products, as we are. Figure 7, shows a flake taken off a piece of bronze furniture from Nimrud, a complete cross-section (not very well polished but sometimes this is not possible in the time available). Under crossed polars the corrosion products present in that quite beautifully layered structure are clearly visible.

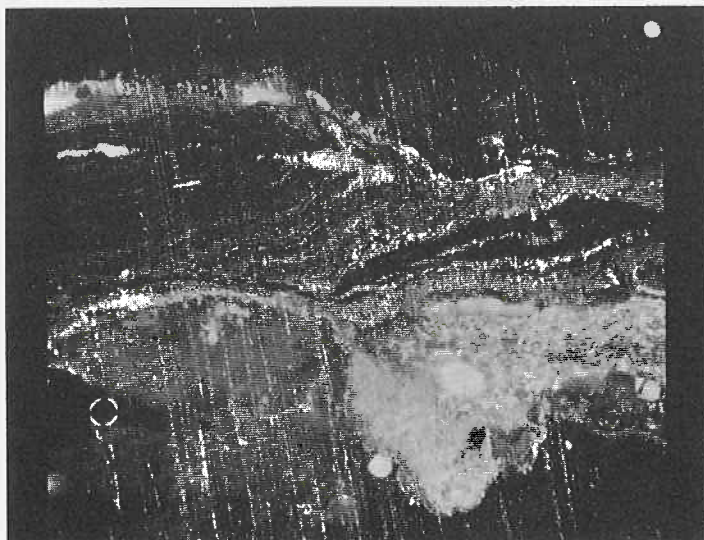


Figure 7. Corrosion products are studied in a flake taken off a piece of bronze furniture from Nimrud. See color plate 1.

Some curator might be interested in that aspect of an object, or he may want to look at figure 8 to consider its macro-structure. This is a bronze, from Igbo in Nigeria [1]¹. It has beautiful rope-work, cast in bronze, on the surface. The archaeologist was particularly interested in finding out how it was made. So we were allowed in this case to cut a little out--very unusual this. Figure 9 shows this cross-section through the rope which is cast in one with part of the body. The left hand side of the section in figure 9 is cast as a second part of the body. Such a micro-structure may be of great interest to students of materials.

Curators may also be interested in analyses of different materials. Figure 10 shows a typical analysis selected from a book [2], of the elements present in iron objects. You will notice in the list of elements sought, items like phosphorus, copper, and chromium, all of which might appear in inhibitors that we might want to apply to our objects while conserving them.

¹ Figures in brackets indicate the literature references at the end of this paper.



Figure 8. Bronze from Igbo in Nigeria.



Figure 9. Cross-section from figure 8: on right-hand side section through the rope which is cast in one with part of the body.

Analysis of Iron Objects of the Dark Age and Early Medieval Period (%)

Ref.	65	65	21	65	11	12
	Axe R.Kennet, Reading	Axe Stratford (Essex)	Piece York	Arrowhead Wood- eaton	Bloom Down- patrick	Bloom Fermanagh
	6th-7th cent.	9th cent.	Saxo- Norman	Med.	13th cent.	Med.
C	0.23	0.049		0.05	0.08	0.05-0.47
Si	n.d.	0.04		tr.	0.16	0.01
Mn	0.01	0.01		tr.	0.02	0.01
S	0.008	0.011		—	0.038	0.014-0.019
P	0.13	0.445	0.17	—	0.061	0.063-0.081
As	0.049	0.042		0.008		
N	0.005	0.0085		—		
Cu	0.01	0.01		0.01		0.01
Ni	0.02	0.07		0.004		0.01
Ca						0.005
Mg		0.005		0.003		
Al		0.04		0.01		0.01
Cr	n.d.	nil		tr.		0.01
Mo	n.d.	nil		nil		0.02
V	tr.	nil		nil		0.02
Ti						—
Slag					7.25	

Figure 10. Analysis of iron objects of the Dark Age and Early Medieval Period (in percent) [2].

Conservation means keeping the object together--at various levels of achievement: keeping it together physically, so that it does not fall to pieces and be broken so that nobody can study it; keeping it together chemically, so that if the curator becomes very interested in its analysis he will have the intact piece, not changed by application of chemicals. Ideally, we should like to keep it, as it is, forever.

Unpermitted Treatments

There are stories of an archaeologist who had analyses made of Roman bronze and found amounts of chromium in it although chromium was not recognized until the 18th century. This happened presumably because a conservator had been treating the object in an electrolytic bath with stainless steel electrodes. Some chromium from the steel had become transferred to the object. This is a story: I do not have any reference to its publication!

Although we do not wish to confuse future scholars, we do want to clean up the object sufficiently to be able to study it. The situation is something of an impasse for the conservator; what does he do? How responsible is he? To help us with these problems we have a code of ethics in the museum [3]. This was written originally for art objects but we like to use it for any kind of object if it is unique, as is an art object. I will not bore you with the entirety of the code but: one, we must have respect for the integrity of the object; two, we have as far as possible to follow the principle of *reversibility*. In other words, what we do now we ought to be able to undo at some distant time in the future, maybe a hundred years hence; maybe a thousand years hence. Reversibility is not always practicable with some of the materials we have to use on objects when we reinforce them. Three, we have to be very careful not to confuse someone. The phrase is, "he (the conservator) can be expected to apply little or much restoration but he cannot ethically carry this to the point of deceptively covering or modifying the original." Four, it is also the duty of a conservator to continue to refresh and enlarge his knowledge and skill (that is why we are here!) and so on. Thus, there is a Code of Ethics which guides us in our activity. Usually we leave the curator to assume ultimate responsibility because it is only he who knows exactly what is the function of his object in his particular collection.

Treatments Available

A conservator therefore needs to have at hand an enormous number of treatments from which to choose one that will satisfy some of these difficult conditions. I propose to go through the various treatments that are available--not all of them, but the more relevant ones--for objects of silver, copper, lead, tin and iron, roughly in that order, which is roughly the order of the electrochemical series.

Silver Objects

Silver is usually alloyed but sometimes it is base-alloyed with so much copper that, while it is still white, it is almost 50/50 copper/silver.



Figure 11. Iphigenia Cup, dates from about 0 B.C.

Figure 11 shows the Iphigenia Cup. It dates from about 0 B.C. Most interesting, it is 2000 years old but clean! You may wonder how it got that way! Our treatment for an object like that would be to keep the air around it pure--keep it free from H₂S so that the silver will not tarnish, because if silver tarnishes it has to be cleaned and that may rub something away. Thus, we are interested in purifying the air, using things like molecular sieves to absorb tarnishing gases. Or we might be interested in putting an inhibitor on the surface of the silver invisibly. Or we might put a lacquer on the surface, also invisible, but it would have to be non-cross-linking so that we could take it off again in the distant future. An ideal treatment for an object like this cup is *benign neglect*! Instead of treating the object, give *great* attention to its environment. The less we do to an object, in general, the better, if it is to be preserved indefinitely.

If the silver had been tarnished, treatments normally used would have been dissolution of the tarnish in one of the Dips (the acid-thiourea mixtures) or possibly electrochemical reduction. One would not really want to rub away an object of so great an age with rouge.

Figure 12 shows another example, a little farther advanced in corrosion. Again silver--although it may not look like it because it was base silver--from Enkomi in Cyprus [4], date, supposedly 14th century B.C., it was crusted over with carbonates. This is a hand-colored slide: we did not always have color photography available!

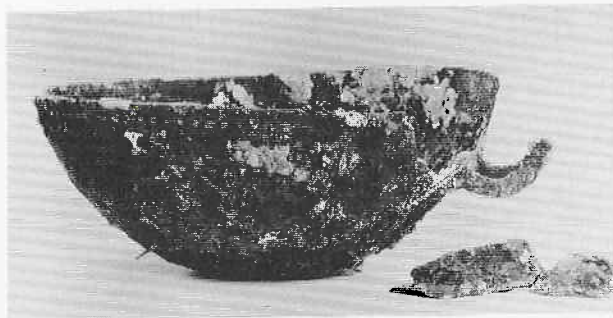


Figure 12. Base silver from Enkomi in Cyprus probably 1400 B.C (see color plate c).



Figure 13. Base silver object in figure 12 after cleaning (see color plate d).

Cleaned, we see (fig. 13) results obtained by the use of dilute formic acid. The crusts on that object developed because the copper in the base alloy diffused out of it and was fixed on the surface as copper carbonates. Thus, the surface of the metal object was left unchanged--we still had the shape of the object and that unchanged shape is now less rich in copper than it was. The surface of the metal is purer in silver--it is whiter than originally. The carbonates could probably have been cracked off very easily and stored if we had wanted to keep samples. The surface made visible by treatment is sometimes called the *epidermis*, in other words the original surface. We shall talk about that later. The process of getting down to it is sometimes called *cleaning*. There is another process called *treatment* which goes below the surface, below the epidermis. These usages of words derive from A. France-Lanord [5].

Figure 14 shows another silver object, from St. Ninians Isle in the Shetlands [6], dating about 800 A.D., crusted over again with copper carbonates, because the metal was base silver. This had been in a different environment--not so old as the Enkomi Cup--only twelve centuries--yet it has corroded so far that great areas have crusted away and vanished. Nowadays, conservators can replace the losses with a synthetic resin, clean up the surface to its original appearance, and present it thus (fig. 15).

In fact, this restored shape is still highly corrodible and if it is left in a damp atmosphere it will turn green. It must therefore now be stored perpetually in an artificially dried environment. There is nothing much else a conservator can do about this because the residual silver is held together only by the wax-like mineral, nantokite, cuprous chloride.

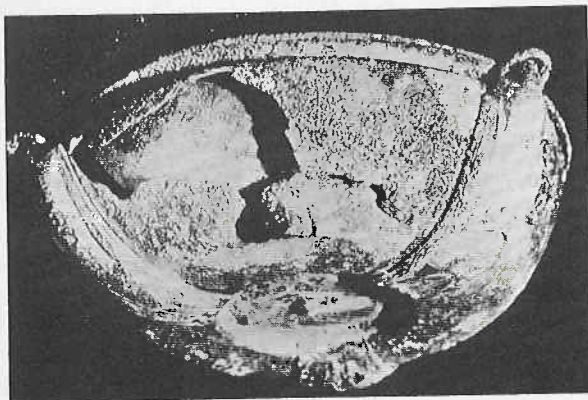


Figure 14. Silver object from St. Ninians Isle in the Shetlands, dating about 800 A.D.

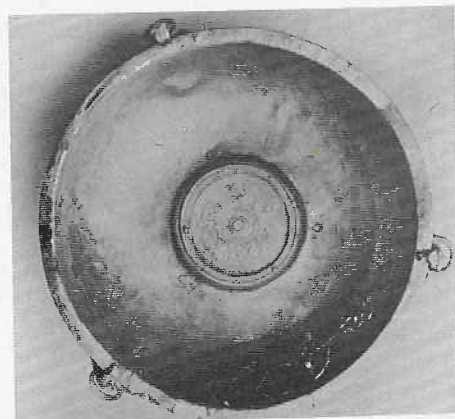


Figure 15. Silver object in figure 14 after conservator has replaced losses and cleaned.

In order to learn what really happens inside such objects, one has to take cross-sections. These are not normally permitted.

Cross-sections of Mineralized Silver

Figure 16 shows another bowl, this one from Ur. Again made of silver, it dates from about 2500 B.C. It is grey in color because it is crusted all over with silver chloride. It has lost an enormous area where corrosion processes have gone all the way through, and there is no metal remaining and no crust even. This sort of situation does enable the conservator to provide material for a cross-section because if he has to replace all of the missing area he may just as well take a little more off: the curator is usually perfectly happy to allow this.

Figure 17 shows a cross-section taken from an edge of one of the losses. You may observe the remaining bright shiny silver. You also see crusts on both sides. The crusts consist of silver chloride. There are one or two things to notice especially about this. First, the epidermis, the original surface, is preserved, although there is a great crust on both the outside and the inside. Also, there is *mineralisation* present: silver chloride has penetrated within the metal--you see the patches of grey. Notice also that we have substantially a mirror image outside, in the crust, of the area inside that has been penetrated by mineralisation. So, if the conservator values this observation made of a cross-section, then he knows that if he sees a great wart on the outside of an object, then it is very likely that just beneath that wart the metal is particularly fragile. But the epidermis is still present! So there is still hope for restoration, for so-called cleaning.

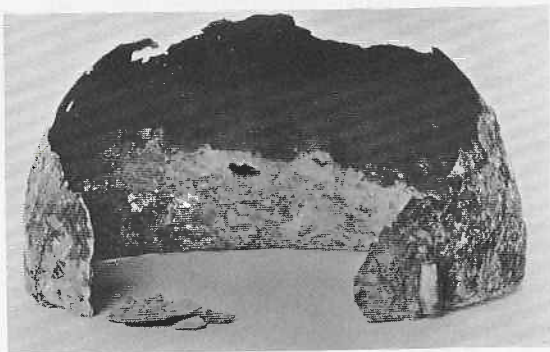


Figure 16. Silver bowl from Ur, dates from about 2500 B.C.

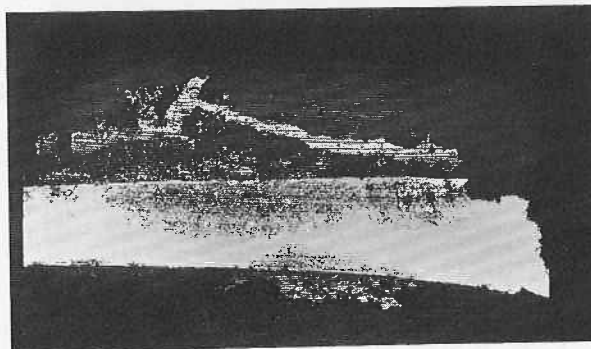


Figure 17. Cross-section taken from an edge of a loss of the bowl in figure 16.

This phenomenon of the mirror-image must happen because some silver has diffused out of the metal to form the crust on the outside. It is interesting that the total volume of the brown crust, the silver chloride, is about twice the volume of the original silver--the mass inside the metal has about the same area as the mass outside the metal. This reflects the fact that the density of silver is 10.5. The density of silver chloride is about half this, 5.5, so we now have the silver redistributed: half of it has stayed inside as silver chloride, half of it has diffused out and become silver chloride. This is an interesting point. Notice also that it has diffused out almost vertically--that is how we form a mirror image.

Now we could as conservators expose that original surface, that epidermis, as shiny silver. You will realise, if we could crack off the crust from the outside and look at the surface revealed, we should then see silver: it would be bright except at places where silver chloride had formed inside.

How can we do this practically? We can dissolve away the outer crust with suitable solvents such as ammonium thiosulphate [7], which I have used in the past because it is available freely in the photo shops, as rapid-photo-fixer, but in Russia they have different systems of supply and there they have used ammonium thiocyanate [8], which they find to react faster than ammonium thiosulphate.

Figure 18 shows a buckle in a corroded condition. It is made of silver and inlaid with gold and niello, Saxon, about 7th century A.D. After careful treatment with ammonium thiosulphate on a glass-bristle brush it comes out as shown in figure 19.



Figure 18. A corroded silver buckle inlaid with gold and niello, Saxon, from 7th Century A.D.



Figure 19. Silver buckle shown in figure 18 after treatment with ammonium thiosulphate in a glass-bristle brush.

Sometimes we wish to expose detail which is finer than is present here, where the decoration is comparatively coarse and it does not matter about using a fine glass bristle brush (which scratches slightly) on the surface. In contrast, Mühlethaler [9] in Zurich had a more difficult situation: he had Roman spoons (fig. 20) from Kaiseraugst, dated to 4th century A.D. He wished to clean them in order to discover detail. He used a Dip--one of the thio-urea/acid mixtures. In order to avoid altering the surface mechanically he used ultrasonics and was able to expose all of the details in a soldered joint (see fig. 21). Here are visible the different metals and structures present where the cup of the spoon was soldered onto the handle.

There is another method of removing silver chloride other than by dissolving it and brushing the solution and debris away. Figure 22 shows a situation where there is a very

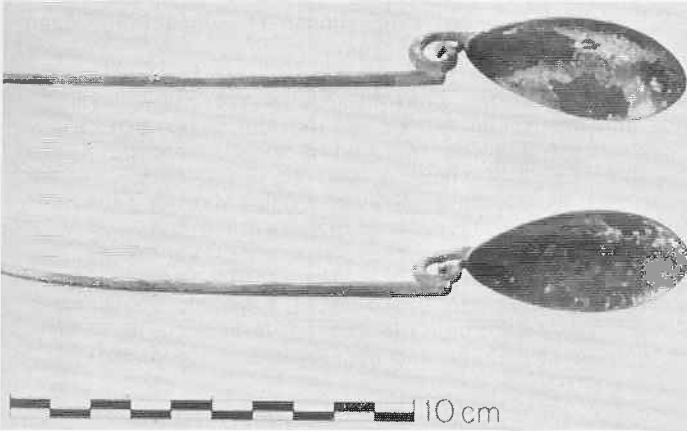


Figure 20. Roman spoons from Kaiseraugst, dated to 4th Century A.D.

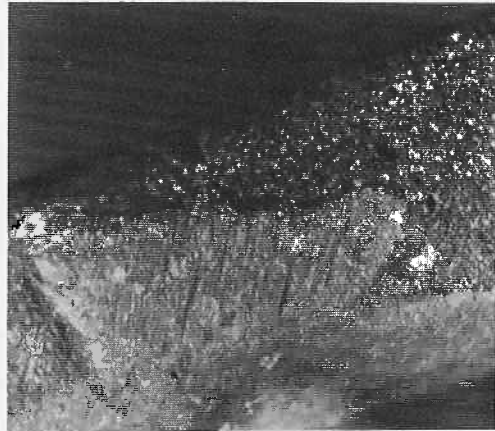


Figure 21. Detail in a soldered joint of Roman spoon in Figure 20 showing the different metals and structures present.

fine silver cage with a blue glass beaker blown inside it [10]. The cage is crusted over with silver chloride. It is Roman, about first century A.D. and the problem is to remove the soil and the silver chloride from the outside without damage to the glass. The problem was solved by using an electrolytic method, making the object the cathode in a solution of formic acid and electrolyzing it at a fairly low current density, about 30 to 50 mA per square decimeter, until the silver chloride on the outside was converted into metallic silver, using a carbon anode, although stainless steel can be used less satisfactorily. Figure 23 shows the result. It was so good that the spin marks caused while making the silver cage can still be seen.

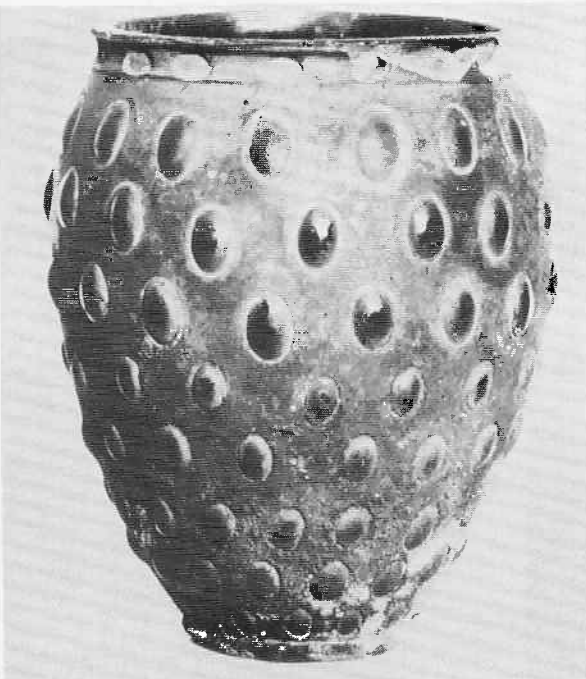


Figure 22. A fine silver cage with a blue glass beaker blown inside it, Roman, about 1st Century A.D.

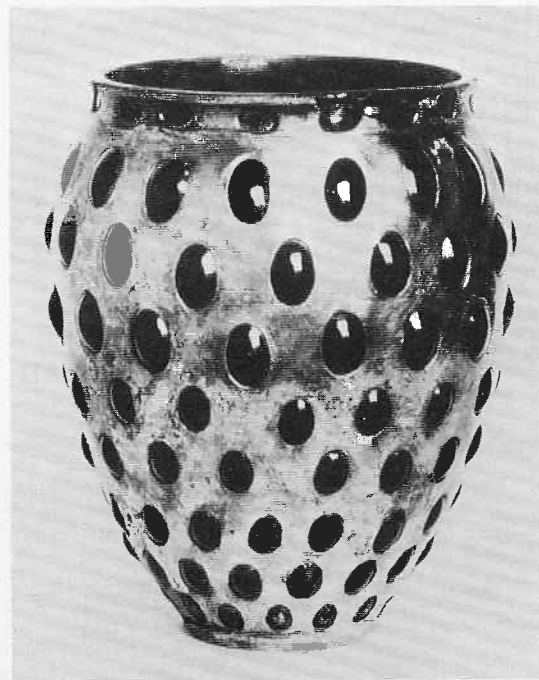


Figure 23. Silver cage shown in figure 22 after treatment by electrolysis.

There was another mark that I cannot see now, still preserved even though the object has been cleaned. It is clearly possible to clean without losing information.

In this example the silver chloride on the outside was converted to silver in a form that could be brushed away. We can also use another technique of making the outer mineral crust into coherent metallic silver using cathodic reduction in caustic soda or sodium carbonate at 30 to 50 mA per square decimeter. Figure 24 shows a bowl to which this method was applied [11]. It is made of silver, from the Royal Graves at Ur, dating from about 2500 B.C. There was only a thin metallic core of silver remaining within the object. At the rim (fig. 25), thickened by the maker's skill, there was no silver at all. So, if we had been incautious we could have lost that information. The result is shown in figure 26. We have been able to convert silver chloride back into metal right up to the edge, where there had been no metal at all, yet the crust outside the epidermis could still be brushed away in order to recover the original shape and appearance. The photograph shows the stage before final re-shaping.

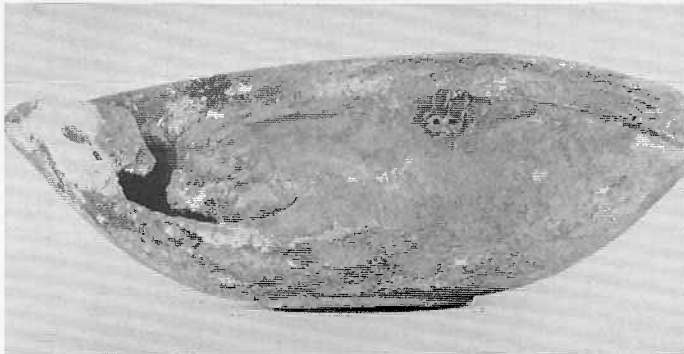


Figure 24. Silver bowl from the Royal Graves at Ur, from about 2500 B.C. before restoration.

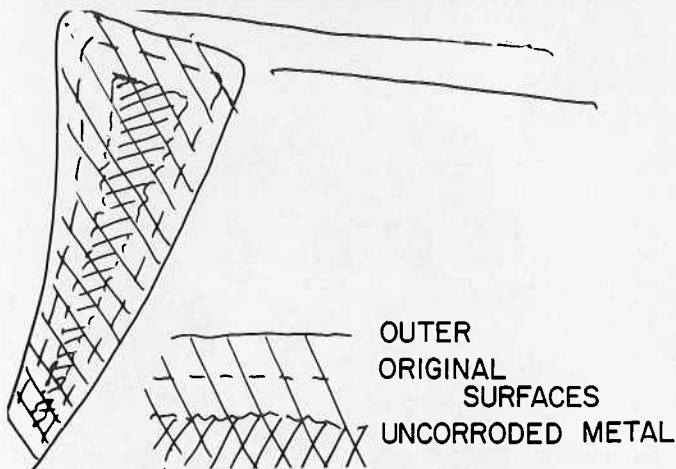


Figure 25. Diagram of the rim of the bowl shown in figure 24, where there was no silver.

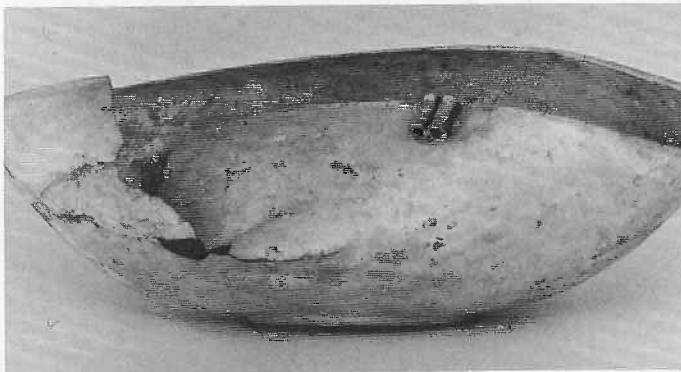


Figure 26. Bowl in figure 24 showing the silver chloride replaced by metallic silver up to the rim of the bowl, using the cathodic reduction technique, using fully rectified current.

The structure of silver which has been recovered electrolytically is of some interest. Figure 27 shows a cross-section of another piece of silver after regeneration. The object was recovered from the same dig at Ur. The recovered silver is porous. This reflects some of the things we were told yesterday about the changes that can be made to corrosion products.

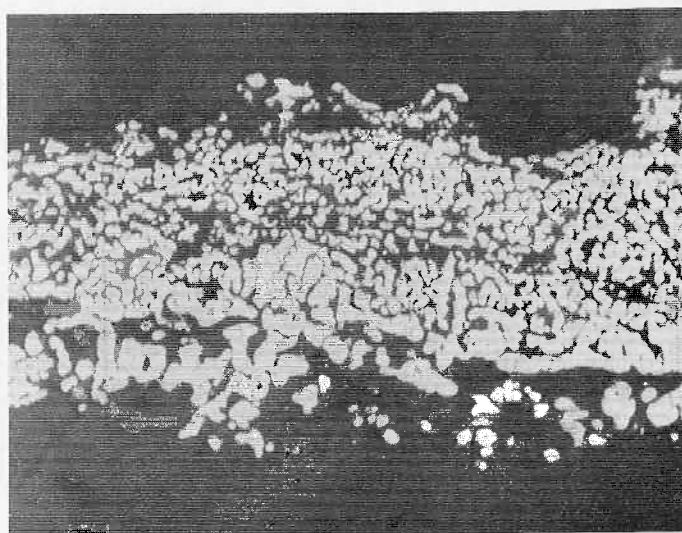


Figure 27. A cross-section of a silver object recovered from the Royal Graves at Ur, (about 2500 B.C.) after regeneration. Note the silver is porous.

A further stage of treatment in handling silver chloride arises in the situation where there is no metal left at all. Then, one can make a coherent and polishable silver by a cathodic reduction technique in weak sodium hydroxide at a low current density (15 mA per square decimeter) but in partially rectified current.

One object to which this had been applied [12] was the lyre from Ur (fig. 28), of the same date as the bowl. The photograph shows its state as found in the museum, only rein-



Figure 28. Silver lyre from the Royal Graves at Ur (about 2500 B.C.) before treatment by the cathodic reduction technique.

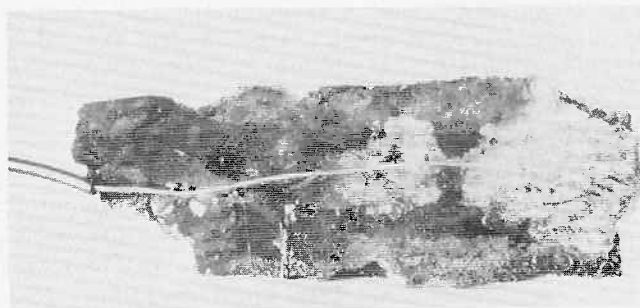


Figure 29. Metallic silver is replacing the silver chloride on this sample by the electrolysis process.

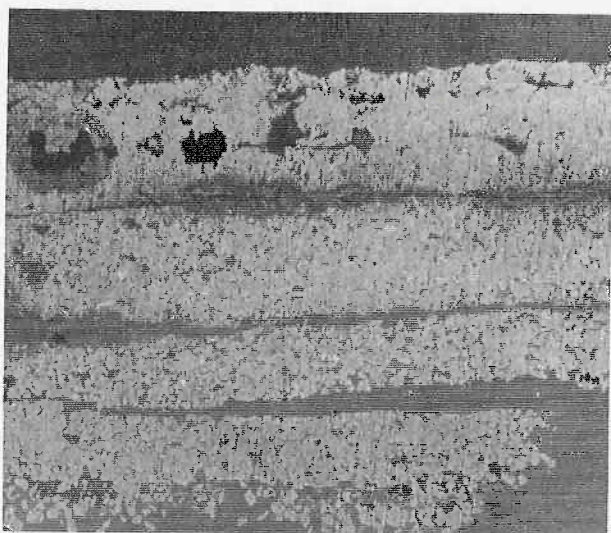


Figure 30. A cross-section of silver metal regenerated by the electrolysis process using partially rectified current. Note the difference in size of the pores compared with the size of the pores in figure 27.

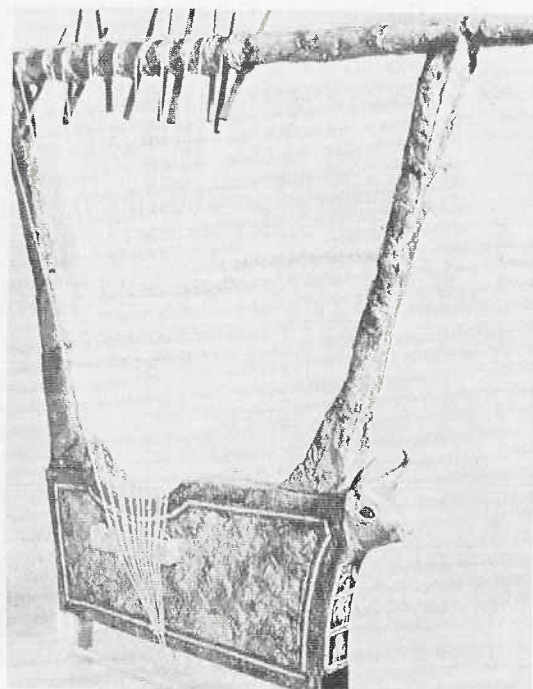


Figure 31. The lyre shown in figure 28 after complete restoration. See color plate i.

forced since the time of excavation. It is in a terrible condition. No one was even sure that it had been assembled properly. The curator was very insistent that he could not continue to show this, partly because it was falling to pieces in the display case, and partly because it did not look like silver.

Figure 29 shows an example of the process in which you can see that the grey silver chloride is being converted into two spreading patches of bright metallic silver, just by laying a thin silver wire on the surface into close contact with the silver chloride, holding it down by insulating polymethacrylate, and electrolyzing. The cross-section of metal treated thus, using partially-rectified current, is shown in figure 30. It is much less porous, much more substantial, than the structure shown before, obtained with fully rectified current. This picture, by the way, represents actually two pieces of silver corroded together, each being split into two laminae. After such treatment one can actually bend without cracking the metal that has been regenerated from silver chloride. In addition, every mark present on the lyre, including evidence for the matting that it had lain upon in the Great Death Pit, was preserved--very important for archaeologists. The only thing that was changed by this process was the grey appearance of silver chloride, changed back into metallic silver. The final appearance of the lyre is shown in figure 31 as it is displayed now. Of course, there was a lot more to the whole process than cathodic reduction: the parts had to be reassembled in their *correct* locations, not in the way that they had been hurriedly put together after excavation for immediate display.

There are questions about this treatment. Is it really permissible to take silver chloride and change it back into metallic silver? My attitude to this is that it took about 3000 years to change from silver to silver chloride and had then begun to fall to pieces. Now that it has been turned back into silver and its shape reinforced it has another 3000 years of life, even if we return it to the same excavation that it came from.

The technical problem of making the change from mineral to metal has been studied further by Charalambous and Oddy [13]. This was reported at the Stockholm meeting of the

International Institute for Conservation in 1975. Charalambous and Oddy made very interesting pictures indeed, showing the transportation of silver from inside silver wire to the outside during the process of corrosion and its subsequent reconversion to metal in its new shape. They concluded that we do not know enough about this method, so we ought not to use it. In fact, I believe it is being used by Curtiss Peterson--who is in the audience--to treat many silver objects recovered from underwater in Florida. He can tell you all about it, more than I know, in fact, at question time.

Doing this sort of thing to silver leads to other difficulties. I am reminded that there is a problem that we call *brittle silver*. This is silver that just falls to pieces in the hands. It does not respond to the silversmith's annealing because, among other things, of intergranular corrosion. Figure 32 shows a specimen like this at the bottom of the screen. We find that this kind of silver can be restored by sintering it just below its melting point underneath charcoal. That probably means in an atmosphere of carbon monoxide such as we were learning about yesterday. The picture shows a vessel from Nuri, of very early date, 530 B.C., which was falling to pieces, literally. On the left, the picture shows numbers of little fragments. Every time it was touched, another similar fragment came off. After our treatment it was possible to bend mis-shapen areas back and to add the missing area. On the right, it may be seen in its finished state, quite strong and tough again. One could, of course, have been extremely conservative about treatment and have taken all the little bits shown in picture No. 1 and have fixed them together on a reinforcing backing and supported them in register. Then we should have had all our pieces ready for study. The owners, however, wanted something done with it because they did not consider it safe to handle--as indeed it was not. This work was reported at the Museum of Fine Arts, Boston, Seminar, Application of Science in Examination of Works of Art, 1965, 131-132.

Further work on the problem of brittle silver was mentioned in a paper by A. E. Werner [14], because the sintering method was found to be unsuccessful on some silver from

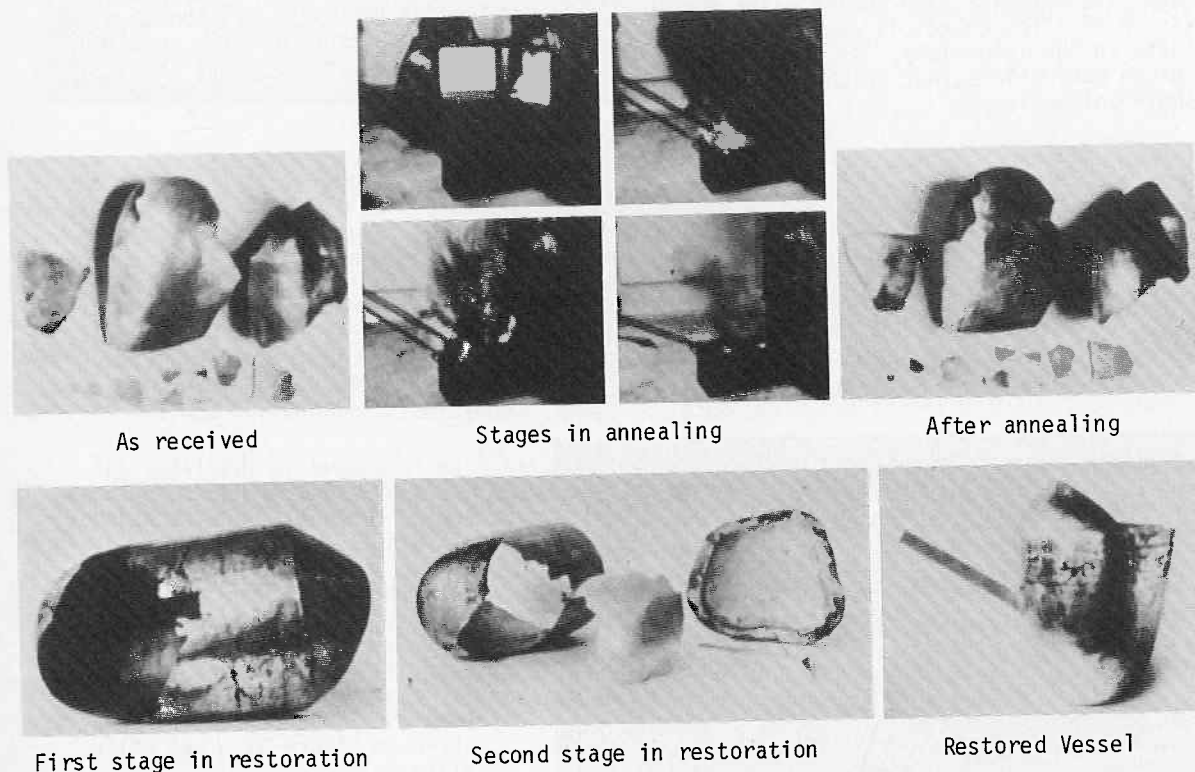


Figure 32. Restoration of silver libation vessel from Royal Cemetery at Nuri, about 530 B.C.

Pakistan. H. Barker, working in the same laboratory, found that he could strengthen similar silver by reducing it in hydrogen gas at atmospheric pressure for 30 minutes at a temperature of 300 to 400 °C--well below red heat. After this preliminary, he then had to apply the sintering process.

All of the above leads to consideration of lifting silver objects, which may be exceedingly brittle, out of the ground. When Woolley lifted the Ur lyre he stuck it together with paraffin wax and burlap in order to remove it in one piece. Part of the difficulty that made the curator want to change the lyre as exhibited arose from this operation: it had not been put together correctly and no one could see how it should be put together properly. The laboratory treatment was needed to recover the original shape. I have come under criticism from several sources for doing this and you should be aware that the method, though practicable, is not necessarily permissible in a museum.

The Russians have faced the same problem of lifting from the ground many beautiful, very thin silver items [8]. They have solved it by pouring over the object, in the ground, very pure ethanol and igniting it, repeating several times. Presumably this treatment heated the silver chloride enough to melt (AgCl melts at quite a low temperature, 455 °C) and flow in order to consolidate the objects. Then they were lifted and treated subsequently by further heating in a furnace and then by cleaning the surfaces with their aqueous ammonium thiocyanate solution and a glass-bristle brush.

Copper and Bronze Objects

Figure 33 is a slide that many of you have seen before but I shall continue to use it because it is immensely valuable. It represents a chisel from Jericho. The excavator considered its date to be 6000 B.C. but it may possibly be not quite as old as that. The picture shows two chisels corroded together within a crust and dropped in transit. The crust cracked through and exposed what was said to be a sewing needle inside: made of copper. The vertical line to the right indicates the location of the micro-section shown in figure 35. The object is shown in figure 34 after deliberate exposure to high relative humidity in the laboratory. At one place it turned green, at a location close to the metal. The green material is that which curators call *bronze disease*, arousing horror if observed in their collections.

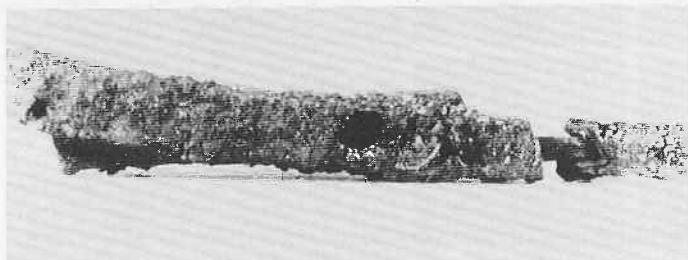


Figure 33. Two chisels corroded together from Jericho and considered to be from about 6000 B.C.

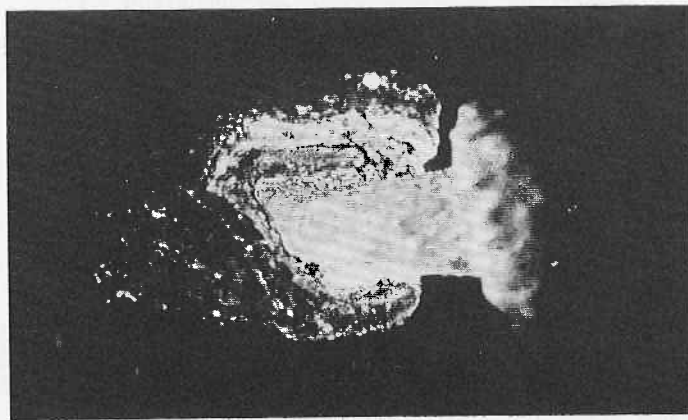


Figure 34. Close-up of the chisels shown in figure 33. See color plate f.

Notice also that the crust is a double layer; there is an epidermis located in the middle of that thick crust of cuprous oxide. There are green corrosion products on the outside (this, by the way, was a hand-colored photograph).

The cross-section through this was extremely informative (fig. 35)². First, you see the green on the outside, carbonates, and within, the pink cuprous oxide. You see the epidermis as a black regular line all around within the pink. Notice also that when the object was dropped, part of the crust was cracked off mechanically, and very important for the conservator, this cracked off along the epidermis surface. Thus, just by cracking, one could recover the original shape. Remember the crust consists of oxide both outside the epidermis and inside the epidermis.

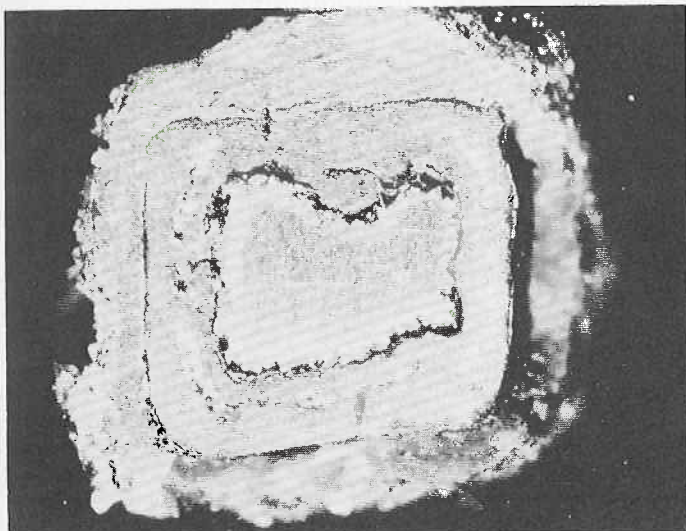


Figure 35. Cross-section taken from chisel sample shown in figure 34.

Notice also that further down between the cuprous oxide and the residual core of metal, there is a black layer which by test with a needle point beneath the microscope, may be observed to be waxy in structure: it is cuprous chloride. This is the material that expanded into the green powdery mass when exposed to high relative humidity. Notice also within the inner of the two crusts of cuprous oxide a line of some green material. This is paratacamite--the green bronze disease--and it happened there, presumably during antiquity, when some cuprous chloride was left behind as the interface between cuprous oxide and metal moved on inwards, leaving this, no longer in contact with metal, to be converted by oxygen and moisture from the air into the stable green disease. Metal is now present only in the middle: it is copper, not containing tin, so far as I know.

The existence of bronze disease has, in my opinion, done great things for museum science. The curator considers its appearance to be an evil. In fact, if it had not been for bronze disease stimulating the curiosity of curators, we should probably not know so much about the corrosion of bronzes as we do now.

Figure 36 shows bronze metal at the top and an incrustation at the bottom. In this copper-tin alloy we find a situation similar to the crusts on silver. Figure 37 shows a typical kind of bronze disease. On the left-hand side you can see several patches of light green at the edge of the crust. That is the location of the grey waxy cuprous chloride where, when it becomes exposed to the air, it forms the green paratacamite that the curator deplures.

² For a color reproduction of figure 35, see R. M. Organ, *The conservation of Bronze Objects*, in *Art and Technology: A symposium on Classical Bronze*, Suzannah Doeringer, *et al.*, color plate V(B) p. 78), Cambridge, MA, 1970.

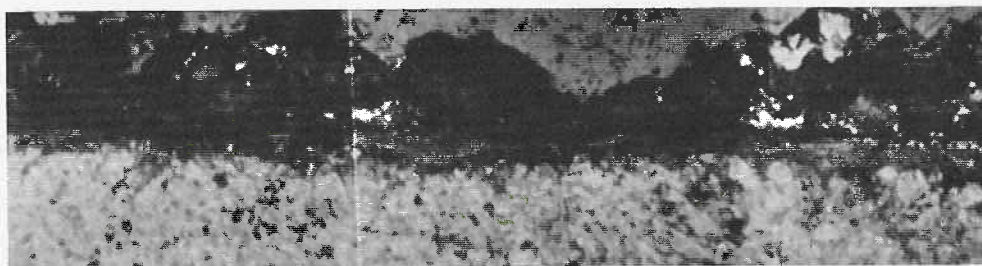


Figure 36. Bronze metal showing bronze disease. See color plate k.



Figure 37. A copper-tin alloy object showing typical bronze disease. See color plate h.

Figure 38 shows a diagram that indicates the options that the conservator has when he is asked to *clean* a copper object in this condition. There are four quadrants: the first possible option (upper left-hand quadrant) is to stabilise the object without changing it; perhaps to do something so that the cuprous chloride can never be exposed to high relative humidity and oxygen. Then it can never change to bright green paratacamite. The second (upper right-hand quadrant) is local cleaning; that is, removing the outer crust down to the epidermis. The lower right-hand quadrant shows just cleaning but also stabilisation by some method serving to prevent bronze disease from appearing. The fourth quadrant represents complete stripping of all corrosion products right down to the metal and beyond, into any corrosion pits in the surface of the metal, so that nothing can happen to it again unless we do it deliberately or are careless in storing it.

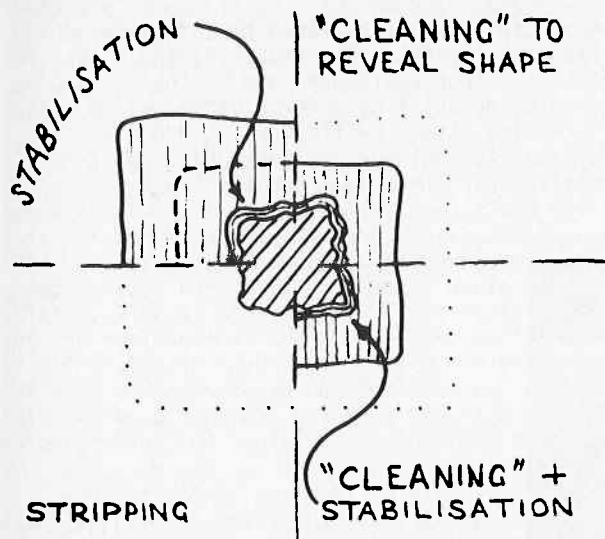


Figure 38. Diagram showing four options the conservator may choose in cleaning a bronze object such as is shown in figure 37.

Methods

Let us then look at methods of stabilisation appropriate to the upper left-hand quadrant: doing *nothing* except stabilising, to prevent cuprous chloride from erupting. A very old method due to Rosenberg, 1917 [15], is described in principle in figure 39. One coats the surface with a mixture of agar jelly and the moisturiser glycerol. Then, apply aluminum foil all over the surface and expose the object in a wet place. The chloride is supposed to diffuse out and attack and be fixed by the aluminum foil. The foil develops holes which we re-cover with foil until eventually there is no longer attack on the foil. The effect is supposedly to fix and prevent further reaction of cuprous chloride that is near the surface. The process does a little more than that. Figure 40 shows results. Condition before is shown on the left and after is shown on the right. As you see, there is a rather unpleasant crop of coppery spots. I do not believe that these photographs are fully representative of the technique. I should hope for a much better all-over appearance given a suitable corroded object.

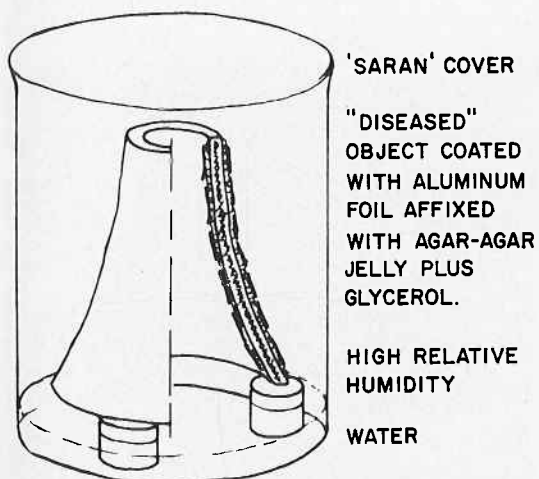


Figure 39. Diagram technique used [15] for stabilisation of a diseased bronze object.

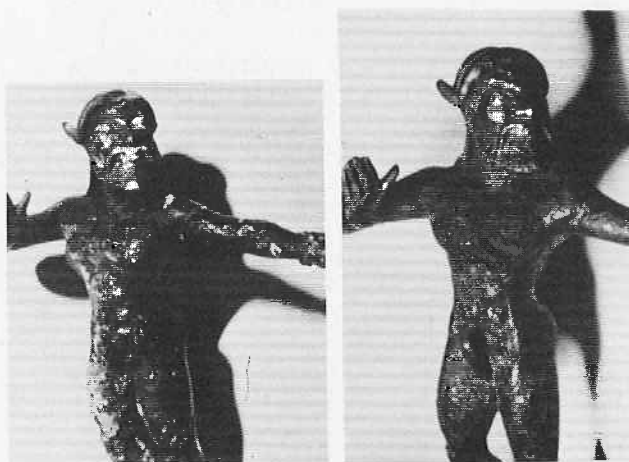


Figure 40. A before and after view of a bronze object treated according to the method in figure 39.

A technique of stabilisation that has been much used, almost hallowed by antiquity, is just to immerse the object in dilute aqueous sesquicarbonate [16]. Figure 41 shows an object in a solution that is going green, showing that things are coming out or that reaction is taking place. One keeps changing the solution until no more chloride can be found in it by repeated tests--three years after starting it may be finished. Then one rinses it off and puts in in a dry place. Nobody likes the method any longer because it involves too much labor. This is really substantially unskilled labor and if this were the only objection, then the method would not be too bad.

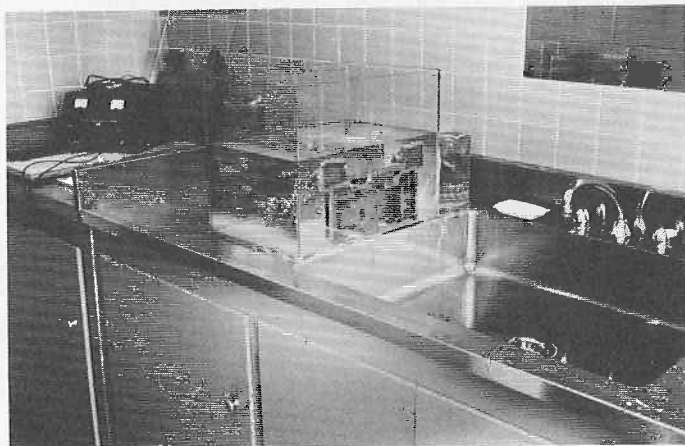


Figure 41. Object being stabilised by immersing the object in dilute aqueous sesquicarbonate.

Another technique, to avoid the protracted sodium sesquicarbonate process, is the silver oxide method shown in figure 42 [17]. This method appeals to the craftsman: he likes to get his fingers on an object, to take a needle and dig the disease out--just like a dentist! Then one puts a little silver oxide in the cavity and makes the oxide react at its interface with the cuprous chloride by putting it in a damp place. This supposedly seals over the edge (by formation of silver chloride). On test this behaves very well indeed. The little spots of dark silver oxide are not really obtrusive. Figure 43 shows a bronze from Nimund going a little blue now as the color-film ages (you noticed that the hand-colored slides had not changed their color?). One cannot really notice that the

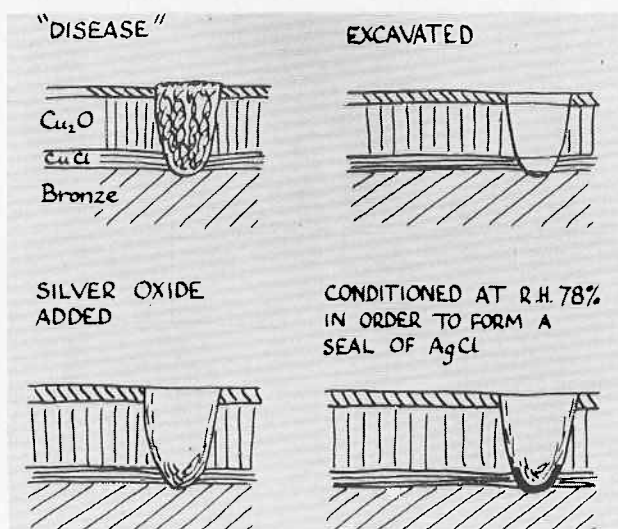


Figure 42. Diagram of the silver oxide method for stabilising diseased bronze.

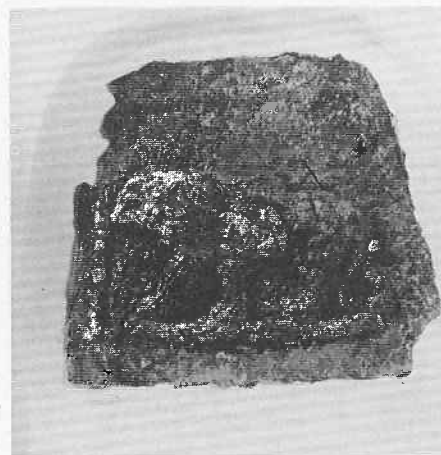


Figure 43. A bronze from Nimund stabilised using the silver oxide method.

spots are brown silver oxide because they are quite similar to the purplish spots of cuprous oxide that are often exposed on the surface. Apart from the fact that silver is introduced where silver should not be, this is quite a reasonable technique if one has the manpower to do it, once the kind of man power is available that wants to do it--in fact, cannot be kept away from doing it.

Another method, later than the silver oxide method, is the use of benzotriazole. I am sure you have heard about this: one just soaks the object in the solution, and nothing seems to happen but afterwards, magically, the object does not seem to corrode anymore. This has been explored by many people: Madsen [18], Greene [19], Richey [20], Marabelli [21], and others. It works in many cases but in others it does not. We would really like a method that does work and always works, if we could possibly have it. We are therefore still looking at the problem of benzotriazole inhibition of corrosion on copper objects. But you realise that the method has really been misused. It was originally devised, and is still used in industry, for the prevention of corrosion of bare metal. But here we do not have bare metal--we have millimeter thick crusts limiting access of oxygen; we have a thick layer of cuprous chloride and high concentration of chloride usually requires high concentrations of inhibitor if they are to be effective.

Another method for dealing with this problem is a particular electrolytic method in distilled water--proposed by Gettens as far back as 1936. Figure 44 is actually by France-Lanord but is after one by Gettens [22], late of the Freer. It shows a micro-section of a corroded bronze which has been made the cathode and exposed in distilled water at six volts against a platinum anode and has made its own electrolyte by dissolution of cuprous chloride, the current rising to 60 mA in two days. By this treatment the cuprous chloride and other copper minerals within the metal have been reduced to the white line visible between the crystals--representing metallic copper. Here the process has been applied to a ready-prepared cross-section. It is not what we should have in the museum, applying it to a whole object. It does not show, what we ought to see, a cross-section through the whole object after it has been treated. It does, however, give an idea of what ought to happen. This kind of stabilisation is not supposed to alter the mineral crust--the green carbonates and the cuprous oxide--on the outside. I am a little dubious about this. Gettens himself said that the method should not be used without much more exploration. It might work with particular care taken to monitor progress.

Now, another type of treatment, see the second quadrant of figure 38, cleaning to reveal shape. What methods do we have? An obvious method is to crack off the crust above the epidermis--a method used by Ternbach and by many Italians--in which one actually cracks off the crust using a needle, perhaps oscillated in a Vibrotool. This is always permissible, because one can always stop if things appear to be going wrong. It is unlike a chemical treatment where you put it in and hope that you have pre-tested *everything* so that nothing will go wrong.

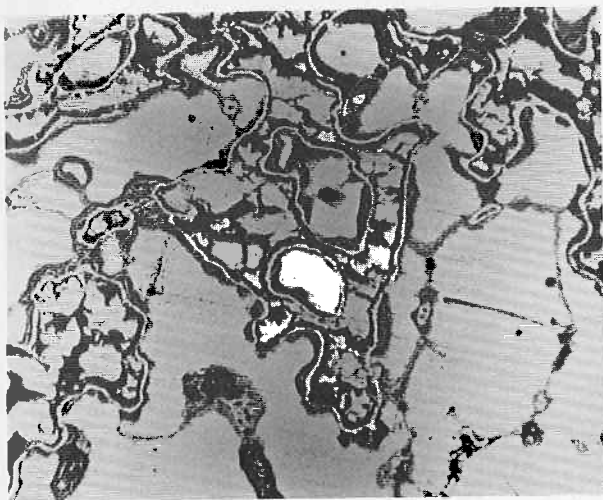


Figure 44. A micro-section of a corroded bronze stabilised by an electrolytic method proposed by Gettens [22].

Another method devised by Fink and Eldridge [23] (fig. 45) is described as an electrolytic method. What actually happened has been rather lost from sight since 1925 when they wrote about it. They said that you wrap the encrusted object in a bare wire then connect the wire as a cathode. What happens then is that some electrolytic action starts at the wire and then spreads inwards to the object. After treatment in this way one could then crack off the crust. So there are two parts to this: electrolytic preparation and then mechanical cleaning.

Figure 46 (see colorplate) shows a bronze we treated in this way in C.A.L.; the crust was very far developed--you can see the bare cathode wire lying against it as a spiral. It was held together by a cellulose sponge, appearing here as pink spotted material. The sandwich has been opened up and copper has visibly formed around the wire, just as silver formed around the silver wire on the object shown above made of silver chloride. This process was not taken to completion; the number of coulombs needed was calculated and at the stage shown the object had received this amount. Obviously the efficiency of the process was very low, because we have not converted all of the mineral. After this treatment it was possible to crack off the crust and we did find the inscription we were seeking. The electrolyte was 5 percent aqueous sodium carbonate and 1 amp/dm² was applied for four days.

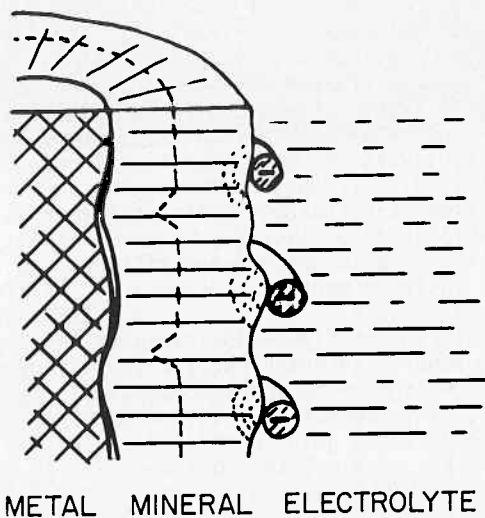


Figure 45. Diagram of an electrolytic method [23] for cleaning diseased bronze to reveal shape.

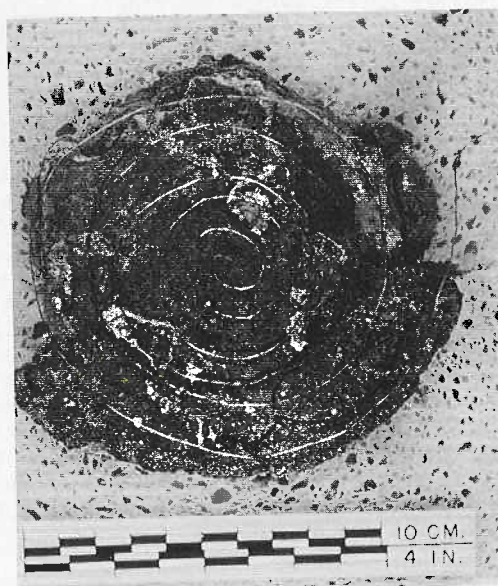


Figure 46. A bronze treated by the method shown in figure 45. See color plate q.

Next let us consider the third quadrant, clean down to original surface and then try to stabilise it. The methods available for stabilisation have been described before, either keep the object very dry or treat with sesquicarbonate or with silver oxide with activation in moist air or with benzotriazole.

Finally, in the fourth quadrant, complete stripping is a possibility. This is permissible sometimes. If one has a collection of weapons for example, then the curator may not mind having them stripped right down. You may remember the Isis and Horus shown earlier. This was stripped right down to the metal. The process used in that case was a serial method, starting off with alkaline glycerol to take off the green carbonate. Then dilute sulphuric acid to remove the cuprite as a mud. Then going a little further, electrolysis to really remove every scrap of chloride out of the surface so that it will never corrode again [24], followed by intensive washing [25].

There are other methods of achieving the result; it does not have to be a serial method. The object can be immersed in sodium hexametaphosphate and the copper ions be sequestered away [26]. One can use the disodium salt of ethylene diamine tetra acetic acid to sequester it away [27] or, more recently, Cejka has used this same technique in Czecho-Slovakia with the addition of hydrazine sulfate and ammonia to expedite the reaction [28]. People do use dissolution techniques.

Other States of Mineralized Copper Alloys: Bronze

There are other varieties of corroded copper alloys, less simple than the one described. Figure 47 presents an example from a Romano-British funeral pyre in Dorset, England [29]. The object was originally a drop of bronze melted from the deceased's accoutrements, incinerated with his remains. The metal melted and dripped down into the charcoal in the fire. The photograph shows one of the many droplets found together, all having a similar rounded but laminated exterior. When cross-sectioned the lower part is found to consist of unchanged bronze where it has been in contact with the charcoal. The copper part has corroded. There is here no original surface, no epidermis; there are just repeating layers of particular corrosion products. The cuprous chloride is again down at the bottom between the crust and metal; this section was exposed to high relative humidity and a row of white dots can be seen--they were pale green really--which indicates the location of the cuprous chloride. Now if anyone wishes really to stabilise this bronze he has to reach down to this level. Whatever technique he uses--sesquicarbonate, silver oxide, benzotriazole, whatever it is--this is the level at which the source of trouble lies. If cuprous chloride was once present anywhere else in the crust it has already changed to paratacamite; it is stable, it will not change anymore. Such a corrosion situation can proceed to completion; figure 48 shows the shape but there is not a scrap of metal left. It is now all mineral; you can see this clearly at the fracture. It might be pseudomorphic of the metal; it might still display the shape and the metallographic structure of the original. There is no guarantee of this at all in a completely mineralised bronze. From the foregoing it is quite clear that objects underground are not protected by their natural patina. The Jericho chisel had an interface that was moving down through the metal during some 8000 years. The presence of so-called patinas may slow down the rate of reaction but it certainly does not prevent it.

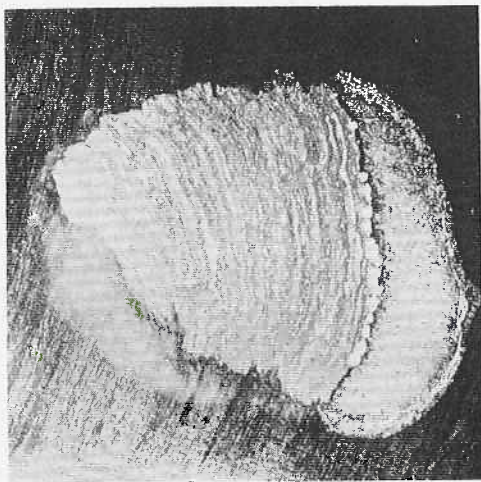


Figure 47. A bronze sample from a Romano-British funeral pyre in Dorset, England [29].

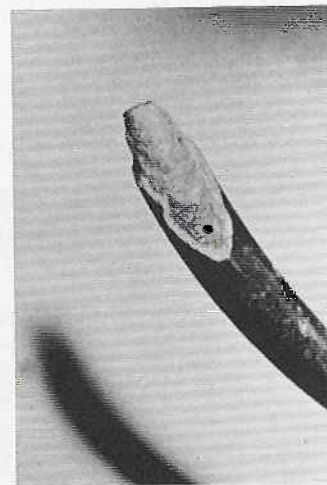
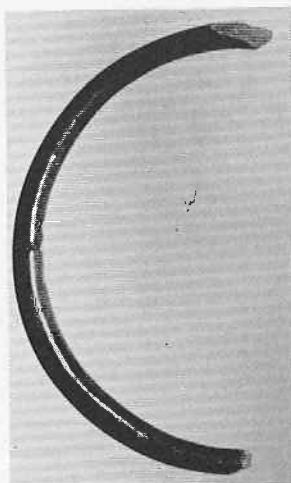


Figure 48. Example of corrosion developed under the epidermis of a bronze with high tin content. See color plate n.

A similar situation occurs underwater. Figure 49 is a cross-section through a flake of copper sulphide, viewed under crossed polars, which came off a bronze spearhead found in the river. The thickness of the crust is about 4 mm (1/6 inch). It has quite a beautiful structure. This has been growing, eating away into the bronze, as is shown by the layered structure, parallel with both the outer surface and the face of the metal, showing continuing and steady attack.

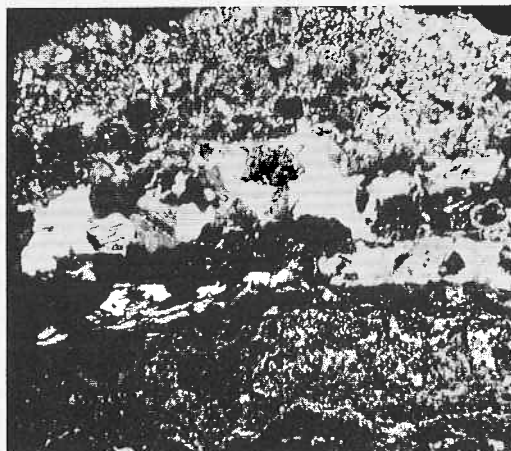


Figure 49. Cross-section of a flake of copper sulphide taken from a bronze spearhead found in the river.

Now people in Moscow are interested in the protective properties of patina. Kalish has reported [30] to the Conservation Committee of ICOM her experiments in making artificial patinas. She has concluded, as a result of her tests, that artificial patinas are never as protective as natural ones which as you see are not very protective either. So I do not believe that we can rely solely upon corrosion crusts as protective agents although, once formed, some varieties do not change in nature but only grow thicker. These present a stable appearance and are therefore valuable to artists for their bronze sculptures.

Tin Objects

Tin as found in museum objects is usually alloyed. It is made into all kinds of useful things, sometimes just intended for decoration. If it is buried underground it grows thick films [31]. Figure 50 shows a cross-section through a coin from Malaysia. The total height of the picture represents 2 mm of thickness. The only metal remaining is



Figure 50. Cross-section through a coin from Malaysia.

shown in part at the bottom. Everything above represents corrosion products--a layered structure, partly broken out during the making of the cross-section because the corrosion products are quite brittle and friable. Analysis showed that the crust contained some sulphate and a little chloride. Both sulphate and chloride are corrosion stimulators if they are found on tin. We did not find them in that crust by use of the microscope but they were shown to be present by analysis.

Figure 51 shows an insignia or cap badge, from the 1812 war. The metal was substantially tin with a little copper. We were asked to stabilise it but there was a thick corrosion crust. Figure 52, made by Martha Goodway, represents a cross-section in which the remaining metal is identified by the scratches on it. Above it is the mineral crust. In between is a peculiar appearance unlike the other minerals, which has been identified by x-ray diffraction (Walter Hopwood) as basic stannous chloride. Here we have actual evidence of the existence of a corrosion stimulator, again lying between metal and mineral crust. It begins to look as though conservators must always penetrate to basic metal in some way if they wish to stabilise objects against continuing chemical change.



Figure 51. An insignia or cap badge from the War of 1812.

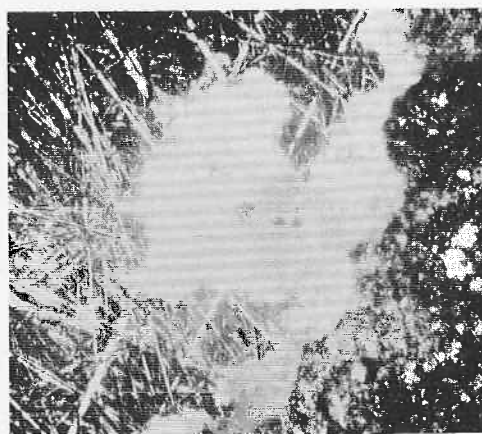


Figure 52. Cross-section showing remaining metal identified by the scratches.

This sort of thing happens to tin not only underground but also underwater. Figure 53 shows a tin pannikin found 15 feet below the surface in waterfalls in Boundary River, Winnipeg, apparently lost from an over-turned canoe. Marks on the bowl show that it was made in London between 1801 and 1821. The pannikin was one of a stack. You can see marks around the side made by the next one in the stack. On the pannikin are numerous crystals, small black ones and small white ones. How should we clean such a bowl when requested? In this case we did not actually clean it at all. We identified the crystals (fig. 54), and found that the black ones were stannous oxide and the white ones were hydrated stannous oxide $5\text{SnO} \cdot 2\text{H}_2\text{O}$, which had not been observed in so-called nature before. So we were able to have new mineral names assigned to them: the black crystals became Romarchite, the white crystals became Hydroromarchite--ROMA from Royal Ontario Museum, Archaeology Department [32]--and the pannikin now has to be preserved exactly as it is, as the type specimen of these two minerals: one way of evading conservation treatment! It is not an economical way: it took at least 100 times the effort to satisfy the International Mineralogical Association than it would have taken to remove the crystals!

There are, however, other things one can do. Figure 55 shows at top left; a tin hat coin as received. It has been buried underground in Malaysia, dating from about the mid 19th century or later. Made of cast tin, it was cleaned to the condition shown on the top right using a common electro-chemical method, surrounding by zinc granules and heating in dilute aqueous sodium hydroxide. It came out beautifully clean--free from all of its crust, but slightly bluish in color--coated with zinc. This was taken off. I am sure that the corrosion experts would have much preferred to have it left on, as a protective



Figure 53. A tin pannikin found 15 feet below the water's surface in Boundary River, Winnipeg, Manitoba, Canada.



Figure 54. Crystals found on pannikin shown in figure 53 were never observed before in nature. Pannikin was preserved as it was found. See color plate g.

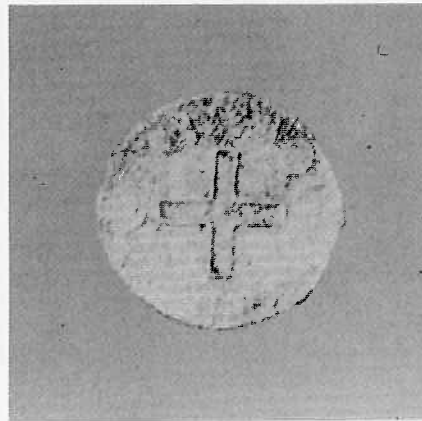
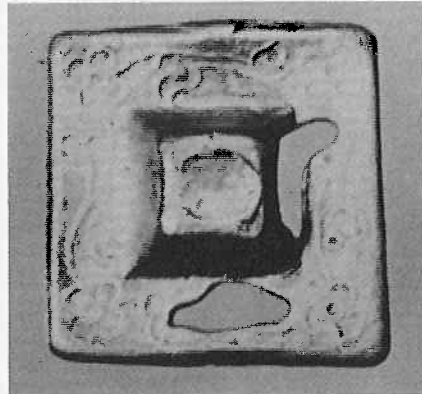
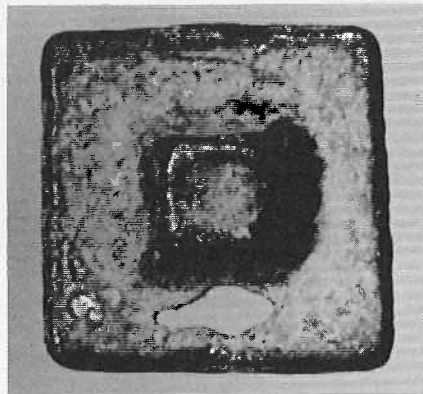


Figure 55. The tin hat coins shown at the top were recovered from underground in Malaysia. They are from the mid 19th century or later. The objects at the bottom are John of Portugal coins brought up from underwater. They are from the 16th century.

film, much like galvanising iron. However, we really could not accept the idea of giving back a tin object looking like zinc, so we took it off.

The objects at the bottom are John of Portugal coins, 16th century, brought up from underwater. The one on the left is uncleaned, the one on the right has been cleaned using, this time, sodium hydroxide with magnesium filings. It has come out beautifully clean and has preserved its color. I am not at all sure that the magnesium did anything to help. It is possible that sodium hydroxide alone would have served but that is the way it was, in fact, done.

There is an interesting fact about coins. You might think that, if a crust 2 mm thick has grown on a metal surface that is itself now only 2 or 3 mm thick, then all the detail would have been lost. This might be true of cast objects but it is not true of stamped objects. In a stamped object the metal is in some places more compressed than in others. It is this compressed metal that corrodes faster. So, in fact, a stamped object will have sharper detail in the remaining metal after corrosion than before. In this event the crust can be taken off in every confidence that detail will not be lost--but only if it has been stamped.

Tin presents another possibility. Figure 56 shows two shoe buckles. The object on the left has been treated. The one on the right has not. It is made substantially of tin with a little silver and a little copper. It is not very old but has acquired a crust--grey and brittle--on the surface, about 1/5 mm thick. The buckle on the left has been treated electrochemically with magnesium ribbon in sodium hydroxide. Gale Wever, who is present, did this. The process was carried out hot, for about two hours. The interesting thing about this object was that after the treatment and the washing we tried to put a protective film on the tin--we tried to form an epitaxial film which would delay further change. This was done by a method published by Shah and Davies [33] at the First Interna-

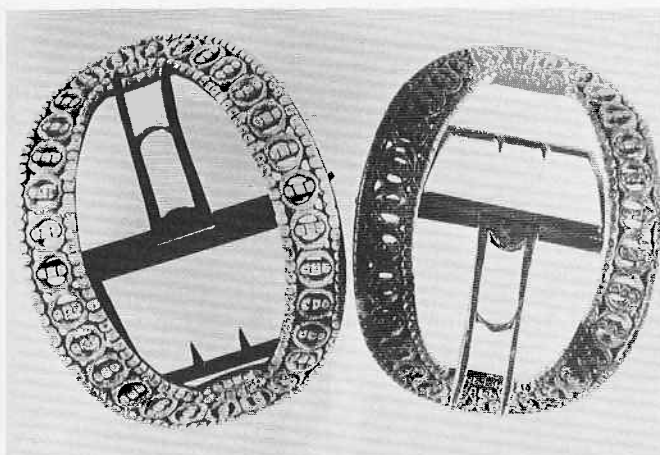


Figure 56. Two shoe buckles, the one on the left has been treated by the method of Shah and Davies [33].

tional Conference on Corrosion in 1961. This involved, essentially, reducing electrolytically to ensure that the surface really was clean, then removing the object out of the electrolyte through the oxygen-rich area around the anode. We hope that this particular treated piece will survive unchanged longer than other tin objects. Normally, of course, one abrades slightly to an acceptable pewter color and finish, waxes it, and looks after it afterwards.

Leaden Objects

Lead characteristically decays in museum storage by developing a white crust of basic lead carbonate that falls off as loose particles. Figure 57 shows an object with cerussite. Lead may also develop monoxide, dioxide, sulphate, chloride, crusts in appropriate environments.

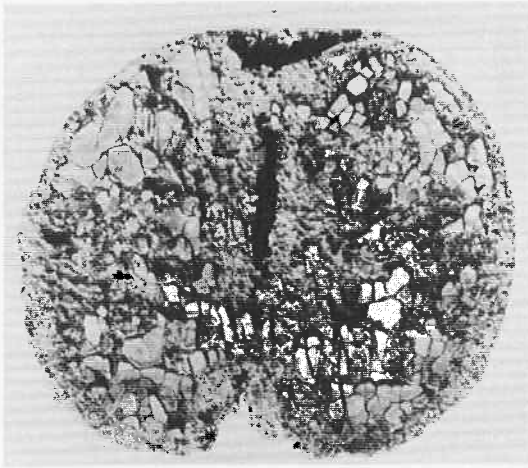


Figure 57. Lead object showing characteristic decay.

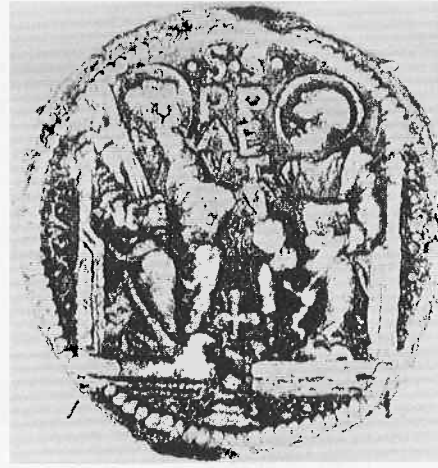


Figure 58. A lead bulla, seal of Pope Paul III, showing corrosion by lead carbonate.

Figure 58 shows the corrosion we hate most. Sometimes it goes to completion. This is a bulla--I am not sure of its date--the surface is just a corrosion crust and difficult to read. Often these leaden things have been saved for us by earlier conservators who brushed shellac varnish all over it as a consolidant. It is wonderful if they did that then, not knowing what else to do, because we can now recover the object. The change would have happened as a result of corrosion stimulants--things like acetic acid, formic acid, which come out of the woodwork, literally, in a display case or in a storage cupboard, or from the cafeteria next door, where they eat mayonnaise on their salads. This stimulant is fatal: all the lead objects very quickly fall into little piles of white powder. We hope that some conservator will have spotted the condition in time and have sprayed it with shellac--which is a safe varnish--in order to hold the powder together until we can deal with it.

The kinds of treatments available are fairly numerous. They aim at cosmetic results: they must remove the crust. We must also remove the corrosion stimulants--the acetates and the formates--or else the corrosion will continue in the presence of moisture and carbon dioxide from the air. When we remove crusts we must also avoid leaving the lead in a corrodible state. There are many objects made of lead which have been treated by chemists who were not conservators and who knew that carbonates were dissolved by acids, so they immersed them in acetic acid, in vinegar, to clean them all up beautifully. Then two years later, they were corroding again. Now we know better!

Actual methods of treatment: first, that dissolve the crust, are: 10 percent aqueous disodium ethylene diamine tetracetic acid, used first so far as I remember, by Kuhn [34] in Munich but there are several other sequestrants that will serve. We have been warned by Hannah Lane [35], working in the British Museum Research Laboratory, that this is not always a good method because sometimes the sequestrant creeps under the crust and attacks the metal directly. She also has some evidence that objects treated in this manner re-corrode faster than objects treated in other ways. I think we need more evidence on that point. Subsequent corrosion is probably related to the presence of corrosion stimulants in the atmosphere at the time of cleaning.

A second method of dissolution is to put the crusted-over object in hot distilled water, which as you know attacks lead, but here it is done in the presence of ion-exchange resins which are in the hydrogen (acid) form [36]. Figure 59 shows a lead medal whose inscription can really not be read--it appears to be the siege of some castle but is crusted over with lead carbonate. We may just immerse it in beads of hydrogen-form ion-exchange resin, heat it enough to boil off all the liberated CO_2 , to boil off all the



Figure 59. A lead medal crusted with lead carbonate.



Figure 60. The lead medal shown in figure 59 after restoration.

acetic acid, to boil off all the formic acid, and it comes out as in figure 60. Then we can dry it off and wax it and it is completed. Nothing has been done to the surface except to remove accretions and stimulators. But there is no protective film formed apart from added wax, unless one adopts one of the special techniques. These are, of course, possible.

A third good method is one due to Caley [37]; it is good in the laboratory but not in the ordinary museum. Figure 61 shows some lead coins treated in this way. The colors here are poor--the coins should look more like lead than green. The method is to use dilute hydrochloric acid, which in the cold does not attack lead, except for formation of a thin protective crust of lead chloride. Then one uses ammonium acetate, which I am not too happy about, but it has to be used in case there is some lead peroxide present, that will not dissolve in any other way. Caley has treated ancient lead in this way and has kept it for at least seventeen years without change in appearance, so it is a possible method. It does, however, require careful attention and I do not advocate its use in museums because we cannot give anything really careful attention, with telephones ringing all the time.

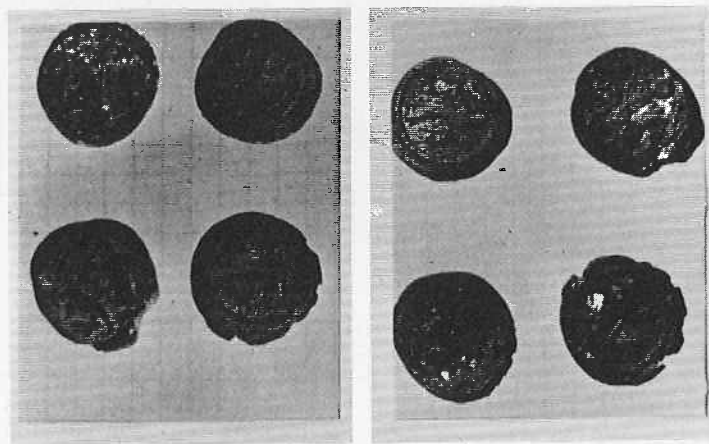


Figure 61. Lead coins treated to remove lead carbonate using Caley's method [37].

Other methods dissolve away the crust. There is also an electro-chemical method. Figure 62 shows a seal of Pope Paul III, seen before in the untreated condition (fig. 57), that has been treated in aqueous caustic soda solution with some metallic zinc [38]. It comes up beautifully clean if you wash it out afterwards. However, I do not know quite how long this will last because there are often residues of zinc salts present on the surface and there are difficulties in washing them away. One has to use tap water for washing because distilled water corrodes the exposed lead. Therefore, we do not normally use this method except in the field or where this is the best that funds allow.



Figure 62. Seal of Pope Paul III after cleaning using an electro-chemical method. (Figure 57 shows this bulla before treatment.)

Then there are methods of more controlled reduction using cathodic techniques. We have three of these, more, in fact. If you want to finish with a lead object that appears blue-grey in color then you electrolyse in 5 percent aqueous sodium carbonate at a current density of two to five amperes per square decimeter using stainless steel or platinised titanium anodes. The resulting blue-grey color is liked very much by some curators. Then it has to be washed. Washing is recommended initially in water, but then in very dilute sulphuric acid, which leaves a protective film of lead sulphate on the surface. This process [39] overcomes most of the problems of electrolysing lead in alkali.

If, however, one wants a finished object dark-grey in color--you notice our aesthetic tastes, now--the same process is carried out but in 10 percent sulphuric acid at about the same current density. Then there are no problems of subsequent corrosion because the surface automatically becomes crusted over with an invisible thin film of lead sulphate.



Figure 63. A bulla that has corroded completely. The portion on the left is restored; the portion on the right is held together with shellac.

In a situation where nothing remains of the metal--where it has changed completely to lead carbonate--but the carbonate is held together with shellac varnish, there is still something that can be done with it. Figure 63 shows a bulla. A bulla is a lead seal clamped around a string attached to the document and bearing impressions. The part clamped around the string is thin and corrodes through first. The one half on the left has been treated. The other half on the right is in fact completely non-metallic; it is just lead carbonate, held together with shellac. It can be changed into the condition of the one on the left by the method of consolidative [40] reduction which now-a-days makes use of 10 percent sulphuric acid as an electrolyte. A lead strip is attached around the crust that remains, to serve as the current-conductor, the cathode. A lead anode is used with a current density of 6-12 mA/dm², leaving it for about 14 days, resisting any temptation to examine it, because if lifted out it will probably fall into fragments. Then it is taken out and found to be quite solid again--more porous than it was, of course. Then it has to be washed a little--but not too much because there is a protective film of sulphate on it and finished with wax in the usual way. This is a good way of dealing with completely lost leaden objects provided that the powder has been held together with varnish.

Iron Objects

We are all familiar with iron. Figure 64 shows a rusty old chariot wheel, just to remind you; perhaps to make you feel that you should go home immediately. Rusted iron seems to be the worst possible thing conservators encounter and some of us have literally tons of it brought to the door every week in need of treatment. The rust of course, contains corrosion stimulators--chlorides, sulphates, perhaps acetates. I do not believe there is ever a true original surface preserved in rusted objects. Many of my colleagues in Europe, however, believe that there are and that they can find them. I am not convinced of this at all, although a lower layer of black oxide can usually be found. Evidence for probable further corrosion (chemical instability) is the presence of wet brown globules of ferric chloride solution which appear on the surface. This has been known for a long time. Krause [41] recognised in 1882 that the ferric chloride content was the source of trouble with rusted iron that had been excavated. What treatments are available?



Figure 64. Rusty chariot wheels with the rims entirely corroded.

Figure 65 shows mechanical methods; we just grind away the thickest part of the crust, then prick away the thin residue. In order to provide an epidermis, one is shown here defined by the presence of inlay, which does happen. It is a purely mechanical method.

How otherwise can we remove this crust? Well, there are many solvents for rust, none of them very good when the rust has been present for a few centuries: things like acids--phosphoric acid, citric acid, oxalic acid, with an inhibitor present to prevent attack on bare metal when it is exposed. Then we have alkalis--sodium hydroxide, usually used hot

in the presence of sequestrants, such as some Versenes that act at an alkaline pH. These methods may be quite good because they not only dissolve the rust but may also dissolve away the corrosion stimulators, which, of course, we must do.

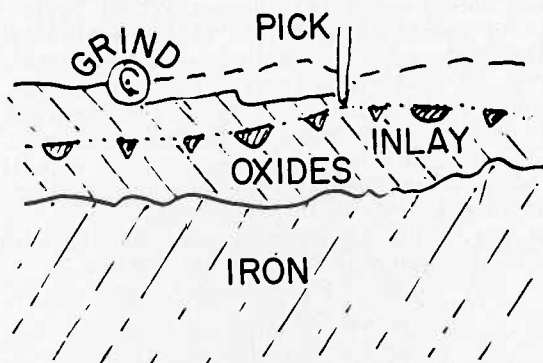


Figure 65. Diagram of a mechanical method for treating corroded iron.

INLAY MARKS THE ORIGINAL SURFACE

There is also a method using tannin which is a good folk method: the early trappers boiled their tools in extracts of bark in order to give a nice blue-black finish which did not rust easily. Some people like the tannin treatment [42]. Archeologists love the black color, normally. In fact, iron treated by other methods is sometimes deliberately painted with a lacquer containing black pigment just to make it appear acceptable. Of course, it is useful also, because it provides some kind of partially permeable barrier between the atmosphere--the environment--and any remaining metal. So it is useful--not only aesthetically satisfying.

If the crusts are very thick we use the electrolytic method. These alter the rust in a helpful manner. Sometimes it goes to a pyrophoric material which glows red-hot when the object is taken out of the tank and allowed to dry. Electrolysis could be good because it may remove the corrosion stimulators--which one really must remove. The process is commonly done at far too high a current density. It is usually done on dry crusts which are very difficult to re-wet. Both difficulties can be avoided if one knows that there is a problem.

Iron recovered from underwater is best kept wet so that the liquid phase never loses continuity. Literally, it should be kept wet at all times and then electrolysed at a very low current density in a weak sodium carbonate solution, usually with stainless steel anodes in the hope that one will really get down to the location of the chlorides. This might require months and months of treatment and testing.

The shape of iron objects can be recovered in ways other than mechanical. An early method is due to Rosenberg [43]. He took his rusted iron object and wrapped it carefully with iron wire, being particularly careful to locate the wire at places where there were pustules of ferric chloride. On top of this he applied thick wet asbestos, which was intended to serve as a kind of mould to hold all together. This was wrapped with more iron wire so that the crusts present were carefully reinforced. After an intermediate stage of drying the whole was heated to red heat, 800 °C, for 15 minutes. This should evaporate away any ferric chloride present in the crust. Then he plunged it into cold saturated sodium carbonate solution. After that he boiled it in dilute potassium hydroxide--intended mostly to wash it while preventing flash rust. Eventually he was able to open it up and he found a beautiful shape where previously it had been a warted-over unsightly rusted object. Knud Holm can probably tell us more about this at question time. The process is probably still being carried out at the National Museum in Copenhagen.

Another method of removing ferric chloride, similar in principle, involves taking the object and, so-called, anneal it at 850 degrees for 8 to 10 hours in a closed furnace. The Military Museum in Copenhagen has been using this technique [44]. I shall not discuss hydrogen reduction because Lars Barkman will do that later in the program.

The crudest method of removing chloride is to wash the object in hot water. Much effort has been spent in making machines to do this. These appear, so far as we know at present, to be doomed to only about 90 percent success. There are some failures because we cannot always penetrate to the ferric chloride layers.

An advance on hot washing is to use an electrolytic method. The object is placed between two stainless steel plates, cathode and anode, in distilled water, and electrolysed. The electric field is believed to assist ions which diffuse out of the crust to move away [45]. One keeps changing the water and keeps it hot, at 40 °C.

Another rather similar method, named cathodic desalination [46], involves putting the object inside an iron screen which serves as the cathode. Surrounding this is a stainless steel anode. A chloride ion which diffuses out of the object beyond the screen moves down the potential gradient and is lost whenever the solution is changed. Wihr, in Mainz, finds these two latter techniques very satisfactory, alternating the two.

If one washes rusted iron, as some people do, in very dilute sodium carbonate, with the idea of moving the equilibrium of the hydrolysis $\text{FeCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$, in the direction of converting the iron salt FeCl_3 to chloride ions, then difficulties are made because the sodium carbonate necessarily also forms much colloidal ferric hydroxide. This lies in the pores obstructing diffusing chloride. A method has been proposed using lithium hydroxide dissolved in ethanol, 90 vol plus methanol, 10 vol to overcome this trouble, the theory being that when the ferric chloride is converted to lithium chloride, this just dissolves in the alcohols and can diffuse away. But the theory does not seem to cope with the ferric hydroxide which is the real obstructant.

Long ago in 1952, I tried to remove ferric chloride by extraction, hot, in chloroform, which does dissolve ferric chloride. I was never able to prove that the method was an improvement over others, but someone might look for a better organic solvent that would serve.

The very latest idea for iron objects raised from sea water, and a very promising one when it works, has been published by Pearson [47], Australia. His method is to convert the Fe_2O_3 , the red oxide, into the black oxide Fe_3O_4 . Thus, we do not really lose the shape of the mass. We merely change from red to black (and we like black on iron!). We hope that something happens to remove the corrosion stimulants as well, and it does. He does this by immersing the object in alkaline sodium sulphite under nitrogen gas in order to prevent atmospheric oxygen from oxidising the sulphite. It is done in an oil drum purged with nitrogen gas, changing the solution every day or whenever needed as the chloride concentration increases. Finally, he washes in water and fixes any sulphite remaining in the object with a bath of tenth molar barium hydroxide, which reacts to form barium sulphite and barium sulphate. The object is then dried.

All of these processes require a final removal of water. If any metallic iron has been exposed by the process, trouble will arise from flash-rusting. There are various ways of avoiding this. Commonly, one rinses out with acetone or ethanol, successively, or one can use dewatering fluids. In the Smithsonian we use a popular commercial fluid containing a substance which is left behind to serve as a corrosion inhibitor. The use of de-watering fluids has great possibilities; they do not dilute the water then evaporate with it as an azeotrope, but actually physically separate the water from the metal by penetrating into the interface. If there is some inhibitor in the fluid it should be very effective. It has been found that on cast-iron machinery it serves better than anything else.

It is strongly urged that anyone who wishes to follow the treatment of iron should read a paper by Fenn and Foley published at the IIC Stockholm Conference, 1975. It is an excellent review of the situation that enables one to see what are the real problems. These are not all technical; some are problems of interpretation.

In epilogue: clearly, there are numerous methods available to conservators but there are also innumerable problems. Therefore, there are still innumerable needs. We have to choose a method, suitable on the one hand for tons of excavated objects or on the other hand for a single art object. Obviously, a single method is unlikely to serve for both. So conservators have to have in mind very clear objectives for their processes and they do need the support of curators because a curator has to state the nature of the ultimate objective; he, or the archaeologist, is the one in charge of collections. Now in order to help conservators to choose a path between the various boundary conditions of his particular problem we need more methods of examination--many more methods of non-destructive testing--to enable us to discover the real situation before we decide what we can do and what we are permitted to do. We also need a great many simple monitoring techniques, not only to evaluate the objects before we start but also to tell us what is happening during the process so that we can satisfy ourselves that what we hoped we were doing is actually taking place. On many occasions at present it is not!

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Corrosion and Metal Artifacts—

A Dialogue Between Conservators and Archaeologists and Corrosion Scientists

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