

NAT'L INST. OF STAND & TECH



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# NBS SPECIAL PUBLICATION **479**

**U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards**

## **Corrosion and Metal Artifacts—**

**A Dialogue Between  
Conservators and Archaeologists  
and  
Corrosion Scientists**



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OCT 28 1977

# Corrosion and Metal Artifacts—

## A Dialogue Between Conservators and Archaeologists and Corrosion Scientists

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Issued July 1977

## PREFACE

In March, 1976, conservators of cultural property, archaeologists, curators, museum scientists, corrosion scientists, corrosion engineers, and metallurgists traveled from many countries to meet at Gaithersburg, Maryland, in the United States at the National Bureau of Standards. Our meeting was entitled "Corrosion and Metal Artifacts: A Dialogue Between Museum Conservators and Archaeologists and Corrosion Scientists." This volume is the formal report of the proceedings.

This meeting in 1976 was the direct outgrowth of the first Rutherford John Gettens Memorial Seminar of the Washington Conservation Guild, held in 1975 at the Freer Gallery of Art on the same topics. The late Rutherford John Gettens was a pioneer in the study of ancient metals, especially the study of ancient bronzes and their corrosion. He set a high standard in a lifetime of work on the technical examination of artifacts.

The success of the 1975 meeting was such that the Washington Conservation Guild joined Professor Marcel Pourbaix of the Centre Belge d'Etude de la Corrosion (CEBELCOR) in suggesting that a "Corrosion Week," one in a continuing series of Corrosion Weeks which have been held on both sides of the Atlantic for a number of years, be devoted to the same topic. We are especially grateful to Dr. Jerome Kruger for obtaining the generous support of the Bureau for this meeting and for the publication of these proceedings.

The conservators, the scientists, and the archaeologists set the stage for our dialogue with lectures in which they gave their backgrounds and their points of view. The discussions these papers elicited have been included substantially as they occurred. Many of the ideas presented are set down for the first time here. Questions for the structured discussions had been collated by the program committee from questions submitted in advance of the meeting by the participants; the discussion of these questions is given in full, and we hope by reporting the discussion faithfully this report will be a substantial addition to the technical literature which has issued from the laboratories of the world's museums for many decades. Those who would see more of this literature should consult the *Art and Archaeology Technical Abstracts*, published twice a year by the International Institute for Conservation.

We hope that as you read this volume of proceedings you will be carried beyond the methods of conservation and the techniques of the scientific laboratory, however interesting, to consider our fundamental interest in the objects. They represent the material heritage of mankind. These tangible things must be preserved and so our first preoccupation is with the conservation of these objects by the best means we can devise. Solving the problems of conservation is one step, an important step, toward a larger purpose. This larger purpose is the study of man through the things he has made.

The study of human culture through material artifacts is gradually becoming recognized as a distinct discipline. It is a discipline to which the skill and insight of the conservator and the instrumentation of the scientist are indispensable, but it is a discipline which has its own structure, methodology, difficulties and rewards; one which demands serious commitment.

Those who were fortunate enough to take part in the Dialogue are well aware of the splendid arrangements made for them by Ron Johnson and Paul Fleming of the Institute for Materials Research, assisted by Gloria Serig and others of the Institute Office, as well as Sara Torrence and the other members of the NBS conference staff. We appreciate the efforts of Ellen Ring and the staff of the Institute Text Editing Facility in preparing the copy, and especially those of Rosemary Maddock for preparing the illustrations, laying out the copy and coordinating the preparation (and the editors).

This volume contains much material which has not been published before. We hope that the publication of so many useful ideas will prove stimulating to the old hands, and that this volume will be a helpful guide to the worker new to the study of artifacts.

The Editors

## ABSTRACT

This book is the formal report of the proceedings of the seminar on Corrosion and Metal Artifacts. It contains the tutorial lectures on the aspects of corrosion science and Engineering of relevance to conservators and archaeologists, background lectures which are addressed to corrosionists with activities and problems in the conservation of metallic artistic artifacts and the full discussion (attendee) of the structured questions distributed before the meeting. The report is well documented with illustrations.

Key words: Archaeological finds, preservation of; conservation of metal artifacts; corrosion, inhibiting of; corrosion, treatment methods; metal artifacts, restoration of; patina, artificially produced; patina, natural.

Disclaimer: Although the editors have reviewed all the papers and discussions contained in these proceedings, the views expressed are entirely the responsibility of the individual authors.

In order to specify the procedures adequately, it has been necessary to identify commercial materials and equipment in these proceedings. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.



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a



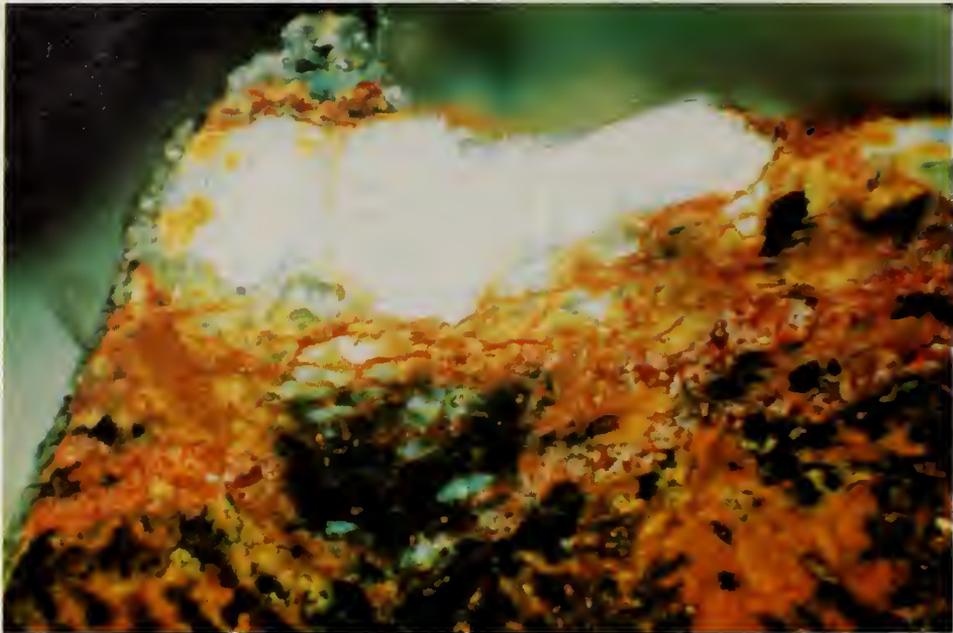
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k



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r

ELECTROCHEMICAL CORROSION AND REDUCTION

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The following text was adapted from tutorial lecture notes, prepared by Prof. Pourbaix expressly for the dialogue to accompany demonstration experiments. The figures are adapted from reference [1]<sup>1</sup> (except fig. 14, which is taken from ref. [2]). References [3] and [4] give further tutorial material. The demonstrations were performed by M. Jean van Muylder (also of CEBELCOR), who also made the oral narration at the dialogue.

Figure 1 indicates schematically some corrosion experiments demonstrated by M. van Muylder. In 1 to 12 (experiment a), an iron piano wire is immersed in water and in several solutions. In 1, distilled water corrodes iron in the presence of air, with the formation

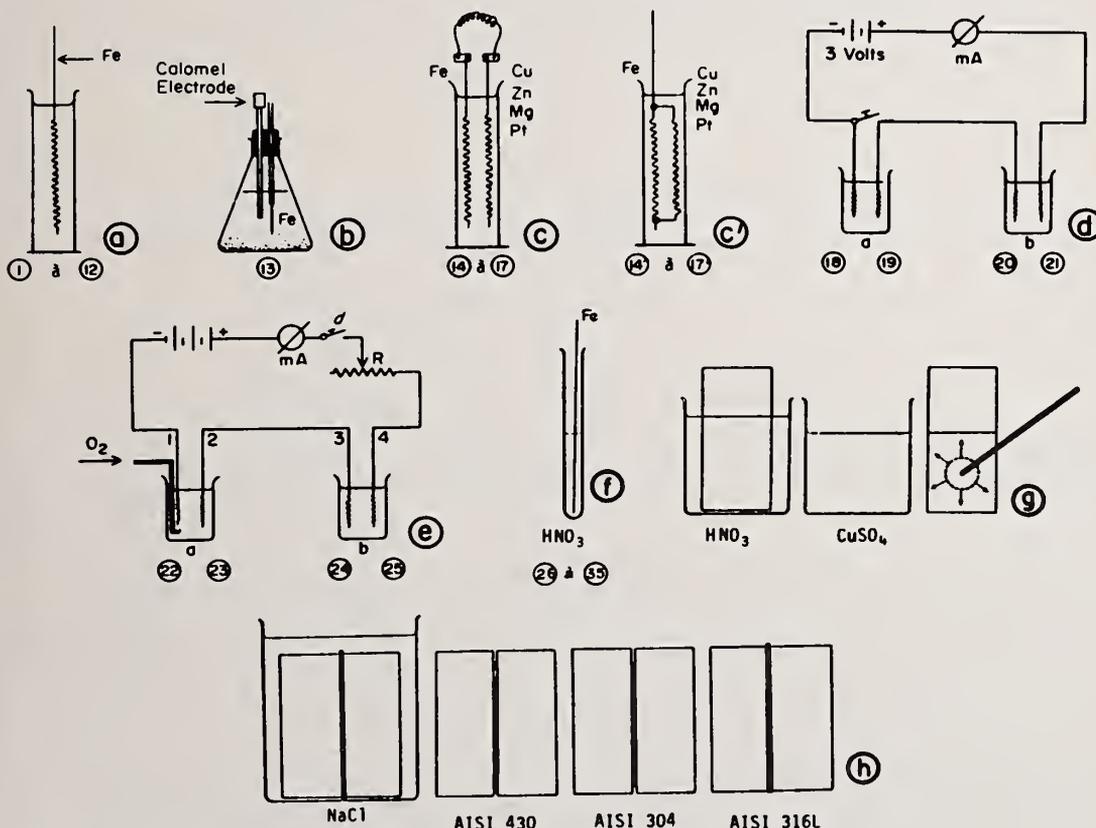


Figure 1. Demonstration experiments.

<sup>1</sup>Figures in brackets indicate literature references at the end of this paper.

of brown rust (ferric oxides). In 2 and 3, the corrosion velocity is enhanced by chloride or by sulfuric acid. In 4, the corrosion may be decreased by a reducing substance (bisulfite); the rust then becomes black magnetite. In 5 and 13 (experiment b), corrosion may be suppressed by caustic soda if air is present, but may be completely suppressed by chromate; but chromate may lead to severe pitting (7) if chloride is present and if chromate is not sufficiently concentrated ("dangerous inhibitor"). In 8 to 11, oxidants such as potassium permanganate and hydrogen peroxide may suppress any corrosion if their concentration is sufficiently high; on the other hand, they may very much intensify corrosion if their concentration is too low. In 12, it is seen that the Gaithersburg tap water is corrosive when stagnant; it is not corrosive when running. It is shown in 14 to 17 (experiment c) that the corrosion of iron is increased by contact with some metals, such as copper and platinum, but it is suppressed by contact with zinc or magnesium. In 18 to 21 (experiment d), an electric current is passed through two electrolysis cells, between two iron wires dipped in a 0.10 molar solution of sodium bicarbonate. Both the two negative electrodes and one of the positive electrodes (in the right-hand cell) remain uncorroded, but the other positive electrode (in the left-hand cell) corrodes heavily, although the metals, the solution, and the intensity of the current are the same in both cells. We have thus, under similar conditions, *anodic corrosion* in the left and *anodic protection* in the right-hand cell. The only difference between the two cells is that there is, on the left one, a switch which does not exist on the right one, and which was closed for a few seconds at the beginning of the experiment. A device similar to that described above is shown in 22 to 25 (experiment e). An electric current is passed through the same two cells, between the same iron electrodes dipped into the same solutions; but instead of having placed a switch on the left one, we are passing there some oxygen around the negative electrode. It is observed that under these conditions, both the two positive electrodes and one of the negative electrodes (in the right-hand cell) remain uncorroded, but the other negative electrode (in the left-hand cell) corrodes. As was the case in the previous experiment, the metals, the solution, and the density of the current are the same in both cells. We have here, under similar circumstances, *cathodic protection* in the right cell, and *cathodic corrosion* in the left one.

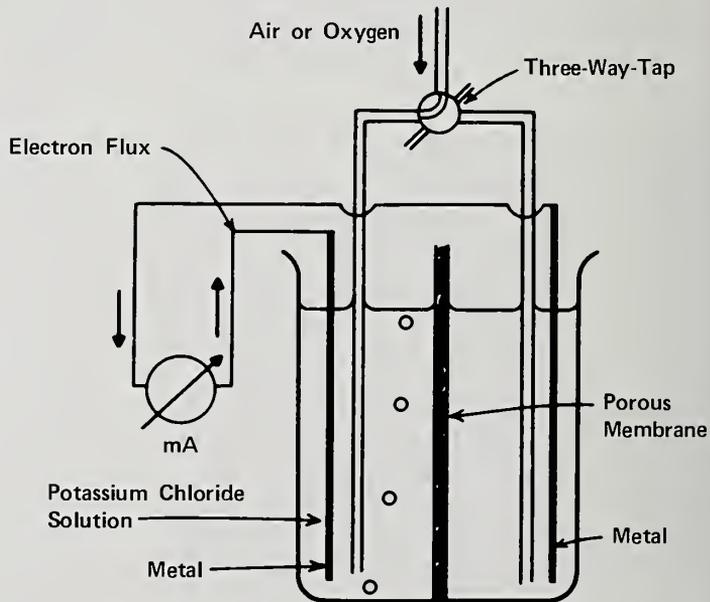


Figure 2. Production of a current by differential aeration (Evans experiment).

Figure 2 shows the famous historical experiment of differential aeration which was performed in 1923 by Ulick R. Evans. Two iron specimens connected through a galvanometer with center zero are placed in a solution containing some chloride and separated by a porous membrane. When air or oxygen is passed into the left hand compartment, electric current passes through the galvanometer, and it is evident that oxygen is promoting the corrosion of the iron in the *right* hand compartment, *where it is absent*. If the three-way cock is turned so that oxygen is passed into the right hand compartment instead of the left, the direction

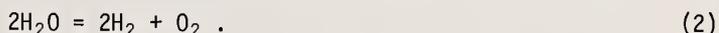
of the current progressively changes and, once again, corrosion of the iron is promoted in the compartment where oxygen is absent.

Such facts, as well as some others, sometimes funny ones, have often led to the opinion that corrosion phenomena are strange and often not understandable, and even do not obey the laws of thermodynamics. However, these facts may be easily explained if one considers that most of the reactions involved are not chemical, but rather electrochemical.

*Chemical reactions* are reactions in which only chemical species are taking part, for example the chemical dissociation of liquid water into  $H^+$  and  $OH^-$  ions:



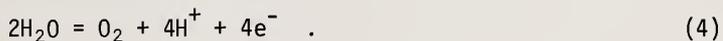
or the chemical dissociation of water into gaseous hydrogen and oxygen:



*Electrochemical reactions* are reactions in which not only chemical species, but also electric charges, *i.e.*, negative electrons,  $e^-$ , are taking part; for example, the reduction of hydrogen ions to gaseous hydrogen:



and the oxidation of water to gaseous oxygen:



The combination of these two electrochemical reactions leads to the overall chemical reaction of the dissociation of water (eq. (2) above)

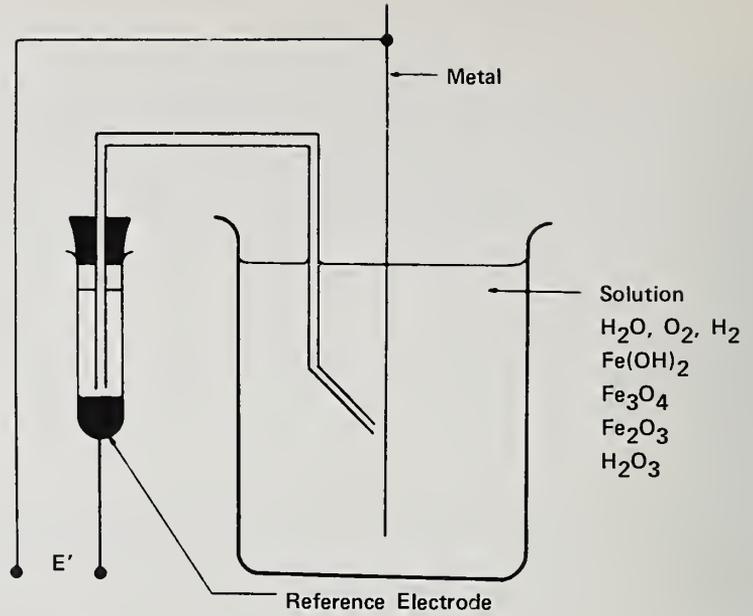


which may thus be performed either chemically or electrochemically.

Concerning the *chemical reaction*  $H_2O + H^+ + OH^-$  (1), it is very well known that, at 25 °C, an aqueous solution is neutral as far as its acidity and its alkalinity are concerned when its activities in  $H^+$  and  $OH^-$  are both equal to  $10^{-7.00}$  gram ions per liter, *i.e.*, when its pH is 7 (at 25 °C).

For studying *electrochemical reactions*, it is convenient to use the concept of *electrode potential*, which may be measured as shown in figure 3. If a metal is in contact with an electrolyte (for example an aqueous solution), its electrode potential is the electric potential of this metal measured versus the electric potential of a *reference electrode* (on which a reversible electrochemical reaction, such as  $H_2 = 2H^+ + 2e^-$  for a hydrogen electrode, or  $2Hg = Hg_2^{++} + 2e^-$  for a calomel electrode, is taking place under conditions of equilibrium), the solution in contact with the metal and the solution of the reference electrode being connected with an electrolytic siphon presenting no diffusion potential (for instance a gel of agar-agar saturated with potassium chloride). The value of this electrode potential is, in fact, a measure of the *oxidizing or reducing power of the interface* between the metal considered and the solution in contact with it, at an area close to the extremity of the siphon (salt bridge).

Figure 3. Measurement of the electrode potential.



The concepts of pH and of electrode potential may be represented as in figure 4, valid for 25 °C. Note the vertical line in this diagram at pH 7: along this line the solutions are neutral as far as their acidity and their alkalinity are concerned; on the left side of this line, where the pH is less than 7, the hydrogen ion concentration is higher than the hydroxyl ion concentration, and the solution is acid; on the right hand side of this line, where the pH is greater than 7, the hydroxyl ion concentration is higher than the hydrogen ion concentration, and the solution is alkaline.

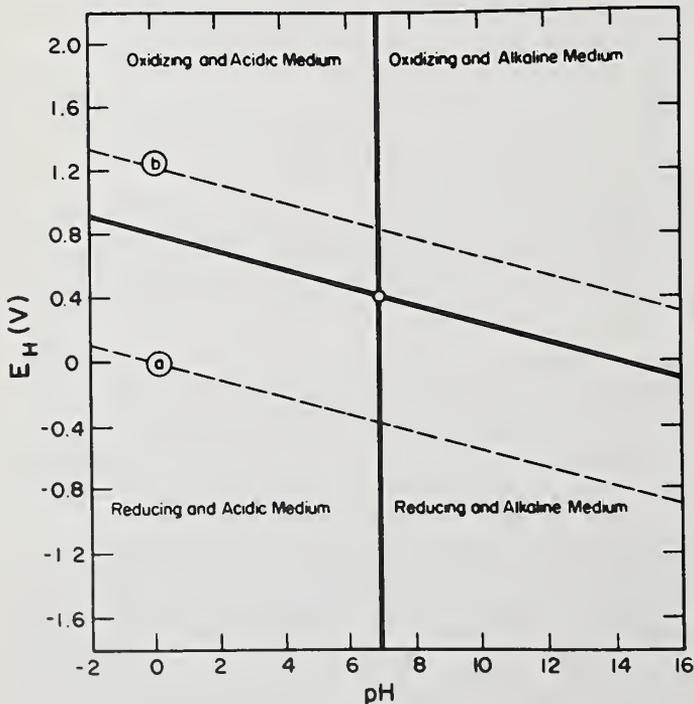


Figure 4. Acid, alkaline, oxidizing, and reducing media.

The oblique line of equation  $E = +0.813 - 0.0591 \text{ pH}$  v (SHE) (volts versus the standard hydrogen electrode) indicates the conditions where the partial equilibrium pressure in gaseous hydrogen is twice the partial equilibrium pressure in gaseous oxygen:  $P_{H_2} = 2P_{O_2}$ ; along this oblique line, aqueous solutions may be considered neutral as far as reduction and oxidation are concerned. The conditions of absolute neutrality, as far as acidity and alkalinity, and oxidation and reduction are concerned, is thus represented by the point of intersection of these two lines, whose coordinates are  $\text{pH} = 7$ ,  $E = -0.400$  volts (SHE). The area of figure 4 is thus divided into four regions: top left, oxidizing and acidic media; top right, oxidizing and alkaline media; bottom right, reducing and alkaline media; and bottom left, reducing and acidic media.

Along line a of figure 4, which represents the equilibrium conditions of reaction  $H_2 = 2H^+ + 2e^-$ , and whose equation is  $E = 0.000 - 0.0591 \text{ pH}$  volts (SHE), liquid water is, at 25 °C, in thermodynamic equilibrium with gaseous hydrogen under one atmosphere pressure; below this line a, water may be reduced to hydrogen, but this may not occur above line a. Along line b, which represents the equilibrium conditions of reaction  $2H_2O = O_2 + 4H^+ + 4e^-$ , and whose equation is  $E = +1.228 - 0.0591 \text{ pH}$  volts (SHE), liquid water is, at 25 °C, in thermodynamic equilibrium with gaseous oxygen under one atmosphere pressure; above this line b, water may be oxidized to oxygen, but this may not occur below line b. Between these lines a and b, water may be neither reduced nor oxidized and is thus thermodynamically stable under one atmosphere pressure. The area between lines a and b is thus the *area of thermodynamic stability of liquid water* at 25 °C and under one atmosphere pressure (fig. 5). And such areas of stability exist not only for liquid water but also for all the other species (solid, liquid, gaseous or dissolved) likely to occur in the presence of water.

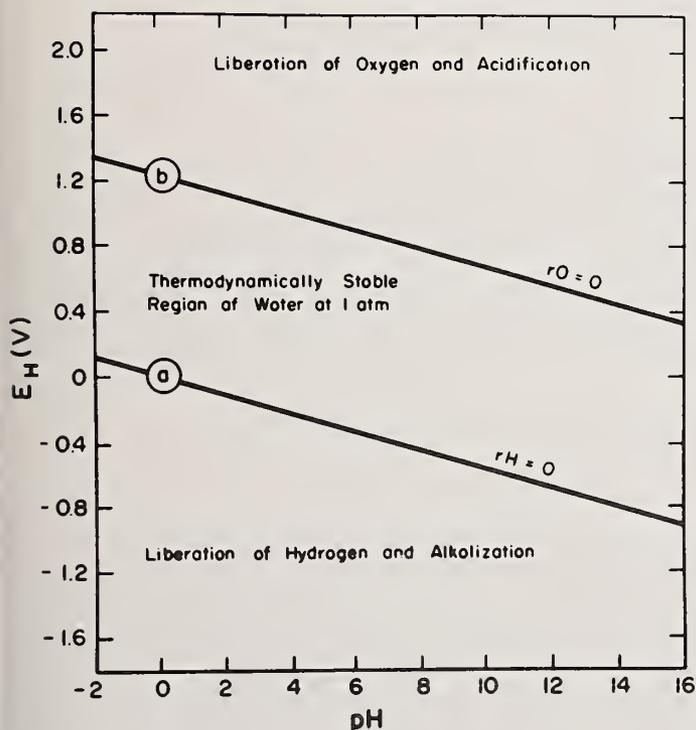


Figure 5. Region of thermodynamic stability of water under a pressure of 1 atmosphere at 25 °C.

Figure 6 shows a potential-pH diagram for the iron-water system. This figure shows that the oxidation of iron may lead to soluble products (green ferrous ions  $Fe^{++}$ , yellow ferric ions  $Fe^{+++}$ , and green dihydro-ferric ions  $FeO_2H^-$ ) or to insoluble products (white ferrous hydroxide  $Fe(OH)_2$  unstable to black magnetite  $Fe_3O_4$  and brown ferric oxide  $Fe_2O_3$  which may be variously hydrated and is the main constituent of rust). We shall consider, for fixing the idea, that iron is *corroding* in the presence of an iron-free solution where the quantity of solution which this solution may dissolve is greater than a given low value (e.g.,  $10^{-6}$  gram atom/liter, or 0.056 ppm), and that iron may be rendered *passive* if it

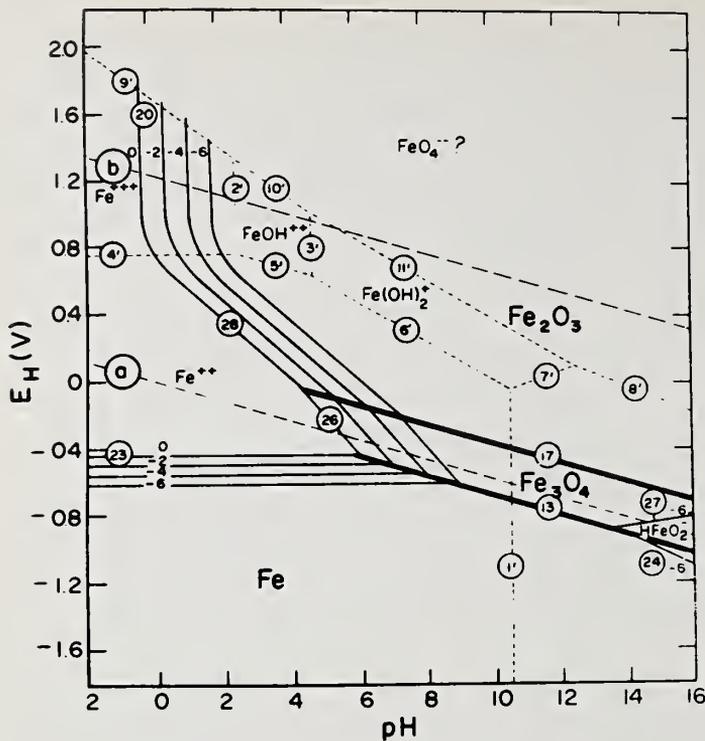


Figure 6. Potential-pH equilibrium diagram for the system iron-water at 25 °C.

becomes covered with a protective insoluble oxide or hydroxide (*e.g.*,  $\text{Fe}_2\text{O}_3$ ). Then the lines, which are drawn in figure 6 corresponding to a solubility of metal and its oxide equal to  $10^{-6}$ , delineate two areas where corrosion is possible (areas of corrosion), an area where corrosion is impossible because the metal is thermodynamically stable (area of immunity), and an area where passivation is possible (area of passivation). Figures 7a and 7b represent the theoretical conditions of corrosion, immunity, and passivation of iron, assuming that the insoluble oxides  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are sufficiently adherent and impermeable so that corrosion of the underlying metal is essentially stifled and that the metal is then "passive."

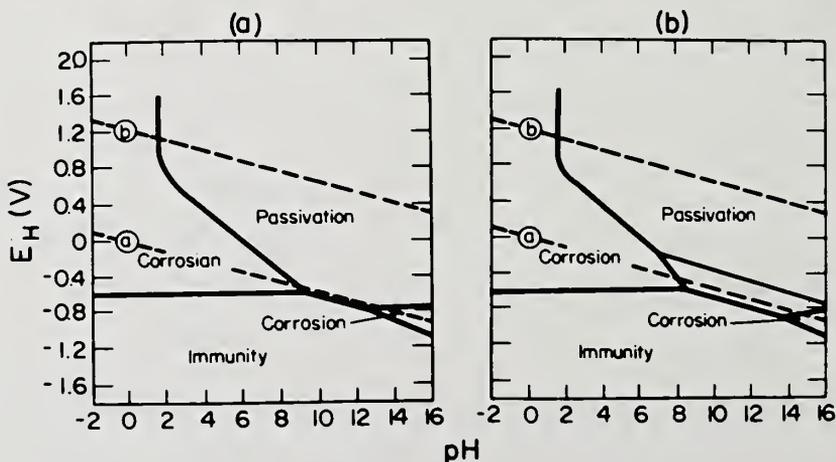


Figure 7. Theoretical conditions of corrosion, immunity and passivation of iron: (a) assuming passivation by film of  $\text{Fe}_2\text{O}_3$ ; and (b) assuming passivation by films of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .

If the pH and the electrode potential of the experiments of figure 1 are measured, and the results of these measurements plotted in figure 8, with notation made of general corrosion ( $\bullet$ ), of local corrosion ( $\circ$ ) and of absence of corrosion ( $\circ$ ), one observes that the conditions under which there is effective corrosion or absence of corrosion are in good agreement with the theoretical predictions. Especially this figure shows that an oxidizing action either protects iron, or causes increased corrosion, depending on whether the particular value of electrode potential of the metal falls within the area of passivation or not. Also the figure shows that the corrosion of iron in a degassed solution of caustic soda is due to an area of corrosion in alkaline solution free from oxidants. In experiment d, (fig. 1) the effect of the switch has been to move down the electrode potential of the passive anode 21 to the corrosion value (19). Also in experiment e, (fig. 1) the effect of bubbling oxygen has been to move the electrode potential of the immune cathode 24 to the corrosion value 22.

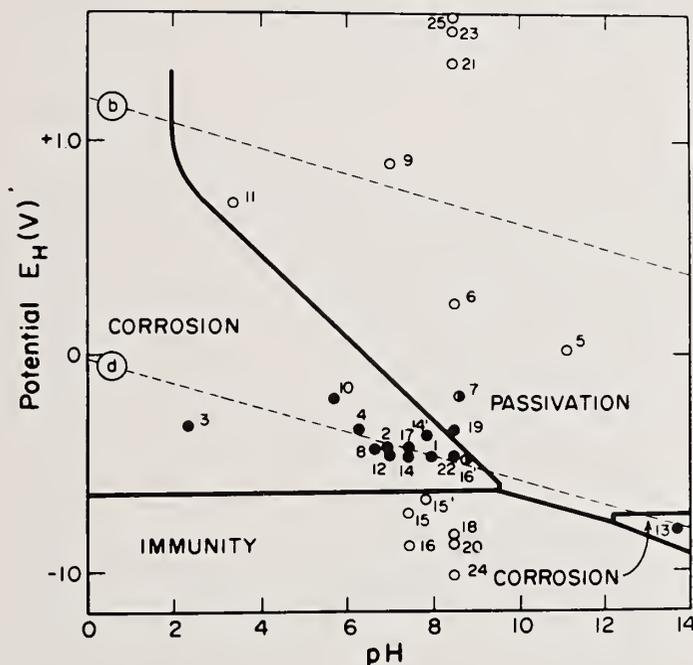
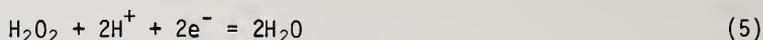


Figure 8. Theoretical and experimental conditions of corrosion,  $\bullet$ , and noncorrosion,  $\circ$ , of iron at 25 °C.

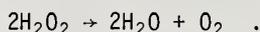
Many other, somewhat funny, experiments may be explained by such diagrams; notably, referring to figure 1, (experiment f): behavior of iron in nitric acid solutions of different concentrations. At low concentrations, considerable corrosion with continuous evolution of nitrogen and of oxides of nitrogen; at high concentrations, no corrosion; at intermediate concentrations, alternate periods of corrosion with gas evolution and of no corrosion. Experiment g: behavior of carbon steel successively immersed in a solution of concentrated nitric acid and in a solution of copper sulfate; the steel becomes passive, but its passivity is destroyed by a blow from a glass rod. Experiment h: "stainless" steel in the presence of a solution of sodium chloride. A simple rubber band may cut chromium steel AISI 430 and a chromium-nickel steel AISI 304 by crevice corrosion; AISI 316 steel, containing chromium, nickel, and molybdenum, is more resistant.

As has just been shown, the potential-pH equilibrium diagram for iron may help to understand the corrosion behavior of iron in the presence of different substances. Similarly, potential-pH equilibrium diagrams for these different substances may yield useful information on the behavior of these substances; we shall consider how in the behavior of hydrogen peroxide in experiments 10 and 11 of figure 1, and in the behavior of potassium permanganate in experiments 8 and 9.

Figure 9 represents the conditions of equilibrium for the reduction of hydrogen peroxide  $H_2O_2$  (and its ion  $HO_2^-$ ) to water and for the oxidation of hydrogen peroxide according to the reactions:



In the area below the family of lines (2,3), hydrogen peroxide may be reduced to water according to reaction (4); in the area above the family of lines (4,5), hydrogen peroxide may be oxidized to oxygen according to reaction (6); in the area between these two families, both reactions are simultaneously possible. This corresponds to the decomposition of hydrogen peroxide by the overall chemical reaction



Concerning, in figure 9, point 10 (dilute peroxide solution) and point 11 (concentrated peroxide solution), it is evident that point 10, for which there is corrosion of iron, is in the area of reduction of hydrogen peroxide to water. Then, the reaction of hydrogen peroxide in dilute solution results from a combination of the corrosion reaction  $Fe \rightarrow Fe^{++} + 2e^-$  with the reaction  $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$  corresponding to the overall reaction  $Fe + H_2O_2 + 2H^+ \rightarrow Fe^{++} + 2H_2O$ .

Point 11 (see figs. 8 and 9), for which there is no corrosion of iron, is in the area of double instability (or of chemical decomposition) of hydrogen peroxide; iron passivated

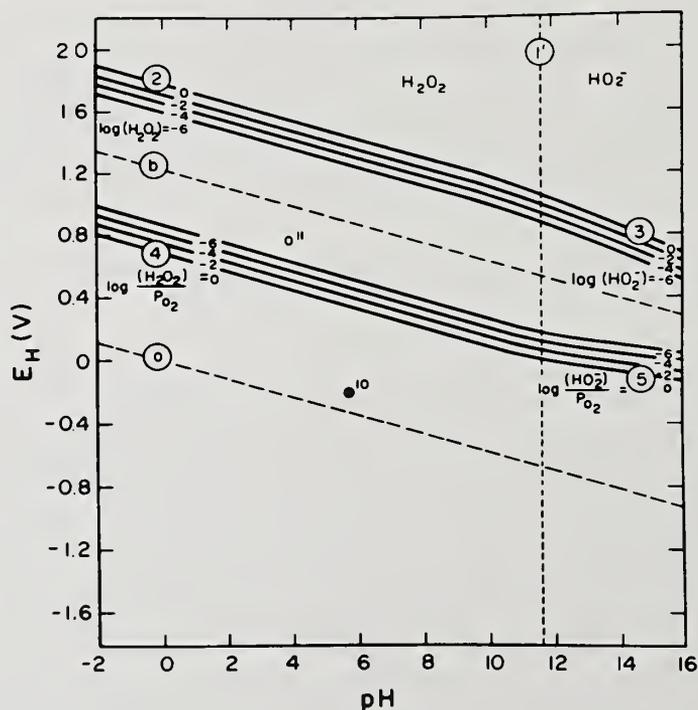


Figure 9. Equilibrium potential-pH diagram for the system  $H_2O_2$ - $H_2O$  at 25 °C.

by the formation of a film of  $\text{Fe}_2\text{O}_3$  there catalyzes the decomposition of hydrogen peroxide according to the reaction  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ . This reaction accounts for the evolution of oxygen which is effectively observed on the surface of passive iron in experiment (11).

Understanding the activating or passivating action of permanganate is based on the manganese-water equilibrium diagram (fig. 10). Comparing example 8 (dilute solution) and example 9 (concentrated solution), shown in this figure, it is observed that point 8, for which there is corrosion of iron, is in the area of stability of soluble  $\text{Mn}^{++}$  ions; and that the point 9, for which there is no corrosion of iron, is in the area of stability of insoluble manganese dioxide  $\text{MnO}_2$ . Thus the activating action of dilute permanganate solution results, from the combination of the corrosion reaction  $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^-$  with the reaction  $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O}$ , corresponding to the overall reaction  $2\text{MnO}_4^- + 5\text{Fe} + 16\text{H}^+ \rightarrow 2\text{Mn}^{++} + 5\text{Fe}^{++} + 8\text{H}_2\text{O}$ .

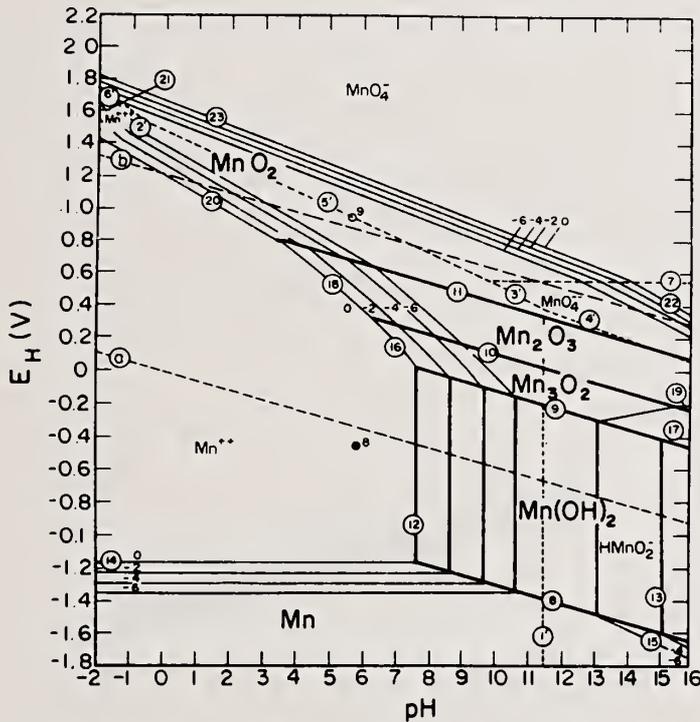


Figure 10. Equilibrium potential-pH diagram for the system Mn-H<sub>2</sub>O at 25 °C.

The passivating action of concentrated permanganate solutions is due to the combination of the passivation reaction  $2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$  with the reaction  $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ , giving the overall reaction  $2\text{MnO}_4^- + 2\text{Fe} + 2\text{H}^+ \rightarrow 2\text{MnO}_2 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ . Hence, the passive film is made up not only of iron oxide as is generally the case but of a mixture of iron oxide and manganese oxide.

\* \* \* \* \*

I am now coming to the corrosion behavior of artistic or architectural structures of carbon steels or of low alloy steels. Probably you all know that certain high strength low alloy steels HSLA of the ASTM type A-242, known in the USA mostly as Corten steels or Maraging steels, may sometimes resist atmospheric corrosion without being painted, due to the formation of a protective rust.

The first building made of such steel was in Moline, Illinois. Other structures built with this type of steel include the Picasso sculpture in front of the Chicago Civic Center.

Some difficulties are often encountered when steels are used, notably because they do not resist corrosion by stagnant water and because it usually takes several years before the rust is really protective; in the meantime severe staining may occur which can be unesthetic, particularly where the staining occurs on adjoining concrete or stone. Several architects may sometimes overcome these difficulties as has been done in Castel Romano, Italy, where a conveniently located metallic grate allows the staining solutions to be drained away out of sight.

Several problems are still to be solved before the scientific and technical aspects of these so called "weathering steels" may be considered as fully elucidated and mastered, mainly concerning an acceleration of the patina formation, which would avoid staining and its damaging consequences, and concerning the production of patinas of different colors. These are two problems we are working on in Brussels.

Figure 11 represents the influence of pH on the electrode potential of iron in the absence and in the presence of oxygen. One sees that oxygen may, according to the concentration, promote corrosion (area 2a) or stop corrosion (area 2b), so that the problem of forming quickly a protective patina on a low alloy steel is, in fact, the problem of increasing quickly and in a stable manner the electrode potential of the steel in the presence of rain water of pH about 6 to about +450 to +550 mV (SHE), *i.e.*, about +200 to +300 mV (SCE). We have been conducting extensive research work along these lines and the results seem to be satisfactory. It has already been possible to produce protective patinas within a few hours instead of a few years, thanks to some pretreatments, and to produce patinas of different colors. This work is presently funded within the frame of a joint program of the European Coal and Steel Community ESCC.

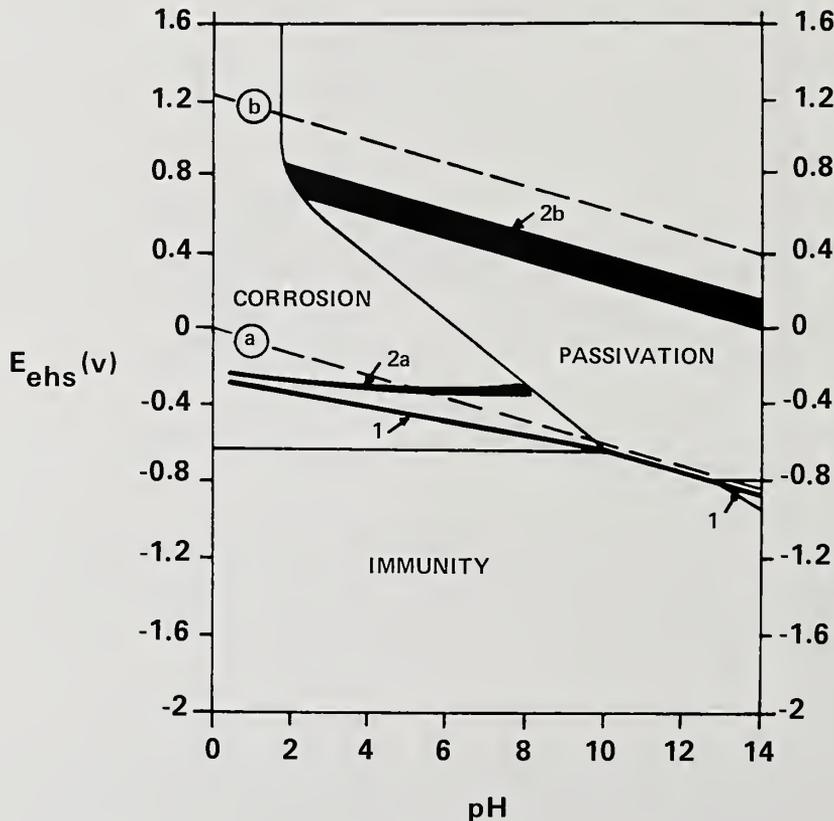


Figure 11. Conditions for immunity after general corrosion and for perfect passivity of in the absence of oxygen (line 1) and in the presence of oxygen (lines 2a and 2b).

Potential-pH equilibrium diagrams similar to the ones we have been showing for iron, hydrogen peroxide and manganese have been drawn for all the metals and metalloids, and notably for the metals which are of interest for metal artifacts: gold, silver, copper, tin, lead and aluminum. Figure 12 shows the diagram for the system copper-water. It may be seen that, in the presence of an atmosphere of absolutely pure air, practically free from both  $\text{CO}_2$  and  $\text{SO}_2$ , that is at pH about 6 and somewhat below the oxygen line  $b$ , the stable form of copper is the black cupric oxide  $\text{CuO}$  (tenorite); copper is thus covered with a black patina.

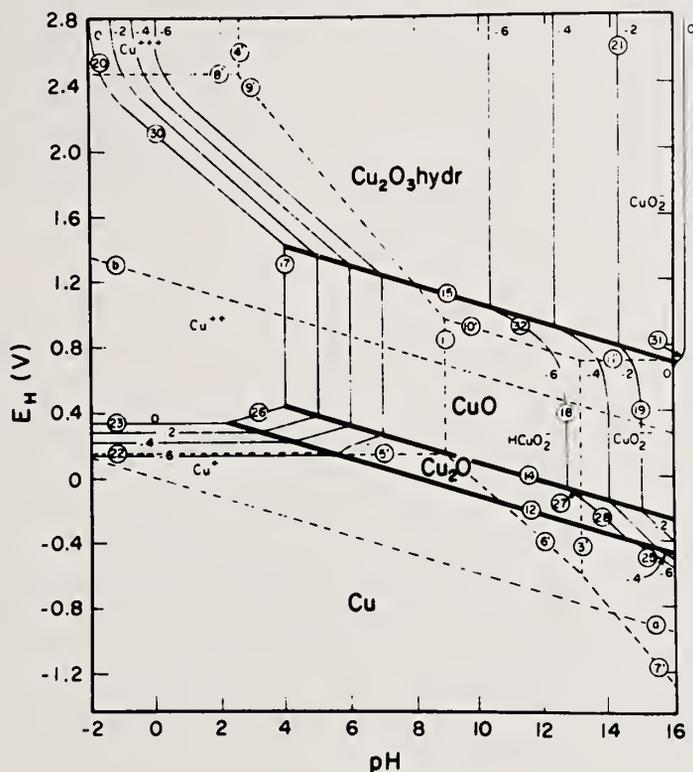


Figure 12. Potential-pH equilibrium diagram for the system copper-water at 25 °C.

Diagrams relating to the system  $\text{Cu-CO}_2\text{-H}_2\text{O}$ , such as those of figure 13, show that, if the amount of  $\text{CO}_2$  in an atmosphere exceeds about 0.04 percent, corresponding to a rainwater of pH about 5.8 containing about  $10^{-5}$  mole  $\text{CO}_2$  per liter (*i.e.*, about 0.4 ppm  $\text{CO}_2$ ), the patina may consist of green basic carbonate  $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$  (malachite) together with black tenorite. According to figure 13a, green malachite is the stable form of copper in an aerated city water of pH about 8 containing about 44 ppm dissolved  $\text{CO}_2$  (*i.e.*, about 10 French degrees of temporary hardness), and this is why, when used for delivery of cold city water, copper pipes are often internally covered with a green deposit of malachite.

Diagrams such as the one in figure 14 [4] relating to the system  $\text{Cu-SO}_3\text{-H}_2\text{O}$ , show the patina formed on copper in an atmosphere polluted by  $\text{SO}_2$ , may consist of black tenorite or of green basic copper sulfate  $\text{CuCO}_4\cdot 3\text{Cu}(\text{OH})_2$  (brochantite) depending on the amount of  $\text{SO}_2$ .

The diagrams of figure 15, relating to the system  $\text{Cu-Cl-H}_2\text{O}$ , show that, in the presence of an aerated and acid solution containing chloride, the stable form of copper is the basic copper chloride, gamma  $\text{CuCl}_2\cdot 3\text{Cu}(\text{OH})_2$  (paratacamite), which is the copper mineral existing in Chile in huge quantities. But where no oxygen is present, the stable copper derivative is the white cuprous chloride  $\text{CuCl}$  (nantokite). This occurs, for instance, at the bottom of



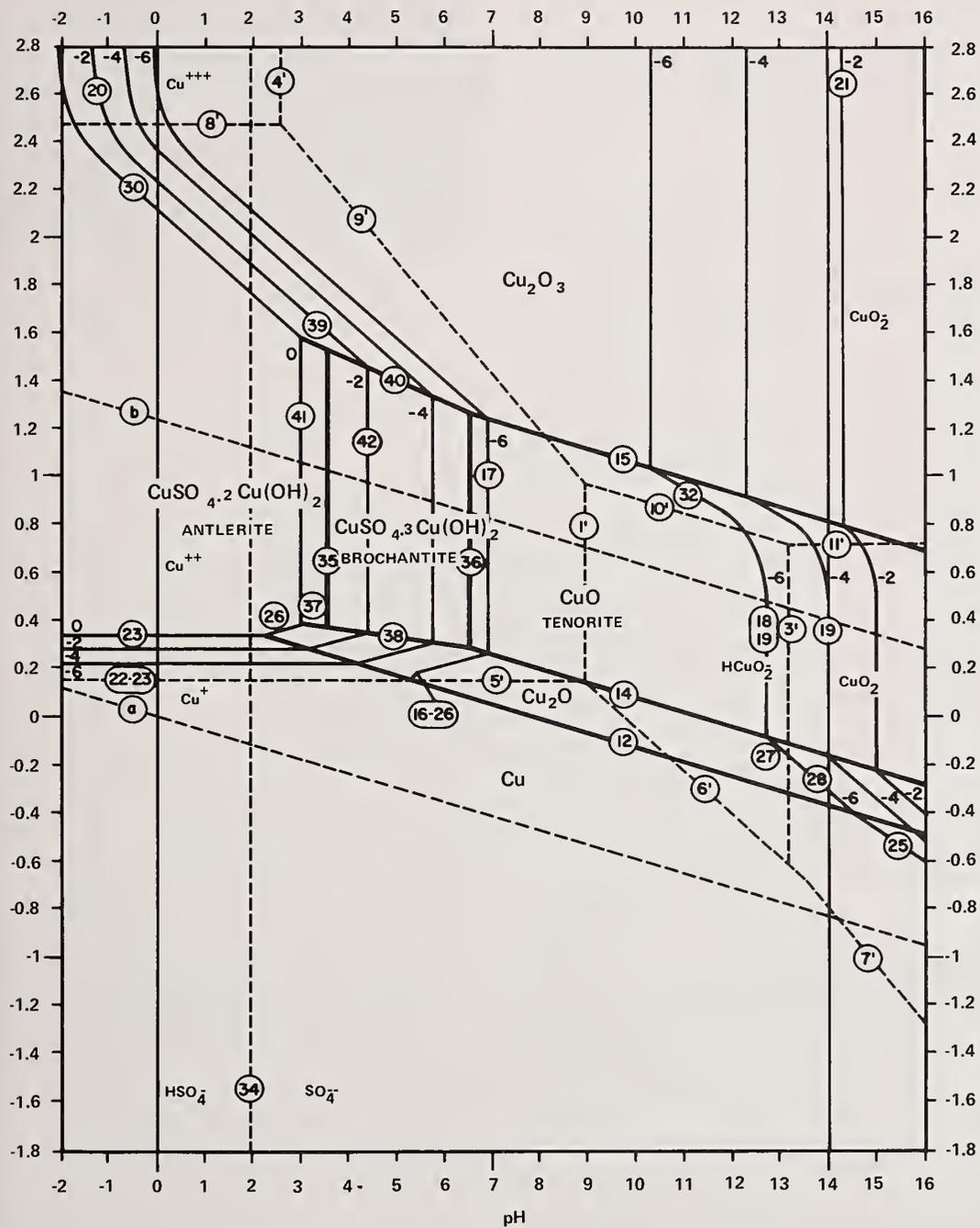


Figure 14. Potential-pH equilibrium diagram for the ternary system Cu-SO<sub>3</sub>-H<sub>2</sub>O at 25 °C for 10<sup>-3.24</sup> mole dissolved SO<sub>3</sub> per liter (46 ppm), ref. [2].

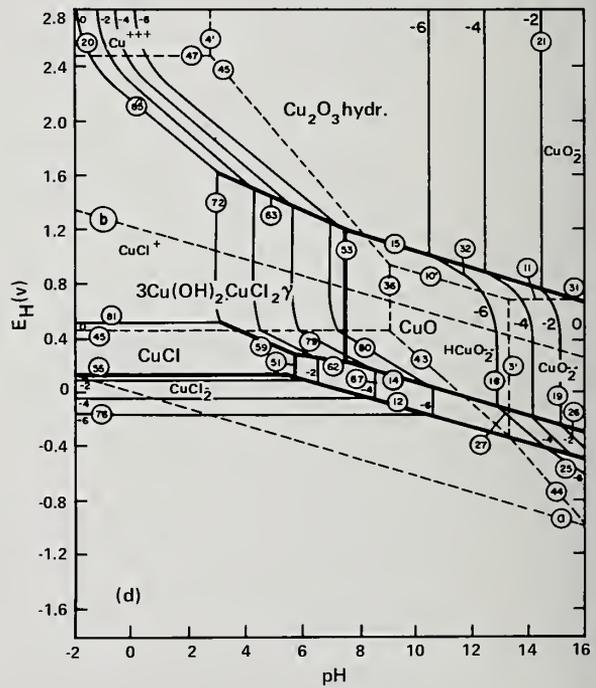
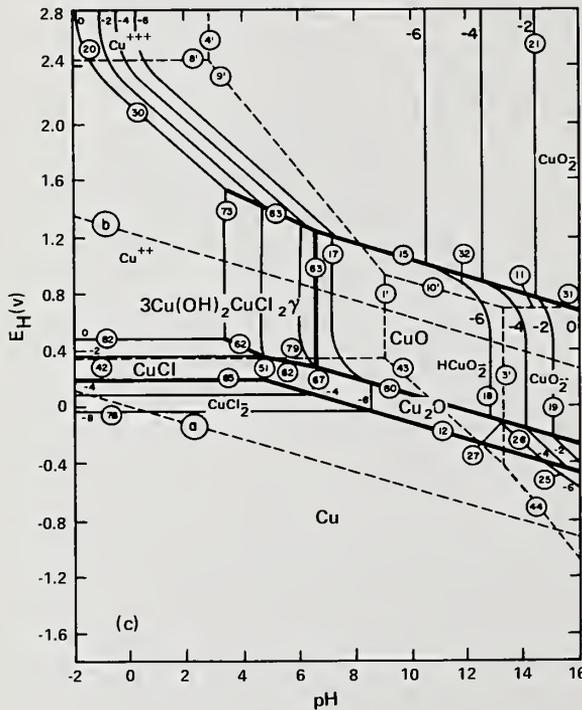
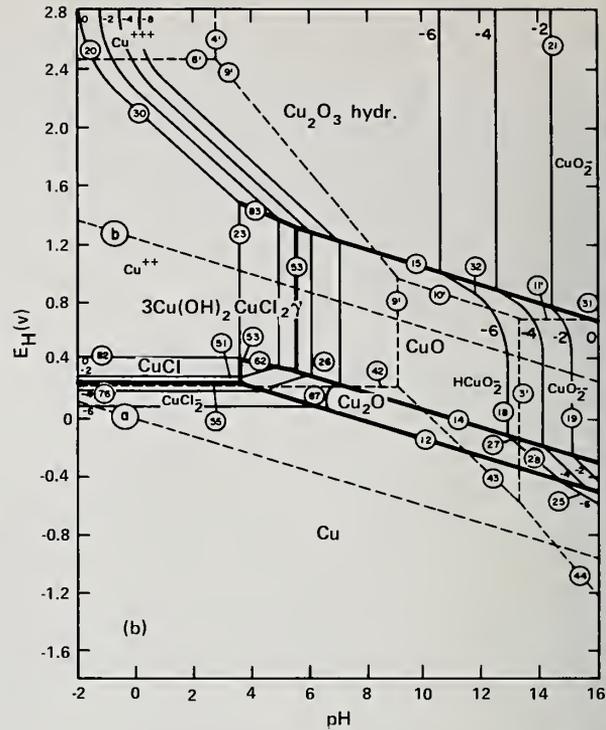
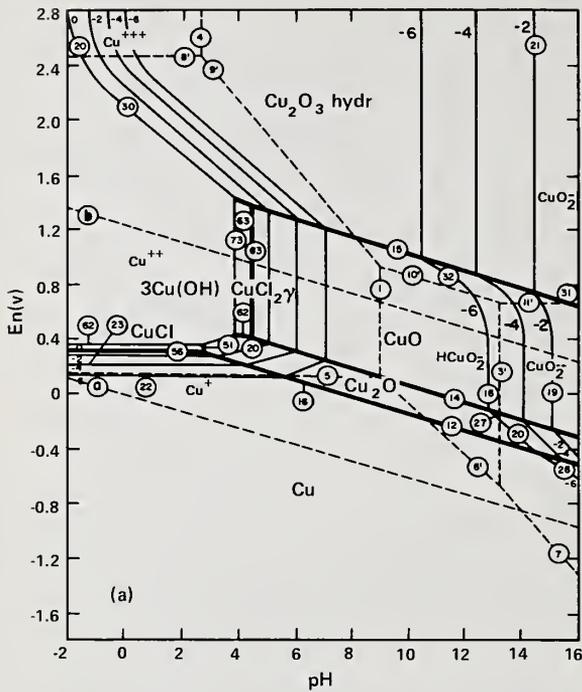


Figure 15. Potential-pH equilibrium diagrams for the ternary system Cu-Cl-H<sub>2</sub>O at 25 °C: (a) 10<sup>-3</sup> g-ion Cl<sup>-</sup>/L, (35 ppm); (b) 10<sup>-2</sup> g-ion Cl<sup>-</sup>/L, (3550 ppm); (c) 10<sup>-1</sup> g-ion Cl<sup>-</sup>/L, (3550 ppm); and (d) 1 g-ion Cl<sup>-</sup>/L, (35,500 ppm).

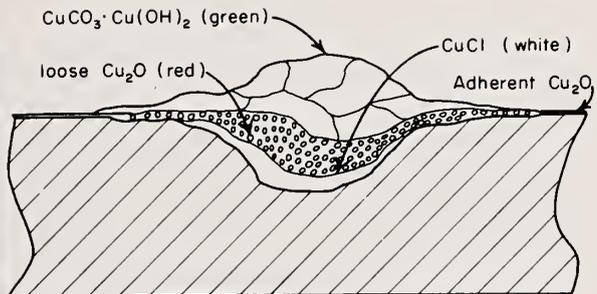


Figure 16. Copper pit in the presence of Brussels water. See color plate m. Cross section shows the presence of red  $\text{Cu}_2\text{O}$  and of white  $\text{CuCl}$  beneath a mushroom of green malachite.

dangerous pits sometimes formed inside copper tubes used for delivering cold Brussels water, shown in figure 16. At the bottom of a cavity containing loose red cuprous oxide  $\text{Cu}_2\text{O}$ , metallic copper is in contact with  $\text{Cu}_2\text{O}$  and with white cuprous chloride  $\text{CuCl}$ . The solution existing inside this cavity is thus saturated altogether with these two substances and the equilibrium conditions of the system at the bottom of the pit are approximately represented in the diagram (valid for  $10^{-2}$  g ion  $\text{Cl}^-$  per liter) by the point of intersection of these straight lines 12 (equilibrium  $\text{Cu}/\text{Cu}_2\text{O}$ ), 51 (equilibrium  $\text{Cu}_2\text{O}/\text{CuCl}$ ) and 55 (equilibrium  $\text{CuCl}/\text{Cu}$ ). The two coordinates of this point are, respectively,  $\text{pH} = 3.5$  and  $E = +270$  mV (SHE) (or  $+20$  mV(SCE)) and the amount of dissolved copper and chloride in the solution are, respectively, about 234 ppm Cu and 270 ppm Cl. As the reaction  $\text{Cu} = \text{Cu}^{++} + 2e^-$ , which may take place in this solution, is reversible, anytime the electrode potential really existing inside the cavity will be greater (more positive) than the equilibrium potential  $+20$  mV (SCE), dissolution of copper according to  $\text{Cu} \rightarrow \text{Cu}^{++} + 2e^-$  will proceed in the cavity, and this means corrosion. On the contrary, anytime the electrode potential inside the cavity will be lower (more negative) than  $+20$  mV (SCE), redeposition of metallic copper will occur according to  $\text{Cu}^{++} + 2e^- \rightarrow \text{Cu}$ , and this means stifling of the corrosion. There is usually a diffusion potential of about 80 to 150 mV between the solution inside the cavity and the bulk of the water; when measured outside the cavity, which is the usual practice, the critical value of electrode potential above which copper pits will develop is thus about  $+100$  to  $+170$  mV (SCE). And this seems to be true, not only for the localized corrosion of copper, but also for the localized corrosion of copper alloys, such as bronzes, brasses and copper-nickel alloys.

Thus, when copper and copper alloys are in contact with an aggressive water, the development of pits and of other localized corrosion essentially depends upon the value of the electrode potential of the metal in the presence of the water: any substance whose electrode potential in this water is higher (more positive) than  $+100$  to  $+170$  mV (SCE) (platinum, gold, carbon ...) may promote pitting; any substance whose electrode potential will be lower than  $+100$  to  $+170$  mV (SCE) (silver, tin ...) may not promote pitting; substances which have a significantly lower electrode potential (zinc) may not only *not* promote pitting, but also stifle previously existing pits.

Thus, reduction of corrosion products formed inside copper pits may be promoted by any treatment which will depress the electrode potential inside pits below about  $+20$  mV (SCE), and preferably lower than this. This may be achieved either by a reactive anode (e.g., zinc) or by an impressed current. Another way to stifle pits is to use corrosion inhibitors (e.g., benzotriazole) which might render the corrosion reaction irreversible.

Due to lack of time, the essentials of electrochemical kinetics have not been considered in the present conference; needless to say, they should be considered with the greatest care.

## References

- [1] Pourbaix, M., *Lecons en Corrosion Electrochimique*, 2nd French Edition (CEBELCOR, Brussels, 1975).
- [2] Pourbaix, M., Some applications of potential-pH diagrams to the study of localized corrosion, Palladium Award Lecture, *J. Elec. Soc.*, 133, No. 2 (1976).
- [3] Pourbaix, M., *Lectures on Electrochemical Corrosion*, translated from the French by J. A. S. Green, R. W. Staehle, ed., foreword by Jerome Kruger (Plenum Press, New York, and CEBELCOR, Brussels, 1973).
- [4] Pourbaix, M., and van Muylder, J., *Laboratory Experiments for Lectures on Electrochemical Corrosion* (CEBELCOR E. 65, 1967).

## Discussion

*C. Peterson:* Is the selection of material for anodes critical in attempting to impose cathodic protection on iron artifacts stored in an aqueous solution?

*M. Pourbaix:* If one uses an outside source for the electrical current, one may use any metal for the anode as long as one calculates the electrode potential correctly.

*E. V. Sayre:* If one has a copper object that is selectively corroding in a number of small pits over its surface, are there any practical methods for inhibiting the corrosion by locally reducing the electrode potentials within the pits?

*M. Pourbaix:* There is a very simple method. If you place a copper rod so that it touches the bottom of the pit, you enforce into the bottom of the pit an electrode potential that is low enough to inhibit further dissolution. One may also use a zinc electrode in the vicinity of the pit but one must be careful that the current flow is between the zinc and the corroded area. As in the case of iron, that was just discussed, one may also apply an external source. Finally, another way to do this is with the use of inhibitors such as benzotriazole.

*G. M. Ugiansky:* I was wondering about the Picasso sculpture in Chicago. I heard several years ago that they were having trouble getting the patina or rust finish on the underside of the sculpture. They were having to hose the underside to get it to discolor. Has that type of problem been solved?

*M. Pourbaix:* I must confess that I have never made measurements on the Picasso monument. We think that to have a good patina you have to have a high temperature, so you need sun. Some research has been done for using C.D. steel for the lower part of cars. According to my experience, the sun only comes to this part when the wheels of the car are turned up. So I do not think that this is a good way to use these steels. So, too, at the bottom of the Picasso monument the temperature has probably not been high enough. But I have no opinion, as I only saw the structure at the beginning, so I don't know how it is now.

I may say this, we have had great success with these steels and I am very much in favor of promoting these steels. There have been, however, many failures because people think that you can use these steels *just* like other steels. This is not true. These steels have a bright future but one should realize that it is a special material that has its own character.

*Unidentified:* I would like to correct one impression. The Picasso monument never had a problem. It weathered very nicely. There was, what is called the "Abraham Lincoln Oasis," a restaurant over a highway on the south side of Chicago. The architect wanted to hose it down daily in order to develop the color in time for a dedication.

## CORROSION PRODUCT CHARACTERIZATION

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The world-wide costs of corrosion, direct and indirect, are enormous, measurable in many billions of dollars annually. Corrosion scientists and engineers are professionally involved in a continuing struggle to reduce industrial corrosion of metallic materials of construction and to preserve metals<sup>1</sup> from the many forms of corrosion attack to which they are susceptible. While much of their work involves materials such as steel, stainless steels, nickel-base and high alloy materials, etc., for which the conservator has little concern, the techniques employed in corrosion research and surface characterization and many of the corrosion phenomena studied can find direct application in the study and preservation of museum material.

The examination of corrosion products is particularly important, because they are present on all metals. Gold is the single exception, thermodynamics indicating that gold oxide will not form at room temperature. Oxidic corrosion products exist in a variety of states. They can provide corrosion protection as thin, invisible barrier films on stainless steels, chromium, aluminum, titanium, and other "corrosion-resistant" metals. They can also form unhindered, entirely consuming a metal as it reverts back to an ore or to a nonmetallic state. Much ancient iron and bronze has been found in this condition, the artifacts totally converted to oxide.

It is, of course, obvious to the corrosion scientist that conservators and archaeologists have a much narrower spectrum of interests in metals and their corrosion products. The number of metals in use prior to the 19th Century was relatively small and corrosion occurred in environments, air, soil and water (including marine), which were relatively pure by our present standards.

In an early (1808) essay on conservation of medals, John Pinkerton [1]<sup>2</sup> wrote:

*Nothing contributes so much to the conservation of brass or copper coins as that fine rust, appearing like varnish, which their lying in a particular soil occasions. Gold admits no rust but iron mould, when lying in a soil impregnated with iron. Silver takes many kinds; but chiefly green and red, which yield to vinegar. For in gold and silver the rust is prejudicial and to be removed; whereas in brass and copper it is preservative and ornamental.*

This statement is an echo of the ancients who recognized that heavy corrosion product layers on copper alloys had the dual function or circumstance of being protective as well as decorative. There was a Greek phrase<sup>3</sup> which termed patina "the flower of brass."

The aesthetic appreciation of a fine patina or a "noble patina," as Gettens [2] spoke of it, remains with us today; but perhaps less so with the corrosion scientist who finds in these corrosion product layers the opportunity to study and analyze a "corrosion test

<sup>1</sup>The term metals is used here to include all alloys.

<sup>2</sup>Figures in brackets indicate literature references at the end of this paper.

<sup>3</sup>ανθος χαλκου

specimen" that has been exposed for centuries or even millenia. It is this time factor which cannot be duplicated in any accelerated laboratory corrosion testing that makes the study of ancient metals so fascinating. It is somewhat analogous to the comparative study (for the physical metallurgist) of terrestrial steel with meteoritic iron-nickel alloys whose cooling rate is measurable in millions of years (and here also the study of oxidation and corrosion products is being undertaken).

In figure 1 is shown a scheme which one investigator, J. B. Cotton [3], devised 20 years ago for the examination of corroded metal specimens. This scheme is perfectly valid and usable today. But new developments in instrumental techniques for surface characterization have, in effect, made obsolete the employment of destructive, wet chemical methods of analysis. Corrosion researchers can easily, quickly, and nondestructively obtain compositional data on metals and alloys and their environmental reaction (corrosion) products.

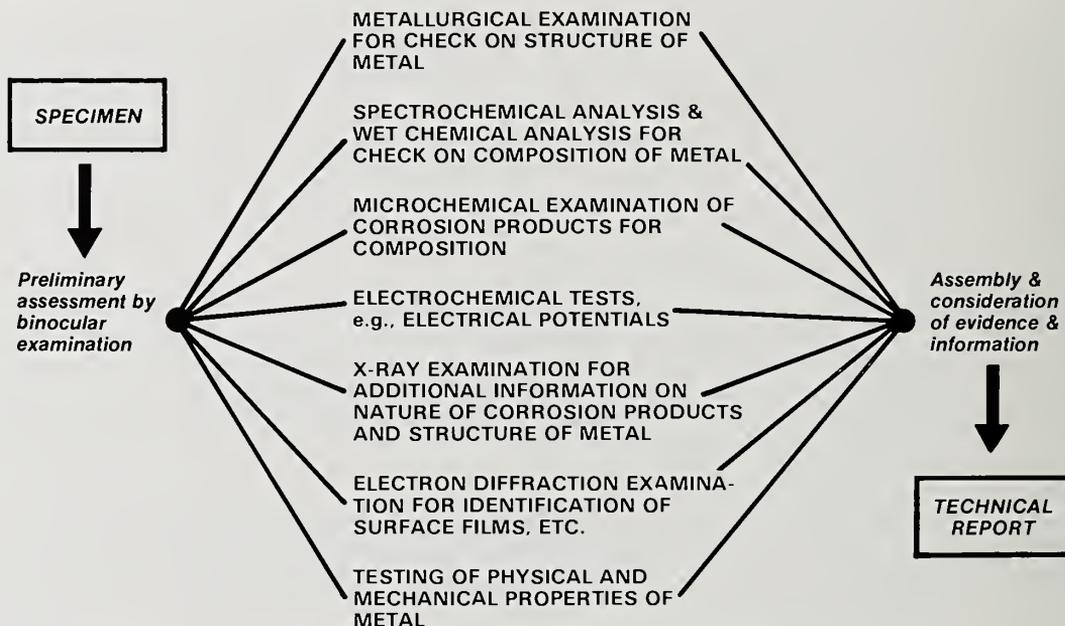


Figure 1. Scheme for laboratory examination of corroded specimens.

More recently (in 1973), the National Association of Corrosion Engineers issued Standard (RP-01-73), Recommended Practice - Collection and Identification of Corrosion Products [4]. It provides guidelines in the methods and techniques of collecting samples of corrosion products and describes some procedures which can be used to analyze and identify the corrosion products. In intended engineering applications, the information is used to resolve a corrosion problem by identifying: (a) the nature and type of attack, (b) the metal or metal phase that is attacked in the alloy, and (c) the environmental conditions that contributed to the corrosion. Obviously, the conservator is interested in similar answers relevant to corroded and oxidized artifacts. In Section 5 on Analysis and Identification Procedures, the Standard covers the following eleven techniques:

- Microscopy (optical, electron and scanning electron)
- X-ray diffraction
- X-ray emission spectrography
- Electron probe microanalysis
- Spark source mass spectrometry
- Optical emission spectroscopy
- Infrared spectroscopy

- Ultraviolet and visible spectroscopy
- Flame spectroscopy
- Differential thermal analysis
- Wet chemical analysis.

A check list for collecting and analyzing corrosion products is included as well as a bibliography on analysis and identification techniques. Altogether, this Standard is a very useful and valuable publication.

Diagnosis of the causes of corrosion has been greatly facilitated as has the development of new information on corrosion mechanisms. A discipline of surface science has in fact come into being in the last 20 years because the advent of ultrahigh vacuum techniques led to a "panoply of electron, ion and x-ray spectroscopic techniques capable of characterizing solid surfaces" [5]. Several of these new tools for surface analysis are summarized below.

1. *Auger Electron Spectroscopy (AES)* employs a spectrometer which measures the energies of secondary electrons, "Auger electrons," ejected from the specimen surface as a result of electron bombardment. The Auger electrons originate in the top 2 to 10 monolayers of the surface and have energies characteristic of their parent atoms. The amplitude of an Auger peak is essentially proportional to the number of the atoms of the specific element present in the area of the specimen surface being analyzed (by a 1  $\mu\text{m}$  diameter beam).

A further development in AES has been made in very recent years which employs a scanning beam as the electron probe. The Scanning Auger Microprobe (SAM) provides Auger images which show elemental distribution over a few square microns in a depth of 10  $\text{\AA}$  more or less. It is an extremely high sensitivity technique and can identify elements present in quantities down to 0.1 percent equivalent monolayer.

It should be noted that AES (and SAM) are analogous to the much older electron microprobe technique in which wavelength dispersive x-ray fluorescence is employed to obtain an elemental analysis of about a 1 cubic micrometer volume element of a specimen surface. The AES technique is of course much more sensitive to chemical species located in the top several atomic layers of the surface. Use of sputter-etching (beam of inert gas ions) to clean surfaces and to permit analysis in depth is essential if unambiguous data are to be obtained.

2. *Electron Spectroscopy for Chemical Analysis (ESCA)* utilizes x-ray photons to ionize inner core electrons whose ejection energy corresponds to that of the photon minus the electron binding energy. The spectrum of ejected photoelectrons is used to identify the elements in the surface. It can also provide additional information on the chemical bonding states present in the surface. It is again a technique highly sensitive to surface composition (in the top 2 to 10 monolayers). An area of about 1 mm is irradiated with an x-ray beam. Since the x-ray beam cannot be used in a scanning mode, the ESCA technique does not permit spatial resolution or element mapping, as do the electron beam spectroscopies.

3. *Secondary Ion Mass Spectrometry (SIMS)* represents a technique developed within the last several years in which an ion beam is used to probe the specimen surface. Secondary ions sputtered and eroded from the surface are collected and analyzed with a mass spectrometer. The SIMS technique has very high sensitivity; its depth of analysis can be the equivalent of 1 to 2 monolayers. It can detect hydrogen and distinguish isotopes. For certain samples, SIMS can provide very useful information on chemical bonding when characteristic fragment ions from known compounds or polymers can be observed.

4. *Ion Scattering Spectrometry (ISS)* examines the energies of the reflected ions (with the same beam that is used in SIMS). These energies are a function of the scattering angle and the masses of the incident ion and the ion from which it recoils. The ion beam diameter is 100  $\mu\text{m}$  for both SIMS and ISS, but the latter spectroscopy provides an energy spectrum in which there is only one peak for each surface element. While this can make the interpretation of the spectra easier, two major problems are peak overlap in a chemically-complex surface and the inability of the technique to provide any information on chemical bonding.

5. *Laser Microprobe Spectrometry (LMS)* employs a combination of mass spectrometer and pulsed laser for pyrolysis studies. The technique is rapid and reproducible. The laser beam diameter can be as fine as 20  $\mu\text{m}$ ; the pulse duration is 200  $\mu$  and a heating rate of about  $10^{10}$   $^{\circ}\text{C}/\text{s}$  can be achieved. The technique is sensitive to inhomogeneities in solids (which can be sighted through a microscope on which the laser is mounted) and composition vs. depth profiles may be obtained by pulsing the same spot. It has been found that a 0.85 J pulse will vaporize  $1.87 \times 10^{-5}$  gram of carbon [6].

(Reference at this point should be made to optical laser microprobe in use in the Museum of Fine Arts Research Laboratory for chemical analyses [7]. This system provides emission spectrographic analysis of material vaporized from a crater 50 to 80  $\mu\text{m}$  in diameter and 80 to 100  $\mu\text{m}$  deep.)

All of these techniques have their strengths and weaknesses. While they are both competitive and complementary in their characteristics, no single technique can completely characterize a surface (or a corrosion product). It is necessary to select the one technique or combination of several techniques which will provide adequate information on the specific problem of the moment.

Three major references pertinent to choosing analytical techniques for metallurgical (artifact) analysis are: *Archaeological Chemistry*, C. W. Beck, Editor [8]; Kruger and Frankenthal's chapter on Oxidation and Corrosion, in Vol. IV of *Techniques in Metals Research*, R. F. Bunshah, Editor [9]; and Authenticity in Art by Stuart J. Fleming [10]. These references present a comprehensive picture of the use of analytical techniques by archaeologists, conservators and corrosion scientists in metallurgical analyses and corrosion product characterization.

#### X-ray Diffraction

The importance of x-ray diffraction techniques and analysis remains as important as ever in the structural identification of crystalline compounds and metallic lattices. In his 1956 article, Cotton [3] discussed how a corrosion product should be carefully removed for microchemical and x-ray examination with precautions being taken to avoid any inclusion of basis metal. The x-ray diffraction examination provides the possibility of determining what the compound species is whose composition is known from chemical analysis.

Vaughan [11] has pointed out the importance of combined use of research tools in the analysis of corrosion products. Phase analysis by x-ray or electron diffraction cannot be overemphasized as a necessary procedure in corrosion research and corrosion product characterization.

Kruger and Frankenthal [9] also provide a good discussion of the identification and measurement of the amount of corrosion products by the x-ray diffraction powder method. Barker has stated that it has been the "experience at the British Museum Research Laboratory that a very good all-round solution to the problems arising from a very wide range of archaeological material is provided by a combination of x-ray diffraction and spectrochemical techniques" [12]. Barker points out very rightly that mixtures of crystalline compounds can provide patterns that are too complex to resolve satisfactorily and that sampling is a very important part of both x-ray and spectrographic analysis. It is wise to use a binocular microscope to separate obvious phases in a complex mixture or corrosion product so that each can be analyzed separately. On valuable objects, it is usually possible to do this using microtools and careful technique such that no visible damage will be done to the object. By combining a series of samplings from a corroded or patinated artifact, a qualitative analysis and a positive structural identification of all of the major constituents can be made. In most cases, the knowledge of composition and of structure of the object can determine authenticity or answer a problem in conservation.

#### Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDXA)

It has been the writer's experience that structure-composition data on corrosion products is very conveniently attainable by applying standard metallographic techniques,

including x-ray diffraction, using a scanning electron microscope equipped with an accessory system for energy-dispersive x-ray analysis.

The SEM did not become a commercial instrument until 1965, but it has received an extraordinarily favorable acceptance as a tool for metallurgical research. It has become (perhaps more so than any other analytical instrument utilizing an electron beam probe) an extremely versatile apparatus amenable to a total systems approach to instrumentation. Its potential application to the study of archaeological material was recognized in 1970 by Brothwell [13] who considered this an important new field.

Figure 2 shows in simple fashion the variety of signals generated in an SEM when a finely focused beam (100 Å diameter) of electrons is scanned over a specimen surface. Each of the electron signals can be used to "image" the sample so that it can be observed visually on a cathode-ray tube (CRT), photographed, or recorded on video tape. Resolution with secondary electrons is commonly better than 100 Å with the newer SEMs. The use of backscattered electrons is desirable when there are compositional differences in the area being imaged. In this case, contrast in the topographic image is enhanced by an atomic number effect.

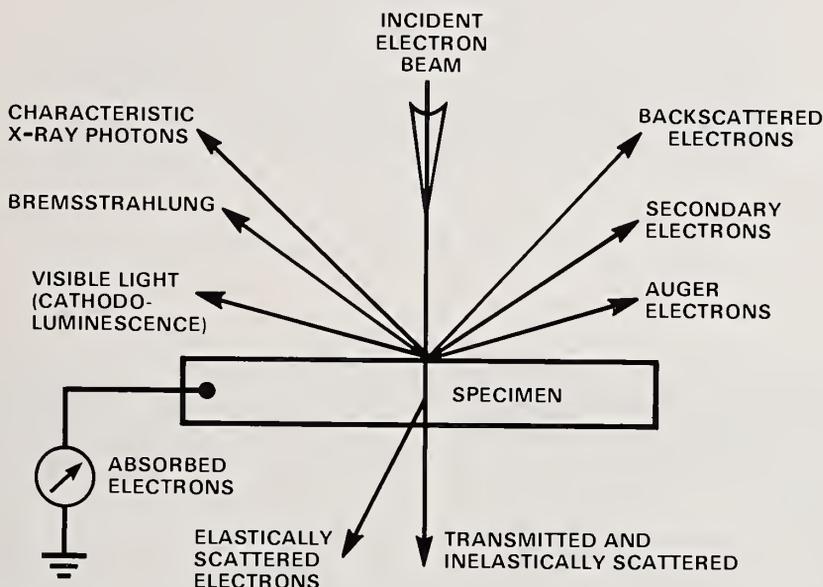


Figure 2. Signals generated in the scanning electron microscope.

With x-ray spectrometers, either energy-dispersive (ED) or wavelength-dispersive (WD), attached to the SEM, the x-ray distribution image becomes a useful method of presenting x-ray analytical information. In practice, as the electron beam scans the surface, the spectrometer is set at the particular element of interest. Whenever, at that energy or wavelength, an x-ray is detected, a dot is brightened at the corresponding point on the display CRT of the SEM. The image that results corresponds spatially to the other (electron) images of the surface but with the density of dots in each area related to elemental abundance. It should be pointed out, however, that the x-ray distribution image gives only very qualitative information on element concentrations and cannot be used when elements are present in low concentration in a surface. More commonly, a standard spectral analysis will be run, requiring no more than 5 minutes by energy-dispersive x-ray analysis (EDXA), and each peak on the energy spectrum separately identified for the element and the specific x-ray emission line producing it. It is, of course, also possible to get integrated counts of all the x-ray emissions in a sample, to photograph the data on a display CRT or to get a computer printout of the tabulated data. Hanson at the Winterthur Museum has carried out pioneering work on the quantitative elemental analysis of art objects by energy-dispersive x-ray fluorescence spectroscopy [14].

On the question of spectral resolution, the wavelength-dispersive (WD) method is clearly superior. For example, the sulfur K and lead M lines at 2.31 and 2.34 keV, respectively, cannot be resolved by EDXA. It would seem that an ideal combination system would be to have an SEM with both types of spectrometers. The WD spectrometer would be used for detailed quantitative work where its high resolution, high peak-to-background ratio and ability to detect light elements (from Be, atomic number 4 upward; the ED system starts at Na, atomic number 11) would provide better performance. This technique, scanning electron probe microanalysis, is discussed by Heinrich [15].

## Corrosion Products on Copper and Its Alloys

In April 1959, the National Association of Corrosion Engineers (NACE) issued a Technical Committee Report, Publication 59-13 on "Identification of Corrosion Products on Copper and Copper Alloys" [16]. This report should be of interest to conservators and archaeologists since it gives a description of microchemical analytical methods by which both soluble and insoluble constituents can be identified. Constituents discussed in detail include oxides, chlorides, sulfates, sulfides, carbonates, silica, calcium, magnesium, sodium, ammonia, and metal constituents of the material being examined. Also a method for spectrographic examination of corrosion products is considered briefly.

In the natural patination of unalloyed (commercial) copper, Schmidt [17] has shown that neither the type of copper nor its hardness or surface is of significant importance. What is important is the total time of exposure to water, its corrosivity and the inclination of test specimens. A patina develops more rapidly on inclined surfaces (compared to vertical surfaces) which dry more slowly and are also subjected to additional attack by dew. Seven years of exposure of test specimens to a mill industrial atmosphere about 8 miles west of Copenhagen and 3 miles from the shore resulted in all inclined specimens showing a bluish-green patination. The vertically exposed specimens showed only faint signs of patination and were all dark brown in color, probably because of a mixed oxide-sulfide tarnish layer.

Analyses of the patina on the inclined specimens corresponded to a composition of  $\text{CuCO}_4 \cdot 6 \text{Cu(OH)}_2$ . (No x-ray diffraction data were reported.) Schmidt pointed out that the patina on old (30 years or more) copper roofs in Copenhagen corresponds to the mineral brochantite,  $\text{CuSO}_4 \cdot 3 \text{Cu(OH)}_2$ . He commented that measurements of rain water collected in 1944-1945 showed a nearly neutral pH (6-8) whereas in 1965 the pH of rain water was 4-5. The presence of  $\text{SO}_2$  in the atmosphere there, as in many places around the world, is causing much earlier patination of copper roofs.

The writer has examined the patination of a copper roof of a 70-year old water tower in Wilmington, Delaware. By x-ray diffraction, the corrosion product layer was found to consist of brochantite, antlerite ( $\text{CuSO}_4 \cdot 2 \text{Cu(OH)}_2$ ), and copper oxide ( $\text{CuO}$ ). In this case, there were 50 x-ray diffraction lines and all were identifiable with known compounds.

Problems, however, can arise when corrosion products on copper alloys, particularly ancient alloys, are analyzed by x-ray diffraction. The patterns can be even more complex, as was found when a problematical Hasanlu bronze (3rd millennium B.C.) was examined. This artifact had been almost entirely converted to oxides and nonmetallics. A typical polished core section photographed with polarized light is shown in figure 3. The same field, at the same magnification, 150X, is again shown in figure 4 where secondary electron (SE) and backscattered electron (BSE) images can be compared, and three elemental distribution maps are included. The latter identify the spheroidal inclusion as being lead-rich (it is actually  $\text{PbCO}_3$ ) and show smaller angular inclusions to be iron-rich phases.



Figure 3. Hasanlu Bronze, 3rd Millenium B.C. (Polished core section of oxidized artifact, photographed with polarized light.)

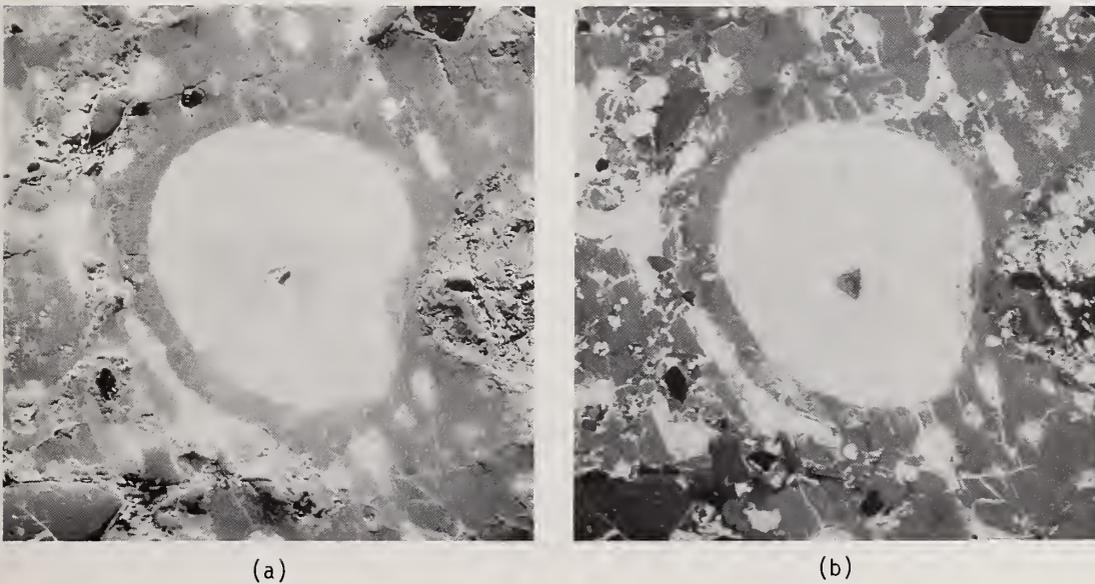
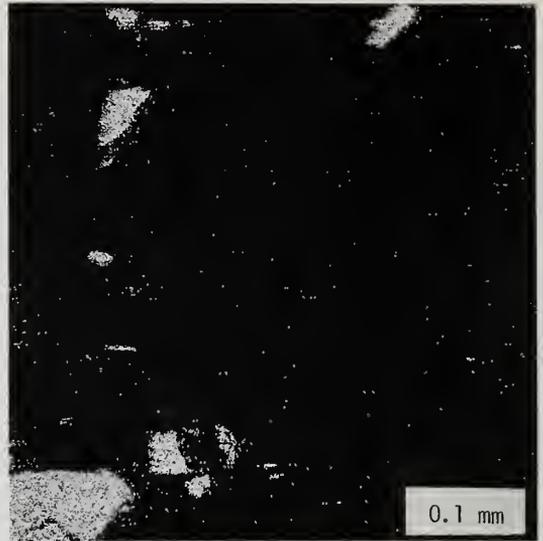


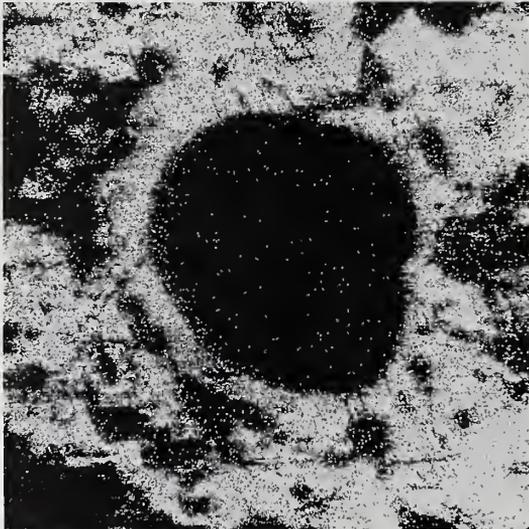
Figure 4. Oxidized Hasanlu bronze:  
(a) secondary electron image,  
(b) CuK $\alpha$  x-ray image,  
(see page 24).



(c)



(d)



(e)

Figure 4. Oxidized Hasanlu bronze:  
 (c) PbL $\alpha$  x-ray image,  
 (d) FeK $\alpha$  x-ray image,  
 (e) CuK $\alpha$  x-ray image.

Because of the structural and compositional heterogeneity of this artifact, originally a leaded-tin bronze, the oxide scale was dissected and separated into separate color fractions which were then examined by x-ray diffraction. Ten different crystalline species were identified:

malachite,  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$   
 atacamite,  $\text{Cu}(\text{OH})_2 \cdot \text{Cu}(\text{OH}, \text{Cl})$   
 paratacamite,  $\text{Cu}(\text{OH})_2 \cdot \text{CuCl}$   
 calumetite,  $\text{Cu}(\text{OH}, \text{Cl})_2 \cdot 2 \text{H}_2\text{O}$   
 cuprite,  $\text{Cu}_2\text{O}$   
 tenorite,  $\text{CuO}$   
 lead  
 lead carbonate,  $\text{PbCO}_3$   
 copper-tin alloy  
 magnetite,  $\text{Fe}_3\text{O}_4$ .

A brown and white phase(s) was not identifiable.

Understanding of the complexities of corrosion product formation in ancient copper alloys is facilitated when the enthalpies of formation of the oxides and hydroxides of copper and tin (and zinc, in the case of antique brasses) are considered; Werner [18] has shown (table 1 below).

Table 1. Enthalpies of formation.

Compound	Enthalpy of formation Kcal/mol
$\text{Cu}_2\text{O}$	- 39.8
$\text{CuO}$	- 37.1
$\text{ZnO}$	- 83.2
$\text{SnO}_2$	-138.1
$\text{Cu}(\text{OH})_2$	-106.7
$\text{Zn}(\text{OH})_2$	-153.5
$\text{Sn}(\text{OH})_2$	-270.5

From these data, it is predictable that tin- (and zinc-) rich phases in copper alloys will oxidize preferentially. Thus, in two-phase bronzes, the  $\delta$ -phase, which is richer in tin than the  $\alpha$ -phase, is more susceptible to oxidation (corrosion). Photomicrographs illustrate this not only for the copper-tin system, but show that the tin-rich phase in old pewter and Britannia metal also is less resistant to oxidation than lead-and antimony-rich phases. For example, an as-polished cross section of a Mesopotamian bronze shaft-hole axe<sup>4</sup> from the 3rd millenium B.C. (10 percent tin) is shown in figure 5. At least 50 percent of the original metal volume has been transformed interdendritically to oxide, which nucleated on tin-rich interfaces and converted the  $\delta$ -phase preferentially to the  $\alpha$ -phase. Where slip traces or deformation bands are present in the solid solution  $\alpha$ -phase and have also undergone preferential oxidation, it is assumed that segregation of tin atoms to these regions was responsible.

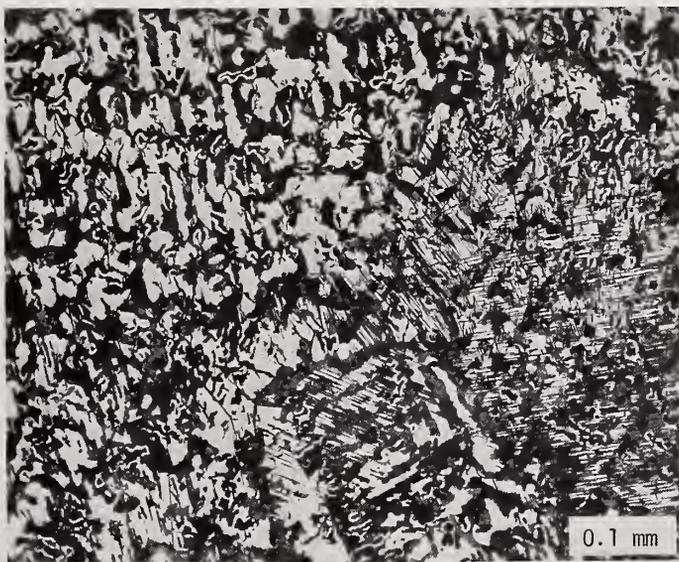


Figure 5. Interdendritic oxidation in bronze Mesopotamian Axe, 3rd Millenium B.C.

<sup>4</sup>University of Pennsylvania Museum Number 31-71-186 (U. 14238).

Corrosion and oxidation occurring over a long-term time span also caused a sharply segregated distribution of copper and tin corrosion products (fig. 6). It appeared that dealloying of tin ("destannification") had taken place. Tin will ionize and oxidize preferentially leaving behind a copper-enriched matrix. There was visible evidence of metallic copper in the corrosion product layers.

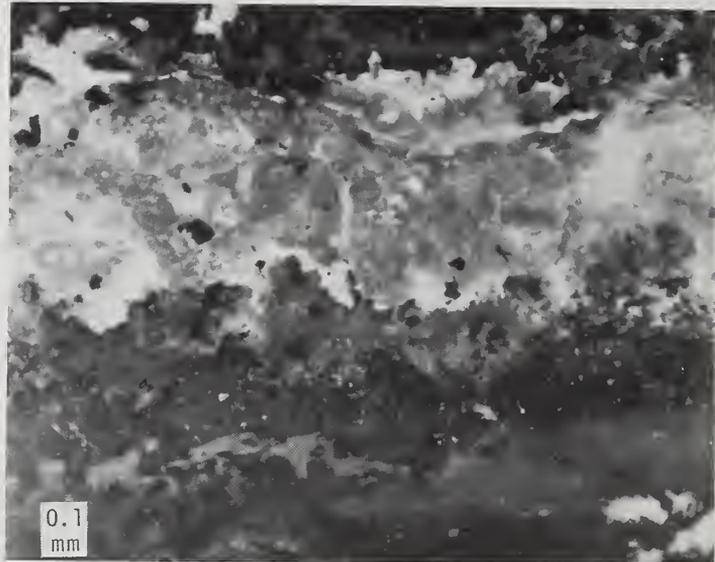


Figure 6. Corrosion product layers in Hasanlu Axe.

(The shaft-hole axe whose oxidation-embrittled microstructure is shown here also provided the opportunity for examination of mineralized wood structure present from the original hafting. The photomicrograph of figure 7 shows the cross-sectional structure of the wood remaining in the axe socket. No identification of the wood has been made.)

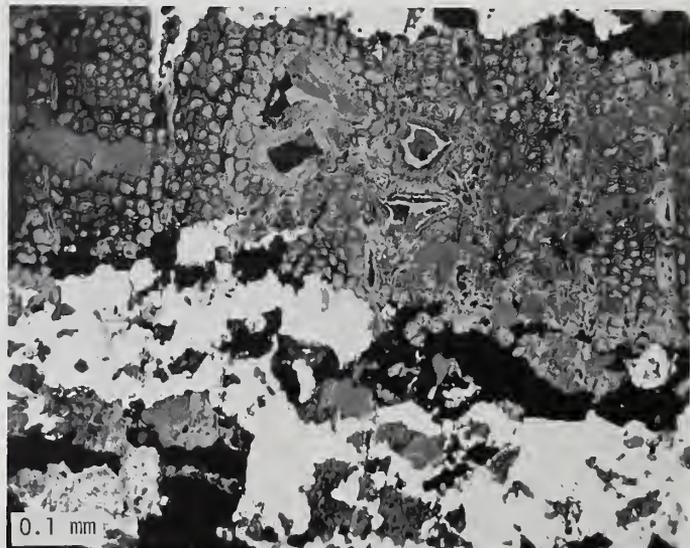


Figure 7. Mineralized wood in Hasanlu Axe socket.

This specimen also showed the presence of transgranular stress-corrosion cracks (fig. 8). At some time in its 4000+ year history, sufficiently high tensile stress was developed by the wedging action of oxidation/corrosion products formed under constraint to trigger crack propagation in whatever aggressive medium (presumably wet soil) the axe was then present and corroding. It is thought that this specimen represents the oldest known example of stress-corrosion cracking found in any alloy.

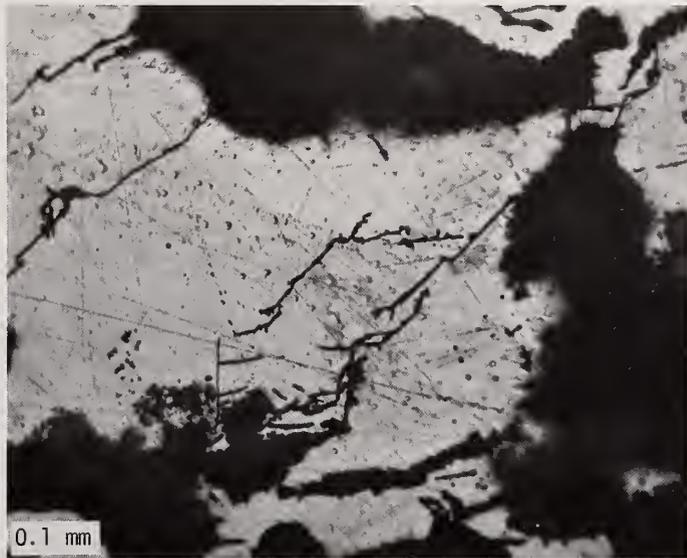
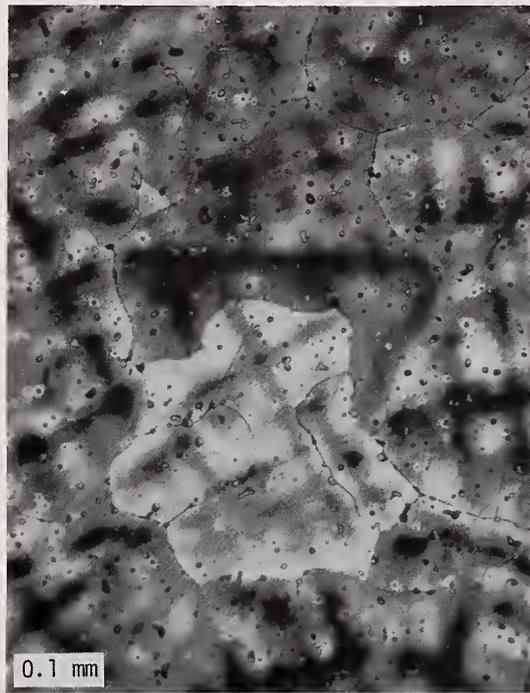


Figure 8. Stress-corrosion cracks in Hasanlu Axe.



(a)



(b)

Figure 9. Microstructure in bronze Amlash Arrowhead: (a) edge structure, (b) center structure.

In figure 9 are microstructures present in a bronze arrowhead (Amlash, 8th to 15th centuries, B.C.). Here it is evident that the structure is one of a leaded, alpha bronze alloy which has undergone intergranular oxidation. The annealing following forging of the arrowhead did not completely obliterate the compositional heterogeneity of the original casting. Metallographic etching (with an  $\text{NH}_4\text{OH}-\text{H}_2\text{O}-\text{H}_2\text{O}_2$ ) system brought out the primary dendritic system of the bronze.

### Dealloying

Literature on the phenomena of dealloying, the corrosion process whereby one constituent of an alloy is removed preferentially from the alloy leaving an altered residual structure, has been reviewed by Verink and Heidersback [19].

Loss of tin from bronze has already been mentioned. However, loss of zinc from brass (dezincification) is the form of dealloying most commonly encountered. Alpha brass (70

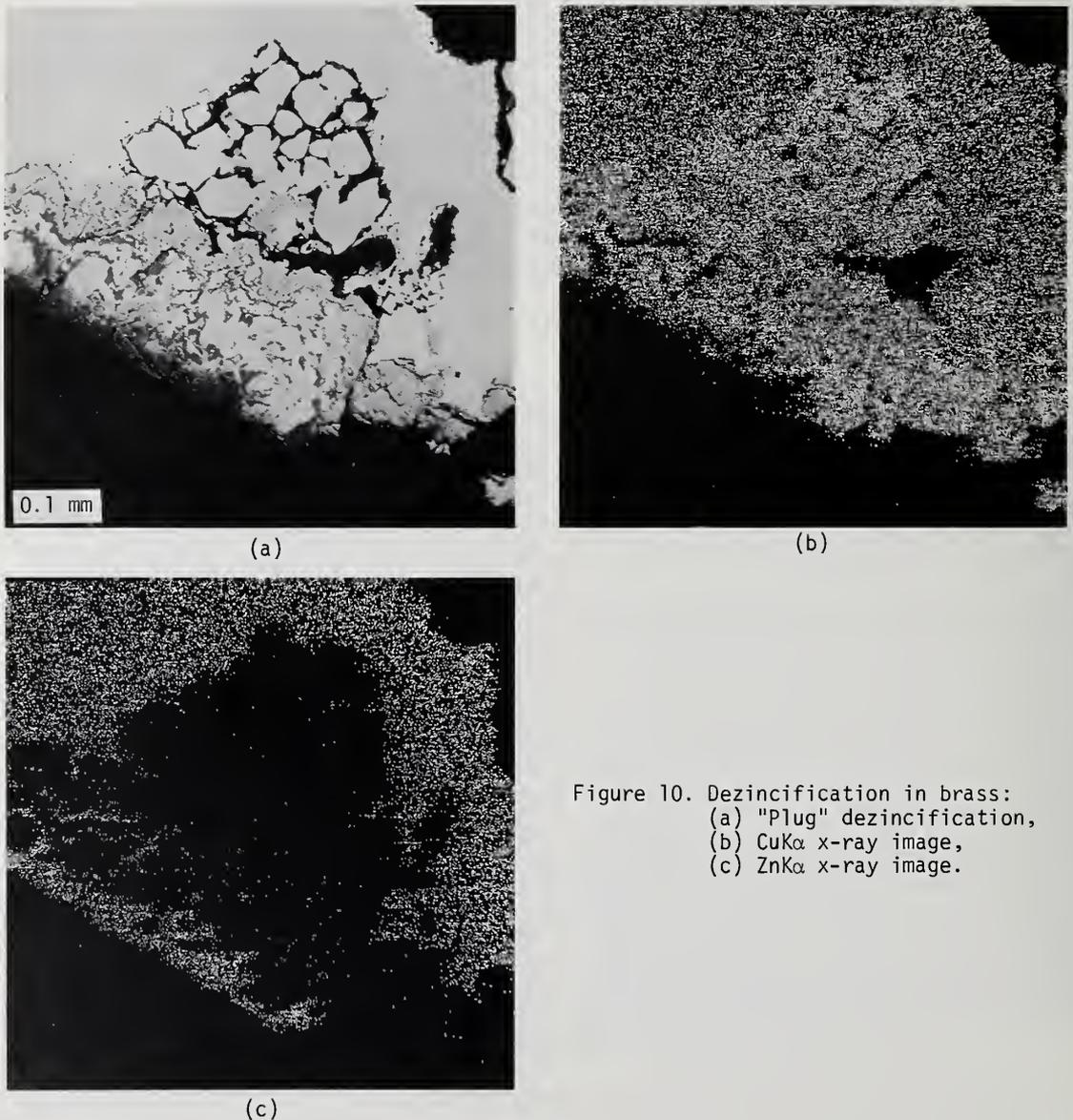


Figure 10. Dezincification in brass:  
(a) "Plug" dezincification,  
(b)  $\text{CuK}\alpha$  x-ray image,  
(c)  $\text{ZnK}\alpha$  x-ray image.

Cu-30 Zn) is especially prone to this type of corrosion attack which results in the development of a weak porous copper sponge, either as a "plug" or a continuous layer in the brass surface. The cited reference [19] discusses recent work on mechanisms and shows how the application of potential/pH (Pourbaix) diagrams has led to new insights.

Examination (by the writer) of brass spoons found in an historical archaeological dig (see next section on Corrosion of Pewter) showed that all pieces had suffered some dezincification from long-term contact with wet soil and ground water. Figure 10 is included to show the nature of the phenomenon. Note that a "plug" of copper has filled in the dezincified region in the brass surface. In the extreme case of alloy failure by this mechanism, dezincification proceeds to the point where a cross section of brass can no longer support the load or applied stress upon it.

#### Corrosion of Pewter and Britannia Metal

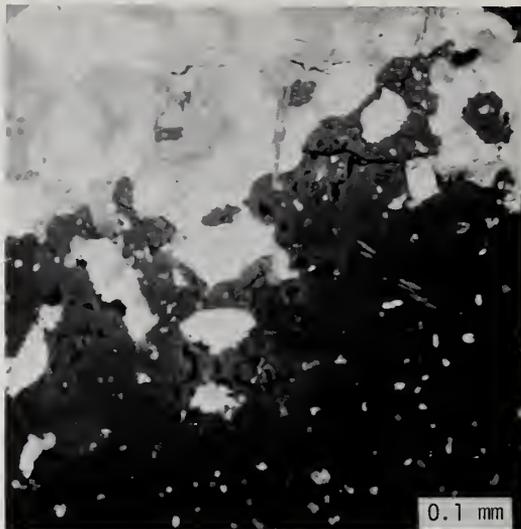
The Archaeological Society of Delaware in its excavations at the Caleb Pusey home in Upland, Pennsylvania, found considerable artifactual material which provided needed information for subsequent restoration of the house (a small, one-and-a-half story cottage built in the late 1600's continuously occupied until the middle of the present century. It was known also as the "Billy Penn House." Penn made many visits there to see Caleb Pusey who was manager and agent for Penn's mill at Upland). Included in the material found were over two hundred coins as well as many spoons and spoon fragments of pewter [20]. The latter were analyzed by J. H. Carlson (Winterthur Museum) using energy-dispersive x-ray analysis who reported that they fell into three categories:

- (1) Three heavily corroded pieces of good quality pewter with tin levels greater than 90 percent.
- (2) A large group of objects and fragments were classified as good to very poor pewter with tin contents ranging from about 80 percent down to less than 20 percent. Many of the poor quality pieces were probably made by the residents of the house at the time, or by a local country pewterer.
- (3) A third group of so-called pewter objects and fragments are actually Britannia, containing 85 to 88 percent tin, 0 to 2 percent copper, 0 to 3 percent lead, and 8 to 14 percent antimony.

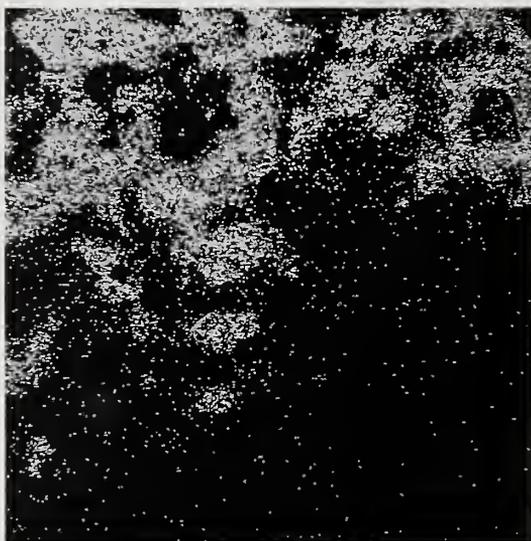
For metallographic examination of pewter spoon fragments, it was convenient to cut, mount and polish a cross-sectional slice from incomplete handles or broken bowls. For example, figure 11 is a cross section of a heavily corroded spoon handle, a pewter containing 24 percent lead, examined in the scanning electron microscope. The four images of the same area compare the secondary electron image with the backscattered electron image which shows greater contrast because the BSE mode emphasizes the heaviness of the atoms in the surface, i.e., responds to atomic number and a lead-rich phase is present. Figure 11 also illustrates the usefulness of element x-ray mapping and shows that the lead-rich regions have resisted corrosion better than the tin-rich matrix phase.



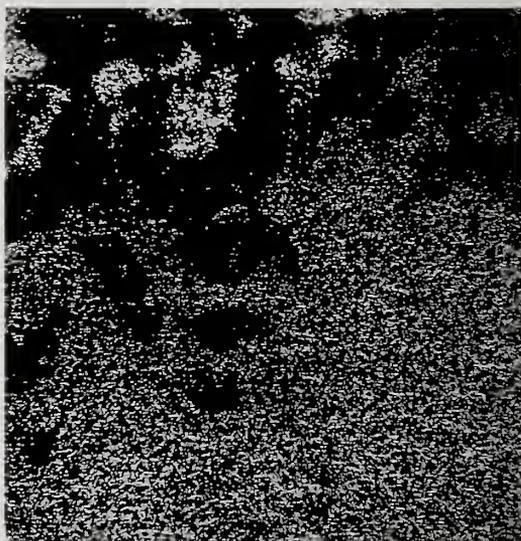
(a)



(b)



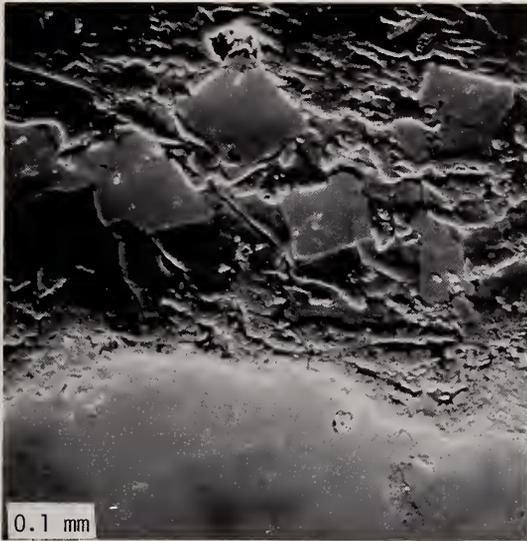
(c)



(d)

Figure 11. Corrosion/oxidation of pewter (24 percent Pb):  
(a) secondary electron image,  
(b) backscattered electron image,  
(c) PbM $\alpha$  x-ray image,  
(d) SnL $\alpha$  x-ray image.

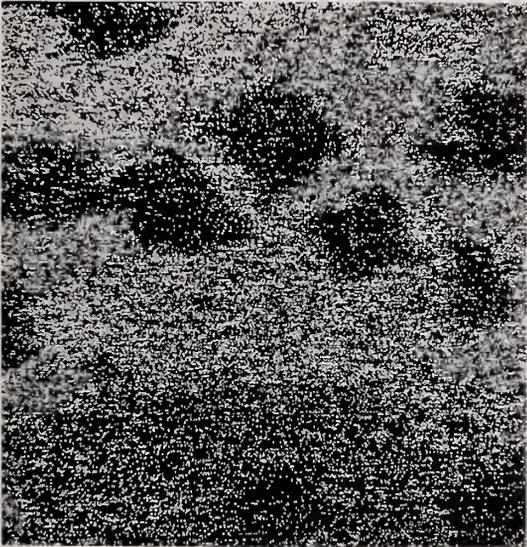
Similar examination of a second spoon fragment identified as Britannia metal from its high antimony content, 14 percent, is shown in figure 12. This specific alloy is essentially a binary tin-antimony system with no copper and no lead. The cuboids, which are deficient in tin and show antimony segregation are, in this case, the corrosion-resistant phase.



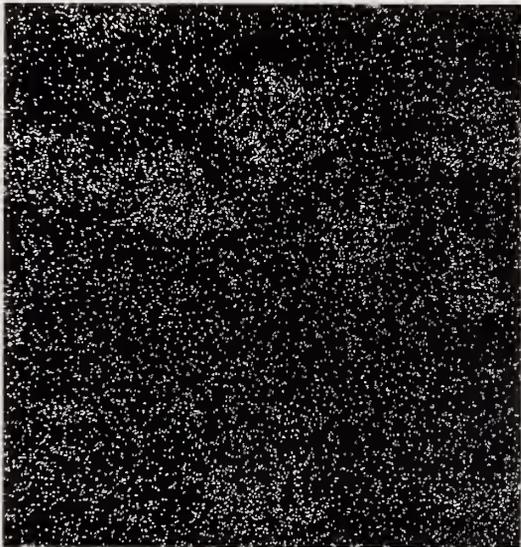
(a)



(b)



(c)



(d)

Figure 12. Corrosion/oxidation of Britannia Metal (14 percent Sb):  
(a) secondary electron image,  
(b) backscattered electron image,  
(c) SnL $\alpha$  x-ray image,  
(d) SbL $\alpha$  x-ray image.

Figure 13 is a micrograph (SEM using backscattered electrons) of a high-quality Britannia metal plate (cross section). A heavy corrosion/oxidation layer exists on the bottom of the plate. This is not an archaeological find but represents what happened to the tin alloy in normal household usage over many years. Only the top surface of the dinner plate was ever cleaned and polished. The corrosion product is mixed SnO-SnO<sub>2</sub> (by x-ray diffraction) and has an onionskin structure. Intergranular corrosion attack has occurred in local areas ahead of the front of general oxidation/corrosion.

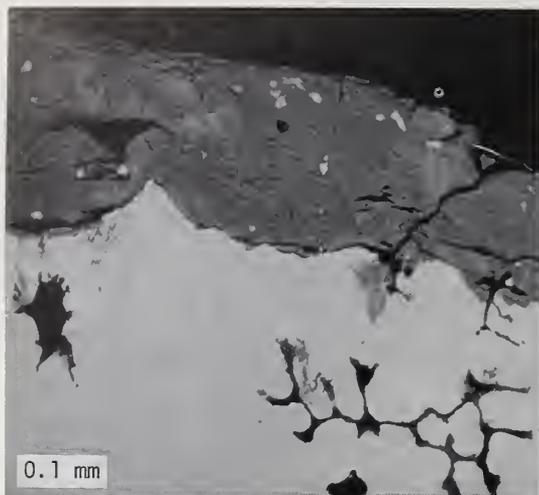
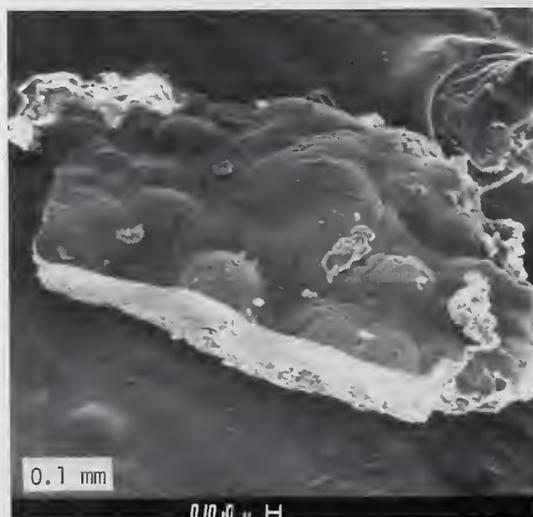


Figure 13. Cross section of Britannia Plate (backscattered electron image).

An interesting analytical problem was posed in the examination and analysis of a 17th century pewter plate found at the bottom of the Caleb Pusey house well. Winterthur Museum analyses (J. H. Carlson) showed that the badly corroded plate contained copper ranging from 2 to 20 percent (depending on the area analyzed). However, on a relatively clean, non-corroded area, a good approximation of the content of the base alloy was obtained (Sn = 95.1 percent, Cu = 3.43 percent, Pb = 0.43 percent, and Sb = 0.62 percent) without resorting to cleaning or scraping the plate. The variability of the copper elsewhere on the plate was puzzling but it was conjectured that an electrochemical displacement mechanism had deposited copper on the plate as tin corroded. Carlson exposed pewter billets to an aqueous solution of  $\text{CuSO}_4$ ,  $\text{Cu}(\text{OAc})_2$  and acetic acid and confirmed that dissolved copper salts can be reduced from slightly acid water to deposit in the metallic state on pewter. Subsequent examination by the writer of a coppery-colored flake spalled off the Caleb Pusey plate revealed copper, iron and sulfur in the deposit (fig. 14). It was concluded that a chalcopyritic layer had formed on cathodic regions associated with areas in the plate that had undergone localized corrosion during the long exposure of the plate to the well water.



(a)

10	750eV	0INT
11	1200eV	9INT
12	1250eV	13INT
13	1400eV	172INT
14	1700eV	41INT
15	2700eV	0INT
16	2250eV	12267INT
17	2700eV	0INT
18	3000eV	0INT
19	3250eV	1INT
20	3700eV	28INT
21	0eV	0INT
22	4450eV	0INT
23	5L00eV	0INT
24	5200eV	0INT
25	5700eV	0INT
26	6400eV	8047INT
27	6750eV	4INT
28	7450eV	15INT
29	8000eV	6047INT

(b)

Figure 14. Corrosion product on old pewter plate: (a) isolated spall, (b) EDXA analysis of spall; columns left to right are atomic number, x-ray energy in electron volts and total integrated x-ray count.

## Wrought Iron Nails

Nails are common finds for archaeologists not only at colonial American sites but also at all Roman occupation sites. Perhaps because of their commonness there have been very few attempts, either in Europe or here in the United States, to study ancient nails in any way other than by classification according to size and form. However, in 1962, Angus, Brown, and Cleere [21] had the opportunity to carry out metallographic examinations of nails found in a Roman legionary fortress (built about A.D. 85) at Inchtuthil, Perthshire (England). Over 875,000 nails varying from 2-1/2 inches to 15 inches in length were found in a 12-foot deep pit. At the time of discovery, the nails received considerable publicity because of the excellent state of preservation of many of them. It was soon shown, however, that the Roman iron makers did not have any secret of producing rusting-corrosion-resistant iron. Actually, the main core of nails was protected over the centuries by the virtually anerobic conditions developed within the mass as the nails on the outside of the mass corroded rapidly and formed a protective, almost impermeable crust. The authors point out also that corrosion of the internal nails was further inhibited by the thermal oxide scale present on most of them. Where these coatings were discontinuous, preferential and severe corrosion attack had taken place.

Similar observations have been drawn by the writer in examination of nails from several 17th century house sites in the United States. For example, the rose head nail shown in figure 15 was excavated by L. T. Alexander at the "Buck site" in Chestertown, Maryland. It is a typical flat-pointed nail of this early period, but in remarkably good condition. In cross section, it can be seen (fig. 16) that the nail is sheathed with a heavy, uniform layer of oxide ( $\alpha\text{-Fe}_2\text{O}_3$  by analysis) and it is believed that the barrier properties of this adherent oxide scale account for the preservation of this particular nail. It is conjectured that the protective oxide scale was formed in a house fire, possibly an intentional one, as it is known that wooden buildings in this period were occasionally set on fire for easier recovery of the nails whose value was considerable at that time. (But still much less than Roman nails in A.D. 85 which were prized by the Scot tribes more highly than silver or gold, because the iron could easily be converted into weapons [21].)



Figure 15. Wrought iron nail from 17th century archaeological site in Chestertown, Maryland.



Figure 16. Wrought iron nail (Maryland) showing protective iron oxide scale.

It is of interest that this Maryland nail was analyzed by optical emission spectrography and found to be different from a similar rose head nail found at the Caleb Pusey house (Pennsylvania) excavations in these two respects.

Table 2. Emission spectrographic data for Maryland and Pennsylvania nails given in parts per million or percent.

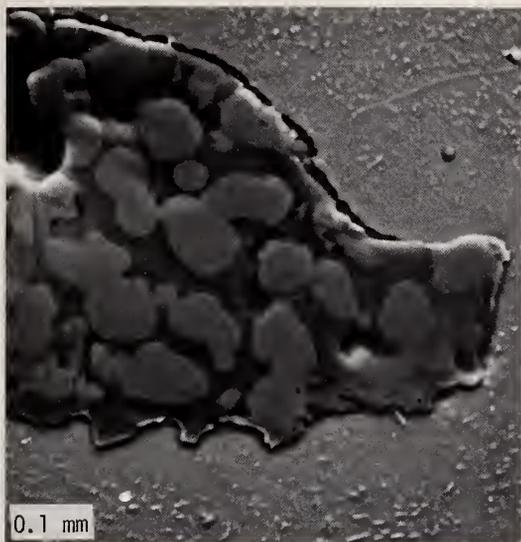
	<u>Ti</u>	<u>Zn</u>
Md. Nail	0.5 - 2%	2 - 10%
Pa. Nail	200 - 1000	0.2 - 1%

The higher levels of titanium, but particularly zinc in the Maryland nail suggest that the iron (ore) for this nail came from Cumberland County, Pennsylvania, where the ores are zinc-containing.



Figure 17. Wrought iron nail with defective oxide scale (Caleb Pusey House, Upland, Pennsylvania).

Figure 17 is a longitudinal section of the Pennsylvania nail mentioned. As can be seen, the oxide scale is imperfect and pockets of rust were present at these surface sites where the protective scale was defective. The metallography of this nail was that of typical wrought iron of the period with characteristic mottled slag inclusions present in a pure iron or ferrite matrix. Figure 18 is included to illustrate again how, with the scanning electron microscope and using the technique of element distribution mapping, it is possible to delineate the partition of Fe, Si and P in the slag inclusions. Comparative studies (metallography and spectral analyses) of early wrought iron nails and of cut nails in their transition period of manufacture and acceptance can provide useful information on the history of local iron making practice. The nail from the Caleb Pusey house was "headed" cold or only warm at the best. The microstructure of the nail shown severe plastic deformation residual from forging, indicating that the forging temperature was not high enough to recrystalline the ferritic microstructure.



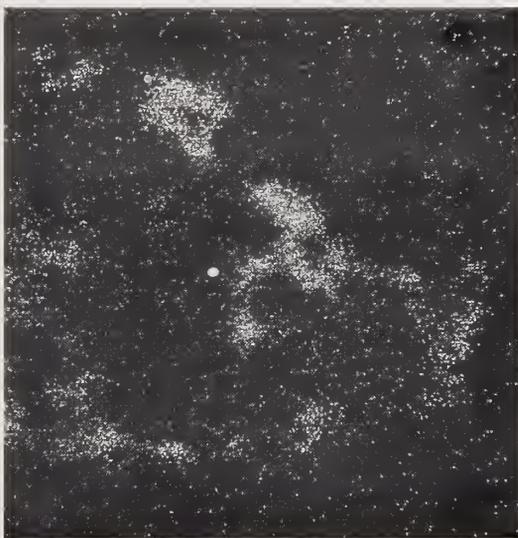
(a)



(b)



(c)



(d)

Figure 18. Wrought iron nail (Pennsylvania):  
(a) secondary electron image,  
(b) FeK $\alpha$  x-ray image,  
(c) SiK $\alpha$  x-ray image,  
(d) PK $\alpha$  x-ray image.

#### Summary

There is no doubt that most of the tools and techniques in use and available to the corrosion scientist can find applications in the study and conservation of metallurgical artifacts. When the archaeologist or metals conservator is uncertain about a course of action to follow, or the potential usefulness of a specific technique in characterization, he is advised to consult an individual or laboratory whose professional work involves the technique(s) in question. In effect, he is advised to continue the dialogue fostered at this meeting.

The writer must necessarily apologize for presenting only an abbreviated overlook of the subject of corrosion product characterization which, covered comprehensively, would require an entire book. The intention here has been to illustrate, in some personal study cases, that structural and compositional characterization of metals and their corrosion products can not only provide information on the early technology of manufacturing metal objects, but additionally, reveal the record of their subsequent history in terms of the changes wrought by long-term environment corrosion and oxidation. A physical and chemical record of this history can be read through the use of appropriate characterization and analytical techniques.

The writer is in complete agreement with this expression of Dr. James A. Charles in concluding his Sir Robert Horne Memorial Lecture on "Arsenic and Old Bronze" [22]:

*It is my view that practical field archaeology and subsequent artifact examination today must combine a whole range of skills if the best possible results are to be obtained. It is my happy experience that active and informed participation on the part of interested scientists is welcomed and that it can be a stimulating and intellectually rewarding part of one's professional life.*

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#### Discussion

*W. T. Chase:* The identification of all the phases in a corroded metal artifact, such as the object from Hasanlu which you showed, is particularly useful. Have you published this any place? If not, I suggest that you include a couple of pictures, with the corrosion phases identified in the proceedings of this meeting.

*N. A. Nielsen:* At the present time there are no plans to publish this material but, perhaps I could follow up on your suggestion.

*M. Goodway:* What is the beam size of the ion scattering technique?

*D. Newbury:* About 100 micrometers.

*C. S. Smith:* The fine photomicrographs shown by Dr. Nielsen make it obvious that microstructure must be considered when interpreting any gross measurements on corroding or corroded materials. Composition, especially when determined on the small samples that are invited by today's ultra-sensitive techniques, is a function of location. The results of both electrolytic or ion stripping techniques, commonly interpreted in terms of depth often depend more on surface distribution than on true variation with depth or thickness.

*N. A. Nielsen:* I do not believe I have any further comments. I agree with what Professor Smith said.



## PRINCIPLES OF GASEOUS REDUCTION OF CORROSION PRODUCTS

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### 1. Introduction

All metals except gold eventually form oxides and, in some cases, sulfides or other compounds because those compounds are more stable than the metallic elements when exposed to the atmosphere. For many metals, the reaction takes place very slowly at or near room temperature, but the rates and the details of the process often are very sensitive to small concentrations of reactant materials in the environment. Old objects that have been in a slowly changing environment or that have spent long periods in a succession of different environments may bear clues to the history of the object in the nature of the reaction products. Removal or reduction of the reaction products may obliterate that evidence. Although the appearance of the object may be closer to its original appearance, it is again in a reactive state.

This paper does not consider whether an object should be treated by gaseous reduction, but only summarizes the principles of equilibrium that place limits on the conditions for reduction. In addition, explicit discussion is included concerning reduction of the products of iron oxidation. This latter subject is interesting for many reasons; it has been studied intensely as a possible method for obtaining iron directly from its ores. In spite of many such studies, there is no simple, sure way to obtain dense iron by direct reduction of its oxides.

### 2. Stability of Oxides

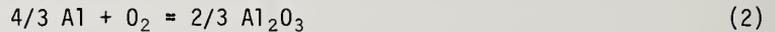
Chemical equilibrium at constant temperature and total pressure is characterized by a minimum value of the Gibbs free energy  $G$  of the system. If the reaction is written as a balanced equation, the change in Gibbs free energy  $\Delta G$  is the weighted sum of the molar Gibbs free energies of the product molecules minus the same sum for the reactants, where the weighting of the sums is in proportion to the coefficients in the balanced chemical equation. The minimum for the Gibbs free energy means that  $\Delta G$  is zero for a very small displacement of the reaction forward or backward when all reactants and products are present in their equilibrium concentrations.

$\Delta G$  is defined in terms of the more familiar quantities enthalpy (or heat content)  $H$  and entropy  $S$  by the equation

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

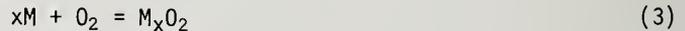
where the difference  $\Delta$  always is taken between the weighted sum of the molar property for products less the weighted sum of the same property for reactants. The enthalpies of compounds are expressed conveniently as their heats of formation from the elements so that

reactants and products both have values based on the same reference states. Thus, for the oxide alumina



the enthalpy change in this reaction carried out at constant T and P is the heat of formation per mole of oxygen. It is advantageous for the comparison of relative stabilities of the oxides to write all equations for the same amount of oxygen. The standard value of any property change is obtained when the metal and oxide are pure and the oxygen is at one atmospheric pressure. These standard reference states are designated as having unit activity, and thermodynamic quantities measured with all reactants and products in their standard states are identified by a superscript zero. For the general case of oxide formation, the standard Gibbs free energy of formation is very simply related to the equilibrium partial pressure of oxygen that is simultaneously in equilibrium with the metal and its oxide, that is to the dissociation pressure of the oxide. The greater the dissociation pressure, the lower is the stability of the oxide and the less negative is its standard free energy of formation.

Writing a generalized equation for the formation of an oxide:



for which the equilibrium constant is

$$K = \frac{a_{\text{M}_x\text{O}_2}}{a_{\text{M}}^x P_{\text{O}_2}(\text{eq})} = \frac{1}{P_{\text{O}_2}(\text{eq})} \quad (4)$$

because the oxide and metal are in their standard states which have unit activity; x can be either a simple fraction or small integer. The equilibrium constant is related to the standard Gibbs free energy change for the reaction by

$$\Delta G^\circ = -RT \ln K = RT \ln P_{\text{O}_2}(\text{eq}) \quad (5)$$

This equation is the basis for the plots of  $\Delta G^\circ$  versus temperature given in figure 1 for oxides and in figure 2 for sulfides.

Unless the equation is given for formation of a higher oxide by oxidation of a lower oxide, the oxide is formed from the metal and oxygen, and the metal and oxide can exist in equilibrium at the dissociation pressure. These diagrams are known as Ellingham diagrams. Analogous plots have been assembled for halides, nitrides, carbides, *etc.*, and they have interesting and useful properties, especially when supplemented by nomographic scales as is done in figures 1 and 2.

The standard heat of formation  $\Delta H^\circ$  varies only slowly with temperature, and nearly linearly. The standard entropy change  $\Delta S^\circ$  also changes very slowly with temperature; this contribution is dominated by the change in the number of moles of gas between reactants and products because the molar entropies of gases are so much larger than those of the condensed phases.  $\Delta S^\circ$  per mole of oxygen immobilized in the formation of a solid oxide is about 190 joules per mole per kelvin unless the metal or oxide is volatile. As a consequence, the lines for solid metals forming solid oxides or for lower oxides forming higher oxides are roughly parallel to one another because the slope is determined by  $T\Delta S^\circ$ , which is about the same for all of these cases. The more stable oxides with large negative heats of formation and low dissociation pressures lie below the less stable oxides on the Ellingham diagram.

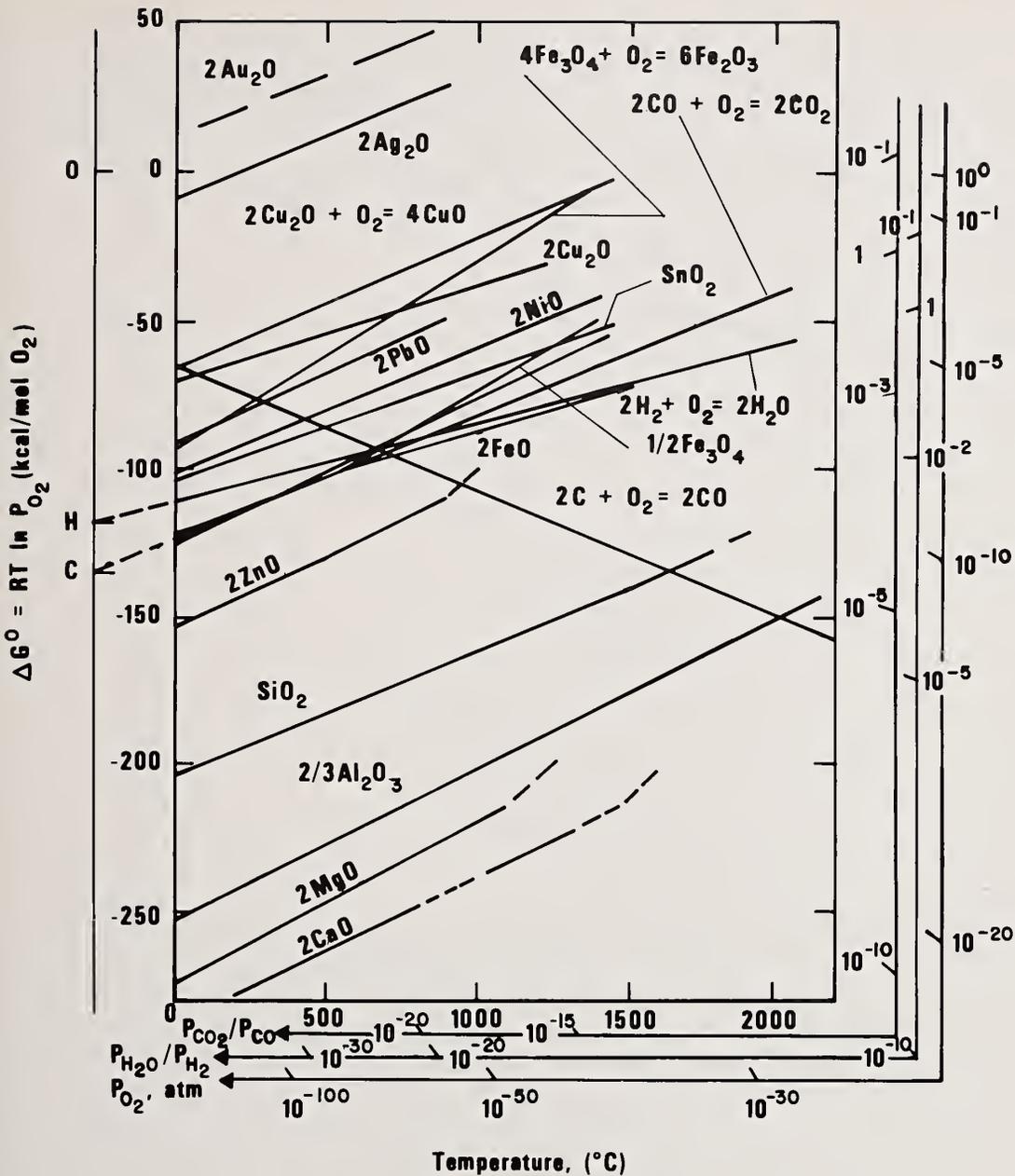


Figure 1. Ellingham diagram for oxides. Based upon the diagram first prepared by Richardson and Jeffes [1]<sup>1</sup> and modified by Darken and Gurry [2]. A few additions and modifications have been made to emphasize the metals used most in old artifacts.

The lines show small changes in slope where a metal or oxide melts and still larger changes in slope where a metal or oxide vaporizes. Analogous statements can be made for the sulfides.

<sup>1</sup>Figures in brackets indicate literature references at the end of this paper.

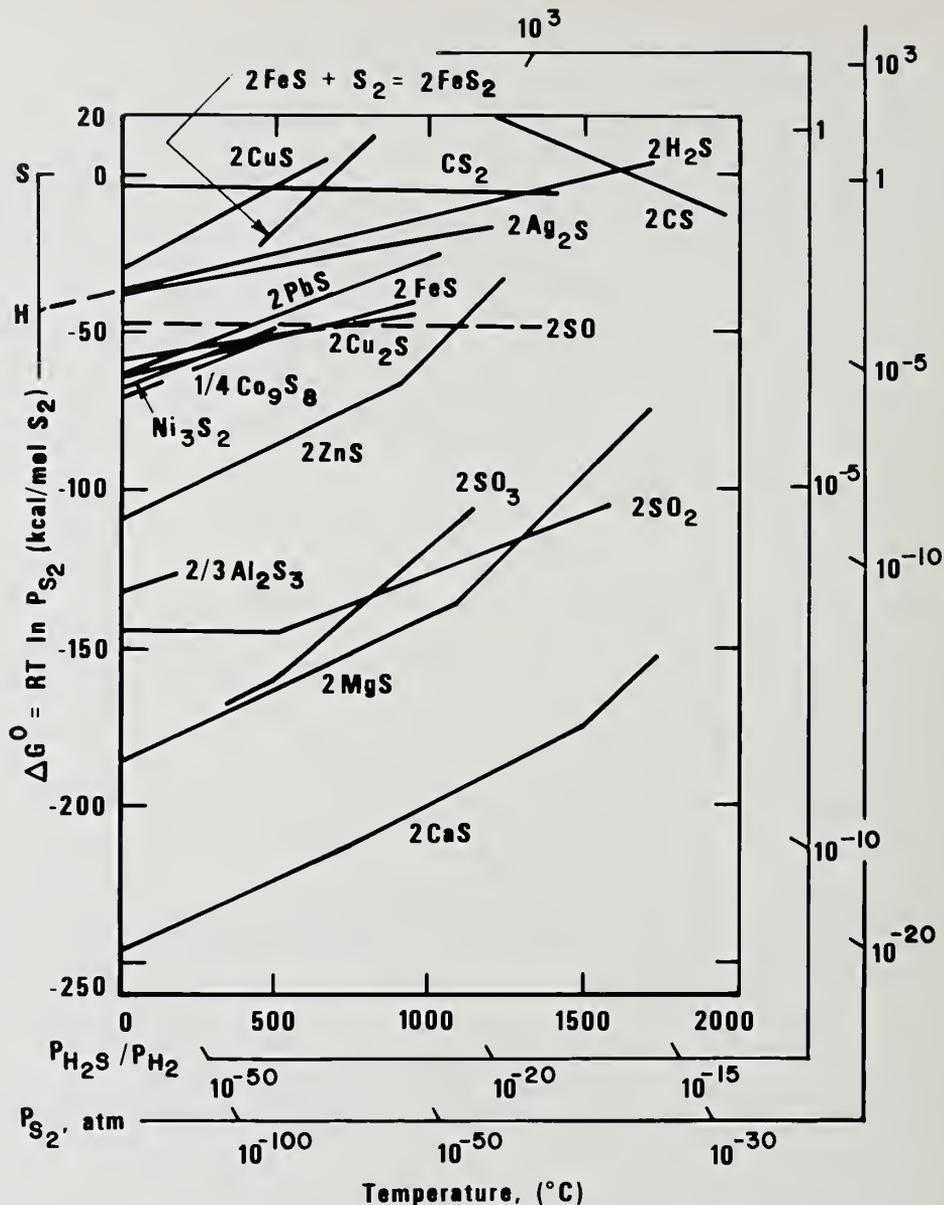


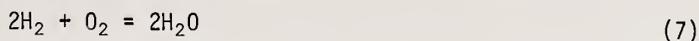
Figure 2. Ellingham diagram for sulfides from the same sources as figure 1, with modifications.

The free energy change, or  $\Delta G$ , for an arbitrary oxygen pressure  $P_{O_2}$  is given by

$$\Delta G = RT \ln P_{O_2}/P_{O_2}(\text{eq}) \quad (6)$$

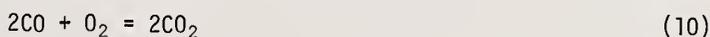
which satisfies the requirement that  $\Delta G = 0$  where  $P_{O_2} = P_{O_2}(\text{eq})$ . It is practical to reduce  $P_{O_2}$  only to about  $10^{-9}$  atm by pumping and somewhat lower by the use of an active metal scavenger (e.g., Al, Mg, or Ti). However, to maintain good control of low oxygen partial pressures, mixtures of hydrogen and water vapor or carbon monoxide and carbon dioxide frequently are used. The lines for these equilibria have similar slopes because three moles of gas react to form two moles. However, oxidation of graphite by one mole of oxygen to form

two moles of carbon monoxide has a distinctly different slope than the metal oxidation lines in figure 1. In fact, this reaction has a negative slope, which is most important for reducing oxides. These three reactions are written below, and the equilibrium constants are written to show how the oxygen partial pressure can be controlled by maintaining the ratios of water vapor to hydrogen, carbon dioxide to carbon monoxide or by controlling the carbon monoxide pressure over hot graphite.



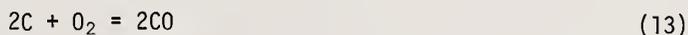
$$K_H = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}} \quad (8)$$

$$P_{\text{O}_2} = \frac{1}{K_H} \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^2 \quad (9)$$



$$K_{2\text{C}} = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2 P_{\text{O}_2}} \quad (11)$$

$$P_{\text{O}_2} = \frac{1}{K_{2\text{C}}} \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 \quad (12)$$



$$K_C = \frac{P_{\text{CO}}^2}{a_C^2 P_{\text{O}_2}} \quad (14)$$

$$P_{\text{O}_2} = \frac{P_{\text{CO}}^2}{K}; a_C = 1 \quad (15)$$

Figures 1 and 2 have been fitted with nomographs. The index marks on the left-most scale of figure 1, labeled O, H, and C, are to be used with the scales at the bottom and on the right for  $P_{\text{O}_2}$ ,  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$  and  $P_{\text{CO}_2}/P_{\text{CO}}$ , respectively. For example, if you wish to determine the dissociation pressure of NiO at 1000 °C, place a straight edge at the O index mark, run it through the intersection of the NiO line with the 1000 °C vertical line, and extend the straight edge until it intersects the right-most line at  $P_{\text{O}_2}$  equal to just less than  $10^{-10}$  atmospheres. Similarly, the mixture of carbon dioxide and carbon monoxide in equilibrium with  $\text{SiO}_2$  and silicon at 900 °C can be found by running a straight line from the C index through the 900 °C point on the  $\text{SiO}_2$  line and reading a ratio of  $P_{\text{CO}_2}$  to  $P_{\text{CO}}$  from the nomograph line closest to the right boundary of the graph equal to less than  $10^{-7}$ . Such a ratio would be very difficult to establish and maintain.

In practice, hydrogen gas can readily reduce those metals that lie above the line marked  $\text{H}_2\text{O}$  or slightly below it if the water is continuously removed. Similarly, CO can reduce about the same metals, although metal with dissolved carbon, or even carbides in some cases, may be the solid product of this reduction. The only reducing agent that becomes increasingly powerful with increasing temperature is carbon, usually introduced in the form of graphite or charcoal. Note that in the neighborhood of 2000 °C and above, such a stable oxide as  $\text{Al}_2\text{O}_3$  should be reduced by carbon to form CO. In a sense, the reaction is even more favorable than the figure indicates because aluminum is volatile below 2000 °C. However, aluminum also forms gaseous suboxides that make its separation as metal very unlikely.

The point that historians have drawn from the principles embodied in figure 1 is that the metals became available for use as soon as furnaces could be built to provide the tempera-

ture at which carbon would reduce the oxide, provided only that the ore was sufficiently abundant to be tested. The sulfide ores were no problem. Although figure 2 shows that CS is not stable enough to be useful directly, the sulfides could easily be roasted to form metallic oxides and SO<sub>2</sub>, after which carbon could be used to reduce the oxide.

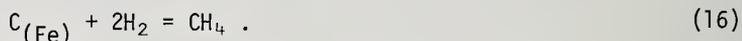
Figure 1 shows that gold has no stable oxide at or above room temperature. The oxides of silver and mercury are readily decomposed in air by a small temperature increase. The oxides of copper, lead, nickel, tin, and iron can be reduced at reasonable temperatures by either hydrogen or carbon monoxide. Build-up of water vapor can be prevented by condensing out the excess water or by reacting it with a more reactive metal. Build-up of carbon dioxide can be prevented in the same way, or by supplying solid carbon at a location where it can react with the hot gases.

### 3. Reduction of Oxides on Iron, Steel, and Cast Iron

Figure 1 shows that the reduction of the lower oxides of iron requires either a temperature in excess of about 400 °C or hydrogen that is thoroughly dried, that is, hydrogen with a low "dew point." For example, the line connecting the H index to the Fe<sub>3</sub>O<sub>4</sub> line at about 250 °C shows that the hydrogen can contain only about 0.1 percent water vapor and remain reducing. Furthermore, at such a low temperature the reaction would be very slow. Slow reaction may be an advantage in the early stages of treatment of a corroded object in order to avoid physical damage from fast evolution of water vapor. Consequently, the reduction process might be started by heating slowly in a stream of pure hydrogen.

However, steel and cast iron are alloys of iron and carbon. Many of these alloys were made intentionally with a nonuniform distribution of carbon resulting from a series of carburizing and oxidizing heat treatments, by hot forging high carbon alloys together with wrought iron, and by a variety of other laborious operations which were parts of a conscious art. The corrosion processes differentially attack these alloys. In the case of cast irons, prolonged corrosion, especially in seawater, may leave behind a residue of graphite infiltrated by silt, mud, or other matter in such a way that the form of the original object is almost wholly or just partially preserved. Much or all of the iron may have been dissolved by the electrolyte. In any of these cases, it is important to determine the condition of the object and to remove any samples that are to give information about the initial alloy content or its thermal or mechanical treatments before any high temperature reduction is attempted.

Hydrogen is a decarburizing agent for carbon dissolved or included in the steel or iron:



Mixtures of carbon dioxide and carbon monoxide may be either carburizing or decarburizing. Strongly oxidizing mixtures always decarburize, but reducing mixtures may carburize or decarburize depending on the carbon activity already in the alloy. Thus, the iron-to-carbon ratio may be disturbed severely as a result of corrosion but, because of the low temperatures, only to the depth that corrosion has penetrated. After high temperature reduction, however, the carbon content may be modified to much greater depths owing to the high diffusivity of carbon and of hydrogen. Corrosion followed by reduction may convert cementite (Fe<sub>3</sub>C) in some steels and cast irons into graphite.

Changes in composition as a result of corrosion and subsequent reduction of products are not limited to steels and cast irons. Both high temperature oxidation and aqueous electrochemical corrosion of all alloys selectively attack the more reactive components. They may form insoluble compounds *in situ* or dissolve away preferentially with more noble constituents later being attacked and removed. When reduction is attempted, the compounds of the more noble elements that still are a part of the object are reduced preferentially. Indeed, compounds of the most active elements may not be reduced at all. The sequence of these processes applied to the surface of an alloy that had been melted and cast, possibly hot or cold forged in addition, results in a surface region that is metallurgically different than the original if it is not chemically different as well. Any reduction heat treatment that exceeds the recrystallization temperature would remove evidence of cold work

and of quenching and tempering irreversibly. For example, cored brasses and bronzes, especially those in which deep-seated corrosion products replaced one phase preferentially, should acquire new surfaces that are chemically different than the original surface. However, the reduced object should look more like the original than the corroded object did, and the removal of deleterious impurities like halides and sulfur-containing ions should contribute to stability against further degradation, provided that additional protective measures are taken. In any case, the chemically and metallurgically altered surface region should be used only with great caution in interpreting the life history of the object.

#### 4. Oxidation Products

Both copper and iron have multiple states of oxidation. The higher valence states are more stable relatively at low temperatures, and the relative stability of the lower valence states increases with increasing temperature. Dry oxidation of copper yields a layer of cupric oxide in contact with air. Valensi [3] found that cupric oxide occupied most of the thickness at low temperature, diminishing with increasing temperature until the dissociation pressure of cupric oxide reaches the ambient oxygen pressure, beyond which only cuprous oxide forms. When the environment contains water or water vapor, the product of oxidation may be a hydroxide or hydrous oxide at low temperatures, but is almost invariably anhydrous oxide at high temperatures.

Table 1. Properties of Fe, Cu, and some of their oxygen-containing compounds.

Material	Structure	Vol/mol Fe (cm <sup>3</sup> )	$\Delta V$ -reduced (%)
$\alpha$ -Fe	b.c.c.	7.1	
$\gamma$ -Fe	f.c.c.	6.9	
FeO	NaCl	11.9-12.5	40-43
Fe <sub>3</sub> O <sub>4</sub>	Spinel	14.9	52
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	(15.2)	53
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	"Spinel"		
$\alpha$ -FeOOH	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	21.3	67
$\beta$ -FeOOH		27.5	74
$\gamma$ -FeOOH	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	22.4	68
Fe(OH) <sub>2</sub>		26.4	73
		Vol/mol Cu	
Cu	f.c.c.	7.1	
Cu <sub>2</sub> O	Cuprite	11.6	39
CuO	Monocl.	12.2	42
Cu(OH) <sub>2</sub>		29.0	76

Iron shows a similar behavior. Some information about its oxides, as well as those of copper, is collected in table 1. It is particularly important to note, from the last two columns, that the oxides are much more voluminous than the metal from which they form. Figure 3 shows some of the chemical interconversions among iron, its chlorides, oxychloride, oxides, hydrous oxides, and hydroxides. At high temperatures, water and halogens are readily driven off the compounds, to leave only anhydrous oxides, if there are no physical barriers that prevent departure of the volatile products. Below the eutectoid temperature in the Fe-O system at 570 °C, ferrous oxide (wüstite) is neither a product of oxidation nor a step in reduction of the higher oxides.

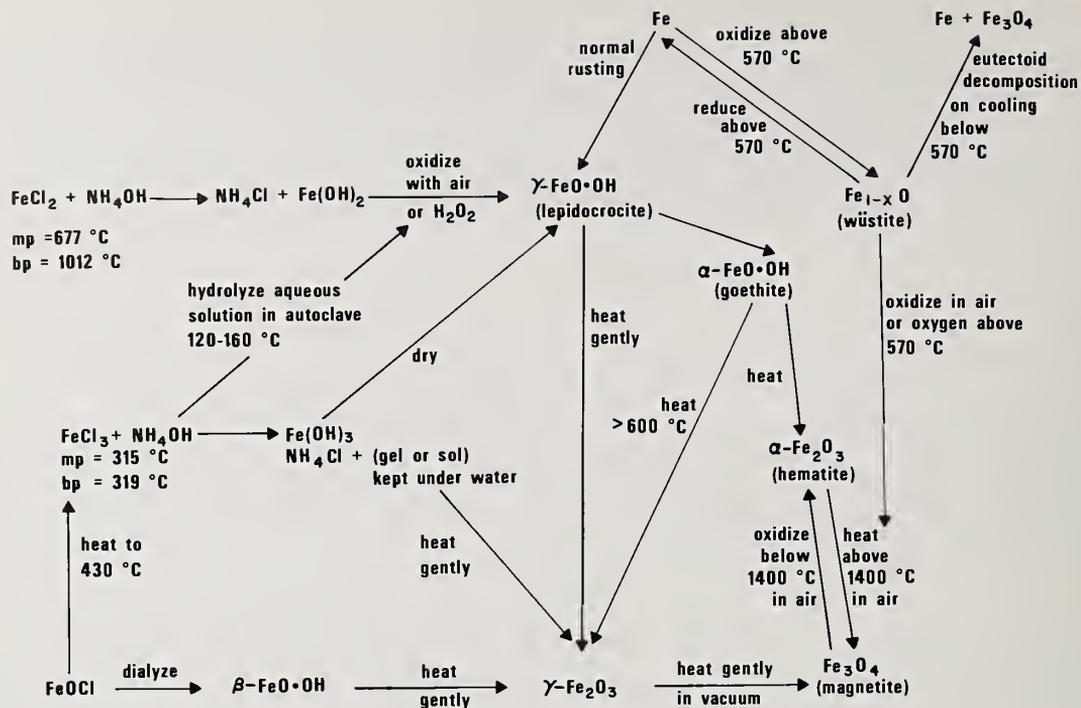


Figure 3. Relations among some iron compounds, adapted from A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., Oxford University Press, p. 545 (1962).  $\gamma$  forms are cubic,  $\alpha$  forms are rhombohedral or hexagonal.

## 5. Reduction of Iron Oxides

Direct reduction of the common oxides of iron, especially magnetite and hematite, which are present in the high grade ores or easily produced in beneficiating the lower grade ores, is a subject of intense interest for possible commercial exploitation. The main drawback to this process is the spongy, reactive nature of the iron that results from reduction. Those who have used the process for conservation of objects of historical value have recognized this problem and taken steps to prevent reoxidation by the use of vapor phase inhibitors and filling the pores with waxes and resins.

Failure to convert the oxides back to solid metal may not be entirely negative however. Many of the objects have lost iron by dissolution or by conversion to gelatinous products that are washed away. Graphite residues of cast irons and some steels may retain the shape of the original object even when most of the iron has been leached away. If little iron remains, there is no benefit to be obtained from a reduction process, although heating in an inert atmosphere may remove undesirable impurities. Some form of stabilization of the porous graphite should be provided. But if iron compounds are the major residue, they also may retain the shape and even the approximate size of the original object. Reduction to a solid mass would change the shape and size greatly, as indicated by a comparison of molar volumes as given in table 1, but the porous mass of iron that results from reduction occupies roughly the same volume as the compounds from which it is reduced. The purpose here is to review very briefly what has been reported about the kinetics of reduction of iron oxides.

Any heterogeneous reaction requires a nucleation stage, the formation of the first particles of the product. If there is an unreacted metal core, Gellner and Richardson [4] showed that reduction of iron oxides under conditions that are very close to equilibrium could avoid the formation of additional nuclei. This permits deposition of iron back onto the unreacted core. This process may depend on the ability of hydrogen to diffuse rapidly to the metal-oxide interface or on the creation of a generally oxygen-poor oxide which can

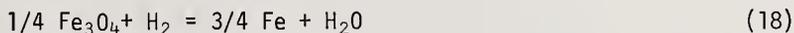
reject iron only where it is in contact with the pre-existing phase. This condition is difficult to maintain, and others [10] have not been able to reproduce it. That is, very careful control of the oxygen partial pressure in the gas phase is necessary to avoid the formation of other metal nuclei where the reducing gas is in contact with the oxide. Indeed, maintaining such control over the whole surface of a large, irregular object probably is not feasible.

It is to be expected that reduced iron nuclei will form at the external surface of a corroded object immersed in hot, reducing gas. The thin nuclei may grow until they impinge in the surface layer. In general, there will be a sequence of reducing gas, metal, lower oxide, higher oxides from every exposed surface. Wherever oxide is in direct contact with the reducing gas, it will tend to be covered with fresh metal. On the other hand, where metal covers the oxide, hydrogen from the reducing gas dissolves in the metal, diffuses rapidly through it to the metal-oxide interface where there is a strong driving force for the formation of water vapor. It may be the evolution of this gas that continuously deforms and fissures the solid layer, leading to the production of a porous, spongy mass instead of dense, solid metal. Hydrogen diffuses in through the iron much faster than oxygen can dissolve from the oxide and diffuse out, but the ability of water vapor to nucleate at the interface has not been demonstrated. Sjostrand [5] reports that the reduced iron is more porous below 570 °C where it forms from the higher oxides without an intervening layer of wüstite.

The first reasonably complete studies of reduction kinetics of iron oxides have been made by McKewan [6], by Quets *et al.* [7], and by Hedden and coworkers [8,9]. They agreed generally about the kinetics and the resulting structures, although the mechanistic details of the process were not clear. When polycrystalline hematite is reduced in hydrogen, the metallic iron nucleates on the outer surface. Above 570 °C, or a little higher, a layer of porous wüstite is next, and a layer of magnetite lies between that and the unreduced hematite. Below 570 °C the wüstite layer is missing. Reduction of polycrystalline magnetite goes directly to iron below 570 °C, with an intervening wüstite layer somewhat above 570 °C. At the lower temperatures for both oxides, there is an induction period which is shortened by increasing the hydrogen pressure or the temperature, but extended by increasing the water vapor pressure in the reducing atmosphere. The induction period is shorter for magnetite reduction than for hematite reduction. It appears to be a period during which reduction propagates rapidly down grain boundaries in the oxide and establishes a pattern of cracks and rifts in the grains. After this period, almost instantaneously at high temperatures, the rate of reduction becomes constant until reduction is more than two-thirds complete in magnetite and more than nine-tenths complete in hematite. The linear reaction rate constant has the form [8]

$$r_a = \frac{k_1 (P_{H_2} - P_{H_2O}/K)}{1 + k_2 P_{H_2} + k_3 P_{H_2O}}, \quad (17)$$

where K is the equilibrium water vapor to hydrogen pressure ratio for the reaction



Above 300 °C, this ratio is given approximately by

$$K = 36 \exp(-8000/RT) \quad (19)$$

For magnetite reduction in one atmosphere pressure of hydrogen,  $r_a$  varies from about  $10^{-5}$  grams of oxygen per  $\text{cm}^2$  per second at 400 °C to about  $10^{-4}$   $\text{g}_0/\text{cm}^2\text{-s}$  at 550 °C. Allowing for some irregularities between 600 and 700 °C,  $r_a$  approaches  $10^{-3}$   $\text{g}_0/\text{cm}^2\text{-s}$  at 1000 °C. These values were measured on magnetites with columnar grains that had cross-sectional areas averaging  $0.035 \text{ mm}^2$ . The rates are slower if the water vapor formed in the reaction is not swept away quickly or if the grain size is larger.

McKewan [6] noted that when  $P_{H_2O}$  is so small that the last term in numerator and denominator can be neglected, the remaining equation has the form of a Langmuir adsorption isotherm.  $k_2$  is nearly independent of temperature, and  $k_1$  has a temperature dependence that yields an activation energy between 40 and 60 kilojoules per mole per kelvin (9.55 and 14.33 kilocalorie per mole per kelvin). On this basis, he concluded that the rate is controlled by weak chemisorption of hydrogen which provides low coverage of the reactive surface at low hydrogen pressures and complete saturation at high pressures.

The introduction of water vapor into the reducing gas, or permitting it to accumulate as a reaction product, retards reduction. There are two possible contributions--an increase in the effective oxygen potential of the mixture, an equilibrium effect that decreases the reducing power, and also the hydrogen in the gas phase increases the diffusion back pressure for the escape (through pores and fissures in the solid overlayers) of the new water produced by reduction. The former (equilibrium) effect could be included explicitly in the calculation of the rate constant. The latter effect was demonstrated by showing that inert gases, nitrogen and argon, added to the gas stream decreased the rate of reduction;  $k_3$  decreases with increasing temperature, becoming negligible at high temperature, and yielding a formally negative value for 'activation energy'.

Hedden and Lehman [8] found that this pattern of reaction kinetics, including the activation energy for  $k_1$ , is about the same for a variety of n- and p-type semiconducting oxides with a wide range of heats of formation. They concluded that the basic rate controlling stages of the reduction mechanism are the same, independent of the nature of the oxide. Their study of magnetite reduction and, with Endom [9], of hematite reduction showed that there was a very strong grain size contribution to the rate. The finer-grained oxides were reduced much more rapidly than coarse-grained oxides because preferential reaction at grain boundaries and the formation of fissures there presented a surface area for reaction that was greater for the fine-grained specimens. Their synthetic oxides had columnar grains, which made the analysis of the problem simpler than it would have been if the boundaries formed a less orderly pattern. They were able to estimate the average thickness of the layer from which oxygen is depleted to be about 65 micrometers during the constant rate period independent of the temperature. This region appears to be microfissured to permit the removal of oxygen by the transport of water vapor.



Figure 4. Porous iron resulting from the complete reduction of magnetite at 423 °C [9]. The average grain cross section is 0.297 mm [2]. 50X. (Reproduced from Endom, *et. al.* [9], p. 635.)

Figure 4 shows a photomicrograph of a magnetite specimen that has been completely reduced to iron below 570 °C. The grain boundary fissures and porous grain interiors are easily



Figure 5. Hematite partially reduced at 590 °C [9]. The bright phase near the top is iron, the light gray interiors of the grains are hematite, and the dark gray bands along the grain boundaries are magnetite. The darkest area at the top is the mounting medium. 200X. Reproduced from Edom, *et. al.* [9], p. 642.)

seen. Figure 5 shows a partially reduced hematite specimen with an external layer of iron, fissured at the hematite grain boundaries, and broad magnetite envelopes growing into each hematite grain after penetrating deeply along the grain boundaries. Wüstite, if present at the iron-magnetite interface, is not resolved. The temperature of reduction, 590 °C, is just above the eutectoid temperature where the wüstite composition range is small. The grain sizes of hematite used in these studies were about 15 times smaller than the magnetite grain sizes, which may account for larger values of  $k_1$  for the magnetite reduction, although activation energies were about the same. The magnetite layer averaged about 10 micrometers in thickness at this temperature and was smaller as the temperature of reaction was lower, but in all cases the variation from place to place was large. In the photomicrograph, the magnetite layer is much thicker along the grain boundaries than on the surfaces where it is covered by a porous iron layer. Edom, Hedden and Lehman [9] note that for each eight iron atoms reduced to metal, the stoichiometric relations provide one iron ion that can diffuse through the  $Fe_3O_4$  layer to the magnetite-hematite interface where it can reduce  $4Fe_2O_3$  to  $3Fe_3O_4$ . This step probably controls the growth of the  $Fe_3O_4$  layer because magnetite is a sufficiently good semiconductor to transport the electron easily. Iron may be super-saturated in the magnetite at its interface with iron if the slowest step is there.

At some temperature between 570 and 610 °C, wüstite intervenes as a product during reduction, and the reaction kinetics change markedly. Hydrogen reacts to form water initially at the wüstite-gas interface, then near the iron-wüstite interface. The rate increases with temperature to about 650 °C, passes through a minimum just above 700 °C, then rises again. Decreasing reduction rate with increasing extent of reduction at fixed temperature shows that diffusion resistance in the growing iron layer cannot be neglected. Grain boundary and pore diffusion affect the rates. Nevertheless, oxygen still appears to be transported from near the wüstite-iron interface as water vapor. Studies on the direct reduction of synthetic wüstite samples showed that the new features are derived from the appearance of wüstite among the intermediate products.

The rate equation of Hedden and Lehman [8] probably is a satisfactory guide for planning a tentative reduction procedure for a corroded object, although the extended studies by Turkdogan and his coworkers [10] have shown that the real processes are considerably more complex. They found that porous small particles of hematite undergo reduction throughout the particles independent of size differences, especially at low temperatures. For larger

hematite particles, the early stages of reduction take place in the pore mouths near the iron-wüstite interface. The boundary between the iron and wüstite particles is not even; the time to reduce a particle completely is proportional to its diameter. However, control of the rate depends on both the rate of reduction at the interface and gaseous diffusion in the fine pores in the iron and wüstite. For larger particles and higher temperatures, diffusion in the pores becomes rate-controlling, and the time to complete reduction is inversely proportional to the square of the particle diameter. As the reduction temperature decreases, the pore size in the iron decreases and its permeability to gases decreases. The pore volume is almost completely interconnected but not uniform in cross section. The surface area per unit mass of iron is much greater when it is formed by low temperature reduction. Not all of the pores seem to participate in the reduction process, but it may be that the gas approaches the equilibrium composition within those pores with little mixing. Even if the original hematite and magnetite are dense, the wüstite that forms on them is porous, and iron grows inside the wüstite as well as on it. It is proposed that reduction of the wüstite takes place by oxygen diffusion through a very thin layer of iron so that the water molecules are desorbed from the iron surface. A mathematical analysis of a simplified geometrical model based on a single porous oxide appears to synthesize the elements of mixed rate control in a way that is numerically consistent with the experimental observations.

## 6. Gaseous Reduction of Corroded Objects

The complexity of both the corrosion process and the variable nature of the foreign matter that can accrue along with corrosion products, together with the incomplete understanding of the reduction process, make it a hazardous task to formulate a recipe for treating or restoring specific objects. This summary is presented only as a check list to ensure that the conservator has thought through the possible pitfalls before embarking on a particular course of action.

1. External foreign matter must be removed by physical means or superficial chemical reactions. The usual silicates and alkaline earth compounds that constitute muds and silts are not reducible under moderate conditions. Any investigation or sampling that is desired for purposes of establishing microstructure and even some aspects of composition should be done before heating. Replacement of small divots may be undetectable after some of the more vigorous reduction treatments.

2. The object should be heated gently to drive off physically and chemically included water without blowing off corrosion products and to minimize cracking from differential thermal expansion. Carbonates and sulfates may decompose, at least partially, and some volatile chlorides may be removed in this step. Removal of halogen and sulfur compounds could be the most important benefit in the whole process. In some cases, a mildly oxidizing atmosphere may be useful; in other cases, mildly reducing or inert gases may be better.

3. If much of the metal core remains, initial reduction in a mildly reducing atmosphere, controlled  $H_2/H_2O$  or  $CO/CO_2$ , may encourage deposition on the existing metal in preference to forming new metal nuclei on the surface. When the atmosphere is made strongly reducing, metallic nuclei may form on any surface to which the reducing gas can penetrate, but particularly the outer geometric surface of the object. Metal grows from these nuclei; the original volume of the object is not restored precisely even when corrosion has dissolved away enough material that the expanded residue occupies the original volume.

4. The freshly reduced product is highly reactive metal with a spongy structure unless it is heated to a high enough temperature for extensive sintering. To prevent quick reversion to the oxidized state and to provide mechanical support for the weak, porous structure, some filling and sealing process must be used. This procedure usually should incorporate inhibitors.

5. The most ambitious and successful practice of gaseous reduction methods appears to be the work of Barkman [11] and his associates in the Wasa preservation program. Their work includes many practical refinements that conservators would be wise to repeat unless a development program can be carried through to prove out variants.

6. Reduction of corrosion products seldom yields a consolidated metal object with the original dimensions. The porous, reactive metal requires protection to prevent immediate reoxidation. In some cases, most of the benefits of treatment might be obtained by careful oxidation to a state that is genuinely stable in the atmosphere against further degradation. Heating gently to drive off water, halides, and the oxides of carbon and sulfur, followed by oxidation in air or oxygen to a sufficiently high temperature to convert all accessible surfaces to a fairly thick layer of anhydrous oxide and to sinter that oxide into a continuous layer (perhaps under an inert or slightly oxidizing atmosphere) that would shield the unoxidized interior, should cause little additional increase in volume or loss in surface detail. Cooling must be done slowly to avoid cracking and spalling. Indeed, a few small cracks might have to be filled with some agent to prevent local corrosion. However, an object so treated should be nearly immune to further reaction because the outer layer would be in a thermodynamically stable state. The nature of the treatment should be evident in the product itself, and it would still be available for a future reduction treatment if that is considered desirable.

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#### Discussion

*P. Gaspar:* Can the change in slope of the rate vs. inverse temperature curve for reduction of magnetite and hematite at the temperature of stability of FeO be interpreted as being due to the involvement of FeO in the rate determining step? Is there a simple interpretation of the dramatic decrease in apparent activation energy for reduction above the stability point of FeO?

*R. A. Meussner:* There have been many attempts to interpret that type of data, but I think that they are all questionable. The activation energies that they get for the low temperatures are in the order of 14000-15000 calories. In the low temperature sensitivity

region, the activation energy we are talking about is 3000. I do not believe one should try to interpret a process as complicated as this is, using data collected that way.

*C. S. Smith:* When applying the high-temperature hydrogen reduction technique to objects of archaeological interest, it must be borne in mind that the resulting permanence is accompanied by the destruction of all internal records of the technical history of the iron. If they are not changed by subsequent heat and reduction, metallic microconstituents such as martensite or pearlite and particles of slag or other nonmetallic inclusions intimately reflect the conditions of refining, shaping, and heat treatment that produced the object. Even the external shape after reduction is only an approximation of the original, and the aesthetic quality of the surface, though it may be attractive, is quite different. Incidentally, a decrease of reaction rate with increasing temperature while the thermodynamic conditions remain unchanged is not uncommon when the temperature is high enough to cause sintering and hence a change in the geometry within which diffusion occurs. The hydrogen deoxidation of solid copper involving no phase changes shows a rate that decreases between 800 and 900° even greater than that observed by Dr. Meussner in his iron oxide system.

*E. V. Sayre:* To your knowledge, have streams of atomic hydrogen been used, possibly at low temperatures, for the reduction of corrosion layers on metals?

*R. A. Meussner:* I am sorry but I really don't know whether this has been tried or not.

*C. E. Birchenall:* The Ellingham diagram, figure 1, when supplemented in the upper left corner by the curve for HgO, provides a very compact rationalization of the history of metallurgy. Those oxides that are most easily reduced, which have the least negative free energies of formation, were the first to yield their metals for man's use.

Most of the reaction lines on Richardson and Jeffes' figure slope upward because the consumption of gaseous oxygen, combining with solid or liquid metal to form solid oxide, results in a decrease in entropy, hence less negative Gibbs free energy change with increasing temperature. The notable exception to this rule is the reaction of solid carbon with one mole of oxygen to form two moles of carbon monoxide. Only that curve slopes downward to more negative free energy change as temperature increases. As it crosses the metallic oxide lines it marks approximately the temperature range in which carbon becomes an effective reducing agent for that particular oxide. As man could build hotter furnaces, more stable oxides yielded their treasure.

The Ellingham diagram for sulfides shows that carbon is not an effective reducing agent for sulfides. The stability of SO<sub>2</sub> makes possible the roasting of sulfide ores to form oxides that can be reduced with carbon. Originally the two steps probably took place in the same fire.

*M. Pourbaix:* It has been said during this presentation that hydrogen may be most helpful for reducing all of the oxides of iron to metal. Perhaps some other treatments, with ammonia, may lead to the formation of gaseous ammonium chloride. All such treatments may also be studied with the help of equilibrium diagrams.<sup>2</sup>

Figure 6 shows as a function of the logarithms of the partial pressure in gaseous oxygen O<sub>2</sub> and of 1/T the equilibrium conditions of the system carbon-oxygen. The slope of every line is the enthalpy of reaction, and the ordinate at origin, for the infinite temperature, is the entropy of reaction. Lines (b) represent the homogeneous equilibria between gaseous CO and CO<sub>2</sub> for different CO/CO<sub>2</sub> ratios; lines (c) represent the heterogeneous equilibria between solid carbon and gaseous CO for different partial pressures in CO; lines (e) represent the heterogeneous equilibria between solid carbon and gaseous CO<sub>2</sub> for different partial pressures in CO<sub>2</sub>. Lines (a) and (b) show the vaporization of solid carbon with formation of carbon vapor e<sub>1</sub> and e<sub>2</sub>.

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<sup>2</sup>See Cebelcor's *Rapports Techniques* 115, RT. 181183. See also *A method of studying involved equilibria and its applications to metallurgical processes*. Proceedings 11th International Congress Pure and Applied Chemistry, London, 17-6 July 1947, 5 871-889 (1953).

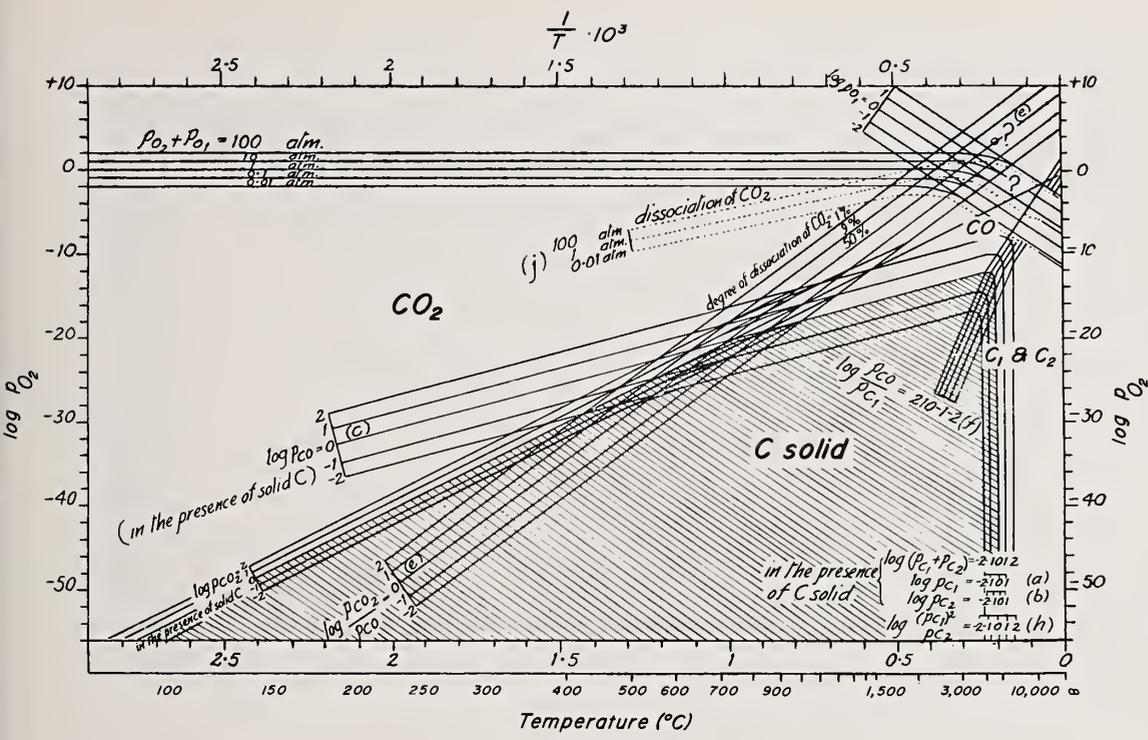


Figure 6. Equilibrium of the system C-O.

Figure 7 shows a similar diagram for the zinc-oxygen system, with indication of the stability conditions of solid Zn, liquid Zn, gaseous Zn and solid ZnO. One may notably see on this figure that, when heated, solid ZnO decomposes along line (f) in gaseous zinc and gaseous oxygen according to reaction  $2 \text{ZnO} \rightarrow 2 \text{Zn} + \text{O}_2$ , with a total pressure of 1 atm at 1949 °C.

By superposing figures 6 and 7 one gets, with addition of equilibrium data for solid  $\text{ZnCO}_3$ , figure 8 which relates to the ternary system Zn-C-O with consideration of solid C, Zn and ZnO, liquid Zn, and gaseous CO,  $\text{CO}_2$  and Zn. This figure shows notably that, by heating a mixture of solid ZnO and C, as is usual in the thermal metallurgy of zinc, one might get directly liquid zinc (corresponding to a zinc blast furnace) provided one could operate at 1052 °C and under a pressure of 7.8 atmospheres.

It is possible to predict easily, with such diagrams, the conditions where any high temperature reaction may occur, including those mentioned by Dr. Meussner for the removal of oxygen and of chlorine by hydrogen.

Figure 9 shows an overall diagram for the system H-O. Figure 10 shows part of this diagram, figure 11 shows part of the Fe-O diagram. Figure 12, obtained by superposing figures 10 and 11, relates to the H-Fe-O system, and shows the conditions where  $\text{Fe}_3\text{O}_4$ , FeO and Fe may be obtained by reduction of  $\text{Fe}_2\text{O}_3$  with  $\text{H}_2/\text{H}_2\text{O}$  mixtures. Figure 13 relates to the Fe-Cl system, and shows notably conditions where  $\text{FeCl}_2$  may be removed in the gaseous form.

Many similar diagrams have already been set up about 40 years ago. We are now discussing with some American friends (John Elliott at M.I.T., G. Simkovitch at State College, Earl Gulbransen at Carnegie Mellon) the possibility of preparing a series of "Atlas of Chemical and Electrochemical Equilibria in the presence of a gaseous phase" which would consist in a series of textbooks in inorganic chemistry for oxides, hydrides, chlorides, sulfides, hydrates, carbonates, sulfates, etc. John Chipman at M.I.T. has already

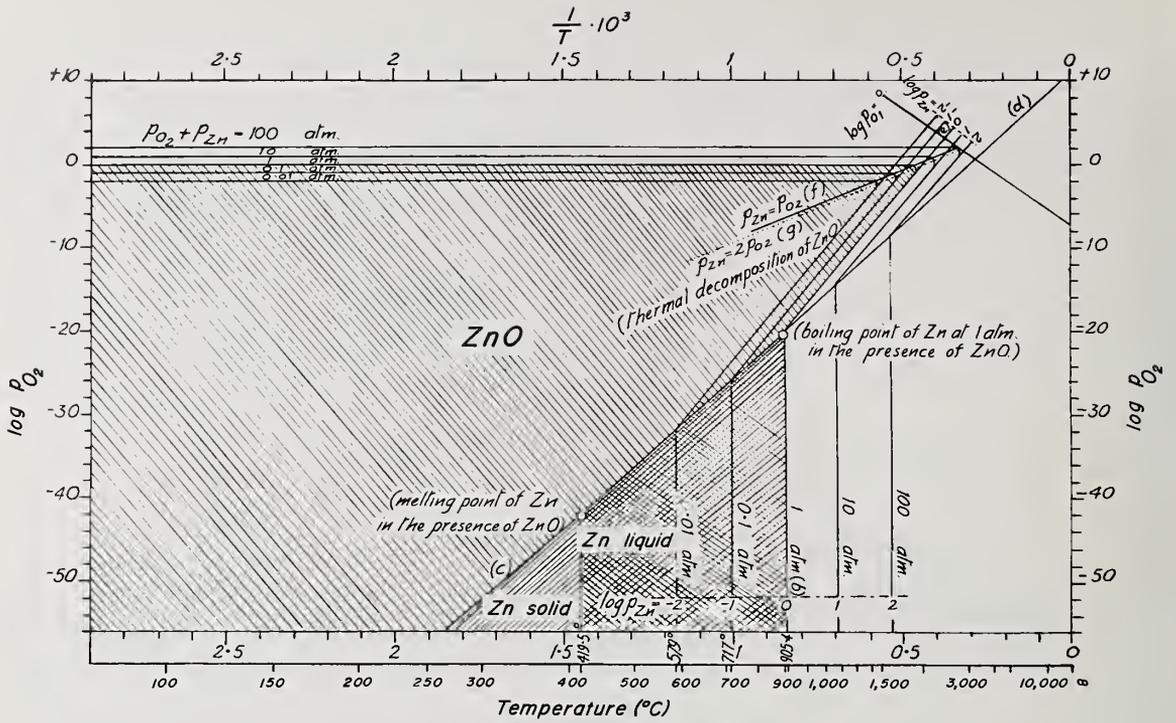


Figure 7. Equilibrium of the system Zn-O.

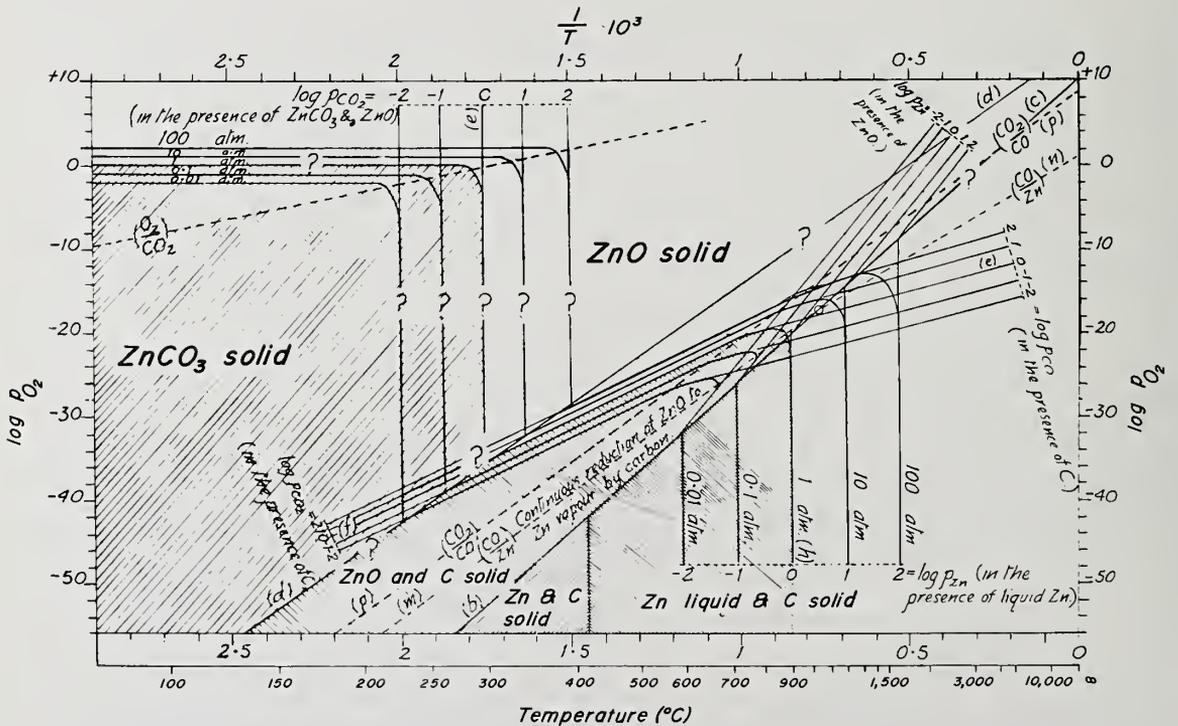


Figure 8. Equilibrium of the system Zn-O-C.

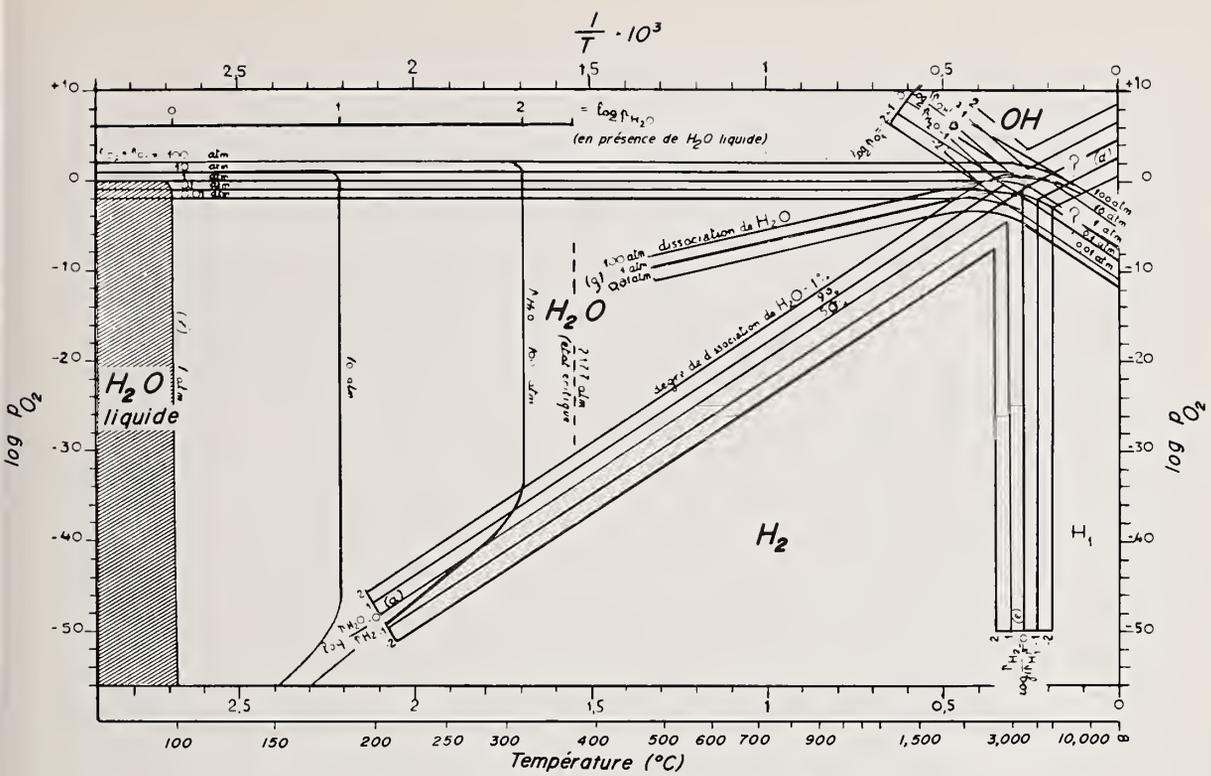


Figure 9. Equilibrium of the system H-O.

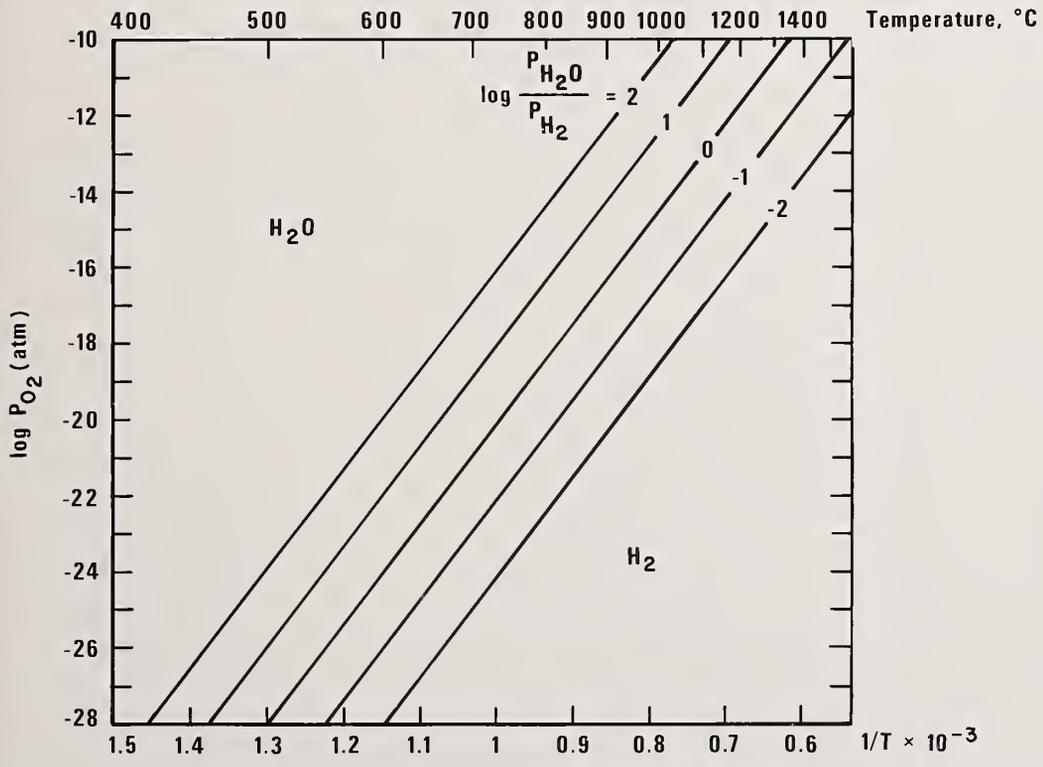


Figure 10. Equilibrium of the system H-O (detail).

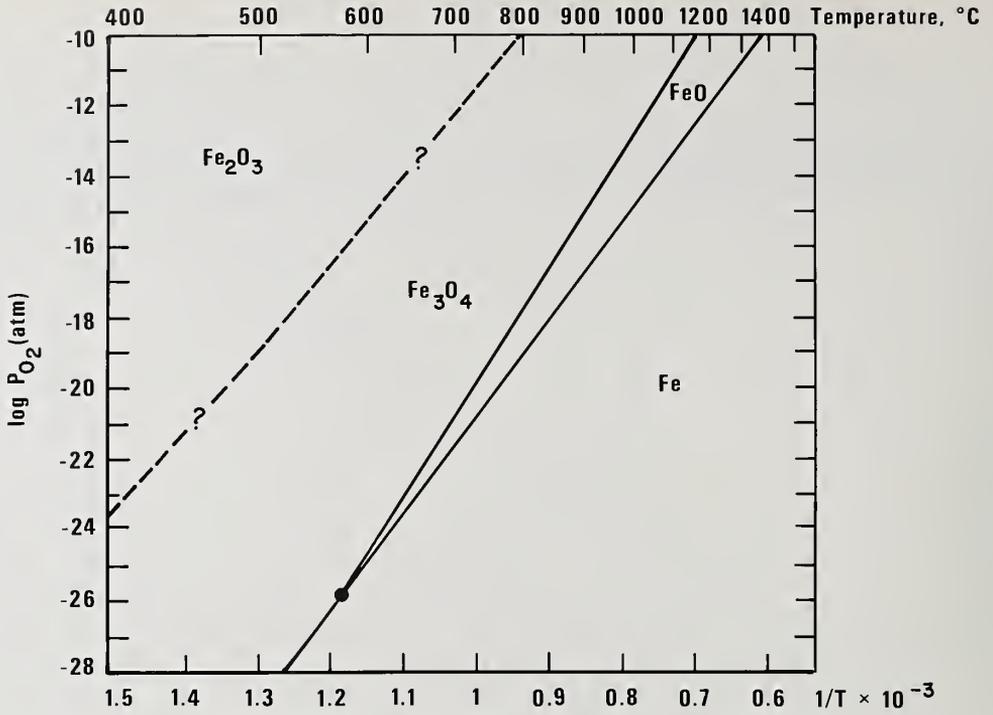


Figure 11. Equilibrium of the system Fe-O (detail).

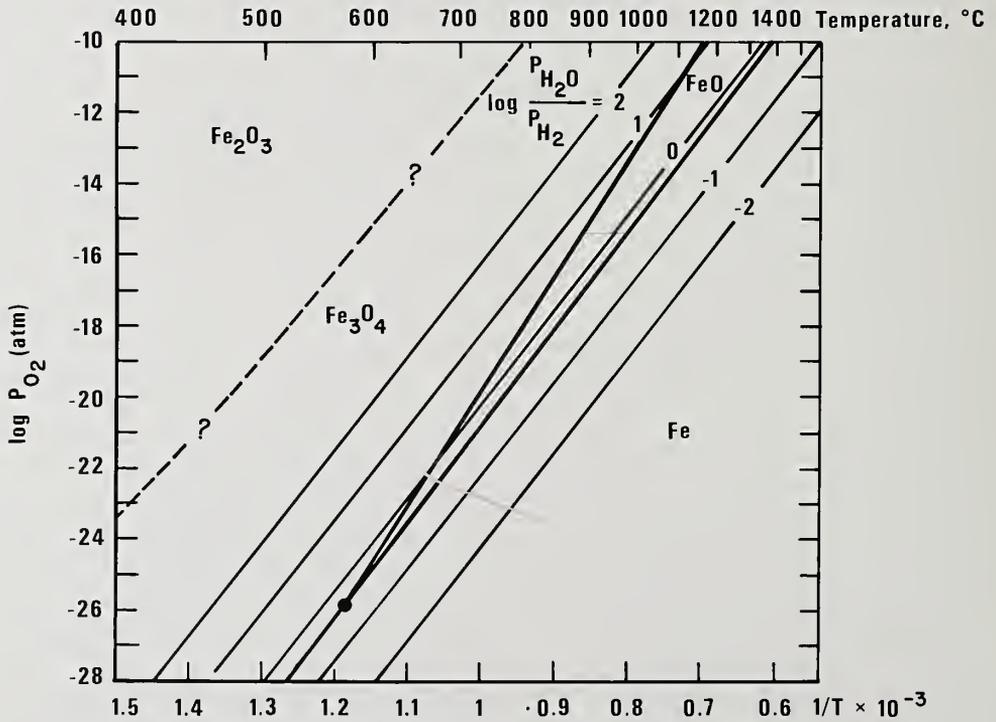


Figure 12. Equilibrium of the systems H-O and Fe-O.





## SOME BRIEF REMARKS ON ELECTROCHEMICAL REDUCTION

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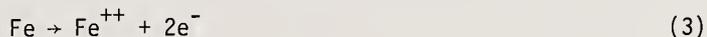
The corrosion scientist uses electrochemical reduction for three reasons: 1) to remove oxide or other corrosion product films in order to do experiments that start with a bare metal surface, 2) to measure the amount of corrosion product present on a metal surface, and 3) to determine the nature of the corrosion products on a metal surface. Because all three of the above reasons for carrying out electrochemical dissolution are of value to conservators and archaeologists but with perhaps different objectives, these brief remarks are directed towards acquainting them with some of the approaches, concepts, and experience developed by corrosion scientists. By no means is this discussion intended to be comprehensive. Those needing further details can obtain them from the literature that will be cited at the end of this discussion.

### 1. Chemical Reactions Involved

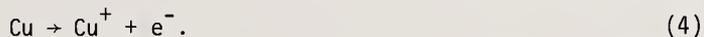
The reduction of corrosion product film is a cathodic process, *i.e.*, electrons must be supplied. The following two equations represent such reduction reactions for one kind of iron oxide layer and for one kind of copper oxide layer:



The electrons taking part in the above reactions are either supplied by a battery, the mode of carrying out an electrochemical reduction on which these remarks will concentrate, or they can be provided by an anodic corrosion process represented by

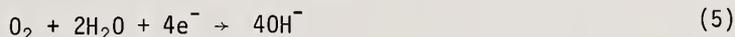


or



The latter mode of reduction is called autoreduction and will be discussed briefly later on.

There are two other cathodic reactions that should be mentioned because they can also occur along with the desired film reduction reactions (1) and (2) and interfere with them in some instances. These are the oxygen and hydrogen ion reduction reactions.



These are problem reactions which can occur concurrently with reactions such as (1) and (2). They therefore compete with the film or layer reducing reactions for electrons and thereby lower the efficiency of the film removal reduction process or prevent it from occurring at all. To lower the possibility of reaction (5) creating problems, a suitable experimental arrangement for carrying out an electrochemical reduction is necessary. This will be the topic of Section 2. Thermodynamic and kinetic considerations determine whether reaction (6) can be a problem. These will be discussed in Sections 3 and 4.

## 2. Experimental Considerations

The experimental arrangement for carrying out an electrochemical reduction is shown in figure 1. The arrangement shown is for carrying out a constant current reduction (galvanostatic).<sup>1</sup> A detailed description of the experimental aspects of cathodic reduction can be found in a paper by Oswin and Cohen [2]. For the purpose of this discussion it will be sufficient to describe the different parts of the arrangement shown schematically in figure 1. The reduction cell will have to be tailored for the object to be cleaned by

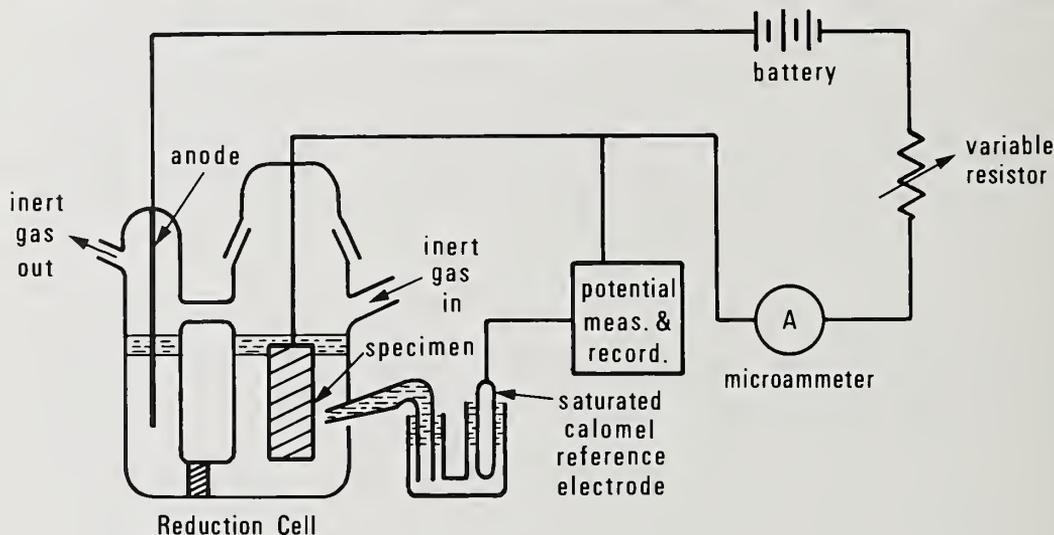


Figure 1. Schematic diagram of constant current reduction apparatus.

reduction but it should also embody the features listed by Cohen and Oswin: a) means for excluding air; b) provisions for carrying out a complete flushing of the cell with an inert gas (usually purified nitrogen) with the specimen in place and immersed in a well de-aerated electrolyte<sup>3</sup>; c) an arrangement that keeps the anode as far as possible from the cathode (the specimen) to minimize oxygen diffusion to the cathode; and d) if a solution analysis for dissolved metal ions is desired, a small as possible cell volume. Items a) and b) listed above are incorporated to remove oxygen from the solution used to carry out the reduction in order to avoid the complications mentioned in Section 1 arising from reaction (5).

The electrical circuit, shown in figure 1, that is attached to the reduction cell is quite simple. The variable resistor controls the current to be applied; it determines the

<sup>1</sup>It is possible to also employ a constant potential (potentiostatic) technique to reduce corrosion products. In this technique, the potential where reduction of a given corrosion product is known to take place is chosen. A potentiostat is needed when this technique is used. A description of the circuit for a simple potentiostat has been given by Green *et al.* [1]<sup>2</sup>.

<sup>2</sup>Figures in brackets indicate literature references at the end of this paper.

<sup>3</sup>See Oswin and Cohen [2] for a discussion of appropriate electrolytes to use.

rate of reduction. This current is supplied by the battery and measured by the microammeter. The saturated calomel reference electrode measures the potential of the specimen where corrosion product films are to be reduced and allows one to determine when the reduction process is completed. By recording the potential of the specimen versus time (chronopotentiometry) one obtains a curve of the sort shown in figure 2. From this curve a number of valuable pieces of information can be obtained. The width of the upper plateau A is a measure of how much material is being reduced at the potential value where

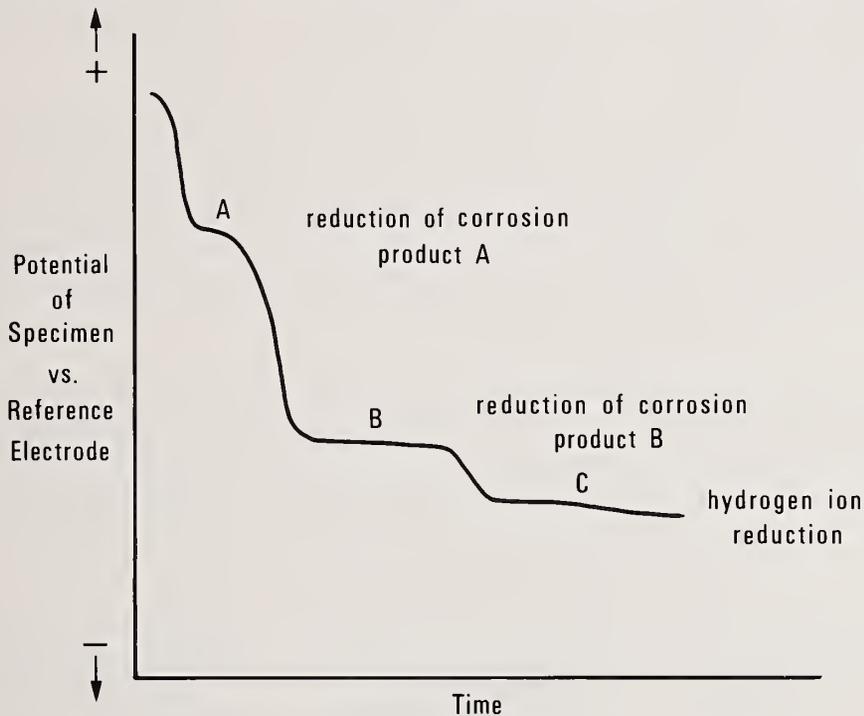


Figure 2. Hypothetical reduction curve for electrochemical reduction of corrosion product layer containing corrosion products A and B.

the plateau is found assuming that the process occurs at 100 percent current efficiency. If the current efficiency is 100 percent, all of the electrons are going into reducing corrosion product A. Because the reduction is being carried out using a constant current for the experimental arrangement shown in figure 1, the product of the number of seconds making up the width of the plateau and the current chosen for the reduction gives the number of coulombs involved in reducing all of A on the specimen's surface. The amount of A can then be calculated from the formula

$$W_A = \frac{i_A t E_A}{F} \quad (7)$$

where  $W_A$  = mass of corrosion product A reduced, grams

$i_A$  = current (in amperes) involved in the reduction of A per unit area

$t$  = width of plateau in seconds

$E_A$  = molecular weight of A (in grams) divided by number of electrons involved in the reduction of the metal atoms in A

$F$  = Faraday constant  $\cong 96500$  coulombs.

The potential at which the plateau for A occurs can sometimes be used to determine the nature of A from a knowledge of the potentials of formation of various corrosion product species. When the reduction of A is complete, the potential changes and its value becomes more negative until, in our example, another plateau is reached where the reduction of corrosion product B commences. The potential and width of the B plateau reveal as before, the identity and amount of B. Usually the final plateau occurs where the hydrogen ion is the species reduced (plateau C). The potentials of the plateaus are determined by thermodynamic considerations, the concern of the next section.

### 3. Thermodynamic Considerations

A valuable aid for looking at the thermodynamic considerations governing electrochemical reduction are the Pourbaix potential-pH diagrams [3]. These diagrams are described and discussed in the paper by Pourbaix occurring elsewhere in this volume. Such diagrams can be used to ascertain the potential of formation (or reduction) of the various oxides or sulfides making up corrosion product layers. Caution should be exercised, however, because kinetic considerations sometimes control the position of the plateau when nonequilibrium conditions prevail and cause the plateaus to occur at different values than those given in the Pourbaix diagram. In many instances, however, the diagrams can provide a useful guide to the corrosion products being reduced at a given potential.

Equally important as the potentials of corrosion product reduction, are the parallel oxygen and hydrogen evolution lines, the upper and lower thin diagonal lines respectively, shown in figures 3 and 4. Above the upper line, oxygen evolution can take place, below the lower line, hydrogen evolution can occur. These lines (especially the hydrogen evolution lines) are of great utility in determining whether it is feasible to reduce corrosion products on a given metal. In figure 3 are shown the Pourbaix diagrams for six metals of interest to those concerned with studying or restoring metal artifacts.

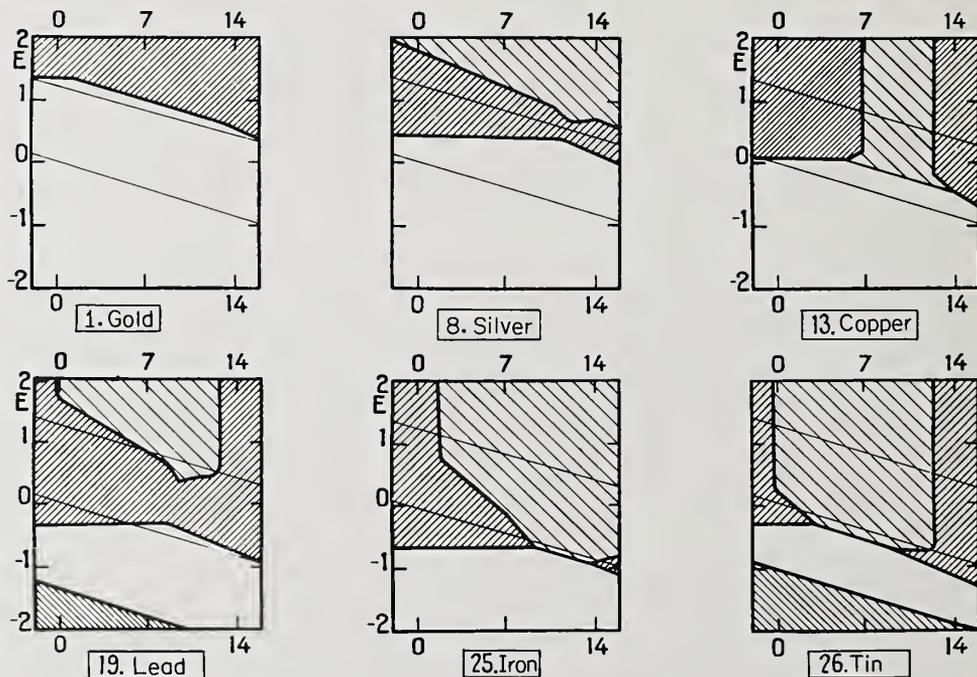


Figure 3. Potential-pH (Pourbaix) diagrams for easily reducible metals. Upper thin diagonal line is the oxygen evolution line, lower is hydrogen. The unshaded regions are those where the metal is the stable phase, the thinly shaded regions are those where corrosion takes place, and the coarsely shaded regions are those where corrosion products are the stable phases (from Pourbaix [3]).

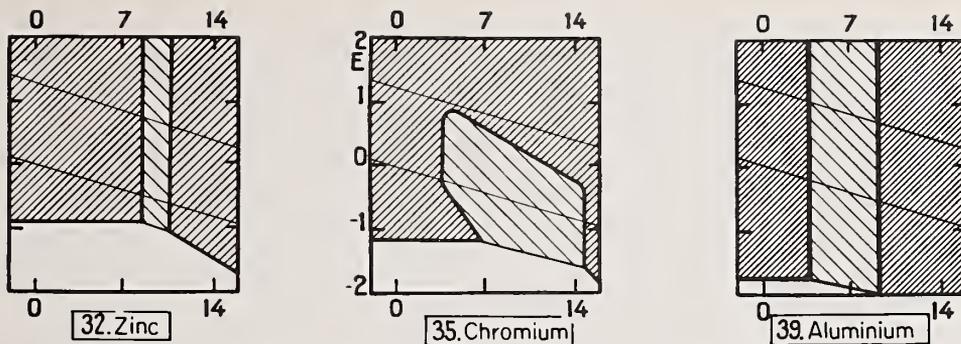


Figure 4. Potential-pH (Pourbaix) diagrams for difficult-to-reduce metals. Upper thin diagonal line is the oxygen evolution line, lower is hydrogen. The unshaded regions are those where the metal is the stable phase. The thinly shaded regions are those where corrosion takes place, and the coarsely shaded regions are those where corrosion products are the stable phases (from Pourbaix [3]).

The unshaded areas are those regions of potential and pH where the metal is stable. In these regions the metal is the thermodynamically stable phase; they are the regions where conditions exist to achieve electrochemical reduction. A crucial consideration is the location of the hydrogen line with respect to the regions where the metal is the stable phase. The diagrams reveal that, unsurprisingly, there is no problem for gold. Likewise, reduction is easy for silver. The corrosion products on copper are also easy to reduce. As one lowers the potential by applying a cathodic current, if the region where metal is stable can be reached before reaching the hydrogen line, then competition between the reduction of the hydrogen ion and the reduction of the oxide on the metal is won by the latter process and there is usually no problem in achieving an efficient reduction of corrosion products. For lead, especially in the middle pH regions, there is no problem. In the case of iron, the oxide reduction potential and the hydrogen evolution line almost coincide and, hence, there is no problem<sup>4</sup>. The situation for tin is also quite good. The metals in figure 3 are metals where theoretically one has a good chance for removing corrosion products by cathodic reduction. For the metals shown in figure 4, however, the situation is different. For example, for zinc, the distance between the oxide reduction potential line and the hydrogen line is much greater than those in figure 3. For chromium, they are even further apart. The situation is even worse for aluminum. (It is because of these thermodynamic facts, among others, that these metals were not produced by the ancients.) Simply put, the electrons supplied by the battery will all be used to reduce hydrogen ions and will not be available to reduce the oxide that exists on a metal specimen. This would indicate that in the future when museum conservators try to restore aluminum beer cans, they will have to employ some other approach than electrochemical reduction.

#### 4. Kinetic Considerations

The rate of corrosion product reduction is crucial in determining whether it is practical to use electrochemical reduction to remove corrosion products from a metal artifact. Thermodynamics determines what reactions are possible under a given set of conditions. Kinetics determines the rate of a reaction and whether, when two reactions are possible, the desired reaction (reduction of corrosion products) will predominate. For example, when both hydrogen reduction and corrosion product reduction are possible, it is necessary that most of the electrons supplied go towards reducing the corrosion product.

<sup>4</sup> It should be noted that the Pourbaix diagram in figure 3 shows a direct conversion of corrosion product to metallic iron. As Oswin and Cohen [2] show, however, the corrosion product can be reduced first to ferrous ions (eq. (1)). This fact will become important in the determination of the current efficiency as discussed in the next section.

An important measure of the effectiveness of carrying out the corrosion product reduction process is the current efficiency. It can be determined from the following expression:

$$\text{Current efficiency} = \frac{W_m F}{E_m i t} \quad (8)$$

where  $W_m$  = grams of metal produced by reduction of the corrosion product

$E_m$  = equivalent weight in grams of metal

$F$  = Faraday's constant in coulombs per equivalent

$i$  = current used for reduction in amperes

$t$  = time of reduction in seconds.

For a metal such as copper the corrosion product is reduced directly to the metallic phase (eq. (2)) and the metal is deposited on the specimen. For such a metal it is usually not possible to measure  $W_m$ . For a metal such as iron the corrosion product is reduced first to a soluble species (eq. (1)) and the quantity of these can be measured by chemical analysis of the electrolytic solution. In this case  $W_m$  can be measured and the current efficiency determined from equation (8). For iron, where the current efficiency can be determined from the quantity of metal dissolved in the electrolytes some of the experimental conditions that can affect the current efficiencies can be listed as follows:

1) Presence of oxygen dissolved in the electrolyte--if oxygen is dissolved in the electrolyte, the reduction of oxygen competes with the reduction of corrosion product. It is for this reason that the experimental arrangement shown in figure 1 includes provisions for working in an inert atmosphere.

2) Electrolyte buffering--Oswin and Cohen [1] have shown for iron that working in an unbuffered solution can give current efficiencies greater than 100 percent because in addition to adding metal ions by the reduction of the corrosion product process, additional ions are added because of corrosion. This occurs because of the process called "auto-reduction." This process results when, as mentioned earlier, reactions such as those given by equations (3) and (4), supply electrons that are in addition to the electrons supplied by an external source of current. A valuable discussion of autoreduction is given by Pryor and Evans [4]. Autoreduction can be decreased if a buffered electrolyte is used whose pH is in the neutral range of values. If, however, a buffered or unbuffered solution is used with a high pH, autoreduction is less of a problem, but other reactions, especially oxygen reduction, can become a problem.

3) Presence of a complexing agent--a complexing agent such as a salt of ethylenediaminetetraacetic acid is a chemical which complexes the metal ions that go into solution and ties them up so that they cannot use up current, for example, by electrodepositing on the surface of the specimen and thereby impede the reduction of the corrosion product. Complexing agents can increase current efficiency a great deal [2], even in solutions with a high pH.

4) Temperature--lowering the temperature of the electrolyte used for electrochemical reduction decreases the rate of autoreduction [4] and thereby improves current efficiency.

## 5. Possible Applications

Two final suggestions need to be made with regard to possible applications of electrochemical reduction to the study of metal artifacts other than the usual one of removing corrosion products for restoration purposes. These suggestions are rather speculative and need to be thoroughly researched before they can be applied, but they are worth mentioning.

1) Establishing the similarity between corrosion products on different artifacts--it would be useful to know if the corrosion product on an artifact A is the same as the

corrosion product on artifact B even though they both exist on the same kind of metal, were found together, but may have corrosion products produced under different conditions. An attractive possibility which should be backed up with a great deal of research, is to use the sort of information shown in figure 2, the position and width of reduction plateaus, to help establish similarities or differences between corrosion products. For example, Hoar and Stockbridge [5] were able to measure the proportion of oxides to sulfides present in films on copper using reduction plateaus.

2) Determination of age of corrosion products--Sato and Cohen [6] have examined oxides on iron aged for different lengths of time. They related the amount of charge to reduce the oxide to the aging time, and found differences in reduction times for different aging periods. Their aging periods were extremely short (5000 minutes ~ 3.5 days) in archaeological terms but perhaps with sufficient research such an approach may prove to be a useful tool for artifact examination.

The above examples serve to emphasize that electrochemical reduction has the potentialities to serve as a tool for gaining valuable information about an artifact in addition to its main use for the conservator, the removal of corrosion products for restoration purposes.

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## MEASURES FOR PREVENTING CORROSION OF METALS

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The objective of this paper is to summarize some of the methods that have been used to protect metals against environmental corrosion with particular reference to museum articles.

Traditionally, methods of protection have been based, more or less, on the definition of corrosion, *i.e.*, the interaction of a metal with its environment leading to deterioration of the metal. Accepting such a definition, it then appears logical to protect a metal by:

- a) treating the metal to render it corrosion resistant, or
- b) treating the environment to render it non-corrosive, or
- c) separating the two.

### 1. Some Restrictions

Because we are dealing with the corrosion of metal artifacts, things of interest to museums, it would appear that certain measures of great usefulness in corrosion technology would be non-applicable to the present problem. Specifically, reference is made to hot-metallizing processes, such as galvanizing and aluminizing, wherein the metal structure is immersed in molten zinc or molten aluminum and the surface is reacted and converted to a zinc or aluminum alloy. Another method of doubtful value might be alloying, although some mention is made of tarnish-resistant silver alloys later because of the wide and continuing interest in this subject. But the use of alloys as a protection measure is limited because, first, the alloy for the metal artifact might have been selected several centuries ago, and secondly, if the corrosion scientist were to attempt to specify that the artist work not with bronze or iron but, rather, with stainless steel, Hastelloy C, or titanium, this suggestion, I suspect, would be ill-received.

Also, the second method, the treatment of the environment, might pose some problem because, at the start, we do not always know what the environment will be. It should be possible to control the atmosphere in a museum case, and the example of the control of humidity in the preservation of bronzes at the Freer Gallery is cited. But, it would be much more difficult to control the environment in the rotunda of the U.S. Capitol.

In spite of certain restrictions, there are useful protective measures that can be considered in the preservation of metal artifacts.

### 2. Protection by Natural Corrosion Products

It should be recognized that, whereas the environment is often considered as the ultimate adversary in the destruction of metal objects, this destructive capability is more often due, not to the natural environment but more to foreign objects which we propel into the environment, such as soot and sulfur dioxide molecules. The atmosphere can be effective in developing its own natural means of protection and a few cases may be cited of the development of passive films in nature and how the electrochemist would use the same principle to achieve protection.

Iron, for example, which usually rusts at an excessive rate, in certain environments will develop a passive film of oxide, probably 10 to 25 Å thick. Iron statues have been known to exist for centuries in relatively uncontaminated atmospheres. One of the classical cases is the Iron Pillar at Old Delhi, India, pictured in figure 1. The Iron Pillar is a shaft, about 24 feet high, of inscribed wrought iron, erected in 400 A.D. and still preserved [1]<sup>1</sup>.



Figure 1. The Iron Pillar of Mehrauli, near Delhi, erected about 400 A.D., and showing no signs of rusting.

The green patina formed on copper roofs in some cases offers protection for many years. The determination of the chemical composition of this green patina was one of the first systematic corrosion studies ever made. This investigation was conducted in England by Vernon and his associates [2,3] and involved collecting and analyzing the corrosion products from roofs that had been exposed to the weather anywhere from 12 to 300 years. The composition of the green patina varied considerably depending on the location of the structure and the approximate composition varied with the atmosphere as shown in table 1. The figures do not add up to 100 percent because there were many other minor constituents in the film. Also, it should not be inferred that  $\text{CuSO}_4$  exists as a distinct and separate compound. These compounds were found as double salts since many of these copper compounds are isomorphic. Several general conclusions were drawn from the study. A green patina was present in all cases of considerable age although a brown film was formed at first. The copper sulfate compound was usually predominant, with the copper carbonate present in low concentration. Where industrial pollution is low in the urban-marine environment,  $\text{CuCl}_2$  may predominate over  $\text{CuSO}_4$ . The composition of these naturally formed corrosion product films was well summarized by Leidheiser in his monograph on the corrosion of copper alloys [4].

The observation of such cases as these has led the corrosion scientist to attempt to reproduce the behavior of Nature and protect metals by the formation of anodic films. The principle is illustrated in figure 2. As an anodic current is first applied, the iron electrode tends to dissolve. At a critical potential, passivation sets in and the corrosion current drops to a very low value. In this range of anodic passivity the active metal is essentially corrosion resistant. A method based on this principle has been used to protect ferrous alloys from corrosion in concentrated acids [5]. The anodizing of aluminum in sulfuric acid solutions is another example of the application of this principle. Aluminum forms a naturally protective oxide film of a thickness of about 25 Å thick.

<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

Table 1. Composition of green patina from different locations.

Location of structure	Age of Structure (years)	Composition of green patina (%)
Urban	30	CuSO <sub>4</sub> (49.8) CuCO <sub>3</sub> (14.6) Cu(OH) <sub>2</sub> (9.6)
Rural	300	CuSO <sub>4</sub> (25.6) CuCO <sub>3</sub> (1.4) Cu(OH) <sub>2</sub> (58.5)
Marine	13	CuSO <sub>4</sub> (2.5) CuCO <sub>3</sub> (12.8) CuCl <sub>2</sub> (26.7) Cu(OH) <sub>2</sub> (52.5)
Urban-marine	38	CuSO <sub>4</sub> (29.7) CuCl <sub>2</sub> (4.6) Cu(OH) <sub>2</sub> (61.5)

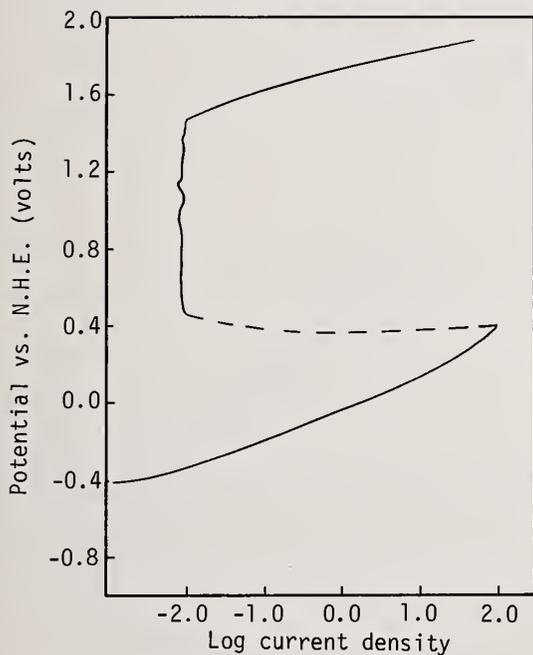


Figure 2. The protection of iron by anodic polarization.

Relatively thick anodized films are produced by electrolysis in 5 percent sulfuric acid and "sealing" in hot water. So-called "non-porous" films are produced by electrolysis in tartrate solutions. The art of anodizing is well-founded and procedures have been worked out to develop corrosion resistant oxide films on aluminum objects without loss of definition. Some procedures of coating metals with hydrous oxides, a closely related process, are discussed below.

### 3. Inhibitors

The employment of inhibitors may involve, in one case, the altering of the environment, but usually involves separating the metal from the environment. There are cases, for

example the addition of alkali to an acid solution, which merely serve to neutralize the agent responsible for metal dissolution. More common, however, are the inhibitors that function through the adsorption of molecules on the metal surface. This subject has been appraised by Foroulis in his excellent review paper on inhibitors [6].

Inhibitors might be either inorganic or organic compounds. Examples of inorganic inhibitors are chromates, molybdates, phosphates, silicates, nitrites and tungstates. These compounds are usually effective in low concentrations, in the range of 100 to 1000 ppm by weight. Organic inhibitors cover a very large number of organic compounds which may be characterized [6] by the type of bonding which is achieved with the metal. Certain compounds, such as nitrogen-containing compounds as aniline, butylamine, and pyridine, are thought to function by electrostatic attraction as does benzoic acid. A second type of compound is thought to adsorb and form a chemisorption bond. Some sulfur compounds and possibly some amines are chemisorbed. Benzotriazole and tolytriazole, both effective inhibitors of copper alloy corrosion, are believed to operate through chemisorption [7,8]. A further type of bond is thought to operate through pi bond interaction with the corroding metal. The so-called pi bonds exist in unsaturated compounds and the electrons forming the bonds instead of being localized, *i.e.*, tied to specific carbon atoms, float over the whole molecule. Thus, table 2, taken from the work of Foster *et al.* [9], shows that several compounds of very similar composition but varying degrees of saturation are dramatically different with respect to their effectiveness as inhibitors.

Table 2. Corrosion inhibition data with 1020 carbon steel in 2.8 N HCl at 65 °C.

Inhibitor (0.4 wt %)	Corrosion rate (metal loss, mg/cm <sup>2</sup> /d)
Blank	> 48,900
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	> 48,900
CH <sub>2</sub> =CH-CH <sub>2</sub> -OH	13,200
HC≡C-CH <sub>2</sub> -OH	146
H-C≡C- $\begin{matrix} \text{CH}_3 \\ \diagup \text{C} \text{---} \text{OH} \\ \diagdown \text{CH}_2\text{-CH}_3 \end{matrix}$	1,956

These inhibitors function to some extent in providing a physical barrier separating the metal from the environment. But it is important to note that monomolecular films are effective and that, in certain cases, fractions of monolayers reduce the corrosion rate to very low values suggesting that the compound, instead of forming an impervious barrier, acts by blocking selective sites that would catalyze specific reactions, as the reduction of hydrogen, which are key steps in the multi-step corrosion process.

#### 4. Treating the Environment-Vapor Phase Inhibitors

The most straightforward way to protect metals by the treatment of the environment is through the reduction in the water content necessary for aqueous corrosion mechanisms. It has been found that if the relative humidity of the atmosphere is below about 60 percent, such normally detrimental atmospheric pollutants as sulfates and chlorides do not corrode iron, copper, zinc, or aluminum. Therefore, the practical goal has been to keep the relative humidity below 50 percent. This can be achieved by using desiccants of which silica gel and activated alumina are among the easiest to use [10]. Moreover, these materials may be regenerated by heating: silica gel to 130-300 °C and activated alumina to 150-170 °C. Formulas have been worked out giving the amount (weight) of the desiccant in terms of the volume of air to be treated, the surface area of the metal, the type of barrier, and other factors.

A more positive method involves vapor phase inhibitors. These are compounds with a significant vapor pressure so that in a closed area they will volatilize and later condense on the metallic surface. The compound contains functional groups, nitrites, or amines that, when present in the condensed moisture film, will inhibit corrosion. The two original vapor phase inhibitors were dicyclohexylamine nitrite and cyclohexylamine carbonate [11,12]. The dicyclohexylamine nitrite has a vapor pressure of 0.0002 mm Hg at 25 °C and a solubility of 3.9 g in 100 g H<sub>2</sub>O which gives a solution of a pH of about 6.8. The carbonate has a higher vapor pressure, 0.4 mm Hg at 25 °C, a solubility of 55 g in 100 g of H<sub>2</sub>O, and produces a solution with a pH of 10.2. These compounds have been used to protect ferrous materials and may attack certain non-ferrous materials such as lead and cadmium. On the other hand, these compounds offer excellent protection for aluminum. In principle, there appears to be no reason why specific vapor phase inhibitors should not be developed for the protection of copper, brass, tin, lead, or any other alloy.

These vapor phase inhibitors have been incorporated into papers with which machined parts, for example, may be wrapped and stored for a period of years. One volatile corrosion inhibitor is marketed by Shell under the name VPI 260.

### 5. Protection by Electroplating

One intriguing question in science is how far back metal coating goes. Or, more specifically, when did artisans first use electroplating to protect or ornament baser metals. In the thinking of contemporary electrochemists this cannot go back before 1800 when Volta constructed his battery. In 1806, Davy electroplated sodium and potassium from their hydroxides, in the 1820's and 1830's Faraday did his important experiments on electrolysis, and only in the 1850-60 period were practical cyanide baths described in the literature. So, in terms of our more recent records, we would say that electroplating for the protection of metals does not go back much over 100 years. On the other hand, one might make a case for the existence of a certain amount of electroplating art approximately 2000 years ago<sup>2</sup>.

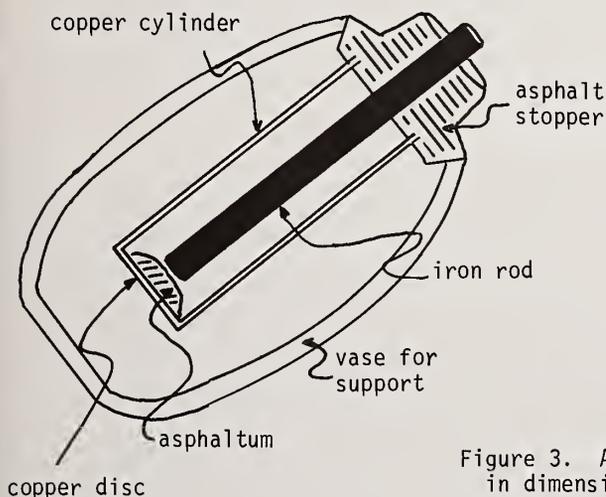


Figure 3. A battery assembled from pieces identical in dimensions to those unearthed by König.

<sup>2</sup>In the presentation of this paper at the Conference on March 17, 1976, the Gundestrup Cauldron was cited as a silver-plated metal artifact dating from the first century B.C. This observation was supported by reference to MacCana's monograph [13] wherein the Cauldron is described in great detail. More detailed investigation and correspondence with people who have studied the original Cauldron at the Danish National Museum in Copenhagen definitely indicate that it is constructed entirely of silver and not silver plated. The Author suspects that the difficulty may have come from translation. In the booklet, *Gundestrup Kedelen* by Ole Klindt-Jensen, the Cauldron is described as "an embossed silver-gilt vessel," meaning a silver vessel partially gilded with gold, rather than a vessel gilded with silver.

In 1935, the German archeologist, Wilhelm König, was excavating near Bagdad and found the remains of a Parthian town [14]. The Parthians dominated this region in the period 250 B.C. to 224 A.D. König found the remains of what has been concluded to be copper-iron batteries. Ceramic vases, copper cylinders, iron rods, asphalt stoppers, and connecting wires were found on the site. Similar pieces were assembled into a working battery using a copper sulfate electrolyte and this battery is depicted in figure 3. Other electrolytes, such as acetic acid and citric acid, were known to people in those days. A large number of these vases and parts were found and it is easy to visualize a series assembly of several batteries to produce a reasonable voltage. With this evidence one must leave open the possibility of electrodeposition being available for metal protection in earlier times.

In modern technology the silver plating of copper and copper alloys is well known. The more recent effort has been directed toward the development of plating baths that would yield non-tarnishing or non-corroding deposits. A recent U.S. Patent [15] describes a Ag-Sr-Ni alloy containing 70 percent Ag, 26 percent Sn, and 4 percent Ni which has the appearance of Ag but excellent tarnish resistance. This alloy was plated from a bath with the following composition and under conditions indicated:

Silver cyanide	0.65 g/l
Tin hydroxide	5.3 g/l
Nickel hydroxide	0.13 g/l
Sodium hydroxide	15 g/l
Sodium cyanide	100 g/l
Temperature	120-150 °F
Current density	15-45 A/ft <sup>2</sup>
Potential	1-1.5 V

The composition of these plating baths is usually arrived at in an empirical manner as the deposition of each element is controlled by its particular potential-current density relationship.

A recent Japanese patent [16] describes a procedure by which a tarnish resistant alloy is prepared by electrodeposition followed by thermal diffusion. The brass object is plated with 12  $\mu\text{m}$  of silver, 0.2  $\mu\text{m}$  of zinc, 0.3  $\mu\text{m}$  of indium, and 1  $\mu\text{m}$  of tin, in that order. The electroplated brass is heated in argon at 750 °C for 15 minutes, and slowly cooled. The alloy then has a composition of 88.1 percent Ag, 8.2 percent Sn, 2.2 percent In, and 1.5 percent Zn.

## 6. Protection with Hydrous-Oxides

There are a number of reports in the literature describing the production of non-tarnishing surfaces by hydrous oxides. These oxides have been deposited electrophoretically, by immersion treatments wherein a salt was hydrolyzed, or by selective oxidation of an oxidizable metal in an alloy. Fath *et al.* [17] described the protection of silver from tarnishing by the electrophoretic deposition of alumina from a bath containing aluminum sulfate and ammonium oxalate. Burkhardt [18] used a solution of 1.5 percent tin chloride in anhydrous methanol and deposited a stannic oxide solution by hydrolysis of the chloride. In some work done in our own laboratory with The Silver Institute it was found that the combination of these two techniques was successful in rendering silver relatively free of tarnish. The codeposition of Mg, Be, or Al with silver is described by Saifullin *et al.* [19], but it is not clear whether the metal or some compound is codeposited. From the conditions of the experiments, one would conclude that a metal hydroxide was deposited. The electrolyte and conditions used by Saifullin and coworkers were as follows:

AgCl (freshly precipitated)	40
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	200
$\text{K}_2\text{CO}_3$	30
pH	9.4
Current density (A/dm <sup>2</sup> )	0.1-1.0
Additive ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ )	0.001-0.1 g eq/l

Silver plated from baths with 0.01 g eq/l  $\text{MgSO}_4$  as an additive is claimed to be greatly resistant to tarnish.

Another oxide treatment is described by Yamazaki [20]. The silver surface is treated cathodically in a solution containing  $\text{SnCl}_2$  (20 g/l) and HCl (50 ml/l). A film of tin oxide or hydroxide is formed in 3 minutes at a current density of 0.02 amp/cm<sup>2</sup>. Alternate electrolytes are tin borofluoride and tin fluorosilicate.

A further oxide treatment [21], this one depositing beryllium oxide, is used to protect silver, copper, or brass against tarnishing. This bath contains 0.7 g/l of beryllium as a beryllium salt and the pH of the bath is maintained between 4.5 to 6.2.

## 7. Vacuum Deposition of Metals

The vacuum deposition of metals offers a method with several apparent advantages. The surface preparation need not be as stringent as required for electrodeposition and the details of the surface will be faithfully followed. Metals such as platinum, rhodium, and iridium may be deposited [22]. Certain metals such as chromium may be deposited in vacuum from the decomposition of a salt, *e.g.*, chromous or chromic iodide. Some metals, such as aluminum are deposited in large-scale commercial operations on both metallic and non-metallic substrates.

## 8. The Silver Tarnishing Problem

Over the years one of the problems that has received a tremendous amount of attention is the prevention of tarnishing of silver. Special attention should be given to this problem as virtually every method known has been explored, most in great depth.

A large number of silver alloys have been made and tested in sulfur atmospheres, in fact, alloys incorporating every metal with appreciable solubility in silver have been tested. Many investigations have been restricted to an upper limit of 7.5 percent alloying element to qualify as a sterling silver composition. Another specification is appearance. The alloy should look like silver, *e.g.*, not have a gold or steely cast. In a typical investigation [23] a large number of alloys was prepared and tested in a sulfur atmosphere. Alloys containing 15 percent zinc, 20 percent cadmium, and 10 percent indium were highly resistant to tarnishing. In this investigation a series of silver-copper alloys were prepared--recall the composition of sterling silver is 92.5 percent silver and 7.5 percent copper. All of the Ag-Cu alloys tarnished at a more rapid rate than Ag itself. In fact, of all the silver alloys available, the silver-copper represents the poorest possible selection for a tarnish-resistant composition. For tarnish resistance alone, a very good alloy would be one with a composition of 8-10 percent indium. With that result in mind, a number of years ago the Indium Corporation of America made up a number of sets of silver services with a tarnish resistant silver-indium alloy replacing the sterling composition. This development was never accepted commercially. Although quite resistant to tarnish, it had a slightly steely appearance, *i.e.*, it did not look *exactly* like sterling silver.

One of the most successful tarnish resistance treatments has been the use of electrolytically deposited coatings, such as those produced by depositing alumina or beryllia on the surface. It should be noted that rarely, if ever, does a coating render silver tarnish *proof*. The coating may give to the silver surface considerable resistance but, in a matter of time, it will tarnish. One objection to the electrolytic deposits is a loss of reflectance of a highly polished surface. This might not be apparent to the layman but is readily evident to the expert at the Franklin Mint as he examines his proof coin.

Certain inhibitors are effective in postponing the onset of tarnishing of silver. It is reported that silver plate, if treated with the phosphoric acid ester of a hydroxy fatty acid, tarnishes less readily. The silver article is immersed in a 3 percent solution of the ester dissolved in trichloroethane and then dried at room temperature.

A proprietary solution claimed to produce an anti-tarnish film includes thiourea and phosphoric acid.

Silver has been successfully protected against tarnish and corrosion by extremely thin coatings of rhodium, *e.g.*, 0.0001 to 0.0002 inch thick. Such coatings insure that the silver surface will not suffer a loss in reflectivity which is a critical item in many

silver applications. Finally, to prevent tarnishing of silver, and copper as well, a technique [25] has been employed which uses air-filter pads impregnated with finely divided Cu, Pb, or Zn hydroxide to absorb and react with the sulfide.

## 9. Acknowledgement

The Author would like to acknowledge the considerable help furnished by Mr. Richard L. Davies, Executive Director of The Silver Institute, in assembling the literature on silver tarnishing. Dr. Sarada furnished the photograph of the Iron Pillar in Delhi.

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#### Discussion

*Phoebe Weil*: Concerning the protective properties of basic copper sulfate on outdoor copper and bronze, we and others (for example Reiderer in Germany) have found that contrary to what has been observed in the case of copper roofing, where the green basic copper sulfate formed is highly but not totally protective of the metal beneath, that this same corrosion product on outdoor bronzes is *not* protective. The explanation is thought to arise from the differences in metallic structure (wrought in the case of roofing vs. cast for statues) and perhaps the greater likelihood in the case of statues for the presence of impurities and rougher surface finish (*e.g.*, filed). We have observed surface attack on statues approximately an order of magnitude or more greater than that reported for wrought specimens exposed in atmospheric exposure tests in similar urban environments.

*R. T. Foley*: Thank you.

*S. K. Coburn*: To confirm the use of vapor phase inhibitors, a revolution in packaging steel is taking place wherein a large barge load of coils of unwrapped steel are being protected by fogging the confined area with a vapor phase inhibitor and transporting the barge through areas where temperatures can result in condensation of moisture. The experimental results have been encouraging enough for us to send box cars and trucks loaded with unwrapped carbon steel to customers. Of course, the recipient, likewise, has to find an area in his plant where he can cover the steel with some sort of a shroud and fog the air space within the shroud to continue the protective atmosphere.

Experiments of this sort are continuing in different parts of the country where a variety of daily temperature differences characterize the respective locations.

*R. T. Foley*: Thank you. That was a very useful comment.

*M. Pourbaix*: You have shown a slide of a silver plated copper bowl that has been found buried in the soil in Denmark and appeared to be in exceptionally good condition. Is anything known about the corrosivity of the soil where the bowl was found?

*R. T. Foley*: No. I am sorry but I have no information about the soil.

*K. E. Holm*: This is a correction to what has just been said about the Gundestrup cauldron.

This cauldron, which is one of the most famous objects of the National Museum of Denmark, is made essentially of silver and is not manufactured out of silver plated copper.

Several authors have written about the cauldron, the find of which was originally published by Sophus Muller in *Nordiske Fortidsminder* Vol. I, 1892 (with a summary in French). The analysis made then give the figures 97 percent silver and *ca.* 3 percent gold. The rest is unspecified. The silver plates have been soldered together with tin-solder. The cauldron is partly gilded with a gold foil which in some places does not adhere very well.

*F. Halahan*: I wonder if the speaker could give any information on the use of mercaptans for the protection of silver and whether he knows if they are used in long-term polishes.

*R. T. Foley*: Under most circumstances mercaptans will corrode silver in much the same manner as sulphur. However, thiourea, which of course is not a mercaptan but very close to it, and some compounds like benzotriazol are used.

*F. Halahan:* I thought that the Long Tarnish-shield polishes for silver had mercaptans in them. At least according to the patent in England.

*R. T. Foley:* It is very possible that proprietary compositions do have mercaptans.

*R. M. Organ:* Mercaptans are supposedly present in Goddard's "Tarnish Preventive--Not a Lacquer". Long chain mercaptans with 15-23 carbons in the chain. The tarnish inhibitor "SEL-REX" contains the same substance, nominally, and analysis by infrared spectrophotometry in CAL confirmed the presence of mercaptans.

*W. T. Chase:* (Added in proof) Use of mercaptans as anti-tarnish agents incorporated into silver polish is covered in a U.S. Patent granted to James G. Murphy (U.S. Pat. 2,841,501; re-issue 24,819 (May 3, 1960)). He shows as examples n-hexadecane-1-thiol, n-dodecane-1-thiol, and other thiols.

## A REVIEW OF THE HISTORY AND PRACTICE OF PATINATION

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The word *patina* today is most commonly associated with the handsome green corrosion products found on certain ancient bronzes recovered after long burial in the soil, or with colors intentionally produced on bronze using various chemicals either with or without heat. My discussion will focus on the latter sort, commonly termed artificial patination. For a proper study of the history of artificial patination of metallic artifacts, particularly bronzes, one must consider as well the larger question of historical attitudes towards the interaction of color and form. Such a study serves several useful purposes: first and most important, it serves as a step toward achieving the objective that is the basis for all aesthetic decisions for connoisseur, curator, and conservator alike, namely that of attempting to see the object through the eyes of its maker or makers--of discovering the artist's original intent. What evidence do we have to call upon that will enable us to see antique bronzes through the eyes of the ancient artisans of the Berlin Foundry Vase, (fig. 1), here shown putting the final polish and burnish on a colossal bronze sculpture;



Figure 1. Berlin Foundry Cup, detail showing polishing and burnishing of a bronze statue (*Corpus Vasorum*, Berlin, II).

Foggini, here seen (fig. 2) in his studio around the year 1700, beginning the first clay sketch-model or *bozzetto* that will later be perfected, enlarged, and translated into bronze? Further, such an inquiry will assist us in distinguishing as the ancients did, between *aerugo nobilis* or "noble patina" and *virus aerugo* or patina that is destructive either

Figure 2. Foggini at work (Lankheit, *Florentinischer Barockplastik*, Munich, 1962, Fig. IV, caricature by A. D. Gabbiani, Florence, Uffizi).



visually or physically or both; and will provide a basis for deciding what, if any, treatment will most appropriately bring the object closest to its originally-intended appearance.

The problem of treating metallic objects is complicated by the fact that patina, *i.e.*, corrosion, is formed at the expense of the substance of the object itself, even occasionally to the point of complete mineralization, and once severe alteration or corrosion has occurred it is impossible to determine original coloration or finish from physical evidence. Further, these corrosion products and accretions can in themselves contain highly important historical information, whether they be the corrosion products and layers of soot and dust on an urban bronze that can perhaps reveal valuable information about past environmental history, or, in buried artifacts, a bit of soil that can help to identify provenance and establish authenticity.

This dilemma, the problems of determining original appearance, of identifying changes that have occurred during the course of time, and of judgment in distinguishing disfiguring foreign material from authentic substance of the artifact or work of art are among the most keenly debated problems in Art Conservation. The most publicized articulation of this dilemma that we might call "The Patina Dilemma" came about as a result of the so-called "Cleaning Controversy" in London, with articles published in the *Burlington Magazine* between 1949 and 1962 [1]<sup>1</sup>. The Cleaning Controversy related not to metallic artifacts but to paintings, for which the changes wrought by time have been summarily identified as *patina*. The arguments begin with rather polarized points of view of the Aesthetician versus the Scientist, the former speaking against "the raw and brutal surface laid bare by cleaning" and presenting a definition of *patina* for painting in terms of glazes or tinted varnishes claimed to have been purposely added by artists throughout the centuries to "tone down brightness" [2]. The Scientists held that treatment could be based on a purely scientific distinction between *genuine patina* or the alterations wrought by time on the authentic substance of the painting and *other* disfigurements wrought by discoloration of once water-clear varnishes, overpaint and restoration and accretions of various sorts [3]. These thesis-antithesis viewpoints were brought to rather elegantly stated synthesis in the articles by Stephen Rees-Jones and Denis Mahon who stressed the absolute necessity, to quote Mahon,

<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

of "the genuine pooling, without distrust and *arrière-pensée* of the most diverse forms of knowledge" [4]. Rees-Jones stressed the *necessity* for interplay between the methods of the laboratory and aesthetic and historic criteria on the question of patina, and quotes Paul Coremans in emphasizing the fact that chemical analysis and physical method, "should be viewed in relation to one another, and in the light of historical, aesthetic, stylistic and technical data to be derived from the curator's, aesthetician's, and restorer's examination of a picture" [5].

It is surely this total-view that we must ideally bring to bear on our approach to the consideration of patina on metallic objects as well. Perhaps in no other area of connoisseurship is one's judgment of beauty so dependent upon scientific understanding, for, as we often see, one man's "handsome patina" can be another man's "ugly corrosion products." The aesthetician will find that an acquaintance with the intellectual processes necessary to understand structure and cause and effect, instead of interfering with his sensory reaction, will rather enhance it; and the scientist will become more acutely aware of the demands made by historic and aesthetic criteria.

Turning now more specifically to our concern with the coloration of bronze, let us begin with a consideration of the material itself. Most of us are familiar with the bright, salmon-colored appearance of the highly-polished metal, as well as with the dark, red-brown of the oxidized surface of the metal. It is precisely the difference between the appearance of a new penny and that of an old penny. Now something different happens when bronze is exposed to increased amounts of moisture and various chemical substances, either gaseous or solid, that will react with the metal. Chemical reactions will occur that will tend to bring the metal into equilibrium with its ambient condition whether above or below ground, inside or out. Moisture is the essential ingredient for further change to take place, and if moisture could be excluded no further chemical changes other than the formation of the thin coating of red-brown oxide would occur. Once moisture becomes accessible to the bronze artifact, what happens is far from simple and still not entirely understood. Lewin and Alexander, in the introduction to their annotated bibliography on the composition and structure of natural patinas, published in *Art and Archaeology Technical Abstracts* [6], point out the considerable complexity of the chemical systems, as an example of which they mention that there are at least eight sulfate-containing copper compounds that can form when copper alloys corrode in the presence of sulfur compounds, and that some twenty-five copper-containing minerals have been identified in natural patinas. Furthermore, ambient conditions can change, as it must be remembered that prior to the Industrial Revolution in the 19th century, outdoor bronzes developed natural patinas described as attractive, thin, compact, translucent, generally red-brown and more or less tinged with green depending upon accessibility of moisture [7]. This stands in contrast to the mottled green and black appearance of modern urban bronzes (fig. 3) whose surfaces have been attacked by various components of urban air, particularly sulfur compounds.



Figure 3. George Washington, LaFayette Square, St. Louis: a typically disfigured outdoor bronze.

Thus, when we read Webster's current definition of *patina* as: "1. a fine crust or film on bronze or copper, usually green or greenish blue, formed by natural oxidation and often valued as being ornamental," and "2. any thin coating or color change resulting from age, as on old wood or silver" [8], we have a definition that, rather than being definitive, contains all of the elements that contribute towards present confusion on the subject:

1. "Natural oxidation" is an imprecise way to describe the extraordinarily complex variety of chemical reactions, of which oxidation is only one, that can occur on a metallic bronze surface as it works its way toward equilibrium with its environment.

2. The results are only rarely a "fine crust or film," but more often range from thin to thick, warty, and multi-layered; from compact to porous; from finely-crystalline to containing crystals of large size; smooth and enamel-like or rough and varied in texture; containing one or two simple compounds to a large number; and in colors spanning the entire spectrum: reds, grays, blacks, greens, blues, browns, purples, yellows, and oranges.

If patina is valued as an indicator of age, when, if ever should it be removed?

What are the criteria for the ornamental qualities of patina?

A revealing way to begin a study of historical attitudes towards patination is by having a look at the origins and use of the word itself. Most dictionaries give the origin of the word as deriving from the Latin word for *plate* or *pan* (*patena*) [9], though it is often mentioned that the connection is uncertain. The key is perhaps to be found in the first known printed use of the word which occurs in Filippo Baldinucci's *Art Dictionary* of 1681 where *patena* is defined, without reference to corrosion products of metals, as "a term used by painters, called by others a skin, namely that general dark tone which time causes to appear on paintings, that can occasionally be flattering to them" [10]. William Hogarth's depiction of Time Smoking a picture provides a good illustration of Baldinucci's definition (fig. 4).



Figure 4. William Hogarth, "Time Smoking a Picture" (George, Hogarth to Cruikshank: *Social Change in Graphic Satire*, fig. 10).

The most likely origin of the word *patina* is the old Italian word *patena* used to refer to a shiny dark varnish applied to shoes [11]. Balducci's use of the term indicates that it came to refer generally to the effects of time and only later was applied to such effects on metallic objects. The first appearance of the word in a dictionary with the definition referring to green corrosion products on bronze occurs in the French *Encyclopédie* of 1751, where *patine* is defined as follows: "There is no French word to express that beautiful and brilliant color of verdigris that copper does not always assume; the attractiveness of this color to the eye and the difficulty in describing it (because all coppers do not uniformly develop it) is highly valued by the Italians who call it *patina* as one dares to do here after their example and by the example of M. le Comte de Caylus who states correctly that one should be allowed to adopt a foreign word at least in the language of the arts of which this Encyclopedia is the Dictionary" [12]. Webster would have done well to emulate French caution.

The term *patina* used to refer to green corrosion products on bronzes was most likely stimulated by the expanding and heightened interest in archaeology in the 18th century. According to the *Oxford English Dictionary*, the earliest recorded English usage of *patina* to describe green corrosion products on bronze is as late as 1797. According to the Italian etymological dictionaries, the Italian verbs meaning *to give a patina*, *patinated*, and *patinator* are all 19th century in origin [13].

The philological aspects of the word appear to reflect the historical situation: while coloristic effects were achieved in bronze sculpture and other metallic artifacts by a variety of means from earliest times, it was not until the 19th century that artificial patination of bronzes by chemical means, with or without heat, was generally and widely practiced.

Observation of, indeed a fascination with the colored corrosion products of copper and copper alloys dates back to ancient times. Experimental artificial production of these substances from copper and other metals was perhaps even fundamental to the development of alchemy and thereby of chemistry itself [14]. The most convincing studies regarding the problem of patination of bronzes in ancient art have been made by Erich Pernice in 1910 [15], followed by the discussion by Gisela Richter in the 1915 catalogue of the ancient bronzes in the Metropolitan Museum [16], and a more recent study by H. Otto in 1959 [17] based on x-ray diffraction analysis of patinas. Both Pernice and Richter provide rich documentation from ancient literature and inscriptions as well as from the objects themselves, and Pernice goes a further step in having himself recreated the ancient method of finishing bronze. Both Pernice and Richter's work have been frequently overlooked in recent studies.

The most important of the ancient literary sources on the subject of patination are to be found in Plutarch, the Greek biographer and historian, and the Roman, Pliny the Elder (Gaius Plinius Secundus), both of whose writings date from the first century A.D. Richter's account of the passage from Plutarch's *De Pythiae oraculis* is worth quoting here: "A number of visitors to the sanctuary of Apollo at Delphi are made to discuss the question whether the patina on the bronze group in front of which they are standing is natural or artificial. One of them is admiring the beautiful surface of the bronze, which resembles neither dirt nor rust, but looks as if it had been dipped in a bath of brilliant blue color. 'I wonder,' he adds, 'whether the ancient masters used a certain mixture or preparation on their bronzes?' In the discussion that follows, various suggestions are made to explain the presence of the patina by physical conditions, for instance, that it is due to the action of the atmosphere which enters the bronze and forces out the rust (or rather corrosion); or that the bronze itself when it gets old exhales the rust." Miss Richter goes on to point out the great importance that Plutarch, "had no reason to believe in an artificial patina, but clearly decides in favor of a patina acquired by natural causes" [18].

To answer the question, "How did the ancients normally finish their statues?", both Pernice and Miss Richter marshal an impressive array of evidence supporting the thesis that the ancients finished their objects in bronze by giving them a painstakingly careful, high, lustrous polish. All seams and welds of the separately cast pieces were ingeniously and carefully hidden so that all exposed surfaces could be polished to perfection by specialists in the foundry. When one considers the great value of bronze metal in ancient times, it is not so surprising that the high lustre of the smoothed and polished metal itself was admired and judged the most desirable and normal method for finishing bronze artifacts of all kinds.

This is not to say that sculpture and other bronze artifacts were not without a variety of coloristic and textural effects, they were, but these were achieved by using alloys of contrasting colors, and other materials, such as ivory, stone or glass, as inlay or in juxtaposition, in combinations such as niello, silver and copper. Such contrasting effects were entirely dependent on a bright and untarnished appearance of the whole. The Delphi *Charioteer* has, for example, inset glass paste eyes and separately inserted bronze plate eyelids with eye lashes. This is consistent with the evidence we have for the appearance of Greek marble sculpture that was not only painted in bright colors, but often was fitted with accessories of different materials such as glass, ivory or metals of various sorts such as necklaces and earrings or diadems. And as the marble sculpture was provided with a protective coating of what was probably a wax-resin mixture (Vitruvius' Punic wax) [19], so was the bronze sculpture provided with a coating designed to exclude moisture and preserve the bright polish of the metal [20]. For both marbles and bronzes it was considered normal to remove and renew these coatings in order to maintain the original dazzling splendour of the sculptures. As Miss Richter pointed out in the passage from Plutarch, that it "follows indirectly that in his own time bronzes were kept in their natural finish; otherwise why should the Delphic visitors be surprised at the presence of a patina on Greek bronzes?" [21].

Several inscriptions survive from ancient times documenting provision for maintenance of bronzes. Pernice mentions an inscription from Chios of the fourth century B.C. in which the clerks of the market are told to see to it that a bronze statue of a tyrannicide be kept free from corrosion, and further the clerk is instructed to see that the statue be provided with a garland and kept bright [22].

The writings of Pliny [23] relevant to the finishing of bronze have been variously interpreted, but in the light of preceding remarks he is found to be entirely consistent. The Latin term he uses to describe the green corrosion products of copper is *aerugo*, *aeruginis* that is to say the rust (*robignine*) of bronze (*aes*). Pliny speaks of a method of producing it artificially, by hanging copper metal in casks over strong vinegar [24]. The uses and purpose of producing this *aerugo* are primarily medicinal and cosmetic, such as for anointing eyes and the healing of sores and ulcers, and not in any way related to the finishing of statuary. When Pliny speaks of bronze and the varieties of bronze alloys he consistently speaks of the color of the metal itself, for example the addition of lead to Cyprus copper "produces the purple color seen in the bordered robes of statues" [25], and that certain bronzes had special value because of their color [26]. A particularly good case in point is Pliny's account of the statue of Athamas by Aristonidas: "When the artist Aristonidas desired to represent the madness of Athamas subsiding in repentance after he had hurled his son Learchus from the rock, he made a blend of copper and iron, in order that the blush of shame should be represented by rust of the iron shining through the brilliant surface of the bronze (*aeris relucente*)" [27].

As to bronze treatments, Pliny mentions the use of vinegar and the urine of a child (*urina pueri*) for cleaning bronze [28]. For copper and bronze utensils he recommends frequent polishing and rubbing with oil or coating with vegetable pitch to preserve them from corrosion [29]. Perhaps the most frequently misinterpreted passage has to do with Pliny's statement about providing a protective coating for bronze statuary, the key words of which are: "bitumine antiqui tinguebant eas," which has frequently been interpreted to mean that the ancients painted their statues with a dark black coating of bitumen [30]. Considering the care taken in inlay work and in contrasting colors of metals this would be unthinkable inappropriate. Pernice has demonstrated the correct interpretation of this passage based on experiments using pitch diluted with turpentine to brushing consistency which was then painted in a thin coating onto a piece of brightly polished bronze. "The wash," he claims, "increased rather than diminished the brightness of the bronze, and at the same time protected the surface from atmospheric effects" [31]. The entire passage in Pliny runs: "The ancients painted their statues with bitumen, which makes it more surprising that they afterward became fond of covering them with gold" [32], because, as Pernice has demonstrated, the bitumen coating gave the same appearance to the bronze as gilding, and therefore made gilding unnecessary. This is reminiscent of the discussion of ancient picture varnishes and the varnish of Apelles as described by Pliny that occurred during the London Cleaning Controversy. Those who supported the idea that the ancients applied a tinted varnish to obscure their bright colors pointed to the descriptions of the dark resin solutions apparently used [33]. Those arguing in favor of the ancients not having veiled their colors pointed to the fact that such natural resins most likely to have been used by the ancients, while

appearing murky brown in a container, had the appearance of a shiny, essentially water-clear, transparent coating when applied to the painting [34].

We have even an inscription as late as 1076 A.D. on the bronze doors of the church of S. Michele at Monte S. Angelo in which the sponsor of the doors, Pantaleone d'Amalfi, instructs those in charge to clean the doors once a year so that they will always be shiny and bright [35].

So all evidence points to the fact that bronzes of all kinds, from artifacts to sculpture, normally received a high polish in the ancient Western world, and apparently in the East as well, and effort was made to maintain this polish. Those that were not maintained turned the familiar reddish-brown, and the old bituminous coating (if present) turned to a darkish color. Those statues exposed to damp outdoor or underground conditions later became tinged with greenish corrosion products. Above and below ground, and apparently beneath the ocean as well, the original high polish itself afforded a certain degree of corrosion resistance, for the smoother the metallic surface, the less well it can retain water, and the rubbing and burnishing process removes the softer constituents from the metallic surface to produce an exposed surface that is both enriched in the harder constituents and, most important, has greater structural and compositional uniformity. Gettens has, for example, pointed out this phenomenon in explaining the thicker, reddish corrosion products found in the unpolished recesses of relief patterns on certain bronze Chinese vessels, compared with the smooth green formed on the polished areas of relief [36].

With the rebirth of bronze casting during the Renaissance a new element of value entered the picture, namely "antiqueness" of a bronze object. There is even some evidence that this concept was valued in Roman times by collectors of Greek bronzes. During the Renaissance, however, it becomes clear that corrosion products had acquired a value, not only because occasionally the color effects of excavated antique bronzes could be quite alluring in themselves, but also because they testified to the age and therefore genuineness of an ancient bronze. And once this value was established, the imitators and forgers were not far behind.

Coloristic effects were still primarily achieved through gilding or the use of contrasting alloys on small objects, and by far the most popular and most common finish for bronzes large and small was the application of a dark lacquer, as can be seen in Donatello's *David* of ca. 1430, which was the first free-standing, full-length bronze figure cast since Antiquity. The use of this dark lacquer may have been a misinterpretation of Pliny, or an imitation of an ancient, discolored, bituminous coating, or, more likely, such a coating served the important purpose of providing visual uniformity to conceal numerous casting flaws and repairs that are reportedly characteristic of Florentine 15th century bronzes. When, for example, the dark coating plus accretions and corrosion products were cleaned from the bronze doors executed by Filarete between 1433-45 for St. Peter's basilica in Rome, they were found to be not only full of numerous original repairs but also made of a patch-work variety of alloy compositions clearly not intended to be seen [37]. In Donatello's earlier *St. Louis of Toulouse* of 1423, the statue was ingeniously cast in pieces small enough so that each could be gilt separately and the whole then put together much as a tailor constructs a suit [38]. The variety and experimental qualities of Donatello's approach to coloration of sculpture is exemplified as well by the wooden statue of the *Magdalen* which was covered for many years with a uniform brown paint to resemble bronze until the cleaning after the Florence flood revealed Donatello's bright polychromy [39].

The first modern account of the subject of the coloration of bronze occurs with the *De Sculptura* published in 1504 by Pomponius Gauricus, an amateur who made observations in the bronze foundries at Padua: "All beauty," he says, "appears perfect in the polishing and coloration. In the polishing we remove all harshness of the filing by means of a scraper, and we add the shine with pumice or with a point or with a burnisher. For coloration we give the color to each part whether in the cast itself (*i.e.*, by alloying) or, he goes on to describe the following colors: "white is achieved by the application of silver leaf, yellow, *i.e.*, gold, with gold leaf; green by wetting with salted vinegar, and black by a varnish of liquid pitch or smoke of wet straw. These colors will do for now, in waiting for the time that we will learn others" [40].

Our other principal literary source for Renaissance practice comes from the writings of the painter Vasari whose Preface to his *Vite* or *Lives of the Great Artists*, published in

1550 and revised in 1568, describes various artistic techniques. Vasari simply states that bronze, "assumes through time and by natural change a color that draws toward black... Some turn it black with oil, and others with vinegar make it green, and others with varnish give it the color of black so that everyone makes it come as he likes best" [41].

Though Vasari mentions green formed by exposure to vinegar, artificial green patinas are rarely found until well into the 19th century, at least one reason for which is the lack of stability of artificially formed greens, particularly under outdoor conditions.

The dark, shiny lacquer was most typical during the Renaissance, with certain exceptions, for example in the coloristic effects, particularly in small bronzes, achieved through combinations of metals and other materials seen in the work of such artists as Benvenuto Cellini, and Antico, and in the exquisite, translucent, reddish-brown lacquers typical of the work of Gian Bologna and his followers in the late 16th century [42].

As to stone and marble sculpture, it appears that in Roman times where carved representations were largely derived from Greek originals from which the polychromy had disappeared, a dichotomy developed for the first time between high-class, unpolychromed sculpture and more popular and conservative works that were polychromed in the old tradition. This tendency was followed, by and large, through the Renaissance onward, and marble carvers adhered to the progressive classical tendency following the Roman traditions and never used color. For coloristic effects it was necessary to rely upon textural variation.

Rudolf Wittkower's discussion of the problem of the polychromy of sculpture, in an article about Bernini's bust of Louis XIV, points out the problem of the eye as having always presented sculptors with one of their greatest problems in representing a head, for, "of all parts of the human body, the eye alone has a design in it which exists only in terms of color and not of shape--(that is) the iris and pupil. The problem is to translate this colored design into colorless sculptural form... Not until the Hellenistic period was a way found of representing the eye by purely sculptural means. Sculptors then depicted the iris by a circle cut out of the eyeball and the pupil either as one or two small holes in the center. While the shadow of the two holes gives the effect of the dark pupil, the ridge between them stands out clearly and produces an effect similar to the dash of light which enlivens the human eye. Since in real life this spot of light shifts with a person's angle of vision, the ridge enabled the sculptor to fix the direction of the look. The Romans accepted at certain periods the Hellenistic sculptured eye, while at others they preferred the simple Greek eyeball; but since they had abandoned polychromy, they left the eyeball unpainted... (During the Renaissance) one and the same sculptor would revert to the simple convex as well as to the sculptured eye... Michelangelo used the sculptured eye for his *David*, where he wanted the stare in the eyes to be fixed and determined. The same applies to his *Moses*. But in his Madonnas and statues in the Medici chapel he left the eyeball unworked" [43].

Few sculptors have expressed the general problem of polychromy in sculpture as well as has Gian Lorenzo Bernini in the 17th century, who was, to quote Wittkower, "always meditating upon the central question of portraiture in stone, namely how to translate the colors and the complexion of a face into uncolored marble," or we might add, into monochromatic bronze. Bernini stated that, "If a man whitens his hair, his beard, his lips, and his eyebrows and were it possible, his eyes, even those who see him daily would have difficulty recognizing him." He explained that, for instance, "in order to represent the bluish color which people have round their eyes, the place where it is to be seen has to be hollowed out, so as to achieve the effect of this color and to compensate in this way for the weakness of sculpture which can only give one color to matter. Adherence to the living model therefore is not identical to imitation" [44], presaging Picasso's famous statement that, "We all know that Art is not truth. Art is a lie that makes us realize truth..." [45].

A document referring to a bronze portrait bust by Bernini states specifically that he wished to reserve the final chasing of the face, hair and beard for himself, and that he preferred the bust without any type of coloring, "since time will give the metal a true and natural color" [46]. He was referring in this case to indoor bronze. In Bernini's immense bronze decorations for St. Peter's basilica in Rome, the *Baldacchino*, the *Cathedra Petri*, and the *Cappella del Sacramento*, the bronzes were either all or partially gilt or highly polished and allowed to darken naturally to a rich red-brown. Coloristic effects were achieved by gilding and the contrasts with other richly colored materials such as marbles and lapis lazuli.

It is not until the 19th century and particularly in France that we find the development of what can be called true artificial patination practiced on a large scale. As late as 1802, Francesco Carradori's book on sculpture technique written in Florence describes only filing and polishing the bronze surface [47]. By mid-century, in Paris, it has been estimated that about 6,000 men were continuously employed in bronze casting [48]; among them were the Master *Patineurs*, artistic specialists in their own right, who developed the art of coloring bronzes by application of heat and chemicals, and who, for the most part, carefully guarded their secrets. It was the exception for the artist himself to apply his own patinas. The Limet brothers, shown here (fig. 5) in their Paris studio, did much of the patination of Rodin's bronzes. An exceptionally fine example of artificial patination is seen in this small horse by Degas (fig. 6) cast by the founder Hébrard after Degas' death in 1917. Degas' use of polychromy in sculpture is exceptional but explainable by the fact that he was primarily a painter. Many of the small sculptures he left after his death were in multicolored waxes. The bronze caster Hébrard stated that particular efforts were made to duplicate the colors of the waxes in the coloration of the bronze. The horse is a particularly beautiful example of color variation by chemical means, with the horse colored a rich chestnut brown and the base tinged with green. Degas' interest in the coloration of form is perhaps best exemplified in the *Little Dancer, Fourteen Years Old* from 1880-81, exhibited in wax form during Degas' lifetime. The *Dancer's* shoes and bodice were real objects covered with colored wax and the sculpture was fitted with a real cloth ribbon and *tutu*. Such innovative effects were received with a certain amount of shock during Degas' lifetime [49].



Figure 5. Limet brothers, "Master Patineur," (Malvina Hoffman, *Sculpture Inside and Out*).



Figure 6. Horse by Degas: a small indoor bronze with patina in good condition.

While the Master Patineurs delighted in creating artistic effects on a small scale, large works were normally given the simplest of treatments, normally uniform and depending, it seems, largely on the quality of the cast. For example at the von Müller foundry in München, the bronzes were left uncolored and probably simply waxed. Harriet Hosmer's statue of Senator Thomas Benton, cast by von Müller in the 1860's was described as being a bright golden color at its unveiling [50]. Otherwise, large scale sculpture was normally chemically treated to turn a dark brown or black.

Efforts to study the change in appearance of outdoor bronzes wrought by atmospheric pollution at the dawn of the industrial age and to provide a more scientific base for the chemical coloration of bronze appears to have begun in Berlin in the 1860's. The various milestones can be found for the most part in the Lewin-Alexander "Patina Bibliography" [51]. Alongside this tradition is that of the sculptor's or craftsman's handbooks that present the various methods handed down in the workshops or, more often, simply lifted without acknowledgement from previously published handbooks. I have collected some eighteen or so books and articles by sculptors or metal-workers, the earliest dating from 1873, and there must be many more [52]. Malvina Hoffman's book, *Sculpture Inside and Out*, first published in 1939, is among the most comprehensive accounts drawing on her experience as a student of Rodin and work with Master Patineurs in the Rudier foundry in Paris. For the most part these are simply recipe collections, with ingredients often described in obscure, arcane or imprecise fashion, for example: salt of sorrel, sulphhydrate of ammonia, uric acid (for urine), wine vinegar, and the like. Explanations of the chemistry involved, when provided, are usually incorrect. It is no wonder that the various sculptor-authors often speak of the element of chance or luck in achieving desired results. Occasionally these handbooks provide a statement regarding desirable aesthetic qualities of artificial patination, all of which agree with that of Slobodkin who states that artificial patinas, 1) should appear natural, and 2) the patina should be very thin and transparent, and should emphasize the metallic qualities of the medium [53]. Uniformly absent is any discussion or even concern with maintenance other than the usual suggestion that bronzes should receive an occasional application of beeswax or commercial paste wax. One author, J. Rood, goes so far as to state: "If a sculpture is of sufficient importance that subsequent generations would like to preserve it indefinitely, a way can certainly be found" [54]. To this we should certainly exclaim, "Such faith!"

Most modern sculptors in bronze believe in the romantic myth of a benevolent Nature that will in time provide their sculptures with a handsome patina. For example, Henry Moore has stated that, "...bronze, naturally in the open air (particularly near the sea) will turn with time and the action of the atmosphere to a beautiful green. But sometimes one can't wait for nature to have its go at the bronze, and you can speed it up by treating the bronze with different acids which will produce different effects. Some will turn the bronze black, others will turn it green, others will turn it red. I usually have an idea, as I make a plaster, whether I intend it to be a dark or a light bronze, and what colour it is going to be. When it comes back from the foundry I do the patination and this sometimes comes off happily, though sometimes you can't repeat what you have done other times... It is a very exciting but tricky and uncertain thing, this patination of bronze" [55].

Those of us who must be concerned with the preservation of bronzes and therefore with the problems of patina have a difficult task indeed, demanding the broadest use of scientific, historical and aesthetic tools available. For sculpture the problem of patination is particularly subtle and acute, for when one considers the traditional way in which the sculptor has worked since the Renaissance in monochromatic wax or clay translated to plaster, translated to bronze or marble, his coloristic effects, as Bernini has stated so well, are dependent upon textural variation. For the eye to see these variations in texture and form requires a reasonable uniformity of coloration. By comparing the appearance of sculpture before and after conservation treatment, the camouflaging effect of a deteriorated patina is plainly apparent (figs. 7 and 8).

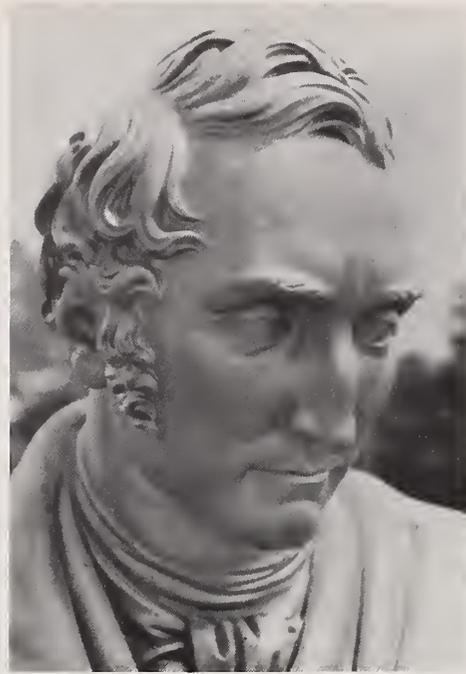


Figure 7. Thomas Hart Benton, Lafayette Square, St. Louis: before conservation treatment.

Figure 8. The same sculpture after conservation treatment.

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- [10] Filippo Baldinucci, *Vocabolario Toscano dell'Arte del Disegno*, Florence, 1681.
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- patine* "Il n'y a point de mot françois pour exprimer cette belle & brillante couleur de vert-de-gris que le cuivre ne prend pas toujours; l'agrément de cette couleur pour l'oeil & la difficulté de la raconter (car tous les cuivres ne s'en chargent pas également), la rendent très-recommandable aux Italiens, qui la nomment patina, comme on ose ici le faire d'après eux, & par l'exemple de M. le comte de Caylus. "Il doit être permis, dit-il avec raison, d'adopter un mot étranger au moins dans la langue des arts". Or l'Encyclopédie en est le dictionnaire."
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- [24] Pliny, *op. cit.*, XXXIV.xxvi.
- [25] Pliny, *op. cit.*, XXXIV.xx.
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"Questo bronzo piglia col tempo per se medesimo un colore che trae in nero e non in rosso come quando si lavora. Alcuni con olio lo fanno venire nero, altri con l'aceto lo fanno verde, et altri con la vernice li danno il colore di nero, tale che ognuno lo conduce come più gli piace. Nel che si vede questa arte essere in maggior eccellenza che non era al tempo degli antichi."
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"Après qu'elles sont bien nettoyées & réparées, on leur donne si l'on veut une couleur. Il y en a qui prennent pour cela de l'Huile & de la Sanguine: d'autres les font devenir vertes avec du Vinaigre. Mais avec le temps la bronze prend un vernis qui tire sur le noir."  
The French *Encyclopédie* of Diderot (*op cit.*) states (under sculpture): "Quant à la poix dont les anciens couvroient leurs bronzes, nous n'avons rien à desirer; les fumées & les préparations de nos artistes sont d'autant préférables, qu'elles ont moins d'épaisseur."

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"Finalmente ripurgasi il lavoro, e conducesi alla dovuta perfezione, prima con lime diverse, più o meno fini, e capaci di entrare in tutte le parti; indi con acqua e pomici di varie grossezze; e per ultimo con dell'istessa pomice pesta, e stecche di legno, e con tripolo."

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#### Discussion

*J. Olin:* Does the corrosion on outdoor bronzes serve as a form of protection against future corrosion?

*P. Weil:* We have examined and photographed the surfaces of a number of outdoor bronzes 60-100 years old and have found them to be very badly pitted. The pits average up to 2 mm in depth. While a certain degree of protection is provided by the basic copper sulfate, it appears that it is not total and in fact corrosion is still going on, much more actively in some places than in others, particularly in green areas.

*T. D. Weisser:* I am not sure that the green product should be removed; however, after working on several outdoor bronzes, I would agree with Phoebe Weil, that the green corrosion product on these bronzes is not necessarily protective. On the bronzes I have worked with, the areas with green corrosion are lower than the areas under the black spots, which could indicate that the green areas have corroded more heavily than those covered with the black product. Often there is a difference of 1/16 inch in the levels of the metal under these two areas.

*K. E. Holm:* You might be interested in knowing that we in our museum have examples of bronze spearheads colored with what is supposed to be a bitumen. The bitumen decoration is well preserved and stands black in contrast to the now somewhat green bronze. The spearheads are dated to about the 3rd-5th century A.D.

## THE PRODUCTION OF ARTIFICIAL PATINATION ON COPPER

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Patination on copper is a natural process that has been observed for centuries on copper roofs and on copper-base metal artifacts that have been exposed to the action of the atmosphere. The colors developed during natural patination are generally a pleasing green, though each local area often will have a particular shade of green that is its own characteristic. The shade of green may be modified by impurities in the copper as well as by the local form of air pollution (fig. 1).

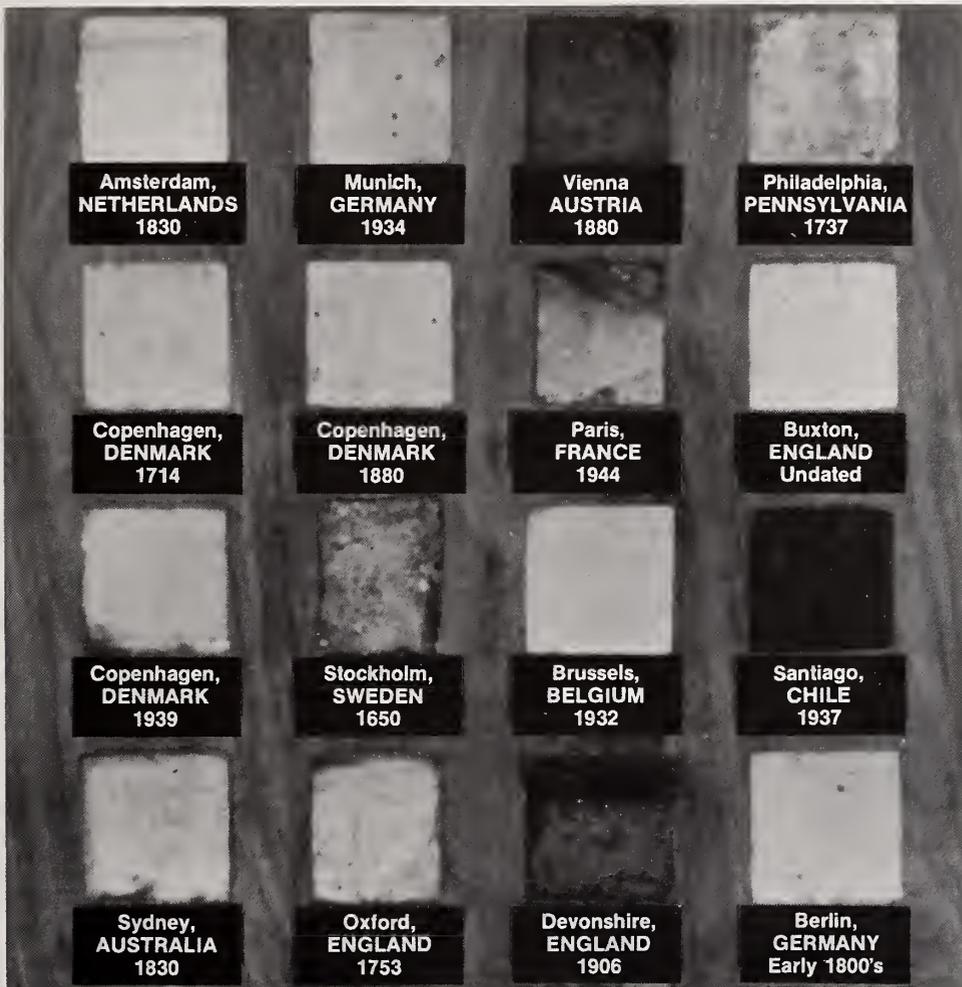


Figure 1. Range of possible shades of patinas on copper (see color plate r). Natural patinas formed on copper after extended atmospheric exposure in various parts of the world, International Copper Research Association, Inc.

This figure was furnished by the International Copper and Brass Research Association and illustrates the range of possible shades of green. The specimens were assembled from worldwide locations. In the top row from the left, we have represented Amsterdam installed in 1830, Munich in 1934, Vienna in 1880, and Philadelphia in 1737. The second row includes Copenhagen in 1714, Copenhagen in 1880, Paris in 1944, and Buston, England, undated. The third row consists of another from Copenhagen in 1939, Stockholm in 1650, Brussels in 1932, and Santiago in 1937. The bottom row has specimens from Sydney in 1830, Oxford in 1753, Devonshire in 1906, and Berlin in 1800.

It was thought, for many years, that natural patination consisted of basic copper carbonate either in the form of azurites or malachite. This misconception has persisted for a long time even though as early as 1908, it was reported by Loock that the patina on the Jan Wellem Memorial in Dusseldorf was basic copper sulfate rather than basic copper carbonate. From 1923 to 1933, W. H. J. Vernon and collaborators investigated natural patinas extensively and came to the same conclusion that the major constituent of most natural patinas was brochantite or basic copper sulfate. Vernon and Whitby sampled patinas from urban, rural, marine, and urban marine locations in England. Careful chemical analysis established that copper carbonate was only a minor constituent and that the only exception to the predominance of brochantite occurred in a marine environment that was free from atmospheric pollution. Natural patinas formed in a clean marine environment were found to consist of basic copper chloride.

As recently as 1962, F. L. LaQue and W. D. Mogerma referred to the patina on the Statue of Liberty as being a "handsome protective layer of green, basic copper sulfate." This statement aroused opposition from several quarters and was finally resolved by chemical and x-ray diffraction analysis performed by D. H. Osborn of American Brass who confirmed that the patina was composed predominantly of basic copper sulfate with less than 5 percent basic copper chloride and less than 0.1 percent basic carbonate.

There have been many methods developed to produce a green coloration or patina on copper or copper base artifacts by accelerated means. The natural process takes approximately ten years and for most of that time the surface has a dark brown to black appearance that is not particularly pleasing. Copper will form green or blue colored salts with most of the common acids, therefore, it is not surprising that the reagents used in the solutions devised for artificial patination seem to represent a large proportion of the stock found on many laboratory shelves. Some of the formulations that have been used are:

- |    |                    |           |    |                    |            |
|----|--------------------|-----------|----|--------------------|------------|
| 1. | Ammonium chloride  | 10 parts  | 4. | Ammonium chloride  | 10 parts   |
|    | Sodium chloride    | 20 parts  |    | Sodium chloride    | 40 parts   |
|    | Copper carbonate   | 30 parts  |    | Copper nitrate     | 80 parts   |
|    | Cream of tartar    | 10 parts  |    | Cream of tartar    | 10 parts   |
|    | Acetic acid 1:1    | 100 parts |    | Acetic acid        | 1000 parts |
| 2. | Ammonium chloride  | 8 parts   | 5. | Sodium chloride    | 20 parts   |
|    | Sodium chloride    | 8 parts   |    | Copper nitrate     | 20 parts   |
|    | Ammonium hydroxide | 15 parts  |    | Water              | 100 parts  |
|    | Acetic acid        | 500 parts | 6. | Ammonium chloride  | 250 parts  |
| 3. | Sodium chloride    | 20 parts  |    | Ammonium carbonate | 250 parts  |
|    | Copper acetate     | 20 parts  |    | Water              | 1000 parts |
|    | Ammonium carbonate | 60 parts  | 7. | Copper nitrate     | 25 parts   |
|    | Cream of tartar    | 20 parts  |    | Zinc chloride      | 25 parts   |
|    | Acetic acid        | 100 parts |    | Water              | 100 parts  |

It is recommended that all the preceding solutions be brushed on thinly to the grease-free copper surface and allowed to air dry. After drying, the surface is rubbed with a soft cloth. This process must be repeated several times in order to develop the depth of color desired. The skill and artistry of the person doing the work play a large part in its quality.

Freeman and Kirby have proposed an alternate immersion process that used a 10 percent solution of ammonium sulfate at 140 °F. This solution must be conditioned or saturated

with copper at a pH of 5.5 to 5.7. The process is said to require at least 24 hours and a final dip in hot water to develop a natural color in the basic copper sulfate coating.

The Incra Patine I Process is the spray application of an ammonium sulfate, copper sulfate, lithium chloride, sodium dichromate, and hydrochloric acid solution that is thickened with a silicate. This process can be adversely affected by the occurrence of inclement weather too soon after application.

Svenska Metallverken, Sweden, has developed a prepatination process under the direction of Dr. E. Mattsson. In this process, the reaction product from cupric nitrate, ferric sulfate, and sodium hydroxide is applied to the preoxidized copper sheet. The coated sheet is dried under carefully controlled conditions and coated with a sealer. The coating resembles natural patina and is designed to last until the natural patina develops. It is claimed that adherence improves with exposure time and that the presence of sulfate can be detected in the coating after five years exposure.

The preceding methods are and have been used more or less successfully, but none of them are as satisfactory and simple as the one bath dipping processes that are available for coloring copper and its alloys brown and black. In 1966, Professor C. K. Hanson of the University of Utah began a research program for Incra, directed towards the preparation of inorganic coatings on copper. The early months were devoted to finding combinations of reagents that would produce colored adherent coatings on copper. This was a trial and error procedure and employed elevated temperatures and pressures.

It was found that a number of reagents would produce colored coatings provided an oxidizing environment at the proper pH was maintained. Recognizing that a pressurized system would be impractical, efforts were directed towards developing an effective cheap aqueous oxidizing system. It was found that potassium chlorate was the most efficient of the reagents that were tested. The coating produced on copper by potassium chlorate was determined to be cuprous oxide. When copper sulfate was added to the system a green layer formed that was identified as brochantite, the basic copper sulfate found in most naturally patinated copper. Cleaned copper panels immersed in dilute solutions of potassium chlorate and copper sulfate developed a coating of brochantite in about 20 days at room temperature. Further work indicated that the time required for brochantite formation could be reduced by agitation, increased solution concentration, and elevated temperature.

As a result of this work, Revere Copper and Brass began work for Incra on a program designed to scale up this method of patination from the test tube/breaker size to a pilot operation in which several 3 foot x 4 foot sheets of commercial 16 ounce ETP copper (CDA110) could be patinated at one time. It was proposed to investigate the effects of variations in agitation, temperature, and solution concentration on the rate of brochantite formation. Determination of solution stability, and the feasibility or need for rejuvenation of used solutions would be made by conducting frequent analyses for copper, sulfate, chloride, and chlorate ion concentrations. Redox and pH would be monitored during each run. The patinas formed would be evaluated with regard to color, uniformity, and adherence. Atmospheric exposure tests would be started using representative panels from each run.

Initial experiments conducted on a beaker scale confirmed that the Utah Process could be reproduced in Revere's Laboratory. A solution concentration of 2.5 g/l each of copper sulfate pentahydrate and potassium chlorate was adjusted to pH 3.0 with sulfuric acid. Three cleaning methods were investigated, sulfuric acid pickling, ammonium persulfate etching, and mechanical cleaning with abrasive-impregnated nylon pads. Mechanical cleaning produced the best results in a 20-day still exposure. Agitation by stirring reduced the time required for patination confirming observations made previously at the University of Utah.

The pilot equipment consisted of a stainless steel tank, 60 inches long, 24 inches wide, and 49 inches deep. Its working capacity was 1060 liters. An overflow weir at one end fed a stainless steel centrifugal pump with a pumping capacity of 40 gallons per minute at 35 feet of head. The output of the pump flowed through a heat exchanger equipped with a thermostatically controlled immersion heater. After passing through a flow meter, the solution was distributed from a header to four perforated pipes located at the bottom of the tank. All materials in contact with the solution were Type 316 stainless steel. The maximum flow rate proved to be 17 gallons per minute, somewhat less than anticipated.

When charging the tank, a mixer was installed on the end of the tank. Deionized water was added to the working level and the pump and stirrer started. Additions of reagent grade copper sulfate and potassium chlorate based on the 1060 liter volume of the system were made and stirring was continued until the salts were dissolved. pH adjustment was made by adding 10 percent sulfuric acid while monitoring with a pH meter. The auxiliary stirrer was then removed and agitation continued by pump.

Four holes were punched on the long side of the 3 foot x 4 foot x 16 ounce copper sheets and they were cleaned mechanically on both sides with abrasive impregnated nylon pads. The sheets were rinsed and suspended in the tank by stainless steel hooks on insulated cross bars. Twelve 3 inch x 3 inch cleaned copper panels were taped to one of the sheets for daily removal to check on the progress of patination. A solution sample was removed daily and checked for pH, redox potential, copper, chloride and potassium chlorate.

A total of nine runs were made in this pilot equipment. The initial runs established that mechanical cleaning of large areas by hand was not satisfactory. The patination was soft and nonadherent and the nonuniformity appeared to be associated with cleaning. The agitation provided by the pumping system was also contributing to the nonuniformity (fig. 2a). This result is typical of the mirror image patterns developed on adjacent sheets by turbulent flow. By increasing the copper sulfate concentration and raising the temperature, we were able to develop a fairly heavy patina, but it was soft and nonadherent (fig. 2b). During these runs, the solution became turbid at about the same time that patination began to develop. Analyses of the soft nonadherent patina indicated that chloride ion was being incorporated in the patina. A run made without agitation at ambient temperature yielded a dense adherent patina with no chloride present.



Figure 2. Patinas produced in pilot equipment:  
a. typical non-uniform mirror image patterns developed on adjacent sheets when turbulent flow is present (see color plate b);  
b. heavy but soft and non-adherent patina produced when copper sulfate concentration and temperature were increased.

The analyses and measurements made on the daily samples showed that the copper concentration increased rapidly during the oxidation stage and as patination proceeded, decreased to nearly the initial value. The redox potential fell rapidly during oxidation from 600 mV to 300 mV and then rose to 350-400 mV during patination. The pH increased rapidly during oxidation from 3.0 to slightly higher than 5.0, then leveled off at 5.0 during patination.

As the pilot runs were in progress, considerable time was devoted to bench work in an effort to solve the coverage problems associated with agitation and surface preparation. Variations in the mode of exposure to the patination solution were also investigated. In one approach a cleaned 3 inch x 5 inch copper panel was supported at a 10° angle in a PVC box. The patinating solution was pumped from a heated battery jar over the panel and returned to the battery jar at velocities ranging from 50 to 1000 in/min and at temperatures from ambient to 130 °F. Results were negative, oxidation started normally, but then changed from a brown to yellow colored film.

At the conclusion of this test it was observed that brochantite crystallization had developed on a submerged PVC surface that had been in contact with the heated bottom surface of the battery jar. A 3 inch x 3 inch cleaned copper panel was placed flat in the bottom of the battery jar, covered with a liter of fresh patinating solution and held at 130 °F. A dense adherent green patina developed on the upper surface of the copper panel in 64 hours. A shallow pyrex tray large enough to hold a 5 inch x 8 inch panel and equipped with a cover was then used in place of the battery jar. Using a solution of 25 g/l copper sulfate and 2.5 g/l potassium chlorate at 180 °F, a dense adherent patina was developed in 6 to 8 hours. This experiment was repeated using six 2 inch x 2 inch panels. A panel was removed each hour for 6 hours. The following series of figures are from a scanning electron microscope study of these panels that was made at the Pulp and Paper Research Institute of Canada. The magnification on the figure is X1000. Figure 3a is a copper surface as prepared for patination. In figure 3b, a panel was exposed for 1 hour in the patinating solution-cuprous oxide forming. At 2 hours (fig. 3c), the cuprous oxide formation is nearly complete. In figure 3d, brochantite formation has started at 3 hours. It is visible as clumps of monoclinic crystals. At 4 hours (fig. 3e) brochantite growth continues. As the development of brochantite continues (fig. 3f), the cuprous oxide is absorbed. At 6 hours (fig. 3g), the growth of brochantite is complete with very little cuprous oxide visible.

The acceleration in patination gained through the horizontal exposure is believed to be due to the heat flux through the panel generated by contact of the panel with the heated bottom of the tray. Panels suspended in a horizontal position, but not in contact with the heated bottom surface of the tray did not patinate any more rapidly than the vertical panels. This approach was not pursued further as its application on a larger scale did not appear feasible.

The bench work on vertical exposure led to the installation of an immersion heater in the bottom of the pilot tank. This arrangement provided gentle thermal agitation while heating the solution. Dense, adherent patinas were produced in four days. The solution concentration was 25 g/l copper sulfate and 2.5 g/l potassium chlorate and was operated at 150 °F. Figure 4a is representative of the patina developed. Figure 4b shows a natural patina said to be 50 years old.

As a follow-up to the Incra Patine II program, Revere installed a small scale commercial operation. This was intended to establish operating procedures and costs while processing full size copper sheets (36 inch x 96 inch x 16 ounces). It was expected that experience gained in operating this line would determine whether a full scale operation would be feasible technically and economically. Installation of the prepatinated sheets by commercial roofers would indicate the response of the product to standard roofing practices.

The small scale prepatinating line was designed to process 36 copper sheets, 3 foot x 8 foot x 16 ounces, racked back-to-back per load. The spacing between racks was 2 inches. The design production was to be one load per week. This allowed one day for unloading, loading, precleaning, and solution adjustment. The patination cycle was four days.

Three processing tanks 4 foot x 4 foot x 10 foot (1.2 m x 1.2 m x 3 m) were constructed. Two tanks were mild steel and one was Type 316 stainless steel. The three tanks were installed adjacent to each other with the long dimension of the tanks at right angles to an overhead hoist line. A one ton hoist and accessory facilities for racking and drying serviced the line. A work handling carrier was loaded from the top and held 18 racks on 2 inch centers. Two sheets were clamped together using appropriate lengths of slit tubing along each of the four sides. Stainless steel bolts and nuts provided the clamping pressure required to hold the double sheets firmly.

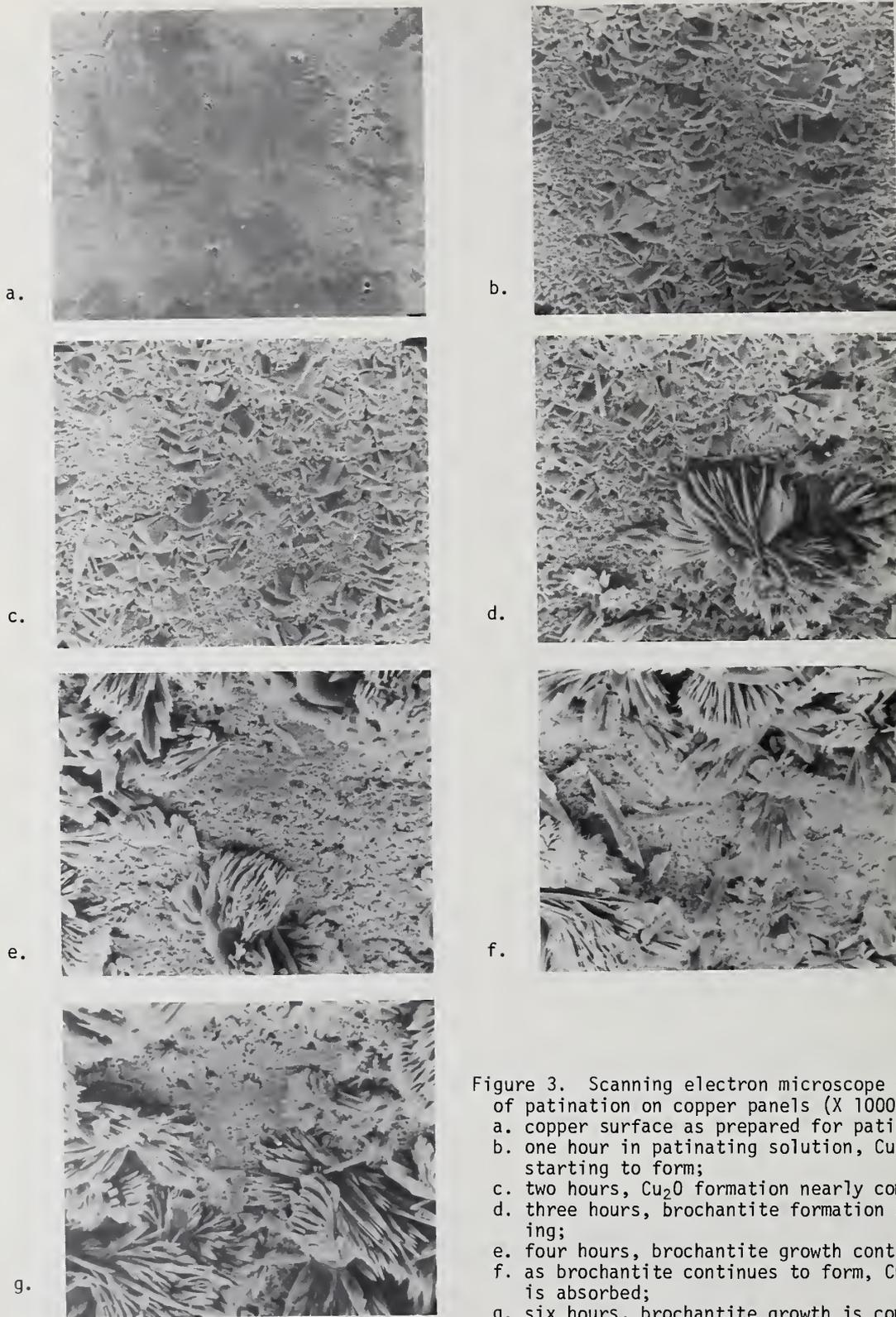


Figure 3. Scanning electron microscope study of patination on copper panels (X 1000).  
 a. copper surface as prepared for patination;  
 b. one hour in patinating solution,  $\text{Cu}_2\text{O}$  starting to form;  
 c. two hours,  $\text{Cu}_2\text{O}$  formation nearly complete;  
 d. three hours, brochantite formation starting;  
 e. four hours, brochantite growth continues;  
 f. as brochantite continues to form,  $\text{Cu}_2\text{O}$  is absorbed;  
 g. six hours, brochantite growth is complete.

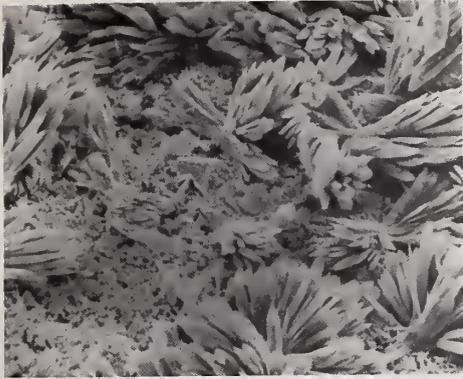


Figure 4a. Four day patina (scanning electron microscope, X 1000).



Figure 4b. Fifty year old natural patina (scanning electron microscope, X 1000).

The first tank in line was heated and used to hold the cleaning solution. The second tank was equipped with an overflow weir to the drain. This tank served as the rinse after cleaning and after patination. The third tank was Type 316 stainless steel and was equipped with a steam coil and temperature control. Cold water was provided at each tank and each tank had a bottom drain and valve.

The cleaner was Northwest Chemicals AC-5 used 10 percent by volume at 165 to 170 °F (74 to 77 °C) and a pH of 5.0 to 6.0. This is a mildly acid detergent solution that was very effective in removing residual rolling lubricant and any light tarnish that may have been present. The patinating solution concentration used was 20 g/l copper sulfate pentahydrate, and 2.0 g/l potassium chlorate at an initial pH of 3.0. The copper sulfate was a commercial grade as supplied by Phelps-Dodge Refining. The potassium chlorate was a technical grade, supplied by Sargent-Welch Scientific. Battery acid grade sulfuric acid was used for pH adjustment. Rome tap water, which is relatively soft was used for make-up and to replace evaporation losses.

A typical operating cycle included the following steps:

1. The copper sheets were racked and loaded into the carrier.
2. The loaded carrier was immersed in the cleaner for 30 minutes.
3. The carrier was rinsed for 60 minutes.
4. The carrier was immersed in the patinating tank. The tank was covered and the steam turned on.
5. The temperature of the patinating tank was checked daily and water added to make up for evaporation losses.
6. At four days immersion time, the carrier was removed, rinsed for 30 minutes, and transferred to the load-unload area.
7. When dry the patinated sheets were unracked and packed in a shipping box.
8. The patinating solution was analyzed for potassium chlorate and chloride. Additions of potassium chlorate were made to bring the total of  $KClO_3 + Cl$  to 2.0 g/l and the pH was adjusted to 3.0 with sulfuric acid.

This cycle took a week under ideal conditions and was repeated on a weekly basis. Figure 6 is a view of the loaded carrier in the rinse tank. Figure 5 is a finished sheet on the way to the unranking area. Figure 7 is the finished work being replaced in the shipping box.

Of course, ideal conditions did not prevail all the time; in fact, at times conditions were just the opposite. We soon found that our design spacing of two inches was too close



Figure 5. Loaded carrier of copper sheets with artificial patina in rinse tank.



Figure 6. Finished sheet on way to unranking area.

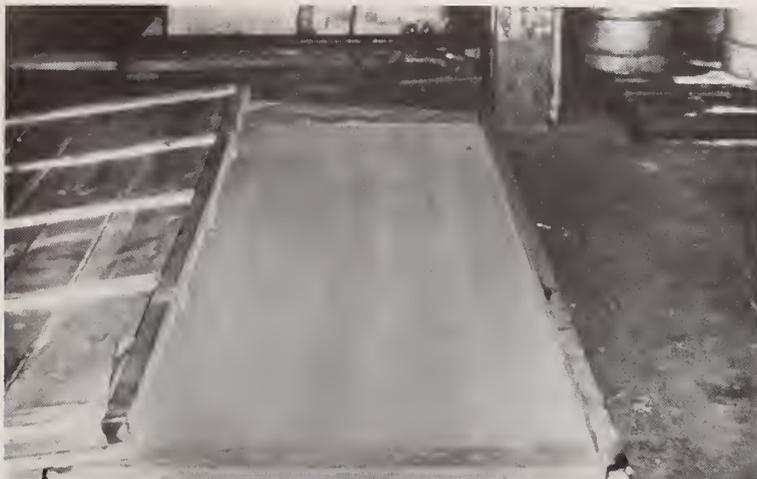


Figure 7. Finished sheet being replaced in a shipping box.

and that to get good coverage the sheets had to be spaced four inches apart, thus cutting our production by half.

In the large tank, the chloride ion produced during the oxidation of the copper by the potassium chlorate increased regularly with each load of sheets that was patinated. When the chlorides reached 0.6 to 7.0 g/l, the patination became dusty and nonadherent and the solution had to be discarded. A modified solution was developed using hydrogen peroxide as the oxidizer, but while this worked well on the laboratory bench it was unsuccessful in the production tank.

We investigated several methods for chloride removal and settled on a procedure in which the copper was precipitated as basic copper carbonate using soda ash. After settling, the clear supernatant was discarded. The precipitated copper was redissolved with dilute sulfuric acid, potassium chloride was added at 2.0 g/l and patination resumed. The chloride removal procedure was repeated three times on one solution when the chloride concentration reached 0.6 g/l. The time for patination became longer after chloride removal, so we abandoned the process except for the use of soda ash to recover the copper when it was necessary to discard a solution. A new solution would process six loads before it was necessary to change it.

Another troublesome characteristic of the solution was the generation of loose or tramp brochantite crystals which accumulated in the bottom of the tank. The stainless steel rack members developed an adherent brochantite layer after a time. This adventitious brochantite made it difficult to adjust the pH to 3.0 as it reacted slowly with the sulfuric acid to raise the pH. This could be partially counteracted by periodically dissolving the brochantite off the rack members and by removing the accumulated loose brochantite during a solution change.

We experienced a leakage problem in the stainless steel patination tank. This occurred during the early usage of the equipment at a time when the chlorides reached 1.0 g/l and the tank was idle for a time. The leak was caused by pitting attack. After repairs, we had no other major problems with corrosion, though I feel that the process could have been improved by eliminating all dissimilar metals from contact with the solution and the copper.

A total of 630 3 foot x 8 foot x 16 ounce sheets were processed. Thirty-six of these sheets were installed by a commercial roofer on a porch roof in Ontario, Canada. Another use was the 375 sheets installed on the Borough House, Sumter, North Carolina that is shown in figure 8.



Figure 8. Roof on Borough House, Sumter, North Carolina, constructed from artificial patina sheets (see color plate a).

The color of the patina formed by this process is a dark green and does not resemble a natural patina initially. Our exposure tests which have been in progress for four years show that the Incra Patine II weathers very well, does not bleed onto adjacent surfaces, and gradually develops a softer green appearance.

#### Discussion

*G. M. Ugiansky:* In light of the information given this morning by Prof. Pourbaix on the stability of phases using potential-pH diagrams, I would like to know if you have considered the ternary Cu-S-H<sub>2</sub>O potential-pH diagram in formulating your process for artificial patination of copper. If the above-mentioned diagram is considered, one could theoretically put the Cu on the proper pH, potential, and S species concentration to produce the wanted patina.

*D. C. Hemming:* I may have skipped too quickly over the point where I mentioned that this patina was identified by x-ray diffraction as brochantite which has the copper sulfate and the three copper hydroxides. So that would put it in the proper range on Pourbaix's diagram for brochantite.

*G. M. Ugiansky:* What form is this patina?

*D. C. Hemming:* As near as we can determine by x-ray diffraction, it is the same as the natural patinas. It is basic copper sulfate.

*G. M. Ugiansky:* If it is a sulfate, then one would have to have a diagram that is not just copper-water. It would have to be the copper-water-sulfur system. A ternary diagram.

*D. C. Hemming:* I believe that it was covered on the Pourbaix diagram that was shown earlier for copper.

*G. M. Ugiansky:* Thank you, I may have missed that part.

*D. C. Hemming:* Our part in this was to attempt to commercialize a process that was developed at the University of Utah and we did not feel that we should digress too far from that which they had given us to work with. There could be other systems developed, I am sure.

*U. Bertocci:* You have shown that during the formation of the patina, Cu<sub>2</sub>O is first formed. Since the stability, as well as the electric potential, of Cu<sub>2</sub>O is affected by light, have you ever detected any effect of illumination on patina formation?

*D. C. Hemming:* We have tried that on a bench scale and could not detect any difference. Perhaps, we did not use the right wavelengths or intensities.

BETA IRON OXIDE HYDROXIDE FORMATION IN LOCALIZED  
ACTIVE CORROSION OF IRON ARTIFACTS

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As a part of a research program on the restoration of buried iron artifacts, we have recently examined a series of iron objects of a type which was already known to be very difficult to restore. The objects in question were three spearheads and two axes found in a gallic tomb of the 4th century B.C. at Pianetto, Forli, Italy. All the objects are heavily corroded, but with a substantial iron nucleus. The thick layer of iron oxides embedding the ground silicates is not uniform, owing to the presence of typical aggregates of corrosion products; the aggregates are fine-grained and brighter than the surrounding oxide layers, as can be seen in figure 1. These are points of active corrosion. In fact, even if the corrosion products of these zones are removed during the restoration, they will develop again by simple exposure to humid air.



Figure 1. Aspect of nonuniform layers of iron oxides.  
The fine-grained and brighter aggregates consist of  $\beta$ -FeO(OH).

We thought it would be of some interest to establish if the corrosion products of the active zone were systematically different from those of the surrounding regions. For each object, two different samples were drawn: the first from the active zones and the other from the surrounding oxide layer. The composition of the samples has been determined by x-ray diffraction using a diffractometer and CoK radiation. The different compounds were identified by comparison with the cards of the Powder Diffraction File published by the Joint Committee on Powder Diffraction Standards.

The results of the analyses are summarized in table 1. They show that the only significant difference between active and inactive zones is connected with the presence of beta-iron oxide hydroxide ( $\beta$ -FeO(OH)). It is systematically present in the active points and absent in the inactive ones. This result can be interpreted in terms of what we know about the formation of  $\beta$ -FeO(OH), which, unlike  $\alpha$ - and  $\gamma$ -FeO(OH), is not a common corrosion product on iron.

Table 1. Relative components found in the active and inactive region of fine artifacts.

Artifact Zone	1		2		3		4		5	
	a	i	a	i	a	i	a	i	a	i
Goethite $\alpha$ -FeO(OH)	+	++	+	++	++	++	+	++	+	++
Akaganeite $\beta$ -FeO(OH)	++		++		+		++		++	
Lepidocrocite $\gamma$ -FeO(OH)	(-)					(-)	(-)			+
Magnetite Fe <sub>3</sub> O <sub>4</sub>		++	+	++	(-)	++	(-)	++	+	++
$\alpha$ -Quartz SiO <sub>2</sub>					++	++				

Notes: a = sample drawn from the active region.

i = sample drawn from the inactive region.

++ = component present in large amount.

+ = component present in medium amount.

- = component present in small amount.

( ) = uncertain identification owing to the peaks overlapping.

$\beta$ -FeO(OH) has been found in the rust layers of steels exposed in marine atmosphere [1-4]<sup>1</sup> or submerged in sea water [5]. Keller [6] proved that a prerequisite of the formation of  $\beta$ -FeO(OH) was the presence of Cl<sup>-</sup> ions and that it is formed in the presence even of small quantities of Cl<sup>-</sup> ions. If these ions are localized in small areas, the remaining metal surface will be covered by  $\alpha$ - and  $\gamma$ -FeO(OH), while the Cl<sup>-</sup> ions are fixed in the lattice of  $\beta$ -FeO(OH) already formed. In contact with metallic iron,  $\beta$ -FeO(OH) has the effect of accelerating the corrosion process because of the release of Cl<sup>-</sup> ions. The role played by Cl<sup>-</sup> ions in the corrosion of iron in different environments has been discussed by Pourbaix [7] and Feitknecht [8].

Although detailed studies of the relationship between Cl<sup>-</sup> ions and formation of  $\beta$ -FeO(OH) are not available for the underground corrosion of iron, we think the results obtained in other environments can be safely extended to this type of corrosion. That is, the presence of  $\beta$ -FeO(OH) is, by itself, sufficient to say that a corrosion attack is in progress on the metal and that such a process is caused by chloride ions, which have to be removed at restoration time to stop the active corrosion.

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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.

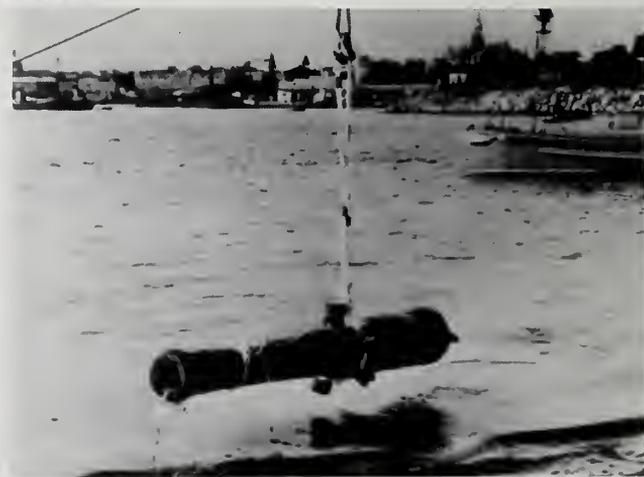


Figure 2. Cannon is transferred from its underwater environment.



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.

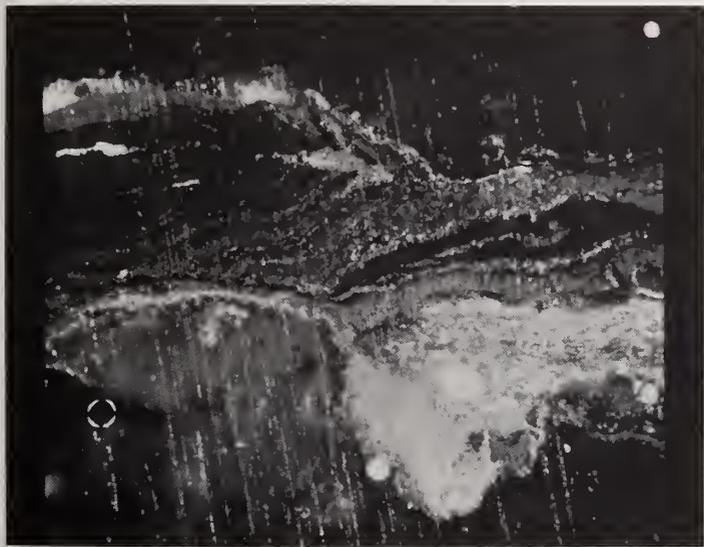


Figure 7. Corrosion products are studied in a flake taken off a piece of bronze furniture from Nimrud. See color plate 1.

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]<sup>1</sup>. 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.

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<sup>1</sup> 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
	<i>Axe R.Kennet, Reading</i>	<i>Axe Stratford (Essex)</i>	<i>Piece York</i>	<i>Arrowhead Wood- eaton</i>	<i>Bloom Down- patrick</i>	<i>Bloom Fermanagh</i>
	<i>6th-7th cent.</i>	<i>9th cent.</i>	<i>Saxo- Norman</i>	<i>Med.</i>	<i>13th cent.</i>	<i>Med.</i>
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-.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		
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  $H_2S$  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.

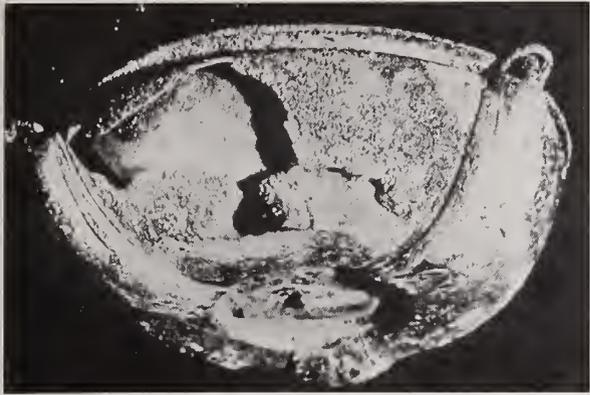


Figure 14. Silver object from St. Ninians Isle in the Shetlands, dating about 800 A.D.

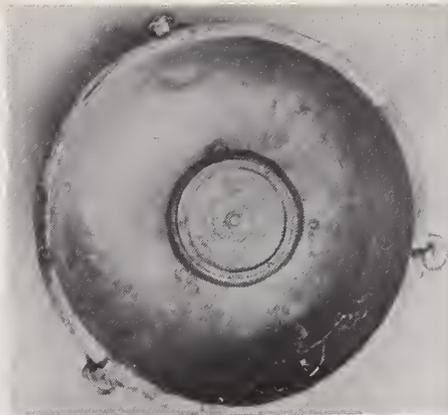


Figure 15. Silver object in figure 14 after conservator has replaced losses and cleaned.

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.

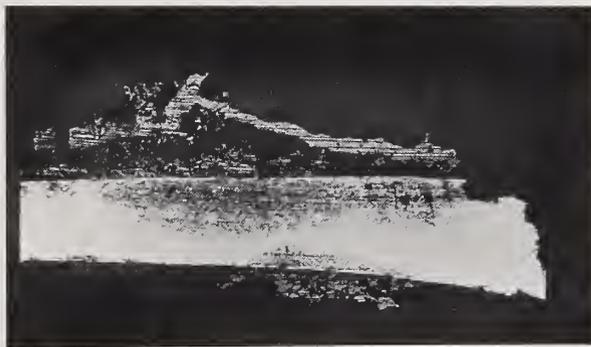


Figure 17. Cross-section taken from an edge of a loss of the bowl in figure 16.

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

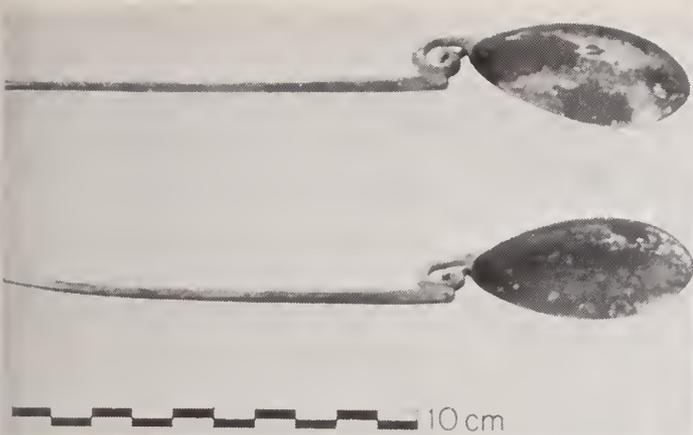


Figure 20. Roman spoons from Kaiseraugst, dated to 4th Century A.D.



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.

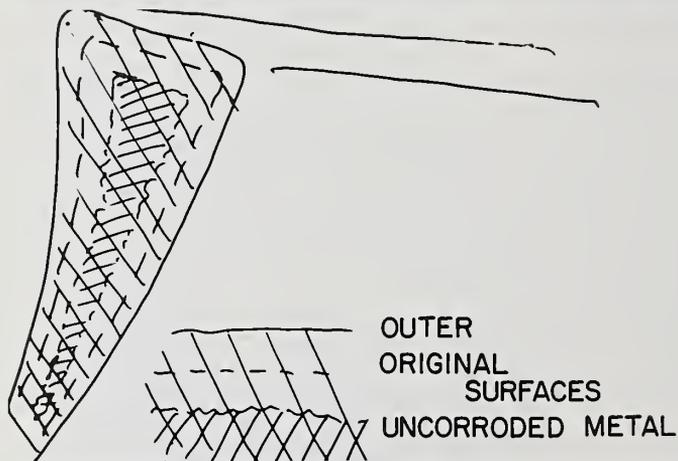


Figure 25. Diagram of the rim of the bowl shown in figure 24, where there was no silver.



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 electrolysing. 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

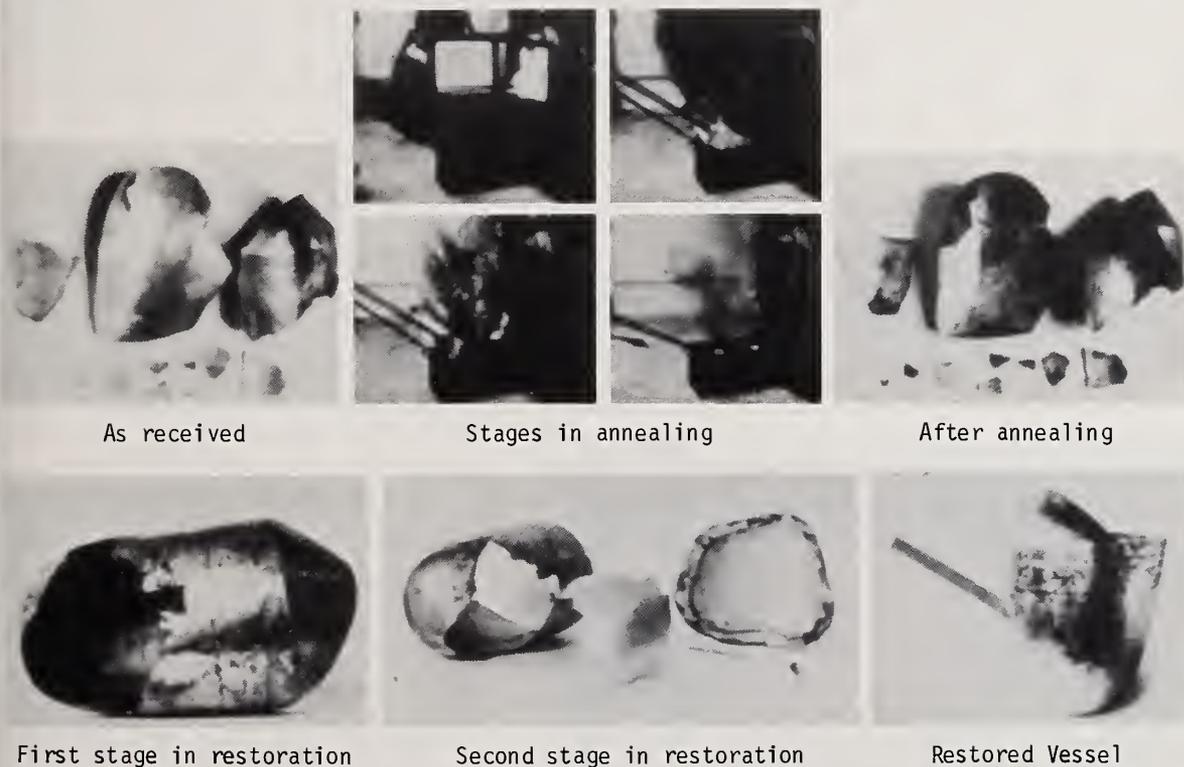


Figure 32. Restoration of silver libation vessel from Royal Cemetery at Nuri, about 530 B.C.

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)<sup>2</sup>. 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.

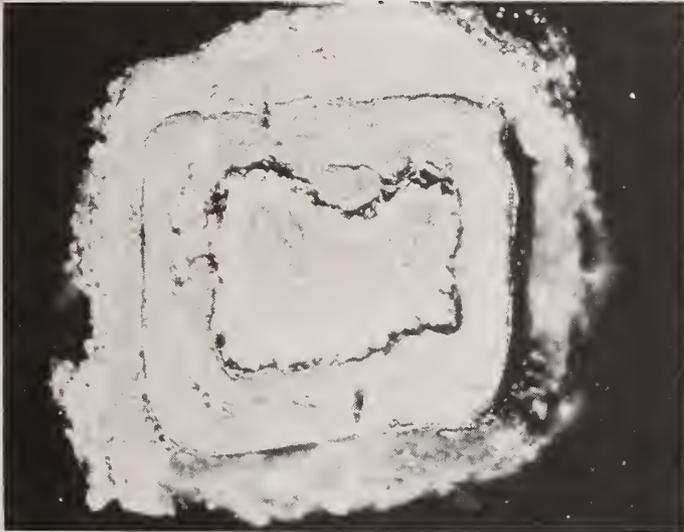


Figure 35. Cross-section taken from chisel sample shown in figure 34.

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.

<sup>2</sup> 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.

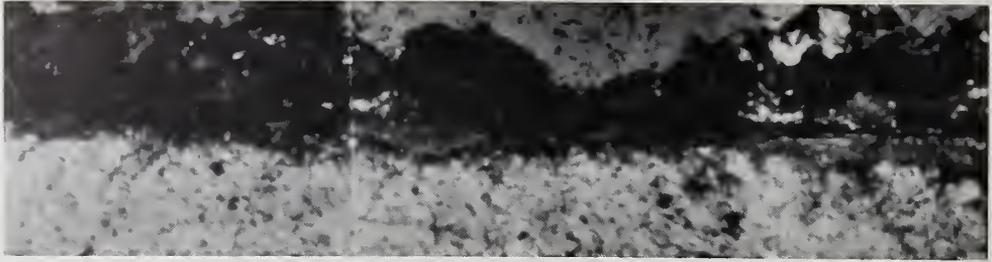


Figure 36. Bronze metal showing bronze disease. See color plate k.



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.

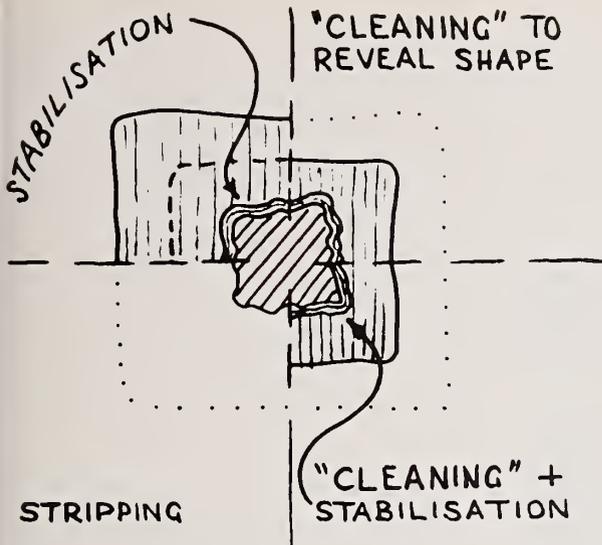


Figure 38. Diagram showing four options the conservator may choose in cleaning a bronze object such as is shown in figure 37.

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

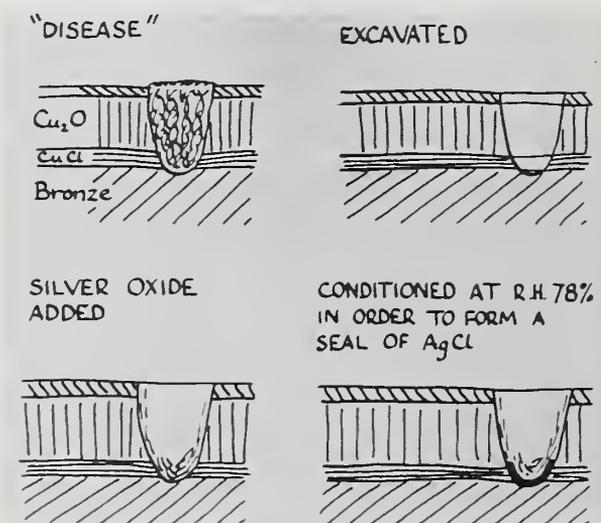


Figure 42. Diagram of the silver oxide method for stabilising diseased bronze.



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.

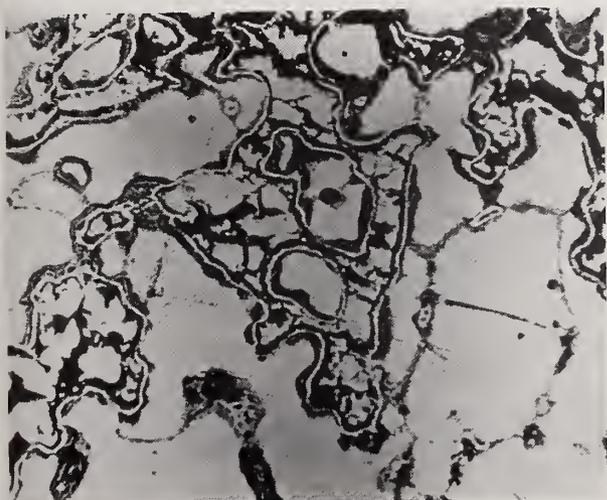


Figure 44. A micro-section of a corroded bronze stabilised by an electrolytic method proposed by Gettens [22].

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/dm<sup>2</sup> was applied for four days.

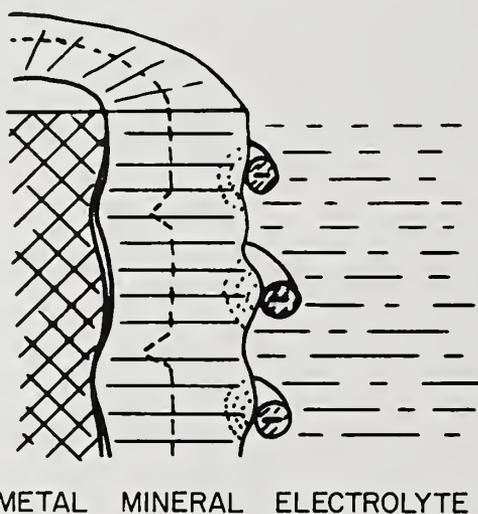


Figure 45. Diagram of an electrolytic method [23] for cleaning diseased bronze to reveal shape.

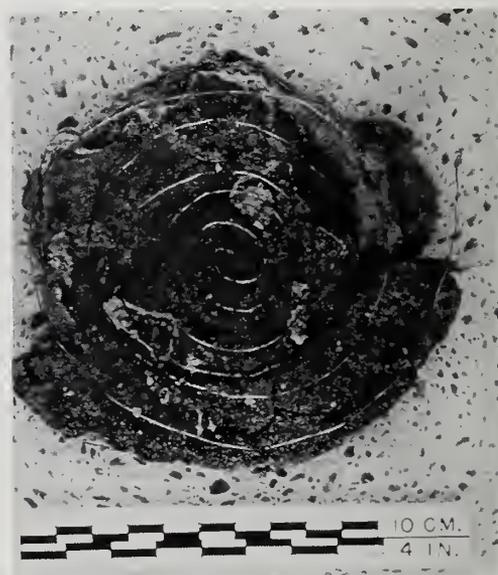


Figure 46. A bronze treated by the method shown in figure 45. See color plate q.

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.

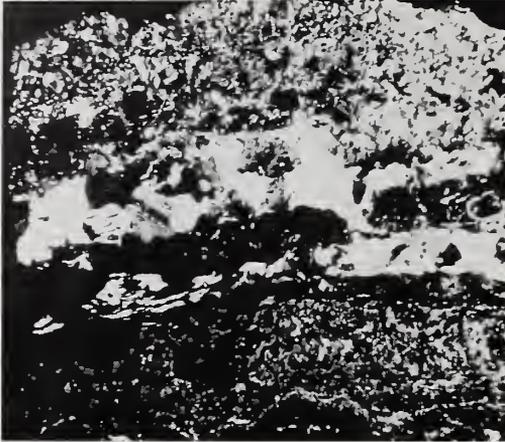


Figure 49. Cross-section of a flake of copper sulphide taken from a bronze spearhead found in the river.

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

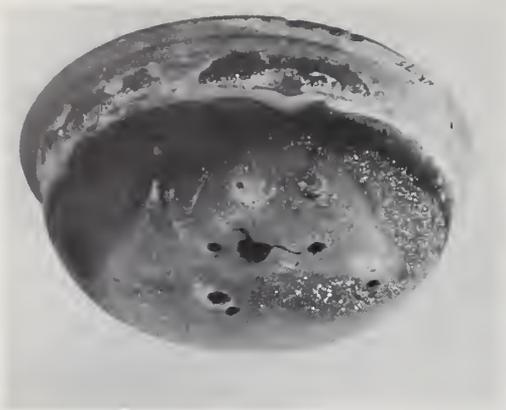


Figure 53. A tin pannikin found 15 feet below the water's surface in Boundary River, Winnipeg, Manitoba, Canada.

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.

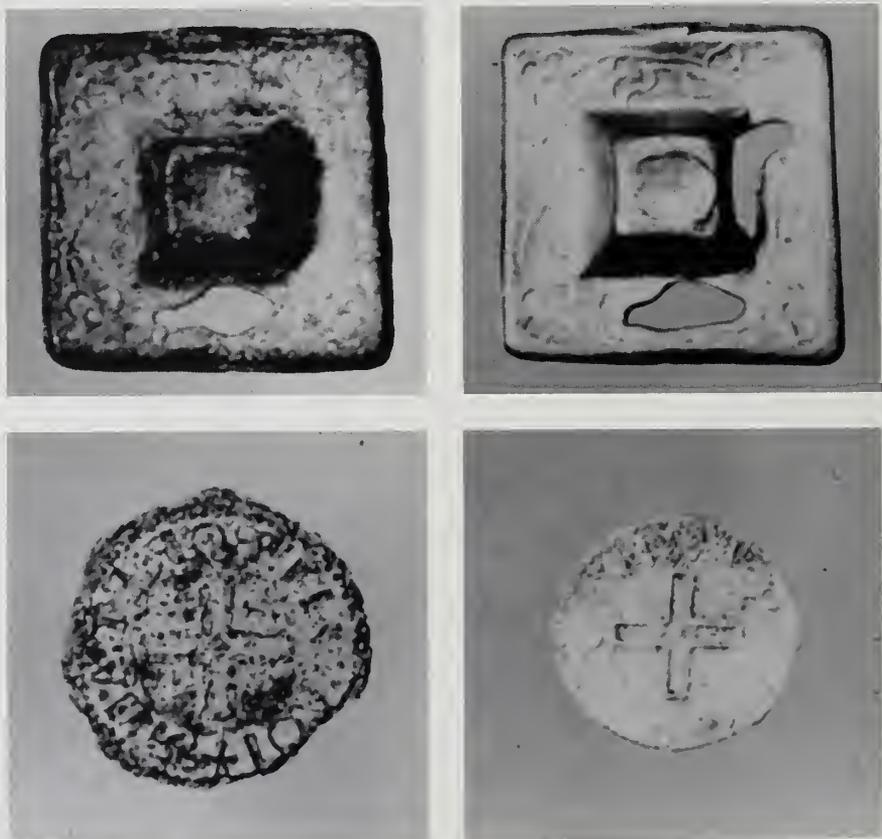


Figure 55. The tin hat coins shown at the top were recovered from underground in Malaysia. They are from the mid 19th century or later. The objects at the bottom are John of Portugal coins brought up from underwater. They are from the 16th century.

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-

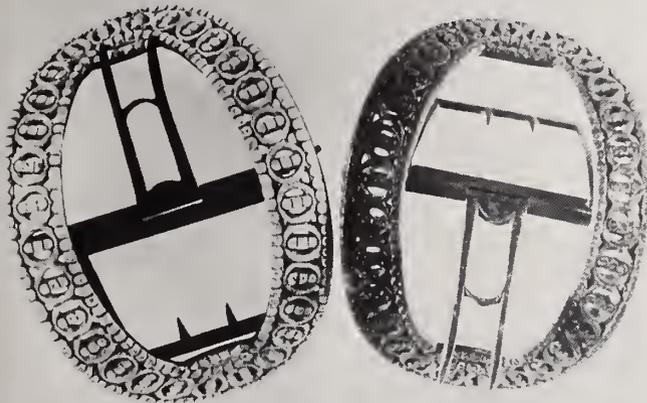


Figure 56. Two shoe buckles, the one on the left has been treated by the method of Shah and Davies [33].

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.

#### Lead 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.

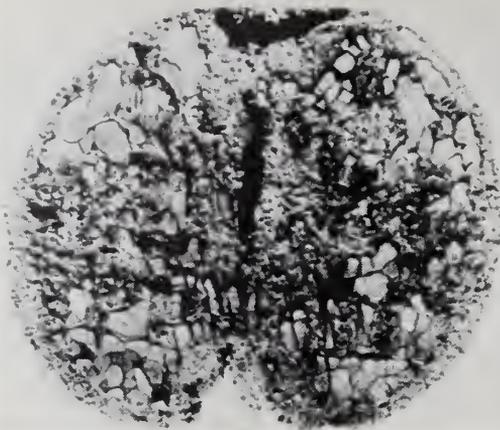


Figure 57. Lead object showing characteristic decay.



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 recorrode 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  $\text{CO}_2$ , 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.

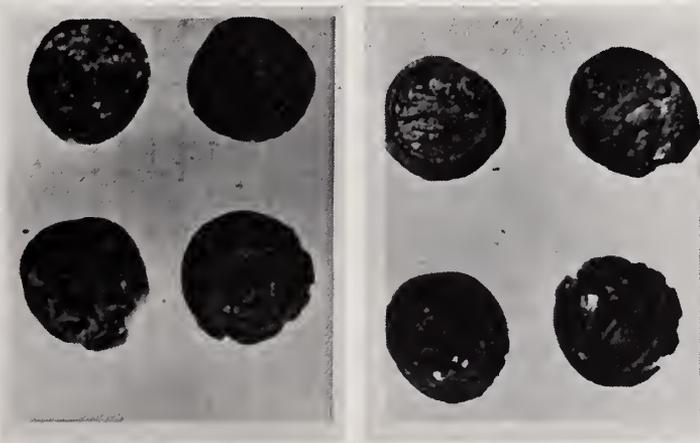


Figure 61. Lead coins treated to remove lead carbonate using Caley's method [37].

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.

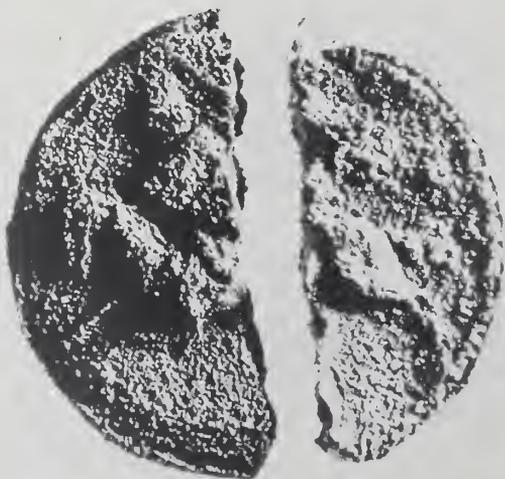


Figure 63. A bulla that has corroded completely. The portion on the left is restored; the portion on the right is held together with shellac.

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/dm<sup>2</sup>, 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.

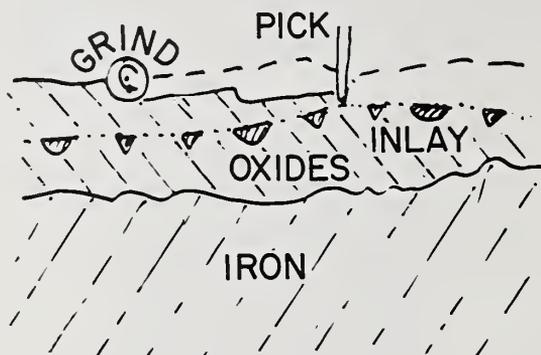


Figure 65. Diagram of a mechanical method for treating corroded iron.

### 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  $\text{FeCl}_3$  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  $\text{Fe}_2\text{O}_3$ , the red oxide, into the black oxide  $\text{Fe}_3\text{O}_4$ . 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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## SOME CONSTRUCTIVE CORRODINGS

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As the other papers at this conference show, corrosion is generally regarded as evil, destructive, or at least undesirable. But, like the electrolytic couple that underlies it, corrosion has two sides. A glance at history shows that corrosion has stimulated much useful science and has been central to many useful processes and the making of many useful objects. One of its principal applications is in the prevention of corrosion, for the products of initial reaction, when they have the right structure, block further attack. Indeed, since the underlying electrochemistry is already fairly well understood, and is immutable, future research in the field will increasingly find opportunity in problems involving the microstructural, interfacial, and mechanical aspects of passivity. The unresolved problems are more akin to diffusion-controlled mineralogenesis in the earth's crust than to basic electrode behavior.

Corrosion can be broadly considered as the movement of interphase interfaces--its chemistry is that of heterogeneous systems in general. The first corrosion was the weathering of rocks after the primaeval formation of the earth's crust, with the accompanying redistribution of the available atomic species into new materials or new arrangements of the old, including the formation of beautiful landscapes and gemstones as well as the ores of useful metals.

Some of the constructive uses of corrosion have historically included the following, listed in no particular order:

- To obtain a solution for use in later chemical processing, as in making pigments, inks and mordants
- To obtain directly a useful mineral corrosion product, such as the pigments verdigris and ceruse and fine abrasives such as crocus or rouge
- To remove superficial layers of the products of prior corrosion; e.g., in pickling tarnished or heat-blackened metals
- To obtain an adherent superficial layer of corrosion product, either for decorative purposes or to confer resistance to corrosion; e.g., the bluing of steel, the chemical coloring of bronze, the anodising of aluminum and the formation of alloy coatings by diffusion
- To roughen or to smooth a surface for decorative or technical purposes, or, when locally restrained, to produce controlled designs as in etched armor, plates for the graphic artist or photoengraver, the manufacture of integrated circuits, and "chemical milling" to predetermined shapes
- To expose the internal textures in materials for decorative purposes or to reveal their macro- and micro-structures for scientific study and process control
- To obtain electric current for uses involving electrochemical, electrothermal or electromagnetic effects

and doubtless others.

The earliest evidence of the use of many of these processes lies in archaeological objects, but the earliest literature on the chemical arts, for example, the Leyden manuscript of the third century A.D. and the *Mappae Clavicula* which began to take form early in the ninth century, are rich in recipes for producing color changes by corrosion [1]<sup>1</sup>. The *Mappae* tells us how to make the pigments ceruse and verdigris by corroding lead and copper respectively, while iron is corroded to yield crocus powder, or put into solution for making ink and it is etched with a copper-bearing solution to obtain a rough copper-plated surface as a basis for amalgam gilding. Fluxes are used to clean metal surfaces for both soft and hard soldering.

The selective removal of copper from its alloys with the noble metals is a most interesting process. Today it is used, in the Western World, only in refining and to improve the color of solid gold very superficially; in earlier times, it was employed to obtain thick layers of pure gold on the surfaces of objects made of cheaper alloys. Chemically, this is identical with the inquartation and parting operations of the assayer--in mechanism, it is related to the dezincification of brass. For corrosion to proceed to a significant depth the presence of 50 atom percent or more of the baser metal is necessary. The Old World beginnings are uncertain. Wasteful of gold, the process could not compete with gilding processes in which thin layers of gold were externally applied in the form of foil or amalgam, but it remained in use as the basis of the alchemist's method of "multiplying" gold. A good summary of this and similar "alchemical" operations is given by Joseph Needham in his general discussion of colored alloys [2].

It was in South America that this type of selective corrosion particularly flourished (fig. 1). Most pre-Columbian "gold" objects are actually made of alloys that contain less than a third of the precious metal, but they were given a pure gold surface after shaping by treatment with corrosive natural minerals, probably one of the varieties of basic ferric sulphate such as copiapite,  $\text{Fe}_3(\text{SO}_4)_4\text{OH}\cdot 13\text{H}_2\text{O}$ , mixed with salt. Known to early metal workers in the West as *misy*, ferric sulphate is almost as potent a corrodant as sulfuric acid itself. When used on Cu-Au alloys by the metalworkers of Peru and Ecuador it left on the surface a sub-microscopically porous layer some 50 to 200 micrometers thick of pure gold which was



Figure 1. Mask of sheet "gold," Lambayeque, Peru. ca. 1100 A.D. The mask is actually about 35 percent copper, 36 percent gold, and 27 percent silver treated chemically to yield a pure gold surface. See Lechtman, reference 3. (Museum of Primitive Arts)

<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

consolidated by burnishing or by annealing to close the pores. The process, which the principal student of it, Heather Lechtman [3], calls "depletion gilding," can be identified by the composition gradients beneath the surface of the object. The gold content increases in a stepwise manner, quite distinct from the sinusoidal gradient left in the metal by cementation processes which are done hot and involve bulk solid-state diffusion.

The enrichment of silver on the surface of silver-copper alloys is a process with somewhat similar results, but this involves oxidation of the copper to form an external layer of scale which is subsequently removed by pickling. This process, known as blanching, was often used by mints to make debased coins appear to be of higher value [4].

The reaction of copper with arsenic vapor to produce silvery coatings of  $Cu_3As$  was used in the third millennium B.C. [5]. The earliest of such reactive coatings were the alkaline-glazed steatite and quartz beads produced in the fifth millennium B.C. In the third millennium B.C., patterns in contrasting colors were produced on carnelian beads by local reaction with alkali [6] (fig. 2).

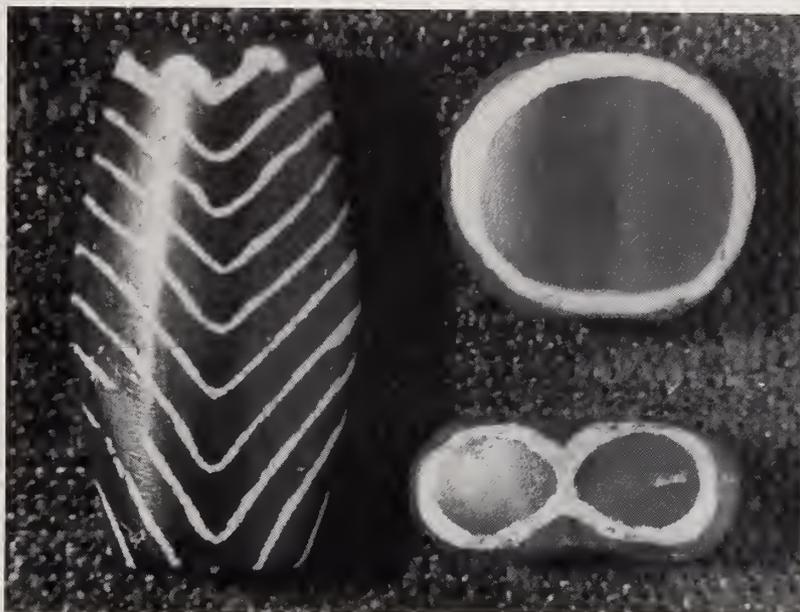


Figure 2. Carnelian beads decorated by "etching." Indus Valley culture, 2000 B.C. probably from Chandhu-daro. (Museum of Fine Arts, Boston) The bead on the left is *ca.* 15 mm long.

The production of colored oxide films on steel by heating it in air is well known and ancient. The fact that the kinetics of the reaction closely parallel the softening of quenched steel enables the color to be used to control the tempering operation with considerable precision. Sixteenth century recipes describe the necessary knowledge of the two colors, the appropriate red for quenching and the yellow through blue colors that characterize steel tools of the different hardnesses appropriate to different kinds of service [7].

Less well known than the colors of tempered steel are the oxidation colors produced on the copper alloy foils that were used to back gems in the days before they were cut to obtain total internal reflection. There are excellent instructions for obtaining purple, green, blue, and other colors on foils of various copper-silver-gold alloys that were carefully burnished in a dust-free room and heated over a smoke-free charcoal fire. "It is very admirable how on a suddain these copper rays will change into several colours: Wherefore, when they have attained the colour you desire, take them off the fornace presently, for otherwise they will alter into another" [8].

The electrochemical replacement of one metal by another was noticed in antiquity. Pliny mentions that iron when smeared with "vinegar or alum" becomes like copper in appearance [9]. Replacement seems to have been used in Roman times for tin-plating bronze and it definitely underlies the recipes for the preparation of iron surfaces to receive amalgam gilding that are given in the ninth century *Mappae Clavicula*. One of these (Chapter 146H) reads:

"Rounded alum, the salt that is called rock salt, blue vitriol, and some very sharp vinegar are ground in a bronze mortar; the cleaned iron is rubbed with these [materials] using some other kind of soft little point. And, when it has taken on the color of copper, it is wiped off and gilded, and then, after the quicksilver has evaporated, it should be cooled in water and rubbed with a tool that is very smooth and bright until it becomes brilliant."

The conversion of iron objects into copper when they were immersed in certain mine waters was sometimes thought to be a proof of the possibility of alchemical transmutation of one metal into another. The Chinese writer Shen Kua in 1086 A.D. refers to a mountain spring whose waters contain a bitter "alum" which becomes copper when it is heated and an iron pan containing it is slowly changed into copper [10].

In the seventeenth and eighteenth centuries, cement copper was commercially produced in Erzgebirge. At Herrengrund the copper was unusually pure and it was used to make charming dishes and cups (fig. 3), often incorporating models of mining and smelting buildings and bearing rhymed reference to their former life as a baser metal [11].



Figure 3. Cup made from cement copper. Herrengrund, ca. 1700 A.D. The inscription reads: "*Ein Pferd mich vor mit füssen trat, / da ich noch Eisen ware, / durch ziment wassers baad / bring ich gut freünd zu baare,*" in reference to its origin as iron in the form of scrap horseshoes. (Author's collection)

The recovery of silver from waste parting-assay solutions by reaction with copper bowls was a standard procedure described in Ercker's great treatise on assaying [12] of 1574. By the early eighteenth century, assayers knew of the successive replacement of silver from solution by copper, of copper by iron, and of iron by zinc. In 1718, Geoffroy published his famed table of chemical affinities (fig. 4), which was an important step in the development of the theory of chemical reactions [13]. The columns listing the experimentally observed



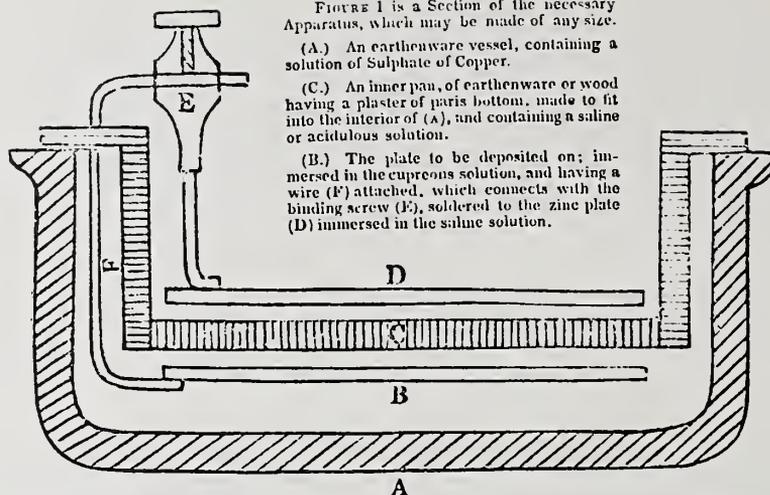
## FIGURE 1.

FIGURE 1 is a Section of the necessary Apparatus, which may be made of any size.

(A.) An earthenware vessel, containing a solution of Sulphate of Copper.

(C.) An inner pan, of earthenware or wood having a plaster of paris bottom, made to fit into the interior of (A), and containing a saline or acidulous solution.

(B.) The plate to be deposited on; immersed in the cupreous solution, and having a wire (F) attached, which connects with the binding screw (E), soldered to the zinc plate (D) immersed in the saline solution.



A

\* \* \* The above engraving has been produced (in relief) by the Electro-chemical Process and is the first result of that process appearing in print.

Figure 5. The first regularly-published print from an electrotype plate, showing the cell used to produce the plate. From *Annals of Electricity*, William Sturgeon, ed., No. 4, 4 January 1840. (Courtesy Burndy Library)

The etched plate of the graphic artist with its intaglio lines is probably the best known use of localised corrosion. Prints made by the process first appear around 1500 A.D. [17]. Leonardo da Vinci used it in 1504 and Albrecht Durer in 1515, but there was a long prehistory in the decorative etching of metal surfaces particularly those of steel arms and armor (fig. 6), but also of copper alloys [18]. The first printed book on iron and steel is mainly on etching them [19].

Although in Europe, etching was mainly used to bite in patterns previously drawn by an artist, in the Middle East and Far East the etching was used almost entirely to reveal the texture of the metal itself, thereby giving surface indications of both gross heterogeneities resulting from casting and forging procedures as well as the finer structural features that depend upon crystalline separations of the kind that, when they were later studied under the microscope, provided the basis of today's material science [20]. Although the internal structure of any material can be seen to some extent in the fine detail of fractured surfaces (and observations of these almost certainly prompted the first "atomic" or corpuscular theories of matter), the subtler details of microstructure can only be seen on carefully prepared sections that have been submitted to etching.

The discovery of carbon in steel occurred in 1774, after centuries of good steelmaking guided by the natural though mistaken belief that heating iron in a hot charcoal fire must purify it [21]. One of the many results of the stimulus given to European science by contact with oriental materials occurred when a Swedish metallurgist came to look closely at the blackish residue responsible for the visible pattern on "Damascus" gunbarrels, which were finished by etching (fig. 7). A few decades later the same etching technique was used to reveal crystal structure in metals for the first time, initially in a meteorite, then to make fancy bibelots of crystalline tinplate, and, almost fifty years later, for the first scientific studies of the microstructure of terrestrial steel, from which stem modern metallography and much more [22].

It is interesting to note that the discoverers of the meteorite and steel structures--Widmanstätten in 1813 and Sorby in 1864--both first published their results in the form of prints made directly from inked metal surfaces etched in relief (fig. 8), as Leonardo had



Figure 6. Hunting sword with etched decoration, pictured in sections to show detail. Made by Ambrosius Gemlich in Munich in 1540. (Wallace Collection, London)



Figure 7. Etched gunbarrel with so-called Damascus texture. Turkish, eighteenth century. (Victoria and Albert Museum)



Figure 8. Print from the etched and inked surface of the Elbogen Meteorite, made by A. von Widmanstätten and C. von Schreibers in Vienna in 1813. The original is 21 cm high. (Author's collection)

proposed over three centuries before. By the 1880's, many engineers and chemists were studying etched metals under the microscope and relating the structures to problems of utility and understanding. Not the least of the consequences of the new method of study was a deeper understanding of the process of corrosion itself, though to this day a metallographer cannot help but feel that there is not enough attention paid to the microstructural aspects of the corrosion process.

Finally, the intentional coloring or patination of metals in jewellery, sculpture, and architecture is an enormous field with a large literature, much of which is worthless. Here



Figure 9. Japanese sword guard (*tsuba*), nineteenth century. Several different alloys are combined by intricate inlaying technique and given their different characteristic colors by a final treatment in a pickling solution. See color plate p for detail of lower right corner. (Museum of Fine Arts, Boston)  
Author's photo.



Figure 10. "Instantaneous Light Box" with case made of tin-plated iron, crystallized, etched, and lacquered. Made in London about 1820 by "J. Watts and Co., Chymists, No. 478, Strand" (Photo courtesy Bryant and May Ltd. and The Science Museum, London)

more than in most areas an examination of objects in a museum laboratory is more revealing than reading about them in a library. Not all such patinations are simple sulphides or oxides. Particularly in need of further study are the Chinese black bronzes of the late Chou and Warring States periods [23], the hot-forged high-tin bronzes of Soghdian Iran with their brownish black coating which seems to have been formed by oxidation prior to the final quench [24]; the fine black finish given to zinc alloy castings known as Bidri ware, originating in the Hyderabad district of India; and, towering above all these in both technical ingenuity and beauty, the colored metals used by Japanese tsuba makers especially in the eighteenth and nineteenth centuries (fig. 9) [25]. Prominent among the alloys used are *shakudo* and *shibuichi* which after pickling acquire, respectively, a beautiful warm purplish black color and a slightly frosty dark greenish brown (fig. 10). These are alloys of copper with gold (ca. 5 percent) and silver (ca. 25-30 percent). Technically, if not historically, their ancestry includes the more gaudy finishes of metallic silver and gold that the metalworkers of South America many centuries earlier had obtained by corroding more concentrated alloys.

All these corrodings, and many more, constitute an integral part of the story of man's discovery of the wonderful diversity of the properties of materials which he can enjoy, incorporate in his philosophies, and employ in innumerable devices.

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#### Discussion

*J. Kruger:* You showed a Japanese work that showed the cherry blossoms floating and you said that it was all part of the texture. How did they do that?

*C. S. Smith:* You start by taking a composite or multilayer sandwich of different metals or alloys. You join these by soldering and then you hammer it out to get a fairly thin sheet. Now if you want to produce a real pattern you make one layer of the metal a little thicker than the other, to allow some tolerance, then with a sharpened punch you depress part of the surface so that when you cut a section through it you will expose areas in the shape or pattern that you want. It is rather like a contour line on a map.



## CONSERVATION OF RUSTY IRON OBJECTS BY HYDROGEN REDUCTION

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It may well be that some are not familiar with the story of the Warship Wasa. I shall therefore give a brief outline of its history before dealing with its preservation. The Swedish King, Gustavus Adolphus, ordered the building of the ship in 1625. The Thirty Years' War was raging in Europe, and Sweden was striving to assert herself as a Great Power. The Baltic separated Sweden from the Continent and a strong fleet was essential to the successful prosecution of the war.

The 38-metre keel of the ship was laid in 1626 and only two years later, in 1628, the Wasa set out on her maiden voyage. This ended in catastrophe after only two nautical miles: the Wasa capsized and sank in Stockholm harbour. The exact location of the wreck was pinpointed by Anders Franzén in 1956, and salvage work started soon afterwards. On April 24, 1961--after admirable work by divers--the Wasa broke surface after fully 333 years on the sea bottom. She was pumped dry and towed on her keel into Beckholm dock in Stockholm harbour. She was placed on a concrete pontoon and the archaeological excavation of the hull began. Figure 1 shows the Wasa in dry dock. The ship was presently furnished with an aluminum housing and in the autumn of 1961, well before the onset of winter, she was towed--inside her new housing and on the pontoon--to the present Wasa Yard in Stockholm. On February 1, 1962, the Yard was thrown open to visitors.

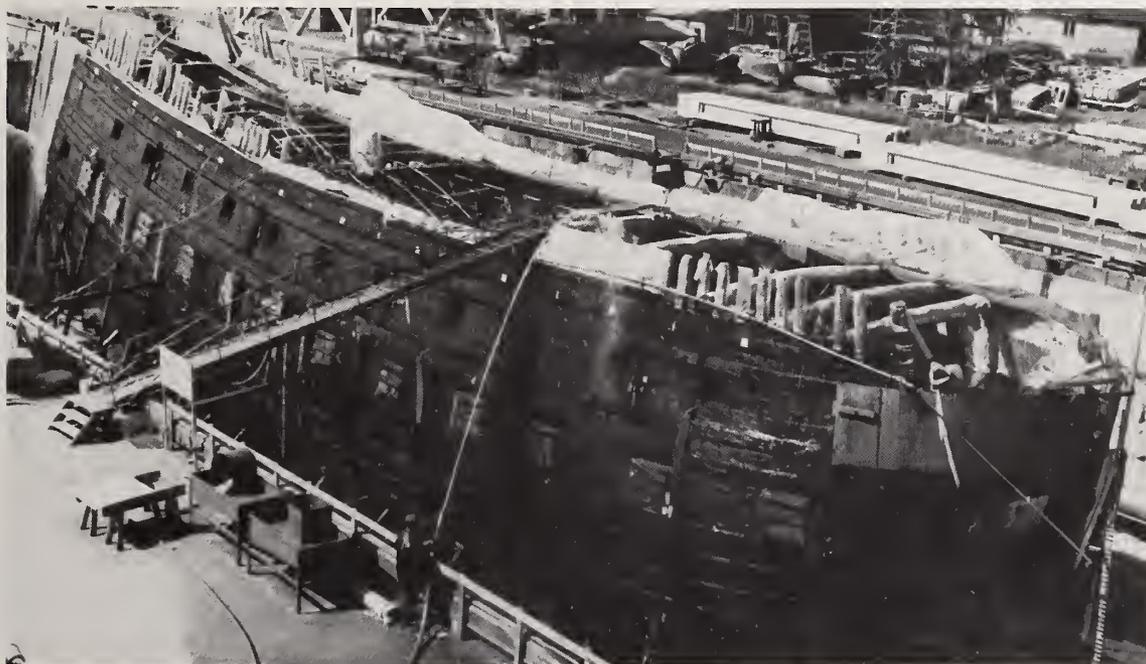


Figure 1. The Wasa in dry dock, 1961.

This massive find of waterlogged wood is the largest of its kind ever recovered. The vessel's displacement was 1300 tons, overall length including bowspit 230 feet, maximum beam 38 feet 4 inches, height of aftercastle 65 feet, and draught 15 feet 5 inches. We were confronted with a formidable task: the preservation of a volume of 25,000 cubic feet of waterlogged wood with a total surface area of 150,000 square feet and containing some 25,000 loose finds.

Early in 1961, the Wasa Preservation Department was formed, together with a panel of experts, into the Wasa Preservation Committee. In July 1964, it was reorganized into the National Maritime Museum's Preservation Committee for the Wasa.

The iron objects constitute the major finding after wooden objects on a volume basis. Most metals do not occur as pure elements in nature but must be extracted by the application of energy. According to the laws of nature a system strives to attain the lowest possible state of energy, which for metals usually means that they tend to return to their oxidized state and hence to their stable energy form. That iron corrodes under certain conditions is therefore as natural as that a stone falls to the ground.

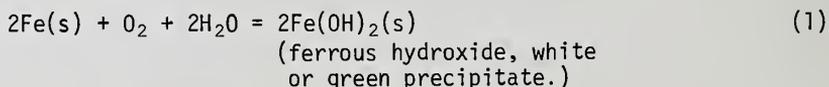
The extent of corrosion is to a high degree dependent on the environment. In archaeological contexts, a distinction must be made between corrosion in a maritime environment, in air, and in soil. A metal corrodes if it is exposed simultaneously to oxygen and water. Corrosion takes place electrochemically, as the corrosion medium is an electrolyte. The dissolution of the metal is an anodic process occurring simultaneously with a cathodic process in which oxygen, and sometimes hydrogen ions, are consumed. Examples of the amount of corrosion in micrometers per 10 years for unprotected steel in different environments are shown below.

Air			Sea			Soil (relative corrosiveness)		
Industrial	Urban	Rural	River	Sea	Tap	High	Medium	Low
1000	500	100	500	1000	100	1000	300	50

Corrosion proceeds in the soil at different speeds due primarily to differences in its specific electrical resistance. The lower the resistance, the greater the quantity of water and salts. Measurement of the resistivity therefore gives a good idea of the corrosive effect of a soil. Another factor affecting corrosion is the presence of oxygen. If the content of oxygen diminishes at greater depths in the soil, the speed of corrosion diminishes correspondingly. The amount of corrosion in soils thus varies according to whether, among other factors, they were formed in salt water, fresh water, or through weathering, and is much higher below than above the marine limit. In judging the corrosion of an object, therefore, it is important to find out whether it has been buried and in which marine deposit. As is evident, sea water is very corrosive. Of fresh waters, river water is more corrosive than, for example, hard tap water, in which the relatively high content of calcium provides some protection against corrosion.

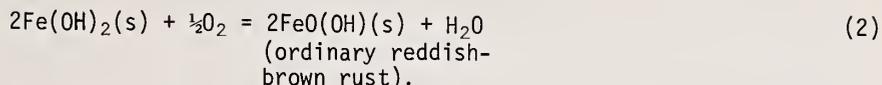
Rusting takes place in humid air when the relative humidity is above about 60 percent. For rusting to start in humid air, however, it is necessary that water layers adhere to the iron object during a long period. If these conditions are fulfilled, one may imagine the rusting to take place in two stages:

First oxygen, dissolved in the water, oxidizes iron to Fe(II):

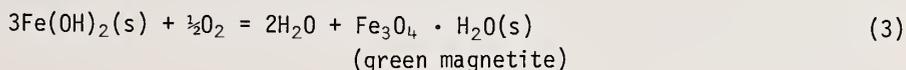


This reaction is promoted both by impurities in the metal surface and by the increased degree of acidity of the atmosphere caused by, among other factors, the combustion gases  $\text{SO}_2$  and  $\text{CO}_2$ .

In the second stage, oxygen from the atmosphere oxidizes the Fe(II) further to Fe(III):



At the outset, therefore, the rust may be considered to consist of iron (III) oxide hydroxide with varying water content. For the sake of simplicity,  $2\text{FeO}(\text{OH})$  may be written  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . But if the available quantity of oxygen is limited, reaction (2) may be modified, leading to the formation of different intermediary oxidation products of ferrous hydroxide, as appears from reactions (3) and (4).



The local accumulation of reddish-brown rust on an iron object through reaction (2) suffices to reduce the supply of oxygen to the ferrous hydroxide formed. It is therefore common to find laminated corrosion products on iron, consisting of an inner core of black magnetite, a thin shell of its green hydrate, and finally, an outer coating of ordinary reddish-brown rust. Such a coating can be produced in practice either by reducing the partial pressure, *i.e.*, volume fraction, of the oxygen over the solution or by placing the objects at a greater depth in the solution so that the resupply of oxygen through diffusion from the liquid surface is retarded. In the Wasa case, the conditions on the sea-floor were undoubtedly sufficiently anaerobic for the aforesaid formation of magnetite to take place.

The chlorides, mostly in the form of iron chloride, are the most dangerous enemy of iron. Iron chloride on most artifacts is difficult to wash out. If water vapour is present, it is absorbed and the  $\text{FeCl}_3$  solution migrates to the iron, dissolves it, and forms  $\text{FeCl}_2$ . Under the action of oxygen from the air, iron hydroxide is precipitated and  $\text{FeCl}_3$  is formed again. Heavy destruction of the iron in the form of pitting occurs.

Examinations of the water at the place where the Wasa sank show that the salt content was 4‰, the oxygen content zero, and the hydrogen sulphide content 7 mg/l in 1943. The temperature has varied between +1 and +5 °C.

During the 16th century, the King Gustav Vasa had the Oxdjupet Inlet closed in order to prevent vessels from entering Stockholm by that route, which must have considerably contributed to a reduction of the water flow; in 1838-39, Oxdjupet was closed completely, after which Kodjupet became the only inlet to Stockholm. In 1867, the first clearing of Oxdjupet started, and in 1919, was continued to a depth of 10.5 metres. The channel was further deepened in 1929 to 12.5 metres. Stockholm harbour had served for a long time as a sewer for domestic and other waste. Everything suggests, therefore, that the conditions had remained the same, *i.e.*, anaerobic with content of hydrogen sulphide.

The conditions for corrosion of the Wasa are known, and therefore the corrosion can be studied under known premises. It is also of interest to study where the iron that rusted away has gone and, finally, how the remaining iron objects should best be treated in order to be preserved. Both wrought and cast iron have been found on the Wasa. Of the roughly 800 iron objects surviving, only a score or so have been wrought iron; the rest are made of cast iron.

Wrought Iron

<u>Iron objects</u>	<u>Upper gun deck</u>	<u>Lower gun deck</u>	<u>Orlop deck</u>	<u>Hold</u>	<u>Total</u>
Bolts				3	3
Pump handles				4	4
Capsquares	1				1
Eyebolts				7	7
Saws				2	2

Cast Iron

Pots			5	6	11
3 pound cannon-balls			82		82
24 pound cannon-balls		7	64	230	301
Iron hook		1			1
Chain shot, 24 pound		2	225		227
Chain shot, 3 pound			12		12
Pike shot, 24 pound			133		133
Pike shot, 3 pound			4		4

Of more than 5000 one-inch bolts--many are more than one metre in length--fragments remain of only two. All iron nails in the decks had rusted away. The original number of nails was even greater than that of the bolts. Other wrought iron parts which have practically entirely disappeared are the forgings for the 64 gun carriages and also for the 52 gunports. The speed of rusting is shown by the corrosion of the bolts which the divers placed in the hull during salvaging of the Wasa. At the point of greatest attack the diameter of one bolt had diminished to one-third in a year's time. The rapid rusting of the gun carriage forgings is a probable explanation of why, during the 17th century, the guns could be released from their carriages and salvaged with the primitive means then available.

All cast iron objects on the other hand have been preserved, although many are corroded right through. Among other items preserved was a pot of 190 liters volume and 80 centimeters diameter from the galley. The corrosion of the cast iron objects varies. Some objects have practically not corroded at all, while others of the same composition and volume are corroded right through. This is exemplified by the distribution of the degree of corrosion of cannon-balls.

<u>Iron residue in the balls, percent</u>	<u>Percentage of the total number examined (228)</u>
2	3
12.5	9
27.5	9
40	11
52	17
67.5	27
85	17
90	6

The cannon-balls were found in two stores in the hold. The outermost balls and those not covered by a thick layer of mud are those which are most corroded. The average corrosion of the balls is 14 mm during 333 years, or 0.042 mm per year. This average corrosion is thus lower than for the bolts which had not been covered by a protective layer of mud. The mud had a pH value between 2.8 and 3.2 and a specific conduction resistance of 100 to 140 ohm cm.

By way of comparison the following analysis for the compact iron core from forgings and castings are of interest:

	Amount found, in percent					
	C	Fe <sub>tot</sub>	Si	Mn	P	S
Shaft of sheave (14577)	0.3	99.1				
Bolt, 1 inch (unnumbered)	0.5	98.8				
Bolt, 1 inch (20083)	1.06		<0.1	0.01	0.02	0.015
Iron support in main mast (22014)	0.6		<0.1	0.01	0.03	0.010
Cannon-ball, 24-pound (13698)	3.58	95	1.21	0.07	0.04	0.5

The higher content of carbon, in the form of graphite, of the cast iron balls was probably the main cause why they have retained their volume regardless of the degree of corrosion. It has been possible to check this by comparing the present volume with archival data, *e.g.*, for the 24-pound cannon-balls which have retained their diameter of 5-1/2 inches or 14 cm. Similar tests made on the bolts of wrought iron show a fairly large variation of carbon content. Examples of analyses of the rusty iron:

	Amount found, in percent						
	Fe <sub>tot</sub>	C	Si	Mn	P	S	Cl
Porous material of:							
Hub (14576)	57.5	2.2					
Cannon-ball (14309)	72.0	15.5	3.51				
Cannon-ball (13698)	ca 43	12.4	5.35	0.09	0.06	0.02	0.7-1.2
Cannon-ball (22900)	47.9	15.3	2.3	0.55	0.13	0.79	
	(Fe <sub>met</sub> 11.8)						
Chain shot (A)	40.2	15.5				0.15	1.2
Chain shot (A), duplicate test	42.5	15.8					2.0

For the same reason, apart from the high carbon concentration, the percentage of silicon has risen. This may be an additional contributory reason why the cast iron findings have retained their volume despite corrosion. The main element in the rusty iron is Fe<sub>2</sub>O<sub>3</sub>. The low sulphur content shows that there are few sulphates or other sulphur compounds in the corroded layer. The analyses show high chloride contents. According to investigations made by the Copenhagen Tøjhus Museum, the chlorides exist mostly in the form of iron chlorides, *i.e.*, the chlorides in the water have been converted into iron chlorides under formation of sodium hydroxide and hydrogen in accordance with the formula  $Fe + 2NaCl + 2H_2O \rightarrow FeCl_2 + 2NaOH + H_2$ . This is of significance from the conservation aspect, as the iron chlorides are less soluble in water than sodium chloride but have a considerably lower melting point.

The iron dissolved from the metal objects in the corrosion process has, to a large extent, been precipitated on material in the ambience because of the virtual absence of water flow. When, therefore, the *Wasa* was raised to the surface and the investigations started, the planking was resplendent with all manner of yellow, brown, black, and red shades. Stalactite deposits of up to half a metre in length hung from the ship's sides in the hold and on the orlop deck, usually down to a knee or strake of ceiling. The stalactite deposits have been analyzed in order to determine their composition and find out how they arose.

The investigation showed that the stalactite formation consists of an inner core of magnetite, siderite, and pyrrhotite. The outer varicoloured fine powder appears to consist of oxidation products of these phases--iron sulphate, iron hydroxide, goethite and lepidocrocite. The formations have an extremely light and porous structure and appear to be caused by the fact that the precipitation of iron took place on timber. This is confirmed by the presence of organic carbon. From the geological aspect the crystallization of magnetite is of interest through this 333-year-old "laboratory experiment".

The investigations of the material reveal the following. The layer of mud on all decks had an estimated total weight of 700 tons. In appearance, it was partly black and partly

grey. The iron content in these layers of mud was 22 and 2 percent, respectively, or between approximately 14 and 144 tons. Furthermore, practically the entire hull was impregnated with iron, which resulted in the very much admired colour of black oak. The mean concentration of iron in the hull is 0.63 percent or about 3 tons of iron.

In the drying out of the wooden sculptures, a deposit was formed on the surface. As there was doubt as to whether it consisted of a conserving agent or the like, or of precipitation of salts in the wood, an x-ray crystallographic analysis was made. This showed that the white deposit consisted of mixtures of iron sulphates ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $7\text{H}_2\text{O}$ ) and a greyish brown deposit which, after heating, had the diffraction pattern of pure iron oxide,  $\text{Fe}_2\text{O}_3$ .

Analysis of textiles showed the iron concentration to be as much as 45 percent. The composition of precipitates on skeletal parts, sculptures, etc. after conservation and in the form of stalactites has been determined. Precipitates on skeletal parts consist of about 95 percent of an iron phosphate, vivianite,  $\text{Fe}_3(\text{PO}_4) \cdot 8\text{H}_2\text{O}$ . Apart from iron, zinc was found in a concentration of about 1/20 of that of the iron, and also traces of manganese and phosphorus. Carbonate groups were also discovered, which renders it probable that the zinc is in the form of basic zinc carbonate. In the form of bivalent iron the vivianite is colourless, but is quickly oxidized in air to the trivalent iron phosphate without change of the crystal structure. In one case, a skeleton was found close to a gun carriage. Iron from rusted iron objects has reacted with the phosphate ions in the bone. The zinc probably derives from a bronze cannon. When the skeleton was exposed, the uncoloured white bivalent iron phosphate was converted into blue trivalent iron in half an hour.

The reason for the continued corrosion of the iron objects after their salvaging from the sunken vessel has been explained earlier. I shall merely illustrate this condition by means of two practical examples. The speed of rusting varies. The disintegration can be delayed by means of various surface treatment methods. The cannon from the "Riksäppet", which foundered in 1676, was salvaged in 1953. It was scraped, brushed, and treated with antirust oil and placed in the museum in 1954 (fig. 2a). After 18 years, the corrosion had proceeded so far that all ornamentation had disappeared (fig. 2b). The large iron pot from the Wasa was rusted to different degrees at the time of salvaging. Part had rusted all through, while other parts had their iron core intact. Attempts were made to rinse the parts with water, extract water with acetone, dry in vacuum, and vacuum impregnate with acrylic lacquer. The result was unsatisfactory, and continued corrosion was observed already within a few weeks. In the case of improper conservation or lack of conservation of the 24-pound cannon-balls from the Wasa, total disintegration may occur within a month.

There has, therefore, been a great need to find a reliable method of conservation for iron. The desire has been for a method with which, after the treatment, one knows that all recesses, cavities, etc., which are inaccessible by conventional methods, are treated; also that one is not then forced to remove the rust but can instead preserve the surface which gives the object its correct form, and which often is ornamented. We chose reduction with hydrogen gas at raised temperatures. By means of this treatment, rusting is arrested completely by eliminating water and oxygen in the material and, which is perhaps more important, all the chlorine. This is difficult to attain completely by other methods.

The carbon content in the corroded part of the find varies very much depending on how much iron which has simply disappeared during the corrosion. Ten to 20 weight percent is very normal. Calculated on the reduced find, that is without oxygen, values up to 35 percent of carbon might be obtained. This means that the carbon content is far higher than in the original find. When choosing the reduction temperature, it is desirable that the carbon content should be retained intact. We recommend normally a reduction temperature of between 600 and 700 °C, and the closer to 600 °C the better. These temperatures related to the reduction of objects solely of iron, and give the best results for this purpose. The decarbonization at 600 °C is negligible. If the iron object contains other metals, one may be forced to reduce at a lower temperature, *e.g.*, 300-400 °C, which takes a longer time. At higher reduction temperatures, 800-1000 °C, the speed of reduction is higher but leads to decarbonization in the rust layer of the find. Figure 3 shows the hydrogen furnace used at the Wasa laboratory.

For the reduction it is best to use 100 percent dry hydrogen gas or a mixture of hydrogen and nitrogen. With the pure gas, reduction time is shorter. An important point to be stressed is that the hydrogen must be dried from water before entering the reduction vessel



Figure 2a. Cannon from the Riksäpplet, founded 1676, salvaged 1953. As the cannon appeared, after soaking in water and boiling in paraffin, when placed on view in 1954.



Figure 2b. The same cannon after 18 years on exhibition. Expansion caused by the continued production of rust has caused the surface to crack and the ornamentation to drop away.



Figure 3a. Hydrogen furnace at the Wasa laboratory, with a second retort at the right.



Figure 3b. Automatic time and temperature regulation of the furnace.

to avoid decarbonization. As no drying is done of the find before the reduction process, the heating period to get rid of the free water must go very slowly to avoid cracking when the water evaporates. Also, the cooling time after reduction must be rather long. To be on the safe side, cooling in the furnace should be allowed to go to room temperature as, in some cases, porous superficial layers may have converted into a more or less pyrophoric iron which on admission of air may start to oxidize and form oxides once again. A good help in keeping a check on the reduction process is if one can check for water in the exhaust gas or arrange for suspension of the find in a scale during the reduction. A normal schedule for, for example, cannon-balls of 24-pound weight and with a total weight of charge of up to 60 kg can be run in a week as follows:

<u>Operation</u>	<u>Time (hours)</u>
Heating to 200 °C	8
Maintenance at 200 °C	for ~16
Heating to 400 °C	8
Maintenance at 400 °C	for ~16
Heating to 600 °C	5
Maintenance at 600 °C	18
Heating at 650 °C	5
Cooling to room temperature	48 hours

To prevent the rusting beginning again, the reduced objects were vacuum-treated with paraffin. The antirust agent used was 2 percent VPI (Shell patent). Accelerated rusting tests in a humidity chamber with admission of air during 10 months showed that the object tested had acquired a fully satisfactory protection against corrosion. The aim of the vacuum treatment of the reduced objects with molten paraffin is, as far as possible, to fully fill the pores in the entire object. Antirust agents with solvent can also be used. The degree of filling for the antirust agent in question is proportional to the concentration in the solution. This implies that one attains a degree of filling of 25-35 percent. This method is used when the requirements of increased mechanical strength of the objects are not unduly strict.

Though the furnace was specifically designed for Wasa finds, it has since come into use for the conservation of other valuable finds. Among these is a viking sword (fig. 4). After the hydrogen reduction of the sword, brass threads decorating the hilt can clearly be seen.

Hydrogen reduction is not an entirely un Hazardous procedure and a few words should be said about the use of hydrogen as a reducing agent. In the first place, it must be remembered that hydrogen is very liable to unite with oxygen of the air. This reaction, if it is at high temperature, is very violent and is referred to as an oxy-hydrogen explosion. Very careful precautions must therefore be taken when working with hydrogen. For work with gases which may explode, there are certain relations, among which the flammability range is one of the most important. The concentration range within which not only combustion but also explosion is possible is called the flammability range and its limits, the lower and upper limits of flammability. The limits for gases are usually stated in percentage by volume and for hydrogen the limits are 4 to 75 percent. The mixture of hydrogen with air is thus nonflammable so long as the content of hydrogen exceeds 75 percent; between 4 and 75 percent, the mixture is flammable and explosive; below 4 percent it is again nonflammable. For the inflammable mixture to ignite or possibly explode, however, the gas mixture must be heated to, or come into contact with, substances which have attained the minimum spontaneous ignition or auto-ignition temperature of the gas mixture, which in the case of hydrogen and air is around 510 °C. If such an inflammable gas mixture is ignited inside a closed chamber, an explosion will take place. If, on the other hand, the gas mixture is allowed to flow freely out of the burner (as for example, a bunsen burner) a very high speed reaction admittedly takes place between the gases but it is not explosive.

If, however, one always carefully drives off all of the *oxygen* in the air from, or to express it more simply, ventilates the reduction vessel before the reduction, one can then without risk admit the hydrogen into the red hot vessel. Ventilation is done most simply by flushing out the vessel with an inert gas such as nitrogen during the time of heating to the desired temperature.



Figure 4a. Hilt of a viking sword before hydrogen reduction.



Figure 4b. The viking sword ready to be loaded into the retort.

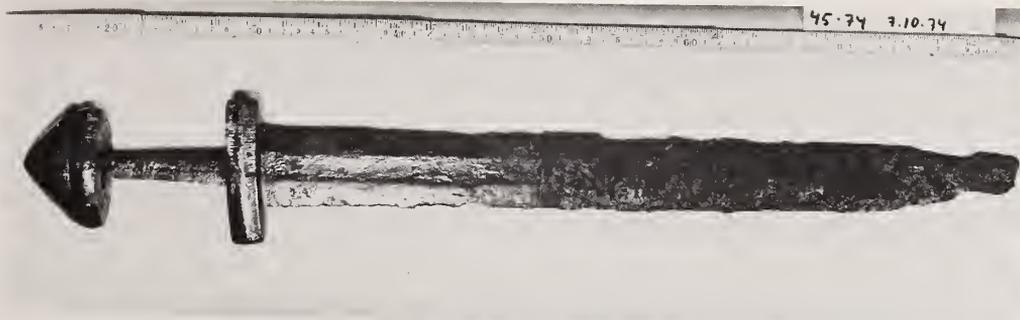


Figure 4c. The viking sword after hydrogen reduction.



Figure 4d. The hilt of the viking sword after treatment, showing the decoration of brass threads.

#### Problems And Ethics In The Conservation Of Iron Objects

The question is, will there be any changes by using the reduction method in the hardening of the find and will there be any other metallographic changes of significance or changes in volume.

On heating to 600 °C, hardening disappears almost entirely. One should, however, keep in mind that lower-temperature heating also has an effect on hardening, for example by hot water extraction or wax treatment. Hardening disappears gradually also with time. It must therefore be understood that the degree of hardening possessed today by a find deriving, say from the 15th century, is not the same as its original degree of hardening. It is not possible to extrapolate the initial hardness from the present hardness. A sample taken before any preservation begins is to be recommended if the degree at present of the hardening is to be recorded.

If a metallurgical examination is to be made, a sample must be taken, which means some destruction of a part of the find. This sample should be taken as soon as possible after the excavation and before preservation.

Other metallographic changes, such as the production of austenite, do not happen when using a reduction temperature of less than 600 °C.

In work on conservation, one is interested in restoring the details to their original form. By means of hydrogen gas reduction the volume of the find can be kept the same as when it was discovered.

Concerning the colour, it will, of course, change from the brown rusty colour the find has when it is found, to black, as the colour the find had when it was in use.

It is, in my mind, of the greatest importance for purposes of exhibition and pedagogy to show an intact find. It is obviously unsatisfactory to show a collection of rusty iron objects, giving the viewer the wrong idea of what they once looked like and the impression that our forefathers used tarnished weapons.

In conclusion, it may be said that the experience of reduction of the iron objects at National Maritime Museum - Wasa Shipyard during the twelve years in which this work has been going on is extremely satisfactory. Owing to the great reliability of this conservation method, no new rusting, or consequent cracking, has arisen. Purely aesthetically, and from the museum aspect, the objects have an attractive and correct appearance, *i.e.*, they look as they did in use.

#### Discussion

*M. Pourbaix:* You have made some comparisons between the hydrogen reduction process and some processes with aqueous solutions. Are there cases where processes with aqueous solutions might be preferred? May aqueous processes lead to a complete removal of chloride?

*L. Barkman:* We made comparisons with the various aqueous solution methods, but we did not succeed in removing the iron chlorides. That was a poor conservation method.

*E. Escalante:* Do you clean and recycle the hydrogen or do you just vent it?

*L. Barkman:* We do not recycle it. We use such a slow stream of hydrogen that we simply ignite it after it has passed through the reduction chamber.

*E. Escalante:* In the film it was mentioned that the water has to be replaced as the wood dries. What is it replaced with?

*L. Barkman:* Polyethylene glycol.

*J. Kruger:* Have you looked at the metallographic structure of the reduced cannon balls as compared to the metallography of cast iron that has not gone through this corrosion and then reduction?

*L. Barkman:* Yes, this was done at the Royal Technical Institute in Stockholm, but I do not have that report with me so I can not respond to that question.

*D. Piechota:* On hydrogen reduction, how long is the treatment from the first heating of the specimen until it is removed from the oven?

*L. Barkman:* We normally run one treatment a week.

*H. Bump:* What is the explosive power of one cubic foot of hydrogen?

*L. Barkman:* It will blow away the furnace. (Audience laughter).

## RESTORATION OF LARGE GILDED STATUES USING VARIOUS ELECTROCHEMICAL AND METALLURGICAL TECHNIQUES

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Four gilded bronze equestrian statues, erected in 1951 in Washington, D.C., had, by 1968, shown severe signs of deterioration. Extensive surface pitting and discoloration were observed, steel structural members had disintegrated, severe cracks were evident, and numerous holes were clearly visible from the interior. Restoration included replacing steel members with brass, filling cracks and pits with tin-silver solder, refinishing with gold by electroplating, and sealing the surfaces with an acrylic lacquer (Incralac).

Key Words: Bronzes; deterioration; gilding; metal finishing; refinishing; restoration; statuary.

### 1. Introduction

In Washington, D.C., on the Memorial Bridge Plaza between the Lincoln Memorial and the Potomac River are four large gilded bronze equestrian statues. The statues, which are mounted on stone plinths, are about 6 m long, 6 m tall, and 3 m wide. They were cast in bronze and then gilded by applying a layer of gold amalgam and heating to evaporate the mercury so as to leave a thin layer of adherent gold.

These statues arrived from Europe and were set in place in 1951. They stand above the tidal waters of the Potomac River near two streets carrying very heavy automobile traffic and are subject to about 100 cm of rain each year. In 1971, after some twenty years of exposure to the environment, the condition of the statues had deteriorated to the point where the structural condition and the surface finish both required that action be taken to restore and preserve these works of art.

The four equestrian statues are the responsibility of the National Capital Parks of the Department of the Interior. This organization has had a great deal of experience with the maintenance of roads, parks, public monuments, and statuary. That experience, however, did not include the repair and restoration of massive gilded bronze statuary and it looked elsewhere for advice and guidance. Experts in the fields of mechanical metallurgy, corrosion, electrodeposition, and organic coatings from the National Bureau of Standards were made available to the National Capital Parks and, within the areas of their expertise, provided advice and guidance.

This paper summarizes the observations of the NBS team. The restoration was carried out by the National Capital Parks. The various materials and procedures used were selected by the National Capital Parks on the basis of artistic, economic, and political considerations, as well as the technical advice of the National Bureau of Standards, the Department of the Navy, and the International Copper Research Association.

## 2. Condition of Statues

### A. General Exterior Appearance

The names of the four statues, from north to south, are Aspiration and Literature, Music and Harvest, Sacrifice, and Valor. The last two, Sacrifice and Valor, looked very much alike. The upper surfaces, washed by rain, were heavily encrusted with corrosion products and dirt, dark green to black in color. The vertical and near vertical surfaces were streaked by the runoff of the rain water.



Figure 1. Aspiration and Literature in 1968 before restoration.



Figure 2. Close-up of Music and Harvest showing surface appearance in 1968.

The two northerly statues, by comparison, looked much worse and Music and Harvest was obviously in poorer condition than Aspiration and Literature. Figures 1 and 2 show the condition of these two in 1968. Only the upward facing surfaces were washed clean by rain; all the other surfaces were dirty with corrosion products so that the impression was of black surfaces with some golden highlights.

### B. Condition of Exterior Surfaces

Upon the removal of the dirt and corrosion products, the underlying conditions of the gilded surfaces became evident. No one condition or set of conditions prevailed. Some areas had no objectionable defects and the gold layer was sound and intact and adherent. In

some small areas, gold was not present, but this seems to have been of relatively rare occurrence. More frequently, the gold layer was perforated. That is, there were many breaks in the gold layer. Also, a significant portion of the gold was poorly adherent and could be easily removed by wire or nylon brushes.

The most impressive condition was the very large number of small depressions and pits. Their appearance strongly suggested that most were present in the original castings, some being shrinkage pits and some being the remains of gas bubbles. They were present in many sizes up to several millimeters in diameter and in many shapes and depths. Many extended all the way through the castings. We presume that many of these had been enlarged by corrosion and some may have been created by corrosion. We would expect that galvanic corrosion would be likely wherever there was a break in the gold. Most of our observations of these pits were made after the gold had been removed by sandblasting. Many were evident, however, where the gold had not been removed, but we presume that the gold layer did cover up some of these defects.

Figures 3, 4, and 5 are micrographs of cross-sections of corings taken from the statues. They show the gold layers, some intact, some with breaks, and some looking spongy. The dark layer between the gold and the bronze was always present in the six different cross-sections examined. An electron microprobe analysis shows it to consist of the same metallic elements (Cu, Sn, Zn, and Pb) in about the same proportion as in the bronze, but with oxygen added. The surface of another specimen was examined by x-ray fluorescence after some loosely adhering gold was lifted off. Sulfur and arsenic were found to be present. The sulfur could have come from the atmosphere or from a sulfuric acid treatment reported to have been given the bronze just prior to fire gilding.

The micrograph in figure 4 shows porosity within the cast bronze. For the most part this is of no particular significance except for the exterior surface condition described earlier.

The surface of one specimen from one of the statues was analyzed for residual mercury and 0.6 mg/cm<sup>2</sup> of mercury was found, but we have no assurance that this is representative of all surfaces.

X-ray diffraction patterns of the green black materials that had formed over the gold surfaces demonstrated the presence of CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) and CuSO<sub>4</sub>/3Cu(OH)<sub>2</sub> (brochantite). Brochantite is the major constituent of natural patina. The only probable source of the gypsum would be the mold materials used to cast the bronze. There was considerable gypsum



Figure 3. Micrograph of cross-section of piece removed from Aspiration and Literature in 1968 showing spongy gold deposit on surface of bronze casting.



Figure 4. Micrograph of cross-section of plug removed from Sacrifice in 1968 showing broken gold layer over porous bronze casting. X240.



Figure 5. Micrograph of cross-section of piece removed from Aspiration and Literature in 1968 showing gold coating over bronze casting.

inside the statue from which an analyzed sample was taken and it is reasonable to expect that the gypsum was deposited on the outside from water seeping from the inside through cracks and pores.

### C. Structural Conditions of Bronze

Several cracks in the bronze shell of Music and Harvest, and of Aspiration and Literature were evident (figs. 6 and 7). Generally, there was no gold within the cracks suggesting that many of them either formed or grew after the gold had been applied. These cracks may have contributed to the exterior corrosion, but only two of them appeared to be structurally significant. One crack was about 2 m long, extending more than halfway around one way of



Figure 6. Crack in Music and Harvest.



Figure 7. Crack in Music and Harvest.

Music and Harvest. Another was extended most of the way around a feather on the lower right wing of Aspiration and Literature. These two cracks were potential sites of structural failure.

#### D. Condition of Interiors

Three of the statues could be entered through the supporting plinths with the aid of a ladder or scaffolding. The fourth statue, Valor, was entered through a hole cut in the back of the horse. It is, however, open to the hollow plinth through the legs.

Upon examining the statue from the inside, with no light in the interior, one became immediately aware of numerous holes letting in pinpoints of light. Some of these were associated with cracks, seams, and welds. Some were simple pores extending through the casting.

The interior surfaces seemed perpetually damp or even wet. Any blind cavities or recesses that could hold water were filled with water. Some of this water may have come through holes from the exterior, but it seems more probable that most came from condensation. The situation in these statues is very favorable to condensation because of the large temperature changes that the bronze would undergo almost daily, the rapid heat transfer characteristics of bronze, and the ready source of moist air from the Potomac River through extensive chambers under the bridges which connect through the plinths to the interiors of the statues. At night, condensation over the entire interior surfaces can be expected and air circulation would bring in moist air from under the bridges. Much of the condensate could easily run down and collect in the recesses. During the day, evaporation of that water would be restricted if for no other reason than that air circulation would be limited. The air would be heated from the top and the hot air would be trapped in the essentially closed system. This air, of course, would contain considerable water.

The interior surfaces of Aspiration and Literature and of Music and Harvest were covered with corrosion products and residual mold materials. The latter is presumed to be mostly gypsum, possibly mixed with sand (fig. 8). It was present in considerable quantity, especially in the wings of the horses, and may have played a part in holding water inside the two statues. Sacrifice and Valor were relatively free of the molding materials and a green patina was present over most of the surfaces.

The statues were cast in a number of pieces that were subsequently fastened together. The two southerly statues, Sacrifice and Valor, were welded together and the other two were bolted together at flanges integrally cast on each piece. Music and Harvest also has several pieces held together along a centrally located seam. This seam is held together by



Figure 8. Interior of Music and Harvest showing flange, rusted bolt heads, corrosion products, and molding materials (gypsum and sand).

"tie-plates" bolted to the pieces being joined. The bolts, nuts, studs, washers, and "tie-plates" throughout the two statues were predominantly steel with some being of brass or bronze. These steel members, in contact with the bronze in a wet environment, undoubtedly formed an active galvanic couple. As would be expected, the steel was badly corroded and many of the parts no longer served a useful purpose (figs. 9 and 10).



Figure 9. Collection of corroded pieces removed from Music and Harvest.



Figure 10. "Corrosion Rose." Remains of corroded steel bolt head.

The statues contained steel tie rods or braces and each was anchored to its plinth with a steel framework. These steel members had been coated with a bituminous material, but had nevertheless corroded (figs. 11 and 12). In some places the coating had come off in local areas. In other places the corrosion had taken place under the coating. Some of these structures were still sound, but others were obviously not. One tie-rod had corroded all the way through.



Figure 11. Steel tie rod with remains of bituminous coating.



Figure 12. Interior of Music and Harvest showing steel tie rod with remains of bituminous coating, flanges, and corrosion products.

### 3. The Restoration

The restoration of Aspiration and Literature and of Music and Harvest was carried out during the fall of 1971 and that winter. The restoration of Sacrifice and Valor was started in November of 1972 and completed that winter.

#### A. Interior Repairs

Mold material was removed to the extent practical with reasonable effort. This was done principally to facilitate the other work to be done. It was hoped, however, that its removal might reduce the corrosiveness of the inside environment by reducing the surface areas for condensation and water absorption, and might reduce the formation of gypsum deposits on the outside surfaces.

All the steel fasteners, braces, tie rods, anchoring structures, etc., were replaced with naval brass. This should provide a more durable structure. Some 1000 bolts were replaced in Music and Harvest and Aspiration and Literature, the two northerly statues.

## B. Repairs to the Bronze Shells

The bulk of the dirt and corrosion products on the exterior surface was removed by treatment with steam and a detergent. The remaining corrosion products and the loose gold were removed with motor driven rotary wire wheels. The more adherent gold was removed by sand blasting with No. 1 grit sand.

It had been planned to fill all cracks by welding and/or brazing. It was found, however, that only a few of the cracks could be welded, as it was not possible to preheat the metal at many of the cracks to a suitable temperature for welding. These latter cracks were filled with a solder, 97 percent tin - 3 percent silver (fig. 13), which was used instead of lead solder because it is stronger and more corrosion resistant. The large crack on Music and Harvest was tied together by bolting plates across the crack on the inside (fig. 14). The threaded studs penetrating the shell were ground and smoothed to the contour of the outside surface.

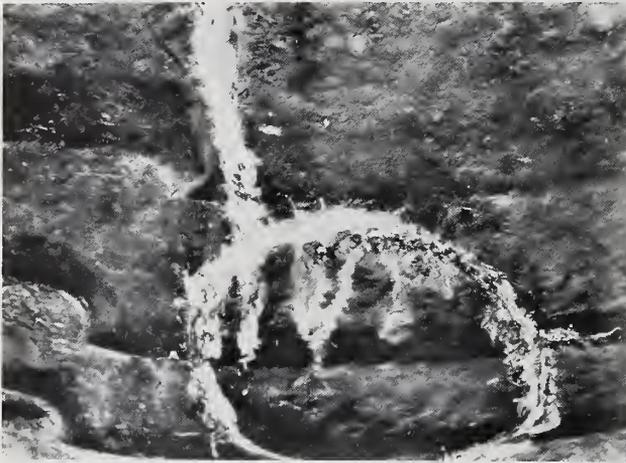


Figure 13. Crack filled with tin-silver solder.



Figure 14. Inside view of crack held together by brass tie plates and of one end of a brass tie rod.

Many pits were routed out and filled with the same solder. There were, however, far too many of the small pits to make this a feasible method of filling all of them. A conducting epoxy was used to fill some of the pits, but because it was difficult to electroplate over that surface, most of the pits were left unfilled.

## C. Surface Finishing

The exterior surfaces were refinished by electroplating with nickel and then with gold. This was accomplished by the brush plating technique which has found considerable use for repairing plated surfaces of machinery and aircraft equipment. It has been used for gold plating new church domes, but we are not aware of its having been used to gold plate statuary

and large bronze castings. For this application the process is unique. In brief, a carbon rod is wrapped with absorbent cotton and cotton gauze and connected to the positive pole of a direct current power source. The negative lead is grounded to the statue. The cotton covered rod is dipped in the plating solution and then swabbed back and forth over the surface to be plated (fig. 15). As the current flows from the rod through the solution to the bronze, the nickel or gold is deposited as a smooth adherent layer. The actual process is, however, more sophisticated than indicated here.



Figure 15. Nickel Plating.

For this application the nickel and gold were each applied in two or more layers and each layer was buffed with a greaseless abrasive pad. The purpose of the buffing was to minimize the porosity of the coating and to provide a surface with an appropriate appearance.

For the nickel plating, the following sequence of operations was typical. This was carried out over small areas at a time. The area might be anywhere between a few square centimeters and about a square meter, depending on the shape and accessibility of the surface and the skill of the plater.

1. Mechanically clean with a rotary wire brush and/or a rotary abrasive flap brush.
2. Cathodically clean with a proprietary alkaline electrolytic cleaning solution
3. Water rinse.
4. Nickel plate.
5. Water rinse.
6. Buff and activate with an abrasive pad.
7. Nickel plate.
8. Water rinse.

The solder and some areas that were particularly difficult to plate were first plated with about 10  $\mu\text{m}$  of copper.

A typical sequence for the gold plating was as follows:

1. Buff and activate the nickel with an abrasive pad.
2. Clean cathodically with an alkaline cleaner.
3. Water rinse.
4. Gold plate.
5. Water rinse.
6. Brunish with an abrasive pad or levigated alumina.
7. Water rinse.
8. Repeat steps 4 to 7 two more times.
9. Air dry.
10. Apply acrylic lacquer (Incralac).

These finishing cycles were not always followed, but varied from place to place, depending on the surface conditions, surface contours, accessibility, and operator technique.

By the nature of the process and individual variability, the thickness of the metal coatings can be presumed to have varied widely from place to place. Also, there was a deliberate effort to plate more heavily over the pitted areas than over the smooth surfaces. The thickness averaged about 12  $\mu\text{m}$  of nickel and 4  $\mu\text{m}$  of gold, as judged by the quantity of plating solutions used.

A clear acrylic lacquer containing benzotriazole was applied over the gold, at least two coats by brush and two coats by spraying. This lacquer, "Incralac" was developed by the International Copper Research Association for use on bronze. It is corrosion inhibiting, is not degraded by ultraviolet light, does not discolor, and does not flake off.

It has been anticipated that weathering of the restored statues would develop local corrosion sites that were not, for one or another reason, adequately refinished during the initial restoration. Consequently, Aspiration and Literature along with Music and Harvest were closely examined in the fall, some 10 months after completion of the initial refinishing. Numerous small holes, cracks, and seams were sites of bronze corrosion products and/or of white deposits which, presumably, were gypsum. Water saturated with gypsum seeped through pores from the interior to the outside and evaporated, leaving a white powder. These defects were not serious, but did require repair.

The smaller defects were cleaned off and lacquered. The larger ones were routed out, filled with solder, replated, and lacquered.

This retouching was repeated two years later, but the number of sites involved was very much less and were too small to be seen from the street.

#### 4. Renewal of Lacquer

Within a few months after the initial refinishing of the first two statues, there was a distinct darkening of extensive areas of the gilded surfaces. The discoloration was very irregular and uneven, and it continued to develop for awhile and then stabilized. A close examination revealed that some dark materials had formed at the gold-lacquer interface. When the lacquer was removed with a solvent, this dark material came off with the lacquer. The darkening did not recur after relacquering the clean surfaces.

After making several tests, it was concluded that the darkening was associated with residue from spent gold plating solution; that the gold plate had not been adequately rinsed after plating and before lacquering. With time the residue underwent a change and became dark and opaque.

This conclusion was confirmed by preparing laboratory specimens with various amounts of residue left on them, lacquering and exposing. Darkening of the specimens with spent solution was obtained, but not on those that had been thoroughly cleaned.

In 1974, all the darkened areas were cleaned off and relacquered. Since then there has been no evidence of further difficulty of this nature.

## 5. An Evaluation of the Restoration

With respect to the texture of the refinished surfaces, we do not detect any significant difference from the original. The color is somewhat different and there is a soft sheen or gloss imparted by the lacquer (fig. 16). With the gold less yellow than originally and having a brownish cast, the overall appearance is less brilliant. Whether the refinished appearance is superior or inferior to the original is a matter of taste, but it is immeasurably better than that existing just prior to the restoration. The appearance of the two restored statues did meet with the approval of members of the Commission of Fine Arts.



Figure 16. Aspiration and Literature after restoration. Winter, 1972.

Structurally, the restored statues should be sounder. There is some concern that some detrimental corrosion on interior surfaces may occur where the tin-silver solder comes through to the interior of the statues. The bimetallic couple in the wet environment may have adverse effects, but they should not be very serious.

The crucial aspect which requires observing closely in the future is the behavior of the gilded surface. There is, undoubtedly, some porosity in the gold coating, especially in those areas which have less than the average thickness of gold. More significant, however, is that there are a large number of pits which could not be gold plated. That is, the gold would not completely plate over the inside surfaces of the pits (fig. 17). These spots or



Figure 17. Pitted surface after gold plating.

pores where the bronze is exposed to the atmosphere at points of contact with the gold are potential sites for severe galvanic corrosion. The acrylic lacquer (Incralac), of course, will inhibit such corrosion, but only as long as it is there. It is expected to be worn off by the elements in about five years and there is always the possibility that it will not be reapplied when it should. Fortunately, the pits are pretty well filled with the lacquer so that the greatest thickness of the lacquer is where it is needed most. Also, we anticipate that the erosion of the lacquer in the pits will be much slower than over the general surface.

With periodic inspection, cleaning, repair of individual flaws as they develop, and periodic lacquering every five to ten years, the statues should keep virtually the same appearance indefinitely without expensive repairs.

#### Discussion

*F. Brown:* What is the mechanism of the cracking in those horses?

*J. Kruger:* Since the cracks occurred at areas adjacent to where the sections were bolted together and under some stress coupled with presence of ammonia like species in the environment, we felt that some of it may have been stress corrosion cracking. Of course with bronzes it is not as likely as with brass but I think that there was some stress corrosion cracking.

*M. Pourbaix:* I cannot speak about this specific problem as I am not familiar with the details. I can say, however, that the problem of pollution exists everywhere. We all know of the problems now existing in Italy and in France. It is also true that when you have the combination of a polluted atmosphere and a porous gold coating, the structure will be destroyed due to the high electropotential. This may be avoided if a completely non-porous gold coating is applied.

I also wish to mention that in some countries such as the German Democratic Republic, the corrosion aspects of a structure *must* be considered in the planning and design stage. I do not wish to propose that this is an example that we should follow, however, Professor Sweible at the Center of Corrosion in Dresden, has a staff of 200 corrosion engineers. Anyone who is building a metallic structure in Eastern Germany must ask the advice of this organization and apply the specification recommended. We all know that 80 to 90 percent of all corrosion damage may be prevented if the proper steps are taken in the beginning. I might also add that Professor Sweible will be coming to Brussels next April on the occasion of our 25th Anniversary.

The horses are wonderful structures and perhaps the procedure that was used is the best, provided that the brush system leads to a non-porous coating and that the Incralac is permanent.

## PROBLEMS OF RETRIEVAL AND RETENTION OF ARTIFACTS IN FIELD EXCAVATIONS

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I feel obliged to make some preliminary remarks, not by way of apology, but as preface. I must state at the outset that the corrosion of metal artifacts does not absorb the prime time on any archeological excavation of which I am aware. It can, however, be a matter of greater or lesser importance with respect to the individual dig, and these circumstances are highly variable. I am informed, for instance, that an Arctic archeologist may have a serious problem with the disintegration of metal artifacts removed from a zone of permafrost. That is not a problem I have ever faced in the deserts of Syria or Afghanistan during the last twelve years.

It is quite impossible for any two archeological excavations to be as alike in dealing with investigative problems as two laboratories in one country, or even in separate countries. While laboratory conditions can be duplicated exactly, or precise equivalent tests conducted concurrently in the same, or separate laboratories, it remains as true today as ever that all archeology is a process more akin to destruction than to conservation, in spite of the virtuous and ecologically conscious feeling which may be derived from mandatory back-filling in some countries today. It is by no means clear that all excavations have as their ultimate goal the elucidation of some direct or correlative aspect of human presence on earth. It may be no more than a personal prejudice that believes they *should* have such a guiding principle. Beyond this, every excavation is highly individual, governed by geography, climate, politics, local economic imperatives, varying cultural pressures, ethnic, age, cultural, and intellectual diversity of staff, all existing as probable greater determinants in a field excavation than in the more readily achieved ideal laboratory. Except for the fact that any excavation normally entails digging, there may be little or no common ground, a point which for the last hundred years and more has been forcefully exhibited in the way in which archeologists speak of each other's work. It is, perhaps, to this well-known circumstance I allude in stressing that what follows here is a personal view. I sail upon this sea of corrosional erudition under the much more palid colors of the generalist, which is what the practice of archeology in the field, irrespective of one's normal penchant, requires one be. Perhaps my remarks may be looked upon as a not altogether irrelevant diversion from the sobriety of this occasion.

In 1815, the Honorable Mountstuart Elphinstone, who was not able to visit Sistan, enthused: "There is no country to which an admirer of Persian poetry and romance will turn with more interest than to Seestaun, and there is none where his expectations will meet with so melancholy a disappointment." Nearly a century later, Lord Curzon, who chose not to visit Sistan, wrote: "Seistan is one of the most unattractive, the most inhospitable, the most odious of places in the world. It is a country of marshes and of swamps, of sands and solitudes, of extreme heat and extreme cold, famous for a wind the most vile and abominable in the universe, presenting at all seasons of the year dangers to life which can scarcely be realized by those who only read of them at a distance."

In February 1971, I signed, on behalf of, I believe, the Smithsonian Institution, a contract with the late Royal Government of Afghanistan to undertake the archeological exploration and excavation of the southwestern portion of the country (fig. 1). This was not quite as mad an act as it at first seems, since it was assumed the inhabited portion of this region would be defined by the Helmand River Valley, much as the Nile Valley contains virtually all the vestiges of ancient Egyptian civilization. In point of fact, I was wrong in this belief. Irrigation canals 100 miles in length, a few perhaps longer, and utilization of run-off from high mountains to the south in Pakistan, meant that people in very early times lived at great distances from the river.

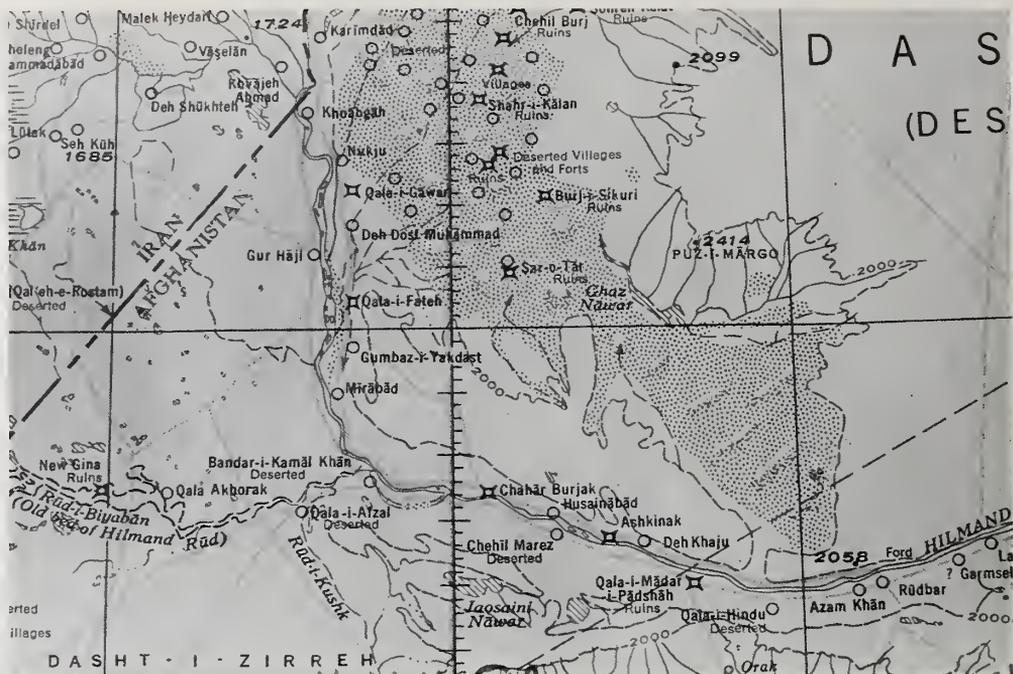


Figure 1. Map showing southwestern portion of Afghanistan.

From the very beginning, we felt very much as we imagined archeological explorers felt entering the Nile Valley, or the Tigris-Euphrates region, early in the 19th century. The comparison may be easily extended. For our work, we had no model; for our project, no paradigm; and for our scope, no parameter. (These are loan words from the New Archeology.) This is at once the project's limitations and weakness, and, we hope, its breadth and value. We worked within a time frame of unknown termini. No written sources, copious as they may be, had any immediate relevance, and in the final analysis, no significant pertinence to anything we found. This has, in the end, resolved itself into a matter with which others who may follow can cope; we have no explanation for it. We liked to remark, ironically, sitting around the campfire, that our labors were conducted with all the advantages of a 19th century exploratory mission to Inner Asia. But that is not the truth. Those missions were, in the main, far better outfitted and financed. For the thousands of exposed burials covering the playas and spoil banks of great and small canals, we had no physical anthropologist; for the rich and puzzlingly varied, curiously clinging, flora and fauna of the basin, we had no botanist or zoologist. For the life of the *hamun*, or land-locked fresh water lakes, and the Helmand River, no limnologist. With the more arcane subjects of the modern day paleobotany, sedimentology, etc.--we could do nothing. Certainly we had no conservator, and if put to it, I believe a corrosion scientist would have been pretty far down on our want list.

Because of an enlightened policy on the part of at least a few individuals, first at the Johns Hopkins University, and afterward at the U.S. Geological Survey, we have had from the beginning an environmental geologist. The amazing success of his work on the formation of dunes and transport of sand by water and wind, of his studies on deflation and aggradation, does indeed cause me to lament that we had with us specialists in so few disciplines. But there was virtually nothing to be done about this.

After more than a year spent in the field thus far, in an area of forty thousand square miles, without a town, without a road, without telephones, electricity, food, or potable water, we know at least something of how much we do not know, which we think is an appropriate first step. Our work is far from finished. Archeologically, we have surveyed in some detail more than one hundred and fifty sites and excavated wholly, or in part, seventeen. This is no more than a non-random sampling. The time range ends certainly around 1500 A.D. It may begin in the 4th or 5th millennium B.C.

Our tasks are similar in that the problem of confronting continuously altering materials intelligently is always with us. Our tasks are separate in that for the conservator, the problem is the profession, whereas for the field archeologist, circumvention of the problem is the expedient. The conservator devotes as much time to an object as it may require--ten minutes, ten days, ten weeks. In the field, the archeologist has to deal daily with perhaps a thousand objects, very few of which present exactly the same problem, and have to be studied minimally to determine even this basic bit of data. I no longer wonder why final reports of excavations are often so late in coming out; I marvel that they ever appear.



Figure 2. The Shahr-i Gholghola site.

The foremost problems in the field are those of retrieval. Without the object, all the rest is moot. The major component of this aspect of our work is simply logistics. Ever mindful of the dire forebodings of Lord Curzon, when we go out into the desert we bring with us everything we need for a minimum of ten weeks: all the food, all the water, all the gasoline. The country through which we must travel is frequently rough and extreme desert, and it takes two long days of driving to negotiate the 275 miles to our base camp. Some of the sites in the region, such as Shahr-i Gholghola (fig. 2) are quite visible, and though they present insurmountable problems of sand removal, much can be learned from surface indications. It is impossible to move this sand at a rate faster than it accumulates. Because of the high winds that exist in the area, we have to grab at sites when they appear from under sand dunes. That is, we have to be ready to deflect our attention, if possible, onto a site such as the 2000-year-old sanctuary complex in figure 3 when it is available. We did clear the major portion of this in 1973, and when we returned the following year it was largely covered by fresh sand. We have to complete every year what we start because most excavated areas cannot remain open from one year to the next. Smaller sites may be completely sand-buried during a given field season. Certain other sites are so deeply covered by permanent sand dunes, owing to the aerodynamics of the area, that we cannot contemplate excavation of them. The most dramatic indication of the wind and sand problem is represented by a small group of mausolea in an Islamic period cemetery (fig. 4). In 1971, when we first saw them, they were sand free. When we returned in 1972 the cemetery was almost completely concealed. The following year, the area was again emerging. For over about five hundred square miles of the Sistan Basin, it is almost impossible to put a foot down without stepping upon an artifact of some sort. Ours is a problem of selection, not of paucity. This concentration of surface sherds is caused by deflation in the area. In other



Figure 3. A 2000-year-old sanctuary complex.



a

Figure 4a. Small group of mausolea in an Islamic period cemetery.  
View taken in 1971, shows them sand free.



b

Figure 4b. Small group of mausolea in an Islamic period cemetery.  
View taken in 1972, shows them almost completely covered with sand.



c

Figure 4c. Small group of mausolea in an Islamic period cemetery.  
View taken in 1974, show the mausolea again emerging.



Figure 5. Illustration of destruction of ceramic artifact by the abrasive action of wind-driven sand.

parts of the region we find aggradation proceeding at a faster rate than deflation, and the concentration of potsherds exists at varying depths below the present land surface.

In our excavations, most of our retrieval problems are related to ceramics rather than to metal. When these are exposed on the ground surface for long periods, they may be almost entirely destroyed by the abrasive action of wind-driven sand (fig. 5). The rate of deterioration of the ceramic, or its response to the abrasive action of the wind, depends directly on the hardness of the ceramic in the first place, and we have found that some of the latest ceramic in our area deteriorates much more rapidly than other much older wares.

But even if we do get the object out of the ground, what happens to it then? What are the problems of recording and retention? One of our basic problems of recording can be summed up by figure 6, a notebook with very acid paper which is not going to last very long. With a stationery budget of 20 dollars, we are forced to rely upon the locally available paper and that happens to be such Chinese student notebooks. Much more expensive, but equally unsatisfactory, were display albums with plastic envelopes (fig. 7). They are electrostatic, so that in a very short while they are completely covered with the blowing silt; and worse still, in the heat of the area they begin to melt and the paper sticks to them. It is especially bad in the case of the xeroxed materials. When you remove the Xerox, the ink stays behind on the plastic, and when you put it back in you have to line it up exactly, otherwise you have two images.

Closely allied with the problems of retrieval and retention is that of transport. For some expeditions, that may not be as great a problem as it is on ours. Every object we find is at least 600 miles from the storerooms of the Institute of Archaeology in Kabul, which constitute a wholly separate problem. The first 275 miles, or so, of this distance is over extremely rough terrain. We cannot hope to transport a reassembled bowl such as the one in figure 8, no more than a millimeter thick in places. It has to be taken apart after the field record photograph, which is why more care is not taken in the initial assembly. Getting everything out whole is certainly something we do not expect and something we have certainly not achieved. That is why the first field photographs are of such prime importance.





Figure 8. Bowl is assembled at the site, photographed and then unassembled for transporting out of the field.

Surprises for the field archeologist do not always come before those of the conservator. For the last five years, we have been finding a great many coins of the Islamic dynasties of this region belonging to the tenth to thirteenth century. No gold coins have been found, but they do exist. We have many coins with oxidized surfaces we believe to be silver (fig. 9) because they so closely resemble in appearance known silver coins of the 3rd-century Sasanians who also lived in this region. Even larger quantities of copper coins have been found, singly or in hoards of up to 406 (fig. 10). We have also found smaller quantities of coins we believed to be lead since Sistan did have one of the few known lead coinages (fig. 11), but this information is quite restricted. Most writers on Sistan coins recognize only gold, silver, and copper. In fact, almost all the "silver" and "copper" coins are lead, some with a thin copper covering partly intact. All of these coins, kept in standard paper coin envelopes and stored in wooden drawers exhibit signs of an alarmingly rapid disintegration owing entirely, it seems, to their contact with wood, or paper manufactured from wood pulp (fig. 12). Their environment has now been changed, but they can be saved only by treatment in the conservation laboratory. It seems to make no difference whether the coin was a surface find or recovered from four meters down; the disintegration rate appears to be the same. These 700 to 1000-year-old coins appear to have suffered more in the last four years



Figure 9. Islamic coin believed to be silver showing oxidized surfaces.



Figure 10. Islamic copper coins were found singly and in hoards of several hundred.



Figure 11. Islamic coins believed to be lead.

than the preceding hundreds. In their natural environment, if on the surface, they are subjected to a daily temperature differential of approximately 20 degrees Celsius, with summer highs in excess of 55 degrees and winter lows of down to -20 degrees, to intense dryness and week-long periods of wet. Those deeply buried, on the other hand, had a constant environment.



Figure 12. Islamic coin showing disintegration caused by contact with wood or paper made from wood pulp.

I might hazard the guess that no one became a field archeologist through an interest in the corrosion of metal, and perhaps in most digs, metal corrosion is not so pressing a problem that it cannot wait until objects reach a laboratory. But many objects, and increasingly so, never become the concern of conservators in museums because they never reach museums. They stay in the countries where they have been found, where there are, most often, no laboratories, no educated conservators, and often not even an awareness of the importance of conservation. This is a problem that is going to require much more attention on the part of conservators rather than field archeologists. It is true now, and will be ever more so, that the laboratory is going to have to go to the object, not the reverse. I cannot think of an archeologist who would not esteem having a conservator as a collaborator in the field. Adding an additional person to a dig is not as simple as buying another plane ticket and twenty pounds of spaghetti. While that may be the case with the vacation excavation, it can be more like expanding a laboratory to accommodate more researchers. I know that for our project the addition of one person would have required another \$300 tent, another \$8,000 vehicle, more field gear of all sorts and increased volumes of water, food, gasoline, and the storage capacity for handling these, all quite apart from that person's specific essential work supplies and equipment. To my knowledge, our most enlightened granting organizations still frown upon budgetary items for a conservator associated with an archeological excavation. They certainly will not countenance sums for restoration of cultural properties, which says something about the values of our society today, though this attitude is not without its causes. The storerooms of the museums throughout Asia are packed with disintegrating objects, some of which may be saved at little cost by a conservator who knows what is required. But, the initiative to save these objects is going to have to come from those who are capable of saving them, and it is a task for which little money is presently available, with a gratification quotient only personal and small, the victory still a Pyrrhic one.

#### Discussion

*J. Kruger:* We have heard several references to the use of vapor phase inhibitors. Has anyone ever tried to store lead coins in containers containing these vapor phase inhibitors? I do not know whether it would work for lead, but it is very inexpensive and easy to use.

W. Trousdale: No attempts have been made to save them as it was only within the last few weeks that it was discovered that they are disintegrating. First, we have to photograph them and then they will be submitted to the Conservation-Analytical Laboratory for treatment. I hope that they will be preserved in such a way that they can still be read.

W. T. Chase: You remarked that the coins have corroded more in the past six years than they had in the previous 600. From your slides of this region, it would appear that there is very little wood and other vegetable matter to supply the organic acids to attack lead; the more likely source of the present corrosion would be the paper, probably kraft paper, of the envelopes and the wood of the storage drawers.

W. Trousdale: They have been far from wood as there is very little wood in that area. The only kind of wood in that area are alkali bushes.

W. T. Chase: Is Mr. Organ here? What about altering the environment to stabilize the lead until treated. Do you have any suggestions along those lines?

R. M. Organ: That was an extremely interesting lecture and I appreciate it. The lead problem is relatively simple if you have enough space to carry some Perma-life envelopes with you. You just pop the lead into those. The Perma-life paper contains a percentage of calcium carbonate which will absorb any organic acid on its way to the coin. That is the critical moment. Once organic acids get to the lead they stimulate corrosion and continue it. Once back in the lab, of course, we can deal with this. We can regenerate the material in exactly the position that it is now. The other thing you can do in a hurry is to put shellac varnish on it. That will hold everything in place so that you can still read them and we can still work with them and get them back for you afterwards.

M. Goodway: This phenomenon seems to have been first observed at the British Museum or at least the publications imply that. How does one get that kind of observation into the kind of literature that the archeologist reads rather than just the literature that the conservators read?

R. M. Organ: That is a very good question, indeed. Of course, it has been observed for a long time. Plenderleith's<sup>1</sup> first book on conservation published in 1936, I believe, showed pictures of moldering lead bullae in wooden drawers. They were photographs so one could leaf through the pages and see that this was something of importance. The difficulty is that within museums, curators and archeologists don't necessarily come into contact with the conservators, or haven't done so in the past. At least, they come in contact when they have some particular problem: they come and get it solved and then go away again. What they really need is some kind of persistent contact so that they know all of the ins and outs of the problem. That is one reason why, in the Smithsonian, we have a lot of lectures on video tape of conservation processes. These are supposed to be sufficiently entertaining to persuade people to keep on watching them. A number of curators have, in fact, watched these things years ago and I hope that they will come back and watch them again. This is, of course, a problem in communication and it is really very serious. A lot of these metals problems we know all about. There are one or two books now for archeologists in the field. There is an early one by Dowman<sup>2</sup> which suggests things that you can do.

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<sup>1</sup>The latest edition of which is: Plenderleith, H. J. and Werner, A. E. A., *The Conservation of Antiquities and Works of Art*, 2nd Edition (London, Oxford University Press, 1971).

<sup>2</sup>Dowman, E. A., *Conservation in Field Archaeology* (London, 1970).



## STRUCTURED QUESTIONS

Question 1: What is the smooth lustrous black surface on ancient bronze mirrors?

*W. T. Chase:* This will be a minilecture on mirror-black. The person who should be giving this is Professor Ursula Franklin of the University of Toronto. She has worked on this problem much longer than I, but she is presently attending the archaeometry meeting in Edinburgh. (Comments contributed by Prof. Franklin will be found at the end of this discussion.) This particular black patina occurs on Chinese bronze mirrors and some weapons from the late Chou Dynasty (about 350 B.C.) until perhaps as late as the T'ang Dynasty (ending in A.D. 907). The questions are: what is this patina; and why is it black?

The material is very corrosion-resistant, but, where it does corrode, a typical warty corrosion can be seen. Figure Q-1-1 shows a mirror now, in the study collection of the Freer Gallery of Art, with four warty areas; one at the rim can be seen in side view. For other views of the warts, see the photograph of the spearpoint (fig. Q-1-12) and figures Q-3-3 and Q-3-4 (p. 206).

Those who studied it before World War II include: William F. Collins, (The corrosion of early Chinese bronzes, *Journal of the Institute of Metals*, 45, 23-55 (1931)); Harold J. Plenderleith, (Technical notes on Chinese bronzes with special reference to patina and incrustation, *Oriental Ceramic Society, Transactions*, 16, 33-55 (1938-39)); and R. J. Gettens, (Some observations concerning the lustrous surface on ancient Eastern bronze mirrors, *Technical Studies in the Field of the Fine Arts*, 3, 29-37 (1934)). For more recent studies one should consult the following: Tsurumatsuru Dono, (*The Chemical Investigation of the Ancient Metallic Culture*, Tokyo, Asakura, 1967); A. G. Bulling and I. Drew, (The dating of Chinese bronze mirrors, *Archives of Asian Art*, 25, 36-57 (1971-72)); I. Drew, (Dating and Authentication: Chinese bronze mirrors, *MASCA Newsletter*, 7, 1, 2-3 (1971)); Ursula Franklin, (Chinese black patinas, paper presented at 182nd Annual Meeting of the American Oriental Society, Chapel Hill, NC, April 20, 1972).

Some typical examples of this black patina include the mirrors from the tombs of Liu Sheng and Tou Wan, discovered in Lingshan Mountain in the western suburb of Man-ch'eng, Hopei Province, China, in 1968. For information of the excavation see *Man-ch'eng Han mu fa chieh chi yao* (A report on the excavations of the Han tombs at Man-ch'eng), *Kaogu (Archaeology)*, 1972, 1, 8-18; a rubbing of one of the mirrors is shown in figure 14 on page 17. See also Ku Yen-wen, Han Tombs at Mancheng, *New Archaeological Finds in China*, Foreign Languages Press, Peking, 1973; Hsiao Yün, *Man-ch'eng Han mu chu tu ti tso ching ying niao ch'ung shu t'ung hu* (Two bronze vases with gold inlaid bird-tracks inscriptions found in Man-ch'eng), *Kaogu*, 1972, 5, 49-52; *Man-ch'eng Han mu 'ching-lou-yü-i' ti chin li han fu yüan* (The cleaning and restoration of jade suits found in Man-ch'eng), *Kaogu*, 1972, 2, 39-47; Jan Fontein and Tung Wu, *Unearthing China's Past*, Boston, 1973, pp. 100-102; *Historical Relics Unearthed in New China*, Foreign Languages Press, Peking, 1972, p. 94 ff.; *Wen-hua-ta k'e-min ch'i chin*, *Ch'u-tu wen-wu*, Wen Wu Press, Peking, 1972, p. 25; *The Genius of China*, an exhibition of archaeological finds of the People's Republic of China held at the Royal Academy, London ..., London, 1973; p. 99 ff.; *The Chinese Exhibition and The Exhibition of Archaeological Finds of The People's Republic of China*, both Washington, D.C., 1974, pp. 65-71 and pp. 31-33, respectively. Figure Q-1-1A shows three of the mirrors from these tombs on exhibition in Peking during 1973. The mirrors are large; the middle one in our plate is about 21 cm in diameter. Two of the three have a fine black patina. It appears to have been fairly dry in this tomb. Objects with other patinas appear from these tombs as well (see Question 6). Some of the later Han mirrors have a much more silvery look to them; they may not be the same material or patina. This is another question for study; is there more than one type of mirror black patina?



Figure Q-1-1. A Chinese bronze mirror dating from about 200 B.C. Ex-collection James M. Plumer (JCP 2), now Freer Gallery Study Collection SC 551. This mirror is 8.9 cm in diameter (3 1/2 inches), and is covered with a deep-green to black patina with four bright-green warty spots. The front surface is shiny black with numerous warty areas.



Figure Q-1-1A. Three mirrors from the Man-ch'eng tombs (see text for references). The large mirror on the right has a particularly fine black patina. See color plate o.

This patina also occurs on weapons, often on weapons with pattern decoration from the late Chou and Han Dynasties. The pattern may be black or part of the pattern may be black and part may be green. This sword (fig. Q-1-2) in the collection of the Hong Kong City Museum and Art Gallery has a shiny black blade and a matte green haft. No joint can be discerned between the blade and haft. The weapon, from the tomb of Liu Sheng (fig. Q-1-3) has black spots on a bronze ground. A bimetallic sword in the Shanghai Museum (fig. Q-1-4) is very similar to the one shown by Cyril Smith. The analyses listed in the figure caption show that the outside has a higher tin content. The tin content varies from the outside, blacker area to the inside, greener area. One can form an idea of the hardness



Figure Q-1-3. A bronze dagger-axe (*ko*) from the Man-ch'eng tomb of Liu Sheng, *ca.* 20 cm in length. The object is bronze-colored with black spots; the mount for the shaft is gilded.

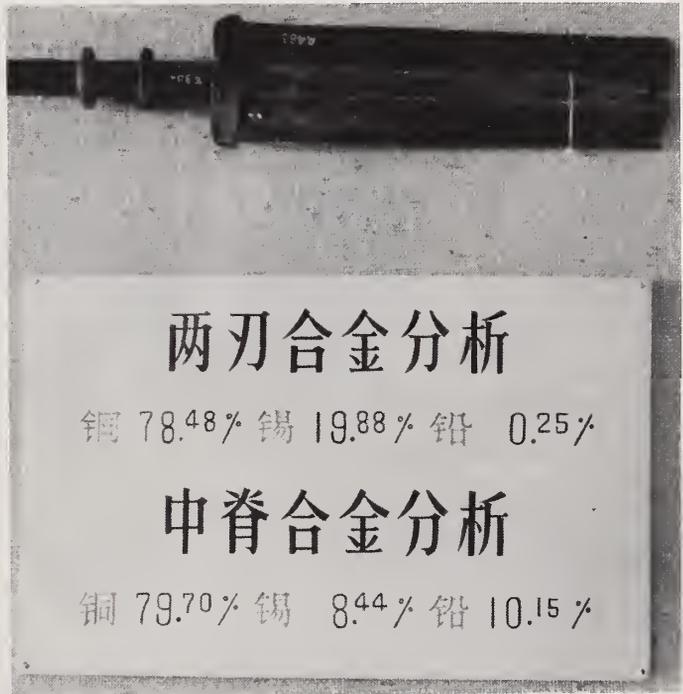


Figure Q-1-2. A bronze sword from the late Chou period (or Warring States period, 4th to 3rd century B.C.). This sword has a shiny black blade and a matte green guard and handle. No joint could be seen between the two. (From the collection of Hong Kong Museum of Art, Urban Council, Hong Kong.)

Figure Q-1-4. A fragment of a late Chou sword with analysis of the two metals from which it is made, as displayed in the Shanghai museum, People's Republic of China. The outer portions have the composition 78.48 percent Cu, 19.88 percent Sn, and 0.25 percent Pb. The inner or central portion, which is green in color, contains 79.70 percent Cu, 8.44 percent Sn, and 10.15 percent Pb. The analyses were made by the Shanghai Metallurgical Research Institute.

and brittleness of the metal by the fracture along the edges. Further examples of these various types can be seen in the Brundage Collection, the Winthrop Collection of the Fogg Museum, the Singer Collection, and many others.

Since this sort of patina almost invariably occurs on high-tin bronzes, it is worth looking at the occurrence of high-tin bronzes in China. Figure Q-1-5 shows a ternary plot of some of our analyses of Chinese bronzes. As you can see, the mirrors form a distinct, high-tin group. We have not yet included weapons in this diagram.

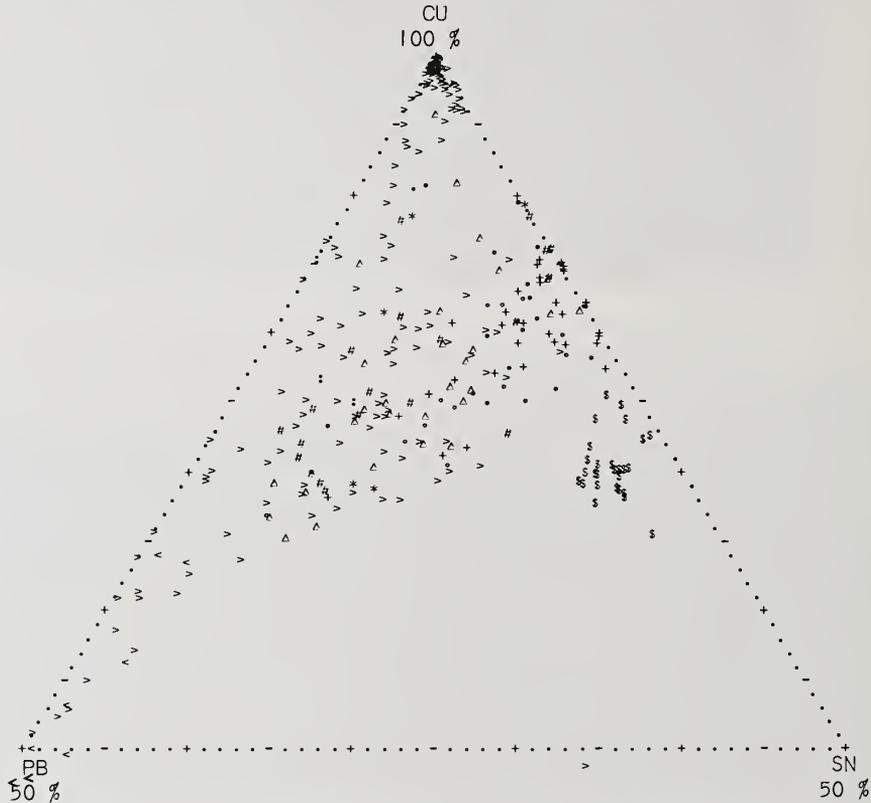
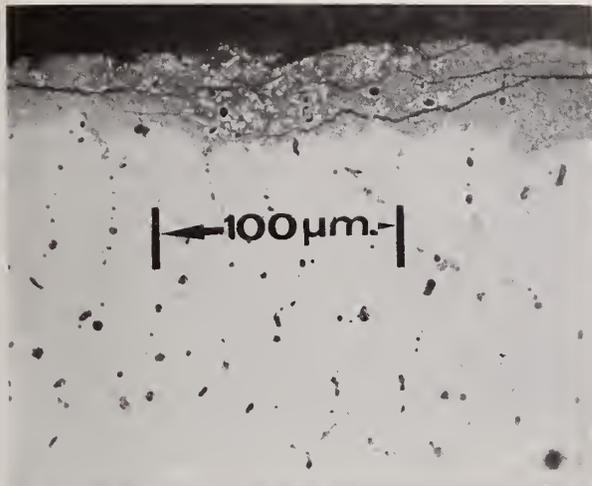


Figure Q-1-5. A ternary plot of Chinese bronzes analyzed at the Freer Gallery of Art. The mirrors (represented by \$ here) form a distinct, high tin group.

Now to return to the black patina; the analytical work done by Ursula Franklin at the University of Toronto and by myself at the Freer, has failed to get any x-ray diffraction pattern for this black material at all. I have put a piece of mirror in the x-ray diffractometer and got only a pattern of distorted alpha-bronze. The black areas seem to give no x-ray diffraction pattern at all. In x-ray fluorescence analyses done by Maurice Salmon in the Conservation-Analytical Laboratory of the U.S. National Museum, we found increased concentration of tin, lead, and iron at the surface.

When microprobe analysis was attempted (with the assistance of Charlie Obermeyer, Mineral Sciences, U.S.N.M.), the tin trace (fig. Q-1-6 and Q-1-7) showed an extra concentration of tin at the surface. Iron and silicon also concentrate at the surface (figs. Q-1-8 and Q-1-9). It appears to be an iron-tin-silicon diffusion into the surface.

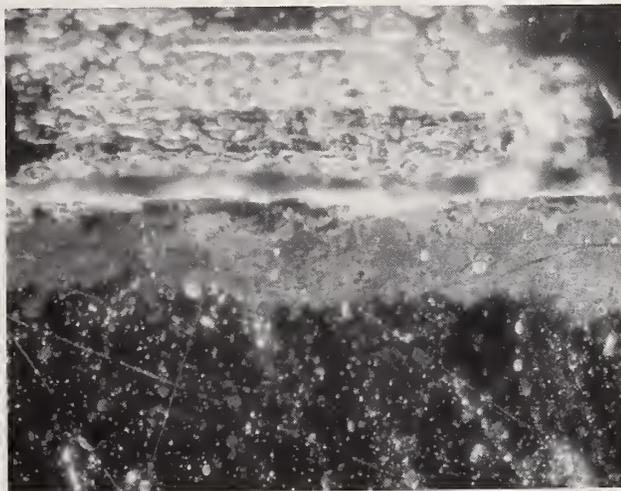
We often see in cross-sections that the outer layer is quite transparent, green or greenish-black, and glassy in appearance. Under the transparent, colored layer lies the uncorroded delta phase of the metal, which can usually be seen partly down through the transparent material. The transparent material also shows a conchoidal fracture and looks very smooth under the scanning electron microscope (fig. Q-1-10). The warts, shown in figure Q-1-1 above, often lift this transparent, colored layer up; it can be seen in flakes in the warts.



(a)



(b)



(c)

Figure Q-1-6. Three photomicrographs of the surface layers of a Chinese bronze mirror dating from the late Chou period. (JCP 11; FGA SC555). The remarkable polished thin section across the thickness of the mirror from which these photographs were taken was made by Grover Moreland of the Department of Mineral Sciences, U.S.N.M. The photographs match the electron microbeam probe photographs below in magnification (figs. Q-1-7, 8, and 9). (a) shows, in bright field reflected light, the dark grey layer of the glassy black patina on the outer (upper) surface. Under this is a lighter grey, partly mineralized layer, and then the bright, uncorroded metal. (b) shows the same area in a combination of bright field reflected light and transmitted light illumination. The dark rectangle at the top is the remains of damage caused by the electron beam in the probe, left here for location. The sample was repolished after the probe work was done. The upper, glassy layer of the patina can be seen to be quite transparent, and not completely continuous. (c) shows the same area in dark field reflected light. The upper surface of the patina can be seen to be quite smooth.

The spear point shown in figures Q-1-11 and Q-1-12 was given to the Freer Gallery by Sir Harry Garner for study purposes. It is shiny green in tone, with a diaper-pattern decoration in brown. The warty corrosion concentrates along the mould joint line at the central rib, around the tip, and along the edge of the blade. These are the areas in which there is the greatest chance of mechanical damage to the protective patina during use.

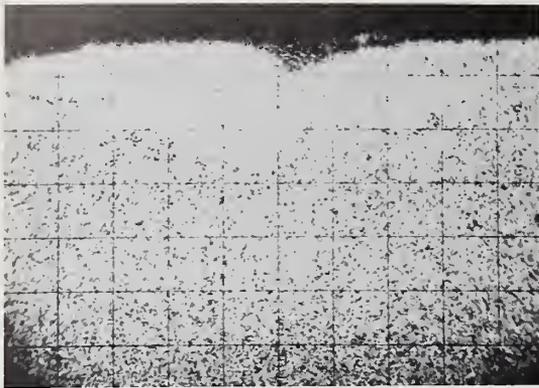


Figure Q-1-7. Tin concentration in the area of figure Q-1-6 (a,b,c) as revealed by the electron microbeam probe. The cracks in the specimen show vaguely. The outer surface and the corrosion penetration zone are enriched in tin.



Figure Q-1-8. Iron concentration in the same area as Q-1-7 revealed by the electron microbeam probe. The iron concentrates in the glassy surface layer.



Figure Q-1-9. Silicon concentration in the same area as Q-1-7, by electron probe. Silicon concentrates in the outer surface, but also appears to be diffusing inwards into the mineralized zone. The lower edge of the mineralized zone (as seen in Q-1-6 (a)) can be seen to be the lower boundary of the silicon diffusion.



Figure Q-1-10. A photograph of the surface and fractured edge of mirror JCP11, taken with the scanning electron microscope (Walter R. Brown, National Museum of Natural History). The outer surface can be seen, in the left portion of the photograph, to be smooth and somewhat cracked. At the center of the photograph the fracture between the outer surface and the mineralized zone underneath it can be seen (arrow). The mineralized zone has fractured roughly. On the right can be seen the sawcut where the sample used for the polished thin section (above) was taken. Magnification 2/3 that of figure Q-1-6 above.



Figure Q-1-11. A Late Chou Dynasty spearpoint, given to the Study Collection of the Freer Gallery of Art, by Sir Harry Garner (SC-B-88). Length = 24.4 cm. Much warty corrosion can be seen on the piece, concentrating along the sharpened edges of the blade and at sharp corners on the median rib and shaft. The sides of the blade are decorated with a diaper pattern in a brown color.



Figure Q-1-12. A detail of figure Q-1-11, showing more clearly the warts and the decoration.

The brown-and green decoration on the surface may well be etched. The green may be the same sort of material as the black mirror patina. It has a glassy appearance. This decoration is probably an example of etching for decorative purposes such as Cyril Smith has mentioned. The cutting edge of the blade has corroded so that the center part of the dendrites has remained, but the alpha-delta eutectoid has been removed. Redeposited copper and a thick corrosion crust can also be seen (fig. Q-1-13).

Seen in more detail (fig. Q-1-14) there are two types of corrosion; in one the delta phase is removed, and in the other the alpha is removed. Further from the blade edge you can see this effect more clearly (fig. Q-1-15 and Q-1-16). The outer surface is at the top of the figures. The outer surface of the patina (which I believe in this case to be really an artificial patina) is very smooth. Beneath this can be seen the uncorroded

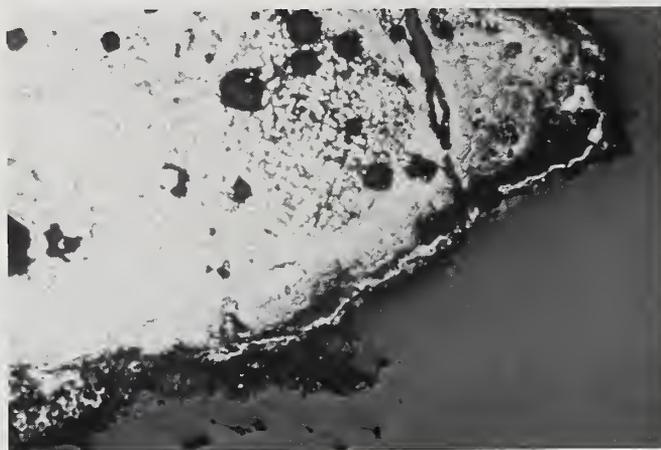


Figure Q-1-13. A bright field metallograph of the blade edge of the spearpoint, showing corrosion with removal of the alpha-delta eutectoid in the triangular area of the cutting edge. Magnification *ca.* X16.

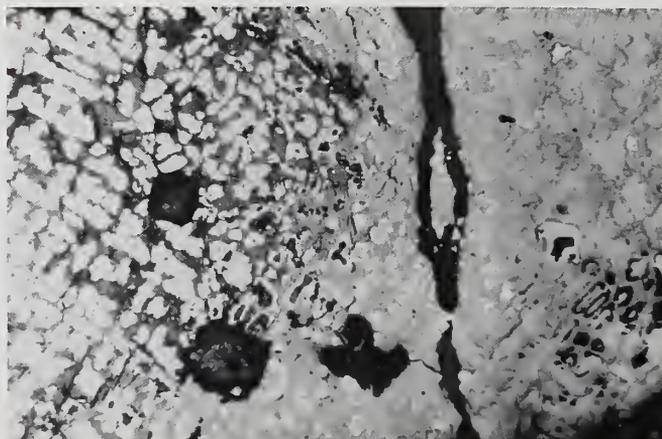


Figure Q-1-14. The same area as Q-1-13, detail in the center of the blade edge; magnification *ca.* X48.



Figure Q-1-15. Photomicrograph of a section taken of the spearpoint in figure Q-1-11 shows the area in bright field illumination. The sharp line of the shiny patina on the outer surface shows at the top; below this lies an area which has been mineralized by the removal of the alpha-phase, leaving shiny patches of delta phase. At the center and lower right, an area can be seen which has corroded inwards from a crack at the right. This area has corroded with removal of the delta phase, leaving the alpha. Voids and patches of cuprite can also be seen. Magnification *ca.* X48.



Figure Q-1-16. Photomicrograph of the same sample in dark field reflected illumination. Magnification *ca.* X48.

delta phase. The sides of the sample were formed by cracking in the spear point. Corrosion has worked in from the sides; this corrosion has removed the delta phase first. The common type of corrosion that we see in ancient Chinese bronzes usually proceeds by removal of the delta phase first. We can see both the usual type and the inverse type on this one sample. My contention is that the corrosion on the outer surface was synthetically produced, and where it has chipped or cracked, normal corrosion has proceeded.

The outer surface at higher magnification shows that, in the alpha-delta eutectoid under the outer surface, the delta phase remains, but the alpha phase has corroded away (fig. Q-1-17). One can see a very similar structure on the mirrors, except that it is black instead of green (although sometimes it may be green as well). Leaving aside the question of how the pattern-etching or mineralization was done, which we would also like to know, how was that shiny black or green patina produced?



Figure Q-1-17. A photomicrograph of the spearpoint in figure Q-1-11 showing the outer surface and mineralized zone at higher magnification (ca. X300) and bright field. The remnant delta, quite uncorroded, can be seen in the central portion of the photograph.

The process has to remove the alpha phase of the bronze, possibly precipitating tin oxide (which I think may be at least one component of the outer layer); it must deposit pseudomorphically with the dendrites that were there; and the iron and silicon diffusion into the surface have to be explained. Ursula has said that the temperature of the process cannot be much above 300 °C or one would see changes in the metallography of the objects, which she has not observed. What is the process, and how can we duplicate it in the laboratory?

One feature that may be of interest to the industrial people here, and might be commercially applicable, is that this patina has done an awfully good job of stopping corrosion on the mirrors for 2000 years.

*T. D. Weisser:* I do not know what the black substance is. In doing my experiments on the effects of 5 percent sodium sesquicarbonate at room temperature on various compositions of bronzes, I noticed a similar surface effect of a black, smooth, lustrous material on a modern, 80 percent copper-20 percent tin polished bronze sample after it has been in the solution for about 24 hours. The microstructure of my sample is similar to your sample, and the alpha phase is preferentially removed in the sodium sesquicarbonate, while the delta phase eutectoid is left behind. The composition of my sample is almost identical to the composition of the outer layer of your Chinese bronze example. Perhaps the preferential attack of the alpha phase is due to artificial patination with something such as cyanide or ammonia or a double carbonate such as sodium sesquicarbonate. Or perhaps it is due to a burial situation setting up similar conditions.

*W. T. Chase:* I am bothered because I am not so sure it is artificial; were the Chinese so sophisticated in 200 B.C.? So we may be seeing a combination of natural and artificial processes, and will have a hard time sorting out which is which.

*M. Fourbaix*: Terry has just said that something very similar to what I have in mind. Assuming that the patina existing on these mirrors is mainly amorphous hydrated tin oxide, it might be possible to produce it artificially by dealloying in some chloride-free running solutions, without stagnation preferably. Such thin films might be studied with Auger spectroscopy. Has this been done?

*W. T. Chase*: No.

*C. S. Smith*: The black finish on Chinese bronzes was probably intentional, for, as on the Brundage short sword mentioned by Mr. Chase, it is terminated at a specific point in the design, not irregularly as it would with natural corrosion. The reaction that produced it was an unusual one, for the alpha phase was completely replaced with an exact pseudomorph in reaction product, while the delta phase remains completely untouched. Even the fine alpha lamellae within the eutectoid are changed within a matrix of uncorroded delta. The surfaces of the delta particles (visible under the microscope through the somewhat transparent structureless corrosion product) are shiny bright and retain all the detailed surface contours left by their formation. There are no visible channels for corrosion around it at all.

The contemporary swords with geometric patterns resulted from a similar but probably not identical chemical treatment. On a sample in the Fogg Museum dendrites, or rather dendritic pseudomorphs after alpha, can be seen extending uninterruptedly between the two regions, now appearing as two different kinds of corrosion product.

*C. E. Birchenall*: Silica can provide the basis for a glassy layer, but to be low melting borax and phosphate additions might contribute. Have boron and phosphorus been looked for in the analyses?

*W. T. Chase*: I think phosphorus has, but not boron. I hope to do a materials balance analysis to see if we have most of what is in there. It is hard to get enough material to do wet chemistry because the layer is always so thin.

*C. S. Smith*: It is very thick as patinas go.

*J. Kruger*: Why not use electron diffraction to identify the black material? Even though it may be amorphous to x-ray diffraction one can sometimes see small crystallites with electron diffraction.

*W. T. Chase*: I might add that during electron microprobe analysis we observed light emission as the beam traversed the black area, a definite blue glow. It is very non-conducting.

*J. N. Andre*: The absence of x-ray diffraction patterns using the mirror as sample may be related to an amorphous compound, but a preferential orientation of the film can also perturbate the result considerably and cause diffraction peaks to be weak or missing. It can happen when there is a preferential growth direction of the product film or a kind of epitaxy with a substrate having a fiber structure; diffraction on a powder sample removed from the surface would probably be free of this problem.

*L. van Zelst*: A black patina like the one discussed has been observed in Islamic high tin bronzes from the Near East. In general, the problem has always been assumed to be related to high tin bronzes, with perhaps amorphous hydrated tin oxide in the layer.

Recently I found it on two "Luristan" bronzes, one with 18.7 percent tin but the other with much lower tin content (approximately 9.3 percent). The metallurgical examination revealed that the mechanism of the corrosion was the preferential attack of the alpha phase, as it is for mirror black. It has in general been the opinion that this was an artificial patina. In the case of the "Luristan" bronzes, however, the possibility of natural patination must be considered. An outline for a possible mechanism was suggested by Richard Stone. It involves changes in pH in the burial conditions, starting out with slightly acidic soil, preferably high in ferric ions (remembering that there is an enriched iron content in the top layer) which might preferentially attack the alpha phase, and then later the pH changes and becomes basic and freezes the whole system and even will help precipitate silica, which is pretty mobile during most neutral conditions.

*W. T. Chase:* We hope to get this material into print so that people can question and discuss it. More input of ideas as we have had at this conference will be very valuable. It may be that someone has had experience in producing corrosion films like these on high-tin bronzes; we would like to hear of their experiences.

*C. S. Smith:* I have two more points to add. It seems that the fine black only occurs on high tin bronzes, yet it is the alpha phase that has been corroded, and the alpha phase has the same composition regardless of how much tin there is above, about 10 percent.

In both the Brundage sword and the similar one in the Fogg Museum, the alpha dendrites are continuous from the black areas to the green areas, and you can see the shape of the dendrite in both the dark and the light green patina.

I find it impossible to believe that these are accidental patinas; their outlines have all the earmarks of something done intentionally.

*W. T. Chase:* I have a thesis, with which Ursula Franklin does not agree, that these surfaces may have been initially shiny metal color with some very light surface treatment which is then partly corroded and partly stained to black or deep green.

There is a sword, not yet examined that I know of, from the Man-ch'eng tombs, which was in the Chinese archaeological exhibition (*The Genius of China*, p. 160, no. 160; *The Chinese Exhibition*, p. 70, no. 160), which has a glassy, bronze-colored surface. In the case in the exhibition, this surface had a very strange and glassy appearance; I've never seen another one like it. Perhaps these things had colors like this sword or glassy-silvery surfaces; due to staining or other things, over the course of time the surfaces may have turned to the black and deep greens. As I said before, the effect may be a combination of natural and synthetic patination.

*J. S. Olin:* For a non-crystalline material the use of infrared spectrophotometry is often helpful. If the black surface referred to does not give an x-ray diffraction pattern, it is possible that the anion might be identified using infrared spectrophotometry. There are characteristic peaks for the silicates and phosphates which have been suggested as possible compounds.

*C. S. Smith:* The uniform appearance of the black patina on the forged high-tin Iranian bronzes when seen in section under the microscope is much more like that of a high-temperature oxidation layer than one produced by electrolytic corrosion. There is no deep selective penetration into the alpha phase or along grain boundaries such as occurs in the cast Chinese bronzes.

*R. M. Organ:* Does it have to do with tin sweat?

*W. T. Chase:* The difficulty is the iron and silicon content, not the tin content. Most of these bronzes, especially the mirrors, have a very high polish, some a very high selective polish. Such abrasive polish (not a burnish) would have removed surface tin.

*B. F. Brown:* Has anyone determined the refractive index of the black layer?

(No response)

*Ursula Franklin:* In the following paragraphs you will find a few additional comments that I would have made, had I been present; all of my remarks are based on experimental work with black mirrors, since I never have had a chance to work with a "pattern-etched" sword.

(1) The fact that most mirrors are high-Sn bronzes (chosen because of colour, hardness and ease of polish) and that some of these mirrors have a black surface finish (again in my opinion for functional or decorative reasons) should not drive us to the conclusion that the black finish depends chemically on a high Sn content. After all, it is the  $\alpha$ -phase that is altered.

(2) All I have seen has convinced me that it is a purposefully executed surface finish. Look at three areas of evidence: (1) its chemical inertness, (2) its microstructure, (3) its external application on the mirrors.

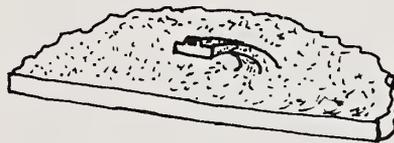
With regard to point (1) the surface layer is an amorphous non-conducting oxide or silicate layer, amorphous even to electron diffraction as far as we can see; it is not an isomorphous film of preferred orientation. If one were to assume the formation of a protective film formed by some type of preferential corrosion (as in the case of stainless steel) one would expect to find the film *enriched* in certain constituents, that have diffused preferentially to the surface to form the protective film (such as Cr in stainless). Below the surface of the film one might find a depleted layer until one reaches the equilibrium bulk concentration. In the black surface finish, however, the elements present are *not* part of the alloy. Si and Fe is present in the surface but not in the bulk, Sn is enriched in the surface but not noticeably depleted below. We have lots of microprobe traces, taken on cross-sections, so that the distribution of Cu, Sn, Fe, Si, S, O, etc., can be documented quite consistently. If the black surface of the mirrors had been produced by an accidental reaction with a specific environment, as Collins thought, it is difficult to see why this reaction would stop at a certain point, leaving a chemically inert, tightly adhering and insulating surface on the object. Furthermore, when interaction with the environment occurs, resulting in the "warty" corrosion, it is the bronze below the surface layer that reacts, not the black surface itself.

Point (2). Looking at cross-sections, one has two overriding impressions. One is the very gradual transition between the altered surface layer and the bronze proper. There is no abrupt change in the micro constituents, in their orientation or their size, no discontinuity of any sort. One sees occasionally cracks with altered inner surfaces, but the general impression is one of a partially etched sample. Secondly, it becomes clear that the non-metallic translucent layer is on the very outer edge; it is quite thin and never penetrates very deeply. When this layer is broken, corrosion products such as malachite can be seen beneath the surface.

I have not seen any electrochemical interaction between the bulk alloy and the altered layer, for instance a reaction of the type that one observes at the contact of dissimilar metals.

Point (3). Looking at black mirrors one can often see polishing marks and scratches on the non-ornate side *below* the finish. The loop on the decorated side shows black surfaces on the inner and on the outer surface as well as on the mirror under the loop (see sketch in fig. Q-1-18). It would be difficult to imagine that this would happen randomly. In cross-section, one can see that the altered layer follows the topography of the ornamentation.

Figure Q-1-18. Idealized section through loop of mirror--black surface present on top and bottom and around loop. Black surface shown here by dots.



We have checked carefully for any influence of Hg or S. While some mirrors contain small amounts of S, it is in the form of sulfide inclusions, more or less evenly distributed through the casting. We found no Hg.

Until I know more, I think that we have to envisage a two-step process. First, some type of sedimentation or etching, that attacks the  $\alpha$ -phase, basically replacing Cu by Fe (or its compounds). This might be followed by a process that involves temperature and a glazing or enameling reaction, which produces the stable outside surface and the gradual, fairly deep transition zone which I have called "the altered layer." (It may be that the thickness of this layer has increased with time.)

During this phase the Sn might have migrated to the surface, producing a low melting, mixed oxide as the coating and the Sn enrichment in the altered layer. Of course, the two steps could be part of one process, akin to Wulff's explanation of the Persian bead making. But whatever it was, I am convinced that it is an intentional process applied to the fully finished and polished object.

Question 2: What was the patina on outdoor bronze statuary during Roman times?

*J. Kruger:* Brochantite.

*B. F. Brown:* Vesuvius would have been a copious source of sulfur (as might also open sewers).

*P. Weil:* It appears that prevailing practice during Roman times was to gild major outdoor bronzes. Recalling Pliny's remarks that the ancients (*i.e.*, the ancient Greeks) used to coat their statues with bitumen to protect their luster, it was all the more surprising that the Romans came to gild them to achieve the same effect. The reason for gilding appears to be that with gilding no maintenance would be required.

*R. M. Organ:* The polished copper might have become tarnished from hydrogen sulfide. After all, there were people there. Then the copper sulfide could oxidize up to brochantite; perhaps they were green if neglected.

*W. D. Richey:* The question of sulfur balance in the air is complex. There are natural and everpresent sulfur sources. Kellogg, *et. al.* (W. W. Kellogg, R. D. Cadle, E. R. Selen, A. L. Lazrus, and E. A. Martell, *The Sulfur Cycle, Science*, 175 587-596 (1972)) has attempted to provide a sulfur balance. Man provides much less than half the sulfur burden from fossil fuels. Some sulfate is postulated to be aerosoled from seas and bodies of water and so would have been present in antiquity.

*R. M. Organ:* There were sulfur springs...

*C. S. Smith:* ...and sulfur from copper smelting.

Question 3: What is the black corrosion product associated with the initial intergranular attack of bronzes?

*W. T. Chase:* The question was asked by John Gettens in his article, "The Corrosion products of an ancient Chinese bronze" (*Journal of Chemical Education*, 28, 68-71 (1951)). His statement of the problem is worth quoting. He is describing the corrosion layers on the "Kelley Bronze", a broken and much repaired Chou dynasty bronze vessel of the type hu, presented to Gettens by Charles Fabens Kelley, then Curator of Oriental Art at the Art Institute of Chicago. Dr. Kelley gave Gettens permission to cut sections and use the bronze for technical study with no restrictions. The fragments of the bronze now reside in the Study Collection of the Freer Gallery of Art, with the number SC548 (see also, R. J. Gettens, *The Freer Chinese Bronzes*, Volume II, Technical Studies; Smithsonian Institution, Freer Gallery of Art, Oriental Studies Series, No. 7; Washington, 1969, p. 127 and p. 183).

The corrosion zones and the several mineral layers were of chief interest. Most striking is the intermediate penetration zone where the eutectic (tin-rich phase) has been converted to a black product leaving dendrites of alpha bronze (copper-rich phase) unattacked. It is a natural etch. In the casting this bronze has apparently cooled slowly, allowing alpha dendrites to form freely and nearly perfectly (fig. 3-2). This zone of interphase penetration is generally 1 to 3 mm thick, but in places it goes entirely through the metal. Because it is so intimately mixed with uncorroded alpha it was quite impossible to isolate the black material for microchemical tests. It was possible, however, from a polished section, to isolate chips free from outer corrosion product and to subject them to x-ray diffraction analysis. The powder pattern showed mainly an expanded copper lattice, but in addition it showed faint lines characteristic of cassiterite and also one unidentified line. No lines of the copper chlorides were observed. Tin oxide could be expected, and indeed, white tin oxide is plentifully seen in the outer corrosion layers. The faintness of the cassiterite lines indicate that the tin oxide is in a cryptocrystalline state. Why does it seem to be black here? It is possible that it is stained black with cupric oxide, and it is well known that some forms of cupric oxide (like

melachonite) are so nearly amorphous that they give undistinct diffraction patterns or none at all. If the black is cupric oxide it is doubtful if it is formed by direct oxidation of copper especially under the reducing conditions that seem to prevail in the interior after corrosion attack is well along. There is a remote possibility that the black is formed from cupric hydroxide precipitated at cathodic areas of local cells set up by electrolytic action in the salt environment. J. W. Mellor (*A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, Volume III, p. 144, London, 1923), cites evidence that cupric hydroxide hydrogel in contact with water or salt solution can eventually dehydrate and turn black even below room temperatures, although several months may be required to bring about the change. Bengough and May (Seventh report to the corrosion research committee, *J. Inst. Metals*, 32, 103, (1934)) state that in copper corrosion dark brown or black hydrated cupric oxides are important constituents of scales that form on the copper surface. This explanation of the initial black corrosion product is, however, highly conjectural since we have so little direct analytical information bearing on it.

The Kelley bronze has the general corrosion structure shown in figure Q-3-1. A more detailed view, figure Q-3-2, shows the intermediate penetration zone that we are interested in, along with cuprous chloride and cuprite. What is it?



Figure Q-3-1. Cross-section of the wall of the Kelley Bronze (FGA SC-B-18), magnification *ca.* X10. From the top can be seen; a thick corrosion crust (dark); a layer or redeposited copper (broad, bright line); a thin line or corrosion product, possible cuprous chloride (dark); the original metal, now corroded with the alpha-dendrites remaining, and surrounded by the black material in question; and more layers of redeposited copper and corrosion products.



Figure Q-3-2. Another metallograph of the Kelley Bronze, magnification *ca.* X65, bright field, showing the remnants of the alpha-dendrites surrounded by the black material.

A similar sample comes from this later Chou (*ca.* 400 B.C.) tube (fig. Q-3-3). A cross-section of the whole tube, near the break (fig. Q-3-4), shows one of the warts of corrosion often seen on these bronzes. You can see some of the black product on the inside of the ring of the tube. On the outside is some of the greenish, glassy material that may be an artificial corrosion product (see Question 1). In bright field, the cross-section through the tube wall shows the outer layer at the left. You can see the uncorroded



Figure Q-3-3. Bronze tube, dating from the late Chou period (FGA X71), *ca.* 10 inches long overall.



Figure Q-3-4. Cross-section of a wart in the sidewall of tube (fig. Q-3-3); the section also shows the entire circumference of the tube.

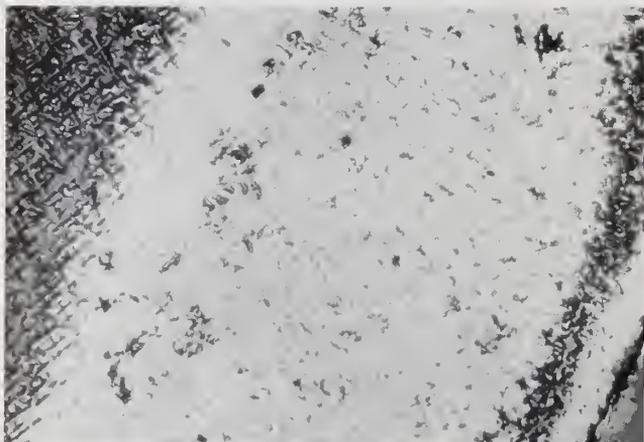


Figure Q-3-5. Cross-section through tube (fig. Q-3-3), bright field illumination, unetched, magnification *ca.* X30.

delta phase (fig. Q-3-5). It is interesting that the delta phase is the only uncorroded metal here. The sample is unetched; the only etching seen on the cross-section comes from the corrosion which the sample has undergone.

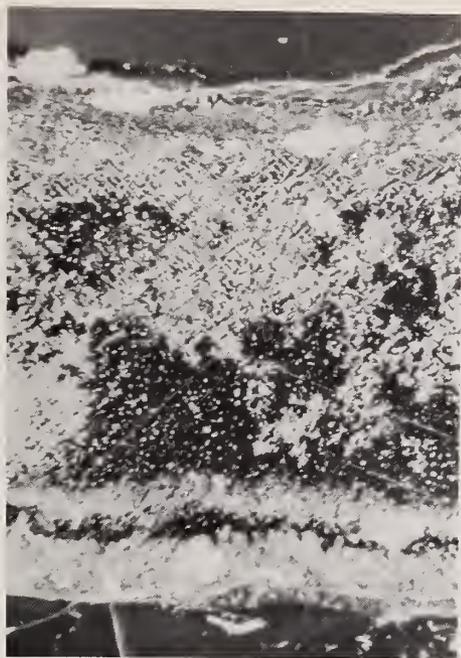


Figure Q-3-6. Cross-section through tube (fig. Q-3-3), dark field, magnification *ca.* X30. The sampling hole in the cuprite layer near the upper left corner of the picture is 130  $\mu\text{m}$  long and 50  $\mu\text{m}$  in width.



Figure Q-3-6A. A detail of the patina on the inner surface of the tube, dark field illumination, *ca.* X60. Compare with Q-3-6. See color plate j.

The corrosion has worked through from the inside of the tubes in a more normal fashion. Let us examine the inside in some detail. Figure Q-3-6 and figure Q-3-6A show some lovely azurite, cuprite, and then this black stuff.

Using a technique developed by Dr. Walter McCrone of the McCrone Research Institute in Chicago (*Techniques, Instruments and Accessories for Microanalysts, A User's Manual*, eds., Walter C. McCrone and R. I. Johnson, McCrone Associates, Chicago, 1974, p. 61; *The Particle Atlas Edition Two*, eds., Walter C. McCrone and John Gustav Dely, Ann Arbor, Michigan, 1973, Vol. I, pp. 225-227), we have made tungsten needles with a diameter at the point of a few micrometers. Five samples were removed from the marked areas on figure Q-3-6. The layer of interest was powdered with the needle, after coating the sample with a thin layer of collodion. The needle was stuck through the collodion to dig into the corrosion layer. The collodion was again dampened with acetone and allowed to dry. This incorporates the particles into the collodion film. The film was then cut with a clean needle, and picked up on a glass fiber for x-ray diffraction. By applying a small drop of acetone to the collodion plus sample on the fiber, the collodion will ball up at the end of the fiber and hold the sample there for diffraction. This way you can sample the individual corrosion layers quite precisely. Camera exposures are of the order of 20 hours.

Diffraction has been done on samples from sites 1 and 2 at the top of figure Q-3-6. In the sample from site 1, I penetrated a little into the cuprite layer and all I got was a weak but classical cuprite pattern. Site 2, the red layer in the color plate, gave us a stronger cuprite pattern. If there is anything else in the sample from Site 1 other than cuprite, it is amorphous; at least it did not give us a pattern.

*J. Kruger:* Your discovery of weak cuprite lines suggests comparison with the stress corrosion of brasses which in ammonia solutions yield black corrosion products that do not look at all like cuprite but yield  $\text{Cu}_2\text{O}$  x-ray patterns. Those have zinc in them; this may be cuprite with tin in it. Perhaps your weak cuprite lines are not accidental.

*W. T. Chase:* Can this black product of stress corrosion be turned red?

*J. Kruger:* No one has done it. (Perhaps it requires a bronze treatment.)

*R. M. Organ:* Very fine comminution may make it black--a very fine particulate?

*C. S. Smith:* Only if it is an electrical conductor.

*R. M. Organ:* Well, cuprite is a conductor.

*C. E. Birchenall:* Something ought to be said about the copper sulfides. At low temperatures chalcocite,  $Cu_{1.99-2.0}S$  has a slightly variable composition, and there are two other phases  $Cu_{\sim 1.96}S$ , djurleite; and digenite. At high temperatures only a single broad phase exists, which spreads from about  $Cu_{\sim 1.8}S$  to  $Cu_2S$  at high temperatures. Because of the variable compositions sharp x-ray diffraction lines are not always obtained. Furthermore, the copper diffusivities are high, or they are in  $Ag_2S$ , so the rate of sulfide growth can be fairly high on copper. The cuprous sulfides are predominately black in color.

*P. Gaspar:* The deeply colored amorphous substance might possibly reflect the intimate association of several valence states of copper--either  $Cu^{II}$  and  $Cu^I$  or possibly  $Cu^I$  and  $Cu^0$ . It is well known that association of two valence states of the same element leads to deeper colors than either valence state alone.

*R. M. Organ:* All the other minerals in that area are in the lower valence state..

Question 4: What is the composition of the thin black layer between the metal and cuprous chloride in many ancient bronzes?

*R. M. Organ:* This question has already been spoken to above. However, I would wish to remind conservators that regardless of the identity of this thin black layer the source of "bronze disease" is the cuprous chloride below the crust of cuprite and above this black layer on the metal--all in an area of lower valency. I have always thought of the black as resulting from the fine state of subdivision.

Question 5: How do artificially produced corrosion products differ from naturally formed corrosion products, if at all?

*L. Fitzgerald:* Artificial and natural patinas on copper cover a range of colors through brown and black to a green weathered appearance. Sulfides and oxides are typical compositions of natural patinas that are brown or black. The green natural patinas have already been discussed.

Artificial patinas are not limited to sulfides and oxides; a much broader range of compositions is possible. Today even selenides are used. Most of the chemical techniques for putting down a patina do not necessarily relate to naturally formed corrosion products. However, in all cases we are looking at de-zincification or some other enhancement of the copper layer as a first step in getting a good black or dark patina, whether done naturally or artificially.

Secondly, the normal chemical reaction is similar to that used to form INCRAPatine II, mentioned before, where an oxidation was used to go through the cuprous-cupric states, and then a copper salt introduced to give a brochantite. If we are going strictly to black or dark layers, today this is done principally by selenides. For a fast black the common technique is to use a selenide at a low pH of 3 to 4, giving a very effective surface on the bronze. This of course, does not relate in any way to a naturally formed corrosion product.

You can get any color you want from copper metal. Experiments have shown that a full range of colors are obtainable through the use of selenide surface treatment. These colors range from yellows and reds through blues to dark purples and black.

*J. Kruger:* By making statistical studies of many patinas one could perhaps separate the different groups using many different techniques of analysis or different techniques of patination. For example, consider the following: (1) ion probe spectroscopy to get concentration profiles; (2) determine electrical properties, p or n character of semi-conductive patinas; (3) optical constants by ellipsometry; and (4) mechanical properties, such as hardness.

*R. M. Organ:* To follow up these suggestions, refer to the three reports of Mrs. Kalish, Moscow: Examination of the Protective Properties of the Natural Atmospheric Patina on Bronze Monuments, Madrid Conference, 1972; Investigation on Protective Properties of Artificial Patina on Bronze Artifacts, Venice Conference, 1975, made to the Conservation Committee of ICOM, comparing the mechanical properties, *i.e.*, the ability of the patina to be bent around a radius, wear of the surface, and the resistance of the surface to pollutants (ammonia, acetic acid, sodium chloride). These reports can be obtained from the International Centre for Conservation, 13 Via di San Michele, Rome 00153, Italy, for ten cents per page.

*P. Weil:* Attention is called to the bibliography on The Composition and Structure of Natural Patinas by S. Lewin and S. Alexander, published in Art and Archaeology Technical Abstracts, 6, (4), December 1967, and 7, (1), June 1968. One point brought out in this bibliography is the frequent presence of nitrates in artificial patinas not commonly found in natural patinas.

*T. Weisser:* Is there a difference between the natural and artificially formed patinas with respect to the adhesion of the corrosion products, the depth of the corrosion, the crystal size or crystal formation in the patina, since one is formed slowly and the other quickly?

*J. Kruger:* Morphology can be an important element in determining age even though there are ways to promote grain growth. Hemming showed SEM's of the surface structure of an artificial patina and that of a naturally formed patina. The morphologies were strikingly different, the artificial one being looser and the natural one being much more close-knit.

*L. Fitzgerald:* Concerning the artificial patina (INCRAPatine II) morphology compared with natural patina, the SEM photos shown of the INCRAPatine II were newly grown, fresh crystals. The natural patina had been exposed to the weather for ten years and the crystals were understandably beaten down and compacted.

*D. Piechota:* Can we use the common mineral term for a corrosion product when it was not formed in the context of natural geological processes, independent of human manipulation?

*C. S. Smith:* Give the mineral name so as to identify the crystal structure and the chemical composition, as an aid to our memories.

*R. M. Organ:* The chemical composition can be the same for several minerals.

*W. T. Chase:* Is the abundance ratio of atacamite to paratacamite indicative of the authenticity of a patina; atacamite being indicative of a forgery? (See S. Z. Lewin, A new approach to establishing the authenticity of patinas on copper-base artifacts, in *Applications of Science in Examination of Works of Art*, William J. Young, ed., Boston 1973; and J. B. Sharkey and S. Z. Lewin, Conditions governing the formation of atacamite and paratacamite, *American Mineralogist*, 56 (1-2) 179-192 (1971).)

*W. D. Richey:* I have had difficulty in reproducing the work--which may tell you more about my work than about Lewin and Sharkey. Both mineral forms were apparently present on objects that seem naturally patinated. It is not as easy to distinguish the two minerals as those articles seem to suggest.

*E. V. Sayre and L. van Zelst:* Because of this question of atacamite/paratacamite has been raised regarding the Greek bronze horse at the Metropolitan Museum, Kate Lefferts, Larry Majewski, Pieter Meyers, and I have been trying to gather information on the frequency with

which particular abundances of atacamite/paratacamite have been observed on ancient bronzes which are thought to be above reproach. Most laboratories have reported both minerals being present. Tony Werner reported in a personal communication that the majority of the authentic bronzes he had examined at the British Museum had a combination of both atacamite and paratacamite. Pieter Meyers and Bert van Zelst report that more often than not on the many bronzes they have examined at the Metropolitan Museum there is a combination of both. Flossie Whitmore and Bill Young at the Museum of Fine Arts, Boston, have observed the same. Direct conservation observation has not proved the presence of atacamite to be a reliable indicator of forgery. One might ask why.

What conditions would produce a mixture of both minerals? In Lewin's first paper, it was stated that paratacamite could be produced under conditions where there were small concentrations of copper complex ions present, but atacamite only when there was an appreciable concentration of copper complex ions. This, therefore, raises the question of the basic solubility parameters for these two substances. I believe literature exists only on the solubility product of paratacamite obtained from precipitation measurements. If you calculate using this solubility product for any system where there is much buffering, as certainly occurs under soil conditions, you find that atacamite and paratacamite should be fairly soluble materials, surprisingly as most conservators tend to think of them as being very insoluble. We indeed have found this to be the case. Bert van Zelst has taken over a research at the Metropolitan Museum in which Pieter Meyers and I have tried to determine solubility products for both minerals in various buffered solutions. In preliminary studies we found that in something like an acetate buffer, with a pH of 5, you get bright blue solutions, with a corresponding high complex copper ion concentration. Even when you have fairly basic conditions, adding some sesquicarbonate (with a pH of 11) to pure paratacamite, you get a distinct blue solution.

*R. M. Organ:* I believe the first paper on this subject was done by Helmut Otto (Freiberger Forschungshefte B37, 66-77 (1959)), who made x-ray diffraction patterns and thought this was a clear way of distinguishing between ancient and modern patination.

*E. V. Sayre* then gave a demonstration prepared by *L. van Zelst*: As a demonstration a freshly prepared mixture of pure paratacamite with a 5 percent aqueous solution of sodium sesquicarbonate was compared with a similar mixture which had been combined some two weeks earlier, and with a mixture of pure paratacamite with water. It was observed that the freshly prepared solution of paratacamite in aqueous sodium sesquicarbonate had a quite pronounced blue color, that the identical but aged solution has a much less intense blue hue, and that the mixture of paratacamite and water was nearly colorless. It was also observed that the residual solid in the aged sesquicarbonate-paratacamite solution was more granular and more blue in color than that in the other two solutions. It has been found through x-ray diffraction that upon aging the paratacamite in the sesquicarbonate solution was slowly changing to malachite.

From these observations the following could be inferred:

- (1) That, contrary to much accepted opinion, paratacamite itself is appreciably soluble in the normally employed sodium sesquicarbonate treatment solution. Nantokite, of course, also dissolves in this solution.
- (2) That not only is chloride removed in part by direct solution of paratacamite, but by direct conversion of the paratacamite to malachite. Nantokite is not required for this conversion.
- (3) The fact that the concentration of the cupric complex ions in solution responsible for the blue color first reaches a maximum and then quite slowly decreases with time indicates that the physical chemical process, *e.g.*, complex ion formation, precipitation, *etc.*, which are bringing the system to equilibrium are occurring so slowly that there is time for many processes affecting the final nature of a corrosion layer, *e.g.*, corrosion itself and the diffusion of ions, to take place under nonequilibrium conditions.

Pieter Meyers, Lambertus van Zelst, and Edward Sayre are in the process of making quantitative studies of the solubility parameters and rates of change of various corrosion products of copper alloys in buffered solutions.

It has been observed that paratacamite has the same sort of inverse solubility that calcite does, *i.e.*, it becomes less soluble by a factor of 10 from that reported in the literature. There has been little success approaching stable conditions from the super-saturated side so as to establish that equilibrium has indeed been obtained. There has been difficulty in getting material to precipitate out of the saturated solution.

They have found the solubility of atacamite and paratacamite in some buffered solutions of pH closer to that of normal soil than sodium sesquicarbonate has been as great as a few tenths of a gram per liter. Thus, the basic premise of Lewin's conclusion that atacamite should not appear on naturally corroded bronzes because such natural corrosion would normally take place under conditions in which the concentration of complex cupric ions was extremely low appears to have been incorrect. There is good reason to expect appreciable amounts of copper-containing ions to be present in solution during natural corrosion, and hence, that both atacamite and paratacamite will be formed as has been found to be true on many ancient bronze objects.

*R. M. Organ:* The sesquicarbonate treatment for "bronze disease" is meant to be used only for the  $\text{CuCl-Cu}_2\text{O}$ -copper carbonates (azurite-malachite) systems, NOT for a basic cupric chloride system, which can be a green patina in its own right, with paratacamite not evidence of bronze disease. "Bronze disease" consists of the paratacamite on or in a cuprous oxide crust, appearing and developing, spot to area. Perhaps Ed Sayre could consider the place of azurite in his research, because we do observe that malachite greens sometimes change toward blue (azurite) in sesquicarbonate solution.

*S. Reisman:* Is there a stratigraphy to the artificial patination of copper, or is the copper sulfate formed directly on top of the metal?

*L. Fitzgerald:* In almost any kind of patination system there is an oxide structure from cupric to cuprous to metal. I know of no system without a microlayer; you just don't drop two electrons that quickly. The layer may only be one molecule thick, but it will be there.

Question 6: How satisfactorily can the history of an object be inferred from its corrosion products?

*C. J. Jack:* In the before-cleaning view of the Graeco-Roman silver wreath shown in figure Q-6-1, there is an appearance of lamination (not visible in the photograph). We have no knowledge of its age or origin. An analysis by Dr. Ursula Franklin found silver and copper sulphide on the wreath before cleaning. Upon cleaning (fig. Q-6-2) the analysis showed the leaves to be a silver copper alloy of the same composition as Roman coinage of about 400 A.D. A number of treatments were tried to clean the wreath: (a) 30 percent hot formic acid; (b) Goddards silver dip; and (c) electrolytic reduction, ultrasonic cleaning, silver dip, quick drying in alcohol and coating with Inralac. The last treatment (c) was the most satisfactory one. It removed all of the two outside laminated layers, leaving only the inner silver copper alloy.

The question posed by this work is, could the laminating layers be produced in the laboratory, or would it take exposure going back to 400 A.D?

*W. T. Chase:* A number of the objects from the Man-ch'eng tombs of the Former Han Dynasty (see Question 1 for sources) show different patinations. These include the shiny black mirrors, a matte black censer, a gilded lamp with green spots, and some objects with reddish corrosion which looks like cuprite. These all came from the same, rather dry tomb, apparently without earth fill, but they have different corrosion products. Why? How can we relate these corrosion products back to burial conditions?

*E. Escalante:* An important factor is the nature of the environment. Our work on metals buried in soils indicates that one can produce layers of many different thicknesses, not only as a function of time, but as a function of the nature of the environment. Therefore, the nature or amount of the corrosion product cannot be used as a reliable guide to judge the age of an object.



Figure Q-6-1. Wreath of Bay leaves. Graeco-Roman, silver with a small amount of gold foil. Front view before cleaning.



Figure Q-6-2. Wreath of Bay leaves. Graeco-Roman, silver with a small amount of gold foil. Front view after cleaning.

*Van Zelst:* A question of important practical value for the museum laboratory is in how far corrosion structures are indicative for authenticity. Especially, the phenomenon of intergranular corrosion is often regarded as a sign that shows natural corrosion processes have taken place. Thus, does everybody think about the usefulness of the observation of intergranular corrosion as an argument in favor of authenticity?

*Kenneth Morris:* We have seen intergranular cracking in parts of one artifact thought to be ancient when another part of the same object thought to be a new repair did not show cracking. Both parts showed similar outer corrosion products and were from adjacent areas of the same object.

*C. S. Smith:* Someone ought to do some experiments on the important question as to whether intergranular corrosion indicates long exposure. It seems reasonable, for example, that corrosion at elevated temperatures in an autoclave at 150 °C or so would produce effects that are similar to long time corrosion including diffusion down grain boundaries.

*M. Goodway:* The metallurgical literature contains references to stainless steel instruments having failed by intergranular corrosion in autoclaving.

*T. D. Weisser:* I have been able to produce intergranular corrosion in brass with sodium hydroxide.

*J. Kruger:* Corrosion engineers see failures by intergranular corrosion in many situations when the time of exposure is not very long when compared to that undergone by ancient metal artifacts. If anyone wants intergranular corrosion, I can produce it on order for a number of different alloys.

Question 7: What is the mechanism of the preservation of an original surface in heavily corroded bronzes and silvers?

*C. S. Smith:* I suspect that the retention of the topographic details of the original surfaces in many corroded bronze objects is a result of the interaction of two factors. Corrosion of most copper alloys begins by deep penetration along grain boundaries and (in castings) along the course of dendrite cores, and thereafter it proceeds laterally under conditions of rigid mechanical and volumetric restraint. Since the mineral corrosion products have a volume greater than the metal from which they form, some of the positive ions must migrate by diffusion to the outside of the piece, where they precipitate without restraint in a softer, loosely packed, less coherent form. Mineralogists have long known that the replacement of one mineral by another (for example, zinc sulphide, ZnS, replacing pyrite, FeS) occurs volumetrically, not in the amounts called for by chemical equivalents. The vanishingly thin but continuous layer of liquid maintained by capillarity between the old and the new phases is enough to allow the unwanted cations to diffuse out and oxygen or other anions to diffuse in. The slow rate of growth and the mechanical restraint combine to give a dense mineral product. The outer crust of the corroded object forms under quite different conditions away from direct contact with the metal, and the two zones are usually easy to separate. Iron, in which intergranular penetration rarely occurs, does not preserve surface details. It would be interesting to see what happens with a homogeneous single crystal of alpha bronze, or with an amorphous alloy.

The corrosion of metals over archaeological time periods is more akin to mineral formation than it is to the industrial corrosion mechanisms with which scientists and engineers today are mainly concerned. The next interdisciplinary conference on corrosion and conservation of archaeological objects should include a petrologist interested in ore formation. We could even tell him something, for we at least know the composition and structure at one earlier stage of history.

Question 8: What is the mechanism of the pseudomorphic replacement of the bronze structure with stannic oxide?

*W. T. Chase:* Figure Q-8-1 shows a Shang Dynasty Chinese broad-axe which we recently restored at the Freer Gallery. During the restoration we were able to take a number of cross-sections. Figure Q-8-1A (also see color plate e) shows one of these cross-sections. The tin oxide on the outside of the axe preserves the dendritic structure of the casting. A detail of the inner transition zone at greater magnification (fig. Q-8-2) shows uncorroded remnants of alpha dendrites, with what looks like cuprite filling in between them. Just outside of this is a black corrosion product, with the dendritic structure preserved in what looks like a diffusion banding of some sort. I do not really have an understanding at all of what is going on here. It would be very helpful if someone would work up a computer simulation of what is going on in terms of the various ions and molecular species in a corroding bronze like this one.

*K. Z. Holm:* I cannot answer the question but would like to point out, that according to my experience, one never finds the cuprous chloride together with this form of pseudomorphic mineralization. You can find the characteristic formation of warts connected with the chloride-induced corrosion in some parts of an object and, in other parts of the same object, the pseudomorphic change we talk about here.



Figure Q-8-1. Broad-axe of the type *ch'i* in the collection of the Freer Gallery of Art (FGA 46.5). The axe is 12 7/8 inches long (32.7 cm). It was recently repaired by the Technical Laboratory of the Freer Gallery. The length of the tang was increased, with the intention of correcting previous erroneous restorations. The restored area can be seen just below the animal mask.



Figure Q-8-1A. Cross-section from the haft of *ch'i* 46.5 (see fig. Q-8-1 and color plate e). The section was removed during restoration. The outer surface of the haft is at the top. White tin oxide can be seen to have pseudomorphically replaced the original dendritic structure. Below this is a banded red layer, probably containing cuprite, and below this is a black transition zone, where the dendritic structure is preserved. The dendrites and their coreing are seen to carry through from the metal into the black material. At the left side is an artificially ground edge made by the previous restorer. Dark field, polarized, magnification *ca.* X100.



Figure Q-8-2. A detail of the black material on the inside of *ch'i* 46.5. At the center of the photograph can be seen remnant metal and an orange (light) material, which may be cuprite. Above this is the black material which pseudomorphically replaces the original dendrites. Dark field, unetched, magnification X200.

Question 9: What are the critical temperature and relative humidity for the conversion of cuprous chloride to paratacamite?

and

Question 11: What are the environmental conditions favoring the formation of paratacamite over atacamite or *vice versa*?

*M. Pourbaix*: The conversion of cuprous chloride to paratacamite is not only a question of relative humidity and temperature. Oxygen concentration or partial pressure is also important. Cuprous chloride exists only in the absence of oxygen at a low pH (see fig. Q-9-1). Paratacamite, on the other hand, needs oxygen in order to exist. This then is an important difference in the set of conditions that determine which substance is stable. A diagram such as that shown in figure Q-9-1 allows one to predict the stability of paratacamite. On this diagram are the partial pressures of water represented as different lines. The slope of these lines on a plot of  $1/T$  vs.  $\log pO_2$  ( $T$  = temperature K, and  $pO_2$  is the oxygen partial pressure) is a measure of the enthalpy of condensation of water vapor. If you have a substance which is hygroscopic for one atmosphere, there is an increase of the boiling temperature and a decrease in the partial pressure. Another line can be drawn that represents the partial pressure of the saturated solutions of the compounds shown in the diagram. On this diagram one can point out regions of stability for these

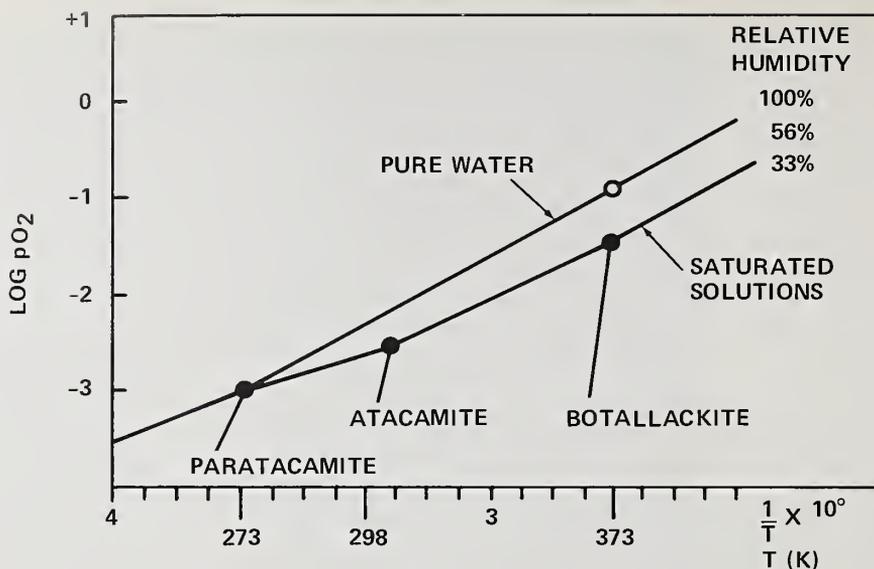


Figure Q-9-1. Stability conditions for  $\text{CuCl}_2 \cdot 3\text{CuO} \cdot n\text{H}_2\text{O}$  in the presence of water vapor.

compounds. To determine the condition, environmental conditions favoring the formation of paratacamite over atacamite or *vice versa*, one can use the enthalpies of formation of these compounds which can be determined on a diagram such as figure Q-9-1 which shows regions where these compounds may be formed. All one needs is to have good values for the thermodynamic properties, *i.e.*, free enthalpies and enthalpies of formation, of paratacamite, atacamite and other corrosion products of interest.

*R. M. Organ:* I did a very crude experiment in 1960 where I put a small amount of cuprous chloride on a watch glass and exposed it to steadily increasing relative humidities and found that below about 39 percent relative humidity it did not change. Above 39 percent, it went to green paratacamite.

Question 10: For the stabilization of pockets of cuprous chloride on bronzes from the Near East is anything better than control of relative humidity to below 40 percent?

and

Question 12: What are the criteria to judge the success of treatment of bronze disease?

*C. S. Smith:* Though control of relative humidity is an established procedure for stabilizing the corrosion of chloride-containing bronzes on display, control of temperature also should be considered for long time storage of research materials. Below about minus ten degrees centigrade almost all relevant biological and chemical processes proceed at extremely slow rates. Change is virtually prevented. One might envision a kind of Shoshoin under UNESCO auspices storing a fraction of mankind's most valued objects and records in an ice cave in the Antarctic. This would be self-preserving in the event of a breakdown of political stability, and could have high ceremonial access only once a century, otherwise. I believe Mr. Organ has studied low-temperature storage and I hope he will comment.

R. M. Organ: In order to control corrosive attack on an immense number of objects, such as is found in Smithsonian museums, numbering between 15 million and 15 billion, control of environment, such as very low temperature or very low relative humidity (for metals), is the only practicable method--individual attention to so many objects is impracticable. Storage in the Antarctic could be ideal!

B. F. Brown: Is it not possible to use a surface active compound (e.g., SPRA-DRI or CRC) to displace the moist chloride from the metallic surface? Such materials have been useful in preserving metal surfaces which have been in sea water without the benefit of rinsing.

C. E. S. Hett: In parks in Canada, we have experience with the watering fluids; these are commercial products made by Sunbeam Auto-Corrosives in Toronto. There are two classes, one water miscible and the other not water miscible. In all, about six or eight types are produced under the trade name of Ferromedes. The non-water miscible types have the advantage of an oil or wax in the solvent and are designed to hold corrosion of the iron after air drying until lacquering. We use the Ferromedes both on cast and wrought iron artifacts after boiling chloride free and have had satisfactory results so far in stabilizing when this treatment is followed by a phosphating lacquer, produced by the same company.

J. Kruger: I would like to enter into the proceedings some other information bearing on the treatment of bronze disease that I recently received from Dr. U. R. Evans of Cambridge University, who is considered by many to be the founder of corrosion science. The letter goes as follows:

Dear Dr. Kruger:

I am most interested in the dialogue between Museum Conservators and Corrosion Scientists which you, with my good friend Prof. Pourbaix and others, are organizing for March 17, and wish it every success.

Had there been more time, I would have written to you to inquire whether a paper from someone who could not attend in person would be welcomed. Had your reply been "yes", I would then have suggested to Mr. Rayner of the Fitzwilliam Museum, Cambridge, that he should send you an account of his success in dealing with a virulent outbreak of bronze disease 25 years ago. The 500 specimens treated in 1951 are today in good condition, and I think that we may assume that the cure is permanent.

Unfortunately, Mr. Rayner has been on leave and only returned today. Clearly it is too late for a paper, but he has produced a short statement of his procedure, which I enclose, along with xerox copies of the four accounts on the situation, printed in my books of 1960, 1968 and 1976 and in a lecture which I delivered in 1951<sup>1</sup>. If you are interested and have time, you might care to look through this and convey your impressions to the meeting. I do not press this; you may have no time, or it may be against the rules governing the meeting.

The circumstances were these. At the outbreak of the second world war in 1939, the most valuable bronze antiques in the museum were sent to a place in the West of England considered to be relatively safe from enemy bombing. After the war was over, they returned, but apparently owing to acetic acid vapor picked up from wood shavings in the packing cases, local corrosion broke out, sometimes leading to perforation in a matter of weeks. There was a serious risk that these exceptionally beautiful and extremely valuable objects of art would be utterly ruined. We had to

<sup>1</sup>U. R. Evans, *Chemistry and Industry*, April 25, 1951, p. 710-711.

U. R. Evans, *The Corrosion and Oxidation of Metals* (Edward Arnold Publishers Ltd., London, 1960) p. 402.

U. R. Evans, *Ibid.*, First Supplementary Volume, 1968, p. 373.

U. R. Evans, *Ibid.*, Second Supplementary Volume, 1976, p. 274.

move quickly, and I worked out roughly a method based on the application of HCl, H<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, in turn, on a zinc nib. Rayner put this into practical form and treated 500 specimens without decay. The treatment worked will, and the acetate anions were fetched out of the corrosion pits under the E.M.F. Zn/bronze. Rayner has written that it is "far the most effective treatment that I know and also the simplest."

With our wishes for success of the meeting and greetings to my friends, including Dr. Floyd Brown.

Yours sincerely,

Ulick R. Evans

*N. C. Rayner*: Treatment of Ancient Bronze Artifacts Suffering from "Bronze Disease." Cut out a "nib" from sheet zinc and join this to the negative terminal of a galvanometer. Scrape the specimen at some unobtrusive point until metallic lustre appears (do not confuse red cuprous oxide with the true metal) and connect this point to the positive terminal. (See fig. Q-12-1.) Wet the nib with *dilute hydrochloric acid* (2 parts to 5 parts) and rub the disease spot until the green material is removed. As far as possible, confine the wetting to the spot (or spots) to be treated, if necessary, grease the surrounding area with vaseline and rub away the vaseline with the nib at the point to be treated. As soon as the green powder is destroyed, remove the hydrochloric acid on blotting paper, then apply *syrupy phosphoric acid* with the nib and blot off. Finally apply *sodium carbonate* with the nib and blot off. Treatment is then complete.

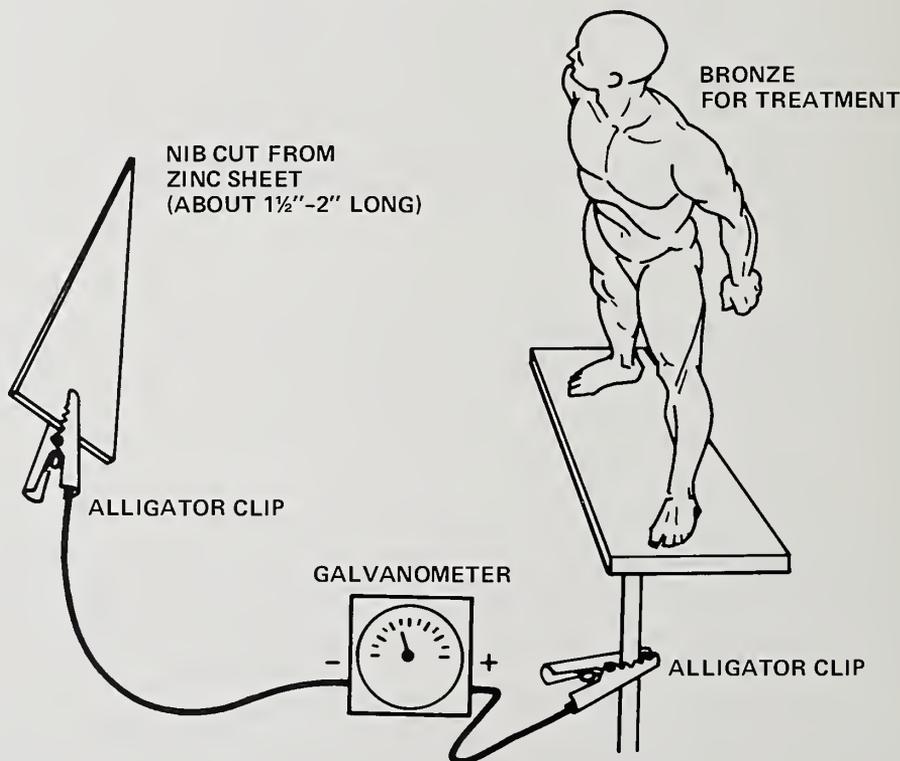


Figure Q-12-1. Sketch of system for treating ancient bronze artifacts for "bronze disease."

*F. M. Organ:* I have always had the impression from some of the published accounts of Rayner's treatment that the zinc nib was simply touched to the affected spots without any electrical connection to the metal, as shown in the sketch on page 218. This information that an electrochemical cell must be made between the zinc and the bronze is thus quite a valuable contribution. One hopes that the treatment is permanent because the treatment of individual spots on a large object can be quite a lengthy process with four or five spots per square centimeter under the best of conditions.

*W. T. Chase:* The following three figures show a section from a Thai bronze of the Ayudhya Period (ca. 300 years old) which contains a thick cuprous chloride layer. These photomicrographs were taken with the intent of showing the rapid progress of bronze disease; they appear in color in a catalogue entitled *Bronze Disease and Its Treatment* which I wrote for a joint project on treatment of bronzes in Thailand. The catalogue is available from the Thai National Museum, Bangkok, and was printed in 1975. Figure Q-12-2 shows the section after exposure to 100 percent relative humidity for 15 minutes; no bronze disease can be seen. After two hours, one can begin to see a change in the cuprous chloride layer (fig. Q-12-3). The change can be seen to begin within the cuprous chloride layer, and not at the interface between the bronze and the cuprous chloride. After four hours, the transformation of the cuprous chloride is more pronounced, (fig. Q-12-4), and it continues to grow on further exposure to high humidity.

The main thing to note from these figures is that the green spots which are the outward manifestations of bronze disease have nothing to do with the corrosion of the metal, but are simply due to the change (oxidation and hydration) of the cuprous chloride layer. All of the criteria for judging success in the treatment of bronze disease depend on the green spots not reappearing after treatment. These figures serve to point out that these green spots have nothing to do with the corrosion of the underlying metal. Thus, the usual criteria for success are not really satisfactory, although I continue to use them.

In the case of the benzotriazole treatment, when a bronze has been treated with benzotriazole and sectioned, the bright green can be seen to break out again in the cuprous chloride layer on exposure to high humidity. It may be that benzotriazole only penetrates to the outer surface of the cuprous chloride layer, and not through it. If it does this, it may be stopping the transformation of the cuprous chloride to cuprous oxide; this would mean that the  $\text{Cl}^-$  ions are not freed to react again with the copper metal. If benzotriazole does indeed work in this way, it may really be a successful treatment for bronze disease. It would be nice to have some experimental corroboration for this hypothesis.

*M. Pourbaix:* There was, as you know, a meeting at Faerrara on September 15, 1975. There were several questions raised concerning the protection of bronzes and gilt bronzes with benzotriazole. Something that is presently not known is what is the mode of action of the benzotriazole and of other inhibitors with copper.

I had up till now no opportunity to work on the action of benzotriazole on copper and on copper alloys. The opinion I presently have on this subject is the following one: it is probably not true that benzotriazole, as has been very often said, is really working by simple adsorption. I believe that its action may be merely a chemical action on the cuprous oxide, which very often exists on the surface of the metal. We know, and you know, that cuprous oxide exists on corroded copper and bronzes as both an adherent and somewhat protective coating, and a nonadherent and loose nonprotective sludge, formed as an hydrolysis product of cuprous chloride or of dissolved copper ions. I have the feeling that benzotriazole is efficient when  $\text{Cu}_2\text{O}$  exists as an adherent coating, and that it is not efficient when  $\text{Cu}_2\text{O}$  exists as a sludge. This concept, which might be rather easily checked, might perhaps help to clarify, as has just been said by Tom, the method of action of benzotriazole and of similar compounds; this might help to elucidate the conditions where these compounds may be successfully used for the protection of copper and of copper alloys.

*R. M. Organ:* While the cuprous chloride changes into green paratacamite, *i.e.*, the onset of bronze disease, the cure of the disease is also taking place because the production of paratacamite is destroying the cuprous chloride. When all the cuprous chloride goes away by converting to paratacamite, it cannot react anymore and bronze disease is stopped. What is not stopped, however, is the continuing corrosion of the metal under the crusts of



Figure Q-12-2. Photomicrograph of sample containing a thick cuprous chloride layer after exposure to 100 percent relative humidity for 15 minutes. No bronze disease can be seen.

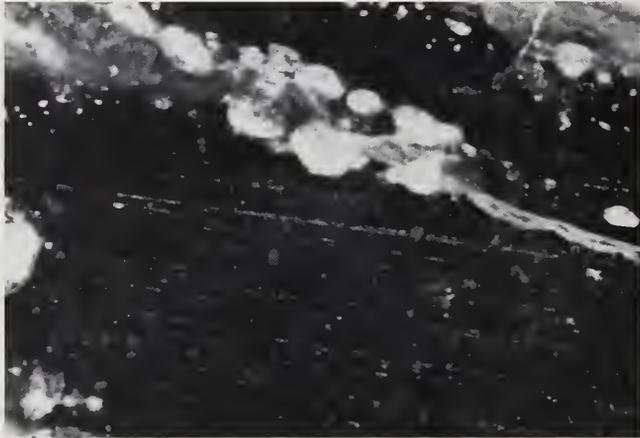


Figure Q-12-3. After two hours a change can be seen in the cuprous chloride layer, not at the interface between the bronze and the cuprous chloride.



Figure Q-12-4. After four hours the transformation is more pronounced.

cuprous chloride. That corrosion can only be prevented by benzotriazole or by controlling the relative humidity to a value so low that the cuprous chloride cannot react. Cuprous chloride does not convert to paratacamite below a relative humidity of 39 percent, but

what is not so well known is the relative humidity below which the continuing penetration of cuprous chloride will be halted. This penetration is the real danger in the museum. It is because bronze disease stops this penetration that I have made the heretical statement that bronze disease is good.

*T. D. Weisser:* Isn't hydrochloric acid a by-product of the conversion of cuprous chloride to other products? If so, can't this hydrochloric acid react with the remaining copper to form more cuprous chloride?

*R. M. Organ:* If you do, I would guess that it vaporizes into the air. It is a valid point that should be looked at.

*L. Barkman:* If one takes identical sesquicarbonate solutions and adds identical quantities of paratacamite to them, it can be seen that such a combination prepared now is considerably more blue than the similar solution prepared a week ago. The conversion to malachite has proceeded much further in the latter solution. The point is that we are dealing with slow processes and that it is to be expected that there will be intermediate stages where non-equilibrium conditions prevail. Therefore, to understand the chemistry of processes involved in bronze disease, it is important to take rate considerations into account.

*M. Pourbaix:* If one assumes that bronze disease continues only in the presence of a humid environment, then a consideration of the hygroscopic nature of the solid compounds formed on the surface is of utmost importance because it influences the critical relative humidity above which the surface becomes wet. One can get some idea of the hygroscopic nature of paratacamite, for example, by measuring the vapor pressure of a saturated solution of it at various temperatures. If one then keeps the relative humidity below these values for the vapor pressure, the solid will dry out and bronze disease is stopped.

Question 13: What are the prospects for the hydrogen treatment of corroded bronze containing cuprous chloride at less than 300 °C?

*E. Birchenall:* A valuable reference that would help with answering this question is a paper by H. H. Kellogg, *Trans. AIME* 188, 862-872 (1950). The compilation, *Thermodynamic Tables for Process Metallurgists*, by C. Jörgensen and I. Thorngren, published by Almqvist and Wiksell, Stockholm, 1969, also contains useful tables of free energies and enthalpies of chlorides as well as oxides, sulfides and other compounds that one might be tempted to reduce with hydrogen.

*D. Piechota:* I thought it was possible to sublime iron chloride from iron at around 300 degrees or so centigrade. In an appropriate environment you might not oxidize or reduce the oxide layer, but you could merely sublime out the chloride. Is that not so?

*R. M. Organ:* I think that was the annealing process, so called, at a temperature of 800 °C described very fully in Eriksen, E. and Thegel, S., *Conservation of Iron Recovered from the Sea*, Copenhagen, 1966, 29 to 41.

*W. T. Chase:* What can be done in the way of changing the environment to stabilize lead objects until they can be treated?

*R. M. Organ:* If the excavator can carry along Permalife envelopes, he can just pop the leaden objects into them. The Permalife paper contains calcium carbonate which will absorb any volatile organic acid on its way to the lead coin. Once organic acids reach the lead, they stimulate corrosion and rapid decay sets in. Once the lead is in the laboratory we can regenerate lead from any corroded material in the exact position it is in now. The other thing you can do in a hurry, if the lead is already corroded, is to put shellac varnish on it. That would hold everything in position until it can be treated and you could still read any inscription.

*M. Goodway:* Since the lead corrosion problem (in wooden drawers) was first observed in the British Museum, how do you get that information back to the archaeologists rather than just to the conservators?

*R. M. Organ:* That's a problem. In the past there has been little interaction between conservators and archaeologists. That is the reason why at the Smithsonian we have lectures on conservators' techniques on videotape (available for archeologists to view). There are some books that suggest things to do, such as one by Dowman, but they won't do for a site such as the one Mr. Trousdale described.

Question 14: Are there any differences between bronze disease caused by chloride and that caused by acetate? (No discussion)

Question 15: What are the cleaning, stabilization and storage procedures applicable to 500 early iron age fragments of bronze from a Hallstatt culture site? These have a discontinuous, unoxidized metal covered by a vile powder layer and then a noble chipable layer.

*P. V. Piechota:* These slides are views of selected pieces of the Peabody Museum's Hallstatt period bronze collection known as the Duchess of Mecklenberg Collection. The pieces come from the Weinitz cemetery in Austria, excavated in 1907 to 1917. Mr. Gettens analyzed the corrosion layers in 1936, finding that there is commonly a fine but crumbling tin oxide layer which covers a troublesome powdery blue layer. He found that this layer is similar to a rare tin silicate called Arandisite. He found no chloride, sulfate or carbonate on the pieces with the above corrosion products. There has been no treatment of these pieces apart from superficial dirt-removal and repair. How have these layers formed? What is the state of the art of the plastics and waxes usable for consolidation of these pieces? Is it possible that there is still a corrosion process going on?

*R. M. Organ:* The only case in which I have seen silicates on bronze was in the Institute of Archeology in London--it was treated satisfactorily in fused sodium carbonate mixture<sup>2</sup>. We don't have any consolidative reduction techniques for copper corrosion products such as you would need for these. Is there any evidence of disease apart from cracking off of the crusts?

*D. V. Piechota:* Yes, on some pieces where we have chloride but doesn't show the tin oxide layer. I feel it is stable, the major problem is consolidation.

*R. M. Organ:* I think what I would do is to get the pieces thoroughly dry in a desiccated atmosphere and then consolidate them with a microcrystalline wax. Take care that everything unwanted is taken off the surface. Don't try it on any object too large to go into a Soxhlet extractor because someone in the distant future will wish to remove the wax.

*D. V. Piechota:* Our museum is dirty and we wouldn't want dirt in the wax.

*R. M. Organ:* In order to be sure of ability to remove a resin coating, one would want to choose one which has a proven ability to be removed, probably an approved polyacrylate, one which will not cross-link with oxygen in time. I think by far the best prospect is afforded by a microcrystalline wax on several counts: it is consolidative coating, it is always removable, and it has minimal permeability to moisture so that if your dry atmosphere gets out of control there is still some protection. To control the problem of getting dust on it you'd have to choose a hard wax.

*D. V. Piechota:* We went to a softer wax because of brittleness in hard wax.

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<sup>2</sup>Cornwall, I. W., and Gedge, I., A new Method of Cleaning Corroded Bronzes, the Annual Report of the Institute of Archaeology, London Univ., 10, 34-36 (1954).

*R. M. Organ:* Some people have handled the dirt problem for storage drawers by putting a Plexiglas cover on each drawer so that one could see the objects without opening up the storage space and fingering the objects.

*W. T. Chase:* (1) Gloss on a resin-covered surface can be avoided by drying thermoplastic impregnated pieces over the impregnating tank in a solvent atmosphere. (2) To detect remnant metal in objects of this sort, a miniaturized commercial metal detector (see Question 23) can be used. We use a modified Radio Shack kit to detect remnant metal. Is there any metal left in your objects or are they completely mineralized?

*D. V. Piechota:* No, they are not completely mineralized; in many objects there is a continuous metallic core.

Question 16: What is the effect of benzotriazole on the mineral substances of corrosion crusts on bronze?

*W. D. Richey:* BTA interacts with Cu(II), not Cu(I), in general, when it interacts with a patina. (The exception would be CuCl, nantokite, if the treatment solution reaches that level.) Since Cu(II) BTA compounds are relatively soluble (relative to patina materials), it is probably scavenging free Cu<sup>++</sup> in solution in pores. BTA does not seem to modify Cu<sub>2</sub>O, and only to a modest extent attacks malachite. The relatively soluble copper basic chloride converts to some extent. Cu(I)Cl undergoes a surface reaction but does not completely convert pieces or particles, which may be a good thing if you consider the relatively low density of Cu(I)BTA.

Question 17: Are there any known adverse effects between fixed and vapor phase inhibitors?

and

Question 18: What is the state of the art of vapor phase inhibitors applicable to museum use, and are any of them potentially hazardous to health?

*S. Coburn:* Vapor phase inhibitors (VPI) such as those developed by Shell originally were organic nitrites. Their use are of wide interest. The material functions in a manner similar to "moth balls." A powder is placed in an enclosed space. This powder vaporizes and deposits on the active sites on the surface a protective film. Two references are very useful; Vapor Phase Inhibition of Atmospheric Corrosion, Sexton, *Corrosion Technology*, May 1960, and The Distribution of a Volatile Corrosion Inhibitor on Corroded Iron, Henriksen, *Corrosion Sci.* 12, 433 (1972).

*B. A. Mksic:* The inhibitor that Mr. Coburn mentioned that was made by Shell is dicyclohexyl-ammonium nitrite (DICHAN). It is used primarily for steel and, of interest to museum conservators, is the fact that it is not compatible with non-ferrous metals as such. In fact, nitrites can have adverse effects on non-ferrous metals as brasses, copper and bronzes under conditions of high humidity and temperature. We have been concerned with developing inhibitors that provide corrosion protection to both ferrous and non-ferrous metals. Our experience indicates that the benzoates would be very promising for museum application, providing 10 to 20 years of protection. It has been used in Norway for 15 to 20 years without any problems where carbonates were also used. Humidity, pressure of SO<sub>2</sub>, H<sub>2</sub>S at reasonable concentrations does not affect their ability to protect metals. The benzoates are effective in inhibiting corrosion by chlorides, although the nitrites are more effective against chlorides.

Our research has shown that these inhibitors work by adsorbing as monomolecular layers on less than 1/2 percent of the surface with the sites of adsorption changing from moment to moment in a statistical fashion.

With regard to the second part of the question concerned with toxic effects, our research has indicated that toxicity of vapor phase inhibitors varies between 200 to 2000 mg/kg of body weight depending upon their composition. It was found that benzoates are less toxic than nitrites which are presently in use. The question on toxicity of volatile corrosion inhibitors is a very complex one. Generally, it is believed that compounds derived from carboxylic and carbonic acids are less toxic than salts of nitrous and chromic acids. Nitrites are of primary concern due to the possibility of forming nitrosoamines in the human body.

*M. Pourbaix:* We think that the action of vapor phase inhibitors is exerted by dissolution in the water present on humid articles, so that the efficiency of these inhibitors may be correlated with their inhibitive action on this condensed water. If so, the eventual adverse effect of polluting gases, such as  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , or  $\text{Cl}_2$ , might be evaluated by experiment performed with aerated aqueous solutions of these gases. Can Dr. Miskic comment on this?

*B. A. Miskic:* In answer to Prof. Pourbaix's question regarding the solubility of VPI's, I must say that to the best of my knowledge the functional relationship between water solubility and the effectiveness has not yet been established. There have been some indications in the literature that such a relationship does exist, but I believe that the major factor which contributes to the effectiveness of VPI's in a specific environment is their protective mechanism. For an illustration, it was discovered that VPI's which produce hydrophobic (water repelling) effects often fail in salt atmospheres, probably due to higher conductivity of corroding electrolyte (chloride contaminated water). On the other hand, VPI's whose protective mechanism is based on changing the electrochemical potential of metal substrate have been found much more successful in inhibiting corrosion. Probably the most effective inhibitors are those formulations that combine both above mentioned mechanisms.

The electrochemical behavior of nitrites is schematically shown on figure Q-18-1, diagram C. They are typically anodic inhibitors thus capable of affecting the kinetics of anodic reactions. The inhibitors with highest "generality" of protection are the ones

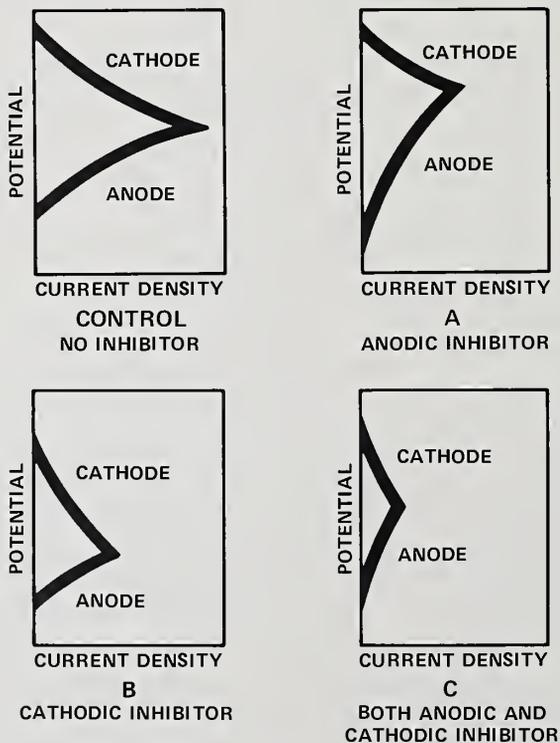


Figure Q-18-1. Schematic showing the electrochemical behavior of nitrites.

that can change kinetics of both electrochemical reactions cathodic and anodic. Some esters of chromic acid and substituted carboxylate salts of heterocyclic amines have been demonstrated to fall in this category (fig. Q-18-1, diagram C). A good source of references on VPI's are the Proceedings of a Symposium on Volatile Corrosion Inhibitors held in Houston in March of 1976, under the Sponsorship of the National Association of Corrosion Engineers (2400 West Loop South, Houston, Texas 77027).

In summary of this discussion, I would like to mention that volatile corrosion inhibitors could indeed be a useful tool in the fight against atmospheric corrosion. However, information on them is scarce and scattered throughout technical literature and many questions regarding toxicity, effectiveness vs atmospheric pollutants, durability of protection, etc., still remain to be answered.

*R. M. Organ:* It is clearly important in museum practice to have something that works with both ferrous and non-ferrous metals. We have avoided using Vapor Phase Inhibitors for many years because we could never guarantee that a storage space would always contain only ferrous metals. Curators keep objects made of various metals together.

*D. V. Piechota:* Is it true that some of the organic corrosion inhibitors, like benzotriazole, deteriorate upon exposure to UV?

*L. Fitzgerald:* With regard to adverse effects of inhibitors, UV degradation of benzotriazole hasn't been a problem. Inralac<sup>3</sup> samples on exposure 8 to 10 years show that the inhibitor is exhausted, but this is believed to be due to migration and volatilization of the inhibitor.

Question 19: Under what conditions can corrosion inhibitors become corrosion stimulators?

*P. D. Weil:* I wish to call attention to two important factors regarding protective coatings for outdoor metals: (1) the structure of the coating and (2) the necessity of a corrosion inhibitor in the coating. Brushed-on coatings, especially without inhibitor, can cause greatly accelerated corrosion, especially in the areas of the striation left by the brush hair in the coating. The coating will deteriorate in these areas first, and corrosion will be promoted by differential aeration in these hair-line fissures. This phenomenon has been observed to cause damage on a plated area of an outdoor sculpture. Protective coatings on outdoor sculpture should be applied by spray and in several thin coats. See P. Weil, The Approximate Two-Year Lifetime of Inralac on Outdoor Sculpture, Venice ICOM Conference Papers, October 1975.

*J. Kruger:* Unless you use enough inhibitor, the inhibitor will stimulate corrosion at the active sites not covered. Unless you use the inhibitor correctly and adequately, it is best not to use any at all.

*R. M. Organ:* You must have an enormous reserve of inhibitor to take care of local pockets of chloride. You shouldn't use inhibitors unless you know what you're doing.

*D. V. Piechota:* Can these organics such as BTA be broken down by ultraviolet light?

*L. D. Fitzgerald:* Outdoor exposure tests on Inralac (with BTA) up to 10 years have shown no real serious breakdown. There is some volatilization of inhibitor, so that after 5 to 6 years the inhibitor is pretty well deteriorated.

*W. T. Chase:* What is the life of Inralac?

*L. D. Fitzgerald:* 1 mil gives a life of 5 years, longer (10 years or so) with touch-ups.

*W. T. Chase:* Indoors?

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<sup>3</sup>A lacquer developed by the International Copper Research Association for the outdoor protection of copper alloys.

*L. D. Fitzgerald:* No data indoors, but it should last indefinitely indoors.

*W. T. Chase:* What about holidays?

*L. D. Fitzgerald:* Catch and repair. Mixed corrosion inhibitors are safe since they do not accelerate corrosion when present in insufficient concentration. The general limitation of inhibitors presently in use is in their anodic nature. In our investigations we succeeded in synthesizing compounds capable of producing protective films on both cathodic and anodic areas.

Question 20: What is a simple, cheap, lasting method for preventing further corrosion?  
(No discussion)

Question 21: What is the state of the art of protective coatings for metal sculptures displayed out of doors? (No discussion)

Question 22: What is the present state of the art of protective coatings, their application, durability and reversibility for indoor or outdoor use on bronze, lead, silver, etc.?

*L. D. Fitzgerald:* The development of INCRALAC, an acrylic finish for copper metals, was discussed in detail, with accompanying slides. This included criteria leading to (1) polymer selection, (2) inhibitor selection, and (3) solvent system. INCRA also examined variations in cleaning techniques. Acrylic polymers were found to be the best for maintenance finishes since they were insensitive to ultraviolet and could be readily stripped. These when formulated with benzotriazole and a non-oxygen containing solvent such as toluene or xylene provided 5 to 10 years exterior durability. A minimum of 1 mil of dry film is required. Other coating systems which have been examined and show promise are (2) aliphatic polyurethanes which provide very hard surfaces for resistance to vandalism but are difficult to strip, (b) polyvinyl fluoride (Tedlar) finishes which must be applied on sheet metal in the plant. These can provide over 15 years of exterior durability. The cleaning and refinishing of the Mexico City Sports Palace and the Zambian National Assembly Building were discussed. Cleaners such as Turco-WO-1 and 5 percent sulfuric acid were used for these jobs. The rinse water contained 1 percent sodium carbonate. The Sports Palace, cleaned with Oakite-WO-1, needed no polishing and was lacquered with 25 percent solid INCRALAC (2 coats). The National Assembly Building, after cleaning with sulfuric acid, required polishing with rouge and prior to application of two coats of INCRALAC. Extended exposure tests at 12 outdoor sites throughout the U.S. have shown INCRALAC to be a durable finish for copper metals over periods up to 10 years. For indoor work when you're not in a hurry for drying, to avoid the orange peel surface with traditional INCRALAC, you can add a little MEK and you get a smooth coating which is great for indoor work. We've looked at the whole gamut of resin types, and we think INCRALAC is best for your purposes, for it is removable, and the other competitive coatings are hard to strip.

Question 23: What nondestructive tests are suitable for field identification of metal objects?

*K. Morris:* We have used an ultrasonic metal thickness gauge to give the thickness of metal objects. It is a sonar-like device, small enough to hold in your hand. This thickness measurement enables identification of various metal parts of a whole object for later reference. It can be particularly helpful to conservators of outdoor bronzes.

*W. T. Chase:* The use of a small, home-built metal detector may be helpful in ascertaining whether a much-corroded metal artifact has any metal remaining or not. Small metal detectors are commercially available for \$5.00 up. The detector coil should be replaced with a small, home/wound coil about the diameter of a pencil; the coil should be wound so that the l-c or other circuit of the metal detector can be made to resonate. We have found a number of uses for one of these devices in our conservation laboratory.

*M. Goodway:* Does anyone have suggestions about telling one metal from another in the field?

*F. Halahan:* Henry Hodges always said that there were only two methods: one was the magnet; the other, if you thought it might be lead, was to wipe it on paper. You will get a grey mark, if it's lead. Generally, in the field, you don't have electricity, you don't have any equipment or facilities for testing. Simple methods like that may be the only ones you can rely on.

*M. Goodway:* (to W. Trousdale) Bill, didn't you have a case where the geologist hefted a piece, and from a knowledge of specific gravities and weight to be expected from volume, make a shrewder guess?

*W. Trousdale:* That was me. (Laughter)...

*R. M. Organ:* May I add one more? If you rub the clean metal object with your hands, and then sniff your hands, there are characteristic odors to the various metals which you get used to quite quickly. You can only do it if you have some means of wiping the hands clean before touching the object. Iron, copper, all these metals have characteristic odors. It might not work for you, but it does for me.

*M. Goodway:* In other words, use all your senses.

Question 24: What methods of cleaning and stabilization of metals are suitable for employment at the archaeological site? (No discussion)

Question 25: What practices should be avoided to prevent stress-corrosion cracking?

*B. F. Brown:* You can't usually do anything about the stress, except assume that it's very high. If it's a copper object, restrain yourself from using ammoniacal cleaning material.

*S. Odell:* Two or three examples of highly worked brass trumpet and horn bells which are badly cracked have come to my attention. Although the cracking in these cases has not been confirmed metallographically as stress-corrosion cracking, it might be wise to avoid cleaning such objects with ammonia-containing solutions and polishes, such as Brasso.

*M. Goodway:* If you can smell the ammonia, it's too much!

*S. Odell:* Right.

Question 26: What precautions need to be taken in the use of metal fastenings for displaying objects? (No discussion)

Question 27: What sort of corrosion problems arise in the display of metal objects?

*R. M. Organ:* We have the usual problems that dissimilar metals should not be in contact. Sometimes display people like to fix metal plates onto vertical surfaces, and they use little metal hooks. This is fine, but the metal hooks may be of a different metal, and we get things happening at the point of contact. Another difficulty is that variations in temperature cause abrasion at those points of contact. Yet another is that when the display person drops it into position, he sometimes doesn't manage to drop it in gently, and it makes a dent on the edge of the object.

To avoid all these problems, what we normally recommend is that each little metal hook be covered with a protective plastic sleeve. This creates another problem. In one place where I encountered this, the brass hook inside the plastic sleeve (probably made of plasticized polyvinyl chloride) which looked satisfactorily yellow and brassy before, had turned black. This is because of corrosion of the brass in contact with the polyvinyl chloride.

What we recommend nowadays is to use the shrinkable sleeves that are sold by the electronics people. Out of the bundle of sleeves that you buy from Radio Shack or Lafayette, for instance, you select one that just fits on. You warm it up and it shrinks tightly into position. Then you have a permanent fixture. I think that these sleeves are made of polypropylene, which is a relatively safe material.

Question 28: What are the conditions which can produce whisker disfiguration?

*T. Weisser:* I am not certain what the person who wrote this question means by "whisker disfiguration." Does he mean whiskers of corrosion, single crystals, or what?

We do get things which one could call whiskers growing on silver objects. We have had rather strange conditions at our museum which have produced silver sulfide crystals, not just tarnish. Long black whiskers first appeared on gold pieces, or pieces of jewelry which looked as if they were all gold. The whiskers seen on the metal parts of this jewelry turned out to be silver sulfide; the silver came from impurities of silver in the gold, from silver solder used in assembling the jewelry, or from silver wire used to attach gems. Why the crystals formed in a whiskery habit, I don't know. Tom Chase may have something to say about this, since he examined them at one point. I doubt whether they would truly be called whiskers.

*W. T. Chase:* I think that the whisker-like crystals on the silver and the brown-to-black mossy-looking substance which forms on some bronzes in the Walters Collection (the renowned Walters Brown Fuzzies) are somehow connected, but I'm not sure just how.

*M. Goodway:* Growth conditions.

*W. T. Chase:* Yes, it must be. I think that the whiskers on the silver objects and on the gold objects with silver solder or silver wire came simply from the fact that they simply were not handled for long periods. As far as we could tell, some of that material was in the cases for 30 to 35 years, without ever coming out or being brushed or cleaned or anything. I wonder if some of the rest of us left things in cases untouched for that long whether we might not get the same effect?

*T. Weisser:* I have noticed that whiskers have appeared on pieces of steel armor where there is silver inlay. I don't know whether or not these had not been handled for a long time.

I also found them on a silver bust of Mr. Walters on the areas closest to the floor of the storeroom. One thing that I discovered in checking the conditions in the storeroom was that there were rubber mats on the floors. The mats had been put down to prevent breakage from dropping of objects. When you say that the "brown fuzzies" are related to the silver whiskers, I think that may be one relationship right there. They might both have been caused by the breakdown of these rubber mats that were put down in the 1930's. A lot of sulfur was being given off by this breakdown, and this might have been enough to

cause the silver sulfide crystals and the brown fuzzies (which do seem to have a lot of sulfur mixed in with them).

*M. Goodway:* These whiskers also appear on bronzes, is that right?

*T. Weisser:* The "brown fuzzies", a mossy-looking brown product, are on the bronzes, and the silver sulfide crystals are on the silver and gold pieces, and on anything that has silver attached to it in any way.

*M. Goodway:* I saw something that looked suspiciously like brown fuzzies on Chinese bronzes in the Art Institute of Chicago, in the exhibition cases. I don't think it's unique to the Walters.

*T. Weisser:* We've had it on all the bronzes: Chinese bronzes, ancient bronzes, Renaissance bronzes, 19th century bronzes, almost every type.

*M. Goodway:* I think it has to do with the enclosure, the stability, the time and so forth, but not necessarily that the enclosure be the Walters Art Gallery!

*T. Weisser:* I'm very glad to hear that!

*K. Holm:* We have experienced the growth of silver sulfide crystals on silver objects which have been held in place in the showcase by plasticine, which contains a fair amount of sulfur.

*M. Goodway:* We still don't know what the conditions are for producing whisker disfiguration, but I'm sure we'll all go home and look for them.

Question 29: What are the characteristics of earlier conservation treatments that might lead to scholarly confusion?

*M. Goodway:* Cyril Smith has one very good example of scholarly confusion.

*C. S. Smith:* Figure Q-29-1 illustrates this. It is a photomicrograph showing the structure of an iron fibula from Slovenia, La Tène period, ca. second century B.C. It is in the Mecklenberg collection at the Peabody Museum at Harvard University, and was one of the objects treated in hydrogen several decades ago by Willard M. Bright who proudly described his technique in the *Museums Journal*, 46, 1-5 (1946); also *Museumion*, 55-56 (1946) 57-53. The fibula was made of tapered wire, about 2 to 4 mm diameter, beautifully coiled in the middle to form a helical spring. The microstructure consists of ferrite grains with particles of cementite ( $Fe_3C$ ) in clusters that retain the outlines appropriate to the pearlite constituent in a steel containing about 0.3 percent carbon after cooling in air from a temperature not much over 750 °C. However, the cementite particles are not in the lamellar form one would expect of such pearlite. The heating in hydrogen has caused it to spheroidize and the boundaries between the ferrite grains pass through the center of these patches in a most unusual way. One can reach no firm conclusions regarding the structure on the metal in the fibula when it left the hand of its maker. One can only guess that the metal had been worked hot, had not been quenched, and that it may have been slightly cold-worked in the finishing stages--all points that could have been read unequivocally from the microstructure of the object before heating. Moreover, the hydrogen treatment seems to have removed iron oxide slag inclusions. The metal is unusually clean. Was it so originally?

No museum conservation laboratory would scrape all the writing off an ancient manuscript in order to have a clean piece of parchment to display, but, at least to someone concerned with technical history, the heating of metal artifacts is equally destructive of useful records of man's past knowledge and actions.

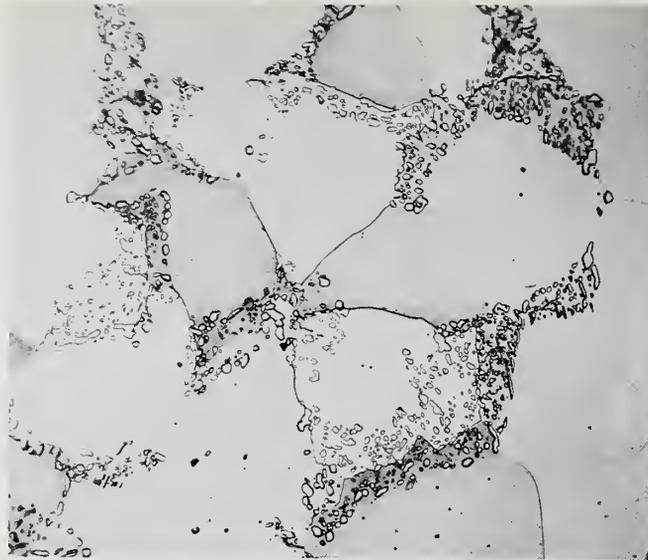


Figure Q-29-1. Microstructure of iron fibula, La Tène period, showing unusual structural details resulting from heating in hydrogen. Longitudinal section X500.

*M. Goodway:* There is one point that I would like to stress in regards to the example that Cyril has shown. When you put an iron object in the furnace for that long at that temperature, it shows signs of being at a controlled high temperature; what this tells the metallurgist is that there was a thermocouple present. Thermocouples have not been with us for even as long as a hundred years. To find that sort of evidence tends to make one believe that there has been fakery involved. When this is in an object that also shows microstructures that are okay for an antiquity it can be extremely puzzling until one knows what particular treatment this sample has been through. Does anyone else have examples of things of this sort that they have run into?

*W. T. Chase:* We run into this problem all the time. One of my favorite examples is in the Freer bronze book. (*The Freer Chinese Bronzes*, Vol. I, *Catalogue*, John A. Pope, Rutherford John Gettens, James Cahill, and Noel Barnard; Vol. II, *Technical Studies*, Rutherford John Gettens; D.C., 1967 and 1969. The bronze referred to here is FGA 24.12, catalogue number 99. It appears in Vol. I on page 508 and Vol. II on page 192.) It is a late Chou *hu* of ovoid, necked form, dating from *ca.* 450 B.C. There is a large area on one side that is absolutely devoid of corrosion. This area looks as if it was made yesterday. The rest of the bronze carries the normal corrosion products. The naked area was painted over, and not discernible at the time of purchase. One day Mr. Gettens got the piece out for examination, and he saw a large area of fluorescence under ultra-violet light. He took some solvent to it, and found underneath it nice, uncorroded bronze. The area he revealed looks dead new. It isn't; this area simply did not corrode.

In the Chinese Exhibition which came to Washington (*The Chinese Exhibition*, An Illustrated Handlist of the Exhibition of Archaeological Finds Of the People's Republic of China, National Gallery of Art, Washington, 1975; bronze rectangular *hu* number 117) there was another *hu* with an area like this on the side of the top of the vessel. This vessel was excavated from a known context, and had not been repaired.

In our examination of Chinese bronzes, we have seen a lot of repaint, repairs, etc. We've had people sample from repaired areas and publish the wrong composition. You constantly have to be on the lookout for earlier treatments.

Question 30: What methods are available for removing tarnish from metallic threads in textiles?

*M. Goodway*: Now there's a real problem. Has anybody got an answer besides the bristle brush?

*R. M. Organ*: The most recent method for cleaning textile threads is to do it while you are washing the textile. You simply make sure that your textile is in contact with an aluminum sheet or screen. If necessary, you sew it down so that the metal thread is in contact with the aluminum wire mesh. Wash it in your usual detergent, which may be Orvus and is undoubtedly alkaline; when the washing is finished, the silver thread is also clean. It is an electrochemical reduction process. I think it was Joe Columbus who noticed this for the first time at the National Gallery, and it is he who should be telling us about it.

We did some tests when we had to deal with a knife box which had silver braid decoration which was all black. We started out with the treatment intending to use this process. The process fails, of course, if you don't get electrical contact. We made tests of electrical conductivity along the length of the braid with a volt-ohm meter to find out how far apart we would have to put our stitches. The braid was broken in some places. We found that usually we had at least a one-centimeter distance which was electrically conductive. We stitched at those intervals, and it came out beautifully.

*J. Columbus*: This is an early sixteenth-century tapestry, about two and one-half by three and one-half meters in size, which we washed. First it was soaked overnight in a 10 percent glycerin solution. The next day it was washed with Orvus. We had it on an aluminum screen, which the washing tank contains for support of the tapestry, but we didn't get the expected results from the aluminum. I think this is chiefly because of the way the silver is woven into the tapestry; it just can't possibly touch all of the surfaces. I then looked for some other method.

In treating textiles with silver in them I have used silver dip. (Gold won't tarnish. For gold, it is just a matter of washing it with detergent.) Silver dip is a very acid, strong solution, but it is also very effective. If it is used fast enough, it can be safely used on a textile. For something as large as a tapestry the amount of time that it would have to remain in the solution might be excessive, and it might cause damage. The silver dip must be washed out with a detergent, quickly.

Figures Q-30-1 and Q-30-2 show one small area in the tapestry before and after brushing with a plastic brush. You can see the difference. The small plastic brush measures about 1/8 inch and about 1/4 inch wide. The ends of the bristle are very soft in feel to your finger. It is used with a rotary motion. It takes the corrosion off the surface, but there are many areas covered with adherent tarnish which the brush will not touch. There are many other areas where the weave is not sufficiently strong to even use the brush on it. Some non-mechanical method would have to be used.

Almost a third of the total area of the tapestry is woven with silver. A fragment of the thread was examined at the Carnegie-Mellon Institute, and they told us that the major component was silver; there were also trace elements of copper, gold, lead, and magnesium, of less than 0.1 percent. It was a fairly pure form of silver. Why it's tarnished on some areas and not others I don't know. The yarns here are wool and silk.

My question is, what are the hazards of using an electrolytic reduction method for removing tarnish from the silver thread?

*M. Goodway*: Do we have any answers to this? What about the use of possibly alkaline solutions on a protein fiber?

*R. M. Organ*: If you're prepared to wash it, then you can do it automatically during the washing process. If you're not prepared to wash it, electrolytic methods cannot be used at all.

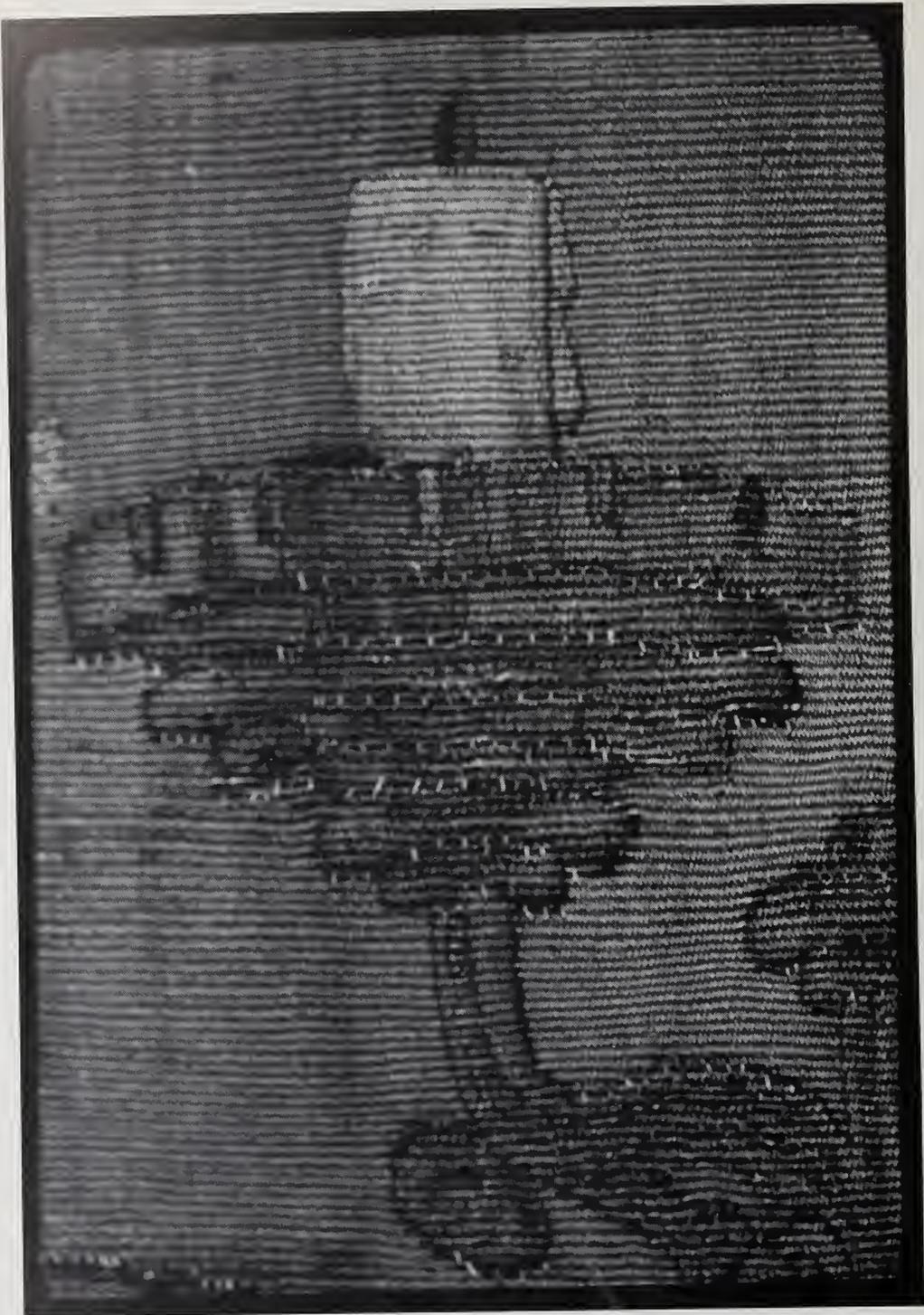


Figure Q-30-1. A detail of a sixteenth century tapestry with silver thread before cleaning with a soft plastic brush.

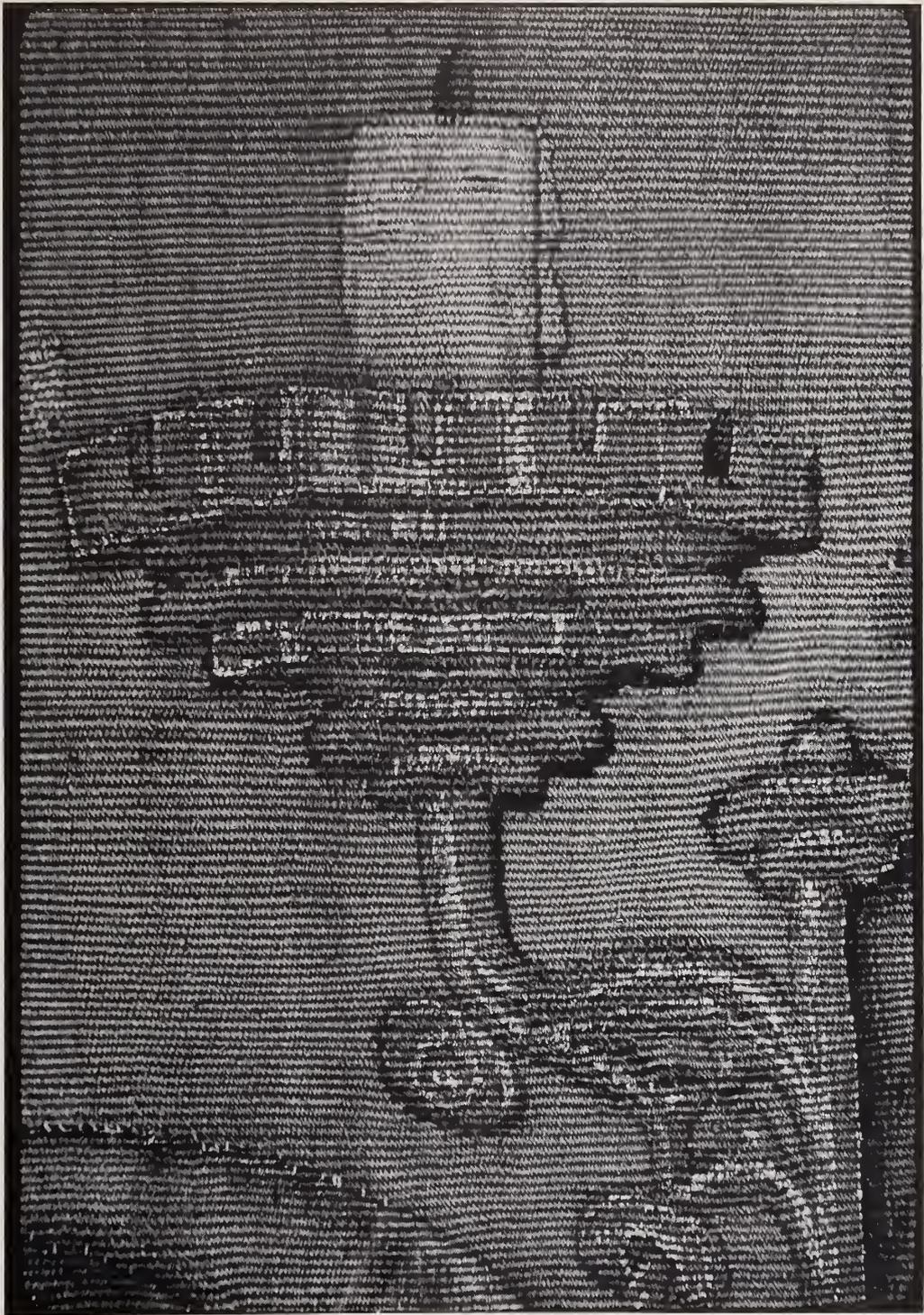


Figure Q-30-2. The same detail, after cleaning.

*E. McMillan:* A mild abrasive technique is the use of a plastic eraser which comes in two forms, a pencil shape and a rectangular form. It is called "Magic Rub"; I believe that the manufacturer is Faber/Castell. Obviously one must be able to clean off the eraser shavings, which may be done with gentle vacuum cleaning, air blower, or soft brush. This technique has been used in our laboratory on the metallic braid decorating saddles, for example. Chemically, this material is a vinyl chloride polymer heavily plasticized with phthalate plasticizer and heavily filled with (calcium) carbonate. We have not observed any ill effects from its use.

Question 31: What are the problems of the methods for consolidative reduction of objects of silver and lead? (No discussion)

Question 32: What are the recommended procedures for the removal or the stabilization of corrosion products found on tin-lead-antimony alloys, especially britannia metal and pewter? What techniques of examination are necessary to distinguish between active and inactive corrosion on these metals? (No discussion)

Question 33: How does one produce an initial protective film on bare metal during treatment?

*J. Kruger:* One possibility for iron and iron alloys is this: after producing the bare metal by some sort of treatment, one should then, by electrochemical means, bring the metal to a potential where a passive film will form on the surface. This can be done by the use of a potentiostatic device, which allows you to select the potential to which you wish to bring the metal surface. You should bring the potential into the "passive" region. At these potentials, a passive film will form on the metal surface.

The metal should be left in the passive region for as long as possible. This will make a good start at forming a protective film on the surface. It is anodization, actually, the production of anodic films. In the case of aluminum, these films are quite protective. They're not that protective for steel, and although there have been some attempts to form anodic films on copper, it is more tricky to do that.

It is also important to remember, in anodic film formation, to use a buffered electrolyte at near neutral pH values.

Question 34: What are the approaches in use by corrosion scientists which are applicable to the examination of metal objects?

*J. Kruger:* I suggest the use of constant potential techniques as an alternative to the constant current ones mentioned in this meeting earlier for electrolytic treatments. These devices can be constructed cheaply from operational amplifiers available in the market. References are given in my paper (p. 59).

*M. Pourbaix:* I remind you of what was said yesterday concerning the reduction of crusts and corrosion products and also of the very nice experiment which was shown by Jerry, on the work of Ulick Evans. I would like to suggest the following, which is very similar to methods being used in corrosion technology and corrosion science (see fig. Q-34-1).

If one has to look to an object with corrosion products on it, one could study and also treat it by a carefully-controlled cathodic treatment which would act on reduction. Having here (a) a calomel electrode and an anode (b) of platinum which may both be moved together on the surface of the object, and here a source of direct current (c), measurement

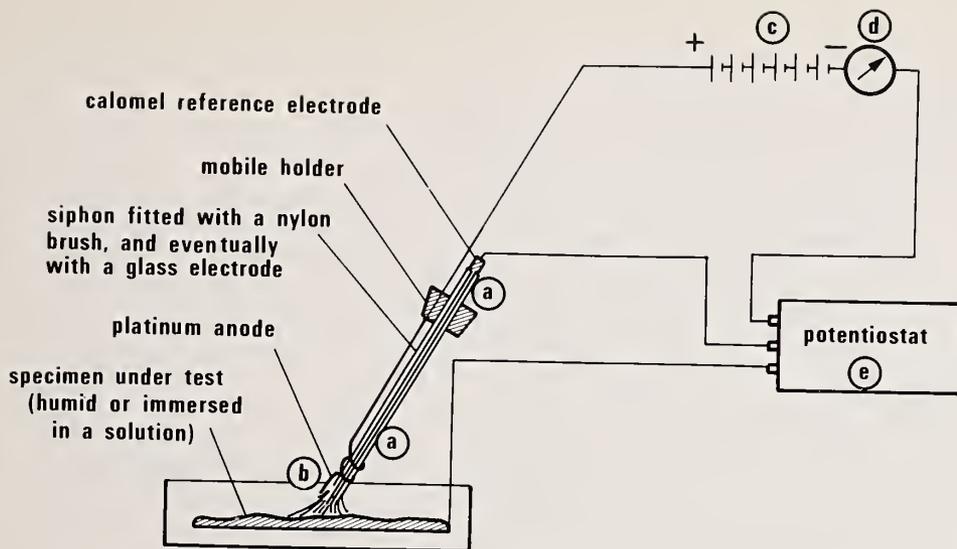


Figure Q-34-1. Device for potentiostatic reduction of specimens.

of the current which is passing (d), and a potentiostat (e) using the specimen as a cathode, it would be possible to impose, during treatment or in tests, a given electrode potential during a given period of time. I am not speaking here about the overall potential difference between anode and cathode, but about the potential difference between the cathode and the calomel reference electrode. It is now possible, with instruments which exist here at the Bureau, and which are gradually becoming very cheap, to make an experiment looking at the whole surface at given electrode potentials; this means that, if you believe in the electrode potential-pH diagrams, you may stay a given moment at a given point on the diagrams, and be sure that you are acting only on a given substance: for instance, only on the paratacamite, only on the cuprous chloride, only on the cuprous oxide, etc. For the examination of objects this might also be helpful. This approach is valid for every compound; you may do this on copper, on tin, on lead, on zinc, etc. Needless to say, the case of zinc is not very important, as zinc is always being dissolved.

When you wish to treat an object by reduction, it may be of interest to know that you have no hydrogen evolved, or, alternatively, that you do have hydrogen. Having here (a) a calomel electrode, which might be made with a plastic capillary, or included in a toothbrush which was used to apply this solution, or combined with a glass electrode with which you can measure the pH, these quantities may be controlled. In addition to the possibilities for analysis of metal and corrosion products, this should assist in controlling the treatment. You may have a selective treatment, you may start with a high electrode potential and then go down. This is being used not only in corrosion studies, but also in analytical chemistry, for instance. I don't know if this has ever been done. I would like to suggest that this be done for looking into the composition of corrosion products and also for the treatment, which may be of greater interest to you.

If you impose on a part of a specimen successively given decreasing values of electrode potential, you may proceed for instance, along line *L-4* in the copper-chlorine diagram given in figure Q-34-2. On point *1* the green paratacamite  $3(\text{CuOH})_2 \cdot \text{Cu} \cdot \text{Cl}_2$  is stable; on point *2* it may be reduced in a red cuprite  $\text{Cu}_2\text{O}$  and in *3* in metallic copper  $\text{Cu}$ ; in *4* this reduction to copper may occur together with evolution of gaseous hydrogen. The intensities of current indicated on the meter (d) of figure Q-34-1 would give an idea of the quantities of chemical species taking part to the different stages of the reduction.

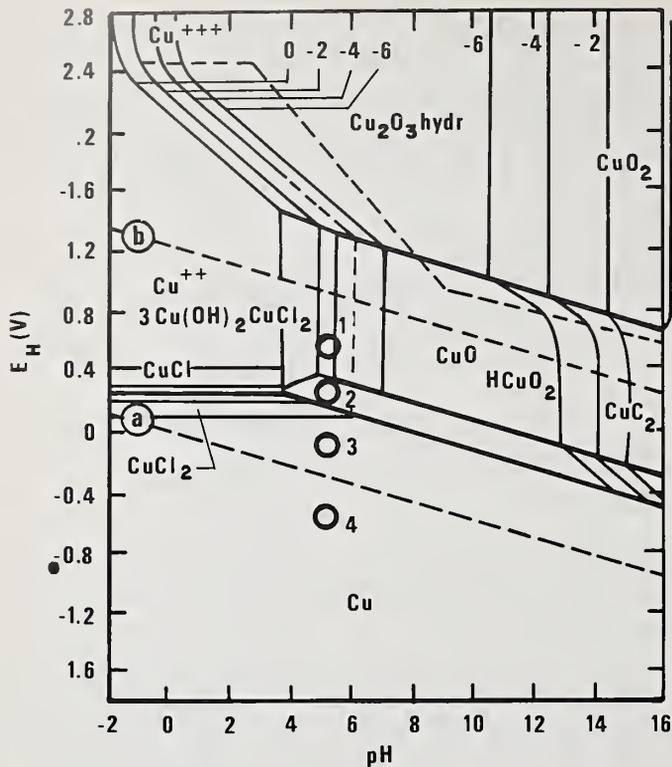


Figure Q-34-2. Potential-pH equilibrium diagram for the ternary system Cu-Cl-H<sub>2</sub>O at 25 °C (355 ppm Cl).

Figure Q-34-3 relates to the tin-water system. On point 1 you are in the region of passivation by SnO<sub>2</sub> (cassiterite). On point 2 this oxide may be dissolved and on point 3 metallic tin may be formed, which will lead on point 4 to the formation of unstable gaseous tin hydride SnH<sub>4</sub>. Below line *a* gaseous hydrogen may be evolved.

According to figure Q-34-4, which relates to lead, due to the high solubility of PbO, the metal is dissolved on point 1 if no CO<sub>2</sub> is present; if there is CO<sub>2</sub>, the white lead carbonate PbCO<sub>3</sub> (cerussite) is stable. On point 2 metallic lead may be formed, leading on point 3 to the formation of unstable gaseous lead hydride PbH<sub>2</sub>.

Figure Q-34-5 shows that zinc will most of the time be leached out from corrosion products, due the high solubility of its lower oxides, carbonates, *etc.* By putting a piece of metallic zinc in contact with corroded bronze in a solution corrosive to zinc, according to the method suggested by U. R. Evans, and shown in figure Q-12-1 (p. 218), the electrode potential at the contact between bronze and zinc will be in the neighborhood of point 1 (about -800 mV or -1050 mV). As shown by figures Q-34-2 through 4, this may reduce the corrosion products of copper, tin and lead with deposition of the corresponding metals.

Concerning silver, a diagram relating to the system silver-sulphur-water, established by Horvath, which I do not have here with me, may be helpful for predetermining the conditions where the black silver sulfide may be reduced to metallic silver.



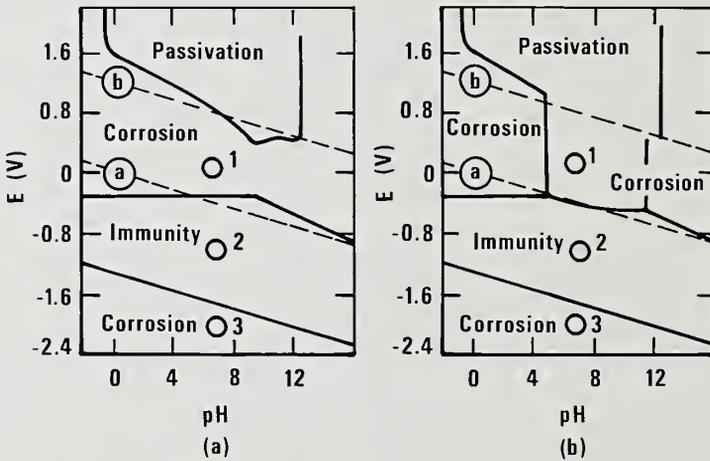
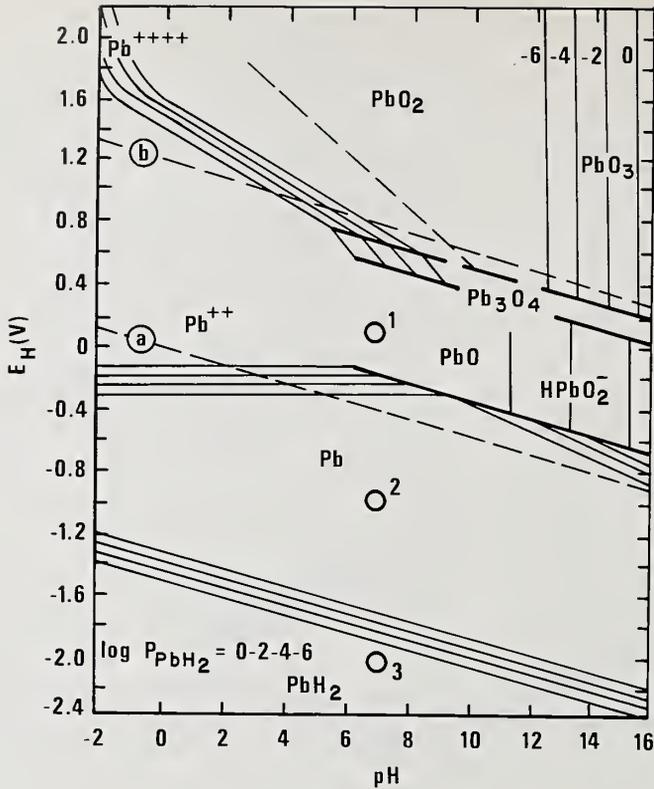


Figure Q-34-4. Potential-pH equilibrium diagram for the system lead-water at 25 °C (top). Theoretical conditions of corrosion, immunity, and passivation of lead (at 25 °C); (a) for solutions free from CO<sub>2</sub>; and (b) for solutions containing CO<sub>2</sub> (1 g-mol/l).

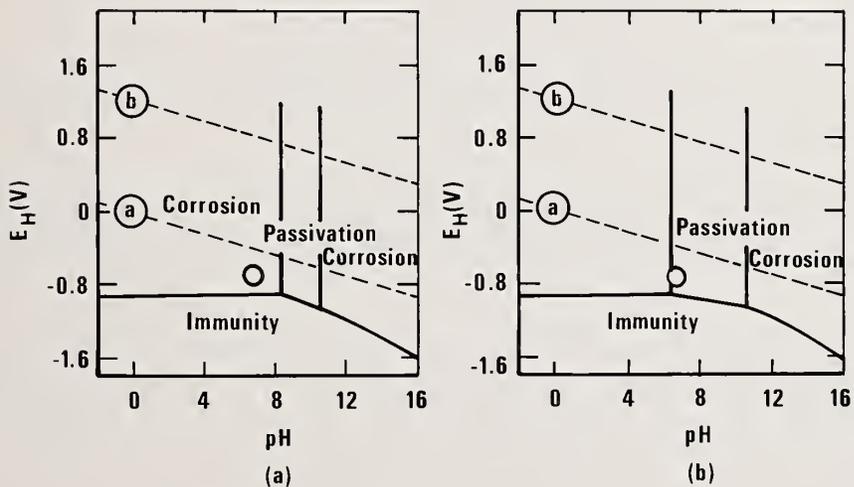
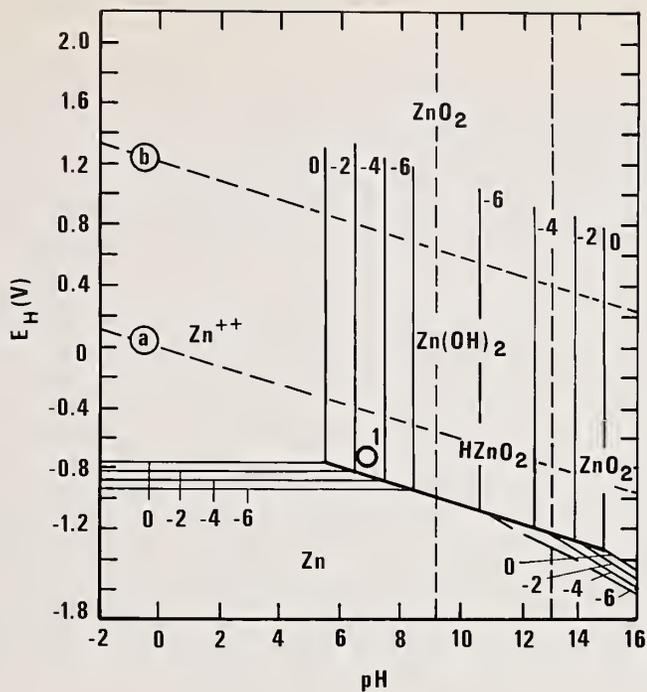


Figure Q-34-5. Potential-pH equilibrium diagram for the system zinc-water at 25 °C (top). Theoretical conditions of corrosion, immunity, and passivation of zinc (at 25 °C); (a) for solutions free from  $\text{CO}_2$ ; and (b) for solutions containing  $\text{CO}_2$  (1 g-mol/l).

Question 35: What sort of research would conservators like to see corrosion scientists do?

*W. T. Chase:* I guess the answer to that is really "a lot." One of the problems that I've been very interested in over the last few years is the treatment of bronze disease with benzotriazole. We talked about the criteria for its effectiveness yesterday. It seems to work, and it seems to stop what looks like ongoing corrosion. At least it stops the bright green stuff from coming out. But the question is, why does it work? Where is it going in the structure of these corroded bronzes? I don't think that at this point anybody knows. Finding out the answers is a project that we would really like to see come corrosion scientist or someone who has access to instruments which would be helpful to pick up and run with.

*M. Pourbaix:* I have learned this morning that some work has been done using INCRAIac, which is made with benzotriazole, on gold. This is also where more research may improve the situation. The color of the structures doesn't seem to be the color of gold.

*R. M. Organ:* A research that I would like to see done is one directed to discovering the conditions under which bronzes are attacked and eaten away invisibly in the presence of cuprous chloride. The sort of experiment that might yield the answers is to set up a system with cuprous chloride on the surface of metallic copper, and measure the corrosion potential under various partial pressures of oxygen. If there is not oxygen present, this might simulate the situation where we have, in a real bronze, cuprous chloride covered over with an impermeable crust of cuprous oxide. At the other extreme, with the partial pressure of oxygen as we find it in the atmosphere, this would simulate the condition where we have the more normal cuprous oxide cover, which is permeable. This experiment would give us a range of conditions, and would tell us whether and how fast the copper is being attacked.

*M. Goodway:* You are suggesting that the cuprous chloride is, perhaps, not so much of a problem except when the oxygen is exhausted.

*R. M. Organ:* Yes, quite. As far as we know, we can stop all this happening just by keeping things dry and free from oxygen. I'd like to know precisely what the conditions would have to be. Alternatively, it would be nice to know at what value of ambient relative humidity does the reaction stop.

*M. Goodway:* Are there some other questions, perhaps, of interest? Well, it seems to me that this is one of the most important questions on the list. In our thinking about the phenomena that we see on objects and in trying to formulate answers, it might be useful to formulate our questions more exactly, and try to marshal our evidence very carefully, and talk to a corrosion expert.

*T. Weisser:* Would it be possible to have a list of those corrosion scientists and other scientists who would be willing to do analysis for museums? Often museums do not have sophisticated equipment or time and funding to do this sort of work, and it would be a great help to know where to get analyses done.

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March 17-19, 1976

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4. TITLE AND SUBTITLE Corrosion and Metal Artifacts -- A Dialogue Between Conservators and Archaeologists and Corrosion Scientists		5. Publication Date July 1977	6. Performing Organization Code
7. AUTHOR(S) B. F. Brown, H. C. Burnett, W. T. Chase, M. Goodway, J. Kruger, and M. Pourbaix		8. Performing Organ. Report No.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		10. Project/Task/Work Unit No.	11. Contract/Grant No.
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) National Bureau of Standards, Washington, D.C., American University, Washington, D.C., Smithsonian Institution, Washington, D.C., Washington Conservation Guild, CEBELCOR, Brussels, Belgium		13. Type of Report & Period Covered Final	14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES Library of Congress Catalog Card Number: 77-608103			
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)  This book is the formal report of the proceedings of the seminar on Corrosion and Metal Artifacts. The volume contains the tutorial lectures on the aspects of corrosion science and engineering of relevance to conservators and archaeologists and, background lectures which are addressed to corrosionists with activities and problems in the conservation of metallic artistic artifacts. The report also contains the full discussion (attendee) of the structured questions distributed before the meeting. The report is well documented with illustrations.			
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons) Archaeological finds, preservation of; conservation of metal artifacts; corrosion, inhibiting of; corrosion, treatment methods; metal artifacts, restoration of; patina, natural; patina, artificially produced.			
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**NOTE:** At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash. D. C. 20056.

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