Methods for Conserving Archaeological Material from Underwater Sites

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Conservation Files

The following conservation files were first posted on the World Wide Web during the 1998 spring semester for use by the students enrolled in ANTH 605, Conservation of Cultural Resources, at Texas A&M University in College Station, Texas. These files constitute the laboratory manual that is used in conjunction with the course. The emphasis of the course is on the conservation of material from underwater sites, especially marine sites, but the conservation of material from terrestrial sites is also discussed. While this laboratory manual is posted for use by students enrolled in the ANTH 605 class, others may download and use the manual; proper credit, however, must be given. (See the proper citation at the end of this page.)

This laboratory manual has been compiled from material gathered over the past 20 years. It consists of much of the data presented in a number of publications by the author, as well as class handouts. Particularly important resources include:

1973-1998: Numerous mimeographed class handouts compiled and distributed to the conservation classes taught by the author at the University of Texas at Austin and Texas A&M University.

1976: *Conservation of Metal Objects from Underwater Sites: A Study in Methods*. Texas Antiquities Committee Publication No. 1, Austin, Texas.

1996: *Basic Methods of Conserving Underwater Archaeological Material Culture*. Legacy Resource Management Program, U.S. Department of Defense, Washington, D.C.

The last publication is largely a compilation of the first two and is very similar in content to this on-line manual. The current manual does differ from the 1996 publication in that material has been added or updated in some sections. This conservation class manual changes each time it is used, and new changes and additions are being planned as preparations are made to post this version. Each time the manual is posted, it will be dated to reflect new changes, and a new revision number will be assigned. Consult the date and revision number to see if you have the most recent version. Revision 0, dated January 1, 1998, starts the series.

The general reference for the entire conservation manual is as follows:

Donny L. Hamilton

1998. Methods of Conserving Underwater Archaeological Material Culture. Conservation Files: ANTH 605, Conservation of Cultural Resources I. Nautical Archaeology Program, Texas A&M University, World Wide Web, http://nautarch.tamu.edu/class/ANTH605.

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Overview of conservation in archaeology; basic archaeological conservation procedures

IN THIS FILE:

Artifact preservation is one of the most important considerations when planning or implementing any action that will result in the recovery of material from a marine archaeological site. It is the responsibility of the excavator or salvor to see that material recovered is properly conserved. The conservation phase is time consuming and expensive, often costing more than the original excavation. Without conservation, however, most artifacts will perish, and important historic data will be lost. The loss is not just to the excavator but also to future archaeologists, who may wish to reexamine the material.

Artifacts recovered from a salt water environment are often well preserved but of a very friable nature. In general, artifacts recovered from anaerobic marine environments (i.e., buried in sediment) are recovered in better condition than artifacts recovered from aerobic marine environments (i.e., the water column and surface sediment). Artifacts not properly conserved in a timely manner are apt to deteriorate at a very rapid rate and subsequently become useless as diagnostic or display specimens. Organic material, i.e., leather, wood, textile, rope, plant remains, etc., if allowed to dry without conservation treatment, can crumble and become little more than a pile of dust and debris in a matter of hours. Iron, on the other hand, can last for a few days to months according to the size and density of the artifact; however, it too will eventually deteriorate and become useless as a display or diagnostic specimen. Bone, glass, pottery, and similar material will, if not conserved, slowly devitrify and, in extreme cases, degenerate to a pile of worthless slivers. For these reasons, conservation must be of paramount concern when the excavation of a marine archaeological site is considered.

Before discussing the conservation of archaeological materials, it is helpful to examine and clarify the various definitions of the term 'artifact.' For the purposes of this manual, the definitions given in the United States Code of Federal Regulations 36, Part 79, section 4 are applicable (U.S. Department of Interior 1991):

1. Collection: material remains that are excavated or removed during a survey, excavation, or other study of a prehistoric or historic resource, and associated records that are prepared or assembled in connection with the survey, excavation, or other study.
    1. Material remains: artifacts, objects, specimens, and other physical evidence that is excavated or removed in connection with efforts to locate, evaluate, document, study, preserve, or recover a prehistoric or historic resource. Classes of material remains include, but are not limited to:
        1. Components of structures and features (such as houses, mills, piers, fortifications, raceways, earthworks, and mounds);
        2. Intact or fragmentary artifacts of human manufacture (such as tools, weapons, pottery, basketry, and textiles);
        3. Intact or fragmentary natural objects that are used by humans (such as rock crystals, feathers, and pigments);
        4. By-products, waste products or debris resulting from the manufacture or use of man-made or natural materials (such as slag, dumps, cores, and debitage);
        5. Organic material (such as coprolites, and vegetable and animal remains);
        6. Human remains (such as bones, teeth, mummified, flesh, burials, and cremations);
        7. Components of petroglyphs, pictographs, intaglios, or other works of artistic or symbolic representation;
        8. Components of shipwrecks (such as pieces of the ship's hull, rigging, armaments, apparel, tackle, contents, and cargo);
        9. Environmental and chronometric specimens (such as pollen, seeds, wood, shell, bone, charcoal, tree core samples, soil sediment cores, obsidian, volcanic ash, and baked clay); and
        10. Paleontological specimens that are found in direct physical relationship with a prehistoric or historic resource.

This section of definitions goes on to discuss what constitutes *associated records* resulting from an archaeological excavation. This manual is concerned only with cultural material or collections resulting from an archaeological excavation; it is does not consider archival or art collections for which there are established standards of conservation that are quite similar in many ways to the federal standards established for archaeological material. What is important is that all relevant documentation be recorded from the start, including all records pertaining to conservation treatment, and that a complete set of records accompany the collection or any artifact separated from the collection.

The following section discusses alternative methods for conserving archaeological artifacts recovered from marine sites. Techniques which may only be appropriate for the conservation of artifacts from terrestrial sites will not be discussed. The section is divided into eight major headings:(1) Introduction to Marine Conservation, (2) Synthetic Resins and Adhesives, (3) Ceramics, (4) Glass, (5) Bone and Ivory, (6) Wood, (7) Leather, and (8) Metals. Appropriate subdivisions will be found under each major heading. All the treatments discussed in this manual do not conflict with any known federal regulations and laws; from this perspective, therefore, there is no limitation on their use.

It is necessary to make a brief statement regarding the level of effort and resources necessary to perform each technique. As each treatment is discussed, the required chemicals are listed, and any necessary equipment is either listed or obvious. For example, if an object is to be rinsed in sodium carbonate, it is obvious that sodium carbonate, water, and a vat necessary to hold the object is required. If the solution and object must be heated during the rinsing process, then a metal vat and a source of heat (i.e., gas stove, electric hot plate, or oven) is required. There are too many variables involved in each treatment to arrive at any specific cost; the cost is dependent upon the size of the artifact and the length of time required for treatment, neither of which can be reliably estimated. How much does it cost to treat by a given treatment a spike from a ship as opposed to a cannon from the same ship? The exercise merely becomes a numbers game that serves no useful purpose.

Any discussion of both near-term and long-term conservation goals is equally meaningless. In conservation treatments, there are no near-term goals as opposed to long-term goals; the only ethical alternative is to treat the artifact so that is stable in the environment in which it is to be stored or displayed. There are some viable alternative conservation treatments for particular artifacts that can be performed by untrained personnel and with a minimum amount of specialized equipment; these treatments, however, are employed only when they will successfully preserve the artifact. For the purposes of this manual, near-term conservation goals will be considered those that deal with the proper storage of an artifact until the long-term goal of suitable treatment can be performed. Where possible, comments relevant to these two goals will be made. Near-term goals are also most relevant when it comes to making decisions such as whether an agency wants to contract out the conservation to existing laboratories or establish its own conservation capability in order to conserve all future artifacts that might be acquired.

BASIC REFERENCES

There is a considerable body of literature on the conservation of archaeological material recovered from all environments, including that from marine sites. However, in recent years, a significant amount of the available data has been compiled in several publications, and the majority of the knowledge that is required to conserve artifacts from marine sites can be obtained from a relatively small number of publications. In addition to this on-line manual, the following publications should be consulted for additional details. These are the most important publications in the field of marine archaeology conservation to date.

Cronyn, J. M. 1990. *The Elements of Archaeological Conservation*. Routledge, London.

Grattan, D. W., ed. 1982. *Proceedings of the ICOM Waterlogged Wood Working Group Conference*.
Waterlogged Wood Working Group, Committee for Conservation, ICOM, Ottowa.

Hamilton, D. L. 1975. *Conservation of Metal Objects from Underwater Sites: A Study in Methods*.
Texas Antiquities Committee Publication No. 1, Austin, Texas.

_____. 1996. *Basic Methods of Conserving Underwater Archaeological Material Culture*.
US Department of Defense Legacy Resource Management Program, Washington, DC.

ICOM Waterlogged Wood Working Group Conference. 1985. *Waterlogged Wood: Study and Conservation*. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference,
Grenoble, France.

Pearson, C., ed. 1987. *Conservation of Marine Archaeological Objects*. Butterworths, London.

Plenderleith, H. J. and A. E. A. Werner. 1977. *The Conservation of Antiquities and Works of Art*.
Oxford University Press, Oxford.

These basic references, combined with various articles and papers from the *Journal of the American Institute for Conservation*, the Canadian Conservation Institute, the Getty Conservation Institute, the International Council of Museum Papers, and the International Institute for Conservation and Artistic Works in London (which publishes *Studies in Conservation*, the major journal for conservation), form the core of the information on the conservation of material from marine sites (see bibliography). These are supplemented by various university theses, papers prepared by conservation laboratories that are not widely distributed, personal communications from conservators, and personal experiences.

The following discussion on conservation is condensed from a combination of the above sources. This discussion, however, cannot replace consulting these references for a more detailed presentation. A 'cookbook' approach to archaeological conservation should never be taken. A range of personal experience and a thorough knowledge of the alternative techniques available is required to contend with the array of material to be treated. Even with this knowledge and experience, there will always be artifacts that simply cannot be successfully conserved; furthermore, there will always be instances when, for any number of reasons, it is simply not practical to conserve an artifact.

CONSERVATION ETHICS

The following are some of the more pertinent conservation ethics adopted by the International Institute for Conservation (IIC) as guidelines for all conservators. These standards were developed for art conservation but are also generally applicable to archaeological conservation. The statements in maroon-colored font are taken directly from IIC. Additional comments follow some of these entries to help clarify them. A knowledge of these ethical considerations helps to understand the reasoning behind a conservator's decision and selection of a procedure for treating an artifact.

1. Respect for Integrity of Object.
   All professional actions of the conservator are governed by unswerving respect for the aesthetic, historic and physical integrity of the object.

   Regardless of an artifact's condition or value, its aesthetic, historic, archaeological, and physical integrity should be preserved. After conservation, an object should retain as many diagnostic attributes as possible. The preservation of the diagnostic attributes of the object being conserved is of utmost importance in selecting a conservation treatment.

2. Competence and Facilities
   It is the conservator's responsibility to undertake the investigation or treatment of an historic or artistic work only within the limits of his professional competence and facilities.
3. Single Standard
   With every historic or artistic work he undertakes to conserve, regardless of his opinion of its value or quality, the conservator should adhere to the highest and most exacting standard of treatment. Although circumstances may limit the extent of treatment, the quality of the treatment should never be governed by the quality or value of the object. While special techniques may be required during treatment of large groups of objects, such as archival and natural history material, these procedures should be consistent with the conservator's respect for the integrity of the objects.
4. Suitability of Treatment
   The conservator should not perform or recommend any treatment which is not appropriate to the preservation or best interests of the historic or artistic work. The necessity and quality of the treatment should be more important to the professional than his remuneration.

   No treatment should be used that is not in the best interest of the object. Any treatment, even if less expensive, extensive, or time consuming should be avoided if there is a possibility of damaging the artifact. For these reasons, near-term and long-term goals are not pertinent when it comes to deciding the best treatment for an artifact.

5. Principal of Reversibility
   The conservator is guided by and endeavors to apply the 'principle of reversibility' in his treatments. He should avoid the use of materials which may become so intractable that their future removal could endanger the physical safety of the objects. He also should avoid the use of techniques, the results of which cannot be undone if that should become desirable.

   No treatment should be used that will result in damage to the object if it has to undergo further treatment. In general, all treatments should be reversible. This requirement recognizes that a conservation treatment may not last indefinitely nor remain superior to all future techniques. If the treatment is reversible, the option to re-treat is always open, and the continued preservation of the material is assured. However, in the conservation of material from archaeological sites and underwater marine sites in particular, this tenet often cannot be followed. The conservator has only one chance to preserve the artifact; in order to do this, non-reversible techniques may need to be used. The concept of reversibility vs. non-reversibility in archaeological conservation is currently undergoing close scrutiny, as it is a well-known fact the many so-called 'reversible processes' are *not* reversible. In fact, there is more potential for successful re-treatment of waterlogged wood previously treated with the 'non reversible' silicone oil process than there is for waterlogged wood treated by 'reversible' processes, such as polyethylene glycol.

6. Limitations on Aesthetic Reintegration
   In compensating for damage or loss, a conservator may supply little or much restoration, according to a firm previous understanding with the owner or custodian and the artist, if living. It is equally clear that he cannot ethically carry compensation to a point of modifying the known character of the original.
7. Continued Self-Education
   It is the responsibility of every conservator to remain abreast of current knowledge in his field and to continue to develop his skills so that he may give the best treatment circumstances permit.
8. Auxiliary Personnel
   The conservator has an obligation to protect and preserve the historic and artistic works under his care at all times by supervising and regulating the work of all auxiliary personnel, trainees and volunteers under his professional direction. A conservator should not contract or engage himself to clients as a supervisor of insufficiently trained personnel unless he can arrange to be present to direct the work.

   In marine archaeology, conservation is not simply a set of procedures and treatments. Often the conservator is the first and, in the case of some very fragile items, the only person to see the actual artifact. The conservator's responsibilities are that of archaeologist, mender, caretaker, and recorder of the artifacts that come into his or her care. Conservation, like archaeology, is a state of mind: a state of mind which holds a deep concern for the integrity of the artifacts and what they represent as remnants of history.

TENETS OF CONSERVATION

When treatment is accorded an object, it can include both conservation and restoration. Conservation refers to the process of documentation, analysis, cleaning, and stabilization of an object. The main objectives of the cleaning and stabilization are protection against, and prevention of, adverse reactions between the object and its environment. Restoration refers to the repair of damaged objects and the replacement of missing parts. A specimen may undergo both conservation and restoration, but in all cases, the former has priority over the latter. Restoration should never be initiated without conservation (Coremans 1969:16). Only the conservation aspect of artifact treatment is considered in this publication.

Because artifacts are a primary element of archaeological inquiry, artifact conservation should not detract from the natural appearance of the object nor alter any of its scientific attributes. The conservator should strive to process specimens so that they retain as much diagnostic data as possible and yet remain chemically stable. Every attempt should be made to preserve as much as possible of the original surfaces, form, and dimensions, i.e., the diagnostic attributes of the object. In addition, all treatments should, if feasible, be reversible when ever possible. This last requirement recognizes that a conservation treatment may not last indefinitely nor remain superior to all future techniques. If it is reversible, the option to re-treat is always open, and the continued preservation of the material is assured.

When objects are treated, the basic attitude and approach should be cautionary and similar to that outlined by Plenderleith and Werner (1971:16-17), who state that the past history of an artifact may impart features of significance pertaining to age and provenience, which can validate the authenticity of the artifact. Therefore, a preliminary examination of the object must be made in order to determine a course of action that will preserve the integrity of the specimen and maintain any significant attributes or any features relating to its manufacture or microstructure. In some cases, a corrosion layer may contain valuable archaeological data, in which case it should be preserved and not indiscriminately removed. Only in those instances where the corrosion is unstable, conceals underlying details, or is aesthetically displeasing should it be removed. Above all, one should heed the cautionary advice offered by Plenderleith and Werner (1971:17): "This work calls not only for knowledge, foresight, ingenuity, and dexterity, but for infinite patience. It should never be hurried."

The recording and preservation of the basic data derived from any given artifact is essential and must be of utmost concern to all laboratories which process archaeological material. In archaeological conservation there is often more to consider than simply the preservation of individual artifacts. One duty of the conservator is to stabilize the artifact so that it retains its form and diagnostic data. When treating archaeological material that requires documentation of context, as well as preservation, the documentation demands equal emphasis and first priority. The interaction between marine archaeology and conservation is a perfect example of the intimate relationship that can exist between archaeology and conservation in general.

It is important to continually stress that the proper conservation of artifacts is critical not only because it preserves the material remains of the past that are recovered, but also because it is capable of providing almost as much archaeological data as do field excavations and archival research. This is possible if the problems of conservation are approached with an archaeologically oriented view of material culture. This view contributes a sensitivity to the nature and potential value of the archaeological record and the importance of various types of association. An underlying premise of archaeology is that the distribution of cultural material, as well as its form, has cultural significance and is indicative of past cultural activities. By studying the material remains of a culture, considerable insight into its workings can be derived.

THE ROLE OF CONSERVATION IN MARINE ARCHAEOLOGY

The development of underwater archaeology is almost entirely a post World War II phenomenon resulting from the development of scuba, which made submerged sites, especially those in shallow water, accessible. Technological progress now allows archaeologists access to even deeper wrecks, such as the CSS *Alabama* and the USS *Monitor*. Nonetheless, underwater archaeology shares common techniques and standards with its terrestrial counterpart. Goggin (1964:302) describes underwater archaeology as " the recovery and interpretation of human remains and cultural materials of the past from underwater by archaeologists"; this definition is acceptable only if it is qualified by a more explicit definition, such as "archaeology can be defined minimally as the study of the interrelationship of form, temporal locus, and spatial locus exhibited by artifacts. In other words, archaeologists are always concerned with these interrelationships whatever broader interests they may have, and these interrelationships are the special business of archaeology" (Spaulding 1960:439). These definitions serve to differentiate archaeology, which is a scientific investigation, from uncontrolled salvage and 'treasure hunting,' which are oriented toward relic or object collecting.

Categories of underwater archaeological sites, in salt or fresh water, include (1) submerged refuse sites; (2) inundated settlements or harbors; (3) shrines or sacred localities, such as the cenote at Chichen Itza; and (4) shipwrecks (Goggin 1964:299). While the conservation of shipwreck material is the topic of this manual, the techniques reviewed here are applicable to metal objects from any underwater site and most terrestrial sites.

Shipwrecks are a special kind of archaeological site which have been compared to time capsules: "The very suddenness of such disasters has made these underwater wreck sites, in effect, accidental time capsules. Thus there is deposited in the waters of the world a mass of materials--dating from the earliest historical times to the present--capable of being located, recovered, identified, and preserved" (Peterson 1969: xiii-xiv). While all of this is true, but it is a very artifact-oriented view. There are much more data available in these 'time capsules' than simply collections of objects and an index to material remains. To an anthropologist or a historian, human activities are of more interest than the ship itself or its contents. It is only through viewing the ship as a component of a cultural system and by structuring the interrelationships of the material remains within the shipwreck site that the story of a social group may be revealed.

When a ship sets sail, it is a self-sufficient, self-contained segment of its culture with samples of what are considered essential commodities for periods of isolated life at a given time. The crew, the officers, and the passengers often represent a cross section of different social classes with class-distinctive quarters and selected material goods. Their distribution in the ship may be represented even after wrecking. It is also possible that data concerning technology, trade, personal belongings of the crew and passengers, armaments, armament policy, monetary systems, navigation, ship construction, shipboard life, and possibly societal and functional implications, as indicated by the distribution of certain kinds of remains, can be obtained. Tax, ownership, mining, shipping, or other types of identification, often stamped or marked on individual artifacts, provide additional leads. This potential wealth of information can often be checked and compared with archival documents for corroboration and reinterpretation.

It is possible to retrieve these data only if well-organized, problem-oriented excavations are conducted. Borhegyi (1964:5), in reference to underwater archaeology, states that "no one today would be forgiven if he employed the nineteenth century excavation techniques." At present, any well-planned underwater excavation should include properly planned conservation prior to the excavation and no one should be forgiven if conservation is cursory or slighted. If conservation plans are not included, more data may be lost than gained.

The recovery of artifacts from archaeological sites destroys the archaeological context, which remains preserved only in the notes, drawings, and photographs made by the archaeologist in the field. Careful recording is a necessity, otherwise the operation is not an archaeological excavation but rather an uncontrolled salvage operation producing a simple inventory of artifacts. Even the limited knowledge derived from uncontrolled excavations can be significant and valuable because it usually can be determined that the materials were associated with a single ship of a certain nation within a certain time span. All associations are not culturally significant, but if one approaches each archaeological excavation with the basic assumption that many associations are meaningful, and excavates accordingly, additional systemic and intra-site problems can be considered.

The conservation of metal artifacts from a marine site, and to a lesser degree metal artifacts from fresh water sites, is only remotely analogous to the conservation problems presented by other fields of archaeology. When artifacts of every variety, but particularly metals, are recovered from the sea (especially warm-water environments, such as the Caribbean and the Mediterranean), they are commonly encrusted with thick layers of calcium carbonate, magnesium hydroxide, metal corrosion products, sand, clay, and various forms of marine life, such as shells, coral, barnacles, and plant life. The term 'encrustation' refers to the conglomerations that may contain one or more artifacts. Such conglomerations may range from the size of a single coin to huge masses weighing several thousand pounds and which contain hundreds of individual objects made of many different materials.

The proper conservation of encrustation with their concealed contents is analogous to an excavation square within a site. Any laboratory that processes encrustation has the responsibility to (1) preserve and stabilize the artifacts as well as conservation technology permits, and (2) recover as much useful data as possible. Considerable information exists in the form of associations recoverable only by in situ observations made by the conservator. Extensive records must be maintained, including notes on the encrustation, the objects it contains, and the preservation techniques used, as well as color, black-and-white, and X-ray photographs. Casts must be made of disintegrated objects and of significant impressions left in the encrustations. Care must be taken with common items, such as potsherds, cloth fragments, spikes, straps, and animal bones. Even less obvious remains like impressions of seeds and insects (such as impressions of cockroaches found in an encrustation from the 1554 Spanish Plate Fleet excavation) must be detected and recorded. In other words, the conservator is in a unique position to supply the archaeologist with valuable evidence and to provide the laboratory with basic conservation data for research. As will be stated again: the investigation of large encrustation with their concealed contents is analogous to the excavation of a structure within a site; the location and orientation of each encrustation must be accurately plotted before it is raised from the seabed so that the data recovered in the conservation laboratory can be related back to the site.

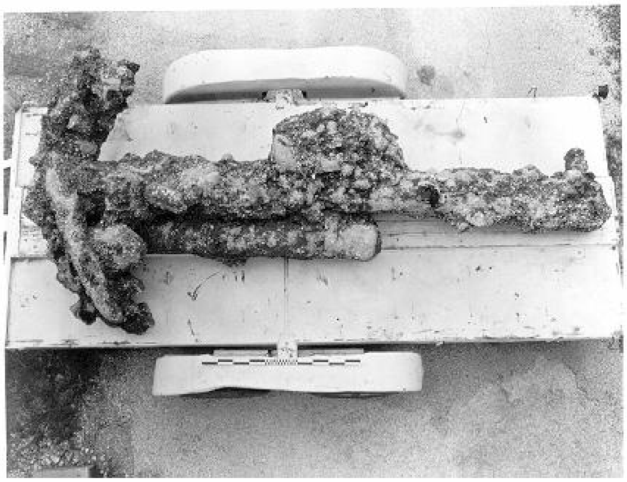


Figure 1.1

Figure 1.1 illustrates one of the several large encrustation recovered from the site of the *San Esteban*, one of the three ships of the 1554 Spanish Plate Fleet wrecked off Padre Island, Texas. This single encrustation, which contained two anchors, a bombardetta gun with its wooden undercarriage, breech blocks, and a multitude of smaller objects, was over 4 m long and weighed over 2 tons. A laboratory must have sufficient space and equipment to accommodate such a large object, mechanically clean it, properly conserve recovered specimens, and, possibly, cast a number of natural molds of disintegrated objects. Furthermore, it may be necessary to prepare the encased artifacts for display. The laboratory must have forklifts, chain hoists, large vats, specialized DC power supplies, hundreds of kilograms of chemicals, and thousands of liters of de-ionized water, among other resources, to perform the job. The conservation laboratory has to take an encrustation such as that depicted in Figure 1 and turn out an array of stabilized artifacts.

The degree and extent of artifact encrustation is dependent upon the local sea environment. Encrustation does not form in fresh water and is extensive in tropical sea water. In the cold sea water of the north, for example, encrustation formation is minimal. In environments where the encrustation is thin, the role of casting is less important, and the number of artifacts associated with any encrustation decreases.

It is often maintained by some treasure hunters that no artifact provenience other than site designation is necessary, since associated relationships are not significant. It is assumed that any patterned distribution of the ship's parts and contents will have been destroyed through years of wave action and shifting sand. This may be true for some wrecks, but such an arbitrary attitude has surely been responsible for the destruction of considerable archaeological data. What is important to remember is that careful documentation, both in the field and in the laboratory, conscientious conservation, and good laboratory records provide data that can be manipulated to solve a variety of problems and conceptual schemes, be they anthropologically or historically oriented. Conservation approached in this manner contributes considerable data to the understanding of any shipwreck.

BASIC CONSERVATION PROCEDURES

Conservation must be a part of any archaeological project; this is especially true for wet sites, i.e., archaeological sites located in bogs, rivers, and oceans. Of the wet sites, those found in salt water present the greatest challenge to the conservator. Artifacts from a marine environment are saturated with salts that must be removed when an artifact is recovered. In addition, the salt water environment accelerates the corrosion processes of many metal artifacts. If the salts are not removed and the artifacts treated in a timely manner, they will, over time, deteriorate and become useless as a diagnostic or museum display specimen.

Prior to any excavation, the archaeological project director should take the following factors into consideration:

1. Anticipate what may be encountered in the archaeological project, be it a survey, testing or a full-scale excavation.
2. Be aware of the types of breakdown, corrosion, and degradation that the recovered material may undergo.
3. Have a person with conservation experience in the field to help with the excavation to ensure that the recovered objects are properly treated.
4. Make arrangements for conservation before initiating any operation where artifacts may be recovered. This may mean contracting with an existing laboratory or establishing special facilities for the project. If the latter, ensure that the laboratory is properly equipped and is headed by a conservator with experience in the field of underwater archaeological conservation. All the artifacts recovered from an excavation should be under the direct control of an experienced conservator until they are stabilized.
5. Always keep in mind that it is an archaeological project, and that an archaeological project does not stop in the field, it continues in the lab. As much basic archaeological data are recovered in the laboratory as in the field. The information and records from both the field and the conservation lab have to be synthesized in order for the archaeological record to be properly interpreted.

FIELD RECOMMENDATIONS

Many projects set up a field conservation laboratory near the excavation site. This is often true for sites far removed from the main laboratory. However, in most cases the field lab cannot compare to the main lab and its capabilities. For this reason, aside from general cataloging, acquisition, and documentation, the minimal use of field conservation facilities is recommended. Proper field conservation procedures can be anticipated by referring to various articles, such as Pearson (1977;1987c), Dowman (1970), and Lawson (1978). During any marine excavation, the following field procedures are suggested (Hamilton 1976):

1. Record the precise position and orientation of every object, i.e., ship timbers, encrustations, individual artifacts, and number each item. Numbering is important so that there will be no confusion as to how each object related to the site after the material has been delivered to the laboratory for processing.
2. Do not remove any encrustation or layers covering the artifacts in the field, since they provide a protective corrosion-resistant layer around the material and preserve associations. Furthermore, considerable data may exist in the form of impressions and natural molds of objects which have completely disintegrated.
3. When dealing with large objects, such as kegs, chests, boxes, etc., it is strongly recommended that they be jacketed or otherwise brought up intact with minimum excavation in the field. This will protect the material while it is being shipped to the laboratory where it can be more effectively excavated. This will save valuable and costly field time, which is always much more expensive than conservation laboratory time. The bottom line is that features such as these are best excavated in the controlled environment of the conservation laboratory.
4. Keep all material wet at all times, either in sea water or, preferably, in fresh water with a sodium hydroxide-adjusted pH of 10 to 12. This will inhibit further corrosion. Keeping the storage vats covered to restrict light will inhibit any algae growth.

LABORATORY CONSERVATION

The laboratory operations from the time a specimen is delivered to its ultimate place of storage or exhibition can be separated into six basic stages:

1. Storage prior to treatment.
2. Evaluation of conservation process.
3. Mechanical cleaning.
4. Treatment to stabilize.
5. Restoration (optional).
6. Storage or exhibition after cleaning.

Only numbers 1-4 will be discussed in this manual.

STORAGE PRIOR TO TREATMENT

Generally speaking, all metal objects should be kept submerged in tap water with an inhibitor added to prevent further corrosion. For long-term storage, excellent results have been achieved using a 1 percent oxidizing solution of potassium dichromate with sufficient sodium hydroxide added to create a pH of 9 to 9.5. Alkaline inhibitive solutions, such as a 5 percent solution of sodium carbonate or a 2 percent solution of sodium hydroxide, can also be used, but they are not satisfactory for long-term storage (Hamilton 1976:21-25). As mentioned above, any adhering encrustation or corrosion layers should be left intact until the objects are treated, since they form a protective coating which retards corrosion. A more thorough discussion of pre-treatment storage techniques can be found under each material-specific chapter in this manual.

EVALUATION OF CONSERVATION PROCESS

Prior to treatment, any artifact, particularly if encrusted with marine carbonates, must be critically evaluated in order to ascertain the possible presence and condition of metal, associated organic material, and/ or other material, such as ceramic and glass. Only after each artifact is evaluated and all options considered is a course of action decided upon.

MECHANICAL CLEANING

X rays are indispensable for determining the content of each encrustation and the condition of any object. They also serve as a guide in extracting the artifacts from the encrustation. The use of chemicals to remove the encrustation is generally a very slow, ineffective process, which may possibly damage the artifact. The use of well-directed hammer blows and assorted chisels are generally the most utilized and effective means of removing encrustation. However, for many objects encrusted together with metal artifacts, especially fragile objects and ceramics, small pneumatic tools are indispensable. Larger pneumatic weld-flux chisels are particularly useful for the removal of large amounts of encrustation. Chisels can be easily fabricated in the laboratory for specific jobs, and their use is often desirable and quite effective in freeing movable parts on artifacts. Sandblasting can sometimes be used for cleaning the bores of cannons or guns but should never be used on the surface of any piece.

TREATMENT TO STABILIZE

First, it must be emphasized that conservation is not an exact science, and in many cases two different conservators may treat the same object in completely different ways. The objective is to treat any given object so that it is stable and does not lose any of its diagnostic attributes. There are often options and some leeway on any conservation procedure that will result in a well-conserved artifact. Therefore, much of what follows is based upon the personal experience and personal preference of the author. Other conservators may not agree completely with everything presented here, but all treatments discussed are within the scope of alternative conservation procedures. When possible, the advantages and disadvantages of each treatment will be presented

Before discussing specific treatments of any given category of material, it is necessary to present a short discussion of adhesives and consolidants. In archaeological conservation, various synthetic resins are used extensively, and they play an important role in the conservation of materials, especially organic and siliceous materials, from marine sites. It is, therefore, important that any conservator working on archaeological artifacts has not only a variety of resins at his or her disposal for use as glues and consolidants but also has a good understanding of their physical characteristics.

Adhesives and Consolidants

IN THIS FILE:

Synthetic resins are widely used by conservators. These resins are polymers constructed of a chain or network of repeating single units, called monomers, that combine with themselves or with other similar molecules or compounds to form polymers. Resins can be divided into two types of polymers: thermoplastic resins and thermosetting resins, both of which are discussed below.

Thermoplastic resins are polymers in which the monomeric units are linked together to form two-dimensional linear chains that are soluble in a range of solvents. They remain permanently fusible and soluble; however, some thermoplastic resins may form insoluble, infusible resins after long exposure to light or heat. Such exposure may cause chemical bonds or links, referred to as cross linking, which become established between linear chains to form three-dimensional networks characteristic of thermosetting resins.

Thermosetting resins are characterized by monomeric units that are linked together by chemical bonds to form three-dimensional networks that are infusible and insoluble in all solvents. The three-dimensional network will not allow solvents to flow between the chains, so thermosetting resins remain permanently insoluble. However, some solvents may cause the resins to swell, forming a gel. Originally, thermosetting resins were hardened by the application of heat, thus the name 'thermosetting.' At present, there are many cold-setting resins, e.g., epoxy, polyurethane, and styrene, that congeal at room temperature when a catalyst is added.

There are innumerable adhesive/consolidants used in conservation and new ones are developed regularly. The ones most commonly used in conservation (UNESCO 1968; Dowman 1970) are:

1. Polyvinyl acetate (PVA), an organic solvent; examples include Vinylite AYAA (V12.5-14.5), AYAC (V14-16), AYAF (V 17-21), AYAT (V24-30), Gelva V7, V15, and V25;
2. Polyvinyl acetate (PVA) emulsions, e.g., CMBond M2
3. Acryloid B-72
4. Cellulose nitrate, also called nitrocelluloid, e.g., Duco
5. Polyvinyl butyral
6. Various polymethacrylates in an organic solvent, e.g., Elvacite 20/3
7. Polymethacrylate emulsions, e.g., Bedacryl
8. Polyvinyl alcohol
9. Elmer's Glue All

POLYVINYL ACETATE

Polyvinyl acetate (PVA) is the most commonly used thermoplastic polymer resin for organic material recovered from archaeological excavations (UNESCO 1968; Ashley-Smith 1983b). This is true in the field as well as in the conservation laboratory.

PVA is used both as a consolidant and as a glue. It comes in a range of viscosities (V) ranging from V1.5 to V60. The lower the number, the less viscous the solution. The lower the viscosity, the lower the molecular weight; the lower the molecular weight, the greater the penetration capability of the consolidant. The lower viscosity PVAs, however, have less bonding strength than those that are more viscous. In addition, the lower viscosity PVAs (below V7) form soft films that attract dust and are subject to cold flow. The finish of PVAs above V25 are very glossy and are often brittle if used alone. V7, V15, and V25 are the most commonly used PVA viscosities in conservation. PVA V7, with its smaller molecules, is frequently used on denser material, such as well-preserved bone and ivory; PVA V15 is a general-purpose resin; PVA V25 is used as a glue. PVA is also heat-sealable; for example, two pieces of cloth treated with PVA can be bound by ironing them together.

PVA has good stability to light and does not yellow. It remains soluble and does not cross link and become irreversible. PVA in strong concentrations, especially V25, may be used as a surface consolidant or as a glue. Many conservators prefer to use PVA V25 as a glue, especially for pottery reconstructions, with good results. Ceramic vessels glued with PVA V25 have, however, occasionally fallen apart because of excessive cold flow of the resin in hot, humid storage conditions.

PVA can be used on any non-metal object, e.g., bone, ivory, shell, antler, teeth, wood, botanical specimens, textiles, murals, stone, etc. In thin solutions, the lower viscosity PVAs (V7 and V15) are used to penetrate and consolidate fragile objects by painting or spraying. In many cases, the object is best consolidated by immersing several times in a dilute solution of PVA. Often there is a tendency for the dried PVA film to have a gloss. This can be eliminated by allowing the object to dry while it is suspended over an open bowl or jar of the solvent used to dissolve the PVA. In addition, the gloss can usually be eliminated by wiping the surface with a lint-free cloth saturated with a PVA solvent. During drying, there is some shrinkage of PVA that exerts contractual forces on the treated object. This can distort fragile thin, pieces, textiles, thin painted surfaces, and other similar objects.

PVA is soluble in a number of organic solvents. Solubility of PVA is directly related to the volatility of the solvent; the more volatile the solvent, the more soluble the PVA. The more soluble the PVA, the better the penetration of PVA into the object being treated. Some of the most common solvents, ranked in order from the most volatile to the least, are listed below.

1. iethyl ether (very volatile, water miscible [WM])
2. cetone (best solvent that is commonly used, WM)
3. benzene (very toxic, WM)
4. ethylene dichloride (very toxic, non-water miscible [NWM])
5. methanol (toxic, cumulative poison, WM)
6. methyl ethyl ketone (MEK) (toxic, NWM)
7. ethanol (denatured alcohols may be toxic, WM);
8. toluene (slightly toxic, NWM);
9. xylene (slightly toxic, NWM);
10. amyl acetate (slightly WM).

The non-toxic water-miscible solvents are the most useful, with acetone and ethanol being the most commonly used.

PVA FORMULATIONS

Slow-Drying PVA Formula	**Fast-Drying PVA Formula**
ethanol	acetone
5-15% PVA	5-15% PVA

Amyl acetate can be added to either to retard evaporation. Acetone can be added to ethanol to speed up evaporation, or ether can be added to either to considerably speed up the setting time.

If cellulose nitrate is used instead of PVA (not recommended) then either 2 percent Triacetin by volume or 5 percent castor oil by volume of cellulose nitrate must be added to plasticize the cellulose nitrate in order to retard, but not prevent, shrinkage, and brittleness.

PVA can also be purchased as an emulsion, such as CM Bond M2. Emulsions are stabilized dispersions of finely divided particles of the resin in water. The resin is merely suspended (rather than dissolved) in the water. As long as the emulsions are liquid, they can be thinned with water; for example, most water-cleanable interior latex paints are actually PVA emulsions. PVA emulsions can be used directly on wet material without drying or driving off the water with a water-miscible alcohol. Emulsions are miscible with water, but after drying, the resin requires the same solvents as the non-emulsified resins. In the repair of pottery, it has been found that PVA emulsions form better optical bridges across cracks than solvent glues. Most commercial PVA emulsions come in a viscosity suitable for use as a glue, so they must be diluted to use for impregnating material. For dilution use, CM Bond M2 has approximately 0.6 grams of resin per 1 gram of stock mixture. PVA V25 and even V15 are often used as a glue. When used as a glue, it only necessary that the PVA be thick enough. One acceptable procedure for making glue is provided by Koob (1996). The procedure described by Koob uses Acryloid B-72, but the process works equally well with any PVA formulation.

ACRYLOID B-72

Acryloid B-72 (referred to as Paraloid B-72 in Europe) is a thermoplastic acrylic resin manufactured by Rohm & Haas, which has replaced PVA in many applications and is preferred by many conservators over PVA. It is a methyl acrylate/ethyl methacrylate copolymer and is an excellent general-purpose resin. Durable and non-yellowing, Acryloid B-72 dries to a clear transparency, with less gloss than PVA, and is resistant to discoloration even at high temperatures. It is very durable and has excellent resistance to water, alcohol, alkalis, acid, mineral oil, vegetable oils, and grease, and it retains excellent flexibility. Acryloid B-72 can be applied in either clear or pigmented coatings by a variety of application methods and can be air dried or baked. It has a very low reactivity with sensitive pigments. Furthermore, it is compatible with other film-forming materials, such as PVA and cellulose nitrate, and can be used in combination with them to produce stable, transparent coatings with a wide variety of characteristics. In stronger concentrations, Acryloid B-72 can be used as a glue (see Koob 1996 for details). This glue formulation is the standard glue used at the Conservation Research Laboratory at Texas A&M University.

Acryloid B-72 is unique in possessing a high tolerance for ethanol, e.g., after being dissolved in acetone or toluene, up to 40 percent ethanol can be added to the solution to control the working time. This property allows its use in applications where strong solvents cannot be tolerated. The alcohol dispersion may be cloudy or milky; however, clear, coherent films are formed upon drying. Friable surfaces of porous, salt-contaminated objects can be stabilized with Acryloid B-72 while the salts are being diffused out in water baths without the adverse effects resulting from the use of soluble nylon discussed below.

Krylon Clear Acrylic 1301 is a formulation of 20 percent Acryloid B-66 in non-water miscible toluene that is easily obtained and is excellent for consolidating or sealing off the surfaces of a wide range of material. It is a ethyl methacrylate resin that is harder than Acryloid B-72 and can be used in place of it in most instances.

CELLULOSE NITRATE

Cellulose nitrate, formerly called nitrocelluloid, has a long history of use in conservation. Recently it has, to a large degree, been replaced by other synthetic resins. Cellulose nitrate is still used, especially as an adhesive. It has many of the same characteristics of PVA, but it is not internally plasticized as are most PVAs. Therefore, cellulose nitrate has a much greater tendency than PVA to become brittle, crack, and peel off.

Cellulose nitrate is soluble in acetone, methyl ethyl ketone, and esters, such as amyl acetate and n-butyl acetate. Since it is not soluble in alcohols, e.g., ethanol and methanol, it is useful on compound objects requiring different consolidating resins with different solvents. A plasticizer is required to prevent the resin from becoming too brittle.

There are a number of proprietary adhesives on the market that utilize cellulose nitrate. Duco cement is one example that is marketed in the USA. Duco cement is cellulose nitrate dissolved in acetone and butyl acetate, with oil of mustard added as a plasticizer. Because of its availability, Duco has been used extensively, with varying success, in pottery reconstructions and general artifact mending. Duco is easy to use and is effective in the short run, but over the years, the glue may yellow and become brittle, resulting in the breakup of glued items. It is not recommended for use in archaeological conservation (Moyer 1988b; Feller and Witt 1990).

Cellulose nitrate is discussed here because of its availability and general misuse in many conservation projects. In a few given cases, it may be necessary to use several resins with mutually exclusive solvents to consolidate some complex object. The use of cellulose nitrate is in this case is only on a temporary basis and should be removed and substituted with a longer lasting, reversible resin. Cellulose nitrate should never be used as a glue. While it still has its drawbacks, diluted Duco can be used to stabilize material such as bone by impregnation. For dilution purposes, Duco has approximately 0.8 grams of resin per one gram of stock mix in the tube.

POLYMETHYLMETHACRYLATE

There are a large number of polymethylmethacrylate (PMM) resins that are easily obtained world wide under different trade names such as Perspex and Lucite (formerly called Plexiglass). There are many different formulations for PMM resin glue, which is commonly made from sheets of Lucite, although good results are also achieved with Elvacite 20/3. Even safety mask shields and motorcycle windshields can be dissolved in solvents. The toxicity of the solvents necessary to dissolve PMM resins restrict their wider use by conservators.

A typical formulation for a 'plexiglass' glue is as follows:

Grind, cut or drill a sheet of Lucite to get a cup of shavings. Place in a jar and add approximately the same volume of solvent, which should consist of 50 percent chloroform and 50 percent toluene. **Caution: heat is generated**. Add acetone to thin to the correct viscosity.

The PMM resins have similar properties to PVA. PMM resins are stronger but have fewer solvents. Many PMM resins require mixed solvents such as 8 parts toluene and 2 parts methanol or a combination of chloroform and ethylene dichloride. In dilute solutions, PMMs penetrate dense material very well. The PMM consolidants are particularly useful when more than one consolidant is required on the same object or cluster of objects. Like PVA, PMM can be purchased as a resin or as an emulsion. Bedacryl is one type of PMM emulsion.

POLYVINYL ALCOHOL

Polyvinyl alcohol (PVAl) is a very useful resin in certain circumstances because water is the only suitable solvent (UNESCO 1968). PVAl resins are used as consolidants and adhesives. They come as a white powder in low, medium, and high acetate grades and have viscosities that ranged from 1.3 to 60. Low and medium acetate grades with viscosities of 2 to 6 are most commonly used in conservation. Concentrations of 10-25 percent are used depending on the viscosity and penetration desired. In general (depending on brand), PVAl dries clearer than PVA. It is more flexible and shrinks less; therefore, it exerts less contractile force than PVA when drying. For this reason, it is often used in textile conservation. It can be used on damp or dry objects. PVAl has been particularly useful for treating wet bone, fragile textiles, and for gluing fragile textiles to plastic supports. It has been used for conserving paper and textiles with water-fast dyes that are alcohol-soluble. PVAl is not recommended for wood.

Since PVAl is soluble only in water, the solution requires the addition of a fungicide such as Mystox LPL (pentachlorophenol), Dowicide 1 (ortho-phenylphenol), or Dowicide A (sodium-o-phenylphenate tetrahydrate) to prevent mold growth. There are indications of a slight tendency for some PVAls to cross link in 3 to 5 years if exposed to strong light, dryness, and heat; especially temperatures over 100°C. If cross linking occurs, the resin becomes less soluble but most likely never becomes completely insoluble. Some conservators recommend that objects treated with PVAl be re-treated every 3-5 years to counteract any possible cross linking.

The high acetate grades of PVAl are soluble in cold water, but the low and medium grades must be dissolved in water heated to 40-50°C. It is particularly useful when more than one consolidant is required on the same object. PVAl is very resistant to oils, greases, and organic solvents, but it has poor adhesion properties for smooth surfaces. Like PVA, it is heat-sealable at 50-65°C.

ELMER'S GLUE ALL

It has generally been thought that Elmer's Glue All is a PVA emulsion. In its original formulation, it was a casein glue, but about 20 years ago, the Borden Co. changed the formula to a PVA emulsion. Recently, there has been an additional change. Now, unlike other

PVA emulsions that are soluble only in PVA solvents after they are dried, the only solvent recommended by Borden, Inc. for Elmer's Glue All is water. They claim that any other solvent would only set the glue more. Because of the uncertainties about Elmer's Glue All, it is not recommended for conservation. It is, however, an excellent glue for wood that is not going to be exposed to outside environments and for consolidating quantities of faunal bone. The stock solution of Elmer's Glue All works fine as glue, but it must be diluted with water in order to use it to impregnate and strengthen material. For dilution purposes, stock Elmer's Glue All has approximately 0.9 grams of resin per one gram of stock mixture.

In conservation, make sure at all times that you are working with a true PVA emulsions, such as Bulldog Grip White Glue. Innumerable problems and additional work have resulted from the use of 'white glues' of unknown formulation.

EPOXY RESINS

There are innumerable thermosetting epoxy resins on the market with many varied properties and special characteristics. Each conservator, through experience, has his or her own favorites. Epoxy resins make excellent adhesives, consolidants, and gap-fillers. There are cold-setting thermosetting resins that set up with the addition of a catalyst. The most desirable characteristic, aside from their strength, is that there is no shrinkage as they set. This is in contrast to all the thermoplastic resins that set through the evaporation of a solvent, thereby undergoing some degree of shrinkage. The main disadvantages of epoxies are that they are essentially irreversible and often discolor with age. In some applications, optically clear resins should be selected. As a general rule, epoxy resins should be avoided; however, epoxies are occasionally required by conservators because nothing else has the necessary strength. They are excellent when a very strong, permanent bond is required. Epoxies are often used in reconstructions of wooden and glass artifacts and are used extensively in all aspects of casting.

Various Araldite epoxy compounds are used extensively in glass conservation and in preparing fossil and other materials that require a permanently clear epoxy. In casting and replicating metal artifacts from marine sites, various Hysol casting epoxies have been used. In all cases, be sure to follow the directions of the manufacturer on the recommended hardeners, mixtures, and thicknesses. If mishandled, a considerable amount of exothermic heat may be generated.

SUMMARY

These are just a few of the most common adhesives/consolidants used in conservation. They have a long, successful track record and are, therefore, widely used for an extensive variety of conservation purposes. Specific applications are discussed in the following files.

Conservation of Bone, ivory, Teeth and Antler

IN THIS FILE:

Approximately 70 percent of bone and ivory is made up of an inorganic lattice composed of calcium phosphate and various carbonates and fluorides. The organic tissue of both bone and ivory is ossein and it constitutes at least 30 percent of the total weight of the material. It is often difficult to distinguish between bone and ivory unless the material is examined microscopically. Bone is coarse grained with characteristic lacunae or voids; ivory is a hard, dense tissue with lenticular areas. Both bone and ivory are easily warped by heat and moisture and are decomposed by prolonged exposure to water.

In archaeological sites, ossein is decomposed by hydrolysis, and the inorganic framework is disintegrated by acids. In waterlogged sites, bone and ivory can be reduced to a sponge-like material; in arid sites, they become dry, brittle, and fragmented. In some circumstances, bone and ivory can become fossilized as the ossein is replaced by silica and mineral salts. Archaeological bone and ivory can only be cleaned, strengthened, and stabilized; satisfactory restoration is often impossible.

REMOVAL OF SURFACE DIRT

1. 1. Wash with soap and water or alcohol (the use of alcohol will facilitate drying). Towel dry.
2. 2. When washing with water, limit amount time in water.
3. 3. Brush lightly with brushes and/or lightly scrape with wooden, plastic or metal tools. Dental tools are particularly useful for this purpose.

Note: Structurally weak bone or ivory must be cleaned carefully and the cleaning method used should be dictated by the specimen's condition.

REMOVAL OF SOLUBLE SALTS

Bone or ivory from a salty environment will invariably absorb soluble salts which will crystallize out as the object drys. The action of salt crystallization will cause surface flaking and can, in some cases, destroy the specimen. The soluble salts must be removed in order to make the object stable. For faunal bone, it is usually not necessary to remove all the soluble salts. It is most efficient to rinse faunal bone in tap water until the chloride level in the material being treated equalizes that of the tap water. For more important artifacts made of any of these materials it advisable to remove all the soluble salts by rinsing for an appropriate length of time in tap water and then in deionized water.

1. If the bone/ivory is structurally sound, the salts can be diffused out by rinsing in successive baths of water. While faunal bone can be put directly into fresh water from seawater (there is a slight chance of cracking), the following succession of baths is recommended for important artifacts:

> 100 percent sea water » 75 percent sea water/25 percent fresh water (local tap water) » 50 percent sea water/50 percent fresh water » 25 percent sea water/75 percent fresh water » straight fresh water.

The object then goes through either running water rinses or numerous changes of the bath water until the soluble salt level reaches that of the tap water or the water supply being used. De-ionized or distilled water is then substituted for the fresh water bath until the soluble salts are removed or reaches an acceptable level.

In order to determine the level of salts in the rinse water, it is necessary to use a conductivity meter. In most cases, one can alternatively use the silver nitrate test to detect the presence of sodium chloride. When sodium chlorides are no longer present, it is reasonable to assume that the bulk of the soluble salts has been removed. The conductivity meter measures the presence of all soluble salts and is thus a much more reliable indicator of the presence and absence of soluble salts in an aqueous solution.

2. If the bone/ivory is structurally unsound, it can be consolidated with a 5 percent solution of Acryloid B-72 and then rinsed. The soluble salts will diffuse through the resin, albeit much more slowly, during the rinsing treatment.

3. Dry bone/ivory in series of alcohol baths (50 percent alcohol/50 percent water, increasing the alcohol content of the baths to 90 percent, 100 percent, and a final bath of 100 percent alcohol). For teeth and ivory, it is sometimes necessary to go through longer dehydration baths in order to ensure that the surface of the material being treated does not delaminate or crack. In such cases, a recommended series of dehydration baths should begin with straight water, followed by 95 percent water/5 percent ethanol (only water-miscible solvents should be used); an additional 5 percent ethanol should be then added to the bath until the artifact is in straight ethanol. To further ensure the integrity of the surface, the artifact

should be placed in a second and even a third bath. The object can then be taken through two baths of acetone. In a few exceptionally critical cases, it may be advisable to take the object through at least two baths of diethyl ether. In most cases, after the object has been taken through two baths of acetone, it is reasonable to assume that all the water has been removed. The object should be then consolidated with a proper resin in order to strengthen it and to make it less susceptible to fluctuations in atmospheric humidity (see below).

REMOVAL OF INSOLUBLE SALTS AND STAINS

If it is necessary to remove insoluble salts or stains from bone/ivory, some means of mechanical removal using picks or other tools is always recommended over any chemical treatment. Inevitably, some damage is done to bone and related material when stains and insoluble salts are removed by chemical means. When chemical agents are used, always make sure that the material is thoroughly wetted with water before any chemical is applied. This ensures that the treating chemical remains on the surface of the artifact and is not absorbed.

Calcium carbonate stains: Structurally sound bone can be immersed in 5 - 10 percent solutions of hydrochloric acid or formic acid. Monitor process closely.

Iron stains: 5-10 percent oxalic acid has been used to remove iron stain stains from bone. For stubborn stains, 5 percent ammonium citrate used alone or 5 percent ammonium citrate followed by 5 percent oxalic acid are effective treatments.

Sulfide stains: 5-10 percent hydrogen peroxide is used to remove sulfide stains. Stained bone may be placed in a hydrosulfite solution followed by dilute hydrogen peroxide to remove any remaining stain.

Unsound bone should be treated with localized applications of the solution with a brush or swab. If unsound bone is submerged, the evolution of carbon dioxide from the decomposition of the $CaCO_3$ will break up the specimen. Very fragile bone may require that the acid be applied locally to stubborn spots, scraped, and blotted; repeat all steps until the area is cleaned.

Following stain removal, it is necessary to rinse the artifact in water to remove all residue of the treating chemical, dry in alcohol baths, and then consolidate with a resin as described below.

CONSOLIDATION

Any resin solution must be diluted to decrease the viscosity and increase its ability to penetrate the material being treated. A 5-10 percent solution of a suitable transparent synthetic resin may be used. When large amounts of faunal bone need to be consolidated, satisfactory results are achieved with water soluble Elmer's Glue All. When bone, ivory, or teeth are treated, slowly dehydrate them in organic solvents as described above then consolide them with PVA (V7) or Acryloid B-72. The use of PVA V7 is encouraged because while the molecules are smaller and are able to penetrate denser material, the resin has enough resilience to mechanically strengthen any object treated with it. For less dense material and large amounts of faunal bone, PVA with a viscosity of V15 is recommended, since it is a stronger, general-purpose resin.

For surface consolidation, apply resin by brush. Good results can be obtained by applying a light coat of resin, allowing it to dry, and then applying a second coat. This procedure should be repeated several times in order to allow for sufficient resin to be absorbed by the material. Complete immersion of the artifact in the consolidating resin gives excellent results, while complete immersion of the artifact in the resin under a vacuum is considered the best method for consolidating most bone or ivory artifacts.

The type of glue used to glue bone, ivory, or teeth together is to some degree dependent upon how the object was treated. If the bone or related material has been consolidated with a resin, a thick viscous mixture of the same resin should be used. PVA with a viscosity of V25, Acryloid B-72, PVA emulsions such as Bull Dog, and in some cases, Elmer's Glue All, are also serviceable glues.

SEEDS AND PLANT MATERIAL

Miscellaneous seeds and plant material are, for all intents and purposes, treated in much the same way, if not exactly the same way, as described above for bone and related material. Once recovered, it necessary to rinse the material to remove any soluble salts that may be present, mechanically clean any material requiring it, chemically treat the material, and rinse out the treating chemical. The material should be dried in a series of water/water-miscible alcohol baths and then consolidated.

SUMMARY

The conservation of waterlogged bone and ivory, as well as most plant material, is a straight-forward process. Complex problems seldom arise, except in cases where bone is so badly deteriorated that it is cannot be treated. In general, intensive rinsing in water to remove the soluble salts followed by complete dehydration through a graded series of water-miscible solvents, and consolidation with an appropriate resin is all that is required. Stains can be removed, but the process may damage bone if care is not taken. The only equipment required is appropriately sized containers, a selection of resins, and a variety of solvents.

Conservation of Pottery

IN THIS FILE:

In general, pottery survives well in marine environments and requires only minimal treatment after recovery (Pearson 1987b). It is necessary, however, that the conservator be able to recognize earthenware, stoneware, and porcelain, and to be familiar with the alternative treatments for conserving them (Olive and Pearson 1975; Pearson 1987d). Stoneware and porcelain are fired at such high temperatures that they are impervious to liquids and thus do not absorb soluble salts from their archaeological environment; therefore, it is not necessary to take them through long rinses to remove soluble salts. However, with certain kinds of stoneware and porcelain, glazes are applied in subsequent firings, and sometimes salts may be deposited between the glaze and the body. If these salts are not removed, the glaze may flake off. So, even caution must be exercised with stoneware and porcelain. Well-fired pottery need only be washed in a mild detergent and the edges and surfaces scrubbed with a soft brush. Care should be taken not to remove traces of food, paint, pigments, or soot that is left on the interior or exterior surfaces. The conservator must be careful not to mark the pottery surface when using a brush or any other object during cleaning. Fragile, poorly fired pottery requires more care, but the procedure is the same. Fragile pieces, pottery with friable surfaces, flaking surfaces, or fugitive paints may require consolidation with a resin.

SOLUBLE SALTS

Earthenware excavated from marine sites becomes saturated with soluble salts, and/or the surfaces often become covered with insoluble salts, such as calcium carbonate and calcium sulfate. In many instances, pottery adjacent to metal objects, particularly iron objects, will be enclosed by the encrustation forming around the metal. Soluble salts (chlorides, phosphates, and nitrates) are potentially most dangerous to the integrity of pottery, and they must be removed in order for the object to be stable. The soluble salts are hygroscopic, and as the relative humidity rises and falls, the salts repeatedly dissolve and crystallize. These salts eventually reach the surface of the pot, where extensive crystallization takes place causing exfoliation of the surface of the pot. Eventually, the pot will break as a result of internal stresses. At times, masses of needle-like crystals may cover the surface, hiding all details. Soluble salts can be removed by repeated rinsing in water (a running bath is the quickest and most effective method but is very wasteful). There are any number of ways of setting up a series of vats so that water runs into one vat and cascades into a series of additional vats. This minimizes water waste, especially if using de-ionized water. Very simple rinsing procedures exist, such as putting soluble, salt-laden sherds in a mesh bag and placing the bag in the reservoir of a toilet. Innumerable volunteers assist you each day in changing the water, and the salt content in the sherds quickly equalize with that contained in the supply water. Then, if necessary, the rinsing can then be continued in several baths of de-ionized water to lower the salt content even further. This is a simple trick that is very effective.

Monitor the rinsing progress with a conductivity meter. If sherds or pottery are too fragile to withstand the rinsing process, surfaces may be consolidated first with Acryloid B-72 then rinsed. Since Acryloid B-72 is somewhat water-permeable, it will allow the salts to diffuse out, albeit significantly more slowly than in non-consolidated material.

REMOVAL OF INSOLUBLE SALTS

In most cases, the safest and most satisfactory method of removing insoluble salts from the surface of pottery is by hand. Most calcareous concretions can be removed easily when wet by scraping with a scalpel, dental tool, or similar appliance. Dental burrs and pneumatic air chisels are also quite useful.

The insoluble salts may also be removed chemically, but it is important to pre-wet the sherd. Nitric acid, hydrochloric acid, and oxalic acid are most commonly used. Before using any acid on pottery, however, make sure that the paste is thoroughly wetted so that the acid will not be absorbed. Although 10-20 percent nitric acid can be used to remove calcareous concretion, it is potentially the most damaging acid of the three. More care should be exercised in its use, as dilute nitric acid will dissolve lead glazes. In most cases, 10-20 percent hydrochloric acid is safer than nitric acid to clean glazed pottery. The sherds are left immersed in the acid until all gas evolution ceases (usually less than an hour); this process may be repeated if necessary. Care must be exercised, since hydrochloric acid can discolor glazes, especially lead glazes, which will turn milky. The samples are then washed thoroughly in tap water and, if necessary, immersed in 10 percent oxalic acid for 10-20 hours to remove iron stains. A thorough rinsing should follow, and the sherds should be then dried. It is imperative that pottery with a carbonate temper (shell, calcium carbonate) not be in immersed in hydrochloric or nitric acid because the tempering material will be removed from the paste, resulting in the weakening of the pottery.

While nitric, oxalic, and hydrochloric acid treatments will remove calcareous deposits (especially hydrochloric), they tend to dissolve the iron oxides from pottery containing iron oxides in the paste or in the glazes (many stoneware glazes contain iron oxides). The use of these acids on glazes containing iron oxides increases their tendency to exfoliate, especially if the glazes are friable. To avoid over-cleaning, the sherds should always be pre-wetted by soaking in water and then by applying the acid locally on the surfaces with a cotton swab or by drops. The excess acid is immediately removed when the effervescing action stops, either by wiping the area or rinsing the object(s) under running water to remove the acid. Earthenware and terra cotta often contain iron oxides, are more porous, and thus more prone to deteriorate when treated with these acids; acid treatments should be used on such materials with some discretion.

A useful chemical for removing calcareous deposits from ceramics is ethylene-diaminetetraacetic acid (EDTA). A 5 percent solution of the tetra-sodium salts of EDTA (pH 11.5) works best for removing calcareous material without seriously affecting the iron content of the pottery. Iron is more soluble at pH 4, while calcareous deposits are more soluble at pH 13. In this treatment, the sherds are immersed in the solution and left until the deposits are removed. Periodically, the solution may have to be replenished. In the process, the iron stains that are usually bound in with the calcium salts are removed along with the calcium. It is a slow but effective treatment.

Soaking calcareous-encrusted sherds in a 5 percent aqueous solution of sodium hexametaphosphate has been used to remove calcareous deposits. Care must be taken, however, since a solution of sodium hexametaphosphate has a tendency to soften the paste of the sherd more readily than the calcareous encrustation.

Calcium sulfate is very difficult to remove from pottery. To test for the presence of calcium sulfate, drop dilute nitric acid on the deposits, then add three drops of 1 percent barium chloride solution. A white precipitate indicates the presence of sulfates (Plenderleith and Werner 1971). These can be dissolved slowly by immersing in 20 percent nitric acid. As the sulfates dissolve, sulfuric acid is produced, which cancels out the reaction of the nitric acid. The nitric acid must be changed often. This technique is not generally recommended, however, and mechanical cleaning is preferred.

Silicates on the surface of pottery can be removed with hydrofluoric acid, but this acid is **very dangerous** and is not recommended to be used by amateurs. Again, mechanical cleaning is recommended.

STAIN REMOVAL

Iron oxide stains can be removed with 10 percent oxalic acid applied locally with cotton swabs on the surface of pre-wetted pottery. This is a generally successful method for removing iron stains from stoneware and earthenware ceramics, although a small amount of the iron in the paste may be removed. A 5 percent EDTA solution is often used to remove stains from pottery containing iron oxide in the glaze or paste in order to minimize the removal of the iron oxide (Olive and Pearson 1975; Pearson 1987d). The disodium salts or EDTA are the most efficient for removing iron oxide stains because of their lower pH.. Either oxalic acid or EDTA will remove iron stains. In all treatments, caution must be exercised to avoid over-cleaning. Intensive rinsing after cleaning is required.

Black metallic sulfide stains are very common on pottery from marine shipwrecks. They can be removed by immersion in 10-25 percent by volume hydrogen peroxide solution until the stains disappear. The time required to remove the stains ranges from a few seconds to several hours. No rinsing is required after treatment with hydrogen peroxide. Hydrogen peroxide can be applied directly to sherds that have been treated with nylon, as the hydrogen peroxide will permeate the nylon film. Hydrogen peroxide is also useful for removing organic stains. Carefully monitor the progress, especially on tin enamel wares (delft, majolica, faience) when the glaze is crazed. Bubbles generated during treatment may lift off the poorly attached glaze.

Glues, such as PVA (V25 or equivalent) and Acryloid B-72, can be used to repair broken pottery. In the past, celluloid glues, such as Duco, have also been used, but they have too short of a serviceable life to be used in conservation. A thick PVA (V25) solution in acetone, acetone/toluene, or acetone and amyl acetate can be used as a glue. Others prefer a PVA emulsion glue in an aqueous base for gluing together porous pottery. It forms a better optical bridge across cracks than a solvent glue, but it has a tendency to give way in damp climates or uncontrolled storage. Alpha cyanoacrylate glues ('super glues') are very handy. These can be dissolved slowly in acetone and toluene after setting. In most instances, it is necessary to consolidate earthenware sherds with a dilute solution of PVA or Acryloid B-72 in order to thoroughly strengthen their surfaces before they can be glued or repaired. This can be accomplished simply by immersing the sherds in a dilute solution of the resin.

GENERAL STEPS FOR THE REMOVAL OF INSOLUBLE SALTS AND STAINS

1. Thoroughly wet the pottery.
2. For sturdy pottery, immerse in 10-20 percent nitric or hydrochloric acid until effervescing ceases. Hydrochloric acid is preferable for glazed pottery. Glazed, friable, or carbonate-tempered surfaces should be cleaned with cotton swabs or by applying concentrated acid, drop by drop. Immediately wipe off the excess acid or rinse in running water when effervescing stops. Continue the process from spot to spot or area by area.
3. Thoroughly rinse the pottery in running water to remove excess acid.
4. Remove iron oxide stains with 10 percent oxalic acid or 5 percent EDTA and rinse thoroughly.
5. Remove iron sulfide and organic stains by immersing in 10-25 percent by volume hydrogen peroxide.
6. For marine-recovered earthenware, it is advisable to thoroughly consolidate the material in a dilute solution of PVA or Acryloid B-72. This is especially important if the artifact will be reconstructed.

STONE CONSERVATION

Small objects made of stone can be treated in essentially the same manner as described for pottery (once pottery has been fired, it is actually a form of stone). Many sedimentary rocks can absorb soluble salts and be stained. The same treatments and chemicals described under pottery can be used, but the acids should be no stronger than 5 percent. Do not use any acids on any of the sedimentary rocks (e.g., limestone, marble, sandstone, etc.), as these can be quickly destroyed by acid treatments. The acids can be used effectively on metamorphic and igneous rock.

SUMMARY

The conservation of ceramics recovered from a marine site is not complicated. When pieces are found encrusted, the most difficult part of the conservation process is the removal of the adhering material without damaging the paste or glaze. For this reason, mechanical cleaning techniques are preferred, but hydrochloric acid is used with some regularity to remove calcareous encrustation. The soluble salts that are invariably present in any porous material recovered from a marine site are removed by rinsing in water. In most instances, tap water is all that is needed, but to the use of de-ionized water in the final baths will remove more soluble salts. Sulfide staining is easily removed with hydrogen peroxide, but other stains, such as iron stains, are more difficult to remove without adversely affecting the material. If the decision is made to remove the more difficult stains, the material should be thoroughly wetted with water before immersing or applying the appropriate chemicals. Monitor the process carefully and rinse thoroughly in water after using any chemicals. After treatment, allow the pottery to air dry. Solvent drying is not required, but it may be used if desired. After drying, consolidate by completely immersing the material in a dilute solution of PVA or Acryloid B-72. Pottery vessels can be reconstructed after the consolidated sherds have dried. Equipment required to conserve ceramics includes appropriately sized vats, tap water, de-ionized water, acetone, ethanol, PVA, Acryloid B-72, hydrogen peroxide, hydrochloric acid, EDTA, dental picks, and pneumatic chisels.

Conservation of Glass

IN THIS FILE:

Glass is usually the most stable of archaeological materials, but glass artifacts, and 17th-century glass in particular, can undergo complex disintegration. Ideally, glass should consist of 70-74 percent silica, 16-22 percent alkali or soda ash (sodium carbonate) or potash (potassium carbonate, usually derived from wood ash), and 5-10 percent flux (lime [calcium oxide]). Soda-lime glass has been the most common glass throughout the history of glass-making, and the modern equivalent is 74 percent SiO_2, 16 percent Na_2CO_3, and 55 percent lime added as stabilizer. Soda glass is characteristic of southern Europe, where it is made from crushed white pebbles and soda ash derived from burnt marine vegetation. Soda glass, which is often used for the manufacture of cheap glass, is twice as soluble in water as potash glass.

Potash glass is more characteristic of interior Europe, where it is made from local sands and potash derived from wood ash and burnt inland vegetation. A little salt and minute amounts of manganese are added to make the glass clear, but potash glass is less clear than soda glass. Most early glass is green because of iron impurities in the materials. Alkali lowers the melting point of the sand, and the flux facilitates the mixture of the components. As long as the original glass mixture was kept in balance, the resulting glass will be stable. Problems arise when an excess of alkali and a deficiency in lime are present in the mixture, for the glass will be especially susceptible to attack by moisture. If old glass contains 20-30 percent sodium or potassium, it may have 'glass disease,' where the glass weeps and begins to break down.

In all glass, the sodium and potassium oxides are hygroscopic; therefore, the surface of the glass absorbs moisture from the air. The absorbed moisture and exposure to carbon dioxide causes the NaO_2 or NaOH and KO_2 or KOH to convert to sodium or potassium carbonate. Both $NaCO_2$ and KCO_2 are extremely hygroscopic. At a relative humidity (RH) of 40 percent and above (and in some cases as low as 20 percent RH), drops of moisture appear on the glass surface. In water, especially salt water, the Na and K carbonates in unstable glass may leach out, leaving only a fragile, porous hydrated silica (SiO_2) network. This causes the glass to craze, crack, flake, and pit, and gives the surface of the glass a frosty appearance. In some cases, there is an actual separation of layers of glass from the body. Fortunately, these problems are not commonly encountered in glass manufactured in the 18th century and later. Pearson (1987b, 1987d) discusses glass deterioration and reviews the various glass conservation procedures.

At our present state of knowledge, the decomposition of glass is imperfectly understood, but most glass technologists agree that glass decomposition is due to preferential leaching and diffusion of alkali ions (Na and K) across a hydrated porous silica network. Sodium ions are removed and replaced by hydrogen ions, which diffuse into the glass to preserve the electrical balance. The silicates are converted into a hydrated silica network through which sodium ions diffuse out.

Decomposed glass often appears laminated, with iridescent layers on the surface. Glass retrieved from an acid environment often has an iridescent film, which is formed by the leached silica layers. The alkali which leached out is neutralized by the acid, and fewer hydroxyl ions are available to react with the silica. This causes the silica layer to thicken and become gelatinized. Glass excavated from an alkaline environment is less likely to have laminated layers because there is an abundance of hydroxyl ions to react with the silica network. Usually a protective layer does not form on glass exposed to alkaline solutions. The dissolution of the glass proceeds at a constant rate. The alkali ions are always extracted in excess of the silica, leaving an alkali-deficient layer, which continually thickens as the deterioration moves deeper into the glass.

There are considerable differences of opinion as to what to do with unstable glass. Some professionals advise that the only treatment should be to keep the glass in low RH environments so the glass does not have any moisture to react with. While a RH range of 40-55 percent is usually recommended, it varies in relationship to the stability of the glass. The weeping or sweaty condition is sometimes made worse by the application of a surface lacquer or sealant. No resin sealants are impervious to water vapor, and the disintegration continues under the sealant until the glass falls apart. Other glass conservators try to remove the alkalinity from the glass to halt the deterioration.

Most, if not all, of the glass manufactured from the 18th century on has been produced from a stable glass formulation, and there are not likely to be any considerable problems presented to the conservator other than normal devitrification. Since the glass is impervious to salt contamination, no conservation treatment other than simple rinsing, removal of incidental stains, especially lead sulfide staining on any lead crystal, and removal of calcareous deposits is expected. The main problems will be related to gluing pieces together. All the problems likely to be encountered are discussed thoroughly Newton and Davidson (1989).

TREATMENT OF UNSTABLE GLASS

Glass that is susceptible to weeping because of unstable glass formulations can be treated in different ways; the technique described by Plenderleith and Werner (1971:345) is representative of the treatments often recommended. It is presented below.

1. Wash the glass thoroughly in running tap water and then soak it in distilled water.
2. Dry the glass in two baths of alcohol. This treatment will retard the disintegration and also improves the appearance of the glass. It does not, however, always stop the breakdown of the glass.
3. If applicable, apply an organic lacquer (PVA or Acryloid B-72) to impede disintegration.
4. For assurance, store the glass in a dry environment with the relative humidity no higher than 40 percent; other professionals say that an RH of 20-30 percent is ideal. The Corning Glass Museum keeps incipient crizzled glass stored at 45-55 percent RH. RH 42 percent is the critical point at which KCO_3 becomes moist.

The above treatment does not attempt to remove any of the glass corrosion products, which often result in layers of opaque glass that may be removed with various acid treatments. The decision to remove surface corrosion products, which often mask the color of the glass, must be made on a case-by-case basis. Removal of corrosion products may also significantly reduce the thickness of the walls and weaken the piece significantly. Indiscriminate removal of surface corrosion products can weaken, blur, or alter surface details. The corrosion layers of a glass object may be deemed a part of the history of the object, and thus a diagnostic attribute, and should not be removed without good reason.

DEVITRIFICATION

Devitrification is a natural process that occurs on siliceous material. It occurs naturally on flint and obsidian and is the basis for obsidian hydration dating. The surface of any glass from any time period, especially soda glass, usually becomes hydrated through time and so will eventually devitrify. Devitrification occurs when the surface of the glass becomes partly crystalline as it adsorbs moisture from the atmosphere or from a submerged environment. As it becomes crystalline, the surface becomes crazed and flakes from the body of the glass. Devitrified glass has a frosty or cloudy, iridescent appearance. Pane glass is especially susceptible.

To prevent further devitrification and to consolidate the crazed surfaces, a coating of PVA or Acryloid B-72 should be applied to the piece. Either of these surface adhesives will smooth out the irregularities in the pitted, crazed surface of the glass by filling in the small cracks and forming optical bridges, making the glass appear more transparent. Merely wetting glass will cause it to be appear clearer for the same reason.

REMOVAL OF SULFIDE STAINS FROM LEAD CRYSTAL

Leaded glass, which includes a wide variety of stem wares and forms of lead crystal, can become badly stained by lead sulfide. Glass that is normally clear may be recovered from marine and/or anaerobic sites with a very dense black film on its surface. A 10-15 percent hydrogen peroxide solution is used, as with ceramics, to remove these sulfide stains. Other than stain removal, strengthening of glass artifacts with a consolidating resin is often required. Fragments can be glued together with a good glue, or if deemed necessary, an epoxy, such as Araldite.

RECONSTRUCTION

Glass can be repaired and reconstructed with the same glues as described for pottery. Optically clear epoxy resins are generally preferred as they adhere to the smooth, non-porous glass more readily. They also dry clearer and shrink less than the solvent resins. The resulting bonds, therefore, are less noticeable and stronger than with other glues. The epoxy resins are, however, usually irreversible. Hysol Epoxy 2038 with Hardener 3416 and Araldite are the two brands most commonly used in glass repair. The new 'super glues,' which are made of cyanoacrylate, are used quite often to piece the glass together quickly. After using the cyanoacrylate, epoxy is flowed into the cracks with an artist's brush to permanently bond the pieces. It is exceptionally difficult and time consuming to gap-fill glass. It requires considerable work and experience. The problem of matching transparent glass colors is equally difficult. All of these problems are adequately discussed in greater detail in Newton and Davison (1989).

As is the case with all conservation, it is necessary for the conservator to be able to recognize what the problems are and to know what may be used to counter them. When lead oxides are found during glass conservation they can be removed with 10 percent nitric acid. A 1-5 percent sulfuric acid solution can be used to remove iron oxide, neutralize the alkalinity of glass that is breaking down, and, occasionally, to remove calcareous deposits. Calcareous deposits are commonly removed with 10 percent hydrochloric acid and, on some occasions, by immersing the glass in 5 percent EDTA tetra sodium. Iron stains are commonly removed with 5 percent oxalic acid or 5 percent EDTA di-sodium.

SUMMARY

Realistically, few problems other than reconstruction and restoration are likely to be encountered on any glass objects found in archaeological sites dating from the mid 18th century to the present. In most cases, the same chemicals and equipment required for treating ceramics are also used for conserving glass.

Wood Conservation

IN THIS FILE:

As an organic material, wood normally decays under combined biological and chemical degradation when buried in earth; it may, however, survive prolonged exposure to extreme dryness or wetness. In shipwreck sites, the wooden components of the hull and small artifacts of wood often survive in good condition, albeit thoroughly waterlogged. The mechanisms of the organic deterioration of wood are succinctly presented in Florian (1987).

Successful conservation of wooden artifacts is dependent upon a knowledge of wood structure and types. Trees are divided into two broad categories: hardwoods and softwoods. Hardwoods are classified as angiosperms, which refers to broadleaf trees which are usually deciduous. Angiosperms are referred to as 'porous' woods because they have vessel pores. Oak and birch are typical examples of hardwoods. Softwoods, or gymnosperms, are needle-bearing trees or conifers. Gymnosperms are considered 'non-porous' because they lack vessel pores. Pines are typical examples of softwood. It is critical that conservators know the category of wood that they are treating; in many instances, it is equally important that a wooden object is identified to the species level in order to successfully conserve the waterlogged wood.

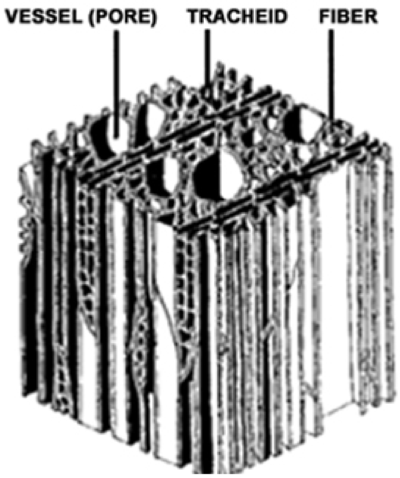


Figure 6.1. Schematic diagram of hardwood, illustrating the relative appearance of vessels and tracheids (vascular cells).

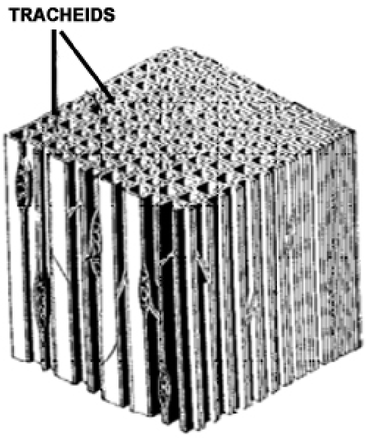


Figure 6.2. Schematic diagram of softwood, illustrating the relative appearance of tracheids.

Through the loss of moisture, freshly cut, sound wood will generally experience a radial shrinkage of ca. 3-6 percent, a tangential shrinkage of 5-10 percent, and a longitudinal shrinkage of - 0.5 percent. Fresh oak shrinks 4 percent radially and 8 percent tangentially when air dried after cutting, while waterlogged oak can shrink 12 percent radially and ca. 24 percent tangentially. Proper conservation treatments can control the amount of shrinkage experienced by waterlogged wood during drying. In practice, a particular conservation technique is often selected because it is known that the treated wood will shrink a desired amount (Patton 1988:43).

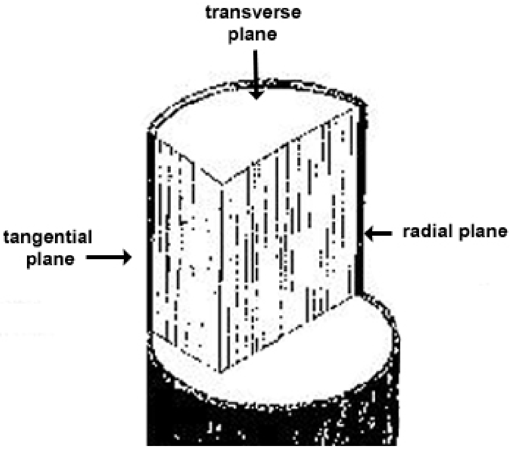


Figure 6.3. Schematic drawing, illustrating the three principal planes in wood: transverse, tangential, and radial.

The manner in which a plank of wood was originally sawn from a log will have an effect on how the plank, or an object manufactured from the plank, will shrink after undergoing any conservation treatment. Flat- or plain-sawn lumber has similar proportions of radial and tangential surfaces with arched grain patterns; these features predispose the wood to warping during drying. In order for lumber to exhibit true tangential and radial planes, it must be rift- or flitch-sawn. Because rift sawing is complex and inefficient, a modified pattern called quarter-sawing was developed. Quarter-sawing results in lumber with predominantly radial surfaces on the faces, a feature which makes the wood less likely to warp during the drying process. In some cases, the manner in which planks were extracted from a log will result in the cracking and warping of a treated wooden object, regardless of the conservation technique used.

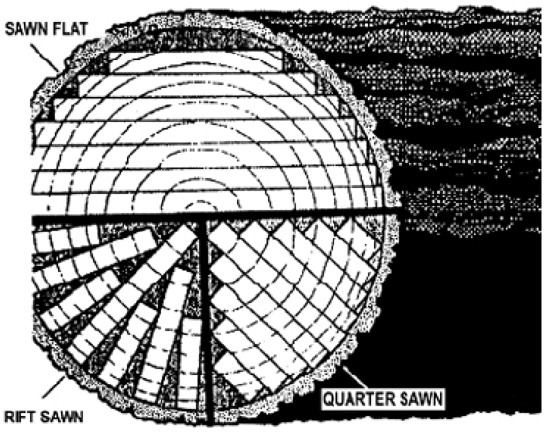


Figure 6.4. Methods of sawing logs for lumber: flat-sawn, rift-sawn, and quarter-sawn.

In most environments the primary factors for the degradation of wood include: (1) physical action (changes in temperature, fluctuations in relative humidity, etc.), (2) insect attack, and (3) fungal decay. Fungal decay can be eliminated as long as the wood is kept in an environment with a relative humidity of less than 65 percent. In anaerobic waterlogged environments, however, wood undergoes profound chemical changes and alterations that result in a significant loss of strength while retaining overall shape and form.

WATERLOGGED WOOD

In all wood, after long periods in wet soil, peat bogs, and marine sites, bacterial action causes a degradation of cell wall components. In general, water-soluble substances, such as starch and sugar, are the first to be leached from waterlogged wood, along with mineral salts, coloring agents, tanning matters, and other bonding materials. In time, through hydrolysis, cellulose in the cell walls disintegrates, leaving only a lignin network to support the wood. Even the lignin will break down over a long period of time. As a result of the disintegration of cellulose and lignin, spaces between the cells and molecules increase, and the wood becomes more porous and permeable to water. All of the deteriorated elements of the wood, including all cell cavities and intermolecular spaces, are filled with water. The remaining lignin structure of wood cells and the absorbed water preserves the shape of the wood. The loss of the finer cellulose tissue does not cause much alteration in the gross volume of wood, but the porosity is increased, and the wood absorbs water like a sponge. A waterlogged wooden object will retain its shape as long as it is kept wet. If the wood is exposed to air, the excess water evaporates, and the resulting surface tension forces of the evaporating water cause the weakened cell walls to collapse, creating considerable shrinkage and distortion. The amount of shrinkage is dependent upon the degree of disintegration and the amount of water present. The amount of water in waterlogged wood is determined by the following formula:

$$\%\ \text{water} = \frac{\text{weight of wet wood - weight of oven-dried wood}}{\text{weight of oven-dried wood x 100}}$$

Wood containing more than 200 percent water is considered to be degraded; it is not uncommon to find wood that contains more than 500 percent or even 1000 percent water. Waterlogged wood is often classed according to the amount of water is contains.

Class I: over 400 percent water
Class II: 185-400 percent water
Class III: less than 185 percent

The Class III hardwoods are the most difficult to conserve.

WATERLOGGED WOOD CONSERVATION

The conservation of waterlogged wood is a two-fold process that involves (1) the incorporation of a material into the wood that will consolidate and confer mechanical strength to the wood while the water is being removed (e.g., PEG- or sugar-bulking treatments), and (2) the removal of the excess water by a method which will prevent any shrinkage or distortion of the wood (e.g., solvent- or freeze-drying). The most common techniques for treating waterlogged wood are discussed below. In any treatment involving wood recovered from a salt water environment, it is necessary that the bulk of the soluble salts be removed first. If the salts are not removed prior to treatment, they will cause a white bloom on the conserved wood and may adversely affect any remaining iron components in the wood and even other material in the same room or environment in which the treated wood is stored.

POLYETHYLENE GLYCOL (PEG) METHOD

Polyethylene glycol (PEG) is a synthetic material that has the generalized formula $H_2OCH\ (CH_2OH_2)\ CH_2OH$. The low molecular weight PEGs (300 - 600) are liquids, the intermediate members (1000-1500) are semi-liquids or have the consistency of Vaseline, and the higher molecular weight PEGs (3250-6000) are wax-like materials. The various PEGs are now designated by their average molecular weight. What was once called PEG 1500 is now called 540 Blend (it is equal parts PEG 300 and PEG 1500), PEG 1540 is now called PEG 1500, and PEG 4000 is now called PEG 3250. Although the PEGs have some of the physical properties of waxes, they are distinguished from true waxes by the fact that they are freely soluble in alcohol (ethanol, methanol, isopropanol), as well as water. PEG 4000, which has a melting point of 53-55°C, was once the most commonly used PEG because it is the least hygroscopic; its large molecules, however, prevent it from penetrating dense wood. Now PEG 1500 and the 540 Blend are more commonly used.

The PEG conservation process was the first reliable method for treating waterlogged wood that was also relatively simple to perform. This method removes excess water while simultaneously bulking the wood. After preliminary cleaning to remove all surface dirt, the waterlogged object is placed in a ventilated vat containing a solution of PEG and solvent (water or alcohol). The vat temperature is gradually increased until, after a period of days or weeks, it has reached 60°C. During this time, the PEG percentage of the solution increases as additional increments of PEG are added while the solvent evaporates. During the conservation process, the wax slowly permeates the wood, displacing the water. At the end of the operation, the wooden object is covered with 70-100 percent molten PEG, depending upon the nature of the wood. The object is then removed, the excess wax wiped off, and the object is allowed to cool. After cooling, any excess wax on the surface of the object is removed with a hot-air gun or with hot water.

In most instances, the wood to be treated is placed in a vat of water containing a small increment of PEG (usually 1-5 percent. The vat is kept at a constant temperature of approximately 52°C. If the solution is not heated, it will solidify when the concentration of PEG in the solution reaches 20-30 percent. Over a period of months (or even years), the PEG percentage of the solution is increased in small increments until a minimum concentration of 70 percent is reached. If this minimum concentration is reached, the wood will remain stable. In some instances, if the percentage of PEG in solution exceeds 70 percent, water may be drawn out of the well-preserved heartwood without being replaced by PEG; this will cause the wood to collapse. The size of the PEG increments is dependent upon the condition, size, and specie of the wood being treated.

An additional method of treating waterlogged wood that is only appropriate for small objects and thus is seldom used in practice involves using a container in which the PEG concentration is increased solely by the evaporation of the solvent. When performing this procedure, it is important that the dimensions of the container be such that the amount of PEG in solution will be more than enough to cover the object at the end of the process.

It has already been noted that PEG is soluble in both water and various alcohols. Water is generally used in PEG solutions for large objects, as it is considerably cheaper than an equal volume of alcohol. When using PEG in water it is necessary to add a fungicide, such as Dowicide 1 (ortho phenylphenol), at .05 to .1 percent of the weight of the PEG used. During the conservation of the 17th-century warship *Wasa,* a fungicide consisting of seven parts boric acid and three parts sodium borate (1 percent of weight of PEG) was used (Barkman 1975:82). For smaller objects, it is often more convenient to use alcohol in the PEG solution. This considerably reduces the overall treatment time, and the finished product is lighter in both weight and color. To further reduce treatment time, the additional step of dehydrating the wood in at least three baths of ethanol before placing it in the first PEG/alcohol solution is recommended. However, it is not critical that all the water be removed from the wood prior to treatment, as PEG is soluble in both water and alcohol. Alcohol treatments save time but are less cost-effective and always pose the risks inherent in heating alcohol. Since all alcohols are fungicidal, no fungicide is required when using alcohol in PEG solutions.

Before a decision is made to conserve wood with PEG, it is important to consider the fact that PEG is corrosive to all metals, especially iron. For this reason, PEG treatments should not be used on wood that will be in contact with any metal (e.g., gun stocks).

Treating small waterlogged wood artifacts with PEG in the laboratory is a simple and straightforward process. Small vats (stainless steel or glass) are readily available and they can be placed in a thermostatically controlled oven to maintain the correct temperature; furthermore, only a small amount of PEG is required. In contrast, when large pieces of wood are treated, there is a considerable investment in PEG (sometimes measured in the tons). A substantial vat must also be constructed with the capability to heat and circulate the solution. Laboratories that intend to conserve large pieces of waterlogged wood must be prepared to make major investments in both equipment and chemicals. Of all of the wood conservation methods discussed in this section, any of the various PEG treatments with water is the most utilized because of its reliability and low cost.

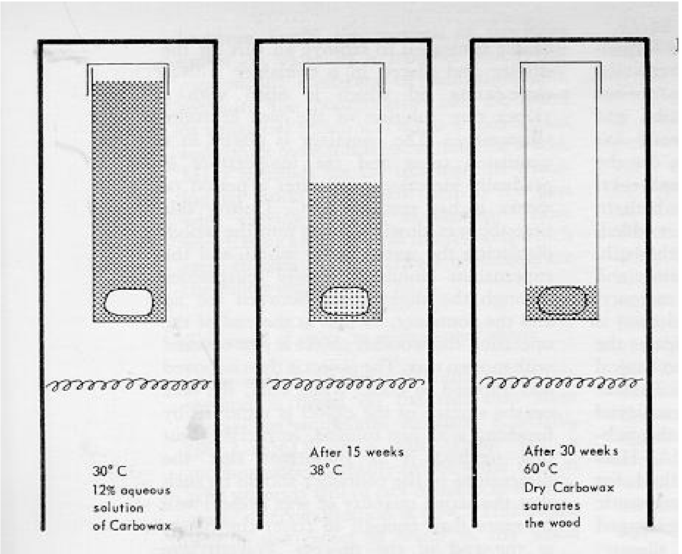


Figure 6.5. Setup for treatment of small specimens of waterlogged wood.

SUCROSE METHOD

The sucrose (sugar) method of conserving waterlogged wood was developed as an alternative to more expensive methods (Parrent 1983, 1985). The procedure is identical to that described for PEG, except that sucrose is used. Wood to be conserved should be carefully cleaned by rinsing in baths of fresh water to remove all ingrained dirt and to remove the bulk of any soluble salts that are present. Once the wood is cleaned, the following procedure is recommended:

1. Prepare a solution with a sufficiently low sucrose (1-5 percent) concentration to prevent the dehydration of well-preserved wood or regions of sound wood within an otherwise deteriorated piece. This necessitates the thorough examination of the wood to be treated in order to determine its state of preservation before treatment begins. With highly degraded wood, it is possible to start with a higher concentration of sucrose; however, if in doubt, start with a 1 percent weight/volume solution. Commence a program of weighing a representative sample of wood in treatment to determine when the wood has reached equilibrium with its solution. Once saturation with a given x percent solution is achieved, increase the sugar concentration by 1-10 percent.
2. Select an antimicrobial agent, such as Dowicide A, and add it to the first mixture of sucrose and water when it is initially prepared. This allows for the complete penetration and protection of the wood by the antimicrobial agent.
3. The incremental percentages of increase can be higher and more closely spaced if the wood is highly degraded. It is best to start with a low percentage increase, e.g., 1-5 percent, until a concentration of 50 percent is reached. Then the solution can be increased in 10-percent increments. Again, if in doubt, the same incremental increases used at the start of the treatment can be used throughout the treatment. The treatment continues until sucrose concentration reaches 70 percent, and the wood has equalized at this concentration.
4. If necessary, select an additive that will discourage insect and rodent attacks on the treated wood. There are many pesticides that will work, and selection depends on local availability. For thorough protection of wood, add the insecticide to the initial solution. If the wood is kept in a museum environment, problems with insects and rodents should be minimal and probably would be controlled by alternative means.
5. When the wood has reached an equilibrium with the highest solution desired, air dry it slowly under conditions of controlled high humidity. Humidity can be lowered slowly as the wood dries. Submitting the wood too quickly to conditions of low humidity will damage it. Slow, controlled drying and adjustment to the prevailing atmospheric conditions, as is the case in all the wood treatments described here, will maximize the success of the overall treatment.
6. Store the wood under conditions of less than 70 percent humidity if possible. The wood should not be subjected to humidity over 80 percent because of the possibility of condensation forming on the wood; this could leach out the sugar.

If sugar is selected as the treating medium, refined white sugar (pure sucrose) should be used. The brown- colored, coarse-grained unrefined sugar (Type A sugar) should be avoided, as it is much more hygroscopic than the white. Each time the relative humidity rises, the surfaces of wood treated in unrefined sugar will become wet. This hygroscopicity is analogous to that encountered when using the medium molecular weight PEGs. The Type A sugar-treated wood, however, remains dimensionally stable.

Maintaining artifacts treated by sugar in a controlled atmosphere will ensure the continued success of the conservation procedure. Artifacts conserved with this method require no more or no less care than those treated with other preservatives. This method constitutes an acceptable means of conserving waterlogged wood and is the least expensive of the methods currently available. Sucrose-treated wood, however, has a dull muted color, and small hair line cracks will frequently form on the surfaces. The treatment will produce dimensionally stable wood and is a viable alternative when the overall cost is a major consideration. The required equipment is the same as discussed above for PEG treatments.

ACETONE-ROSIN METHOD

The treatment consists of replacing the water in wood with a natural rosin, in this case, pine rosin (also called colophony). This treatment was developed to conserve well-preserved hardwoods that cannot be penetrated by the higher molecular weight PEGs (McKerrel and Varanyi 1972; Bryce et al. 1975).

The following procedure is recommended:

1. Wash object thoroughly, removing all dirt. It is usually necessary to store the wood in several rinses of fresh water.
2. Dehydrate the wood completely in three successive baths of acetone. Objects 5-10 cm thick require about four days in each acetone bath, while objects less than 5 cm thick require about two days in each acetone bath. It is important that all the water be removed, as water is incompatible with rosin.
3. Place the wood in a sealed container containing a saturated solution of rosin dissolved in acetone heated to 52°C. Only lump, technical-grade rosin should be used. Do not use powdered rosin, as it is difficult to handle and usually has a powdered substance added to it to keep it from sealing together.

   In a sealed container at a thermostatically controlled 52°C, a saturated solution of rosin in acetone is 67 percent rosin. To ensure a saturated solution, an excess amount of rosin should be placed in the container. This results in a thick, viscous layer of rosin that will settle to the bottom of the container. The object being treated should be suspended or supported above this undissolved rosin. Objects 5-10 cm thick should be left in the solution for four weeks, while objects less than 5 cm thick should be left in the solution for two weeks. These treatment durations are only rough approximations; each piece of wood should be evaluated based upon its own characteristics.

4. Remove the object from the rosin solution, and wipe off excess rosin with acetone-moistened rags.

In some cases, when conserving very well-preserved hardwood, the conservator might consider submerging the wood in a 10 percent hydrochloric acid (HCl) bath after washing the object and before dehydrating the wood in Step 2 (above). Pre-treatment with hydrochloric acid improves the penetration of the rosin into the object by breaking down the organic acids in the wood. Caution must be exercised, however, as hydrochloric acid may result in a checked surface, which is more subject to cracking post-treatment. In addition, hydrochloric acid is supposed to bleach the wood to a more natural or original color, but the bleaching is only temporary and rarely affects the final color of the treated piece. (Hydrochloric acid pre-treatment can also be used to improve the penetration of PEG into wood, although the finished product may be more prone to checking and shrinkage.) To make the pre-treatment bath, mix one volume of HCl to nine volumes of water. The duration of pre-treatment is very variable, but objects 5-10 cm thick should be left in the acid for approximately four days, while objects less then 5 cm should be left in the acid for about two days. After pre-treatment, it is necessary to rinse the wood in running water for three to five days to thoroughly remove all traces of the acid before continuing to Step 2 (above). This pre-treatment is optional and is often eliminated because of the potential damage to the object.

In practice, ethanol is often used instead of accetone as a solvent for the rosin (especially when treatment is carried out in a PVC pipe). Room-temperature treatments, both in acetone and isopropanol, are also commonly employed. If room temperature treatments are used, the treatment time is increased considerably to ensure complete saturation of the object with the rosin solution.

The advantages of the acetone-rosin treatment include the fact that treated wood is light in weight, dry, strong, and can be glued and repaired easily. Because rosin does not react with any of the metals, the acetone-rosin treatment can be used on compound wood and metal objects. It is considered by many to be the treatment of choice for all composite wood/metal artifacts. Disadvantages include the flammability of acetone and the high cost of materials, which make this treatment practical only for small objects. In addition, the treatment would not be an ideal choice in cases where it is necessary to flex the treated wood (i.e., when reconstructing a composite object) because the wood will splinter and break if it is flexed too much.

In general, the only problems that have resulted from using acetone-rosin have occurred when an old solution was used in which the acetone had already absorbed a considerable amount of water from the atmosphere. It is important that dry acetone or alcohol be used. Despite the inherent dangers of the treatment and the relative expense, the acetone-rosin treatment should be used more frequently by conservators, particularly for small pieces. This treatment has one of the better success records in wood conservation and produces the most dimensionally stabilized wood after the PEG 400 and 540 Blend treatments but without the hygroscopic problems of PEG (Grattan 1982b).

ALCOHOL-ETHER METHOD

This method is similar to the process used for drying out biological specimens. If necessary, the wood should be cleaned prior to treatment. The waterlogged object is first immersed in successive baths of alcohol until all the water has been replaced by the alcohol. Isopropanol or ethanol is usually used. This is followed by successive baths of acetone. If necessary, the dehydration progress can be monitored by measuring the specific gravity of each bath. When all water has been replaced by acetone, the object is immersed in successive baths of dimethyl ether to replace all the acetone with ether. When this has been accomplished, the object is dried very quickly by placing it in vacuum to rapidly volatize the ether. Ether is used because it has a very low surface tension of 0.17 dyne/cm compared to 0.72 dyne/cm for water. This means that when the ether evaporates, the surface tension forces are so low that there is no appreciable collapse of the weakened cell wall. If desired, 10-20 percent dammar resin, colophony rosin, or a mixture of the two may be dissolved in the final bath of ether to consolidate the wood and to protect it from warping due to changes in relative humidity. PVA may be used in place of the resins on some pieces.

This method has proved to very successful, producing a very natural-looking wood that is light in both weight and color. The dehydration process is very efficient, but the alcohols and ether must be water-free. For many objects, a dehydration of only alcohol and acetone is effective. Due to the high cost of the materials, this method is practical only for the treatment of small objects. The alcohols and especially the ether are highly flammable, and extreme caution should taken when conserving wood with this method.

CAMPHOR-ALCOHOL METHOD

In essence, this treatment is analogous to the dehydration method described above but with a temporary bulking agent added. The water in the wood is completely displaced by a water-miscible alcohol, which is then displaced by camphor. The camphor fills the cavities and cell walls of the wood, then slowly sublimates (goes directly from a solid state to a gas) without exerting any surface tension on the cell walls. Consequently, the wood does not collapse, shrink, or distort. The treatment results in a very aromatic, lightweight, and light-colored wood. Camphor can be dissolved in any of the alcohols. The following procedure is recommended.

1. Wash object thoroughly and with care.
2. Dehydrate the specimen in a series of alcohol baths. Begin with a 50 percent alcohol/50 percent water bath (50/50 percent), then 75/25 percent, then 90/10 percent, and finally 100 percent alcohol. This is the most conservative procedure and, in practice, the exact strength of the alcohol baths can vary. The dehydration process is dependent upon the condition of the object to be treated.
3. Accurately weigh the object after it has been dehydrated. Leave the specimen in a 95 percent alcohol/5 percent camphor solution heated to 52°C until the object stops gaining weight. Check the progress by weighing daily. Each time the weight levels off, add 5 percent camphor to the solution until a concentration of 75-80 percent camphor is achieved. This process may take several weeks or even months. Throughout the treatment the solution is kept heated to 52°C, and the level of the solution is kept constant by the addition of more alcohol. In practice, the treatment is carried out to completion with little monitoring.
4. After the object is removed from the bath, the alcohol will evaporate over a period of weeks, leaving behind crystallized camphor in the cell walls. Over a period of months, the camphor will vaporize by sublimation. Varnish, wax, polyurethane, dammar resin, colophony, and even PVA can be applied to the surface of the wood to reduce the evaporation of the camphor.

The camphor-alcohol method comes very highly recommended, but like the alcohol-ether method, it is economically impractical for the treatment of large objects and the solution is highly flammable.

FREEZE DRYING

Freeze drying is used with some regularity of small pieces of wood, but the only limitation is access to the properly sized freeze-drying container (Ambrose 1970, 1975; Rosenquist 1975; McCawley et al. 1982; Watson 1982). In the past, the main problem that presented itself was the tendency for the surface of the wood to check and crack. This is caused by the ice crystals expanding and damaging the cell walls. Ambrose (1970) found that if the wood is pre-treated by soaking it in a 10 percent solution of PEG 400 until it is saturated, the formation of ice crystals during the freeze-drying process is essentially eliminated. This pre-treatment has become a standard element of the freeze-drying method for wood, as well as for leather. In addition to inhibiting the formation of ice crystals during freeze drying, the PEG introduced into the object during pre-treatment will act as a humectant after treatment and prevents the wood from undergoing excessive shrinkage.

More recently, Watson (1987:274-275) observed that a 20 percent or higher PEG solution will dehydrate and kill any microorganisms present in the solution through osmosis. He recommends using 20 percent PEG 400 for mildly degraded wood and 10 percent PEG 400 + 15 percent PEG 4000 for more degraded pieces. For severely degraded wood, the PEG 4000 may be increased to up to 25 percent, but treatment time is increased when PEG 4000 is used. If a PEG solution of less than 20 percent is used, a fungicide, such as 1 percent borax/boric acid or Dowicide 1, should be mixed with the PEG solution to stop any slime or mold from growing in the solution during pre-treatment.

Following pre-treatment with PEG, the wood is frozen in a domestic freezer. After freezing, it is recommended that the wood be placed in a freeze-drying chamber at a temperature of -32 to -40°C, and a vacuum applied after the temperature of the wood reaches -25°C. During the process, the frozen ice crystals sublimate, and the water vapor is frozen onto the condenser coils. This continues until all the water is removed, which can be determined by weighing the piece being treated. The treatment is completed when the weight loss stabilizes. After treatment, the wood should be stored in a relative humidity of 45-60 percent. Freeze drying as described here and in the chapter on leather is essentially the same when treating any waterlogged organic material. (See Watson 1987 for additional details.)

Although the freezing can be done in a chest freezer, like biological specimens, a quick freeze is best. This can be achieved by immersing the wood in a container with acetone and dry ice (frozen CO_2). Some acceptable results have been achieved using non-vacuum freeze drying in a domestic freezer (particularly frost-free freezers). When a domestic freezer is used, the pre-treated wood is placed in the freezer and left there until it is dried. In this non-vacuum process, treatment times are in terms of months, as opposed to weeks in a vacuum freeze drier (McCawley et al. 1982).

Of all of the treatments discussed in this section, freeze drying is the most expensive due to the high cost of freeze dryers. Because of the size limitations of most freeze dryers, and the substantially higher costs when investing in equipment capable of treating larger objects, freeze drying is restricted to small objects in most laboratories.

SILICONE OIL TREATMENT

Since 1993, Dr. C. Wayne Smith of the Conservation Research Laboratory and the Archaeological Preservation Research Laboratory at Texas A&M University has been conducting research in the use of polymer media for the stabilization and conservation of organic materials. Waterlogged wood, glass, leather, woven basketry, and cork have been successfully conserved with polymer media, as well as artifacts such as corn cobs, which have been nearly impossible to conserve while maintaining the diagnostic features of the samples. The conservation of animal hides, biological tissues, and archaeological and histological bone samples has also been successful. Electron microscopic and chemical analysis of organic samples, which have been stabilized by the displacement of free water and air with silicone polymers exhibit some unique qualities over water-stored and air-dried specimens. An informal survey of university laboratories and departments has indicated that there are numerous areas where silicone bulking and related technologies would have almost immediate beneficial impact. The same holds true for museum artifact conservation, archival work, and in industrial applications.

A simplified version of the silicone bulking process, which is applicable for the treatment of small wood artifacts and other organic material is as follows:

1. Place waterlogged wood directly into a bath of ethanol and hold under a vacuum (10 kg) for approximately one hour.
2. Place the dried wood into a bath of acetone and hold under a vacuum for approximately one hour.
3. Measure out a suitable amount of SFD-1 silicone oil and mix 4 percent isobutyltrimethoxysilane by weight into the silicone oil. The isobutyltrimethoxysilane is a cross linker that sets the silicone oil up for curing in the next steps. Keep wood submerged in this mixture under a low vacuum (5 kg) overnight. It is important during this stage not to draw too high of a vacuum; this will prevent the collapse of the wood cells.
4. Remove wood and pat dry with a dry rag to remove excess silicone oil on surface.
5. Place the wood in a closed container with a small dish containing a small volume of FASCAT Catalyst 4200 in it. Place everything in a furnace heated to 52°C. The heat of the furnace vaporizes the FASCAT and cures the silicone oil in the wood..

This silicone oil treatment results in a very naturally colored wood that undergoes little to no dimensional changes. The wood is stable and does not require the close environmental controls like some other treated woods. The conservator must keep in mind that this treatment is not reversible; however, few of the other treatments outlined in this chapter are reversible.

Reversibility in Artifact Conservation

Ideally, reversibility is a desirable aspect of any conservation process. In reality, however, the issues of reversibility have been grossly overstated and, in many cases, misrepresented. For example, it is impossible to remove all of the polyethylene glycol from a conserved piece of waterlogged and badly deteriorated wood. During the process of treatment, some of the PEG is chemically bonded to the remaining lignin and cellular structures of the wood, preventing the complete removal of the polymer. In addition to chemically bonding, additional PEG will simply be trapped in cellular voids. Even the best methods that treat wood with PEG cause intracellular damage during treatment. In essence, the process of conserving the wood may undermine the structural integrity of the wood. The process of removing PEG causes additional damage to the already weakened physical structure of the wood. More times than not, the process of re-treating heavily waterlogged, damaged timbers causes more damage than should be desirable.

Too often, the theoretical state of reversibility of an artifact outweighs important issues that include the degree of artifact degradation, effects of attempted treatment reversal, the real potential for successful 100 percent reversibility, and the best interest of the artifact. In contrast, silicone oil treatments for even heavily waterlogged and damaged wood do not cause the cellular distortion that has been associated with PEG treatments. After treatment, thin sections of polymer-treated wood samples are so well preserved that in most cases, post-treatment genus and species identification are possible.

To date, it has been demonstrated that silicone and polymer treatment processes are reversible. In reality, however, the potential for loss of diagnostic attributes is too high. This suggests that a great deal of research needs to be completed in the development of reversible processes. Expected longevity, short time frame for conservation, and ease of curation, however, are invaluable aspects of silicone and polymer processes that make them a serious consideration for the treatment of many artifacts.

The greater issue which conservators need to address is the long-term well-being of an artifact assemblage. Many of the conventional processes which are routinely used for the conservation of artifacts have a relatively short life expectancy. This is why reversibility has always been an issue. In the case of PEG-treated artifacts, permanent curation in climate- and temperature-controlled environments only prolongs, to some degree, the life expectancy of the artifact. Water miscibility and chemical changes within this bulking media inevitably cause slow degeneration within the artifact.

The longevity of silicone and polymer processes is not an issue. Extensive testing and nearly 25 years of data collected by the silicone and polymer industries has demonstrated that the minimum half-life of the polymers used in conservation is at least 200 years. Ease of treatment in using these new technologies, too, is another consideration. Actual treatment times for the conservation of very delicate glass beads recovered from excavations of the Uluburun shipwreck (ca.1300 B.C.) is approximately 20 minutes. Once completed, the beads require only a brief curing period before they can be handled.

The last consideration to bring to the whole issue of reversibility is that strict adherence to traditional technologies is a good way to never discover new, and hopefully better technologies. This manual does not suggest that silicones are the panacea for all conservation needs. Rather, it suggests that these new technologies will, and are, having an impact in archaeological conservation simply because reversibility has never been an absolute fact using traditional processes. Silicone and polymer processes are merely an additional set of tools in the conservator's tool kit. Research has indicated that the following decades will hold exciting new advances in the science of archaeological conservation. Conservation sciences have a responsibility to seek out, define and refine tomorrow's technologies.

SUMMARY

There are several other treatments for conserving waterlogged wood, such as bulking with paraffin in a solution of hexane, but they are not extensively used. What is most important to realize is that the problems of conserving waterlogged wood may be overcome with a number of treatments. The decision to select a treatment may be dependent upon one or many factors: a particular color of wood or enhanced grain is desired; the resulting wood must be glueable, flexible, or rigid; the wood is part of a compound wood/metal artifact; or the resulting product cannot be sensitive to fluctuations of humidity and can withstand storage in adverse conditions. All of these issues may be of concern to the conservator, and there are ways of treating waterlogged wood that provide the desired result for each of these cases. All of the treatments outlined in this chapter are applicable to different situations and all should be considered acceptable alternatives to the conservator.

Leather Conservation

IN THIS FILE:

PRELIMINARY CLEANING

As with all porous material, it is necessary to remove the bulk of the soluble salts present in leather recovered from marine environments. The procedure is the same as that described earlier for bone and ceramics. Prior to conservation, archaeological leather must be washed in order to remove any ingrained dirt. Ideally, leather should be washed in water alone. A variety of mechanical cleaning techniques may be required, depending upon the condition of the leather and the particular cleaning problem. Soft brushes, water jets, ultrasonic cleaners, and ultrasonic dental tools are effective mechanical cleaning tools for leather. If chemical cleaning is necessary to remove ingrained dirt, a small amount of non-ionic detergent (about a 1 percent solution) or sodium hexametaphosphate may be used. If Calgon (a commercial water softener) is used, first ensure that the pH is between 3 and 5; the addition of additives may make it unsafe to use on leather. Rinse the leather well after washing. Do not use any chemicals that will damage the leather's collagen fibers.

A safe storage solution for waterlogged leather, or any organic material for that matter, can be made by preparing a stock solution of 50 percent water/50 percent ethanol. To the solution, add 10 percent glycerin by volume and two to three drops of formaldehyde.

The conservator should always keep in mind that it is often better to leave stable stains on the leather than to damage the leather by trying to remove them. For stain removal, particularly iron staining, 3-5 percent ammonium citrate or ethylene-diamine-tetraacetic acid (disodium EDTA) is used. Commercial trades names for EDTA are Titriplex III and Disodium Deterate. Soak for two to three hours while monitoring closely, then rinse the piece in running water or standing tap water until all chemical residues are removed. Check the pH of a standing bath of water containing the leather to determine if the chemical removal is complete. Always keep in mind that chemicals used to clean rusts and mineral concretions (e.g., oxalic acid, EDTA) may produce further hydrolysis of the proteinaceous collagen fibers in the leather. Furthermore, they may remove tanning and/or coloring agents, painted decorations, and other attributes that are part of the diagnostic attributes of the leather object. Caution should be exercised when using any of these chemicals on leather, as diagnostic attributes should never be removed.

Freeze drying and solvent dehydration are the most common conservation treatments for waterlogged leather. The drying behavior of any piece of leather, however, is dependent upon its condition at deposition, the burial environment, the genus, species, health, and sex of the individual (man or beast), the location of the skin on the body, the production or tanning method used, and finally, the leather object's history. Very good results have been achieved in the conservation of bog bodies through freeze drying using 15 percent PEG 400. The PEG acts as a lubricant to minimize skin and bone shrinkage during drying.

TREATMENT OF BRITTLE and/or DESICCATED LEATHER

The following treatments that involve the addition of lubricants have been used successfully on brittle and/or desiccated leather. Glycerol, which is soluble in water and alcohol, acts as a humectant for the leather.

SMITHSONIAN GLYCERIN TREATMENT

59 percent glycerin (glycerol)
39 percent water
1 percent formaldehyde or 1% Dowicide (TM) 1

OR

25 percent glycerin
75 percent alcohol

Immerse the artifact in the solution until the leather is pliable. (When an alcohol solution is used, it is difficult to determine when the leather is pliable because the alcohol makes the leather stiff.) Treatment may require several weeks. The treatment restores flexibility, but glycerin is hygroscopic and can support mold growth. In spite of this fact, the Smithsonian Glycerin Treatment has been used successfully.

Waterlogged leather recovered from excavations by The Museum of London is conserved in a solution of 30 percent glycerin and 70 percent alcohol (ethanol) for two weeks. The leather is then dried in three successive baths of acetone, each three hours long (glycerin is not soluble in acetone). Similar results can be achieved by using 10-40 percent glycerin mixed in 90-60 percent alcohol or water. Avoid using concentrated glycerin. While the solutions in alcohol can remove tanning agents, alcohol speeds up the conservation process and confers greater mechanical strength to the leather than will a water solution.

The glycerin treatment has also been applied to basketry, matting, sandals, etc. to restore pliability, quite often with disastrous results. It should be kept in mind that there is no reason to make something flexible or pliable if it was not particularly pliable in the first place. The glycerin treatment can be used in combination with PEG. To retreat any object that was conserved with glycerin, such as basketry, remove the glycerin with successive changes of alcohol baths.

BRITISH MUSEUM LEATHER DRESSING TREATMENT (BML)

200 gm (7 oz) anhydrous lanolin
30 ml (1 oz) cedarwood oil (acts as a fungicide)
15 gm (½ oz) beeswax (optional)
350 ml diethyl ether (B.P. 15-25°C) or 330 ml of hexane

Heat the first three items together (beeswax can be omitted, its function is to act as a polish) and then pour the molten liquid into the ether or hexane. Allow to cool while constantly stirring. Exercise extreme caution, as ether and hexane have low boiling points and are very flammable. Apply sparingly to the leather and rub well. Wait two days, then polish the treated leather with a soft cloth. Very hard leather can be soaked in a solution of one part BML: three parts Stoddards Solvent. BML darkens the leather, but it is a treatment with a good success record.

POLYETHYLENE GLYCOL (PEG) TREATMENTS

Dry leather can be saturated with water or alcohol and treated with PEG 1450, PEG 540 Blend, PEG 600, or PEG 400. In the past, leather was treated in PEG which was heated to a temperature of 40-50°C. Presently, most leather treatments are carried out at room temperature because heat is generally detrimental to leather.

The PEG treatment consists of immersing leather in a dilute solution of PEG (i.e., 10 percent) in water or alcohol and increasing the PEG concentration in 10 percent increments as it is absorbed by the leather. A final PEG concentration of 30 percent in solution is adequate for most archaeological leather. Keep the artifact immersed in the 30 percent PEG solution for several days until the leather is flexible. Once pliable, remove from the solution and clean off excess PEG from the leather with toluene or water. Allow treated leather to dry slowly under controlled conditions.

As mentioned in previous chapters, there are several types of PEG, and each has its own characteristics. PEG 540 Blend (equal parts of PEGs 1450 and 300) is slightly hygroscopic and becomes moist at high humidity; for this reason, the surface of the leather treated with PEG 540 Blend is sometimes sealed with a hard wax, i.e., a mixture of 100 gm microcrystalline wax and 25 gm polyethylene wax. PEG 3250 is very hard and is not very hygroscopic. Its main disadvantage (in some cases advantage) is that the treated leather is rigid. When using PEG 3250, form the treated specimen to its final shape while the wax is still warm and then allow the artifact to cool. PEG 1450 gives consistently good results. The various PEG treatments are more commonly used for the conservation of dry leather. A 15 percent PEG 400 solution is commonly used as a pre-treatment when the leather is to be freeze dried.

PEG-treated leather can be hygroscopic, greasy, and dark in color. There is the additional possibility that the PEG may eventually migrate out of the leather.

BAVON TREATMENT

Bavon ASAK 5205 is a water-soluble emulsion, while Bavon ASAK ABP is solvent-soluble emulsion. The exact chemistry of Bavon is unknown. In some sources, it is described as being an alkylated succinic acid-mineral oil blend. Bavon ASAK-ABP is described as being a copolymer of polyhydric alcohol and a partial ester of an unsaturated hydrocarbon. In archaeological conservation, Bavon works as a lubricant that makes leather pliable and gives it a natural brown appearance.

Very hard, desiccated leather has been successfully softened by soaking it in a concentrated Bavon leather dressing consisting of six parts Bavon ASAK ABP to four parts 1:1:1 trichloroethane. Soak until satisfactory pliability is reached, then place the leather between blotters and glass and allow it to dry.

TREATMENT OF WET OR WATERLOGGED LEATHER

Leather, like a lot of organic material from a marine environment, undergoes some complex changes in a marine environment (Florian 1987). The difficulties in achieving natural looking, chemically stable results have long been known by conservators (Jenssen 1983). The best review of the most common treatment currently in use is presented by Jenssen (1987). The most relevant treatments are discussed. below.

Waterlogged leather should be stored in water with 0.1 percent Dowicide 1 prior to treatment. If the leather is to be treated in an organic solvent, the leather can be stored in 50 percent water/50 percent ethanol or straight ethanol; a fungicide is not required.

Treated leather should not be stored in an environment with a relative humidity higher than 63 percent.

POLYETHYLENE GLYCOL (PEG) TREATMENTS

Treat with the method described above for desiccated leather, using PEG 400, 540 Blend, 600, 1450, or 3350. Gradually increase the concentration of PEG in solution up to 30-100 percent. Treatments with aqueous solutions of PEG are slower processes but are less expensive than treatments involving solvent solutions. Some conservators prefer alcohol treatments, while others think that alcohol treatments cause the leather to shrink more than comparable aqueous treatments. Solvent solutions, however, produce a lighter leather with more uniform shrinkage. All the PEG treatments for waterlogged leather are satisfactory by themselves, but treatment is considerably enhanced if the leather is taken through a final step of freeze drying. The freeze-drying process is identical to that described earlier for wood. A commercial freeze-drying vacuum chamber works the best; however, very good results have been obtained using domestic chest freezers. The former takes only a week or so, while the latter may take several weeks. Progress can be determined by regular weighing of the object to determine weight loss as the leather loses moisture.

BAVON TREATMENT

1. Wash leather in a 1 percent solution of Lissapol, castile soap, soft soap, or saddle soap; never use commercial detergents on leather as they may extract tanning materials.
2. If iron stains are present, they can be removed by immersing the leather in a solution of tap water and 3-10 percent disodium EDTA (pH 4) or 3-5 percent ammonium citrate (pH 5) for a maximum of one hour (shorter if possible). EDTA has been reported to damage fibers of leather but is relatively safe if used selectively and cautiously. Ammonium citrate is recommended over disodium EDTA by the Canadian Conservation Institute.
3. If calcareous material is present, place the leather in a 2 percent hydrochloric acid solution for up to one hour.
4. Rinse the leather thoroughly in running water for 30 minutes to lower the pH to 3-6 or to the pH of the rinse water.
5. Dehydrate the object in acetone. Use two or more successive hour-long baths.
6. Air dry until the leather is supple, then place between absorbent tissue and glass to dry for 24 hours.
7. Apply Bavon leather dressing (below) with a brush. Flex and manipulate leather during the application of the Bavon.

Bavon Leather Dressing

1 liter of stabilized 1:1:1 trichloroethane
1 gram Dowicide 1
50 grams anhydrous lanolin
20 grams Bavon ASAK-ABP

GLYCERIN TREATMENT

Waterlogged leather recovered from excavations by The Museum of London is conserved by placing it in a solution of 30 percent glycerin and 70 percent alcohol (ethanol) for two weeks. The leather is then dried in three three-hour long baths of acetone (glycerin is not miscible in acetone and is, therefore, not removed in the acetone baths). Good results can also be achieved with a solution of 10-40 percent glycerin mixed in 60-90 percent alcohol or water.

FREEZE DRYING

Freeze drying is the best method for conserving waterlogged leather. The leather is first immersed in a 15 percent solution of PEG 400, which acts as a humectant and prevents excessive shrinkage (a fungicide, such as 1 percent boric acid should be mixed with the PEG solution). After immersion, the object is frozen to -20 to -30°C. Like biological specimens, a quick freeze is best. This can be achieved by immersing the leather in acetone with dry ice (frozen CO_2). The piece is then placed in a freeze-drying chamber under vacuum for a period of two to four weeks. Some acceptable results have also been had using non-vacuum freeze drying in a (preferably frost-free) freezer chest.

DEHYDRATION USING ORGANIC SOLVENTS

This treatment involves the replacement of water in leather with a water-miscible organic solvent. In most cases, a sequence of solvents with decreasing polarity is used, e.g., a series of baths of x percent water/x percent of isopropanol, followed by a bath of 100 percent isopropanol, a bath of 100 percent ethanol or methanol, 100 percent methyl ethyl ketone, 100 percent acetone, and finally 100 percent ether. Slow desiccation of glutinous collagen fibers allows their surfaces to become less sticky and less brittle and thus more flexible. This example is a very conservative method of treatment. In most instances, fewer baths are used and for some leather, drying only through acetone is necessary. The following solvent dehydration treatment, described by Plenderleith and Werner (1971:34), allows the leather to dry out in a flexible condition without undue shrinkage.

1. Remove iron stains with 5-10 percent disodium EDTA (pH 4).
2. Rinse the leather in clean water, brush lightly.
3. Remove excess water by soaking the object in methyl ethyl ketone or acetone.
4. Immerse the object in carbon tetra-chloride with a fungicide, such as oxide of naphthenate.
5. Dry between blotting paper and glass plates.
6. Apply leather dressing and work the leather into shape if necessary.

Of the treatments discussed above, solvent-drying treatments followed by the application of a leather dressing are the most effective. Controlled air drying from an aqueous state never works. The contractile forces of the escaping water draw the protein fibers together, causing the leather to harden and shrink. Some conservators prefer freeze drying with a pre-treatment of PEG 400. These are the two most common treatments, and both can give acceptable results, but there is always the problem of the leather feeling greasy, overly stiff, and/or too dry and brittle when treated by any of the methods now in general use.

SILICONE OIL

The process of treating waterlogged leather with silicone oil is very similar to the treatment outlined for waterlogged wood. In the treatment of waterlogged leather, however, best results are obtained when the catalyst is painted onto the surface of the leather after it has been saturated with silicone oil and a crosslinker.

Textile Conservation

IN THIS FILE:

The term 'textile' is applied to woven objects and also to fabrics which are the products of other kinds of interlacing of yarns, such as braiding, looping, knitting, lace making, and netting. The textile category also includes materials such as felts and non-woven materials in which the fibers gain coherence by a process other than spinning.

This brief discussion of textile conservation is limited to the natural fibers of animal and plant origin: wool, hair, silk, cotton, flax, jute, hemp, nettle, grass, etc. The animal fibers consist primarily of protein and are more resistant to decay than vegetable fibers, which are composed primarily of cellulose. Flax and cotton, for example, are very susceptible to attack by bacteria under humid conditions and seldom survive in archaeological environments. All textiles are deteriorated by light, insects, microorganisms, and air pollution which, alone or together, cause considerable loss of tensile strength and pliability. The oxygen in the atmosphere affects all organic substances to varying degrees. Prolonged exposure to normal atmospheric conditions will cause textiles to weaken and disintegrate. The speed of the deterioration varies according to environment and the nature of the fibers. The main factors that promote the decay of textiles can be categorized into three groups:

1. Organic: Because textiles are organic, they are subject to attack by molds and bacteria. Decomposition is greatest in situations that favor the growth of these organisms, such as damp heat, stagnant air, and contact of the material with vegetable matter. Attack by destructive insects may also be encountered.

2. Physical: Excessive heat causes desiccation and embrittlement; exposure to ultra-violet light causes a type of deterioration known as 'tendering,' as well as the photochemical degradation of susceptible dyes.

3. Chemical: Exposure to noxious gases can also cause tendering. In some cases, these gases are converted to acids, which are the main cause for the deterioration of some textiles.

In general, textile conservation should be left to specialists; however, many archaeological specimens can be treated even by novice conservators. Fibers that compose a fabric should be identified before any treatment is undertaken, particularly if stain removal is required. Physical tests, such as burning, quickly identify the presence of animal fibers, which do not burn readily and shrivel into a residue of carbon. These fibers usually emit the distinct odor of singed hair. Vegetal fibers burn easily to a fine ash. Many fibers and hairs can also be readily identified by microscopic examination. Animal hairs, for example, can be identified by their characteristic cuticle patterns and medullar cross sections. Simple staining tests enable the conservator to distinguish between the different kinds of fibers.

The textile materials encountered most often in archaeological sites are linen, cotton, wool, and silk. Linen is a spun and woven vegetable-based fiber derived from flax stalks and branches. Linen fibers lie close together and are durable. They withstand moderate alkaline conditions because of their cellulose content, but are readily affected by acids. Moisture easily passes through the fibers of linen, causing the material to undergo dimensional and weight changes as well as changes in the overall strength. Linen does not take dye well and is usually left in a bleached or unbleached white state.

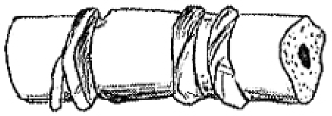


Figure 8.1. Schematic drawing of flax.

Cotton is a vegetable fiber derived from lint on the cotton seed. It can survive in moderate alkaline conditions but is adversely affected by acids. Cotton does not transmit moisture like linen and is very absorbent in its processed state. It is this characteristic which allows cotton to take dyes well. Cotton has a very characteristic clockwise twist; for this reason, it is commonly spun in a 'Z' twist.

Figure 8.2. Schematic drawing of cotton.

Figure 8.3. Schematic drawing of wool.

Wool consists of protein fibers. The majority of the amino acids in the protein of the wool are keratin, which contains insect-attracting sulfur. Wool fibers absorb more moisture and accept dyes better than vegetable fibers. Wool is not a strong fiber and weakens considerably when wet.

Figure 8.4. Schematic drawing of silk.

Silk is an animal (insect) fiber that is derived from the cocoon filament of the silkworm. Because it is basically protein, silk is easily affected by alkalies and various inorganic acids. Like wool, it easily absorbs moisture and will take dyes readily. These dyes, however, are not as light-fast as those on wool. Silk is as strong as a steel wire of the same diameter but is very light sensitive. Therefore, it will break down faster than wool when exposed to ultra-violet rays.

The proper treatment of textiles usually requires the use of flat, shallow pans, hot plates, and racks, or other devices that can support fragile textiles during rinsing, treatment, and drying. Treatment involves documentation, cleaning, reinforcing, sterilization, and proper storage and protection from environmental dangers.

DOCUMENTATION

A thorough documentation, both photographic and written, should record all pertinent information about the textile to be treated. The various features and properties that the conservator should look for are:

1. The nature of the fibers
2. The spin of the yarn (i.e., 'Z' or 'S' twist)
3. The number of wefts and warps per inch (or centimeter)
4. The type of weaving and of dye (water-fast or soluble)
5. Paint
6. Metal threads, and any other features that may be diagnostic or of interest.

CLEANING TO REMOVE SOIL, DISCOLORATION AND STAINS

A great number of substances can be removed from textiles by simply washing the artifact in water. De-ionized water is always preferred. Add 0.4 to 1 percent ammonium hydroxide (0.4 percent for animal fiber, 1 percent for vegetable fibers) to the water for greater cleansing power. If necessary, add 1 percent neutral non-ionic detergent (such as Lissapol N) to remove more stubborn soil. During the washing and cleaning process, the fabric can be bleached in a 4 percent hydrogen peroxide solution. For more stubborn stains (including mildew, mold, black sulfide stains, and organic stains), soak the artifact in one of the following solutions:

Stain Solution 1

1 liter de-ionized water
60 ml 30 percent hydrogen peroxide
2.5 g sodium silicate dissolved in 100 ml hot de-ionized water

Stain Solution 2 (for more stubborn stains)

1 liter de-ionized water
300 ml 30 percent hydrogen peroxide
20 g sodium silicate
5 g sodium carbonate

5 g sodium hydroxide

Soak for ½ to 1 hour or until the stain is removed then place the artifact in a closed bag to oxidize.

Sodium silicate and metasilicate are stabilizers, which are added to control the decomposition of hydrogen peroxide (H202) to water (H20). Whenever possible, a simple solution of hydrogen peroxide (and possibly a stabilizer) is recommended for stain removal because as the hydrogen peroxide loses oxygen, it bleaches and converts to water. Therefore, there is no danger of continuing chemical action. Hydrogen peroxide can be used on all vegetable fibers and its bleaching effect is permanent. Do not use hydrogen peroxide on hair or any fiber that was not white when originally in use. The addition of different sodium or alkali compounds are used to control the pH and to increase the cleaning power of the solution.

Copper corrosion stains can be treated with 1-5 percent ammonium hydroxide. For silver corrosion stains, first soak the stain with potassium cyanide then apply a few drops of iodine. Remove the resulting silver iodide product with a 5 percent solution of sodium thiosulfate. Textiles with iron rust stains can be treated with any of the following chemical solutions:

1. 5 percent hydrochloric acid [muriatic acid (HCl)]
2. 5 percent oxalic acid $H_2C_2O_4$
3. 10 percent hydrofluoric acid (HF)
4. 5 percent EDTA disodium
5. 5 percent acetic acid (CH_3COOH)
6. 5 percent formic acid (HCOOH or CH_2O_2)
7. 2-10 percent ammonium citrate

Oxalic acid and hydrofluoric acid solutions are the most effective for removing iron stains from archaeological textiles. Extreme caution must be taken, however, when handling hydrofluoric acid. EDTA disodium and ammonium citrate solutions are often recommended because their higher pHs (>2.5) potentially do less damage to fibers. These solutions are effective but rather slow. After any chemical treatment, intensive rinsing in de-ionized water will remove all residue from the textile which may adversely affect the fibers over time.

For textiles that cannot be cleaned with water (such as textiles with water-soluble dyes), dry cleaning using organic solvents, such as perchlorethylene or trichlorethylene, or petroleum solvents, such as white spirits, is recommended. The advantages of solvent cleaning are:

1. Unlike water, solvents do not soften textile fibers, minimizing the risk of shrinkage and loss of shape.
2. Dyes not fast in water may be undisturbed in solvent.
3. Solvents are more efficient than water for dissolving grease.
4. In general, solvents are volatile and dry quickly.

The costs of solvent cleaning are much higher, and the problems of toxicity and inflammability must be taken into consideration.

REINFORCING FRAGILE TEXTILES

Quite often, the only practical method of reinforcing fragile textiles is to fasten them to a synthetic mesh of terylene, light cotton fabric, fiber glass, or other substance. Particularly fragile textiles are sometimes mounted between sheets of plastic or glass. In most cases, a heat-sealable adhesive, such as polyvinyl acetate, polyvinyl alcohol, Acryloid B-72, or their emulsions, are used to coat the backing which is then ironed (heat-sealed) onto the textile. Any breaks in the threads either in the warp or weft of the material should be affixed with drops of glue to prevent additional unraveling

The conservator also has the option to consolidate and reinforce fragile textiles with various synthetic resins. Since water softens and makes textile fibers pliable, emulsions and water-soluble resins are preferred for textile consolidation. Water-based adhesives also give the conservator more 'working time' than solvent-based adhesives. The most frequently recommended resins for textile conservation are:

1. polyvinyl alcohol (water-soluble, dries clear with minimum shrinkage)
2. polyvinyl acetate (V7) (**note:** resin shrinkage during drying may distort fibers)
3. ethulose (ethyl-hydroethyl cellulose) (water-soluble, very pliable)
4. polymethacrylate
5. Acryloid B-72, 5 percent in toluene

A mixture of 0.15 percent ethyl-hydroethyl cellulose, 0.6 percent polyethylene glycol (PEG) 400, and 0.2 percent fungicide will consolidate fragile fabrics and restore moisture to dry, brittle fibers. A solution of 20 percent lanolin in toluene can be applied to fibers that have a tendency to shred or lint.

DISINFECTION

For wholesale treatment of mold and insect infestation, place the infested objects in a closed container with thymol crystals. The crystal can be vaporized by holding the container over a light bulb. After treatment with thymol crystals, spray the objects with a 0.5-1 percent Lysol solution. This treatment will remedy most problems. Carbon disulfide can also be used as a fumigation agent.

Disinfectant solution can be prepared in the lab by mixing 0.1 percent Dowicide 1 (ortho-phenylphenol), 68 percent ethanol, and 30 percent de-ionized water. This solution is lethal to most bacteria, fungal spores, and surface mildews. Dowicide 1 has a maximum solubility of 0.1 percent in water and 46-58 percent in the various alcohols. Alternatively, a solution of 2 percent DowicideA and sodium ortho-phenylphenate can be used. Dowicide A has a maximum solubility of 120 percent in water and approximately 350 percent in alcohol. For the majority of textile disinfectant needs, Lysol disinfectant spray will suffice. Lysol spray consists of 0.1 percent Dowicide1, 79 percent ethanol, 8 percent n-alkyl, and 0.035 percent n-ethyl morpholinium ethylsulfates (deodorizers and scents). The conservator should keep in mind that topical treatments are not long lasting.

CONSERVATION OF WATERLOGGED CANVAS AND ROPE

After a series of tests by the Conservation Division of the Western Australia Museum on artifacts recovered from a 19th-century shipwreck, the following sequence of treatment was proposed for the conservation of canvas (and other similar fabrics) and rope.

1. Immerse artifact in 10 percent hydrochloric acid to remove all adhering encrustation and some iron corrosion and stains.
2. Rinse artifact in running water. Watch for any dyes that may be adversely affected.
3. Soak artifact in acetone to remove any tar, pitch, tallow, or other acetone-soluble substances. Watch for any dyes that may be removed.
4. Soak artifact in 5 percent oxalic acid to remove the bulk, if not all, of the iron stains. Treatment time will vary from a couple of hours to a couple of days.
5. Immerse artifact in 5 percent EDTA disodium to remove any remaining iron stains. Soaking time will vary from a couple of hours to up to three days.

   Note: Both Steps 4 and 5 may be required for particularly stubborn iron stains. In other instances, either Step 4 or Step 5 may be used.

6. Bleach artifact in a 5 percent hydrogen peroxide solution. Particularly stubborn stains may be treated for short periods in a stronger (10-20 percent) solution. Perform this step only on cloth, canvas, and textiles that were originally white. Never use hydrogen peroxide on animal fibers.
7. Rinse artifact thoroughly in de-ionized or distilled water.
8. Dehydrate artifact in acetone and air dry.
9. If necessary, consolidate the material with a suitable synthetic resin. In some cases, the textile may have to be treated with heat-sealable resin and either dry mounted or sealed to a backing of another fabric, such as light cotton or a synthetic mesh.

SILICONE OIL TREATMENT OF WATERLOGGED TEXTILES AND ROPE

Waterlogged textiles and rope are currently being conserved using silicone oil. The results have been quite promising. See the Archaeological Preservation Research Laboratory Reports.

STORAGE

Store textiles in an environment that limits their exposure to atmospheric pollutants and ultra-violet light. Relative humidity should be kept at a maximum of 68 percent. (Environments with a relative humidity of over 70 percent encourage mold growth.) Ideally, textiles should be stored in a dark place with a low temperature of 10°C and a relative humidity of 50 percent or less. Moths and other insects should be deterred by keeping moth balls (paradichlorobenzene) in the storage area. This is particularly critical when storing wool.

Metal Conservation: Preliminary Steps

IN THIS FILE:

Archaeological material from marine sites presents some of the most difficult problems that are confronted by the conservator. The techniques of preserving this material have been carefully studied, and various techniques have been developed. The following sections describe the most applicable and useful approaches and conservation techniques that can be used to process and document metals recovered from shipwrecks and other underwater sites.

During most of the history of metallurgy only a few metals have been used. The metals of antiquity (iron, tin, copper, lead, silver, and gold) are those which were recognized and intentionally used with consistent regularity to manufacture tools, weapons, ornaments, hardware, and other paraphernalia. Each of these metals was used individually and in combination with the others, or with zinc or tin, to form more serviceable alloys, such as bronze, brass, and pewter.

From the moment of manufacture, the various metals and their alloys, except for gold, react with their environment and begin a corrosion process that converts them to more stable compounds. Before competent conservation techniques can be applied to a metal artifact, it is essential that the conservator be aware of the corrosion products that result from exposure to different environments. The nature of the corrosion products determines the technique and procedures that can be used effectively.

The corrosion of metals can be discussed in terms of terrestrial environments with temperate, tropical, and desert subdivisions, as well as aquatic environments, with salt and fresh water subdivisions. A more simplified approach is to look at the presence of oxygen and moisture in the environment. In any environment, moisture is a critical variable, and since aquatic environments, especially sea water, are the topic of interest here, dry conditions (where metal corrosion is minimal) are not considered. In sea water, the above variables, along with temperature, pH, and the presence of aggressive anions like chloride, determine the rates and types of corrosion.

The corrosion of iron in sea water will be discussed here; iron conservation treatments are presented in File 10A and File 10B. The corrosion and preliminary conservation of non-ferrous metals is discussed in File 11; the conservation of cupreous metals is discussed in File 12; silver and silver alloys are discussed in File 13; lead, tin, and lead alloys in File 14; and gold and gold alloys in File 15.

FERROUS METAL CORROSION

Iron is usually the most common metal recovered from archaeological sites. Due to the variety of conditions and environments within which corrosion can occur and the number and complexity of the corrosion products, iron presents the conservator with the most difficult problems of all the metals of antiquity. Iron corrosion processes are applicable to other metals and make iron a useful introduction to all metallic corrosion. The following information on corrosion processes relies heavily on Potter (1956), Evans (1961),Pourbaix (1966), Hamilton (1976), and Pearson (1987a).

ELECTROCHEMICAL CORROSION

In electrochemical corrosion, a galvanic cell is created when two different metals, or different areas on the same metal, are coupled by means of an electrical or ion-conducting electrolyte. The result is an electrochemical reaction. In essence, electrochemical corrosion is reserved for those processes where a current flows between anodic and cathodic areas situated at different parts of a metallic surface or between two different metals of the same or different material. The electrochemical oxidation of iron results in the formation of ferrous ions as the initial product.

Iron recovered from land sites that has only been exposed to ground and air moisture corrodes essentially by an electrochemical process. The corrosion of iron in sea water proceeds in a similar yet greatly accelerated manner because water generally becomes more corrosive as its salt content increases. Iron corrodes five times faster in sea water than in soil, and 10 times faster in sea water than in air (Cornet 1970:439).

The corrosion of metals submerged in salt water is a complex process. In the case of metal recovered from shipwrecks, the shipwreck itself has often been explained in terms of a large galvanic cell based upon the electromotive series of metals (Peterson 1969:30, 1972:244). Stated in general terms, all metals are compared in an electrochemical cell with a hydrogen electrode, which is given an arbitrary electrode value of 0. Metals that have a potential more negative than hydrogen in a galvanic cell are said to have a negative electrode potential, and metals having a potential more positive to hydrogen have a positive electrode potential. By measuring the electromotive force (EMF) in volts required to balance a galvanic cell formed by a particular metal immersed in a solution of its salts of normal cation activity and a hydrogen electrode, the metals are arranged according to their relative chemical activity or electrode potential into an electromotive series of metals (see Table 9.1). The least active metals are at the top of the series, the most active are at the bottom. The more negative the electrode potential, the more active the metal, and the greater the tendency for the atoms to lose electrons and form positive ions which go into solution. When the ions of a metal go into solution, the parent metal always becomes negatively charged, regardless of its electrode potential sign. When two metals form an electrochemical cell, the metal with the more negative reduction electrode potential in the electromotive series becomes the anode. It loses electrons and forms positive ions, which then go into solution. The more positive or noble metal in the cell forms the cathode and is given cathodic protection, while the anodic metal is preferentially corroded in any resulting electrochemical reaction.

Table 9.1. Electromotive Series of the Metals of Antiquity: Standard Reduction Potentials in Salt Solutions of Normal Ionic Activity at 20°C, pH 0.

	IONIC REACTION	**ELECTRODE POTENTIAL***	
Noble End (Cathodic)			
Gold (+1 aurous, +3 auric)	$Au^{+3} + 3e^{-} \quad Au$	+1.50	-
Silver (+1)	$Ag^{+} + e^{-} \quad Ag$	+0.799	-
Copper (+1 cuprous)	$Cu^{+} + e^{-} \quad Cu$	-	+0.552
Copper (+2 cupric)	$Cu^{+2} + 2e^{-} \quad Cu$	+0.337	-
Hydrogen (+1)	$2H^{+} + 2e^{-} \quad H2$	0.00	0.00
Lead (+2 plumbous, +4 plumbic)	$Pb^{+2} + 2e^{-} \quad Pb$	-0.126	-
Tin (+2 stannous, +4 stannic)	$Sn^{+2} + 2e^{-} \quad Sn$	-0.136	-
Iron (+2 ferrous)	$Fe^{+2} + 2e^{-} \quad Fe$	-0.440	-0.409
Iron (+3 ferric)	$Fe^{+3} + 3e^{-} \quad Fe$	-	-0.036
Zinc (+2)	$Zn^{+2} + 2e^{-} \quad Zn$	-0.0763	-
Base End (Anodic)			

*Electrode potentials in left column are from Evans (1963:end papers); potentials in the right column are from Hunsberger (1974:D120-125).

As a blanket explanation for the corrosion of different metals in a shipwreck in salt water, the large galvanic cell metaphor and the electromotive position of the metals have been overused and are not completely understood. The large mass of different metals associated with a sunken ship in salt water may consist of thousands of independent galvanic cells, each formed between two metals that have different electrode potentials. In order to establish a galvanic cell, the metals must be in very close proximity or in contact with each other. This requirement necessarily limits the metals that can form a galvanic couple to a single encrustation. Even then, variables, such as conductivity of the electrolyte, aggressive ion concentration, and mass transport, may alter or interfere with expected theoretical or laboratory reactions.

Any metallic surface is almost certainly to contain inclusions of more noble metals; it is very rare that a metal is 100 percent 'pure.' For this reason, a metal need not be in contact with a more noble metal to corrode in sea or tap water. An oxide-scale layer on a metal surface will be cathodic to the metal, which will be anodic in the presence of an electrolyte. A metallic couple between the two can form a number of galvanic cells. Electrochemical cells may also form on a chemically homogeneous metal in areas of mechanical stress, such as a dent or a bend, and concentrate the corrosion along this stress line. In shipwreck sites, stress corrosion is a very important factor in the corrosion and deterioration of given iron artifacts. Iron fastenings that are bent during the wrecking and sinking, for example, will corrode preferentially at the point of the bend, leaving a void but with good metal remaining at each end.

Even if a metal is pure, without an oxide layer or area of stress, immersion in a solution, such as sea water, which contains traces of salts of nobler metals can cause the formation of local cells at the metal surface, which effectively corrode the object (Potter 1956:238; Leigh 1973:20). In addition, the effects of different oxygen concentration, temperature, and pH at a metal surface may cause corrosion.

For iron artifacts buried in the ground, pitting is a prominent feature of the corrosion process. This anaerobic environment tends to be chemically reducing and forms soluble ferrous ions, which often diffuse some distance away from the iron surface. When iron is buried in an aerobic soil or exposed on the surface to the air, the ferrous ions initially formed in the corrosion process oxidize to ferric ions, resulting in layers of ferric oxide scale on the metal surface. This ferric oxide scale tends to form layers that may crack and spall due to the differences in the thermal expansion coefficients between the ferrous and ferric corrosion products and the metal. Alternatively, the corrosion products may inhibit additional corrosion by forming a protective film. Air-oxidized artifacts occupy more volume than the original metal and usually have obvious layers of ferric oxide scale. If salts, such as sodium chloride, are present in the environment, a very conductive solution is formed, and electrochemical corrosion is accelerated.

The electrochemical corrosion of metals has been detailed in a number of sources. In the case of iron, it has been shown that in any electrochemical cell where iron establishes a metallic couple in salt water with a more noble metal, such as copper or silver, or even with another piece of iron or a different part of the same iron object, the anodic and cathodic reactions are the same (see Potter 1956:236-237; Evans 1963:28).

At the surface of the more noble metal (the cathode), the following reaction occurs:

$$2H_2O + 2e \rightarrow H_2 + 2(OH)^-$$

The hydroxides combine with the sodium ion in the solution to form sodium hydroxide as the cathodic product:

$$Na^+ + OH^- \rightarrow NaOH$$

At the anode, the reaction is the production of ferrous ions:

$$Fe^+ - 2e \rightarrow F^{+2}$$

which, in turn combine with chloride in the salt water to form ferrous chloride as the anodic product:

$$Fe^{+2} + 2CI^- \rightarrow FeCl^2$$

On exposure to air, or solutions containing dissolved oxygen, the ferrous chloride oxidizes to ferric chloride and ferric oxide. Ferrous chloride and ferric chloride and are freely soluble and may yield ferrous hydroxide when they combine with the cathodic product sodium hydroxide:

$$FeCl^2 + 2NaOH \rightarrow Fe(OH)^2 + 2NaCl$$

In solutions containing dissolved oxygen, a secondary reaction oxidizes the ferrous hydroxide to a ferric state. In the presence of hydroxyl ions in a neutral or slightly alkaline solution, this hydrated ferric hydroxide (any form of ferric oxide with internal water, i.e., common rust) is precipitated on or around the electrodes of the cell. The sequence of reaction at an iron anode in the presence of oxygen as stated by Potter (1956:236) is:

ferrous ion	$Fe - 2e \rightarrow Fe^{+2}$
ferrous hydroxide	$Fe^{+2} + 2OH^- \rightarrow Fe(OH)^2$
hydrated ferric hydroxide (red-brown rust)	$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3 \cdot H_2O$

The primary anodic reaction of electrochemical corrosion of iron is the production of ferrous ions. The secondary stage, the oxidation of the ferrous ion compounds to a ferric state, is modified in anaerobic environments. Intermediate oxidation products of ferrous hydroxide, such as hydrated magnetite and black magnetite, are formed (Potter 1956:236-237; Evans 1963:28-29, 75):

$$6Fe(OH)_2 + O_2 \rightarrow 4H_2O + 2Fe_3O_4 \cdot H_2O$$

(green hydrated magnetite)

$$Fe_3O_4 \cdot H_2O \rightarrow H_2O + Fe_3O_4$$

(black magnetite)

Depending on the environment, the corrosion products can take on a variety states of division and hydration, as well as a variety of physical forms. It is common to find corroded iron from marine sites with an outer layer of hydrated ferric hydroxide (common rust), which has restricted the supply of oxygen to the ferrous hydroxide briefly formed at the surface of the metal. Laminated corrosion layers consisting of an inner layer of black magnetite, a thin layer of hydrated magnetite, and an outer layer of hydrated ferric hydroxide are formed:

$$Fe_3O_4/2Fe_3O_4 \cdot H_2O \textbf{\textit{ or }} 2Fe_2O_3 \cdot H_2O$$

It is easy to see how two different areas of the same metal object can become anodic and cathodic to form an electrolytic cell. Electrons flow from the anodic area to the cathodic area causing the metal to corrode by forming soluble positive ions at the anode. Millions of these cells over the surface of the metal result in massive oxidation, which continues until an equilibrium state is reached. The corrosion process is halted at the cells when they come into equilibrium but may continue at alternate anodic and cathodic positions on the object until the bulk of the metal is oxidized.

As metals corrode in salt water, there are localized changes in the pH, which upset the equilibrium between the dissolved calcium carbonate and dissolved carbon dioxide in the sea water (Leigh 1973:205). This results in insoluble precipitates of calcium carbonate and magnesium hydroxide. These precipitates intermix with sand, marine life, and corrosion products (especially ferrous hydroxide, ferrous sulfide, and magnetite) to form a hard dense layer of encrustation or concretion around the metal. The encrustation accumulates on the original metal surface to form a perfect mold around the object; furthermore, it will actually separate two metal pieces that were initially touching each other. Such encrustation effectively separates the metals from each other and destroys the electrochemical cell by cutting off the current flow and/or oxygen supply**.** It is rare, in fact, to find any two metal objects recovered from a shipwreck that are in direct contact with each other.

ANAEROBIC CORROSION

Despite the fact that the corrosion processes are impeded by the formation of encrustation, metal deterioration can continue due to the presence of sulfate-reducing bacteria. These bacteria play a large part in the corrosion of metals, especially iron in salt water. They also adversely affect metals in fresh water, as well as metals buried in the soil under anaerobic conditions (Evans 1963:224; Pearson 1972a:35; Leigh 1973:205). Sulfate-reducing bacterial activity accounts for most of the rapid corrosion of buried iron and steel pipelines in waterlogged clay soils in England (Farrer et al. 1953:80). As much as 60 percent of the corrosion of iron in salt water can be attributed to bacterial action (Pearson 1972a:35).

Sulfate-reducing bacteria, particularly the strains known as *Sporovibrio desulphuricans* (Pearson 1972a:35) and *Desulphovibrio desulphuricans* (Farrer et al. 1953:82) are commonly found in salt water, fresh water, and waterlogged soil, where decaying organic material consumes oxygen and creates localized anaerobic environments. Sea water has a large supply of sulfates, and under aerobic conditions, these bacteria use hydrogen to reduce the sulfates $(SO4)^{-2}$to sulfides (S^{-2}) as a metabolic by-product according to the reaction:

$$H_2SO_4 + 8H \rightarrow H_2S + 4H_2O$$

In this process, the hydrogen that accumulates on the iron as a cathodic product polarizes the cathode in an oxygen-free environment. The polarization of the cathode ordinarily halts the electrochemical corrosion process. However, the utilization of hydrogen in the metabolism of the bacteria depolarizes the cathodic areas of the cell, allowing corrosion to continue unabated. In addition, the hydrogen sulfide formed as a metabolic by-product reacts not only with iron but with all of the metals of antiquity (except gold) and accelerates the corrosion process. The hydrogen sulfide reacts with the ferrous ion from the anodic areas to produce ferrous sulfide and ferrous hydroxide, two major corrosion compounds of iron associated with objects recovered from the sea (Leigh 1973:205). On iron, the corrosion process (Pearson 1972a:34-35) proceeds as follows:

$$Fe^{+2} + H_2S \rightarrow FeS + 2H^+ \qquad \text{ferrous sulfide}$$

$$3Fe^{+2} + 6OH\ 3Fe(OH)_2 \qquad \text{ferric hydroxide}$$

———————————————————————————

$$4Fe + H_2SO_4 + 2H_2O \rightarrow FeS + 3Fe(OH)_2$$

(overall reaction)

The life cycle of sulfate-reducing bacteria stimulates both the cathodic and anodic reactions of the electrochemical corrosion process. In some cases, however, the precipitation of a continuous film or layer of iron sulfide may stifle rather than stimulate the anodic reaction (Evans 1963:225). Without the presence of sulfate-reducing bacteria, the corrosion of iron and other metals in anaerobic environments would be inhibited.

One observation that has become apparent is that the presence of wood in direct association with most metals has an adverse effect on them. Apparently, this results from the fact that as wood decays it consumes oxygen, thus creating an anaerobic environment that stimulates the establishment of sulfate-reducing bacteria. The wood also provides nourishment for the bacteria. This corrosion reaction is most evident on iron, silver, and lead in direct contact with wood.

FERROUS ALLOYS

There are comparatively few differences between the corrosion processes of iron and those of mild steel, wrought iron, and numerous low alloy steels (Evans 1963:93). Even cast iron oxidizes by the same processes, including the action of sulfate-reducing bacteria. In addition, when cast iron is submerged in salt water, it undergoes a corrosion process called graphitization (Patoharju 1964:316, 1973:3; Pearson 1972a:10). In this reaction the salt water conducts a current between the anodic pearlite and the cathodic graphite flakes in the iron to form a galvanic cell. The pearlite corrodes, leaving a porous framework of graphite filled with the iron corrosion products discussed earlier. This graphite framework can maintain the original form of the object with little outward change in appearance, but with a considerable loss of density and mechanical strength. The process can proceed until the bulk of the metallic iron has corroded within the graphite framework. Ultimately the graphite framework will become incapable of supporting the object by itself, resulting in the deformation of the object.

SUMMARY

The corrosion processes of iron in aquatic environments are generally known, but the reactions are complex and subject to many unpredictable variables. The majority of the resulting corrosion products, however, are predictable to a considerable degree of accuracy. This knowledge, while not replacing analytical tests for validation on particular objects, is usually sufficient to determine what conservation alternatives are warranted for any given artifact if its history is known.

The most commonly encountered iron corrosion products are:

$Fe(OH)_2$	ferrous hydroxide
$FeO(OH)$	ferro-hydroxide
$FeCl_2$	ferrous chloride, anhydrous
$FeCl_2 \cdot H_2O$	ferrous chloride, hydrated
FeS	ferrous sulfide
Fe_3O_4 ***or*** $FeO\ Fe_2O_3$	ferro-ferrous oxide (magnetite)
$2Fe_3O_4 \cdot H2O$	magnetite, hydrated
$2Fe_2O_3 \cdot 3H_2O$	ferric hydroxide (common rust)
Fe_2O_3	ferric oxide
$FeCl_3$	ferric chloride, anhydrous
$FeCl_3 \cdot x\ H_2O$	ferric chloride, hydrated

On metal objects recovered from shipwrecks, the most prevalent iron corrosion products are ferrous sulfide, magnetite, ferrous hydroxide, and iron chlorides. Many iron objects will completely convert to ferrous sulfide, leaving only a loose slush within a natural mold of encrustation. Other iron objects will completely mineralize to a massive oxide, magnetite, but retain their structural integrity and surface detail; some will be completely degraded to a loose granular oxide. In each case, iron sulfides are present in varying degrees. Also, iron chlorides are always a component part of any of the iron corrosion products. The main difference between exposed and buried iron concretions is the prevalence of magnetite in buried encrustations and the prevalence of ferro-hydroxide and ferric oxide in encrustations exposed to open sea water (North and MacLeod 1987:78), especially in high-energy zones, such as reefs.

Once iron has been removed from a marine environment, the corrosion process will continue, and even accelerate, unless certain precautions are taken. It is essential that iron artifacts be properly stored in an inhibitive solution to prevent further corrosion. If the iron in an encrustation is exposed to the air or to an uninhibited solution, the ferrous compounds can oxidize to a ferric state, which will occupy a greater volume and will scale off the surface. This process can disfigure an object and eventually destroy it. Without exception, it is much better to conserve iron artifacts with ferrous corrosion products rather than one with ferric corrosion products. Every precaution should be taken to prevent the ferrous corrosion products from oxidizing to ferric products through proper storage and treatment.

The greatest damage to marine iron after recovery is caused by the iron chlorides. The formation of ferrous chloride has already been shown by the reaction: $Fe^{+2} + 2Cl^{-}\ FeCl_2$, which, in turn, oxidizes to ferric chloride and ferric oxide in the general reaction: $6FeCl_2 + 3O_2\ 2FeCl_3 + 2Fe_2O_3$. Both of these reactions are gross oversimplifications, but the reaction proposed by Eriksen and Thegel

(1966:90) -- $Fe + 2NaCl + 2H_2O\ FeCl_2 + 2NaOH + H2$ -- is not thermodynamically feasible. Regardless of the exact equation, both the ferrous chloride and ferric chloride combine with water to form hydrates: $FeCl_2 \ x\ H_2O$ and $FeCl_3 \ x\ H_2O$, where x is normally 2, 4, or 6. It is these hydrated chlorides that cause the trouble. Upon exposure to moisture and oxygen, they hydrolyze to form ferric oxide or ferric hydroxide and hydrochloric acid. The hydrochloric acid in turn oxidizes the remaining non-corroded metal to ferrous chloride and hydrogen, or ferric chloride and water. In a simplified form, some or all of the following reactions may continue until no metal remains:

$$Fe - 2e \rightarrow Fe^{+2}$$

$$Fe^{+2} + 2Cl^{-} \rightarrow FeCl_2$$

$$4FeCl_2 + 4H_2O + O_2 \rightarrow 2Fe_2O_3 + 8HCl$$

$$4FeCl_2 + 7H_2O + O_2 \rightarrow 2Fe_2O_3 \cdot 3H_2O + 8HCl$$

$$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$$

$$4FeCl_3 + 9H_2O \rightarrow 2Fe_2O_3 \cdot 3H_2O + 12HCl$$

$$Fe^0 + 2HCl \rightarrow FeCl_2 + H_2$$

$$4Fe^0 + 3O_2 + 12HCl \rightarrow 4FeCl_3 + 6H_2O$$

Of the above corrosion products, it is possible by electrolytic reduction to reduce the ferrous compounds $Fe(OH)_2$, $FeCl_2$, FeS and the ferrous oxide portion of Fe_3O_4, which probably exists as $FeO \cdot Fe_2O_3$. It is not possible to reduce the ferric compounds in an aqueous solution. This problem is discussed further under the Electrode Potential heading of the section on Iron Conservation.

The preceding discussions on metal corrosion are necessarily brief and primarily refer to those corrosion products most commonly found on metals recovered from salt water. An early paper on the major corrosion products of the different metals can be found in Gettens (1963,1964). The most current and detailed discussion regarding the corrosion of marine iron can be found in North and MacLeod (1987).

PRELIMINARY STEPS: DOCUMENTATION, STORAGE, AND MECHANICAL CLEANING

The *Conservation of Antiquities and Works of Art* (Plenderleith and Werner 1971) is an early, general reference for the conservation of archaeological material from any environment. While it contains only a few direct references to the objects recovered by marine archaeologists, many basic conservation techniques are discussed in a general manner. It is regrettable that much of the extant literature on the conservation of iron and other metals from salt water has either been neglected, oversimplified, or is misleading as to alternative procedures, cost, time involved, and problems encountered. (See, for example, Peterson 1964, 1969, 1972; Townsend 1964, 1972; Eriksen and Thegel 1966; Marx 1971; Wilkes 1971.) Presently, the most comprehensive survey of the techniques of conserving iron from marine sites, as well as other material, is *Conservation of Marine Archaeological Objects* (Pearson 1987a).

Sea-recovered metals present the most difficult problems the conservator is likely to encounter, but all of the conservation procedures used on these metals can be applied to metals recovered from other environments. The absence of marine encrustation and excessive chloride contamination considerably reduces the length of time required to process and stabilize objects from non-marine environments.

Regardless of the conservation technique utilized, it is essential to understand that no treatment is sufficient unto itself. It is but a part of a series of conservation processes designed to assure that a lasting preservation will be achieved. The duty of the conservation laboratory is to take the metal specimen as received and deliver a stabilized object. This involves a number of sequential and alterative steps. The major steps in the conservation of metals recovered from marine environments are:

1. Preliminary Steps
    - a. Initial documentation
    - b. Storage prior to treatment
    - c. Mechanical cleaning
    - d. Preliminary evaluation

2. Treatment

3. Final Steps
    - a. Rinse after treatment
    - b. Drying
    - c. Sealant
    - d. Storage
    - e. Periodic inspection

INITIAL DOCUMENTATION

When one is responsible for conserving material resulting from an archaeological excavation, the basic approach to conservation should be that once an encrustation or any artifact has been delivered to the laboratory for treatment the conservator must (1) preserve and stabilize the specimen as well as possible, (2) recover useful archaeological information, and (3) acquire data for conservation research. These are possible only if extensive records are maintained, including detailed description, radiographs, black-and-white photographs, color slides, and notes on the preservation procedures used. Since all photographic negatives and prints are kept as a permanent record, they should undergo archival processing and be stored in a cool, dry, dark cabinet for maximum protection. Digital images are also recommended. All records should be well organized in a well-designed and readily accessible data base.

Proper records will include all the pertinent archaeological data, identifications, descriptions, and the complete conservation procedure for each artifact. Considerable archaeological data exists in the form of associations and provenience of artifacts within each encrustation. This information is recoverable only by in situ observation and recording by the conservator. In other words, the conservator is in a unique position to supply valuable archaeological data necessary to reconstruct details of the past. The conservation data record the treatment history of every specimen, thereby accumulating valuable research records on the evaluation of particular conservation techniques. If any specimen needs re-treatment in the future, the card provides valuable information on why the original treatment failed and how to reverse the process.

STORAGE OF IRON PRIOR TO TREATMENT

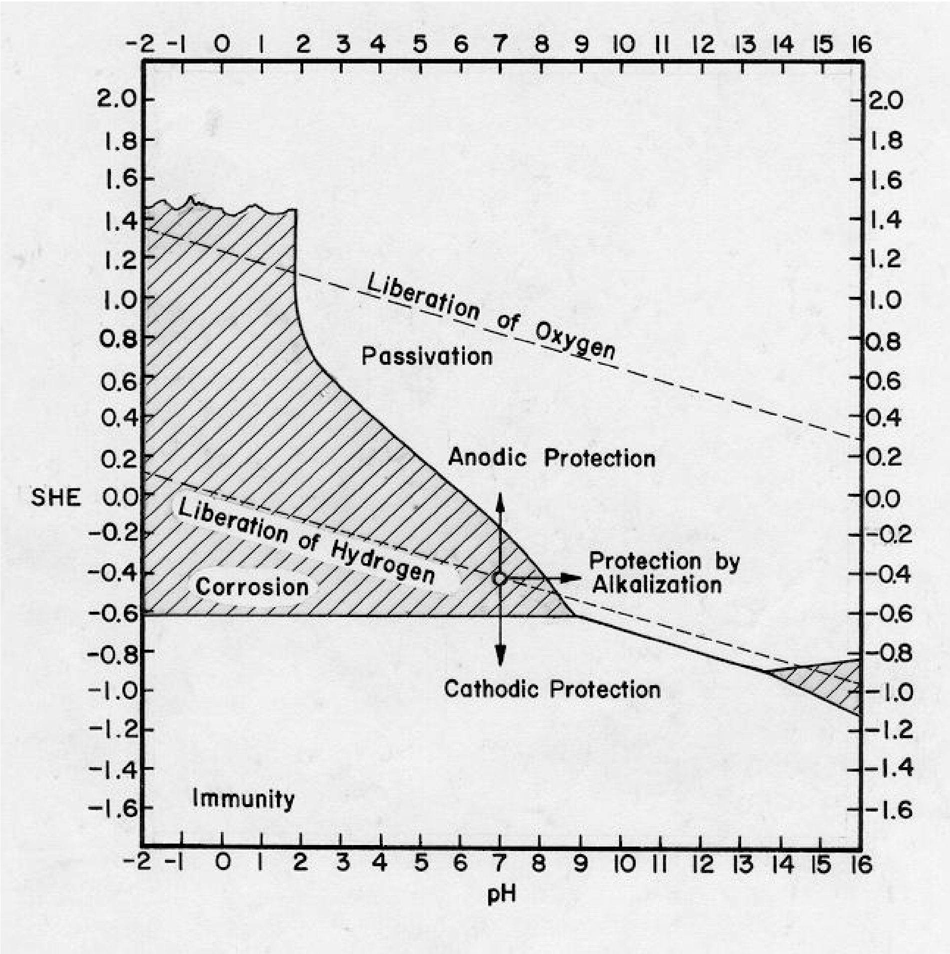
The focus of the following section is upon metals recovered from sea water but is equally applicable to even non-metal artifacts recovered from other environments. The major alternative storage solutions are discussed.

Artifacts from the sea are usually encrusted together; they may even form large masses weighing well in excess of a ton. A single encrustation may contain objects of a variety of materials, including metal, wood, bone, and fiber. In order to prevent further corrosion, disintegration, or collapse, these materials must be kept wet throughout the period between recovery and treatment. It is necessary, therefore, to select a solution in which all materials can be safely stored. Since iron artifacts are likely to be the most common objects found in encrustation, solutions which provide good protection for iron but do not adversely affect other metals and materials should be selected. During storage, the encrustation should be left intact. The encrustation forms an excellent protective coating, which retards corrosion, prevents the chemical conversion of corrosion products already present, protects the artifacts from additional deterioration, and preserves artifact associations until they can be properly documented. Once processing has begun, and the different materials are removed, individual artifacts can be placed in a more desirable storage solution pending further conservation.

Iron recovered from a marine environment should be stored in an inhibitive aqueous solution. An inhibitive solution is any solution containing a substance that diminishes or prevents the corrosion of metals. Alkaline inhibitive solutions or inhibitive solutions containing oxidizing agents are commonly used in conservation.

Alkaline Inhibitive Solutions

The most common alkaline inhibitors used in conservation are sodium hydroxide, sodium carbonate, and sodium sesquicarbonate. Solutions containing these alkalies will prevent the corrosion of iron in oxygenated water as long as they are in concentrations sufficient to maintain a pH which passivates the iron (i.e., makes it chemically inactive) through the formation of an oxide film on the metal. In general, iron can be passivated in a chloride-free solution with a pH above 8. (See Hamilton1976:21-25 for a more thorough discussion of storage environments.) In inhibitive solutions with a pH of less than 8, the presence of oxygen will increase the rate of deterioration; the corrosion will be localized and the attack will be even more intense than if no inhibitor had been used (Evans 1963:151). Passivation of iron is difficult or impossible at a pH below 8, relatively easy at a pH above 8, and very easy between pH 10 and 12 (Pourbaix 1966:312). Iron will corrode by hypoferrate formation in solutions above pH 13 that are free from oxidizing agents. Thus, if iron is stored in an alkaline solution with the pH maintained between 10 and 13, the iron will remain passified and will not corrode. Figure 10B.7



A 5 percent sodium carbonate (pH 11.5) or a 5 percent sodium sesquicarbonate (pH 9.7) storage solution is sufficient for most iron objects if chlorides are not abundant. At high chloride concentrations, prolonged storage in either of these two solutions is not advisable unless additional alkali is added or the solution is changed often. Because the pH of these solutions is borderline to the corrosion domain, they are not recommended for long-term storage of iron objects from a marine environment. They can be used only for short-term field use or other temporary laboratory storage.

Oxidizing Solution

If long-term storage is required, an inhibitive solution containing oxidizing agents can be used, but the difficulties of properly disposing oxidizing agents prevent their more widespread use. From an environmental viewpoint, it is safer to take the extra time required to monitor the storage of iron in alkaline solutions.

Various chromate compounds, such as potassium chromate, potassium dichromate, and sodium chromate make effective storage mixtures. They are more reliable than alkaline inhibitors as long as the concentration and pH are maintained at safe levels. Chromate solutions prevent corrosion by forming a very thin passivating film of ferric oxide and chromic oxide on the surface of the metal (Pearson 1972a:14). This oxidizing solution creates an environment where a much wide range of pHs and electrode potentials of the surface of the metal is in the passivation range of the metal (Pourbaix 1966:74). It must be emphasized, however, that the chromate solution must be alkaline. The natural alkalinity of chromate (i.e., pH 9.1 to 9.3) is an important factor in passivating iron. Dichromates (pH <7) are more acidic than chromates and will not passivate iron unless an alkali is added. The addition of alkali, e.g., NaOH, converts dichromates to chromates and establishes the natural pH of chromate.

Like the alkaline inhibitors, the protection offered by a chromate solution will be suppressed if the pH is too low. Should this occur, the chromate can stimulate an intense localized attack on the surface of the metal and create pits covered with membranous blisters of iron hydroxide. The iron hydroxide inhibits contact between the chromate and the iron surface and allows the anodic reaction $Fe\ Fe^{+2}$ to take place (Evans 1963:141; Kranz 1969:20). It is necessary that the pH of the chromate solution be maintained in a range of 9.0 to 9.5; if the pH of the solution falls below 9, corrosion of the object will be worse than if no inhibitors were used. The concentration of chloride in chromate solutions is not as critical a factor as it is in alkaline inhibitors, as long as there is free hexavalent chrome (Cr^{+6}) present in the solution (Worth Carlin 1975, personal communication). For this reason, chromate solutions are particularly suited for the storage of iron from chloride-contaminated environments.

The pH of the chromate solution must be checked regularly, as some of the chromate in the solution is reduced and the solution may become acidic. If this occurs, additional alkali must be added to convert the dichromates to chromate and re-establish the natural pH range of 9.0 to 9.5.

Chromate solutions have the serious disadvantage of being highly toxic if ingested and inhaled. Chromates are strong irritants, and some are highly flammable if they come in contact with organic material. Chromate solutions should not be discharged into city sewage lines or natural drainages, since they kill beneficial bacteria. Most cities have regulations concerning the disposal of solutions containing hexavalent chrome, and a conservation laboratory must, of course, comply with them. If proper disposal cannot be arranged, chromate solutions should not be used.

There are several methods of treating a chromate solution for disposal. One method is described in Pearson (1972a:62): the chromate solution is acidified with concentrated sulfuric acid to a pH of 4. Sodium metabisulfite is added until the solution turns bright green. This reduces the hexavalent chrome to trivalent chrome. The solution is then neutralized with a 40 percent sodium hydroxide solution to precipitate out chromium hydroxide. The chromium hydroxide is allowed to settle as a sludge in the bottom of the vat. The solution is drained into the sewer lines, and the chromium hydroxide, which is insoluble, is disposed in a chemical dump.

Excellent long-term storage results have been achieved with a 0.1N solution of potassium dichromate ($K_2Cr_2O_7$) with sodium hydroxide. Many wrought iron artifacts recovered from 16th-century Spanish ships have been stored in this solution for more than three years with no apparent corrosion. The pH may have to be adjusted to and maintained at 9.0 to 9.5 by the addition of sodium hydroxide as the chrome is reduced. Sodium chromate also provides good results and has the added benefit of being cheaper than potassium dichromate.

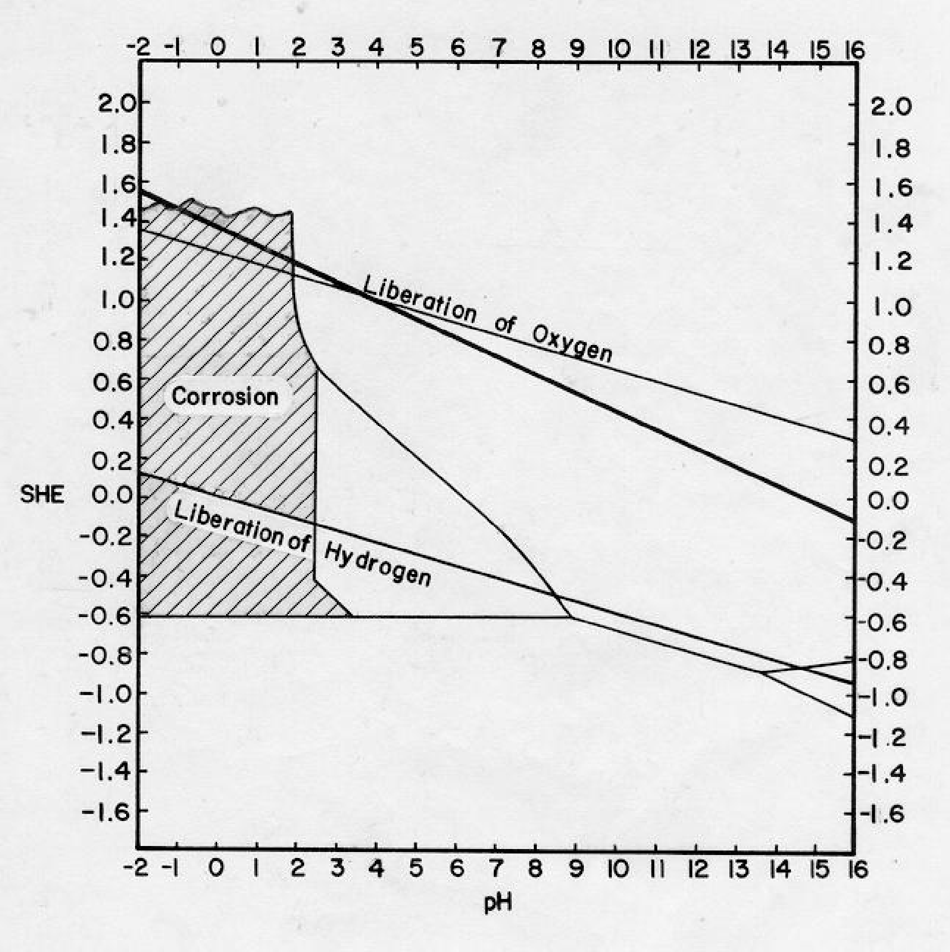


Figure 9.1. Stability conditions of pure iron in a chromate solution.

Use of De-ionized Water

Most conservation literature recommends that all storage solutions be prepared with distilled or de-ionized water. The exception to this rule occurs when the material to be conserved contains more chloride than is present in the local water supply. Tap water should be used for all storage solutions and electrolytes until the chloride level of the solution is less than that of the tap water. Using rain water in solutions as an interim step between tap water and de-ionized water will considerably reduce conservation costs. Following this procedure will result in significant financial savings when a large number of chloride-contaminated materials are to be processed. Unaltered de-ionized or distilled water should never be used as a storage solution for metal artifacts. They are generally slightly acidic and hence highly corrosive. Furthermore, when de-ionized or distilled water is used for rinsing or as a bath for detecting chlorides, immersion of the object should be kept to a minimum and adequate precautions taken.

ENCRUSTATION REMOVAL

Upon delivery to the conservation laboratory, marine archaeological material is typically covered with a dense and often thick encrustation. Removing the artifacts from this tough mass is analogous to removing objects from inside concrete blocks. Since most of the objects are hidden from view, radiographs are indispensable for determining the context of an encrustation and for serving as a guide in extracting the artifacts it contains. In order to x-ray large encrustations, large industrial X-ray machines, such as a 260 KVP water-cooled Picker Industrial X ray, must be used. Small- to medium-sized encrustation, up to approximately 1 x 1 m, can be x-rayed intact, and most of the constituent artifacts identified. It is often desirable to make a tracing or overlay from the individual X-ray plates. On the overlay, all the discernible artifacts are traced. Any specimens not detectable on the radiographs can be drawn, and their correct provenience can be ocated as they are encountered in the encrustation. Useful notations, such as catalogue numbers, condition of specimens, etc., can easily be added to the overlay.

For removing the encrustation, mechanical cleaning is the only feasible alternative. To accomplish this, a variety of hammers and chisels are indispensable, especially on the very large pieces. By hammering and chiseling along cleavage lines, the encrustation can be detached from large objects with little or no damage to the artifacts. For the extraction of smaller specimens, however, pneumatic tools are more efficient and less destructive. Chicago Pneumatic Weld Flux chisels are particularly serviceable for removing large amounts of encrustation and for extracting large, less fragile articles. Smaller, more precisely controlled Chicago Pneumatic Air Scribes, with their more delicate scribes and various chisels, which can be custom-made in the laboratory, are ideal for removing the encrustation from small, fragile pieces and for getting into restricted places. The pneumatic air scribe is much more durable than any comparable electric scribes or vibrotools. Combined use of the two types of pneumatic tools, the chisel and the scribe, is often necessary. They can, for example, be most effective in freeing movable parts, such as loaded breech chambers, iron lifting rings, and swivels on cannons.

When in doubt as to how much to mechanically remove, it is much safer to leave a thin layer of encrustation on the surface of the metal where the original surface cannot be determined. When the object is placed in electrolysis, the evolution of hydrogen bubbles at the surface of the metal will loosen the encrustation and mechanically remove any left on the metal. While electrolysis can be used to remove encrusted artifacts, the whole process of conservation is considerable speeded up if the encrustation removal is aided by mechanically removing by hand as much of the encrustation as possible.

The encrusted bores of cannons present a special problem. Tube drills are ideal, but each caliber gun requires a differently sized tube drill. Since these are quite expensive, they may not be practical for many laboratories. A suggested procedure is to use a hammer or chisel to remove as much as possible of the encrustation from the muzzle of the bore. A sandblaster can be then used to cut through the encrustation. Periodically, a steel rod ground to a chisel-like point should be used to roughen the surface of the encrustation so that the sand will work more efficiently. This technique may sound brutal, but very little, if any, harm is done to the cannon. The sandblaster will actually cut a hole through the encrustation without touching the metal. That is, a layer of encrustation is usually left on the surface of the bore. If necessary, additional encrustation can be removed with iron rods. Once a hole is made through the cannon bore, the cannon can be set up in an electrolytic bath with a center auxiliary anode. Hydrogen evolution in the bore will remove the remaining encrustation. This works very well on wrought-iron breech-loading hooped-barrel guns because cleaning is facilitated by the cannon tube being open at both ends.

The use of acids is generally a slow, ineffective process. Acids, especially hydrochloric acid, attack the metal oxide as readily as the encrustation and so are too damaging to consider. Even if successful, chemical techniques pose problems for recording associations and measurements and for making casts from molds of completely oxidized artifacts.

It has been known for a long time that when encrusted iron artifacts are placed in electrolysis, that the encrustation is loosened off the surface of the metal. This technique, termed 'deganguing' by the French (Montlucon 1986, 1987) can be quite effective on singularly encrusted objects, but can be destructive when used on encrustation containing possible molds of corroded artifacts that can be cast in epoxy. Additionally, some information in the encrustations is in the form of associations that must be visually documented by the conservators. 'Deganguing' is an effective tool, that has been in use, to varying degrees for years, but it should be used judiciously when working with complex, heavily encrusted objects that may contain numerous other artifacts.

PRELIMINARY ARTIFACT EVALUATION

After each artifact is removed from an encrustation, it must be rinsed, carefully examined, and its condition evaluated to determine the most appropriate conservation treatment. It is useful to classify the metal specimens into one of three categories analogous to those suggested by Western (1972:83). These are based upon weight/size ratio, close visual inspection, testing the surface with a magnet, probing the corrosion layers with a dental pick, and occasionally using X rays. The categories include:

1. Metal objects with a substantial metal core and a consolidated surface capable of withstanding chemical, electrochemical, or electrolytic reduction without significant changes in the form or dimensions of the artifact. Electrolytic reduction is the preferred treatment in most cases.

2. Metal specimens that are badly corroded but retain their overall shape. Very little or no metal may remain, and there is little overall supporting strength. Most treatments would alter the original form. The recommended procedure is to stabilize the artifact by diffusing out the soluble chlorides in an aqueous solution of sodium sesquicarbonate and to consolidate the artifact with a substance such as microcrystalline wax or other synthetic consolidant.

3. Metal artifacts that are so badly oxidized and fragile they can only be consolidated. Any further treatment will usually completely disintegrate them. Casting the object itself or making a replica from the natural encrustation mold is often the only means of preservation or recovery.

Only after these decisions have been made should treatment begin.

Iron Conservation: Part I - Introduction and Equipment

IN THIS FILE:

As stated in previous section, the preliminary evaluation of an iron artifact will determine the methods by which the artifact is cleaned. Only after an artifact has been evaluated and cleaned can the appropriate conservation measures be taken. The various treatments available for the conservation of iron can be organized into five general categories:

1. Electrochemical cleaning

    a. Galvanic cleaning
    b. Electrolytic reduction

2. Alkaline sulfite treatment

3. Chemical cleaning

4. Annealing

5. Water diffusion in alkaline solutions

ELECTROCHEMICAL CLEANING

The corrosion of metal, as explained earlier, is an electrochemical reaction. Electrochemical and electrolytic reduction cleaning processes, therefore, are the most common techniques utilized to halt, stabilize, and even reverse the oxidation of the metal. In the field of conservation it has been the general practice to distinguish between electrochemical and electrolytic cleaning. An electrochemical reaction is based upon the association of two metals occupying different positions on the galvanic or electromotive series of the metals without an externally applied electromotive force (EMF); therefore this cleaning process is also known as galvanic cleaning. Electrolytic reduction, also called electrolysis, is an electrochemical reaction maintained by an externally applied EMF or electric current. Basic information on these two processes can be found in Plenderleith (1956), Plenderleith and Torraca (1968) and Plenderleith and Werner (1971). Hamilton (1976:30-49) and North (1987:223-227) provide detailed discussions of electrolytic reduction.

GALVANIC CLEANING

Galvanic cleaning is often mentioned as an effective method for conserving shipwreck material. In two frequently cited works on underwater archaeology, it is the only technique recommended (see Peterson 1969:83-84; Marx 1971:125). For marine-recovered iron artifacts which are severely chloride-contaminated, however, galvanic cleaning is not a favorable alternative. It is often not desirable even for metals from terrestrial sites, where chlorides present no real problems.

To be effective, galvanic cleaning requires that a substantial metal core be present in the object being treated. In most circumstances, this process can be recommended only if a few small objects are to be cleaned and if equipment for electrolytic cleaning is not available. Except for limited use, galvanic cleaning is best considered as an obsolete technique. Since it is used in some laboratories, however, it is briefly discussed here. Some of its advantages and its major disadvantages are presented.

Galvanic cleaning involves placing the iron object in a vat and surrounding it with a more active anodic metal, such as zinc or aluminum, and filling the vat with an electrolyte. In this process, nascent hydrogen acts as the reducing agent as it evolves from the surface of the iron. The chlorides are removed, and reduced metal is left by the reaction. In order for galvanic cleaning to be effective, it is necessary to control the electrode potential of the artifact being treated. In galvanic cleaning this is determined by the couple between the anodic metal and the iron and by the electrolyte; once the electrode potential of the artifact has been established, however, it cannot be manipulated.

The simplest method of galvanic cleaning consists of wrapping the object loosely in aluminum foil and placing it in a glass beaker of 10 percent sodium hydroxide, or caustic soda (NaOH), or a 10 to 20 percent solution of sodium carbonate, or soda ash (Na_2CO_3). (Noël Hume [1969:283] suggests using an electrolyte of baking soda (sodium bicarbonate, $NaHCO_3$), but tests at the Texas A&M Conservation Research Laboratory have shown that baking soda electrolytes are not effective in galvanic cleaning.) The object is left in the caustic solution until the aluminum foil completely oxidizes. The reaction can be speeded up by heating the solution. The object is then rinsed, and the process is repeated until satisfactory results are achieved. Only small, lightly corroded specimens can be treated in this fashion.

The most commonly used method of galvanic cleaning differs from the method above only in that granulated zinc or aluminum granules are used to cover the object and a 10 to 20 percent solution of sodium hydroxide is employed (Plenderleith and Torraca 1968:241; Plenderleith and Werner 1971:194-197). The solution is heated to boiling in a metal pan or heat-resistant glassware, and the level of the solution is maintained with the addition of distilled water. The cleaning continues until the electrolyte is exhausted or the activity of the zinc abates. The process is repeated with fresh or cleaned zinc and fresh caustic soda until all of the materials are reduced and all traces of chlorides have been eliminated. If high levels of chlorides are allowed to remain in the artifact, future outbreaks of corrosion are inevitable.

This process requires facilities to heat the container and an adequate ventilation system, such as a fume hood, to exhaust the caustic vapors. In the reduction process, the caustic solution is exhausted and has to be periodically discarded, and considerable zinc is lost through oxidation. The activity of the remaining zinc is significantly reduced by an accumulated film of oxychloride and carbonate. To be renewed, the zinc must be cleaned with dilute hydrochloric acid solutions, rinsed in distilled water, and then dried (Plenderleith and Werner 1971:196). Alternatively, the zinc can be melted in a ladle under a reducing flame and re-granulated by slowly pouring the molten zinc into water (Organ 1973:193); each time the zinc is reclaimed, slag formation will further reduce the quantity of zinc.

For iron artifacts, or any other metal with extensive chloride corrosion compounds, the galvanic cleaning process is impractical. The artifact is always obscured, so it is not possible for the conservator to observe its progress. Even under ideal conditions, the process requires constant supervision and is messy. The fumes produced are unpleasant and irritating to the skin, eyes, and throat. Furthermore, it is often difficult to provide simultaneously adequate ventilation and adequate heat. Large artifacts, especially those which are chloride-contaminated, require a long processing time and a prohibitive amount of zinc, which has to be continuously cleaned and replenished.

Galvanic cleaning of most metal artifacts should be considered only if equipment for electrolytic reduction is unavailable, and even then, it may be a waste of time for a majority of iron artifacts, especially if they are very large. Noël Hume's comment (1969:276) bears repeating: "Those amateurs who have been told that it is a simple method that can readily be performed on the kitchen stove are advised to forget it."

ELECTROLYTIC REDUCTION CLEANING

Electrolytic reduction cleaning is one of the most efficient and effective methods of conserving metal artifacts. Electrolytic units are very cost-effective and simple to set up and maintain. The cleaning process can be selected exclusively for its mechanical cleaning action of the evolved hydrogen, for the metal reduction process or a combination of the two. Efficient electrolytic reduction, however, involves more than simply wiring up artifacts for electrolysis. A knowledge of corrosion processes and electrochemical thermodynamics is essential. The conservator must be familiar with electrode potentials and pH and know how these variables relate to electrode corrosion, passivation, and immunity. These factors are particularly crucial when dealing with chloride-contaminated metals. This is not to say that satisfactory results cannot be obtained by the novice, but rather that knowledge and experience enables the conservator to understand and better control what is going on in the electrolytic cell and to correct adverse conditions.

The essence of the technique involves setting up an electrolytic cell with the artifact to be cleaned as the cathode. An electrolytic cell consists of a compartment or vat with two electrodes, the anode and the cathode, and contains a suitable electricity-conducting solution called the electrolyte. An electric current from an external direct current (DC) power supply is applied to cause oxidation and reduction. The anode is the positive terminal of the electrolytic cell, to which electrons, negatively charged ions, or colloidal particles, travel when an electric current is passed through the cell. Oxidation occurs at the anode and oxygen is evolved. The cathode is the negative terminal of an electrolytic cell, to which positively charged metallic ions travel. At the cathode, reduction takes place and hydrogen is evolved. In the reduction process, some of the positively charged metal ions in the compounds on the surface of the artifact are reduced to a metallic state in situ. In addition, chlorides and other anions are drawn from the specimen and migrate toward the positively charged anode by electrolytic attraction.

The chief advantage of electrolytic reduction is that the density of the externally applied electromotive force (EMF), or electric current, can be controlled. This control enables the conservator to select a low current density that creates a preselected electrode potential conducive for the consolidation and/or reduction of some mineralized metals. When there is an underlying metal core, it is theoretically possible to reduce enough of the ferrous corrosion compounds back to a metallic state through electrolytic reduction. This will consolidate the corrosion layer while eliminating the chloride components of the compounds. A high current density can be selected so that the evolved hydrogen will mechanically remove any completely oxidized crust.

When using electrolytic reduction cleaning, factors to be considered are the equipment and the experimental variables.

1. Equipment
    - a. Power supplies
    - b. Terminal wires and clips
    - c. Anode material
    - d. Chloride monitoring

        e. Vats

    2. Experimental variables

        a. Types of electrolytic setups
        b. Electrolytes
        c. Current densities
        d. Electrode potentials

Equipment

DC Power Supplies

The regulated DC power supply requirements for electrolytic reduction are wide-ranging, and a well-equipped laboratory should have several units of varying current capacities, each of which is capable of continuous operation. Power units fall into four general current ranges and are capable of cleaning any object from the size of a small spike to a large anchor or cannon.

Most small DC power supplies have an output current with less than 0.1 percent ripple. The larger power supplies have 0.5 percent or more ripple. For well-controlled reduction, the low ripple power supplies are recommended; a little ripple, however, is not harmful. The choice of a power supply depends upon the desired current density control, the size of the artifact, and the number of artifacts on any one unit. Current controls and an amperage meter provide a means of determining and adjusting the current as the treatment progresses. During electrolysis, the current increases as the metallic species are reduced and the resistance of both the object and the electrolyte decreases. The current resistance (IR) drop in the electrolyte is due to an increase in chloride and other ions. This is the main reason for the current increase; the decrease in the resistance of the object plays only a minor role. Therefore, variable adjustments are necessary if an object is to be electrolytically reduced at a fixed current density or a predetermined electrode potential.

Because of the expense of regulated power supplies it is not surprising that many conservation laboratories build their own power units. Foley (1967) and Organ (1968:291-308) give directions on how to build an inexpensive power supply. Alternatively, battery chargers can be employed. Battery chargers, however, are not designed to run continuously for electrolytic cleaning. If they are to be useed in electrolysis, it is usually necessary to remove timers, relays, and charging rate devices to make them serviceable. Since an electrolytic cell for cleaning artifacts lacks the resistance of a battery, and the battery chargers generally do not have the necessary internal resistance controls to compensate for it, the chargers run well above their maximum safe operating amperage. Additional resistance must be added to the circuits to keep them from overheating. Variable autotransformers, such as Powerstats, on the input alternating current (AC) line and variable rheostats, or line resistors, on the outgoing DC negative terminals serve this purpose well. Anyone with a basic knowledge of electrical circuits can easily alter most direct current battery chargers for electrolytic cleaning of metal artifacts.

Terminal Wires and Clips

For most objects, terminal wires made of U.S. National Electric Code Standard 16 AWG, Separation 2, 300V maximum rating insulated copper wire can be used. This wire is the standard two-ply multistrand wire commonly found on many electrical appliances and is quite flexible and easy to use. One strand of the wire is used for the negative connection, the other for the positive connection; or they can be joined at the terminal ends to make one pole connection if a larger sized wire is required. For larger artifacts that need more current, No. 2 to No. 0 AWG multistrand wire is required. Multistrand copper wire is recommended in all cases because it has a larger current capacity and is more flexible and easier to manipulate than comparably sized solid wire. Before using any wire, one should check the amperage capacity of the wire, or, if in doubt, consult an electrician. A good rule of thumb to follow is that the wire should not heat up during electrolysis; if it does, the wire is not heavy enough.

Steel alligator test and battery clips (Mueller clips) are recommended for attaching the terminal leads to the artifact and the anode. Appropriatly sized clips on the terminals facilitate setting up and taking down artifacts in electrolysis. These clips come in a variety of shapes and sizes. The size of the clip selected is determined by the current to be used, the size of the artifact, and the placement of attachments. Mueller clips Nos. 25, 27, 48 and 85 are the most useful sizes and should be kept in stock. Steel clips, which are usually are cadmium- or zinc-plated, should be stripped of this plating by a quick bath in a dilute solution of hydrochloric acid before use (if left too long in the acid, the tempered steel spring is weakened and will break when depressed). The removal of the cadmium or zinc coating prevents any plating of this metal from the anode clips onto the artifact. For this same reason, copper clips should not be used. Copper clips on the positive terminal, like the exposed copper wire attached to the anode clips, eventually go into anodic dissolution when submerged in the electrolyte and plate onto the cathode. In order to prevent anodic dissolution, any copper wire that is exposed in the electrolyte should be coated with an acrylic, polyvinyl acetate, or silicone rubber.

Anode Material

For electrolytic cleaning of iron, 16-gauge expanded mild steel mesh with half-inch openings is an inexpensive but efficient anode material. This steel mesh is easily cut, relatively flexible, easy to form-fit around the artifact and does not conceal the artifact from view. It also permits free circulation of the electrolyte and will not trap any gases. Mild steel plates, and even sheets cut from mild steel drums, make serviceable and cheap anode material, but their rigidity makes them difficult to form-fit around an artifact. Specially constructed mild steel vats, or even 55-gallon steel drums, can serve both as the electrolytic vat and the anode material. When a form-fitted anode is desired, however, only expanded steel mesh is cheap enough and flexible enough for regular use.

Mild steel anodes are surprisingly durable. As long as an adequate alkaline pH (minimum of 8.5) is maintained at the surface of the mild steel anode, it is less susceptible to chloride corrosion and will even outlast stainless steel. To maintain this level of alkalinity, it may be necessary to circulate the electrolyte. Mild steel anodes are commonly used as the oxygen-hydrogen cell electrodes (Worth

Carlin 1975, personal communication).

It is claimed that stainless steel makes a superior anode, and it is often recommended because it is relatively inert and seldom needs to be replaced. All stainless steels, however, do not make equally suitable anode material. A stainless steel with a high percentage of chromium and nickel or even titanium must be selected; Type 316 stainless steel, which is composed of 16-18 percent chromium, 10-14 percent nickel, and 2-3 percent molybdenum, is recommended. Only Type 316 stainless steel resists chloride corrosion and is a good alternative to mild steel anodes in an alkaline electrolyte.

The high cost of stainless steel generally restricts its use as anode material for large objects and makes it impractical to cut and form-fit it to clean a single artifact. The most practical way to use stainless steel anodes is in certain electrolytic setup alternatives that allow for a number of artifacts to be treated at one time. These setups will be described below.

As long as the hydroxyl ion concentration in the electrolyte is kept high, mild steel anodes are more efficient than stainless steel anodes. Regardless of the anode material, it is much simpler and more economical to change the electrolyte before the chlorides build up to such an extent that they alter the pH and electrode potential at the anode, destroying the anode's passivity and causing it to go into dissolution. When this happens, the anode has to be replaced.

Vats

A wide variety of containers can be used in an electrolytic setup. Many kinds of non-conductive vats of various caustic and acid-resistant plastics, such as polyvinyl chloride (PVC), polypropylene (PP), and polyethylene (PE) are widely used. PVC plastic pipes with sealed ends make excellent vats for long, slim artifacts, such as rifle barrels. Fiber-resistant plastics should be avoided unless it is certain that they are alkali-resistant. Glass containers are also suitable for electrolytic setups, as are wooden vats, or frames lined with sheets of PVC plastic (care must be taken not to puncture the plastic).

In addition to non-conducting containers, conducting mild steel vats are frequently used in electrolyte cleaning. The metal vat serves as all or part of the anode and may be substituted as such in any of the electrolytic setups described below. Metal vats also have a distinct advantage over plastic vats in that all stages of the conservation process can be carried out in them. This is especially advantageous for very large pieces, where it is not economically feasible to have different vats for electrolysis, rinsing/dehydration, and wax impregnation.

Mild steel vats can be constructed in various gauges and are surprisingly durable and versatile, even in the lighter gauges. Use a gauge that provides the strength required and does not increase the weight of the setup beyond the laboratory's ability to handle it. A common coffee can, with the can used as the vat and the anode, is a simple and effective container for small artifacts. Mild steel 55-gallon drums, cut lengthwise or in half, make readily available, cheap vats, which can be employed in any of the described setup alternatives, in combination with auxiliary anodes to assure a more even distribution of current. Welded mild steel vats can be constructed cheaply and will last for years. For very large artifacts, such as anchors, a two-piece 5-m long mild steel vat is recommended. This 'T'-shaped vat is constructed of two parts, the stem and the cross, each of which is open at one end. When the parts are joined, the vat is used to clean anchors with auxiliary sheets of expanded mild steel positioned near the top surface of the anchor in order to achieve a better distribution of current. Separated, the two vats can be employed to clean an assortment of large iron artifacts.

When corrosion takes place in a conducting mild steel vat, it will occur at the stress points, such as weld lines and bends in the metal. It is for this reason that North (1987:225) discourages the use of a mild steel vat as an anode. If a metal vat is not hooked up as the anode, the fact that it will not be anodically passivated affords it some protection; however, any chloride ions present will still eventually corrode the vat. Furthermore, if a mild steel vat completely corrodes in 10 years due to its use as the anode, it can be easily replaced many times and still be more economical than stainless steel or plastic alternatives. The recommendation by North is disregarded by most conservators responsible for treating large iron artifacts from marine sites.

Care must be taken to ensure that metal anode vats remain passive during electrolysis; otherwise, the metal will go into anodic dissolution and create perforations, which are difficult to repair. This is sometimes difficult when using low current density electrolysis in the presence of high levels of Cl^- ions; however most of the difficulties can be overcome if a 5 percent sodium hydroxide electrolyte is used until the chloride levels decrease or the current density can be increased to keep the anode passive. This issue will be discussed in more detail later in this section.

Conservators should be aware of some safety issues regarding the use of metal vats as both the container and the anode. Most DC power supplies used in electrolytic cleaning operate in a 6- to 12- or a 24- to 32-volt range and a 0- to 50- or 0- to 200-amperage range, but the actual voltage used during electrolytic cleaning usually does not exceed 6 volts. At this voltage, there is little personal danger in using metal vats. In general, a voltage of less than 32 volts is not hazardous because the IR drop in the human body is such that little or no current would pass through the body. Care should be taken, however, to avoid shorting the two terminals of higher voltage power supplies against each other.

CHLORIDE MONITORING

Chloride concentration monitoring of the electrolyte is crucial to the efficiency and success of electrolytic reduction when conserving metal objects recovered from marine environments. Several methods to quantitatively monitor chloride concentration exist. The mercuric nitrate titration method is recommended in this manual due to its simplicity and low cost.

MERCURIC NITRATE METHOD OF CHLORIDE DETERMINATION

The mercuric nitrate test is a quantitative method used to determine Cl^- or NaCl in parts per million in an aqueous solution. It is a quick and simple test to perform and gives accurate and consistent results. The following procedure is a modification of the method outlined by Furman (1962:331-332).

Equipment:

1. One automatic 25 ml burette
2. Two small amber glass bottles with droppers
3. One 500 ml amber glass bottle
4. One 250 ml beaker
5. A magnetic stirrer
6. Teflon-coated stirring bars

Chemicals:

1. Diphenylcarbazone-bromophenol blue indicator
2. 0.02N mercuric nitrate solution.
3. Sulfuric acid

Transfer the blue indicator and the sulfuric acid to the amber dropper bottles. The mercuric nitrate should be stored in the amber glass bottle for refilling the burette.

Procedure:

1. Take a 20 ml sample of electrolyte or solution to be tested, and place it in the glass beaker.

2. Place the beaker on the magnetic stirrer and put a Teflon stirring bar in the beaker.

3. Adjust the stirrer until the liquid is in a steady swirl.

4. Add five drops of diphenylcarbazone-bromophenol blue indicator. This will change the color of the solution to blue.

5. Add drops of sulfuric acid (usually 18N for sodium hydroxide electrolytes, 9N for sodium carbonate electrolytes, or 4.5N for water solutions) to the solution until an acid end point is reached. The acid end point is indicated by a color change from blue to clear. (The amount of sulfuric acid does not need to be measured as it only acidifies the sample for the next step.)

6. Titrate 0.02N mercuric nitrate, drop by drop, from the automatic burette into the beaker until the solution reaches a violet end point. The color changes gradually from clear to violet. Near the end point, each drop will show a flash of color. Continue until a single drops swirls into a single even violet color through out the solution. **Note:** the sensitivity of the titration can be increased by using a smaller normality solution or decreased by using a larger normality solution of mercuric nitrate.

7. Note the amount of mercuric nitrate titrated to reach the end point.

The concentration of chloride or sodium chloride in parts per million is calculated by the following formulas:

$$\frac{T \times N \times 0.03545 \times 1{,}000{,}000}{20} = T \times N \times 1772.5 = \text{ppm } Cl^-$$

$$\frac{T \times N \times 0.05846 \times 1{,}000{,}000}{20} = T \times N \times 2923 = \text{ppm NaCl}$$

where

T = amount of mercuric nitrate titrated

N = normality of mercuric nitrate

In order to facilitate the calculation of chloride concentrations, a conversion table can be established using the formulas above:

Amount of Mercuric Nitrate Titrated (ml)	ppm Cl^-	ppm NaCl
0.1	3.5	5.8
0.2	7.0	11.7
0.3	10.6	17.5

0.4	14.0	23.4
1.0	35.0	58.5
10.0	350.0	585.0
etc.	etc.	etc.

The mercuric nitrate test gives the total amount of Cl^- or NaCl in the electrolyte. Unused electrolyte solution, however, will already contain a certain amount of chlorides. In order to determine the amount of chlorides expelled from the artifact, the amount of chlorides present in an unused sample of the electrolyte must be determined. This provides a 'blank' which is subtracted from the amount of chlorides present in a sample taken from the electrolytic bath. For example, if a sample taken from an active electrolytic bath contains 24.5 ppm of Cl^- while an unused sample of the same electrolyte contains 17.5 ppm, the amount of chlorides in the electrolytic bath that have been expelled from the artifact is 7.0 ppm.

Comments on the Mercuric Nitrate Test
Throughout this entire process, the glassware must be kept clean and uncontaminated. To prevent cross contamination, a clean beaker and stirring rod should be used for each electrolyte sample, or these items should be washed thoroughly and rinsed with de-ionized water between each sample. Purple mercuric nitrate stains can be removed from the stirring rods by immersing them in dilute solution of nitric acid.

Two notes should be added with regard to the chloride testing procedure. First, the diphenylcarbazone-bromophenol end point is to some degree subjective, but most individuals are consistent about their end point. Therefore, the most reliable and consistent results are obtained when only one individual is responsible for monitoring the electrolyte. To further assure the consistency of chloride monitoring, the reagents should be tested weekly against a known sodium chloride solution.

All of the chemicals in the concentrations required for the chloride test can be purchased from a chemical supply house. Chemical costs can be considerably decreased, however, if the chemicals are mixed in the lab as follows:

18N Sulfuric Acid, H_2SO_4: Dilute reagent-grade sulfuric acid with an equal volume of distilled or de-ionized water. Slowly add the acid to the water, never the water to the acid. Extreme heat will be generated. Let cool.

0.02N Mercuric Nitrate Solution, $Hg(NO_3)2 \cdot H_2O$: Dissolve 3.42 g of reagent-grade mercuric nitrate in 1 liter of distilled or de-ionized water.

Diphenylcarbazone-bromophenol blue indicator: Dissolve 0.5 g of reagent-grade crystalline diphenylcarbazone and 0.05 g of crystalline bromophenol blue in 100 ml of 95 percent ethanol.

1000 ppm Sodium chloride solution (to test reagents): Dissolve 1 g of reagent-grade sodium chloride in 1 liter of distilled or de-ionized water. Dilute in half for 500 ppm NaCl, dilute a second time for 250 ppm, etc.

During electrolytic cleaning, the chloride level should be calculated and recorded at least once a week. These calculations can be used to make a graph that visually depicts at a glance the progress of chloride removal from an artifact. This will save much valuable time and enable the conservator to determine when all detectable soluble chlorides have been removed from the object, as well as when to change a chloride-contaminated electrolyte. Systematic chloride monitoring assures that the artifact will remain in electrolysis for the least amount of time necessary. Chloride monitoring cannot, however, be used to determine the efficiency of the reduction of the iron compounds. This can only be confirmed with analytical tests on samples taken from the artifact before and after treatment.

The graph in Figure 10A.1 presents the progress of a typical iron artifact recovered from a marine environment. It clearly depicts the high initial rise in chlorides released from the artifact and the subsequent decrease as the electrolyte is periodically changed. Drops in the graph to the zero line represent electrolyte changes. The two-week gap in the graph in November indicates when the artifact was taken out of electrolysis in order to mechanically clean the remaining encrustation and loose corrosion products. Occasionally, a drop from a previous high is seen on some chloride graphs, especially when the chloride level is high. This may be caused by chlorides reacting with corrosion products from the anode, chlorate formation, or the actual liberation of chlorine which causes the chlorides to be undetectable by taking them out of solution. Electrolysis is continued until the chloride concentration levels off for several days and does not increase above that present in a 'blank' of the electrolyte.

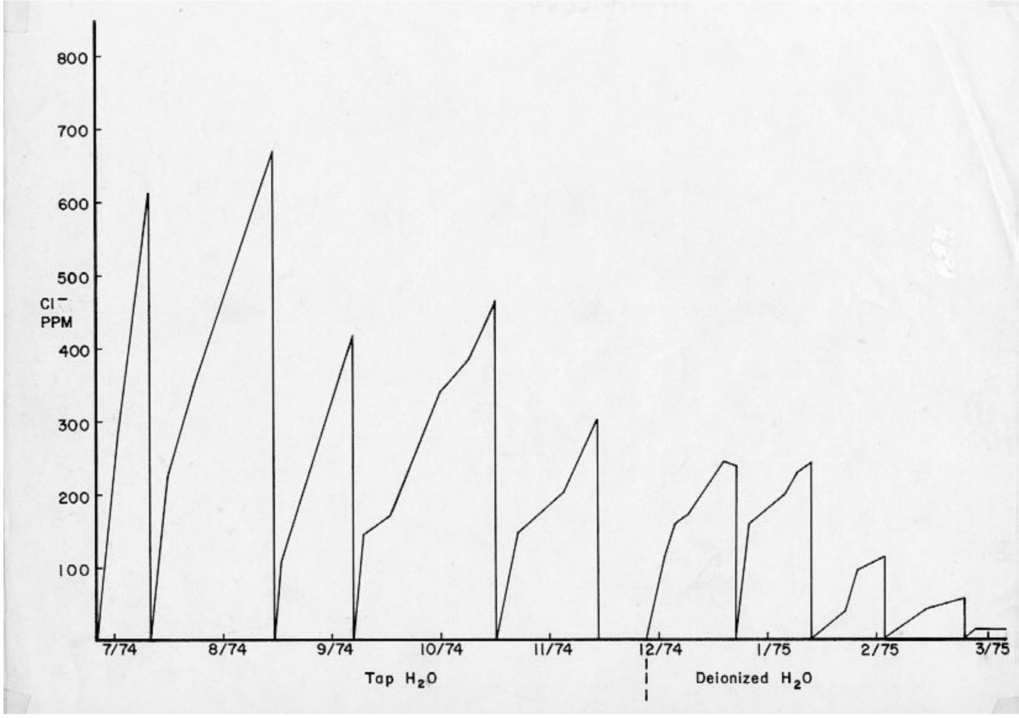


Figure 10A.2. Graph depicting the diffusion of chlorides into solution during electrolysis.

Iron Conservation: Part II - Experimental Variable and Finals Steps

IN THIS FILE:

TYPES OF ELECTROLYTIC SETUPS

The manner in which artifacts are set up for electrolysis is dependent upon the following factors (Hamilton 1973, 1976):

1. the size and condition of the specimens
2. the amount of artifacts to be processed
3. the number of available regulated direct current power supplies
4. the current capacities of the power supply units
5. the number, size and nature of the vats

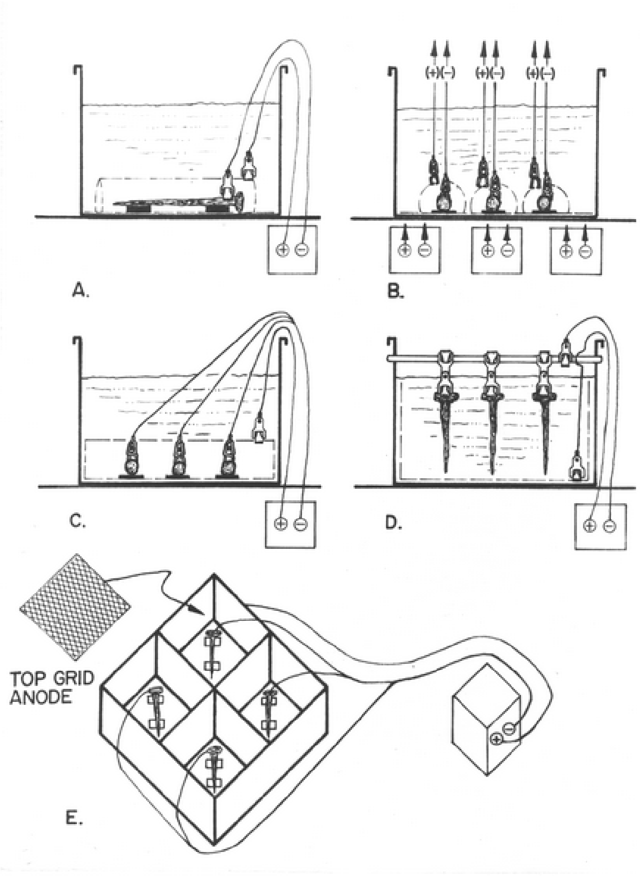


Fig 10B

The 'ideal' electrolytic setup (Figure 10B.1A) consists of a single artifact in one vat, surrounded by a close, form-fitted anode that is equidistant from all surfaces of the artifact and is connected to a single regulated direct current (DC) power supply. With this setup, a conservator is able to precisely regulate the flow of the current to the artifact and maintain a predetermined electrode potential conducive to metal reduction on the surface of the specimen. This setup is used for artifacts that are especially significant and need to be conserved as carefully as possible.

The Type 2 electrolytic setup (Figure 10B.1B has several artifacts in one vat, but each artifact is surrounded by its own close, form-fitted anode, and each is connected to a separate DC power supply. When this arrangement is used, it is important to make sure that the distance between the different anodes is greater than the distances between the artifact and its anode in order to prevent any cross-over current. (This point is not graphically depicted in Figure 10B.1b.) With this setup, the current flow to each artifact can be carefully controlled, and the correct electrode potential can be maintained. Since the chlorides present in the electrolyte come from all the artifacts in the vat, it is not possible to determine exactly when a specific artifact is chloride-free. The chloride test does, however, tell the conservator when to change a chloride-contaminated electrolyte and when all of the artifacts are chloride-free.

If an artifact requires close supervision (i.e., to consolidate a metal-oxide interface or to preserve some surface or structural detail), it is advisable to hook it up in one of the two methods described above. The most critical variable for precision control is the ability to maintain an even current density on the cathode surface by positioning the anode equidistant from all parts of the artifact while maintaining a steady reduction electrode potential. Monitoring the chlorides during electrolysis is of lesser importance.

The most commonly used electrolytic setup involves connecting multiple artifacts to a single power supply. Regardless of how it is configured, Type 3 electrolytic setups (Figure 10B.1C-D) are the least desirable from the standpoint of control, but they have the advantage of processing a number of objects at one time in one vat on a single power supply. In one configuration (Figure 10B.1C), each piece is individually connected to the negative terminal of a single power supply. The artifacts share common anode sheets placed above and below the specimens. An alternative variation of this setup has a common bottom anode and individual top form-fitted anodes to assure a more even distribution of the current to each artifact.

In the most popular Type 3 configuration (Figure 10B.1D), artifacts are suspended from a brass cathode rod conductor (Plenderleith 1956:194-196; Plenderleith and Torraca 1968:243; Plenderleith and Werner 1971:198). Adjustable vertical anode sheets are hung on either side of the vat, and another anode is laid along the bottom of the vat. This is sometimes referred to as the 'sandwich setup.' The oxygen evolved off the bottom anode sheet ensures that the solution is continually mixed, preventing chlorides from concentrating along the bottom of the vat. The increased circulation also helps to maintain the anodes in a passive state by preventing the formation of strongly oxidizing, acidic hypochlorite from forming on them.

Sandwich setups have all of the disadvantages discussed above. An additional disadvantage is that the proximity of the object to the negative terminal connection is a factor in the current flow. The closer an artifact is to the negative terminal the more current it receives. By regularly repositioning the artifacts, each object will receive an average current for the duration of the treatment.

Sandwich setups have the advantage of making it possible to process a number of specimens on a single power supply in one vat. This consideration is important when limited facilities are available to conserve a considerable amount of small articles.

When a metal vat is used as the anode, it is often advantageous to have auxiliary, adjustable expanded steel anode sheets hung along the sides and across the top of the vat to adjust for variations in the size of artifacts. When plastic vats are used, it is desirable to have a bottom anode because the oxygen evolved from the bottom ensures that the solution is continually mixed, thus preventing the tendency for molecular chlorides and hypochlorite to concentrate along the bottom or at the anodes.

Other refinements can be made to improve the sandwich setup for electrolytic cleaning. Most descriptions (Plenderleith 1956:195) recommend that three brass rods be suspended across the top of the vat, with vertical sheets of steel hung by copper wire from the side rods, and artifacts suspended by copper wire from the center rod. It is much simpler to use expanded steel sheets or stainless steel sheets, which extend up to the top of the vat and are bent and extended over the ends of the vat. This eliminates the two brass anode bars and the copper suspension wires, which would in any case go into anodic dissolution and plate the cathode. The anode sheets are attached to the positive terminal with a Mueller clip. Since the copper wire attached to the clip is out of the solution, it does not go into anodic dissolution and disconnect from the clip, which is a common occurrence on anode connections submerged in the electrolyte.

Suspending artifacts from the cathode rod with copper wire is not effective. It is difficult to maintain a good contact between artifact and the cathode; at some point, electrical contact will inevitably be lost. It is more desirable (at least for most small objects) to attach artifacts to the cathode rod with double-ended clips. Such clips can be purchased or made by bolting the ends of two clips together. The clips apply a constant pressure and ensure maintenance of a secure contact on the cathode rod and on the artifacts. The clips also facilitate attaching and removing artifacts without unnecessary difficulty.

In all Type 3 electrolytic setups, the conservator is unable to regulate the electrode potential or the current density to each artifact, which lessens the possibility of reducing the appropriate corrosion compounds back to a metallic state. It is also impossible to monitor the chloride loss from any one artifact in Type 3 setups.

There are also a number of setups that involve multiple artifacts, each in an individual cell, but all connected to a single power supply. In Figure 10B.1E, an example is shown using a mild steel or stainless steel vat with compartments; the vat is connected to the positive terminal and serves as the anode. An artifact can be placed in each of the compartments. When more than one compartment is used, the current to each artifact cannot be controlled, but the chloride level of the electrolyte in each of the compartments can be monitored. This approach takes advantage of limited facilities by using one DC power supply for several artifacts. It also enables the conservator to determine exactly when each object is cleansed of chlorides, keeping the length of treatment of each artifact to a minimum. When an artifact is completed, its compartment can be taken down and set up again without disturbing the electrolytic treatment in other cells.

Many conservation laboratories use an electrolytic setup in which a single power supply is connected to a control panel consisting of a number of amperage gauges and rheostats. Each artifact is placed in a separate vat and the current that runs from the power supply to each vat is regulated by a rheostat wired into the line. Each artifact or vat has a gauge that indicates the incoming amperage. This particular setup can be used to regulate the current to a number of artifacts from a single power supply; it has no particular disadvantages as long as the power supply has an amperage output sufficient for processing the number of artifacts that are being treated.

ELECTROLYTES

The two electrolytes commonly used in conservation for treatment of iron objects are alkaline solutions of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH). Each electrolyte has its advantages and disadvantages and the conservator must know how to choose the electrolyte best suited for the object to be treated. Alkalies (and acids) used in conservation should be concentrated enough to do the required job but no stronger than necessary. This avoids over-cleaning the specimen and helps keep operating costs as low as possible.

SODIUM HYDROXIDE

In most laboratories that treat iron recovered from marine sites, a 2-5 percent solution of sodium hydroxide is the standard electrolyte used in electrolytic cleaning; it is the only electrolyte used when the objective is to maximize the reduction of ferrous corrosion products. Sodium hydroxide is more soluble in solution than sodium carbonate; unlike sodium carbonate, however, it will generate extreme heat when mixed in concentrated solutions. With its higher pH (12.9), sodium hydroxide is much more caustic than sodium carbonate and presents a potential hazard to those working with it. Caution must be exercised, and adequate safety equipment such as gloves, eye shields, eye washes, and safety showers, should be available.

SODIUM CARBONATE

If maximum reduction of corrosion products is not the objective of electrolytic treatment, a 5 percent sodium carbonate electrolyte with a pH of 11.5 will suffice for the cleaning of most iron artifacts.. In terms of safety, it is much less caustic than sodium hydroxide and much safer to handle. It is less conductive than sodium hydroxide, however, and must be used in stronger concentrations (5-10 percent vs. 2-5 percent). The more concentrated solutions of sodium carbonate are only slightly less expensive than their weaker sodium hydroxide counterparts, and sodium carbonate is usually easier to obtain from chemical supply houses than sodium hydroxide.

In experiments comparing artifacts treated in 5 percent sodium carbonate mixed in tap and de-ionized water and 2 percent sodium hydroxide mixed in tap and de-ionized water, chlorides diffused out of the artifacts and reached higher Cl^- concentrations in sodium carbonate electrolytes more quickly than comparable artifacts in sodium hydroxide electrolytes (Locke n.d.).

The major problem encountered with sodium carbonate electrolytes is the precipitation of insoluble carbonate on artifacts during electrolytic cleaning (see below). Another problem commonly encountered with sodium carbonate electrolytes is that the pH and conductivity of the solution are inadequate in keeping mild steel anodes passive in the presence of high chloride levels. In sodium carbonate electrolytes, $(OH)^-$ ions discharge as oxygen at the anode more readily than the dissociation products of carbonate ions $(CO_3),^{2-}$. The anode becomes acidic by the accumulation of hydrogen from the oxygen evolution reaction; therefore, anodic dissolution is more prevalent with sodium carbonate than when sodium hydroxide, with its surplus of hydroxyl ions, is used. To ensure passivity in sodium carbonate electrolytes, mild steel anodes must be cleaned and replaced more often than in sodium hydroxide electrolytes, especially if the electrolyte is not circulated. It also takes longer to rinse out all residue of a sodium carbonate electrolyte from an artifact than to it does to rinse out all residue of a sodium hydroxide electrolyte.

The most important disadvantage of Na_2CO_3 relates to its pH and cathode reduction potentials. Theoretically, more efficient reduction of ferrous corrosion compounds is possible using 2-5 percent sodium hydroxide with a pH of 12.9 than 5 percent sodium carbonate with a pH of 11.5. (This is discussed in detail in the section on electrode potentials.) In general, sodium carbonate can be used as an electrolyte if reduction is not the objective; when treating metals from marine sites, however, a sodium hydroxide solution is the preferred electrolyte.

CARBONATE SEQUESTERING AGENTS

The cathodic precipitation of insoluble carbonate onto artifacts that are being electrolytically cleaned is the major problem encountered with sodium carbonate electrolytes. The carbonate precipitates from the electrolyte; this precipitation is more likely to occur at high current densities and when tap water containing high levels of carbonate is used to prepare the electrolyte. Carbonate precipitation in sodium hydroxide electrolytes is very rare and appears to be directly associated with the use of tap water that contains high levels of carbonate.

Artifacts recovered from salt water that are encrusted with calcium carbonate, magnesium hydroxide, and other minerals can provide the necessary elements to react with the carbonate in the electrolyte to form insoluble carbonates, such as calcium or magnesium carbonate. Once the surface of an artifact is plated with a carbonate deposit, chlorides may remain trapped beneath the surface. This will result in inaccurate chloride level readings in the electrolyte and lead the conservator to incorrectly assume that the removal of chlorides from the artifact is complete.

As a precautionary measure, gluconic acid, sodium gluconate, or sodium glucoheptanate in the amount of 2 percent of the NaOH or Na_2CO_3 in the electrolyte can be added as a sequestering agent to prevent the precipitation of insoluble calcium carbonates onto the artifacts. Gluconic acid and sodium gluconate require an excess of hydroxide in the electrolyte to work effectively; the lower pH of 5 percent sodium carbonate (pH 11.5) electrolytes will inhibit the action of these sequesterants. For both sodium carbonate and sodium hydroxide electrolytes, 50 percent aqueous sodium glucoheptonate has been found to be the superior sequesterant. In addition to preventing undesirable carbonate deposits on the cathode, the gluconate ions will sequester dissolved ferric ions, which would ordinarily precipitate as ferric hydroxide or oxide on steel anodes; gluconate ions will also prevent the formation of rust on artifacts during the rinsing and drying process.

If the local tap water is suspected of contributing to the formation of carbonate precipitate, de-ionized water should be used in the electrolyte. If carbonate precipitate is not observed, there is no reason to go to the trouble of adding a sequesterant to the electrolyte.

If carbonate does precipitate on an object, it is usually impossible to brush off or remove by electrolysis; rather, it can be eliminated by soaking the artifact for several days in a 5 percent solution of sodium sesquicarbonate or sodium hexametaphosphate. Sodium sesquicarbonate complexes with the insoluble calcium or magnesium salts to form soluble salts in the same manner as sodium hexametaphosphates (Plenderleith and Werner 1971:253).

WATER IN ELECTROLYTES

It is generally recommended that only distilled or de-ionized water be used in electrolyte solutions. The exception to this recommendation occurs when the objects to be cleaned are heavily contaminated with chlorides. It is more economical to use tap water in the electrolyte until the chloride level approximates the level of the local tap water; once this level has been reached, the tap water is replaced with deionized water. The use of tap water in the first electrolytic baths may actually reduce the electrolysis time. Preliminary experiments indicate that chlorides are removed more rapidly when tap, rather than de-ionized, water is used in sodium hydroxide and sodium carbonate electrolytes.

EFFECTS OF ELECTROLYTES ON METAL VATS

When iron objects recovered from the sea are cleaned there is a very large buildup of chlorides in the electrolyte for the first few baths. If the metal vat that contains the electrolyte is also used as the anode, high chloride levels (2,000 to 18,000 ppm) and lack of external circulation can cause the vat to corrode extensively through anodic dissolution. Anodic dissolution is best prevented by using a 5 percent NaOH electrolyte with its surplus of hydroxyl ions; after the chloride levels drop below 1000 ppm, 2 percent NaOH can be safely used. Anodic dissolution is more frequently encountered when using a 5 percent sodium carbonate electrolyte and should not be used in vats that are not easily replaced.

CURRENT DENSITY

The current density used in electrolytic reduction is expressed as the number of amperes per unit of artifact surface area that is introduced into the electrolytic cell by an external DC power supply, such as one ampere per square centimeter (1 amp/cm2). Current density ranging from 0.001 to 1 amp/cm2 have been proposed for use in electrolytic cleaning (Plenderleith 1956:195; Plenderleith and Torraca 1968:242; Plenderleith and Werner 1971:198; Pearson 1972a:12; Townsend 1972:252), but guides to the application of specific current densities are seldom given.

The irregular shape of many metal artifacts may make it difficult to determine their surface areas. Although it is seldom stated in conservation literature, the total surface area of the cathode is calculated only when an anode is form-fitted around the cathode and completely encompasses the artifact; otherwise, only the surface area of the object that is exposed opposite the anode is calculated. If the artifact to be treated is solid, well-consolidated metal, or if it has only ferric corrosion compounds, the applied current density is not critical. If the object has ferrous corrosion compounds, an initial high current density that results in the steady, vigorous evolution of hydrogen will quickly flake off the corrosion layer and significantly alter the shape of the specimen. In addition, an initial high current density can disfigure the surface of iron and also seal off the object, preventing the removal of deeply seated chlorides. These problems can be avoided by using a low current density in the early stages of electrolytic cleaning. More importantly, it is possible to reclaim enough of the metal through a reduction process that will consolidate the metal oxide interface, preserving a closer approximation of the object's actual dimensions. This is true even of wrought-iron objects whose corrosion layers are often non-adherent.

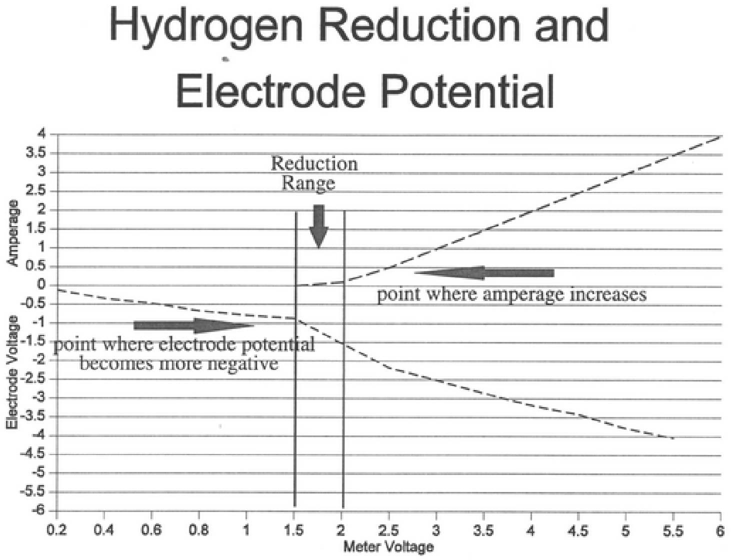
In Hamilton (1976:41), the following current densities and objectives are proposed. These current densities are recommended only as rough guidelines for treating iron artifacts recovered from marine environments. The densities were established by measuring the electrode potential established first on the surface of a rectangular bar of steel and then verified on a number of small artifacts.

1. Low current densities (0.001-0.005 amp/cm2) facilitate the reduction range of ferrous corrosion compounds.
2. Moderate current densities (0.05 amp/cm2) attempt to approximate the optimum conditions for chloride removal without undue evolution of hydrogen.
3. High current densities (0.1 amp/cm2) encourage the vigorous evolution of hydrogen for mechanical cleaning.

If iron reduction is the objective, the specimen should be started off at a low current density. It is followed by a medium current density for the long chloride removal stage. A continuation of low current density would only lengthen the process of chloride removal, while the vigorous production and evolution of hydrogen at high current density interferes with the efficient removal of chloride from the metal and its corrosion products. At both low and medium current density, the marine encrustation and some corrosion products are slowly removed from the object by the mechanical action of the evolved hydrogen. For maximum efficiency, however, the artifact should be finished at a high current density. This ensures the complete removal of any remaining marine encrustation and loose corrosion layers, as well as any remaining chlorides. When high current densities are used only in the last stage of electrolysis, the metal corrosion products that are capable of being reduced have already been reduced, and it is less likely that they will be removed by vigorous hydrogen evolution. While the current density recommendations serve as useful guidelines, they cannot be adhered to rigidly. The conservator should take into consideration the individual peculiarities of the objects being treated and the facilities available to treat the objects. In the case of very large objects, for example, the above current density recommendations may require current in excess of the maximum capacity of an available or practical power supply.

For more direct control over the reduction of metallic corrosion compounds, North (1987:226) recommends that an artifact be placed in electrolysis and the voltage of the power supply slowly increased over the period of a week. The conservator graphs the progression of the treatment by plotting amperage along the x-axis and voltage along the y-axis. The voltage at which the amperage begins to rapidly increase is the hydrogen evolution voltage; this is the voltage at which to conduct electrolysis in order to optimize reduction. By using this technique, some of the difficulties of using current densities are eliminated, and it use is recommended.

In practice, neither measuring current density nor establishing hydrogen evolution voltage is necessary for most artifacts; merely observing the evolution of hydrogen from the artifact is often sufficient. In this technique, as the voltage or amperage is slowly increased, a few bubbles of hydrogen are observed evolving from the surface of the artifact. (In theory, metal reduction does not require any evolution of hydrogen, but the irregular evolution of hydrogen from the surface of the metal is a visual indicator that the current is flowing.) The artifact is treated at this level of low hydrogen evolution to reduce as many of the corrosion products as possible. After a short time, an increase in the evolution of hydrogen may be observed as the resistance of the artifact is broken down and some of the corrosion products in the metal are reduced; if this occurs, the current is decreased to the point at which the irregular evolution of hydrogen is again observed. After most of the desired reduction has been achieved, the current is increased so that there is a steady, yet not vigorous, evolution of hydrogen from the surface of the artifact. This is necessary to remove the maximum amount of chlorides within a reasonable length of time. Vigorous hydrogen evolution indicates a high current density that will mechanically clean the artifact. (As stated above, an artifact should not be mechanically cleaned at high current densities until all desired corrosion products have been reduced and chlorides removed.) In practice, this is how most experienced conservators determine the current density at which to treat iron artifacts as well as artifacts of other metals.



X-axis is divided into two scales: top = amperage gauge reading; bottom = electrode voltage on surface of artifact
Y-axis = voltage gauge reading.

Top line = amperage gauge reading
bottom line = electrode potential measurement on the surface of the artifact

Fig. 10B. Current Density

The applied current density will determine the electrode potential established between the electrodes and the electrolyte, as well as the rate of hydrogen evolution at the cathode. For reduction of metallic corrosion compounds, the establishment of a specific electrode potential on the cathode is essential. Since there is not a corresponding relationship between a given current density and a electrode potential on differentially corroded iron artifacts and different iron alloys, current densities and hydrogen evolution voltages alone are not precise enough tools for the treatment of very select artifacts. In such cases, it may be necessary to actually measure the electrode potential established at the surface of the artifact being treated. An understanding of electrode potentials also clearly demonstrates why one electrolyte is preferred over another when maximum reduction is the objective. This issue will be further discussed below.

In the case of iron, most of the corrosion products, if they can be reduced, are reduced to magnetite. Unlike non-ferrous metals, it has not been shown that any of the iron corrosion products actually reduce back to metal.

ELECTRODE POTENTIALS

Control over the electrode potential at the surface of the cathode is the main objective and advantage of electrolytic reduction of metal artifacts. The normal electrode potential, or relative activity, of each metal is ranked in an electromotive series based upon a normal hydrogen electrode (Table 9.1). The hydrogen electrode is given an arbitrary potential of zero, and all metals are negative or positive to it. The normal electrode potential of a metal represents the electromotive force (EMF) required to balance the cell formed by a particular metal electrode immersed in a solution of its salt of normal cation activity and a hydrogen electrode (Evans 1963:231).

The potential series of the metals represent their equilibrium values at a pH of 0. These potentials change with pH value. In order for a metal to be corroded anodically, an electrode potential more positive than the equilibrium value of the metal must be established; a more negative potential must be created for cathodic reduction. Pronounced cathodic reduction of iron occurs only when the electrode potential is considerably more negative than the equilibrium value of the iron. Dissolution of the anode becomes significant when the electrode potential is made considerably more positive.

The electrode potentials of metals are altered if the [ionic] activity (effective concentration) is not normal. Clearly, if the solution is diluted, the passage from the ionic to the metallic state will be slower, whereas the passage from the metal into solution remains unaltered. Thus the balance will be upset, but a fresh balance may be obtained at a more negative potential. This means that at 18°C, if activity and concentration are regarded as identical, every ten-fold dilution (say from N to N/10, or from N/10 to N/100) will shift the potential in a negative direction by about 0.058 volts for a monovalent ion, or 0.029 volts for a divalent ion. The theoretical shift of potential is approximately realized in the case of the more noble metals; but on some of the less noble metals [iron] the potential actually measured is found to be almost independent of the concentration of the metallic salt in the original solution; this occurs if the metal is capable of reacting with the solution, so that the concentration in the layer next to the metal becomes different from that in the body of the liquid (Evans 1963:234). (See Figure 10B.2.)

The potential of iron immersed in an aqueous solution originally free from iron ions depends on the hydrogen-ion concentration, becoming steadily more negative as the pH value rises (Evans 1963:235).

The electromotive series in Table 9.1 indicates that the reduction reaction of ferrous ions, Fe^{2+} Fe - 2e, occurs at -0.409 volts to -0.440 volts at a pH of 0. The reduction potential increases -0.029 volts for each pH increase. The reduction of ferric ions, Fe^{3+} Fe - 3e, occurs at -0.036 volts and increases -0.019 volts per pH increase. The hydrogen discharge potential, 2H+ H$_2$ -2e, occurs at a voltage potential of 0 and increases -0.058 volts per unit of pH increase. The reduction potential of ferrous, ferric, and hydrogen ions at different pHs at a standard temperature of 20°C are graphically presented in Figure 10B.3. This graph makes it possible to determine the theoretical electrode potential voltage necessary for reduction of ferrous corrosion products in an electrolyte of known pH and ion content. It is thermodynamically impossible to reduce ferric oxide and other ferric iron corrosion compounds in an aqueous solution; this point is also graphically depicted in Figure 10B.3. The electrode potential for the reduction of ferric corrosion products is well out of the range possible for electrolytic reduction in an aqueous alkaline electrolyte with an external EMF.

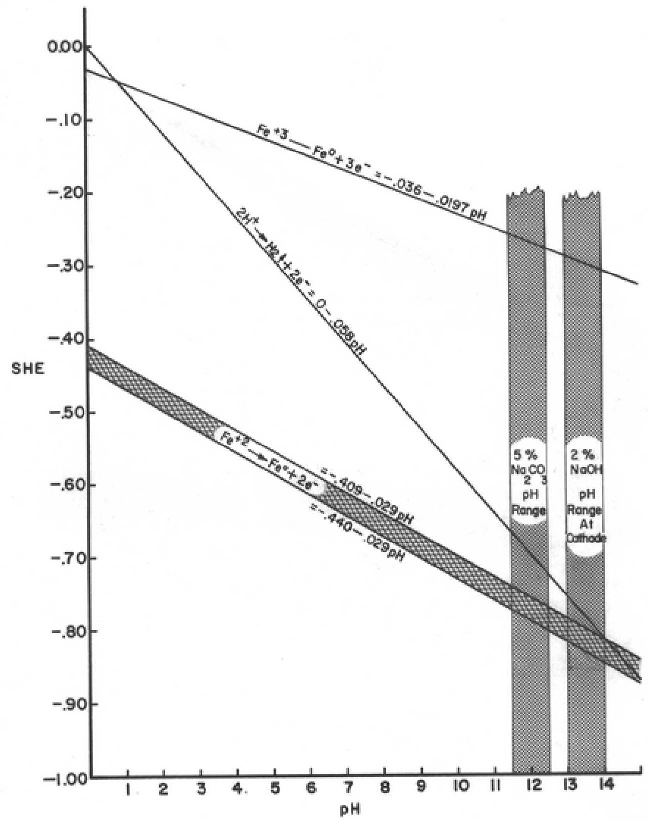
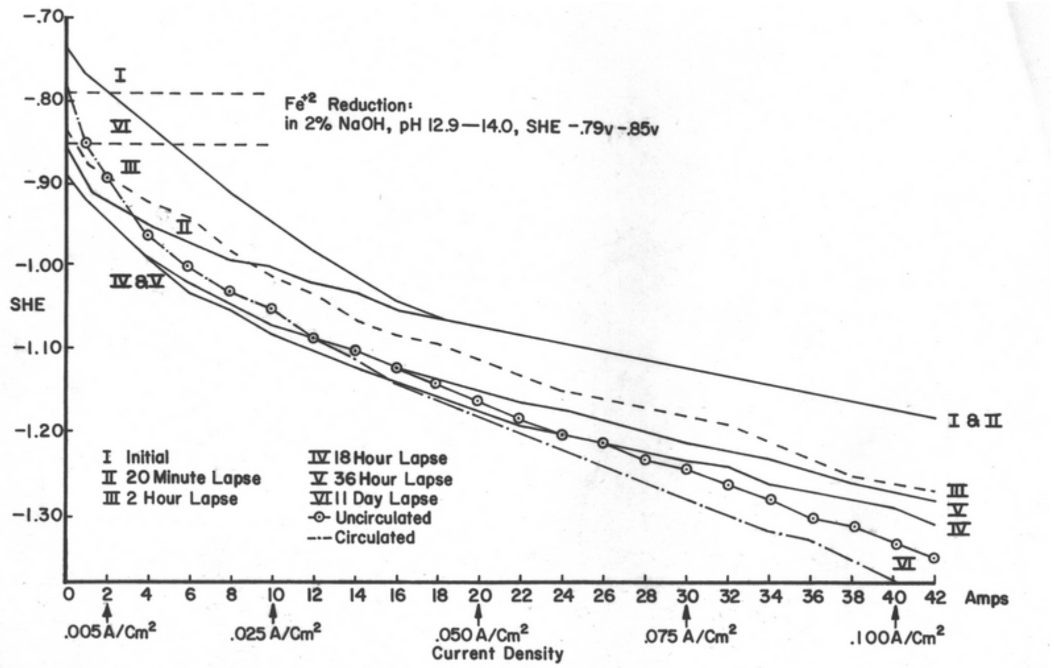
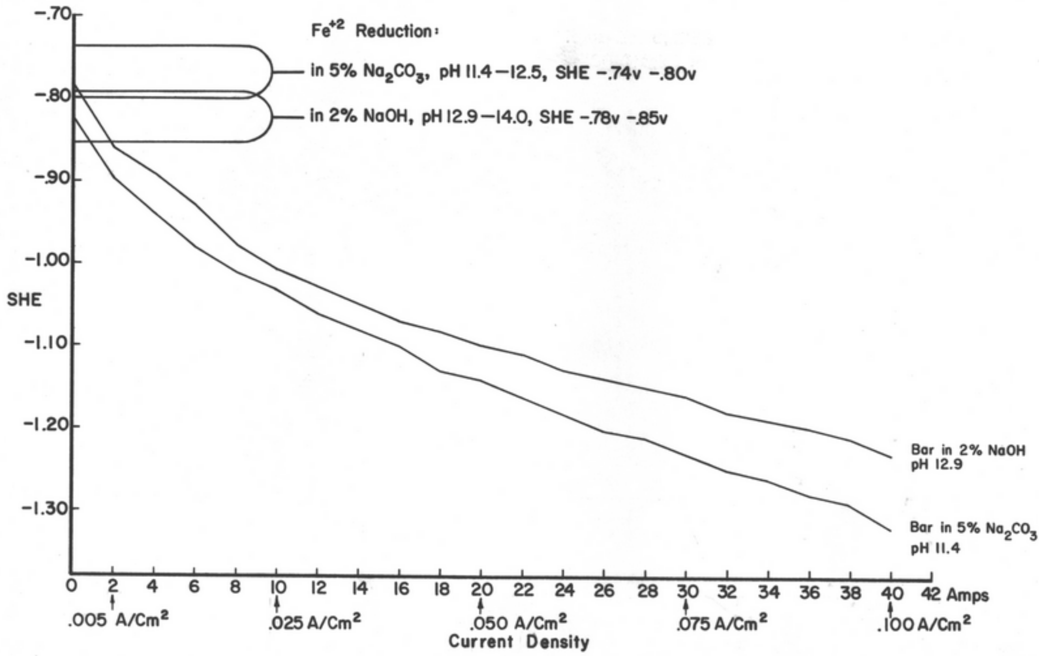


Figure 10B.3. Reduction potentials of ferric, ferrous, and hydrogen ions at different pHs and standard temperature of 20°C. The pH range of a 5 percent Na$_2$CO$_3$ and a 2 percent NaOH electrolyte are shaded.

Electrode potentials are affected by temperature, pH value and electrolyte composition. In the conservation of iron pH is the most important factor. There are several ways to measure the pH of the electrolyte but no simple way of determining the pH at the surface of an electrode; unfortunately, this is the pH reading of concern. It is known that the pH of the catholyte (the solution at the surface of the cathode where hydrogen is evolved) is higher than that of the remaining electrolyte. In order to arrive at a reasonable estimation of the prevailing pH at the cathode, the pH of the electrolyte is measured and a maximum increase of one pH level is assumed; this results in a maximum pH of 14 for sodium hydroxide and 12.5 for sodium carbonate. This approach is imprecise, but there is no direct method by which to measure the pH of the catholyte. These adjusted pH ranges are shown in Figures 10B.3, 10B.4 and10B.5.



[Figure 10B.4](). Reduction potentials at the surface of an iron cathode during electrolysis in a 2 percent NaOH electrolyte at different current densities over an 11-day test period.



[Figure 10B.5](). Comparison of the reduction electrode potential on the surface of the same iron cathode in a 5 percent Na_2CO_3 and a 2 percent NaOH electrolyte.

The electrode potential at the surface of the cathode is a critical factor in the reduction of corrosion compounds during iron electrolysis. As the hydrogen discharge potential of the cell is reached, hydrogen ions are formed which reduce adjacent ferrous compounds. (At more negative electrode potentials, molecular hydrogen will form so rapidly that the molecules will combine with each other and evolve as hydrogen gas; this evolution of hydrogen acts as a mechanical cleaning agent that physically removes any unconsolidated corrosion layers.) The theoretical point at which the maximum reduction and/or consolidation of the ferrous corrosion compounds is achieved is at the intersection of the hydrogen discharge line and the ferrous ion reduction line or immediately to the left of this intersection (see [Figure 10B.3]()). Using the formula $Fe^{2+} + 2e$ Fe and substituting values for the Fe^{2+} reduction potential and the correction for pH [(-0.409)(-0.029)(pH)], this intersection appears at a pH of 14.1 and an electrode potential of -0.82.

[Figure 10B.3]() gives the measured electrode potentials of an artifact in an electrolyte of 2 percent sodium hydroxide with a pH of 12.9 at different current densities over an 11-day period. The initial test was taken before the surface of the artifact was thoroughly saturated with hydrogen, the current resistance of the electrolyte had dropped, and the resistance of the artifact was broken down. After a period of 20 minutes, and throughout the remainder of the 11-day test period, the electrode potentials fell within a rather narrow range. Using the data presented in Figure 10B.3, the potential range for ferrous ion reduction at a pH range of 13 to 14 can be determined as -0.79 to -0.85 volts. In Figure 10B.4, this potential range is achieved at a current density below and up to 0.005 amps/cm2, which is barely within the iron reduction range of NaOH. Figure 10B.5 compares the electrode potentials of the same artifact in 2 percent NaOH and 5% Na_2CO_3; the pH of sodium carbonate is not high enough to establish the desired theoretical electrode potentials for the reduction of ferrous compounds. On theoretical grounds, a sodium hydroxide electrolyte is clearly superior when reduction of the ferrous corrosion products is the objective.

After electrolysis has begun, several hours to a full day are required for the cathode to adjust to an equilibrium state. At the metal surface, a metal/hydrogen bond is established, and the surface becomes saturated with hydrogen, followed by the evolution of hydrogen. Until the metal surface becomes saturated with hydrogen and establishes equilibrium, the electrode potential will remain in flux. After the electrode potential on an artifact has been established, daily adjustment of the current may be necessary to maintain the potential as the current resistance of the electrolyte drops with the addition of dissolved salts, and the resistance of the metal and its corrosion products is altered. The procedure for measuring electrode potentials is described in Hamilton (1976:103-105). Before adjusting the current back to the predetermined potential, however, it must be certain that the shift in potential is due to changes in the cathode and not to the transport system (i.e., changes in the electrolyte due to lack of circulation). In Figure 10B.4, the six series of tests were taken over an 11-day period without circulating the electrolyte. On the last day, the electrolyte was circulated and the test was run again. There are negligible differences in the electrode potential readings of the last two tests, except for the potentials at high current densities. The transport system is still adequate, especially for the electrode reduction potentials of ferrous compounds. If any changes occur in the transport system, it will become visually apparent at the anode, where acidic areas may form. In these areas chloride ions react with the positively charged anode to form hypochlorite ions (ClO-) or hypochlorous acid (HClO), which will oxidize the anode. Adverse reactions are easily detected at the anode, and when this occurs, the cathode is also affected, although it is not as apparent or as detrimental to the operation of the electrolytic cell. The potential at both electrodes, however, is altered. Should a change in the potential occur, the electrolyte should be stirred or circulated and the measurements taken again. If the electrode potential remains the same, then the amperage may be adjusted back to re-establish the optimum range.

From the standpoint of efficiency, electrode potential measurements are necessary for precise control and quality processing of very select artifacts. The areas of advanced or retarded corrosion on the surface of the artifact will be reflected in the electrode potentials, making it possible for the conservator to identify those areas requiring more extensive reduction and to measure the progress of the electrolyte reduction. The data acquired from electrode potential measurements have been used to arrive at realistic current densities for the bulk of the iron artifacts that require treatment but do not warrant the close supervision or the time required for taking electrode potential measurements. Still, there is the difficulty of arriving at the most effective current densities for given artifacts, especially irregularly shaped artifacts and differentially corroded artifacts. For these reasons, using either hydrogen evolution potential voltage or merely visually observing the rate of hydrogen evolution is sufficient for the bulk of iron artifacts.

OUTDOOR ELECTROLYSIS

All electrochemical reduction cleaning processes produce irritating caustic vapors and hydrogen gas, which must be properly exhausted from any room or building for the safety and comfort of personnel. Expensive fume hoods or sealed rooms with exhaust systems are required; alternatively, the electrolytic vats can be placed outside. Most laboratories use variations of all three methods. The smaller artifacts are cleaned in the main laboratory under fume hoods. A few large artifacts are cleaned in a ventilated room in a separate building. Other large artifacts and some small ones are electrolytically cleaned outside, in vats made of mild steel or plastic.

Expensive air exhaust systems are not necessary when electrolysis is performed outdoors. The solutions are changed frequently enough so that any air-blown dirt or sand in the electrolyte will present no problems. Rain is of no concern, unless it is heavy enough to substantially dilute the solution. This problem can be easily determined with a hydrometer to test the specific gravity, and remedied by adding more sodium hydroxide or sodium carbonate. In many cases, rain will only decrease the amount of de-ionized water that needs to be added to the vats daily to compensate for evaporation, caustic vapors, and electrolytic reduction.

If the area is fairly isolated (i.e., safe from human traffic) and has adequate utilities, it is strongly recommended that outdoor electrolytic reduction be performed. The power supplies must be kept out of the weather, but sheds over the vats are optional. Although lower temperatures do not significantly decrease chemical activity, there may be an IR drop in the electrolyte that will increase the cell voltage. All electrolytes should be kept from freezing.

GENERAL OBSERVATIONS ON CLEANING IRON OBJECTS ELECTROLYTICALLY

The following observations are directed primarily towards large iron objects but are not restricted to them. Recommendations for improving electrolytic cleaning procedures and reducing electrolysis time are offered.

Although conservators often avoid cleaning large iron objects electrolytically (because of their size), there are no insurmountable problems. In order to better understand the factors that lead to success or failure in electrolytic cleaning, several case histories are reviewed.

The earliest attempt to electrolytically clean a large, seabed iron artifact was by Lieutenant Nielsen of Norway. The specimen was a wrought-iron gun recovered in 1942 from a ship dating to the 15th century (Eriksen and Thegel 1966:100-102). The conservation was attempted under the adverse conditions of World War II, with inadequate facilities and supplies. The attempt was unsuccessful for a number of reasons, the most important being the following:

1. Failure to remove the wooden undercarriage shielded a large portion of the cannon from the electrolyte and prevented an even distribution of the current.
2. The electrolytic treatment was too brief for complete chloride removal, lasting a total of 69 discontinuous hours spread over a 384-hour period.
3. The placement of the steel anode sheet along only one side of the vat failed to ensure an even distribution of current.

4. After the brief electrolytic treatment, the wooden undercarriage was swabbed with hydrochloric acid to neutralize the 1 percent sodium hydroxide used as the electrolyte. This acid introduced additional chlorides to attack the iron.

Ora Patoharju (1964, 1973) reports one of the first successful attempts to electrolytically clean a large cast-iron cannon. In 1963, two guns from a 1790 shipwreck were treated. One had been recovered many years before treatment and had been allowed to dry out; the second cannon had recently been recovered and had been kept wet. Both served as the cathode with three stainless steel sheet anodes in a 10 percent Na_2CO_3 electrolyte. They were run at a rate of 20 amperes at 4 volts (current density ca. 0.027 amps/cm2) for one month and a rate of 150 amperes at 4 volts (current density ca. 0.2 amps/cm2) for five months.

Not enough details on all aspects of the electrolytic treatment were provided in order to properly evaluate the methods employed. After being displayed outdoors for two years, however, the 'wet' gun was stable and its treatment judged to be successful, although the dry gun continued to deteriorate as rapidly as before electrolysis. The most likely reasons for the successful treatment of one gun is that it was kept wet, preventing further corrosion, and that the six months of electrolysis ensured the complete removal of the chlorides in the metal. The preliminary conclusion of Patoharju is that cast-iron objects coming directly from the sea should be kept wet up to the point at which they are immersed in the electrolyte. If the object is allowed to dry out before treatment, the specimen will undergo further oxidation, and any conservation attempt may be futile.

In another example, a couple of large breechblocks had been successfully treated with electrolysis, with the majority of the corrosion layer left intact on the specimens. A month after completion of the treatment, it was decided to put the breechblocks back into treatment in order to darken the surfaces. The wax that coated the breechblocks was melted off in an oven, which most likely caused increased conversions of FeO to Fe_2O_3 on the artifacts before they were put back into electrolysis. In this case, and that of Patoharju's 'dry' gun, the corrosion layer completely detached and left behind a badly disfigured surface.

The above examples suggest that if there are thick layers of corrosion, the treatment must be successful the first time. Wrought-iron corrosion layers are non-adherent; after they have been removed of water during the drying and sealant steps, these layers apparently undergo additional oxidation and may also lose the electrical couple with the metal core. During subsequent electrolysis, hydrogen will evolve at the surface of the metal and slough off the corrosion layer. This problem may possibly be alleviated by soaking the object in electrolyte for a long time prior to any further electrolysis in order to re-establish the electrical couple.

Pearson (1972a, 1972b) discusses the conservation of six cast-iron cannons and other relics jettisoned in 1770 by Captain Cook on Endeavor Reef, off of the Australian coast. Upon arrival at the laboratory, the cannons were stored in 2 percent solution of sodium hydroxide, and each was placed in an epoxy-coated wooden cradle specifically constructed to support it throughout the conservation process. The coral encrustation was mechanically removed with hammers, and the cannon surfaces were carefully scrubbed with water to remove the loose black corrosion products. The three cannons and their support cradles were simultaneously treated in separate fiberglass-lined wooden tanks with a 2 percent NaOH electrolyte. The vats were hooked up in series on one power supply, analogous to the Type 4 setup described earlier. Each cannon was set up as the cathode and two anodes, a single mild steel sheet along one side of the vat, and a steel rod in the bore, were used. A current density of 10 amps/m2 (0.001 amps/cm2) was applied. Each week, the third cannon was removed from its vat and the electrolyte discarded and replaced with fresh electrolyte. Cannon No. 1 was then placed in this vat; Cannon No. 2 was placed in the vat from which No. 1 had been removed; and Cannon No. 3 was put in the vat formerly occupied by Cannon No. 2. With this method, the first cannon, the one in electrolysis the longest, was always placed in the fresh electrolyte. This rotation was continued weekly until analysis showed that there was no increase for one week in the chloride content of the bath containing the first cannon. This method required six to eight weeks of electrolysis for each cannon.

A current density of 0.001 amps/cm2 was chosen by Pearson because experiments proved it to be the optimum current density value for the removal of chlorides. Pearson found that higher values blistered the graphitic surface layers of the cast iron, and lower values only prolonged the time required to remove chlorides. More importantly, this current density is within the range that is most efficient for the reduction of ferrous iron compounds. A series of experiments (Hamilton 1976:40-46) on wrought iron indicate that 0.001 amps/cm2 to 0.005 amps/cm2 is theoretically most efficient for metal reduction (as is shown in Figures 10B.6 and 10B.7); 0.05 amps/cm2 to 0.1 amps/cm2 is most efficient for chloride removal; and the vigorous evolution of hydrogen produced by a density of 0.1 amps/cm2 and above is used for mechanical cleaning.

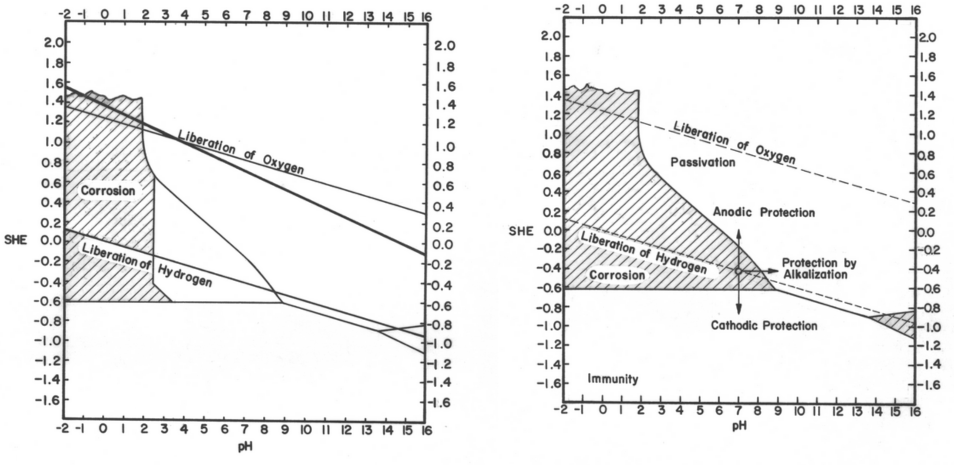


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Fig 10B.6 and Fig 10B.7

EXPOSURE TO ANODE SURFACE

When Pearson (1972a) cleaned Captain Cook's cannons, he placed a single mild steel anode along one side of the vat and used immovable wooden support cradles on the cannons. The placement of the anode failed to create an even current density, and the cradles shielded two areas from what current flow was present. This shielding interfered with the removal of the chlorides and the reduction process. Pearson (personal communication) reports that minor corrosion occurred at these two support points because the cannons were not rotated sufficiently during the treatment. Similar occurrences have occurred even on small surface areas covered with plastic identification tape.

From these examples, it is clear that no portion of the artifact can be covered throughout electrolysis; even a small piece of narrow tape can shield the area beneath it enough to prevent complete removal of the corrosive chlorides. To avoid this problem, cannons should be rotated frequently, and the position of movable supports should be shifted each time the electrolyte is changed. When plastic tape is placed on artifacts for purposes of identification, the position of the tape should be moved at least once during electrolysis.

The importance of using form-fitted anodes in electrolysis should be emphasized. Such anodes, positioned to ensure an even current density over all the surface of the artifact, improves the overall efficiency of the electrolytic process. An exact distance does not need to be maintained between the artifact and the anode at every point; this is nearly impossible for irregularly shaped artifacts. Rather, the anode should be bent and shaped so that is somewhat evenly distanced from the artifact at all points.

North (1987:225), citing Hamilton (1976), states that the use of form-fitted anodes has been suggested, but that they are unnecessary because a satisfactory current distribution will be achieved as long as the artifact-anode distance is between 20-80 cm. However, he further states that this recommendation does not apply when a rod is used as the anode in the barrel of a cannon, as the current will be concentrated in the cannon bore due the small distance between the rod and the cannon. In addition, while discussing the establishment of hydrogen evolution potential voltage, North (1987:226) notes that hydrogen gas evolution is coming from only one area of the artifact may be due to the fact that the anode is too close to the artifact at that point. This clearly demonstrates that maintaining a relatively even distance between the artifact and the anode is essential for proper electrolytic cleaning.

Even if form-fitted anodes are not used for every electrolytic treatment (artifacts are frequently placed between two anodes, particularly when processing a large amount of artifacts at a single time), they are highly recommended. They will maximize iron reduction and chloride removal and will cut down on the electrolysis time.

DURATION OF ELECTROLYSIS

Ora Patoharju (1964) reported an electrolysis time of six months to clean two cannons recovered from a 1790 wreck. In general, wrought-iron objects that approach the size of a cannon require between 6-12 months of electrolysis. As an example of the length of time required to treat large wrought-iron objects, one 198-cm long fully armed swivel cannon required 20 days to remove all of the encrustation and to dismantle the component parts; 251 days of electrolytic cleaning at 20 to 50 amps; 7 days of rinsing in several changes of alternate boiling and cold de-ionized water; 15 days of dehydration in alcohol; and 1.5 days submerged in molten microcrystalline wax. Three hooped barrel cannons processed together in one vat required 480 days of electrolysis, 3 months of rinsing (the rinsing period was prolonged while awaiting delivery of microcrystalline wax), 5 days of dehydration in alcohol, and 5 days submerged in microcrystalline wax. Even small wrought-iron artifacts, such as spikes, often require 60-90 days of electrolysis. If an object is kept in electrolysis for too short a time, the full potential of electrolysis is not achieved, and the time required to rinse the artifact is significantly increased.

Reducing Electrolysis Time

When artifacts are electrolytically cleaned in small vats with a low ratio of electrolyte to artifact volume, the length of electrolytic time is considerably extended. The larger the volume of electrolyte to artifact being cleaned, the shorter the period of electrolysis required.

Two wrought-iron breechblocks that were cleaned in two small vats required 25 months of electrolysis. In addition, more frequent changes of the electrolyte will also considerably decrease the time required to electrolytically clean an artifact.

The stage at which the chloride (Cl^-) level in the electrolyte is reduced to below 50 to 100 ppm requires the greatest amount of electrolytic cleaning time. Below 100 ppm Cl^-, the artifact is assumed to be in the final stages of cleaning. There are at least two explanations for the long amount of time required to remove chlorides during electrolysis: (1) The electrolysis is carried out at high current densities which have a tendency to repress Cl^- migration in preference for H_2 evolution, (2) The Cl^- concentration in the electrolysis is governed by the Donnan equilibrium theory.

The Donnan equilibrium theory pertains to the unequal distribution of ions on two sides of a membrane (Kunin 1958:14-16). Although no membrane exists between the artifact and the electrolyte, the interface between the solid and liquid phases may be considered a membrane. An exchange of Cl^- ions continues until the concentration ratios are equal in both phases. The lower the Cl^- ratio in the electrolyte, the more effective the diffusion of the Cl^- ions from the artifact to the electrolyte. Using the Donnan equilibrium theory, it can be generalized that the rate of Cl^- transfer from the artifact to the electrolyte is negated despite the electrolytic field when the Cl^- content of the electrolyte reaches equilibrium with or is higher than the Cl^- level in the artifact. Chloride tests can be misleading under equilibrium conditions. When the Cl^- content in the electrolyte maintains a steady level in a controlled constant volume of electrolyte, it should be determined that either the chloride removal process has been completed, or that equilibrium conditions have occurred. Unless the electrolyte is renewed to lower the Cl^- concentration, little or no further Cl^- removal from the artifact can be achieved. Either determination can be easily validated by changing the electrolyte and monitoring the chloride levels for a few more days. Frequent changes of the electrolyte and use of as large a vat as possible ensures that the chloride level of the electrolyte is lower than the chloride level of the artifact. This will facilitate chloride removal and make the entire electrolytic process more efficient. For example, two similar wrought-iron anchors were placed in electrolysis, with the electrolyte in one anchor vat changed more frequently than the electrolyte in the other vat. The anchor that underwent more frequent changes of electrolyte required 6 months of electrolysis in contrast to 11 months for the other anchor. Three wrought-iron cannons required 16 months of electrolysis at 100-150 amps and 3 volts to remove the chlorides, whereas a second group of three hooped barrel cannons that underwent more frequent changes of electrolyte were completed in 11 months.

SUMMARY

When sea-recovered artifacts are cleaned by electrolytic reduction, it is recommended that the artifact be started in an electrolyte of 2-5 percent NaOH in tap water. During this period, the reduction of ferrous compounds is attempted at low current density, and high levels of chloride are removed at medium current density. Electrolysis is continued in the tap water electrolyte until the chloride level of the electrolyte approximates the level found in the tap water. Tap water is then replaced by de-ionized water, and electrolysis is continued with 5 percent NaOH or lowered to 2 percent NaOH. A low current density is maintained until the electrolyte is again changed, whereupon a medium current density is used.

The higher pH of NaOH is preferable when the objective of electrolysis is the reduction and/or consolidation of ferrous corrosion products. If this is the case, NaOH should be used as the electrolyte. If the corrosion products are in a ferric state, there is no advantage in using NaOH, and Na_2CO_3 can be used from the beginning. This is applicable to many iron objects that are air-oxidized in archaeological sites, but this generalization should not be carried out too far. There will almost always be some ferrous compounds that can be successfully reduced.

ALKALINE SULFITE TREATMENT

The alkaline sulfite treatment was developed by North and Pearson (1975b) to stabilize marine cast iron, but it is also used on wrought iron. Bryce (1979:21) found that the treatment is effective on iron objects that are moderately to heavily corroded, but the objects still must have a metallic core present for the treatment to be effective; otherwise, the iron object will break apart during treatment. The procedure is as follows:

1. 1. After mechanical cleaning, an iron object is immersed in a solution of 0.5 M (20 g per liter of water) of sodium hydroxide and 0.5 M (126 g per liter of water) of technical-grade sodium sulfite. A glass container should be filled with as much solution as possible and the object quickly placed in it to avoid any oxidation of the solution. The container is then sealed air tight, placed in an oven, and kept heated to a temperature of 60°C. The object is processed through several baths of the solution until chlorides are eliminated; this may take a week to several months and numerous baths. Tap water can be used for the first one or two baths, but de-ionized or distilled water should be used in the final baths. The solution does not attack any residual metal, so there is no danger of too many baths.

   When a marine iron object is immersed in this hot reducing solution, the iron corrosion compounds are converted to magnetite, and the chlorides are transferred to the solution and discarded with each bath change. The object comes out of the treatment with a very black surface coloration. Since the solution is strongly alkaline, contact with the skin should be avoided.

2. Once the alkaline sulfite stabilization treatment is completed, the object is washed for one or more hours in several baths of de-ionized water and then placed in a 0.1 M solution of barium hydroxide (32 g per liter of water). Barium hydroxide is slightly poisonous, so contact with the skin should be avoided. If the object is intensely rinsed in several baths of de-ionized water following the alkaline sulfite stabilization, the barium hydroxide baths can be eliminated.
3. The alkaline treatment has been very effective for conserving iron recovered from a marine environment. The main drawbacks of the treatment are that it must be carried out in an air-tight container, and the container should be kept heated.

CHEMICAL CLEANING

A number of chemical cleaning treatments are used for iron artifacts recovered from non-marine environments that have negligible chlorides present. The most common chemicals used are oxalic acid, citric acid, phosphoric acid, ethylenediamine tetra-acetic acid (EDTA), and other complexing agents. The exclusive use of any of these chemical treatments may improve the appearance of an object, but they do not remove chlorides and hence cannot prevent subsequent corrosion. Therefore, they are not considered as conservation alternatives for treating iron recovered from salt water. Details concerning the use of these and other chemicals are described by Plenderleith and Werner (1971).

Two chemicals, phosphoric acid (and its derivatives in commercial rust removers) and tannin solutions, are often used to form a corrosion-resistant film of phosphate and tannates on the surface of treated iron pieces. The corrosion-resistant significance of phosphate and tannate films was first made apparent when iron articles recovered from an ancient Roman tannery in England were found to be in an excellent state of preservation (Farrer et al. 1953). Before either chemical can be used, however, the chlorides must be removed by electrolysis, alkaline sulfite treatment, or water diffusion.

TANNIC ACID

The corrosion-resistant nature of tannate films on iron was investigated by Knowles and White (1958) and later by Pelikan (1966). In accelerated exposure tests, it was found that tannate films on iron were more corrosion-resistant and lasted twice as long as phosphate coatings. It is important that the right tannic acid be selected, as many are not effective. Argo (1981) provides a discussion of the requirements and benefits of tannic acid solutions. Tannic acid solutions (such as Baker reagent tannic acid, $C_{76}H_{52}O_{46}$) with a pH of 2.5-3.0 provide good, weather-resistant tannate films. Solutions of hydrolysable tannins, such as extracts of chestnut, myroblans, or valonea, with a pH of 2 to 2.5, provide the most weather-resistant protection (Knowles and White 1958:16). If the tannic acid mixture has too high of a pH, phosphoric acid should be added to bring it down to a pH of 2.4. In most conservation laboratories, tannic acid solutions are a standard part of the conservation of all iron artifacts. Although a tannic acid coating is often the final step in iron conservation, it is recommended that an additional sealant, such as microcrystalline wax, be applied over the oxidized tannate film for maximum protection.

In the past, the Conservation Research Laboratory at Texas A&M University has used a 20 percent tannin solution (200 g tannin, 1 liter water, 150 ml. ethanol) on iron artifacts. Logan (1989) states that solutions of tannic acid stronger than 10 percent are much too concentrated and recommends that several coats of diluted 2-3 percent tannic acid (with the addition, if necessary, of sufficient concentrated phosphoric acid to achieve a pH of at least 2.4) be brushed on the object. She also cautions that different brands of tannic acid react differently and recommends BHD Chemical tannic acid as working consistently well. Recent treatments conducted by the Texas A&M Conservation Research Laboratory on iron artifacts recovered from a 17th-century French shipwreck have demonstrated that a 5 percent tannic acid solution permeates the corrosion layers of the artifacts better than a 10 percent solution. In general, a 2-10 percent solution of tannic acid is effective; the concentration of the solution should be determined by the ability of the solution to permeate the corrosion layers of the artifact to be treated.

Several coats of the tannic acid solution should be applied with a stiff brush to the surface of the artifact. A brushed-on film provides better protection than a dipped or sprayed application because the brushing ensures that the solution has access to the metal in areas of loose rust. Brush application also eliminates the polarization of cathodic areas by the formation of hydrogen (Pelikan 1966:112). Objects such as cannon balls have also been successfully treated by vacuum impregnating them with a tannin solution. The object is allowed to completely air oxidize between each application of the tannic acid; after the final application, the object should be allowed to dry for one to two days.

The tannin solution reacts with the iron or iron oxide to form a ferrous tannate, which oxidizes to a mechanically strong, compact, blue- to black-colored ferric tannate. In order to ensure a continuous tannate film, Knowles and White (1958) recommend that all iron oxide products be removed from the surface of the artifact, otherwise there is a possibility that corrosion may start at the junctures of the cathodic iron oxide and the tannate film. Good results can be achieved even if this recommendation is not followed; Pelikan (1966:110-111) found that tannin solutions react directly with the metal base and with the rust if the solution is sufficiently acidic (pH 2 to 3). In addition to forming a corrosion-resistant film, tannin solutions can be used to impart an aesthetically pleasing black color to iron.

A phosphate film is formed on iron objects by impregnating them with a 20 percent solution of phosphoric acid (H_3PO_4). Impregnation under a vacuum is recommended in order to ensure complete penetration of the acid into all porous areas of the metal. The acid complexes with the iron to form an inert film of ferric phosphate film on the surface of the metal. Reese-Jones (1972) describes the above procedure and reports that porous cast-iron cannon balls from a 1588 Spanish Armada shipwreck were successfully treated by this method after the chlorides were removed by water diffusion. Similar results can be achieved on wrought iron or steel.

Data reported by Pelikan (1966:112-113) indicate that a mixture of phosphoric acid and tannin solution can be used on badly rusted iron to appreciably improve the corrosion resistance of a phosphate film. One hundred milliliters of 80-85 percent phosphoric acid solution is added to the 20 percent tannin solution, and several coats are brushed onto the artifact. This is followed by at least four coats of the standard 20 percent tannin solution. Following the treatment of an object with the phosphoric acid-tannin solution, a final sealant should be applied to seal off the tannate or phosphate film. This solution does not result in the rich, dense black coloration that Baker tannic acid does by itself.

Regardless of whether tannic or phosphoric acid is used, it is highly recommended that a sealant, such as microcrystalline wax, be applied over the film formed on the object, The wax will provide a vapor barrier, which the film does not, and will also contribute some strength to corrosion layers on the metal.

ANNEALING

OXIDIZING ATMOSPHERE

Treating sea-recovered iron objects by heating them to a temperature of 850°C was first attempted in Denmark in 1955 (Eriksen and Thegel 1966). It was proposed that at this temperature, the chemically bound water associated with the ferrous chloride corrosion products in the porous matrix of the metal would be driven off, leaving behind inactive anhydrous ferrous chloride. Simply leaving chlorides in an anhydrous state, however, will not prevent subsequent corrosion. Both ferrous and ferric chloride are capable of absorbing water from the atmosphere and reinitiating the corrosion process unless a perfect air-tight, atmosphere-proof coating is applied. The success of annealing is more likely due to the sublimation of the chlorides. Experiments conducted by Pearson (1972a:25) indicate that a temperature of 850°C is well above the melting point of ferrous chloride, and both ferrous and ferric chloride sublimed strongly from a piece of test iron at 700°C. Therefore, it is probable that the sublimation of ferric and ferrous chlorides occurs at a temperature of 700°C and higher.

The apparent absence of corrosion during 20 years of outdoor exposure is testimony to the success of this method. However, there are considerable disadvantages to this method:

1. There is no opportunity to preserve the iron oxide interface. The corrosion layers spall and crumble, obliterating any decoration or identification markings on the cannon and leave behind a badly disfigured surface.
2. The remaining surface is oxidized to an unattractive red iron oxide color.
3. The elevated temperatures alter the metallurgical microstructure of the metal, rendering the artifact useless for future metallurgical examinations.

Because of these shortcomings, the technique of annealing in an oxidizing atmosphere is not recommended.

REDUCING HYDROGEN ATMOSPHERE

Work by Barkman in connection with the preservation of the *Wasa*, the 1628 ship raised intact from the Stockholm Harbor in 1961 (Barkman and Franzen 1972), has demonstrated that annealing iron at a temperature of 1060°C in a reducing atmosphere successfully stabilizes and preserves it, returns it to a metallic state, and eliminates the corrosive chloride compounds by sublimation.

The iron to be treated is placed in a hydrogen furnace and heated in the presence of hydrogen gas. The temperature is slowly raised to 1060°C over a period of one week. At this elevated temperature, all of the moisture is driven off, and all of the chloride corrosion compounds are volatilized. The hydrogen reduces the iron corrosion compounds back to a metallic state and combines with the oxygen in the corrosion products, forming water, which is driven off by the heat. Over the years, the temperature to which the hydrogen oven is heated has been decreased. In the past, objects undergoing hydrogen reduction were placed in a special furnace with 100 percent dry hydrogen gas, or a mixture of hydrogen and nitrogen, initially heated to a temperature of 300°C and over a period of days taken to 1000°C (Barkman 1978:155-166).

Annealing in a reducing atmosphere is said to result in very little damage to the surface of the metal. More experiments are needed, however, to determine the extent of any undesirable surface alteration. From the standpoint of time and final results, the technique appears to be a satisfactory, efficient alternative for cleaning iron recovered from the sea.

The primary drawbacks to this technique are the expense of the equipment and the lack of hydrogen kilns big enough to treat large objects. At present, a few conservation laboratories use annealing to treat numerous small artifacts, such as cannon balls, with a minimum amount of hands-on handling. Another drawback is the large amount of hydrochloric acid produced when the chlorides are driven off from the artifacts; the hydrochloric acid will attack any exposed metal inside of the kilns or furnaces. The detrimental effect the HCl fumes on the metal hardware of the kilns or furnaces has discouraged some companies who own industrial furnaces from volunteering their use to conservators.

All annealing methods present the problem of the changes in the metallurgical characteristics in the metal when heated to high temperatures.

The loss of information by the treatment of totally rusted marine cast iron at 800°C will not be great and there seems to be little objection to the use of the hydrogen reduction process at 800°C for this purpose. The reduction of rust on wrought iron is a different matter. The main problem is knowing whether the residual metal contains, either intentionally or unintentionally, enough carbon to give useful information to the archaeometallurgist. If carbon is absent then treatment at 380°C is acceptable although some change will occur. The slag inclusions will suffer very little microscopic change and no macroscopic change. To ensure the removal of chlorides at 380°C the treatment time must exceed 60 hours (Tylecote and Black 1980:95).

As long as the conservator follows the recommendations cited above, the major objections to annealing in a reducing atmosphere of hydrogen are overcome. The main limiting factor is the high cost of this type of furnace and the inherent safety concerns and potential danger of heating hydrogen to very high temperatures. The treatment does result in stable, chloride-free artifacts.

HYDROGEN PLASMA REDUCTION

Hydrogen plasma reduction is a relatively new technique (see Patscheider and Vepek 1986). Iron artifacts, as well as those of copper and silver, are conserved by placing them in a quartz discharge tube surrounded by hydrogen gas under low pressure. The hydrogen gas is ionized into plasma by the introduction of high-frequency radio waves. Iron is in the center of the hydrogen plasma, and the magnetite and ferric oxide on the surface of the iron are converted to metallic iron. Because the treatment is carried out at a temperature of less than 400°C, there is no change in the metallic structure of the iron.

Although preliminary results have been encouraging, the primary disadvantage of this conservation technique is the high cost of the equipment and the small size of the artifacts that can be treated in all but the most expensive units.

WATER DIFFUSION

In any archaeological excavation of a shipwreck, there will always be some artifacts that cannot be conserved by any the methods discussed above. Little or no metal may remain in the artifact; even if metal is present, any electrochemical or chemical treatment may considerably alter the form of the object. If the methods outlined above are not feasible for conserving a particular object, the conservator has three additional options: the chlorides can be removed by a process referred to as water diffusion; the article can be embedded in plastic; or the artifact can be cast (see the file on Casting and Molding).

The only way that an iron artifact recovered from the sea can be stabilized is to remove the chlorides from the metal. This is most easily accomplished by electrolytic reduction techniques, but if the artifact is very badly oxidized, and its overall form and dimensions are to remain intact, the only alternative is to remove the soluble chlorides by the much slower process of water diffusion (Oddy and Hughes 1970). The name accurately describes the process. The artifact is placed into a container filled with water, and the water is changed frequently, as the soluble chlorides diffuse out of the metal into the solution. The water should be changed weekly or as often as necessary as determined by a qualitative or quantitative chloride test. Because water diffusion does not remove chlorides from an artifact within in any accepted time frame, it should only be considered when attempting to conserve an artifact so badly corroded that there is the possibility that it may be destroyed if it were cleaned by electrolytic reduction or by the alkaline sulfite treatment discussed above.

Since water diffusion requires a lenghty treatment process, the water must be inhibited in order to prevent the metal from rusting. Alkaline chemicals, such as a 5 percent sodium sesquicarbonate, 5 percent sodium carbonate, or 2 percent sodium hydroxide solution will inhibit rust formation on the surface of the artifact; only the water, however, will remove the soluble chlorides. Chloride-contaminated iron should be immersed in successive baths of tap water until the chloride level of the bath approximates that of the tap water; the artifact should then be placed in successive baths of de-ionized water until the chloride count in the bath has leveled off and ceases to rise when it is changed. Uninhibited de-ionized water should not be used in water diffusion because it is very corrosive.

Organ (1955) suggests that alternating hot and cold temperatures will speed up chloride removal by alternately expanding and contracting the capillaries in the metal and the corrosion layer, causing a flushing action that will expel and draw in fresh water. From a standpoint of coefficients of thermal expansion, however, the alternate heating and cooling most likely changes the diffusion gradient of the solution rather than significantly changing the size of the metal capillaries. In some instances, this will decrease the time required to remove the soluble chlorides, but Oddy and Hughes (1970:187) found that there was no significant difference between the time required to wash similar objects of both iron and bronze at room temperature and at ca. 50°C. The alternate heating/cooling cycle may facilitate the removal of chlorides, however, when significant levels of chloride are present, and months to years are required to remove them. After the soluble chlorides have been eliminated, the artifacts must be carried through the same final steps as iron treated by other methods.

FINAL CONSERVATION STEPS

RINSE AFTER TREATMENT

Following any conservation treatment -- electrochemical, electrolytic, chemical, or water diffusion -- it is necessary to remove insoluble oxide sludge, metallic powder, residual chlorides, and chemical residue through intensive rinsing (Plenderleith and Werner 1971:20). In electrolytic reduction or water diffusion, the artifact is removed after establishing that the chloride count in the solution has leveled off and ceases to rise when it is changed. The artifact is then rinsed thoroughly in several changes of alternate boiling and cold de-ionized water to remove any residual electrolyte and chlorides. Boiling water rinses oxidize the surface of the metal to a flat, pleasing black color. Iron artifacts may rust in de-ionized water during prolonged periods of rinsing; this can be prevented by adding gluconic acid, sodium gluconate, or sodium glucoheptanate to the rinse water. The gluconates act as rust inhibitors during the rinsing process and continue to serve in this capacity during solvent dehydration, heat drying, or air drying. Pearson (1972a:13-14) prevented Captain Cook's cannons from rusting during the rinse process by rinsing with a potassium chromate solution (1000 ppm chromate) with a pH not lower than 8.5. The strict disposal requirements for chromate solutions, however, prevent their large-scale use. Neither the gluconates nor chromate solutions are used widely, and satisfactory results are achieved without them. Nonetheless, conservators should be aware of the protection that they can provide, when and if their use is required.

The artifact should stand in the last vat of rinse water for a minimum of 24 hours. A sample of the bath water is taken and acidified with nitric acid and tested with 0.2 N silver nitrate for the presence of chloride. The silver nitrate test is suggested because it is quick, qualitative, and quite sensitive to minuscule amounts of chlorides. If the test is positive the artifact is returned either to electrolysis or further rinsing. If the test is negative, the artifact is ready to be dried and sealed with microcrystalline wax.

Specimens treated by water diffusion are put through a similar rinsing process. Since many of the objects treated by water diffusion are, however, very fragile, they may not be able to withstand the mechanical action of boiling water. The rinse water, if heated, should be kept below the boiling point for such artifacts, and sodium glucoheptanate should be added to the rinse water as a rust inhibitor.

QUALITATIVE TEST FOR CHLORIDES

The presence or absence of chlorides is determined by the silver nitrate test (Plenderleith and Werner 1971:201). The artifact is placed in distilled or de-ionized water for a few hours or overnight. A 10- to 20-ml sample of the solution is placed in a test tube and acidified with a few drops of dilute nitric acid (ca. 10 percent). The solution is mixed and five drops of 0.2 N silver nitrate (17 g of $AgNO_3$/1 liter of H_2O) is added. The test tube is held against a black background with good side lighting. If any chlorides are present, a white opalescence will be apparent. Under ideal conditions, with clean glassware and uncontaminated reagents, the test provides a good qualitative indicator for the presence or absence of chlorides.

DRYING

After rinsing, the moisture absorbed by the artifact must be removed before any sealant, with the exception of certain waxes, which are heated above the boiling point of water, can be applied. When specimens can be immersed in any wax heated above the boiling point of water, drying is an optional step. Artifact drying can be accomplished by heat, vacuum desiccation, or dehydration in water-miscible alcohol or acetone. After treating iron, the metal surfaces are in a reactive state and quickly rust on exposure to air. In order to prevent the rapid formation of superficial rust, contact with air should be minimized until tannic acid or the final sealant or insulating coating is applied to the surface of the artifact. Some exposure to air is inevitable, and it is particularly troublesome when drying by heat (ovens or infra-red lamps) or vacuum desiccation. Infra-red lamps are not very effective on dense objects, and it is expensive to obtain ovens or vacuum chambers to accommodate very large specimens.

An alternative is to use a water-miscible solvent, ethanol, methanol, isopropanol, or acetone. Isopropanol is recommended because it is non-toxic, has a high flash point, and does not have an obnoxious odor. Ethanol and acetone are as effective, or even more effective, as isopropanol but are toxic and have lower flash points. Each of these solvents prevents the problems of rusting when exposed to air and can be used on objects of any size. Drying in an oxygen-free environment, such as that provided by alcohols, is ideal for objects with little metal remaining, since it will prevent the remaining metal from rusting and ferrous compounds from oxidizing to a ferric state. Both reactions will cause artifacts to expand and slough off the oxide layers. Alcohols also have the advantage of enhancing the removal of any remaining soluble chlorides and water in the specimens. In addition, all stains and undesirable features can be removed by brushing them while the objects are still in the alcohol. Artifacts also can be stored indefinitely in alcohol until it is convenient to process them.

When rinsing is complete, the artifact is removed while the water is hot and wiped with rags. This allows most of the water to evaporate. The artifact is immersed in alcohol that has been previously used for drying wet objects in order to remove the bulk of the remaining surface water. It is then submerged in water-free isopropanol to dehydrate for a minimum of 24 hours. By taking these precautions, the water content of the isopropanol bath will remain low and it can be thus used repeatedly. When the water content of the isopropanol becomes sufficiently high, it is used for the preliminary rinse, and fresh alcohol is used for the dehydration bath. This efficiency procedure is important during periods of material shortages and high prices.

SEALANT AND CONSOLIDATION

It is imperative that the surfaces of treated marine-recovered iron artifacts be covered with a protective coating to insulate the metal from the effects of moisture, chemically active vapors, and gases. The right sealant or coating should be chosen to provide a protective moisture barrier and prevent corrosion. In general, the sealant selected should be (1) impervious to water vapors and gases, (2) natural-looking, so that it does not detract from the appearance of the artifact, (3) reversible, and (4) transparent or translucent, so any corrosion of the metal surface can be quickly detected.

Various monomers, acrylates, acetates, epoxies, paints, oils, lacquers, and other sealants have been used in the past, but few have withstood the test of time. Many of these sealants craze, peel, are irreversible, or have a high degree of permeability to water vapor. No single sealant is completely successful and all have some disadvantages, but microcrystalline waxes best satisfy the requirements of conservation. They have a high melting point and are relatively hard; in addition, they are the least permeable to water vapor of any of the sealants commonly used (Rudniewski and Tworek 1963:212). Besides sealing the surface of the artifact from the atmosphere and moisture, they provide considerable stability and strength to the object and are excellent for consolidating those which are fragile. In contrast, some laboratories (North 1987:230) use microcrystaline wax as the final coat only on cast-iron artifacts; its use on wrought iron that is to be stored and displayed indoors is also recommended.

Cosmoloid 80H is the most often-recommended microcrystalline wax mentioned in the conservation literature, but it is not available in the United States. Gulf 75 Micro-wax and Witco180M microcrystalline wax melt at approximately 180°F and make satisfactory substitutes. In some instances it may be advisable to dehydrate the artifact in alcohol before it is placed in a vat of microcrystalline wax; however, when microcrystalline wax is used as the final sealant, it is possible to eliminate the drying process for a great many iron artifacts. Artifacts can be taken directly out of the rinse water and placed in a vat of wax that is heated to 175°C, well above the boiling point of water. The artifact must be kept in the wax long enough and at a high enough temperature to completely vaporize the water and until bubbles stop evolving from the artifact. This may require several days for large artifacts. After complete penetration, the wax is cooled to 93-107°C, the artifact is removed, and the excess wax is promptly wiped off with rags. Since the water boils out of the artifact, this technique should not be used on fragile objects or objects with a loose oxide layer; fragile specimens should be dried by one of the methods mentioned above. With this exception, combining the water removal and the sealant steps remains a very satisfactory approach. Time and expense are saved, and good results are achieved.

The temperature at which the artifact is removed determines the thickness of the wax coating. Too low a temperature results in an obvious layer of wax, while at too high a temperature, all of the wax will run off the surface of the object. If any excess wax should remain after cooling, it can be removed with a torch, a hot air gun, or by scraping lightly with a knife. Scraping is the simplest method and leaves the least obvious scars on the wax film. Additional wax or wax with graphite added to it as a pigment can be used to cover surface defects in the metal and enhance the appearance of badly corroded objects.

In many laboratories, facilities are not available to impregnate large objects, such as cannons and anchors, with microcrystalline wax, so other coatings must be used. There have been experiments with chromate paints, lacquers, clear epoxies, linseed oil, and polyurethane. In general, all but polyurethane are ineffective. Over a period of months they craze, peel, and become permeable to moisture. The opaque coatings hide the surface of the artifact from view, preventing one from observing the corrosion occurring under the coating. In addition, the surface finish of the epoxy is too glossy and is irreversible, causing further damage to a few specimens which have to be re-treated.

Polyurethane-based paints or coatings are thermoplastic polymers that have many favorable attributes for serving as a protective coating on treated iron objects. They form clear, fast-drying, tough, flexible coatings with excellent adhesion and are highly resistant to moisture, salt water, acids, alkalis, abrasions, and weathering. The coatings can be removed with aromatic and chlorinated solvents, such as toluene or ethylene dichloride. Polyurethane comes in gloss and stain finishes. The gloss finish has more resin and is, therefore, more durable. It is recommended for outdoor use. The satin finish has less resin and has silica added to give a more acceptable flat finish, but it is less durable than the gloss finish and is generally recommended for interior use. By using an undercoat of gloss and a second coat of satin finish and by adding graphite to one or both coats, a very acceptable, translucent finish can be obtained that does not detract from the underlying surface color of the specimen being coated.

The use of polyurethane coatings in the manner described above or by themselves can be recommended for maximum protection of large iron artifacts to be displayed outside or in areas of high humidity and salt vapor in the air (North and Pearson 1975:177; Hamilton 1976:55; North 1987:230). For example, a large 18-lb. Civil War cast-iron siege cannon recovered from Galveston Island on the Texas Gulf coast needed to be sealed after treatment, but the cannon was larger than any of the wax vats in the laboratory. The surfaces of the cannon were painted with a 20 percent tannin solution to form a corrosion-resistant ferric tannate film. The painted surfaces were then left to air oxidize for two days. The cannon was then painted with a coat of clear gloss polyurethane, allowed to dry, and then painted with a coat of satin polyurethane. Graphite was added to both the gloss and the satin polyurethane to completely dull any glossiness to the surface finish. The results were very satisfactory.

Success has also been had with using Rustoleum, a fish-oil-based paint, but it has only a 10-year durability span, as opposed to 20 years for polyurethane (North 1987:230). For sealing wrought-iron artifacts that are to be displayed indoors, North (1987:231) recommends using clear- drying zinc phosphate-based anti-corrosion primer as the first coat, followed by up to six applications of high-durability, clear acrylic lacquer, and finished off with a final coat of Krylon Matte Spray Finish (North and Pearson 1975:177, North 1987:230). For large objects that are to be displayed outdoors, Townsend (1972a:253) suggests using a mixture of three parts zinc silicate powder to two parts water. This mixture forms a light beige paint that oxidizes to a light nautical gray. The coating, being anodic, provides cathodic protection of the iron object and is said to be highly resistant to salt spray, rain, sunshine, and temperature fluctuations. Large anchors and other implements painted with zinc silicate have been displayed outdoors in North Carolina without damage for many years.

With the exception of microcrystaline wax, which is easily removed by placing the artifact in a vat of boiling water, all other sealants present some problems in terms of reversibility. Polyurethane must be sandblasted off, and Rustoleum can only be removed with sodium hydroxide. For ease of application, resistance to water vapor, transparency, and the ability to strengthen the surface of the artifact, microcrystaline wax is the best sealant for both cast-iron and wrought-iron objects that are stored and displayed indoors. If an object is to be displayed outdoors, or if it cannot be treated with microcrystaline wax, polyurethane-based paints are recommended.

Artifacts that are so badly corroded that they cannot be treated, and compound objects with metal and organic parts requiring treatment but which cannot be separated, can be embedded in clear plastic blocks. Smith and Ellis (1961:32-35) describe the process of embedding a wrought-iron swivel gun and a Spanish battle sword in Selectron 5000 resins. This technique is drastic, with no hope of ever extracting the artifacts from the blocks, but it remains a possibility for very select, problem artifacts.

STORAGE AND PERIODIC INSPECTION

The conservation of artifacts should produce objects that are chemically stable with an aesthetically acceptable appearance. Treatment should be reversible in the event that the object should require additional preservation. Re-treatment is generally prevented only if the artifact is stored or displayed under optimum conditions. Atmospheric pollutants, sulfur dioxide, hydrogen sulfide, sodium chloride, dust, and soot are detrimental, ubiquitous, and difficult to control even inside a reasonably sealed building. The relative humidity in which an artifact is stored is a particularly critical factor in its stability. The moisture level at which corrosion appreciably accelerates is called the critical humidity and is considered to be 60 percent for iron and steel (Cornet 1970:443). If iron still contains chlorides, a humidity as low as 50 percent may have to be maintained. Subsequent corrosion sometime in the future is inevitable with higher relative humidities. All the potential corrosive factors should be taken into consideration when storage facilities are being planned.

Since metal artifacts can eventually become chemically unstable from a myriad of causes and may need additional treatment, periodic inspections and evaluations of the artifacts are necessary. A conserved artifact of iron from a marine site remains a piece of metal, just as susceptible, and in fact more susceptible, to continued corrosion as any other piece of iron. Proper conservation does not ensure that an object will be preserved in perpetuity. At our present stage of knowledge, perhaps it is most realistic to say that the objective of artifact conservation is to delay eventual re-treatment for as long as possible and to make any necessary treatment simple and brief. There remains a lot of room for improvements in the conservation of iron. Still, at the present state, there are a number of procedures that successfully contend with the majority of problems encountered.

SUMMARY

The majority of iron artifacts recovered from marine sites is treated by electrolytic reduction. This treatment consistently produces stable artifacts with a minimum of inexpensive equipment and chemicals, as well as a minimum of 'hands-on' treatment time. The alkaline sulfite treatment is commonly used for artifacts with badly corroded surfaces that could possibly flake off during electrolysis. Less common, but still used by a few laboratories, is hydrogen reduction of iron, but the cost of the equipment prohibits it more general use; this also applies to hydrogen plasma reduction techniques. Although not a consistently reliable treatment, various forms of intensive rinsing are sometimes employed on problem artifacts, and usually in conjunction with other treatments.

To carry out the above treatments, adequate space and equipment are required. Essential equipment includes various regulated DC power supplies, plastic and metal vats, anode material, wire, clips, fume hoods, pneumatic chisels, air compressors, a fork-lift truck if heavy artifacts are to be treated, a source for heating the rinses and wax, a pH meter, and an X-ray machine. All are easily secured at reasonable expense, and much of the equipment can be secured through federal surplus.

Non-Ferrous Metal Conservation

IN THIS FILE:

Storage of Non-Ferrous Metals

It is not uncommon to find non-ferrous metals, such as copper, silver, lead, tin, gold, and their alloys, in archaeological sites. These metals have been used in the manufacture of art objects, coins, jewelry, and various utilitarian items such as fasteners, navigational instruments, cooking vessels, and small tools. They are more noble than iron and survive adverse environments in better condition than do iron specimens. Nevertheless, the corrosion problems of each metal varies in different environments. Only those techniques applicable to the conservation of sea-recovered metals are considered here.

Sea-recovered materials are often encapsulated by encrustation. When encrustation is present on non-ferrous metals, it is generally much thinner than encrustation found on iron. Artifacts manufactured from these metals, however, are often found encapsulated in the encrustation that surrounds iron artifacts. Prior to any treatment of the metal artifacts, preliminary conservation steps must be completed. These include (1) initial documentation, (2) storage, (3) encrustation removal, and (4) artifact evaluation. The treatment of each metal group, i.e., cupreous metals; silver and its alloys; tin, lead, and their alloys; and gold and its alloys, is discussed in detail.

STORAGE OF NON-FERROUS METALS

A variety of metal artifacts made of different metals are often found encrusted together in marine sites. In these instances, it is necessary to store the material in such a way that the most susceptible metal is afforded protection, and little to no damage is done to the other metals and non-metals found association with it. Since iron artifacts are the most commonly found metal, the storage conditions discussed under iron are most often used. However, gold, silver, pewter, brass, bronze, copper, and lead artifacts, as well as ceramics, stone, glass, bone, cloth, seeds, and wood, are often all associated in various combinations within a single encrustation. In some cases, the best storage for the encrustation may be simply in fresh water. Once the different objects are removed from the encrustation, they are placed in the most appropriate storage environment for each material.While iron artifacts, as discussed earlier, should at a minimum be stored in an alkaline solution protected from light, this solution is not necessary or even recommended for artifacts made of other metals.

COPPER

Copper is corroded by oxidizing solutions and strong alkaline solutions. In neutral or slightly alkaline solutions, the copper is passivated and corrosion is halted by the formation of an oxide film on the surface of the artifact. A 5 percent solution of sodium sesquicarbonate or sodium carbonate is recommended for storing copper.

SILVER

Silver is stable in aqueous solutions of any pH value and in the atmosphere, as long as these environments are free from oxidizing substances. Since chlorides do not affect silver or lead, they do not need to be placed in an aqueous solution and can be stored dry once the encrustation has been removed. Prior to the removal of adhering encrustation, however, it is best to house such objects in an appropriate solution to keep the encrustation from becoming harder and difficult to remove. Silver objects can be stored safely along with iron artifacts in either a 5 percent sodium sesquicarbonate or sodium carbonate solution. When silver that is encrusted to an iron object is stored in a chromate solution, a film of brown Ag_2O will form. This film can be removed during the conservation of the object; chromate solutions, however, are not recommended for the storage of singular silver artifacts.

LEAD, TIN, PEWTER

Lead, tin, and pewter are more easily stored. All are often stored dry; when the encrustation on metals is allowed to dry out, however, it becomes much harder to remove. For this reason, lead, tin, and pewter are stored in aqueous solutions. Lead is corroded by aqueous solutions free from passivating substances, especially soft water, de-ionized water, or distilled water, and should never be stored in them. However, since lead is corrosion-resistant in hard, passivating bicarbonate water, and both tin and pewter are passivated in slightly alkaline solutions, all can be stored in tap water, with the pH adjusted to 8-10 by the addition of sodium sesquicarbonate. Lead and pewter can also be stored in sodium carbonate with a pH of 11.5. Tin will resist corrosion in slightly alkaline solutions that are free from oxidizing agents but will react adversely to strongly alkaline solutions. Any alkaline solution with a pH of above 10 is potentially dangerous to tin. Lead, tin, and their alloys, such as pewter, should not be stored in a chromate solution because of the oxidizing effect of chromate, which will form an orange chromate film on artifact surfaces that is difficult to remove. In the absence of passivating substances, an oxidizing agent, such as chromate, can damage lead, tin, and pewter artifacts.

Cupreous Metal (Copper, Bronze, Brass) Conservation

CUPREOUS METAL CORROSION

The term 'cupreous' is used to designate all metals that consist of copper or alloys that are predominantly copper, such as bronze (an alloy of copper and tin) and brass (an alloy of copper, zinc, and often lead). The term does not imply a valence state as does cupric-divalent copper or cuprous-monovalent copper. The cupreous metals are relatively noble metals that frequently survive adverse conditions, including long submersions in salt water that will often completely oxidize iron. Cupreous metals react with the environment to form similar alteration products, such as cuprous chloride (CuCl), cupric chloride ($CuCl_2$), cuprous oxide (Cu_2O), and the aesthetically pleasing green- and blue-colored cupric carbonates, malachite [$Cu_2(OH)_2CO_3$], and azurite [$Cu_3(OH)_2(CO_3)_2$] (Gettens 1964:550-557). In a marine environment, the two most commonly encountered copper corrosion products are cuprous chloride and cuprous sulfide. The mineral alterations in copper alloys, however, can be more complex than those of pure copper.

The first step in the electrochemical corrosion of copper and copper alloys is the production of cuprous ions. These, in turn, combine with the chloride in the sea water to form cuprous chloride as a major component of the corrosion layer:

$$Cu - e >> Cu^+$$

$$Cu^+ + Cl^- >> CuCl$$

Cuprous chlorides are very unstable mineral compounds. When cupreous objects that contain cuprous chlorides are recovered and exposed to air, they inevitably continue to corrode chemically by a process in which cuprous chlorides in the presence of moisture and oxygen are hydrolyzed to form hydrochloric acid and basic cupric chloride (Oddy and Hughes 1970:188):

$$4CuCl + 4H_2O + O_2 >> CuCl_2 \cdot 3Cu(OH)_2 + 2HCl$$

The hydrochloric acid in turn attacks the uncorroded metal to form more cuprous chloride:

$$2Cu + 2HCl >> 2CuCl + H_2$$

The reactions continue until no metal remains. This chemical corrosion process is commonly referred to as 'bronze disease.' Any conservation of chloride-contaminated cupreous objects requires that the chemical action of the chlorides be inhibited either by removing the cuprous chlorides or converting them to harmless cuprous oxide. If the chemical action of the chlorides is not inhibited, cupreous objects will self-destruct over time.

Copper objects in sea water are also converted to cuprous and cupric sulfide (Cu_2S and CuS) by the action of sulfate-reducing bacteria (Gettens 1964:555-556; North and MacLeod 1987:82). In anaerobic environments, the copper sulfide products are usually in the lowest oxidation state, as are the ferrous sulfides and silver sulfides. After recovery and exposure to oxygen, the cuprous sulfides undergo subsequent oxidation to a higher oxidation state, i.e., cupric sulfide. The whole chemical reaction generally proceeds along the same lines as those described earlier for iron.

Upon removal from a marine encrustation, copper and cupreous artifacts are inevitably covered with varying thicknesses of a black powdery layer of copper sulfide that imparts an unpleasing appearance. Occasionally, the corrosion process will pit the surface of the artifact, but this is more common on cupreous alloys where tin or zinc is corroded preferentially. The stable copper sulfide layer does not adversely affect the object after recovery from the sea as do copper chlorides; copper sulfides only discolor the copper, imparting an unnatural appearance to the metal, and are easily removed with commercial cleaning solvents, formic acid, or citric acid. (See North and MacLeod [1987] for a detailed discussion of the corrosion of copper, bronze, and brass in a marine environment.)

CONSERVATION OF CUPREOUS METALS

Copper and alloys in which copper predominates are all generally conserved by the same methods. Particular care needs to be taken only when there is a high percentage of lead or tin in an alloy; lead and tin are amphoteric metals and will dissolve in alkaline solutions. Although there are a considerable number of chemical treatments for the conservation of copper, bronze, and brass, most are not satisfactory for cupreous metals recovered from marine sites. Three effective chemical treatments are discussed below. Consult the bibliography for further information.

In some instances, it is necessary to mechanically remove gross encrustation and corrosion products from the artifact to reveal the preserved surface of the metal. This step is facilitated for sea-recovered cupreous objects because the marine encrustation will form a cleavage line between the original metallic surface and the encrustation. When the artifacts are removed from gross encrustation, superficial encrustation is often deliberately left adhering to the surface of the artifact due to the fragility of the artifact or to avoid marring its surface. Careful mechanical cleaning and rinsing in water may be all that is required to remove this remaining superficial encrustation. In other cases, all adhering encrustation can be removed by soaking the object in 5-10 percent citric acid with 1-4 percent thiourea added as an inhibitor to prevent metal etching (Plenderleith and Torraca 1968:246; Pearson 1974:301; North 1987:233). Citric acid should be used cautiously, as it can dissolve cupric and cuprous compounds within the artifact. The artifact is completely submerged in the solution until the encrustation is removed. This may require an hour to several days, during which time the solution should be stirred to keep the acid concentration evenly distributed.

When a specimen is very thin, fragile, has fine detail, or is nearly or completely mineralized, any acid treatment may be too severe. In these cases, the artifact can be soaked in a 5-15 percent solution of sodium hexametaphosphate (Plenderleith and Werner 1971:255) to convert the insoluble calcium and magnesium salts in the encrustation to soluble salts, which can be subsequently washed away.

Following any necessary preliminary treatment, the conservation of chloride-contaminated cupreous objects requires that the adverse chemical action of the chloride be prevented. This can be accomplished by:

1. removing the cuprous chloride
2. converting the cuprous chloride to harmless cuprous oxide
3. sealing the cuprous chloride in the specimen from the atmosphere

The possible treatment alternatives include:

1. galvanic cleaning
2. electrolytic reduction cleaning
3. alkaline dithionite treatment
4. chemical cleaning
    a. sodium sesquicarbonate
    b. sodium carbonate
    c. benzotriazole

The first three alternatives can remove cuprous chlorides and reduce some of the corrosion products back to a metallic state; however, they are best used only on objects with a metallic core. If carefully applied, these treatments will stabilize the object and maintain a form approximating its original, uncorroded appearance. If misapplied, they can strip the corrosion layer down to the remaining metal core. Jedrzejewska (1963:135) draws attention to the fact that stripping, especially by electrolysis, may destroy significant archaeological data such as tool marks, engraved lines, and decorative elements, as well as alter the original shape of the object. For these reasons, the corrosion layers of any metal artifact should never be indiscriminately removed. The treatment should strive to preserve corrosion layers in situ through very controlled electrolytic reduction or alkaline dithionite treatment. The chemical techniques described do not strip the corrosion layer. Rinsing in a sodium sesquicarbonate solution removes the cuprous chlorides from the artifact, while benzotriazole and silver oxide seal the cuprous chlorides from the atmosphere. The chemical treatments are applicable to substantial objects as well as to completely mineralized pieces.

GALVANIC CLEANING

This procedure is carried out in exactly the same manner as described for iron. It is generally regarded as an obsolete technique, except under certain circumstances already mentioned in the section on the galvanic cleaning of iron.

ELECTROLYTIC REDUCTION CLEANING

Electrolytic reduction of cupreous metals is also carried out in the same manner as described for iron. Either 2 percent sodium hydroxide or 5 percemt sodium carbonate can be used for the electrolyte. The latter is used most often, although acceptable results have also been achieved using 5 percent formic acid as the electrolyte. A mild steel anode can be used, but Type 316 stainless steel or platinized titanium is required if formic acid is used as the electrolyte. The same electrolytic setups described for iron or for silver (below) are used.

Precise data concerning optimum current densities for cupreous artefacts are not available. Plenderleith and Werner (1971:198) state that the current density should not be allowed to fall below 0.02 amp/cm^2 in order to prevent the deposition of a salmon-pink film of copper on the objects. Keel (1963:24) states that a current density above 0.01 amp/cm^2 will damage cupreous objects. Along these same lines, Pearson (1974:301-302) correctly observes that care must be taken when electrolytically cleaning marine-recovered mineralized bronze in order to prevent damage to the artifact surface by the evolution of hydrogen gas. Current densities, both within and in excess of the given ranges above, are commonly applied to different cupreous objects. North (1987:238) recommends using the hydrogen evolution voltage techniques described for the treatment of iron. In general, the same procedures regarding current density that are described for the treatment of iron apply to the treatment of cupreous artifacts. The main variations in treatment involve the fact that the duration of electrolysis for chloride- contaminated cupreous objects is significantly shorter than that for comparable iron objects. Small cupreous artifacts, such as coins, require only a couple of hours in electrolysis, while larger cupreous specimens, such as cannons, may require several months.

ALKALINE DITHIONITE

This treatment was developed for consolidating mineralized silver. Since then, it has also been found to be effective on cupreous objects. A complete description of the treatment can be found in the file on silver. Alkaline dithionite treatment will destroy any patina on the surface of the cupreous object, but it effectively removes the bulk of the chlorides in the shortest period of time; further, it reduces some of the copper corrosion products back to metal.

CHEMICAL TREATMENTS

Many cupreous artifacts with chloride contamination, such as well-patinated bronzes with bronze disease, extensively mineralized bronzes with or without cuprous chlorides, bronzes without a substantial metallic core, and bronzes with mineralized decorative features, cannot be treated by either of the reduction techniques. There are three different chemical treatments available that are used to stabilize the artifacts while leaving the corrosion layers intact: treatment with sodium sesquicarbonate, with sodium carbonate, or with benzotriazole.

Sodium Sesquicarbonate

The cuprous chloride components of copper and its alloys are insoluble and cannot be removed by washing in water alone. When bronzes or other alloys of copper are placed in a 5 percent solution of sodium sesquicarbonate, the hydroxyl ions of the alkaline solution react chemically with the insoluble cuprous chlorides to form cuprous oxide and neutralize any hydrochloric acid by-product formed by hydrolysis to produce soluble sodium chlorides (Organ 1963b:100; Oddy and Hughes 1970; Plenderleith and Werner 1971:252-253). The chlorides are removed each time the solution is changed. Successive rinses continue until the chlorides are removed. The object is then rinsed in several baths of de-ionized water until the pH of the last bath is neutral.

In practice, the superficial corrosion products are mechanically removed from the metal objects prior to putting objects in successive baths of 5 percent sodium sesquicarbonate. For the initial baths, the sodium sesquicarbonate is mixed with tap water; de-ionized water is used for subsequent baths. If the chloride contamination is extensive, baths prepared with tap water can be used until the chloride level in the solution approximates the chloride level of standard tap water. De-ionized water is then substituted. This procedure is very economical when processing objects that require months of treatment.

Initially, the baths are changed weekly; as the duration of treatment progresses, the interval between bath changes is extended. Monitoring the chloride level by the quantitative mercuric nitrate test enables the conservator to determine precisely how often to change the solution. In lieu of a quantitative chloride test, the qualitative silver nitrate test can be used to determine when the solution is free of chlorides. The cleaning process is slow and may require months and, in some cases, even years.

The sodium sesquicarbonate treatment is often used by conservators because, unlike other cleaning treatments, it does not remove the green patina on the surface of cupreous objects. This treatment may encourage the formation of blue-green malachite deposits on the surface of the objects, which will intensify the color of the patina. If malachite deposit formations occur during treatment, the object should be removed from the solution and the deposit brushed off. On some bronze pieces, this treatment will result in a blackening of the surface, which obscures the original green patina and is difficult to remove. This blackening is attributed to the formation of black copper oxide and appears to be an inherent characteristic in some cupreous alloys.

Sodium Carbonate Rinses

The sodium sesquicarbonate treatment outlined above has been the standard treatment for fragile cupreous artifacts with chloride contamination and for artifacts that have a patina that is desirable to preserve. In practice, however, conservators find that the treatment often enhances the patina, making it much bluer in appearance. In other examples, it has considerably darkened or blackened the patina.

With regard to the sodium sesquicarbonate treatment, Weisser (1987:106) states:

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

Weisser (1987:108) concludes:

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

has not been proven.

Weisser suggests that if previous treatments with BTA have not been successful, the objects can be treated with 5 percent sodium carbonate in distilled water. The sodium carbonate removes the cuprous chlorides and neutralizes the hydrochloric acid in the pits. Sodium carbonate, unlike sodium sesquicarbonate, which is a double carbonate and acts as a complexing agent with copper, reacts relatively slowly with copper metal. Still, in come cases, slight alterations in the color of the patina can occur.

Benzotriazole

The use of benzotriazole (BTA) has become a standard element in the conservation of cupreous metals. BTA follows any stabilization process and precedes any final sealant. In some cases, it can be a single treatment unto itself. When marine cupreous objects are conserved, however, BTA is usually used in addition to some other treatment, such as electrolytic reduction or alkaline rinses, which remove the bulk of the chlorides. For artifacts from a fresh water site, it may be the only treatment required.

Treatment with BTA does not remove the cuprous chloride from the artifact; rather, it forms a barrier between the cuprous chloride and moisture of the atmosphere. In this method of cleaning (Madsen 1967; Plenderleith and Werner 1971:254), the benzotriazole forms an insoluble, complex compound with cupric ions. The precipitation of this insoluble complex over the cuprous chloride forms a barrier against any moisture that could activate the cuprous chloride and cause bronze disease. Tests at the British Museum (Plenderleith and Werner 1971:254) indicate that if active bronze disease is present, all attempts to stabilize the object with BTA may fail due to the widespread distribution of cuprous chloride in the corrosion layers.

The treatment consists of immersing an object in a solution of 1-3 percent BTA dissolved in ethanol or water. In general, the best results are achieved if the specimen is impregnated with the solution under a vacuum for 24 hours. If the artifact is left in the solution for at least 24 hours, 1 percent BTA mixed with de-ionized water works as well as more concentrated solutions. For shorter treatments, 3 percent BTA mixed in either water or ethanol in recommended. In some cases, ethanol is preferred when the BTA treatment is of short duration. The main advantage of using ethanol in the solution is that it penetrates cracks and crevices better than does water. After the artifact is removed from the solution, it should be wiped off with a rag saturated in ethanol to remove excess BTA. The artifact then is exposed to the air. If any fresh corrosion appears, the process is repeated until no adverse reaction occurs. (See Green 1975; Hamilton 1976; Sease 1978; Walker 1979; Merk 1981 for additional information.)

It must be emphasized that the BTA treatment does not remove the cuprous chloride from the artifact. It merely forms a barrier between the cuprous chloride and the moisture in the atmosphere. Therefore, for artifacts heavily contaminated with chloride, such as marine-recovered cupreous objects, BTA treatment should follow the sodium sesquicarbonate or sodium carbonate treatment to ensure long-term artifact stability. BTA is a suspected carcinogen, and contact with the skin should be avoided, and the powder should not be inhaled.

FINAL TREATMENT AND SEALANT

Following electrolytic or chemical cleaning, the objects are put through a series of hot rinses in de-ionized water until the pH of the last rinse bath is neutral. Because copper tarnishes in water, Pearson (1974:302) recommends washing the objects in several baths of denatured ethanol. If a water rinse is used, any tarnish can be removed with 5 percent formic acid or by polishing the area with a wet paste of sodium bicarbonate.

After rinsing, copper objects should polished to any degree desired and treated with BTA. The object is then dehydrated in acetone or a water-miscible alcohol and coated with clear acrylic lacquer or microcrystalline wax. The commercially available KrylonClear Acrylic Spray No. 1301 is recommended for ease of application, durability, and availability. For increased corrosion protection, Pearson (1974:302) recommends that 3 percent BTA can be added to the drying alcohol, as well as to the lacquer. Microcrystalline wax can be used, but in most cases, has no special advantage over acrylics.

SUMMARY

All the treatments discussed here are effective for the treatment of all artifacts from marine sites that contain cupreous metals. Of the conservation alternatives considered in this file, electrolytic reduction, alkaline dithionite treatment, and alkaline rinses are the only ones which actually remove the cuprous chlorides. For this reason, they promise the most enduring protection.

Electrolytic reduction cleaning of copper-alloyed objects, such as brass and bronze, is often avoided because it removes any aesthetically pleasing patina and may change the color by plating copper from the reduced corrosion compounds onto the surface of the alloyed metal. In the case of cupreous metal recovered from marine environments, however, the chemical stability provided by electrolysis often takes precedence over aesthetics. The history of success in applying electrolytic reduction techniques to cupreous artifacts clearly demonstrates that electrolysis is the quickest, most effective, and enduring means of processing copper, brass, or bronze objects from a salt water environment. This statement is especially true for larger objects, such as cannons.

The extremely long time required for sodium carbonate and sodium sesquicarbonate treatments discourages their use. Preliminary treatment of artifacts with sodium carbonate followed by benzotriazole treatment may provide satisfactory results, but more experiments are needed before a final judgement can be made. Alkaline dithionite treatments have also proven effective for conserving cupreous alloys.

Regardless of the preliminary treatment, an application of BTA should be an inherent step in the conservation of all cupreous metal artifacts. In most cases, if the artifact is effectively treated with any of the treatments discussed above, as well as with BTA, and then sealed and stored in the proper environment, it will remain stable.

Silver Conservation

SILVER CORROSION

Silver is a very noble metal and is often found in a native state combined with gold, tin, copper, and platinum. It is completely stable in aqueous solutions of any pH as long as oxidizing agents or complexing substances are not present. In addition, silver is not appreciably affected by dry or moist air that is free from ozone, halogens, ammonia, and sulfur compounds (Pourbaix 1966:393; Plenderleith and Werner 1971:239). Silver is particularly susceptible to the effects of the sulfide radical. This is best demonstrated by the formation of tarnish on silver objects that are exposed to sulfur in any form, particularly hydrogen sulfide and sulfur dioxide, which can convert to sulfuric acid.

In a marine environment, with its abundance of soluble sulfates and oxygen-consuming, decaying organic matter, sulfate-reducing bacteria utilizes available sulfates under anaerobic conditions to form hydrogen sulfides as a metabolic product. The hydrogen sulfide reacts with the silver to form silver sulfide. The overall reaction proceeds in the same process as described earlier for iron:

$$2Ag + H_2S >> Ag_2S + H_2$$

In anaerobic marine environments, silver sulfide (Ag_2S) is the most common mineral alteration compound of silver (North and MacLeod 1987:94). It is commonly reported from shipwrecks in the Caribbean and Australia and constitutes the most prevalent corrosion compound on silver objects from marine sites. Most marine-recovered silver artifacts have a thin sulfide surface layer, which has removed some surface detail, such as inscriptions, marks, and stamps. A large percentage of the artifacts, however, are completely converted to sulfide; others have only minimal metal remaining.

In aerobic seawater, the most commonly encountered corrosion product on silver and silver alloys is silver bromide (AgBr). Varying amounts of silver chloride (AgCl) and silver sulfide (Ag_2S) may also be present (North and MacLeod 1987:94). Silver chloride is generally not extensive on silver recovered from salt water. Gettens (1964:563) notes that silver coins recovered from salt water are sometimes superficially altered to this mineral. In sites where the conditions vary between aerobic and anaerobic, combinations of all the major silver corrosion products are likely to be present (North and MacLeod 1987:94-95). In the case of relatively pure silver objects, silver sulfide (Ag_2S) and silver chloride (AgCl) will predominate. In the case of base silver alloys with significant amounts of copper, the copper will corrode preferentially and form cuprous oxide, cupric carbonate, and cuprous chloride. In such cases, the silver alloy object should be treated as if it were copper.

Regardless of what silver corrosion products are formed, all are stable and do not take part in any further corrosive reaction with the remaining silver. In fact, the corrosion layers impart some degree of protection against further corrosion to the metal. They also often provide an aesthetically pleasing patina, which is often desirable and deliberately preserved. The only reason to treat silver is to remove disfiguring corrosion layers to reveal detail, for aesthetic reasons, to reduce mineral products back to a metallic state, and to remove the chlorides from the copper component part of base silver alloys.

Prior to conservation treatment, marine encrustation should be removed mechanically or, in some cases, by immersion in 10-30 percent formic acid solution. The conservation alternatives for cleaning silver and silver alloys are:

1. galvanic cleaning
2. electrolytic reduction
3. alkaline dithionite treatment
4. chemical cleaning
5. stabilization and consolidation.

GALVANIC CLEANING

Treating silver galvanically can be accomplished by using mossy zinc or aluminum in caustic soda, as described earlier for iron. Variations include using mossy zinc or aluminum granules with heated 30 percent formic acid (Plenderleith and Torraca 1968:241-246; Plenderleith and Werner 1971:197, 221). After treatment, the metal is rinsed thoroughly and then dehydrated in a water-miscible solvent and sealed with clear acrylic lacquer. Galvanic cleaning is effective, but there is no reason to recommend it over electrolytic reduction or alkaline dithionite treatments.

ELECTROLYTIC REDUCTION CLEANING

The electrolytic cleaning of silver takes advantage of the reduction action of electrolysis by removing the chloride and sulfide ions from silver chloride and silver sulfide. When a direct current is applied, the negatively charged chloride and sulfide ions migrate toward the positively charged anode. The chlorides may form as chlorine in the solution, and the sulfides oxidize to sulfates. Since the anions do not react with the inert anodes, they accumulate in the electrolyte and are discarded with it. During the process, the silver in the corrosion compounds is left in a metallic state.

Two methods of electrolytic reduction cleaning have been described in the conservation literature; the methods are referred to by Organ (1956) as normal reduction and consolidative reduction. Normal electrolytic reduction uses a fully rectified direct current (DC) power supply. Consolidative reduction employs a partially rectified (asymmetrical) alternating current (AC) power supply. Both techniques require that a metal core be present in the object. The Conservation Research Laboratory at Texas A&M University deals primarily with the normal reduction process in 5 percent formic acid, essentially as it is described in Plenderleith and Werner (1971:222). Both techniques are discussed below.

ELECTROLYTE

Two electrolytes, formic acid (HCOOH) and sodium hydroxide (NaOH), are used to clean silver. Although electrolyte concentrations of 5-30 percent HCOOH and 2-15 percent NaOH in de-ionized water have been proposed (Organ 1956:129; Plenderleith and Werner 1971:222; Pearson 1974:299), 5 percent HCOOH or 2 percent NaOH solutions are generally used as electrolytes for cleaning silver.

CURRENT DENSITY

Silver is easily reduced in electrolysis, regardless of the voltage or setup. North (1987:240) has observed that good results have been obtained during silver electrolysis with a wide range of applied voltage, and that the voltage applied during electrolysis does not appear to be critical. Since the number and size of items being treated is variable, Pearson (1974:299) adjusts the current to produce a cell voltage of approximately three volts. Plenderleith and Werner (1971:198) state that the current density should not be allowed to fall below 0.02 amps/cm^2 in order to prevent a film of salmon-pink copper from the corrosion materials, cathode screen, or copper leads from being deposited on the artifacts. In a series of experiments, Organ (1956:134) found that a low current density of 30-50 milliamperes/dm^2 (0.3-0.5 amps/cm^2) reduced more silver than higher current densities. Even the extremely low current density of 0.01 amp/cm^2 recommended by Organ (1956:129) provides satisfactory results. In most cases, a very low current density in the range proposed by Organ is best for maximum metal reduction during the electrolytic cleaning of silver.

ANODE MATERIAL

When treating silver, inert anodes, such as expanded platinized titanium and No. 316 stainless steel, are preferable. In some of the older conservation literature, carbon anodes are recommended, but they are no longer used, since they will invariably dissolve in the electrolyte. Platinized titanium can be used in both alkaline and acid electrolytes; it is especially recommended for use in acid electrolytes because it is almost totally inert and will not react with the electrolyte. The extremely high cost of platinized titanium, however, limits its widespread use. No. 316 stainless steel anodes are a good substitute for platinized titanium as long as formic acid is used as the electrolyte. Stainless steel anodes will oxidize after prolonged electrolysis in sodium hydroxide, resulting in the destruction of the anode and the deposition of iron on the silver. Mild steel anodes can be used in sodium hydroxide electrolytes; however, they should not be used in formic acid, as the mild steel will quickly break down and invariably result in iron deposition on the silver.

CATHODE CONTRACT

The electrolytic cell for silver cleaning can be set up using any of the methods described in the section on iron. As for iron, the setup in which artifacts are attached with clips to a cathode rod and sandwiched between two suspended anodes (Figure 10B.1D) is most commonly used by conservators. This electrolytic setup is useful for treating several artifacts at once and can be used for coins and other small pieces. When treating silver by electrolysis, however, the conservator may want to avoid attaching clips to small silver pieces in order to not scratch the surface. This is especially true for fragile coins and delicate pieces of jewelry. Direct, individual clip connections between the artifact and the cathode can be eliminated by using a cathode conductor screen made of copper mesh (see Figure 13.1). The specimen to be cleaned makes an electrical contact through the cathode screen, which is connected to the negative terminal. The areas of the screen not used for making contact between the cathode and the artifact should be covered with silicone rubber. The rubber keeps the objects separated and reduces the amount of exposed copper surface, which will minimize the problem of copper plating on the silver.

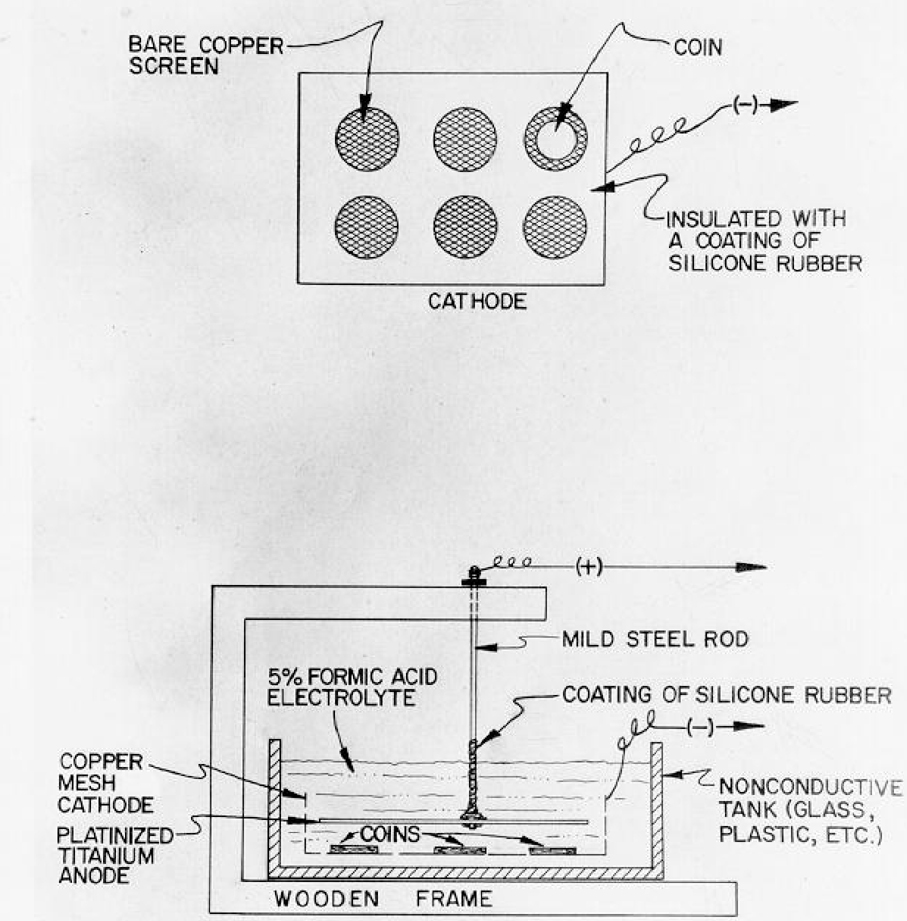


Figure 13.1. Electrolytic setup for cleaning silver coins or other small artifacts.

PROCEDURE

Silver artifacts are ready to be electrolytically cleaned after any encrustation has been removed with a small pneumatic chisel, and the artifacts have been thoroughly rinsed. Small specimens can be set up as shown in Figure 13.1. This setup is designed to clean coins, but it is applicable to any small silver or other non-ferrous metal objects. The setup uses a glass container, a copper mesh cathode conductor screen, a wooden support frame for the anode, and an expanded platinized titanium or stainless steel No. 316 anode attached to a mild steel rod. The rod is covered with silicone rubber to ensure that only the platinized titanium or stainless steel will act as the anode. After the artifacts are placed onto the cathode screen, the current is applied, and an electrolyte of 5 percent formic acid is added. In order to prevent any of the salts in the electrolyte from plating onto the surface of an artifact, the current should never be turned off while the artifacts are in the electrolyte. This will considerably reduce the problem of copper plating on the surface of the silver. While the current remains on, the objects should be periodically removed, brushed under de-ionized water, and dipped in a 0.2N solution of silver nitrate to remove any plated copper and superficial sulfides. The objects are then placed back upon the cathode screen with the opposite side facing up. Electrolysis is continued until each side of the artifact has a uniform appearance, and hydrogen is fully evolving from the surface. Small objects, such as coins, generally require only a few hours of electrolysis. Large silver objects or irregularly shaped pieces can be cleaned in the manner as described above, except that the object is connected to the negative terminal with a clip rather than via a cathode conductor screen.

REDUCTION IN FORMIC ACID

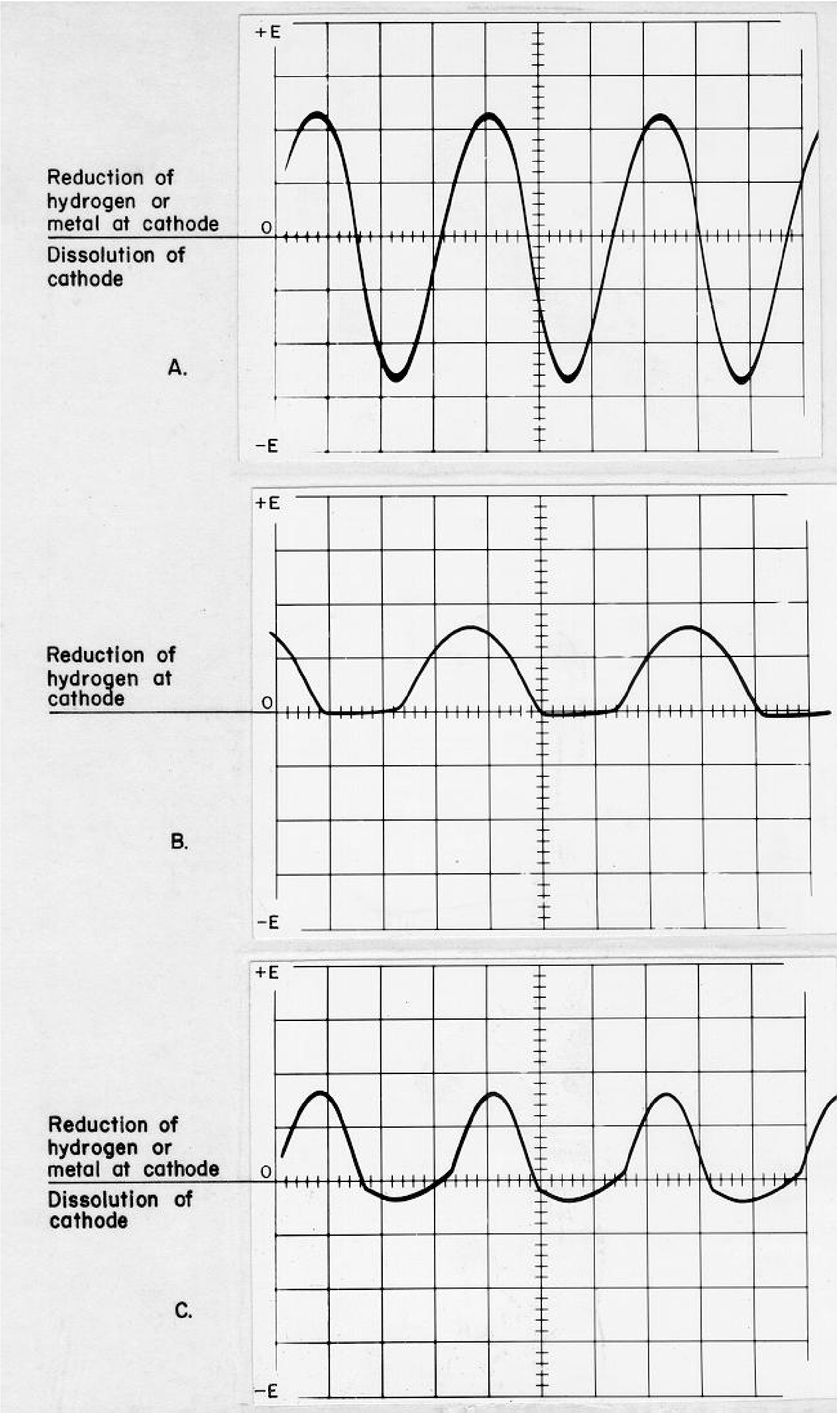
Organ (1956) conducted several detailed experiments on silver reduction techniques and alternatives. He recommends that standard electrolytic reduction be conducted in 30 percent aqueous formic acid because the electrolyte has no detrimental effect on silver and requires only minimum washing after electrolysis. (Tests performed at the Conservation Research Laboratory at Texas A&M University have indicated that a 5 percent formic acid electrolyte is adequate.) Organ observed that the reduced layer of silver ions and corrosion products external to the original surface delaminates and reveals the original surface when a formic acid electrolyte is used at a current density of 1 amp/cm^2. For this reason, treatment in a formic acid electrolyte is often used for silver that has the original surface preserved in the corrosion layer. The treatment is effective as long as a substantive metallic silver core remains. During electrolysis, the reduced silver corrosion layers regenerated on the surface of the metal in formic acid are left in granular or particulated layers, which are physically weak and tend to separate from the metallic core. In order to preserve the detail of the specimen, clear acrylic lacquer should be applied to seal the corrosion layers in place on the surface of the artifact. Because the corrosion layers are particulated, silver that is reduced in formic acid tends to be dark, brittle, and rigid. However, the dark, reduced silver is stable, thoroughly cleansed of corrosion products, and 'antique' in appearance. If a brighter surface is desired, the silver can be lightly polished with a paste of sodium bicarbonate, a fine fiberglass brush, or a silver buffing cloth.

REDUCTION IN SODIUM HYDROXIDE

Reduction in a 3 to 15 percent aqueous solution of sodium hydroxide at a low current density (10-50 milliamps/dm^2) will result in firm, hard, metallic silver capable of being polished (Organ 1956:135). The regenerated silver retains the detail and texture of the original laminated corrosion surface but is full of voids and is not ductile. More recent tests have shown that a NaOH electrolyte is more conducive than formic acid for the thorough reduction of silver.

CONSOLIDATIVE REDUCTION

Fully rectified direct currents have been used in metal conservation, electroplating and battery charging. It was discovered some years ago, however, that a small amount of reverse current (also called partially rectified or asymmetrical alternating current) produces smoother electroplated finishes, faster battery charging time, and increased battery life. The technique was first described in the conservation literature by Organ (1956) as consolidative reduction.



There are three possible kinds of induced electromotive currents: alternating current (AC), direct current (DC), and asymmetrical AC (Figure 13.2). In every cycle of AC (Figure 13.2A), there is an equal amount of forward current (current flow from negative to positive) and reverse current (current flow from positive to negative); therefore, an AC has a symmetrical sine wave form. If an artifact is that is undergoing electrolysis is hooked up to AC, metal and hydrogen are deposited, and metal is reduced from the corrosion compounds at the cathode during the forward half of the cycle. In the subsequent reverse half of the cycle, the metal and hydrogen deposited or reduced at the cathode are dissolved. No progress in reduction takes place.

Because DC flows only in a forward direction, only reduction and deposition reactions take place at the cathode (see Figure 13.2B). In normal reduction using DC, metal and hydrogen are reduced at the surface of the specimen being treated, but in the process, the cathode can become polarized by the accumulation of hydrogen gas bubbles formed and deposited at the cathode surface.

The hydrogen gas can insulate the surface in some areas, while other areas are in direct contact with the electrolyte. Polarization will, therefore, result in uneven metal deposition and microscopic voids in the newly reduced metal.

In consolidative reduction, an asymmetrical AC of 10-20 percent reverse current and 80-90 percent forward current is generally used. During electrolysis, the net effect is a rapid succession of reduction and dissolution cycles (see Figure 13.2C). During the 90 percent forward half of the cycle, reduction of metal in the corrosion compounds and deposition of metal dissolved in the previous reverse current half cycle takes place. During the 10 percent reverse half cycle, there is a partial dissolution of the previously reduced or deposited metal; however, the 90 percent forward current places the emphasis upon reduction and deposition over dissolution as the current reverses 120 times a second. In the process, the polarization of the cathode is minimized.

Organ (1956) used asymmetrical AC in a sodium hydroxide electrolyte to regenerate the completely mineralized silver of the Ur lyre from silver chloride to massive metallic silver while preserving the surface details of the corrosion layers. The reduced silver was ductile and more homogeneous than silver reduced by normal electrolytic techniques using fully rectified DC. Organ used a 3 percent NaOH electrolyte, a carbon rod anode, and a very low current density of 10 milliamps/dm^2 (1 milliamp/cm^2) to reduce the silver and to prevent the rapid evolution of hydrogen that would possibly disturb the reduced silver.

For silver artifacts that are badly or completely corroded, more complete reduction is achieved if the cathode wire is laid against one side of the artifact and the exposed wire covered with wax or polymethacrylate. This ensures that the current passes through the corroded metal while flowing from the electrolyte to the cathode. The hydrogen discharges at the surface of the mineralized metal and reduces it. Organ (1956) used this technique in order to make an electrical contact with the nonmetallic, poorly conducting silver chloride on completely mineralized silver. This arrangement is beneficial even when only a thin core of metallic silver remains. During the process, which may take many weeks, the corrosion layers external to the original surface are reduced *in* situ, and all surface details are preserved. Since this technique preserves all of the outer corrosion surface, it should not be used on specimens with an original surface preserved within the corrosion crust. Following reduction, the artifact is rinsed in cold de-ionized water to remove all alkalis and then coated with a suitable sealant.

Additional details concerning the development and application of consolidative reduction can be found in Organ (1956:137-144). Plenderleith and Werner (1971:223-226) provide a useful summary of consolidative reduction techniques, and additional research is presented in Charalambous and Oddy (1975); the description of the circuit for the partially rectified current is provided in both sources. Asymmetrical alternating current appears to have some advantages over direct current, and may prove to be superior for treating all metal artifacts, including iron. Electrolytic reduction techniques that use asymmetrical alternating current have not been widely adopted by conservation laboratories, however, since efficient reduction of silver corrosion products to metallic silver can be achieved with very low current densities using direct current and a sodium hydroxide electrolyte.

ALKALINE DITHIONITE

The alkaline dithionite treatment is similar to the alkaline sulfite treatment for iron. It is a relatively cheap, simple, and efficient method for the uniform reduction of silver corrosion products to metallic silver (MacLeod and North 1979). The steps involved in the alkaline dithionite treatment of silver are as follows:

1. Immerse the object in 10-12 percent hydrochloric acid to remove any surrounding encrustation that may consist of sand, shell, calcium carbonate, and copper and iron corrosion compounds. This step may take from 12 hours to a week, or until all cleaning action ceases, and no more gas bubbles evolve from the object. During this step, it is necessary also to make sure that the solution remains acidic. If necessary, concentrated hydrochloric acid should be added to the solution to maintain a working strength.

2. Rinse the object thoroughly in tap water to remove all residual encrustation and acid. A pneumatic chisel may be used to mechanically remove any resistant encrustation.

3. Prepare a solution of alkaline dithionite: dissolve 40 g of sodium hydroxide in a liter of water, add 60 g of sodium hydrosulfite (the amount of sodium hydrosulfite in solution is not critical and any amount within the 55- to 65-g range will be effective). Immerse the silver object quickly in the alkaline dithionite solution in order to eliminate oxidation of the solution in the container. The container should be completely full of solution and have an air-tight seal.

4. Agitate and turn the container daily to keep the solution mixed and to expose all surfaces of the object(s) to the solution.

5. After one week, remove and rinse the object(s) in water until the pH of the rinse water remains unchanged.

6. The corrosion products on the surface of the artifact will be reduced to a gray, metallic silver, which can be polished with a wet baking soda paste or a fiberglass brush.

In addition to being very effective for reducing silver corrosion products, the alkaline dithionite treatment has been used successfully on all cupreous artifacts, converting copper corrosion products back to metallic copper.

To dispose of the used alkaline dithionite solution, allow it to air oxidize for several days in order to convert sulfites to sulfates. After oxidation, the solution should be neutralized with hydrochloric acid. The solution can then be safely disposed down the drain; however, it is possible to extract all the silver from the solution through electrolysis, which will plate the metal on the cathode. The silver recovered from the cathode may come close to paying for the treatment.

RINSE AND SEALANT

Following electrolysis, the artifact should be rinsed with de-ionized water. If an alkaline electrolyte is used, the rinsing should be quite intensive in order to prevent the formation of a white precipitate on the object. After rinsing, the silver can be dried with hot air or dehydrated in acetone and then coated with a clear acrylic lacquer, such as Krylon 1301.

CHEMICAL CLEANING

The majority of silver objects recovered from archaeological contexts require only limited treatment. In most instances, the various corrosion products can be removed with simple chemical solutions (Plenderleith and Werner 1971:227-229). Common tarnish caused by sulfur compounds can be eliminated easily with commercial silver cleaning solutions. Alternatively, a mild silver dip solution that consists of 5 percent thiourea and 1 percent non-ionic detergent in distilled water can be prepared. A solution of 15 percent ammonium thiosulfate in distilled water with a 1 percent non-ionic wetting agent is stronger than the silver dip and is effective for removing both tarnish and silver chloride. For base silver with copper corrosion compounds, concentrated ammonia effectively cleans all copper compounds from the silver. Care must be taken, however, because ammonia dissolves silver chloride and will substantially weaken badly corroded silver. A solution of 5-30 percent formic acid in de-ionized water is effective for dissolving copper compounds without affecting silver chlorides. Formic acid can also be used to brighten silver that has already been cleaned with another chemical or technique. Metallic copper films can be removed with a silver nitrate solution. In general, however, simple washing in soapy water or rubbing the silver object with a mild polishing abrasive is usually sufficient.

STABILIZATION AND CONSOLIDATION

Since silver sulfide and silver chloride are stable compounds, corroded silver pieces do not need to be stabilized. Object consolidation, however, is often required. Many of the silver coins and other small silver pieces likely to be found within an encrustation may have been completely converted to silver sulfide. In some cases, all that remains of the silver is a wet, formless slush. In a few cases, an enlarged, deformed, or discontinuous crystalline structure remains, and all that can be done is to record any data contained as an impression of the coin in the surrounding encrustation.

When an artifact is nearly or completely converted to a compact, cohesive silver sulfide, the form and all of the details of the original specimen are retained. Some 'coins' may consist of a light silver sulfide wafer that can be crumbled to powder with slight pressure. If consolidative reduction is not attempted, or is impossible, any cleaning treatment may dissolve the coin or at least destroy all the markings and details that are preserved in the mineralized sulfide layer. In some instances, it may be possible to conserve the artifact in the alkaline dithionite solution described above. In other instances, the only alternative is to consolidate the sulfides. This is easily accomplished by first dehydrating the object in acetone. It should be then placed in a dilute solution of polyvinyl acetate (PVA) and acetone. It is left in the solution until bubbles cease to rise from its surfaces, whereupon it is removed and allowed to partially dry. The process should be repeated two or three times followed by a thorough drying of the object. The process of repeated immersion and drying ensures that a maximum amount of the acetate is absorbed by the object. The PVA will consolidate the sulfide layers, although the aritfact will remain fragile and can be easily broken. If desired, any number of other consolidants, such as butyl acetate, various polymethacrylates, or even wax, can be used in place of PVA.

SUMMARY

Since the corrosion products of silver are stable, the treatment accorded silver artifacts is less critical than for other metal objects, especially iron. In some instances, however, when treating base silver with a significant amount of copper, it is the copper and its corrosion products that can create problems; in these cases, the artifact should be treated as copper. In many instances, silver may be treated exclusively by mechanical means or by various chemical treatments. Because of silver's susceptibility to corrosion in anaerobic conditions that are characteristic of marine environments, a treatment is often employed that will reduce the silver corrosion products back to a metallic state. If reduction is the objective, only electrolytic reduction and the alkaline dithionite treatments are effective treatments. It is for this reason that they are the treatments most often used to conserve silver artifacts recovered from a marine environment. Each is effective in its own way, and the decision to use either one should be based upon the particular resources of the laboratory and the number of artifacts to be treated.

Lead, Tin, and Lead Alloys

TIN, LEAD, AND LEAD ALLOY CORROSION

Articles of tin are seldom encountered in archaeological sites. This metal is found more often in various alloys, particularly in combination with copper for bronze and/or tin pewter. Gettens (1964:560) notes that tin seldom survives in archaeological sites because of the transformation of tin to a mix of stannous and stannic oxide by direct intercrystalline oxidation (SnO and SnO_2) or to a loose powdery gray tin, commonly referred to as 'tin pest,' by allotropic modification The alteration compounds of tin in a marine environment have not been adequately studied; it is known, however, that sodium chloride stimulates the corrosion of tin. Ingots of tin that were completely oxidized to tin oxide were recovered from a Bronze Age shipwreck off the coast of Turkey (Bass 1961). Although not often mentioned in literature, tin sulfide can also be expected to be found where sulfate-reducing bacteria are active in anaerobic environments.

Lead is commonly found in shipwrecks; it was used on ships for weights, cannonballs, sheeting, and stripping. Lead is a stable metal in neutral or alkaline solutions that are free from oxidizing agents, especially if carbonates are present in the water (Pourbaix 1966:488-489). Basic lead carbonate ($2PbCO_3 \cdot Pb[OH]_2$) and lead oxides (PbO and PbO_2) are formed under most archaeological conditions where there is prolonged atmospheric exposure. The gray lead carbonate and lead oxide generally form a protective layer on the artifact that prevents further oxidation. Both these corrosion compounds are found on lead from a marine environment, but lead chloride ($PbCl_2$), and especially lead sulfide (PbS) and lead sulfate ($PbSO_4$), are also common.

Gettens (1964:558) noted that few occurrences of lead sulfide have been reported on archaeological objects, but more recent research (North and MacLeod 1987:89) shows that the primary lead corrosion product in anaerobic marine environments is lead sulfide, while lead sulfate is commonly found on objects recovered from aerobic marine environments. It is not unusual in shipwreck excavations to find the remains of lead straps that have been completely converted to a black slush. The bulk of this corrosion is most likely lead sulfide which results from the action of sulphate-reducing bacteria. Some intermediate forms of lead oxides (PbO and PbO_2) may be formed, and oxysulfides are also present. Lead often exhibits extensive corrosion attack when it is in contact with wood. Lead strips that were nailed onto a ship's keel have been observed in a state of severe deterioration. The oxygen-consuming, decaying wood and the marine encrustation that forms over the lead apparently creates the anaerobic conditions conducive for the metabolism of the sulfate-reducing bacteria; in addition, the decaying wood provides nourishment for the bacteria.

Lead alloys, such as old pewter, which is an alloy of tin and lead, oxidize to the same compounds as the two parent metals. The condition of different pewter pieces varies widely both between and within archaeological sites, primarily because of different local conditions and varying percentages of tin to lead in each individual object. In general, leaded pewter always survives in better condition in marine environments than does lead-free pewter; this is most likely due to the formation of lead sulfate ($PbSO_4$) that protects the surface of the artifact. Lead-free pewter suffers extensive corrosive attack in aerobic sea water and is often completely mineralized as stannic oxide (SnO_2) and lead sulfide (PbS), and various very brittle, mineralized antimony and tin ($SbSn$) compounds are formed. In contrast, in anaerobic environments, both leaded and lead-free pewter survive in good condition through the protective formation of lead and tin sulfide films (North and MacLeod 1989:90-91). In fact, the only corrosion present on pewter recovered from anaerobic marine environments may be a thin sulfide film on the surface of well-preserved metal. Various combinations of lead carbonate, lead oxide, lead sulfide, lead chloride, and tin oxide are possible. Pewter objects often have wart-like blisters on the surface of the metal, which possibly result from localized contaminations of salts (Plenderleith and Werner 1971:278). These should not be removed, for under most of them there are either holes or pits in the metal.

CONSERVATION OF LEAD, TIN, AND PEWTER

Once recovered from the sea, the corrosion products of objects of lead, tin and their alloy, pewter, are stable. The corrosion products may be unsightly or even disfiguring, but they do not take part in chemical reactions that attack the remaining metal. The objects should be cleaned only for aesthetic reasons and to reveal surface details under the corrosion layers. Old pewter, an alloy of lead and tin, must be treated as tin, which is the more anodic and chemically sensitive metal. Therefore, no acids, or sodium hydroxide should be used, unless, in the case of electrolysis, the metal is given cathodic protection.

CHEMICAL TREATMENT OF LEAD

Because of the ease of treatment and the availability of the chemicals, the most widely used conservation treatment for lead from any archaeological environment is the acid treatment described by Caley (1955). The lead is immersed in 10 percent hydrochloric acid, which will remove any adhering marine encrustation, along with lead carbonates, lead monoxide, lead sulfide, calcium carbonate, and ferric oxide. This treatment is good for lightly corroded specimens, and it gives lead surfaces a pleasing appearance. The surface detail that is preserved by this treatment varies with the degree of corrosion when recovered. For more diagnostic lead artifacts, Caley's method has been superseded by electrolytic reduction, which has the ability to convert mineral products back to a metallic state. For the general cleaning of lead without a lot of hands-on labor, however, Caley's method remains an acceptable and much-used technique, provided that the object is thoroughly rinsed after treatment in order to remove all remaining hydrochloric acid residue. This will prevent contamination of any chloride-sensitive material with which the treated lead may be stored.

If lead dioxide is present, it can be removed by soaking the object in 10 percent ammonium acetate. The ammonium acetate will also act as a buffer to protect the lead from the action of any hydrochloric acid that may remain. If treated with ammonium acetate, lead should be left in the solution only as long as necessary, as the solution can etch the metal. For most lead objects, however, the ammonium acetate step is not required.

If the objective is to completely remove all of the lead corrosion products from a lead object, a 5 percent solution of ethylenediaminetetraacacetic acid (EDTA) disodium salt is most effective. After complete immersion in the EDTA solution for two to three hours (up to 24 hours for large objects), the object is rinsed in tap water.

After treating lead by Caley's method, the conservator still has the option to use electrolytic reduction to reduce any corrosion layer that are still in place back to a metallic state.

GALVANIC CLEANING OF LEAD

Any solid object of tin can be cleaned galvanically or by electrolytic reduction in the same way as described for iron and the other metals. Normally, in galvanic cleaning, the vat with the electrolyte, anodic metal, and specimen is heated to speed the reaction; however, since tin is an allotropic metal that is slightly soluble in sodium hydroxide, heating should be avoided and the treatment time kept to a minimum. Tin coins respond well to cold electrochemical reduction, using zinc, aluminum, or magnesium powder in caustic soda (Plenderleith and Werner 1971:275). Magnesium is often substituted for zinc, since zinc sometimes discolors the tin (Plenderleith and Organ 1953). However, if electrolytic reduction equipment is available, there is little reason to use galvanic cleaning for any object of lead, tin, or their alloys.

The only conservation alternative for badly oxidized tin objects is to consolidate them in microcrystalline wax or embed them in a plastic material. Slow, extended diffusion of chlorides in an alkaline solution is not an option due to the solvent action of the solution on tin objects.

ELECTROLYTIC REDUCTION CLEANING

The ability to control the speed of the electrolytic reaction through current controls makes electrolytic reduction especially useful for lead coins and medals or, indeed, any specimen where surface detail is important or reduction and/or consolidation of the corrosive layers is the objective. Two electrolytic reduction techniques, normal reduction (Plenderleith and Werner 1971:267-268) and consolidative reduction (Organ 1963a:131; Plenderleith and Werner 1971:268-270), are used for treating lead.

Normal Reduction

Lead artifacts with substantial metal remaining can be cleaned by the normal electrolytic reduction process using 5 percent sodium hydroxide, anodes of mild steel or stainless steel, and a current density of 2-5 amps/dm^2. Very satisfactory results are achieved by this technique. However, since lead is susceptible to solvent action by the electrolyte, when it is not cathodically protected, the current must be flowing before putting the specimen in the electrolytic tank and must not be cut off while the specimen is immersed in the tank. A good electrical contact, as indicated by evolution of hydrogen from the object, must be made with the lead, and the contact should be sufficiently supported to ensure that the electrical contact is maintained.

Since lead, tin, and pewter are susceptible to attack by strong alkalies, a sodium carbonate electrolyte is safer for use in electrolysis than a sodium hydroxide electrolyte. If the electricity were to go off during electrolysis while the lead or tin object or alloy was immersed in NaOH, the object would be attacked by the alkaline solution. If sodium carbonate was being used as the electrolyte, however, a passivating film of carbonate would form on the object, and the alkaline attack would stop. The attack on tin and tin alloys by sodium hydroxide solution is particularly aggressive. Since sodium carbonate does a reasonably good job on artifacts made of these metals, the use of sodium hydroxide electrolytes should be reserved for consolidative reduction on special artifacts where there is some reason to attempt to achieve the absolute maximum reduction of corrosion products back to metal. For example, when there are inscriptions or marks that are preserved in the corrosion layer of an object, sodium hydroxide should be used as the electrolyte.

Consolidative Reduction

This technique was developed by Organ (1963a:131) to consolidate the inscriptions contained in a fragile corrosion layer of basic lead carbonate on a group of lead seals. The removal of the corrosion layer would have obliterated the inscription. Consolidative reduction converts the basic lead carbonate and other lead corrosion products to a compact mass of lead. The object is tightly compressed between two polyurethane foam pads in order to support and put pressure on the corrosion layers while they are cathodically reduced at a current density of 100 to 200 milliamps/dm^2.

In consolidative reduction, which employs very low current densities, mild steel anodes cannot be used because the current flow is so low that there is no way to keep the anodes passivated against anodic dissolution; therefore, stainless steel anodes and a 5 percent sodium hydroxide electrolyte are recommended. The procedure described by Plenderleith and Werner (1971:268-269), who use a 10 percent solution of sulfuric acid with a lead anode, is not common because of the difficulties of handling sulfuric acid and the deposition of lead from the anodes onto the artifacts being treated. In addition, more recent research has shown that the most thorough reduction is achieved when NaOH is used as the electrolyte.

Plenderleith and Werner (1971:269) suggest using a partially rectified alternating current source, which provides a 'bumping' effect, for better results. As discussed in the section on silver, however, the use of an asymmetrical alternate current is not widely used since low current density electrolysis using straight direct current effectively reduces lead corrosion products back to metallic lead, especially when sodium hydroxide is used as the electrolyte. The use of an asymmetrical alternate current does not appear to increase the degree of reduction (Lane 1975; 1979). The most important thing for the conservator to keep in mind during any electrolytic cleaning process is the importance of maintaining a constant flow of electrons to the lead or tin metal that is being treated to ensure cathodic protection.

Rinsing Procedure Following Electrolytic Reduction

Sodium hydroxide electrolyte residues cannot be removed completely from lead through simple water rinsing; a more complex procedure must by followed (Plenderleith and Werner 1971:269-270). The object should be submerged in a dilute solution of sulfuric acid (4 drops of concentrated (15-18%) H2SO4 per liter of tap water) with a pH of 3 to 3.5 neutralizes the alkalinity of the electrolyte and forms a protective coat of lead sulfate on the surface of the object. The artifact is then taken through a succession of H2SO4 baths until the pH ceases to rise due to the diffusion of alkali from the lead. After removal from the sulfuric acid bath, the residual acidity present on the surface of the lead is removed through immersion of the object in successive baths of cold distilled water with a pH of about 6, until the pH of the water does not drop.

SEALANT

Following the rinsing, the reduced object is dried with hot air or dehydrated in a water-miscible solvent. The fragile reduced metal is then strengthened and protected from atmospheric corrosion by submersion in molten microcrystalline wax.

STORAGE

Lead is particularly susceptible to organic acids, such as acetic acid, humic acid, and tannic acid. Lead artifacts, therefore, should not be stored in oak cabinets or drawers. If so, even small concentrations of vapors of these acids can initiate corrosion, which progresses rapidly. To be safe, lead should by stored in sealed containers or polyethylene bags.

Gold and Gold Alloy Conservation

GOLD CORROSION

Gold is a relatively inert metal and thus undergoes minimum corrosion. It is the copper- and/or silver-based gold alloys that easily corrode, resulting in silver or copper corrosion compounds that leave an enriched and possibly weakened gold surface.

GOLD CONSERVATION

Pure gold and high gold alloys do not require any conservation treatment. Gold objects from shipwreck sites appear to look the same when recovered as the day they went down with the ship. The copper and silver in low- alloy gold do corrode. When present, the copper and/or silver corrosion compounds of low-alloy gold are treated by the processes described for these two metals (see Files 12 and 13). Silver corrosion products can be removed with ammonia; copper compounds with formic acid, citric acid, or alkaline sequestering agents, such as Rochelle salts or alkaline glycerol. All the pertinent comments applicable to silver and copper conservation are made under those headings.

Casting and Molding in Conservation

The techniques of casting and molding are often used to restore and replicate artifacts. Casting replicas for exhibition, distribution, and study is only an adjunct to conservation. This aspect of casting, although of considerable importance, is not considered here, and the reader is referred to publications and brochures that can be obtained from manufacturers of casting materials, and to articles by Rohner (1964, 1970), Rigby and Clark (1965), Hamilton (1976), and Frazier (1974).

In the conservation of marine archaeological specimens, casting is used when the artifact itself cannot be treated. In some cases, only through casting can the object be saved or its form determined. As has been already noted in previous files in this on-line manual, metal objects within an encrustation can continue to corrode until little or no metal remains. In such cases, the original surfaces with identification marks, stamps, letters, or numbers are lost. Fortunately, the encasing encrustation begins to form immediately at the onset of the corrosion process. It forms a mold around the original forms, preserving any surface details. Quite often, the encrustation is more informative than the deteriorated or badly oxidized object.

There are many ways of using casting techniques during the conservation of shipwreck material. Some knowledge of the procedures used is important. A laboratory should also keep a stock of the necessary supplies and casting compounds. A number of different casting materials from many different manufacturers can be used. Products that are particularly recommended include Dow silver chloride (AgCl) silicone rubber, Smooth-On polysulfide rubber, Surgident Neo-Plex Rubber, Permamold Latex, Hysol Epoxy, plaster of Paris, and Coecal plaster. Many similar products could be substituted for those recommended here.

CASTING TECHNIQUES IN MARINE ARTIFACT CONSERVATION

The first published account of casting in marine conservation as a means of retrieving completely oxidized artifacts is that reported by Katsev and van Doorninck (1966:133-141). Using a lapidary saw, they sectioned small encrustation containing natural molds left by oxidized Byzantine iron tools. Some specimens required only one cut, while more complicated objects required several cuts. The corrosion residue was removed from the natural molds, and a piece of cardboard or plastic was made to fit between the sawn halves to compensate for the material removed by the saw. The mold then was filled with a flexible compound and the halves fitted together. The rubber cast was removed once the compound had cured. When the rubber flashing that formed along the seams of the mold was cut away, a replica of the disintegrated artifact was obtained.

Although rubber casts such as these are not permanent nor long lasting, they will last for a number of years. Their life and usefulness can be extended by storing them in plaster mother molds to provide support and to keep them from stretching and losing their form. If a permanent epoxy cast is needed, a mold must be first made of the polysulfide rubber cast; this second mold is then cast in epoxy.

After casting several molds sectioned with a lapidary saw, several disadvantages were noticed by Katsev and van Doorninck (1966). The technique is limited to small encrustation and to uncomplicated shapes, which require only a few cuts. A problem also arises in correctly aligning the two halves and the cardboard gasket required to replace the thickness sawn away by the blade. This problem is compounded when more than one cut is made. When the mold is cut with a saw, the seam flashing is very noticeable.

If X-ray facilities are available, some of the problems of casting natural molds can be overcome. Radiographs reveal the shape of the object and the extent of the corrosion. In certain encrustation, it is possible to use a pneumatic air chisel to cut openings into the distal ends or key points of an object. Through these holes, the corrosion residue can be washed out and the casting compound poured. Alternatively, the air chisel can be used to inscribe a line along or around an encrustation. By hitting along this line with a chisel and a hammer, the encrustation can be broken in a predetermined manner. Simple encrustation are easily opened and cast in this way. Because it is much more effective to break open natural molds in encrustation, the use of lapidary saws is not recommended.

The only way to recover many of the smaller, thin iron artifacts recovered from marine sites is to cast the natural mold left inside the encrustation after the artifact has corroded to a slush. The corrosion residue can sometimes be removed simply by rinsing the mold out with water; in other cases, a considerable amount of mechanical corrosion removal is required. After any residual corrosion product is removed, the void is filled with casting material. Epoxy is recommended as a general casting material, since it does not present the same long-term storage problems to the conservator as does polysulfide rubber. After the casting material has set, the surrounding encrustation can be removed with a pneumatic chisel, revealing a perfect replica of the original artifact.

Using the above technique, conservators have been able to make epoxy casts of corroded hammer heads directly onto the original wooden handles, as well as iron cleavers hafted onto the original wooden handles, a variety of iron keys, and several door locks (see Figure 16.1). It should be emphatically stated that if casting techniques are not being used on otherwise unconservable artifacts, a significant amount of data will be lost. (See Hamilton 1976:72-85; North 1987:231-232; and Muncher 1988 for a more complete discussion of the techniques of casting.)

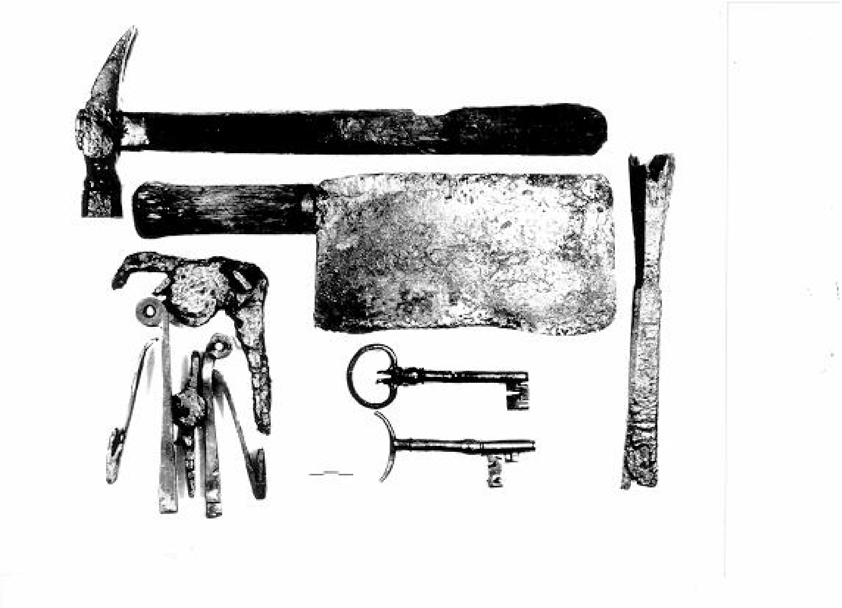


Figure 16.1.

Epoxy casts of iron tools from the submerged 17th-century town of Port Royal, Jamaica.
From top to bottom and left to right: a hammer with the original wood handle, a cleaver with the original wood handle, a door lock, two keys, and a socketed chisel.

Natural molds of disintegrated metal objects are often encountered in very large encrustation, where, even if it were possible to x-ray the piece, they cannot be detected on radiographs. To avoid destroying possibly valuable information about the encrusted artifacts, close observation is required when using air chisels to break apart the encrustation in order to reveal any natural molds. Because of the presence of these natural molds in large encrustation, the use of acids or even electrolysis to remove encrustation (see Montlucon 1986, 1987) is not generally recommended. When natural molds are detected, it is possible to open a small area on one side of the mold, clean it out, and fill it with epoxy.

The casting examples discussed above involved corroded iron artifacts; similar casting procedures are often employed on silver artifacts, which often corrode extensively in anaerobic marine environments. For example, a number of silver discs that are plano-convex in cross section were recovered from two 16th-century Spanish shipwrecks. On the flat surface of the silver discs are usually one or more stamps indicating ownership, mines, and tax marks. Many of the stamps were obliterated in the corrosion process. The encrustation, however, formed a perfect mold of the original surface of the silver, and a reverse impression of the stamps remained in the encrustation. In one example, the encrustation on a singularly encrusted silver disc was removed with an air scribe by chipping along the circumference of the disc and separating the two halves of the encrustation from the silver. The reversed silver stamps were revealed by carefully removing the corrosion products from the interior surface of the encrustation with fine bristle brushes and pointed wooden sticks. A latex peel was made of the interior surface of the encrustation which contained the reverse of the stamp. Plaster casts were made from the latex peel of the stamp impression, and the stamps were highlighted with a soft-lead graphite pencil. It is possible to recover many otherwise lost stamps through this procedure, and this technique is routinely incorporated into the conservation of encrusted silver discs in order to preserve these valuable data. Few historians or archaeologists would deny that the salvage of the stamps is historically more significant than silver discs with obliterated stamps.

The casting examples discussed above present an unquestionably strong case for the value and significance of casting in the conservation of marine shipwreck material. The recovered data are of the type that is lost daily by improper care and conservation of archaeological material. These examples emphasize the reasons why marine shipwreck material should be processed by conservation personnel, who are familiar with the material culture, as well as with the alternative techniques available for salvaging and preserving the maximum amount of data from an artifact.

Concluding Remarks

This on-line conservation manual has attempted to present the current state of conservation of archaeological material from marine environments. Various procedures, chemicals, and types of equipment have been discussed, but many more were not. There are many minor variations, optional steps, and 'tricks' that are learned and used by different conservators. Time and space has not allowed for a thorough discussion of each known technique and the variations within the different techniques; it is necessary, therefore, for the conservator to consult the original published sources for each topic. Individuals interested in archaeological conservation should consult the referenced sources and a trained conservator before attempting the procedures described herein.

The preservation of antiquities should produce objects that are chemically stable with an aesthetically acceptable appearance. All treatments should be reversible in the event that the object should require additional preservation. Simply because an object has been successfully conserved does not mean it will not deteriorate in the future. Artifact stability can be ensured only if the object is stored or displayed under optimum conditions. Metal artifacts, as well as those made of organic or siliceous material, can become chemically unstable from a myriad of causes and, therefore, require periodic inspection and evaluation, as well as possible re-treatment. At our present stage of knowledge, perhaps it is most realistic to say that the objective of archaeological conservation is to delay re-treatment as long as possible through proper storage and to make any necessary re-treatment simple and brief. It is obvious that the conservation laboratory can play a major role in archaeology if the project objective is to produce the maximum amount of archaeological data from the excavation of waterlogged and underwater sites.

During the course of this discussion a clear idea of the facilities required, the treatments available, chemicals used, and various insights on conservation have been presented. This should be helpful in evaluating any conservation proposal or for assistance in establishing conservation facilities designed to conserve the vast array of material found on marine sites. Estimating the costs involved is more complicated. With a knowledge of what equipment and materials are needed, however, it is simply a matter of determining the variety of treatments to be performed and the level or volume of artifact treatment expected of the laboratory.

All of the treatments discussed in this manual are used to conserve material from marine sites. With most treatments, it is not a question of which treatment is preferred or which treatment is better than another. The fact is that each treatment discussed would be the preferred means of treatment for a particular artifact. For this reason, a conservation laboratory must have a conservator who is familiar with the various treatments, who knows in which situations particular treatments are the most appropriate, and who has the facilities, equipment, and chemicals to carry out the treatments.

Conservation Bibliogrpahy

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CCI	*Canadian Conservation Institute Publications and Notes*
GCI	Getty Conservation Institute
ICOM	International Council of Museum Papers
IIC	International Institute for Conservation of Historic and Artistic Works
TC	*Technology and Conservation* (published erratically, now defunct.

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When a conservator writes a conservation manual such as this, much of the data are in his or her head and from personal applications. Common procedures that are used extensively may be so ingrained that the original reference or even any reference may be left out when the procedure is transcribed. To help alleviate any problems that this might create, in addition to the cited references above, a more intensive bibliography, separated by major materials, is included here.

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