Basic Methods of Conserving Underwater Archaeological Material Culture

Donny L. Hamilton

Nautical Archaeology Program,
Department of Anthropology,
Texas A&M University
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TABLE OF CONTENTS

OVERVIEW OF CONSERVATION IN ARCHAEOLOGY

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 excavator/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. 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 in a matter of hours crumble and be little more than a pile of dust and debris. Iron, on the other hand, can last for a few days to months according to the size and density of the artifact but it will eventually deteriorate, fall apart 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 become a pile of useless slivers. For these reasons conservation must be of paramount concern when excavations of a marine historic ship archaeological site are considered.

Before discussing the conservation of archaeological materials, it is important that everyone understand what is meant by the various definitions of the term "artifact" so that there will not be any misunderstanding. For our purposed the definitions given in 36 CFR Part 79, section 4 are applicable (U.S. Department of Interior: 1991):

Section 79.4 Definitions:

(a) *Collection* means 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* means artifacts, objects, specimens and other physical evidence that are 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:

(I) Components of structures and features (such as houses, mills, piers, fortifications, raceways, earthworks and mounds);

(ii) Intact or fragmentary artifacts of human manufacture (such as tools, weapons, pottery, basketry, and textiles);

(iii) Intact or fragmentary natural objects use by humans (such as rock crystals, feathers, and pigments);

(iv) 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);

(v) Organic material, such as vegetable and animal remains, and coprolites);

(vi) Human remains (such as bones, teeth, mummified, flesh, burials, and cremations);

(vii) Components of petroglyphs, pictographs, intaglios or other works of artistic or symbolic representation;

(viii) Components of shipwrecks (such as pieces of the ship's hull, rigging, armaments, apparel, tackle, contents and cargo);

(ix) 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

(x) 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 paper 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, quite similar in many ways to the federal standards established for archaeological material. What is important is that all relevant documentation be taken from the start, including all records pertaining to conservation treatment and that a complete set of records accompany the collection or with and given artifact separated from the collection.

The following section discusses alternative methods for conserving archaeological artifacts recovered from marine sites. Conservation techniques which may be appropriate or the conservation of artifacts from terrestrial sites, but which are not satisfactory for marine sites are not discussed. The following section is divided into Introduction to Marine Conservation, Synthetic Resins and Adhesives, Ceramics, Glass, Bone and Ivory, Wood, Leather, and Metals with appropriate subdivisions under each major heading. All the treatments discussed do not conflict with any known Government regulations and laws; therefore, there are no limitation on their use from this perspective.

First, however, a brief statement should be made about estimating the level of effort and resources necessary to accomplish each option. As each treatment is discussed, the required chemical are listed and any necessary equipment are either listed or they are obvious. For example, if an object is 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 are heated during the rinsing, then a metal vat and a source of heat, be it a gas stove, an electric hot plate or an oven is required. The choices are variable. There are too many variables to arrive at any specific cost, for it all depends 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 that is to be stored or displayed in. There are some viable alternatives that can be used on given artifacts that can be done by untrained personnel and with a minimum amount of specialized equipment, but these treatments are employed only when it will successfully preserve the artifact. If this is the case, then it remains an alternative in any situation. It also depends upon what is meant by near-term and long-term? As I see it a near-term goal would be to properly store an object until it can be proper treated, which is the long-term goal. Where possible, comments relevant to these two requests will be made.

Near-term goals, as opposed to long-term goals are more relevant when it come to making decisions such as whether an agency wants to contract out the conservation to existing laboratories which would satisfy the immediate or near-term goal, or should they establish their own conservation capability to conserve all future artifacts that might be acquired would satisfy all long-term conservation needs.

PRELIMINARY CONSIDERATIONS

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 excavator/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.

There is a vast literature on the conservation of archaeological material from all environments, as well as that from marine sites. However, in recent years, a vast 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 few publications. This report can not replace consulting these publication for additional details. The most important publication in the field of marine archaeology conservation are:

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

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

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

Pearson, Colin (ed.), 1987, *Conservation of Marine Archaeological Object*s. Butterworths, London.

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

CETBGE, 1984, *Waterlogged Wood: Study and Conservation*. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Grenoble.

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

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, 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. These are supplemented by various university theses, papers prepared by conservation laboratories that are not widely distributed, personal communications from conservators, and personal experience. The following discussion on conservation is abstracted from a combination of these sources. This discussion, however, can not replace consulting these reference for a more detailed presentation. A "cook book" approach to archaeological conservation can never be taken. A thorough knowledge of the alternative techniques available and a range of

personal experiences is required to contend with the array of material to be treated. Even with this knowledge, and experience, there are always artifacts that simply can not be successfully conserved, and in archaeological conservation there are always those artifacts that are just not practical, for any number of reasons, to conserve. See the following discussion.

CONSERVATION ETHICS

Artifacts recovered from a salt water environment are often well preserved but of a very friable nature. 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 in a matter of minutes crumble and be little more than a pile of withered fragments. Iron, on the other hand, can last for a few days to months according to the size and density of the artifact but it will inevitably deteriorate, fall apart 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 become a pile of useless slivers as the soluble salts crystallize and exfoliate the surfaces and can even cause the specimen to disintegrate. For these reasons conservation must be of paramount concern when a marine site such as a historic ship is being considered.

The following are some of the more pertinent conservation ethics adopted by the International Institute for Conservation as guidelines for all conservators. These standards were developed for art conservation but are also applicable in as much as it is possible to archaeological conservation. The indented, lettered ethics are taken directly from IIC. I have added comments following 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.

A. *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.

B. *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.*

C. *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.*

The quality of treatment should not be based on an object's quality or value. All artifacts should receive the same high standard of treatment.

D. 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 though 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.

E. 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. All treatments must 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 retreat is always open and the continued preservation of the material is assured. However, in the conservation of material from archaeological sites, especially underwater marine sites, this tenet often can not be followed, for the conservator has only one chance to preserve the artifact and in order to do this, non-reversible techniques must be utilized.

F. 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.*

G. 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.*

H. 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.*

Conservation is not just a set of procedures and treatments; it goes far beyond that. 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 the protection 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.

Conservation should not detract from the natural appearance of the object nor alter any of its scientific attributes since artifacts are a primary unit of study in archeology. The conservator should strive to process specimens so that they retain as much diagnostic data as possible and yet remain chemically stable. For example, 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 retreat 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 espoused by Plenderleith and Werner (1971:16-17). Basically they state that the past history of an artifact may impart features of significance pertaining to age and provenience which can validate its authenticity. Therefore, a preliminary examination of the object needs to be made 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 archeological 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 given 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 concern for the recording and preservation of the basic data derived from any given piece is essential and needs to be expressed by all laboratories which process archeological material. In archeological conservation there is often more to consider than just 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 archeological material that requires documentation of context, as well as preservation, the documentation demands equal emphasis and first priority. The interaction between marine archeology and conservation is a perfect example of the intimate relationship that can exist between archeology and conservation.

It is always important to continually stress that proper conservation in marine archaeology is important not only because it preserves the material remains of the past that are recovered, but that it can and should be an essential part of marine archeology, capable of providing almost as much archeological data as the field excavations and the 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 archeological record and the importance of various types of association. An underlying premise of archeology 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 ARCHEOLOGY

The development of underwater archeology is almost entirely a post-World War II phenomenon resulting from the development of Self-Contained Underwater Breathing Apparatus, SCUBA gear which made the sites, especially those in shallow water accessible. Now even the deeper wrecks such as the CSS *Alabama* and the USS *Monitor* are accessible. Still, underwater archeology shares common techniques and standards with its terrestrial counterpart. Goggin (1964:302) describes underwater archeology 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 archeology, which is a scientific investigation, from uncontrolled salvage and "treasure hunting," which are oriented toward relic or object collecting.

The kinds of underwater archeological 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 paper, techniques to be reviewed here are applicable to metal objects from any underwater site and most terrestrial sites.

Shipwrecks are a special kind of archeological 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. Such a mass of material will give historians and archaeologists a priceless collection of objects that can be identified accurately as to period and that will in turn furnish an index to the material remains of Western man from the beginning of his culture. (Peterson 1969:xiii-xiv).

All this is true, but it is a very artifact-oriented view. There are much more data available in these "time capsules" than just 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 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. Finally, the ship's remains provide valuable details concerning ship construction. Within a shipwreck it is possible that data concerning technology, trade, personal belongings of the crew and passengers,

armaments, armament policy, monetary systems, navigation, ship construction, ship life, and possibly societal and functional implications as indicated by distribution of certain kinds of remains can be obtained. Tax, ownership, mining, shipping, or other types of identification stamps or marks on individual artifacts provide additional leads. This potential wealth of information can often be checked and compared with archival documents for corroboration and reinterpretation.

Written history is always an abstraction of actuality, and as a matter of course is replete with gaps, errors, and misinterpretations. For example, the early colonial period in the New World is poorly documented. Archeological excavation in sites of this period provides additional details to fill the missing pages of history and to correct the misinterpretation. Underwater archeology also can play an important part in interpreting history; the analysis of on any historic period shipwreck, especially when the available documentary evidence which might be available is used to provide us with considerably more insight into the era being investigated.

It is possible to retrieve these data only if well-organized, problem-oriented excavations are conducted. Borhegyi (1964:5), in reference to underwater archeology, stated that "no one today would be forgiven if he employed the nineteenth century excavation techniques . . ." I maintain that 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 conversation plans are not included, more data may be lost than gained.

The recovery of artifacts from archeological sites destroys the archeological context, which remains preserved only in the notes, drawing, and photographs made by the archeologist in the field. Careful recording is necessary, otherwise the operation is not an archeological excavation, but an uncontrolled salvage operation producing simply an 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 archeological 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 freshwater sites is only remotely analogous to the conservation problems presented by other fields of archeology. When artifacts, of every variety, but especially metals, are recovered from the sea, especially warm waters 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 masses weighing several thousand pounds containing hundreds of individual objects made of many different materials. The proper conservation of encrustations with their concealed contents is analogous to the an excavation square within a site. Any laboratory that processes these encrustations has the responsibility (1) to preserve and stabilize the artifacts as well as conservation technology permits and (2) to 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 have to be maintained which include 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 have to be made of disintegrated objects and of significant impressions left in the encrustations. Care must be taken of mundane things such as potsherds, cloth fragments, spikes, straps, 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 must be detected and recorded. In other words, the conservator is in a unique position to supply the archeologist with valuable evidence

and to provide the laboratory with basic conservation data for research. The investigation of large encrustations with their concealed contents is analogous to the excavation of a structure within a site, and the location and orientation of each encrustation needs to be accurately plotted before it is raised from the seabed, so the data recovered in the conservation laboratory can be related back to the site.

Let's look at an example from a marine site. In Figure 1 is one of the several large encrustations recovered from the sites of the "San Esteban", one of the three ships of the 1554 Spanish plate fleet wrecked off Padre Island, Texas. This single piece, with two anchors, a bombardetta gun with its wooden undercarriage, breech blocks ,and a multitude of smaller objects, is over four meters long and weighs over two tons. A laboratory must have sufficient space and equipment to take a piece like this, mechanically clean it, properly conserve recovered specimens, and possibly cast a number of natural molds of disintegrated objects. It may even be necessary to prepare the encased artifacts for display. The laboratory has to have forklifts, chain hoists, large vats, specialized DC power supplies, hundreds of kilograms of chemicals, thousands of liters of deionized water among other resources to perform the job. In areas where there is an abundance of rain water, this can be substituted for deionized or distilled water for most treatments, considerably cutting the cost of the conservation. The laboratory has to take an encrustation like that depicted in Figure 1 and turn out an array of stabilized artifacts.

The degree and extent of the encrustation depends upon the local sea environments. Encrustation does not form in fresh water and is extensive in tropical sea water. In northern cold, sea water encrustation formation is minimal. For instance, Gordon Watts (personal communication) says that the encrustation found on the surface of the iron on the CSS *Alabama* which is about 170 feet of water in the English Channel off the coast of France are thin and crumbly. 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 needs to be emphasized that careful records in both the field and the conservation laboratory are required. No amount of accuracy in the laboratory can compensate for inaccuracies or inadequacies in the field data, nor can competent documentation in the field make up for poor laboratory records. Both the field and laboratory records are necessary for documenting the distribution of the material culture remains.

In contrast, it has been maintained by some treasure hunters that no artifact provenience other than site designation is necessary, since associational 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 archeological data. What is important to remember is that careful documentation in both 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 our knowledge of any shipwreck.

BASIC CONSERVATION PROCEDURES

Conservation must be a part of any archaeological project and 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 and 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.

For the past 20 years I have been responsible for the conservation of archaeological material recovered from a number of underwater archaeological projects. For the past 12 years I have directed excavations at the sunken city of Port Royal, Jamaica and have recovered thousands of artifacts which have been conserved. In addition, I have been teaching courses in artifact conservation since 1973. It is with this in mind, that I propose the following every archaeological project director takes the following into consideration prior to any excavations.

1. Anticipate what you might encounter 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 might undergo.

3. Have a person with conservation experience in the field to help with the excavation to insure 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 is the case, be sure 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 is recovered in the laboratory as in the field. The information and records from both the field and the conservation lab have to mesh together in order to interpret the archaeological record properly.

FIELD RECOMMENDATIONS

Many projects setup 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 it is recommended that field conservation facilities be used as little as possible, aside from general cataloguing, acquisition, and documentation. Proper field conservation procedures can be anticipated by referring to various articles such as Pearson (1977; 1987c), Dowman (1970) and Lawson (1978). From my own experience I recommend the following field procedures during any marine excavation (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; they provide a protective corrosion resistant layer around the material and preserve associations. Also, considerable data can exist in the form of impressions and natural molds of objects which have completely disintegrated.

3. When dealing with features, kegs, chests, boxes, etc. it if 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 the pH adjusted to a reading of 10 to 12 with sodium hydroxide. 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 conveniently 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 are discussed.

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% 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% solution of sodium carbonate or 2% 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. See a more thorough discussion under each material.

EVALUATION OF CONSERVATION PROCESS

Prior to treating any artifact, especially if encrusted with marine carbonates, have to be critically evaluated as to the probably metal, condition of metal, possible associated organic material and artifact of other material such as glass and ceramic. 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 can be damaging. The use of well directed hammer blows and assorted chisels are generally the most used and effective means of removing encrustations. However, for many objects, especially fragile objects and ceramics, small pneumatic tools are indispensable when it come to removing calcareous growth from encrusted metal artifacts. The are by far, more efficient and less destructive than any other possible tool. Larger pneumatic weld-flux chisels are particularly useful for the removal of large amounts of encrustation. Smaller more precisely controlled air scribes, with more delicate chisels are ideal for removing the encrustations from small, fragile artifacts, and for getting into tight places. Chisels can be easily fabricated in the laboratory for specific jobs. Combined use of the two tools is often desirable and is 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 has be emphasized that conservation is not an exact science and in many cases two different conservators might treat the same object in completely different ways. There is often no one and only way to treat an object. The objective is treat any given object so that it is stable and it does not loose any of its diagnostic attributes. Thus 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 on personal experience and personal preference. Other conservators might not agree completely with everything I present here, but everything I discuss is within the conservation bag of alternative procedures. When possible, I will discuss the advantages and disadvantages of each treatment.

Figure 1. Large encrustation over 3 meters long and weighing over a ton containing two anchors, a bombardetta gun and over a hundred additional artifacts from one of the 1554 Plate Fleet shipwrecks

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 extensively used. The use of synthetic resins also plays 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 have a variety of resins at his disposal for use as glues and consolidants and have a good understanding of their physical characteristics.

ADHESIVES AND CONSOLIDANTS

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 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 can 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 (Dowman 1970, UNESCO 1968) are:

     1. Polyvinyl acetate (PVA) which is an organic solvent, e.g.,

          Vinylite AYAA (V 12.5-14.5)

          AYAC (V 14-16)

          AYAF (V 17-21)

          AYAT (V 24-30)

          Gelva V7, V15 and V25;

     2. Polyvinyl acetate (PVA) emulsions, e.g., CMBond M-2 (Elmer's Glue All is not a true PVA emulsion.)

     3. Acryloid B-72;

     4. Cellulose Nitrate, also called nitrocelluloid, e.g., Ducco & HMG;

     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

In general polyvinyl acetate (PVA) is the most commonly used thermoplastic polymer resin for organic material recovered from archaeological excavations (Ashley-Smith 1983b, UNESCO 1968). This is true in the field as well as 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 and the lower the molecular weight the greater the penetration capability of the consolidant. However, the lower viscosity PVAs have less bonding strength than the more viscous ones. Also, 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 only ones commonly use in conservation. PVA V7, with its smaller molecules, is uses on denser material such as well preserved bone and ivory , PVA, V15 is the general purpose resin, and PVA, V25 is used as a glue.

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, can be used as a surface consolidant or as a glue. Many conservators prefer to use V25 PVA as a glue, especially for pottery reconstructions, with good success. In my own experience, I have found that ceramic vessels glued with V25 PVA have occasionally fallen apart because of excessive "cold flow of the resin" in hot, humid, adverse 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 & 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 one of its solvents, especially acetone.

On 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 heat sealable; for example, two pieces of cloth treated with PVA can be bound by ironing the two together.

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. Diethyl ether (very volatile, water miscible [WM]).

2. Acetone (best solvent that is commonly used, WM).

3. Benzene (very toxic, WM).

4. Ethylene dichloride (very toxic, not 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 Formula

1. ethanol 1. acetone

2. 5-15% PVA 2. 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% Triacetin by volume or 5% Castor Oil by volume of cellulose nitrate has to be added to plasticize the cellulose nitrate to retard -- it will not prevent it -- it shrinking and becoming brittle.

PVA can also be purchased as an emulsion, such as CMBOND M-2. Emulsions are stabilized dispersions of finely divided particles of the resin in water. The resin is merely suspended in the water; it is not 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 nonemulsified 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, CMBOND M-2 has approximately .6 grams of resin per 1 gram of stock mixture.

PVA V25 and even V15 is often used as a glue. When used as a glue, it only necessary that it be thick enough. One acceptable procedure for making glue is provided by Stephen Koob (1996) The procedure described here uses Acryloid B-72, but the process works equally well with any PVA formulation. This glue formulation, using Acryloid B-72 is the standard glue used at CRL.

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 twenty 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 .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.

ACRYLOID B-72

Acryloid B-72, in Europe referred to as Paraloid B-72, 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. Acryloid B-72 generally dries with less gloss than PVA. It dries to a water-clear transparency and is resistant to discoloration even at high temperatures. Acryloid B-72 is very durable and has excellent resistance to water, alcohol, alkalis and acid. Acryloid B-72 has exceptional resistance to mineral oil, vegetable oils and grease and it retains excellent flexibility. It 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. Acryloid B-72 is durable and non-yellowing. It is compatible with other film forming materials such as PVA and cellulose nitrate. It can be used in combination with them to produce coatings with a wide variety of characteristic with emphasis on stability and transparency. In stronger concentrations, it can be used as a glue. See Koob (1996) for details on preparing it for use as a glue.

Acryloid B-72 is unique in possessing a high tolerance for ethanol, e.g., after being dissolved in acetone or toluene, up to 40% 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 on drying. It has also been found that the 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% Acryloid B-66 in toluene (NWM) 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. It can be used in most instances in place of Acryloid B-72.

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 most

PVAs are. Therefore, cellulose nitrate has a much greater tendency to become brittle, crack and peel off than does PVA.

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 the 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 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 Cement has been used extensively, with varying success, in pottery reconstructions and general artifact mending. In the past, I have used Duco and have found that while it is easy to use and is effective in the short run, over the years the glue has yellowed and has become brittle resulting in the breakup of the glued items. It is not recommended for use in archaeological conservation (Feller and Witt 1990; Moyer 1988b).

Cellulose nitrate is discussed here because of it availability and it general misuse in many conservation projects. In a few given cases where it might be necessary to use several resins with mutually exclusive solvents to consolidate some complex object. It use is 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 Cement can be used to stabilize material such as bone by impregnation. For dilutions purposes, Duco Cement has approximately .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 (formally called Plexiglass). There are many different formulation. In the past I have had good results with Elvacite 20/3. The glue is commonly made from sheets of Lucite. Even safety mask shields and motorcycle wind shields can be dissolved in solvents. The toxicity of the solvents restrict PMM resins from being widely used.

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

Grind, cut, drill a sheet of Lucite to get a cup of shavings -- approx same volume of solvent. Place in a jar and add 50% chloroform /50% toluene. <u>Caution heat is generated</u>. Add acetone to thin to correct viscosity.

The PMM resins have similar properties to PVA. PMM resins are stronger but have fewer solvents. Two solvents for PMM resins are chloroform and ethyl acetate. 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. In most instance the PMM adhesives are prepared from sheets of resin. 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 with viscosities ranging 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% 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 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 PVAl's to cross link in three to five years if exposed to strong light, dryness, and heat; especially temperatures over 100° C. If cross-linking occurs the resin becomes less soluble, but probably never becomes completely insoluble. Some conservators recommend that objects treated with PVAl be retreated 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 (ca. 125° F). 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 120°-150° F.

EPOXY RESINS

There are innumerable thermosetting epoxy resin on the market with many varied properties and special characteristics. Each conservator, through experience, has his 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, but this is not to say they do not have a use in conservation. In many instances, epoxies are required because nothing else has the necessary strength. They are excellent when a very strong, permanent bond is required. They 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 and follow the directions of the manufacturer on the recommended hardeners, mixtures and thicknesses. If mishandled, a considerable amount of exothermic heat can be generated.

These are just a few of the most commonly used adhesives/consolidants used in conservation that have a long, successful track record and are, therefore widely used for a wide variety of conservation purposes. Specific applications are discussed in the following sections.

BONE, IVORY, TEETH AND ANTLER

Approximately 70% 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 is ossein and it constitutes at least 30% of the total weight. It is often difficult to distinguish between bone and ivory unless examined microscopically. Bone is coarse grained with characteristic lacunae or voids while 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 archeological 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. Archeological bone and ivory can only be cleaned, strengthened and stabilized; satisfactory restoration is often impossible.

METHODS OF CONSERVATION

Removal of surface dirt from structurally sound bone/ivory

1. Wash with soap and water or alcohol. Use of alcohol will facilitate drying. Towel dry.
2. When washing with water, limit amount time in water.
3. Brush lightly with brushes and/or lightly scrape with wooden, plastic or metal tools. Dental tools are particularly serviceable for cleaning.

Structurally weak bone/ivory must be cleaned carefully and the cleaning method used is dictated by the specimen's condition.

Removal of soluble salts

Bone/ivory from a salty environment will invariably absorbs soluble salts that will crystalize 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 have to be removed to make the object stable. For faunal bone, it is usually not necessary to remove all the soluble salt. It is safer to rinse then in tap water until the chloride level in the material being treated equalizes with 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 (it matter little if it cracks) for artifacts it is recommended that they go from seawater to 75%seawater/25% fresh water (local tap water) to 50%seawater/50% fresh water to 25%seawater/75%fresh water to 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. Then deionized or distilled water is substituted until the soluble salt are removed or reaches a level deemed safe. For faunal bone it seldom necessary to go to the extra effort of rinsing them in deionized water. Rinsing them through the local tap water is, in most cases, sufficient.

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 which tests for the presence of sodium chloride.

When sodium chlorides are no longer present, one can be pretty sure -- but not absolutely sure -- that the bulk of the soluble salts have been removed. The conductivity meter measure 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% solution of Acryloid B-72. and then rinsed. The soluble salts will diffuse through the resin, although much more slowly, during a rinsing treatment.

     3. Dry bone/ivory in series of alcohol baths (50% alcohol/50% water, increasing the alcohol content of the baths to 90%, 100%, and a final bath of 100% alcohol) For teeth, and ivory, it is sometimes necessary to go through longer dehydration baths in order to insure that the surface of the material being treated does not elaminate or crack. For example going from a straight water bath to 95%water/5% ethanol (only water miscible solvents should be used), and then increasing each bath with an additional 5% ethanol, until the artifact is in straight ethanol, To be on the safe side the artifact is then placed in a second and even a third bath. The object can then be taken through 2 baths of acetone. In a few exceptionally critical cases, it may be advisable to take the object through at least 2 baths of diethyl ether. By this point, and in most case, after the object has been taken through 2 bath of acetone, one can be assured that all the water has been removed from the article and it should then be consolidated with a proper resin, to strengthen the object and to make is less susceptible to fluctuations in atmospheric humidity.

     4. Consolidate as discussed below.

Removal of insoluble salts and stains---CAUTION!

In all cases, the question should be asked, is it necessary to remove the insoluble salts. If the answer is, Yes, then some means of mechanical removal using picks, or other tools is always recommend over any chemical treatment, for inevitably some damage is done to bone and related material when stains and insoluble salts are removed by chemical means. When chemical means are utilized, always make sure that the material is thoroughly wetted with water before any chemical are applied. If this is done, the chemical is not absorbed and the treating chemical stays on the surface.

Calcium carbonate
     Structurally sound bone can be immersed in 5% to 10% solutions of hydrochloric acid, or formic acid. Monitor process closely.
Iron stains
     5-10% oxalic acid has been used to remove iron stain stains from bone. Also 5% ammonium citrate by itself and 5% ammonium citrate followed by 5% oxalic acid for stubborn stains.
Sulfide stains
     5-10% hydrogen peroxide is used. Stained bone can 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 acid 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 and then all the steps repeated until the area is cleaned.

It is then necessary to rinse in water to remove all residue of the treating chemical, dry in alcohol baths, and then consolidate with a resin as describe below.

Consolidation

1. The resin solutions must be diluted to decrease the viscosity and increase its ability to penetrate the material being treated. A 5% to 10% solution of a suitable transparent synthetic resin may be used. When large amounts of faunal bone needs to be consolidated, I have found that the water soluble, Elmer's Glue All works quite satisfactorily. When bone, ivory and teeth are treated, usually, slow dehydration in organic solvents, as described in I above, then consolidation with PVA (V7) or Acryloid B-72 is recommended. PVA with a viscosity of V7 is recommended, because the molecules are smaller and are able to penetrate denser material, yet the resin has enough strength to mechanically strengthen any object treated with it. For less dense material and a lot of faunal bone, PVA with a viscosity of V15 is recommended since it is a stronger, general purpose resin.

2. For surface consolidation apply resin by brush. Best results can be obtained by applying a light coat of resin, let dry and then apply a second coat. Such a procedure should be repeated several times in order to get sufficient resin absorbed by the material to accomplish consolidation. Repeated applications are necessary.

Complete immersion in the consolidating resin gives the best results. Complete immersion in a vacuum is even better.

3. Reconstruction or Gluing

The glue used to glue bone, ivory, or teeth together depends upon It depends, to some degree, on how it was treated. what the material being glued is It the bone or related material has been consolidated with a resin, then a thick viscous mixture of the same resin should be use. PVA with a viscosity of V25, Acryloid B-72, PVA emulsions such as Bull Dog, and in some cases Elmer's Glue All make serviceable glues.

SEEDS AND PLANT MATERIAL

The miscellaneous seeds and plant material are, for all intent and purposed treated in much the same way, if not the exact same way, as described above for bone and related material. Once recovered, it necessary to rinse them to remove any soluble salts that may be present, mechanically clean the material requiring it, chemically treating the material, rinsing out the treating chemical, then drying the material in a series of water/water miscible alcohol baths, and then consolidating the material.

SUMMARY

The conservation of waterlogged bone and ivory, as well as most plant material, is a straight forward process. Seldom are there any complex problems except in cases where the bone is so badly deteriorated that it is can not 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 can damage the bone if care is not taken. The only equipment required are the right size containers, a selection of resins, and a variety of solvents.

POTTERY CONSERVATION

Generally pottery recovered from marine sites requires only minimal treatment since earthenware survives well in marine environments (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 temperature that they are impervious to liquids, and thus do not absorb soluble salts from their archaeological environment and it is not necessary to take then through long rinses to remove soluble salts. However, in some instances with certain kinds of stoneware and porcelain, glazes are applied in subsequent firings and sometimes salts get between the glaze and the body. If these salts are not removed the glaze can be flake off. So, even caution has to be exercised with stoneware and porcelain. Well fired pottery need only be washed in a mild detergent, scrubbing the edges and surfaces with a soft brush. Care should be taken not to remove traces of food, paint, pigments, and 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, badly 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 will be entrapped by the encrustation forming around the metal, especially iron. The soluble salts (chlorides, phosphates and nitrates) are potentially the most dangerous and they must be removed in order for the pottery 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 can 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 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 over flows into a second vat, and then another, etc. in order to waste the minimum amount of water, especially if you are using deionized water. One should always keep in mind that very simple procedures, such as putting soluble salt laden sherds in a mesh bag and simply place them in the reservoir of a toilet. Innumerable volunteers assist you each day in changing the water and the salt content in the sherd quickly equalizes with that contained in the supply water. Then, if necessary, the rinsing can then be continued in several baths of D. I. 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 can be consolidated first with Acryloid B-72 (formerly soluble nylon was used), then rinsed. Since Acryloid B-72 is somewhat water permeable, it will allow the salts to diffuse out. The diffusion process will be considerably slower if treated with any consolidant such as Acryloid B-72 or PVA.

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 tool. Dental burrs and pneumatic air chisels are also quite useful - especially the latter.

The insoluble salts can 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 make sure that the paste is thoroughly wetted so the acid will not be absorbed into the paste. Although 10-20% nitric acid can be used to remove calcareous concretion, it is potentially the most damaging acid of the three. More care should be exercised when it is used; dilute nitric acid dissolves lead (glazes). In most cases 10-20% hydrochloric acid is safer than nitric acid to clean glazed pottery. Glazed pottery from marine sites is often cleaned of calcareous encrustation with 10-20% hydrochloric acid. The sherds are left immersed until all gas evolution ceases--usually less than an hour--and repeated if necessary. Care must be exercised, for hydrochloric acid can discolor glazes, especially lead glazes which will turn milky. The samples are then washed thoroughly in tap water; then immersed in 10% oxalic acid (very toxic) for 10-20 hours to remove iron stains. A thorough rinsing follows and the sherds are then dried. It is imperative that pottery with a carbonate temper (shell, calcium carbonate) not be in immersed in hydrochloric or nitric acid for 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 sherd should always be pre-wetted by soaking in water and then apply the acid locally on the surface with a cotton swab or by drops. The excess acid is immediately removed when the effervescing action stops by either wiping the area or rinsing under running water to remove the acid. Earthenware and terra cotta often contain iron oxides, are more porous and more prone to deteriorate when treated with these acids; therefore acid treatments should be used with some discretion.

Useful chemicals for removing calcareous deposits from ceramics are ethylene-diaminetetraacetic acid (EDTA). A 5% 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. Generally speaking, 5% EDTA-tetra sodium is recommended. It is a slow but effective treatment.

Soaking calcareous encrusted sherds in a 5% 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 3 drops of 1% barium chloride solution. If a white precipitate forms, it indicates the presence of sulfates (Plenderleith and Werner 1971). These can be dissolved slowly by immersing in 20% nitric acid. As the sulfates dissolve, sulfuric acid is produced which cancels out the reaction of the nitric acid. The nitric acid has to be changed often. This technique is not generally recommended. 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% oxalic acid applied locally with cotton swabs on the surface of pre-wetted pottery. This is generally a successful method of removing iron stains from stoneware and earthenware ceramics although a small amount of the iron in the paste might be removed. A 5% 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 & Pearson 1975; Pearson 1987d). The di-sodium 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% by volume hydrogen peroxide solution until the stains disappear. The time required to remove the stains ranges from just a few second to several hours. No rinsing is required after treating with hydrogen peroxide. Hydrogen peroxide can be applied directly to sherds that have been treated with nylon. The hydrogen peroxide permeates 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 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 Glue) 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 PVA.

GENERAL STEPS FOR THE REMOVAL OF INSOLUBLE SALTS AND STAIN FROM POTTERY

1. Thoroughly wet the pottery.
2. For strong sturdy pottery, immerse in 10-20% nitric or hydrochloric acid until effervescing ceases. Hydrochloric acid is preferable for glazed pottery. Glazed, friable or carbonate tempered sherds should be cleaned with cotton swabs or by applying concentrated acid, drop by drop on the pottery. 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 in running water to remove excess acid.
4. Remove iron oxide stains with 10% oxalic acid or 5% EDTA and rinse thoroughly.
5. Remove iron sulfide and organic stains by immersing in 10-25% by volume hydrogen peroxide.
6. For marine recovered earthenware, it is advisable to thoroughly consolidate them in a dilute solution of PVA or Acryloid B-72 to consolidate them. This is especially important if you are going to reconstruct the piece.

No discussion is presented here on ceramic reconstruction.

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 of the 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%. Do not use any acids on any of the sedimentary rocks (e.g. limestone, marble, sandstone, etc.)- 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 they are found encrusted, the most difficult part of the conservation is the removal of the adhering material without damaging the paste or glaze. For this reason, mechanical cleaning techniques are preferred, but HCl acid is used with some regularity to remove calcareous encrustation. The soluble salts that are invariably present in any porous material recovered from marine sites are removed by rinsing in water. In most instances, tap water is all that is needed, but to the use of D.I. 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 with out adversely affecting the ceramic. If the decision is made to remove the more difficult stains, the material should be thoroughly wetted with water before immersing or applying the chemicals to remove the stains. Monitor the process carefully and rinse thorough in water after using any chemicals. After treating allow the potter to air dry. Solvent drying is not required, but it can be used in desired. After drying, consolidate by completely immersing in a dilute solution of PVA or Acryloid B-72. Any sherds or reconstructible vessel can them be reconstructed.

Equipment required to conserve ceramics include appropriate size vats, tap water, D.I. water, acetone, ethanol, PVA, Acryloid B-72, hydrogen peroxide, HCl, EDTA, dental picks, and a pneumatic chisel is very useful.

GLASS CONSERVATION

Glass is usually the most stable of archaeological materials, but it can undergo some complex disintegration - especially 17th-century glass. Ideally, glass should consist of 70-74% silica, 16-22% alkali or soda ash (sodium carbonate) or potash (potassium carbonate, usually derived from wood ash) and 5-10% flux [lime (calcium oxide). Soda-lime glass is the most common glass throughout the history of glass making and the modern equivalent is 74% SiO^2, 16% Na_2CO_3, and 55 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 inland 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 is 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. The 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 (calcium oxide is used as a stabilizer) is used in the mixture, for the glass will be especially susceptible to attack by moisture. RH higher than 40% can be dangerous. If old glass has 20%-30% sodium or potassium it may begin to weep and break down -- this is called glass disease.

In all glass, the sodium and potassium oxides in glass are hygroscopic, therefore, the surface of the glass absorbs moisture from the air. The absorbed moisture and exposure to carbon dioxide causes the $Na0_2$ 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% and above (and in some cases as low as 20% RH), drops of moisture appear on the glass surface. In water, especially salt water, the Na and K carbonates in unstable glass can leach out leaving only a fragile, porous hydrated silica (SiO_2) network. This causes the glass to craze, crack, flake and pit giving the glass a frosty appearing surface. In some cases there is an actual separation of layers of glass from the body. Fortunately, these problems are not commonly encountered in 19th-century and later glass. When problems are encountered it is on types not expected to be encountered on sites dating from this period. Pearson (1987b. 1987d) discusses glass deteriorations 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 & 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 have an iridescent film which is formed by the leached silica layers. The alkali which leaches 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 as the alkali leaches out. 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. Normally 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 advise that the only treatment should be to keep the glass in low relative humidities so the glass does not have any moisture to react with. While a RH range of 40% to 55% 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.

When it comes to 18th-20th-century sites, we are on much more secure ground, for most, if not all, of the glass that might be found during this period was produced from a stable glass formulation, and there is not likely to be any problem glass present, other than normal devitrification. Thus, 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 envisioned. The main problems will be related to gluing pieces together and possibly some restorations. All the problems likely to be encountered are discussed thoroughly in <u>Conservation of Glass</u> (Newton & Davidson 1989).

While, glass that is susceptible to weeping because of unstable glass formulations, is not expected, when it is encountered is treated in different ways, but the technique described by Plenderleith & Werner (1971:345) is representative of the treatments often recommended.

    1. Wash thoroughly in running tap water.

    2. Soak in distilled water.

    3. Dry in 2 baths of alcohol to dry quickly. 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.

    4. If applicable, apply an organic lacquer-- PVA, Acryloid B-72 to impede the disintegration.

    5. For assurance, store in a dry environment with the relative humidity no higher than 40%, others say 20%-30% is ideal. The Corning Glass Museum keeps incipient crizzled glass stored at 45-55% RH. RH 42% 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 results in layers of opaque glass, which can be removed with various acid treatments. The decision to remove surface corrosion products, which often mask the color of the glass, has to be made on a case by case basis. Removal of corrosion products, which can reveal the true color of the glass as it significantly reduces the thickness of the walls. At the same time, it can sometimes weaken the glass object significantly. Indiscriminate removal of surface corrosion products can weaken, blur or alter surface details. The corrosion layers of a glass object can 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 usually becomes hydrated through time, especially soda glass. It can be expected to be present on any glass after a length of time. Devitrification occurs when the surface of the glass becomes partly

crystalline as it adsorbs moisture from the atmosphere -- and from being submerged in water. 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 surface, a coating of PVT or Acryloid B-72 is applied. Any of these surface adhesives will smooth out the irregularities in the pitted, crazed surface of the glass, making it appear more transparent, by filling in the small cracks and forming optical bridges. 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 will come from marine sites and anaerobic sites with a very dense black film on its surfaces. A 10-15% solution of hydrogen peroxide 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, but optically-clear epoxy resins are generally used as they adhere to the smooth, non-porous glass more readily, they dry clearer and shrink less than the solvent resins and are, therefore, less noticeable and the bonds are stronger. 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" 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 artists brush to permanently glue 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 these problems are adequately discussed in greater detail in *Conservation of Glass* (Newton and Davison 1989).

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

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

WOOD CONSERVATION

Schematic diagram of hardwood and softwood illustrating the relative appearance of vessels and tracheids.

Being of organic origin, wood normally decays under combined biological and chemical attack when buried in the ground. It can, however, survive prolonged exposure to extremes of dryness or wetness. In shipwreck sites, the wooden components of the hull and small artifacts of wood often survive in good condition, although thoroughly waterlogged. The mechanisms of organic deterioration are succinctly presented in Florian (1987). Successful conservation depends upon a knowledge of wood structure and types. Trees are divided into two broad categories, hardwoods and softwoods. Hardwoods are in a taxonomic grouping called Angiosperms and which refers to broadleaf trees which are usually deciduous. They are referred to as porous woods because they have vessel pores. Oak and birch are typical examples of a hardwood. Softwoods, or Gynmosperms are needle bearing trees or conifers. They are called nonporous because they lack vessel pores. Pines are a typical example of a softwood. It is very important to know the category of wood and in many instances, it is critical that one knows the species in order to successfully conserve the waterlogged wood.

Generally speaking, freshly cut, sound wood will, through water loss, shrink ca. 3-6% radially, 5-10% tangentially, and - 0.5% longitudinally. Oak shrinks 4% radially and 8% tangentially when air dried after cutting, while waterlogged oak can shrink 12% radially and ca. 24% tangentially. Proper conservation will control the amount of shrinkage. 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).

The manner in which a board was originally sawn from the log will have an effect on how it is going to shrink after undergoing any conservation treatment. In fact, the method of sawing can make it very difficult to conserve the wood without cracking and warping occurring after treatment.

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, it dries with less tendency to warp. Because, flat or plain sawn lumber has similar proportions of radial and tangential surfaces with arched grain patterns, it tends to warp easily.

In anaerobic waterlogged environments there are profound chemical changes and alterations in the composition and microstructure of woods, resulting in great loss of strength while retaining overall shape and form. In other environments wood decays from; 1) physical action (changes in temperature, fluctuations in relative humidity, etc.), 2) insect attack, and 3) fungal decay. By far fungal decay, along with anaerobic bacteria, plays the largest role in the breakdown of wood. Fungal decay can be eliminated as long as the wood is kept in a relative humidity of less than 65%.

WATERLOGGED WOOD

The tannin in wood protects it from degradation, and allows some wood, especially those with high tannin contents, to survive in good condition. In all wood, after long periods in wet soil, peat bogs and marine sites, bacterial action causes a degradation of the cellulosic components of cell walls. In general, water soluble substances such as starch and sugar disappear from wood first, along with mineral salts, coloring agents, tanning matters and other bonding materials. In time, through hydrolysis, cellulose in the cell walls disintegrates, leaving 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 increases and the wood becomes more porous and permeable to water. All the deteriorated parts, 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. As long as the waterlogged wood objects are kept wet they will retain their shape. If the wood is exposed to the air, the excess water evaporates and the resulting the surface tension forces of the evaporating water causes the weakened cell walls to collapse, causing considerable shrinkage and distortion. As mentioned above, freshly cut, sound wood will, through water loss, shrink ca. 3-6% radially, 5-10% tangentially, and - 0.5% longitudinally. Oak shrinks 4% radially and 8% tangentially when air dried after cutting, while waterlogged oak can shrink 12% radially and ca. 24% tangentially. 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 formula:

$$\% H_2O = \frac{\text{weight of wet wood - weight of oven dried wood}}{\text{weight of oven dried wood}} \times 100$$

Anything greater than 200% is considered to be degraded, and it is not uncommon to find wood that has more than 500% water. 1000% water is not uncommon. Waterlogged wood is often classed according to the amount of water is contains.

Class I, over 400% H_2O

Class II 185-400% H_2O

Class III less than 185% H_2O

The Class III hardwoods are the most difficult to conserve.

WATERLOGGED WOOD CONSERVATION

The conservation of waterlogged wood is a two-fold problem that involves (1) incorporation of a material into the wood which will consolidate and confer mechanical strength to the wood as the water is removed and (2) the removal of the excess water by a method which will prevent any shrinkage or distortion of the wood. All the bulking treatments that use PEG or sugar are examples of the first, while solvent drying and freeze-drying are examples of the last. The most common techniques for treating waterlogged wood are discussed below. In all the treatments discussed below, if the wood was recovered from a salt water environment, it is necessary that the bulk of the soluble salts be removed, otherwise, they will cause a white bloom on the conserved wood and will can adversely affect any remaining iron components in the wood and other material in the same room or environment where the treated wood is stored.

Polyethylene Glycol (PEG) Method

The polyethylene glycol is a synthetic materials that has the generalized formula $H_2OCH (CH_2OH_2)_n CH_2OH$. The low molecular weights (300 - 600) are liquids, the intermediate members are semi-liquids or have the consistency of Vaseline (1000-1500) and the higher molecular weights (3250-6000) are wax-like materials. The various PEGs are now designated by their average molecular weight, but this only came about in recent years and the names have been changed. 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 alcohol (ethanol, methanol, isopropanol), as well as water. PEG 4000, which has a melting point of 53-55° C (ca. 125° F), was once the most commonly used because it was the least hygroscopic, but its large molecules prevent it from penetrating dense wood. Now PEG 1500 and 540 blends are more commonly used.

The development of PEG as a conservation process was the first reliable method for treating waterlogged wood that was simple to carry out. The excess water in wood is removed and the wood is bulked in one operation. The waterlogged object is cleaned to remove all dirt on the surface and is placed in a ventilated vat where the temperature is gradually increased until, after a period of days to weeks, it has reached 60° C (140° F). During this time the PEG percentage of the solution increases as the solvent (water or alcohol) evaporates of by adding increments of PEG. In the process, the wax slowly diffuses into the wood, displacing the water. At the end of the operation, the wooden object is covered with molten 70- 100% PEG, depending upon the nature of the wood. The object is then removed, the excess wax wiped off and allowed to cool. When cooled, any excess wax on the surface is removed with a hot air gun or with hot water. When carrying out this method using a container in which the PEG concentration is increased by evaporation of the solvent, it is important that the dimensions of the container be such that the starting quantity of wax present will be more than enough to cover the object at the end of the process.

This method of treating waterlogged wood is only appropriate for small objects, and thus is seldom used in practice. In most instances, the wood to be treated is placed in a vat of water and a small increment of PEG (usually 1-5%) is added to the water which is kept heated to approximately 52° C (125° F). Over a period of months (even years), as the PEG replace the water in the wood, the PEG percentage is increased in small increments until a minimum concentration of 70% is reached. If at least 70% PEG is reached, the wood will remain stable, and in some instances, if a percentage greater than 70% is reached, it can draw the water out of well-preserved heartwood without replacing it with PEG causing the wood to collapse. The size of the PEG increments is dependent upon the condition, size, and specie of the wood being treated.

As mentioned above, PEG is soluble in both water and various alcohol. For large objects, water is always used, because it is the cheaper procedure. When using PEG in water it is necessary to use a fungicide such as Dowicide 1 (ortho phenylphenol) , 0.1% of weight of PEG used. On the Wasa, a fungicide consisting of 7 parts boric acid and 3 parts sodium borate was used -- 1% of weight of PEG (Barkman 1975:82). For smaller objects, it is often more convenient to use alcohol, such as ethanol. The treatment is considerably reduced, and it results in a wood that is lighter in weight as well as lighter in color. When alcohol is used, it is best to dehydrate the wood in at least three baths of ethanol before placing it in the first PEG mixture. It is not critical that all the water be removed however, for since PEG is soluble in both water and alcohol, the presence of water in the wood does not present a problem. Alcohol treatments save time, but obviously increase the cost and there is always the inherent danger of heating alcohol mixtures. Since all the alcohols are fungicide, no biocide is required when using them in PEG mixtures.

An important consideration that comes into play when PEG is used to conserve wood is the fact that PEG is corrosive to all metals, but especially with iron. For that reason, PEG treatments should not be used on wood that is going to be in contact with any metal, especially iron. Therefore, you would not want to use it on a gun stock that was going to be put back on the iron barrel after treatments, because the PEG would or could then cause the iron to start corroding.

It usually a simple matter to rig up any number of ways to treat the smaller waterlogged wood artifacts in the laboratory. Small vats (metal or glass) are readily available and they can be placed in a thermostatically controlled oven to maintain the correct temperature and only a small amount of PEG is required. In contrast, when large pieces of wood are treated, there is a substantial investment in PEG (sometimes measured in the tons) and a substantial vat has to be constructed that can be heated and the contents circulated with pumps. It is a major investment in both equipment and chemicals when a laboratory elects to get in the business of conserving large wood pieces. Quite often this capacity is the most costly investment of the laboratory. In addition, between treatments, the PEG has to be kept stored.

As am example of cost, if a single piece of wood 6 feet long and 1 foot wide was treated. While a stainless steel vat would be preferred, because PEG is corrosive to all metals, but most laboratories get by with using mild steel vats painted with a good epoxy paint. The cost of a mild steel vat 8 feet long, 2 feet wide, and 2 feet deep would cost approximately $400.00. A vat this size will hold 32 cubic feet, or 1984 pounds of water, and approximately the same amount of PEG. a ton of PEG costs approximately $2000. Either strip heaters or preferably a in-line heated pump is required to keep the solution heated (otherwise it solidifies when a 20-30% concentration is reached). A Chromalox circulation heater will cost approximately $900.00. The other pumps to circulate the solution will cost around $200.00. This comes to an investment of $3500.00 for equipment and PEG. Of the methods discussed in this section, any of the various PEG treatments with water is the most utilized because of its reliability and low cost.

SUCROSE METHOD

The sucrose (sugar) method of conserving waterlogged wood was developed as an alternative to more expensive methods (Parrent 1983, 1985). In practice the procedure is for all intent and purpose, 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 clean the following procedure is recommended:

1. Prepare a solution with a sufficiently low sucrose (1-5%) 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% 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% solution is achieved increase the sugar concentration by 1% to 10%.
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, i.e., 1% to 5% until a concentration of 50% is reached. Then the solution can be increased in 10% 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% and the wood has equalized at this concentration.
4. If deemed 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 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. <u>Slow, controlled drying and adjustment to the prevailing atmospheric conditions,</u> as is the case in all the wood treatment described here, will maximize the success of the overall treatment.
6. Store the wood under conditions of less than 70% humidity if possible. The wood should not be subjected to humidity over 80% because of the possibility of condensation forming on the wood; this could leach out the sugar.

If sugar is selected as the treating medium, I have found that refined white sugar (pure sucrose) should be used. The brownish colored, coarse grained unrefined sugar (Type A sugar) should be avoided for wood treated in it is much more hygroscopic than wood treated in refined, white sugar. Every time the relative humidity rises, the surfaces of wood treated in unrefined sugar become wet. This hygroscopicity is analogous to that encountered when using the medium molecular weight PEG's. 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 thus treated 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 it is very characteristic for small hair line cracks to form on the surface of the wood. The treatment will produce dimensionally stable wood, and is a viable alternative when the over-all cost is a major consideration. The required equipment is the same as discussed for PEG. The only difference being the cost of sucrose as opposed to PEG. Sucrose, from a producer, is in the range of 10 to 15$^{¢}$ as opposed to approximately $1.00 for PEG (when purchased in bulk) otherwise the price increases substantially for both.

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 such as oak where the higher molecular weight PEG could not penetrate (McKerrel and Varanyi 1972; Bryce, McKerrell, and Varanyi 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 3 successive baths of acetone. Objects 5-10 cm. thick require about 4 days in each acetone bath. Objects less than 5 cm. thick require about 2 days in each acetone bath. It is important that all the water be remove, for the water is incompatible with the 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, the dust is annoying and it 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% rosin. To insure a saturated solution, an excess of rosin should be placed in the container so that there is a thick viscous layer of rosin in the bottom of the container. The object being treated should be suspended or supported above this thick undissolved rosin. Objects 5-10 cm.

thick-leave in the solution for 4 weeks; objects less than 5 cm. thick-leave in the solution for 2 weeks. These times are only rough approximations and each piece of wood should be determined based on its own characteristics.

4. Remove from rosin solution and wipe off excess rosin with acetone wet rags. This treatment is feasible only for small objects, because of the cost and danger of using the organic solvent. The treatment has also been successfully applied at room temperatures and using solvents such as isopropanol and any of the other alcohols which are less flammable. The HCL pretreatment is optional, and is often eliminated because of the potential damage to the object.

In some cases, when conserving very well preserved hardwood, the conservator might consider submerging the wood in a 10% muriatic acid (HCL) bath after washing the object and before dehydrating the wood in step 3. To make the bath, mix 1 vol. HCL to 9 vol. water, in conservation terms, this is a 10% solution. It is very variable as to how lone any given piece needs to stay in the acid, but as a rough guide, objects 5-10 cm. thick, leave in the acid for 4 days, objects less then 5 cm., leave in 2 days. Treatment with HCL is supposed to bleach the wood to a more natural or original color, but I have found that the bleaching is only temporary and rarely affects the final color of the treated piece. The HCL treatment improves the penetration of the resin into the wood by breaking down the organic acids in the wood. Caution must be exercised for the HCL treatment can cause the treated piece to have a checked surface and be more subject to cracking after the conservation treatment is completed. Treatment with HCL can also be used to improve the penetration of PEG into wood. Caution is advised for it has been noticed that the surface of the wood tend to checks (have numerous small cracks on the surface) more often and shrink more when treated with HCL. If a HCL pretreatment is used, it is necessary to rinse the wood in running water for 3-5 days to thoroughly remove all traces of the HCL before start step # 2 above.

The advantages of the acetone/rosin treatment include the fact that treated wood is light in weight, it is dry, it can be glued and repaired easily, it is strong, and it can be used on compound wood and metal objects, for the rosin does not react with any of the metals. Thus, it is considered by many to be the treatment of choice for all composite wood/metal artifacts. Disadvantages include high costs, because of the organic solvents, and the flammability of the acetone. In cases where it is necessary to reconstruct a composite piece, and where it may be necessary to flex a piece of wood, acetone/rosin would not be an ideal choice because the treated wood will splinter and break if it is flexed too much.

Over the years, I have had the best success rate with the acetone/rosin treatment. Generally the only problems that have resulted from using acetone/rosin have occurred when an old solution was used and the acetone in the solution had adsorbed a lot 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, especially for small, important pieces. This treatment has one of the better success records and produces the most dimensionally stabilized wood after the PEG 400 and 540 Blend treatments, but without the hygroscopic problems of the PEG (Grattan 1982b).

In practice, ethanol is use as often as a solvent for the rosin as acetone (especially when treatment is carried out in a PVC pipe. Also room temperature treatments, both in acetone and isopropanol are commonly employed. If room temperature treatments are used, the treatment time is increased considerably to insure complete saturation with the rosin solution.

Because solvents are used, this technique is employed mainly for small wood artifacts, although a few laboratories have the facilities to treat objects several feet long. Colophony cost $108.45 for 25 pounds or $4.34 a pound. Acetone and other alcohols, all run about $2.90 a gallon when purchased in bulk.

Alcohol-Ether Method

This method is similar to the process used for drying out biological specimens. If necessary, the wood should be cleaned. The waterlogged object is first immersed in successive baths of alcohol until all the water has been replace by the alcohol. Isopropanol or ethanol is usually used. This is followed by successive baths of acetone. If deemed 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 so that the ether volatilizes rapidly. 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 necessary, 10-20% dammar resin, colophony rosin or a mixture of the two can be dissolved in the final bath of ether so that the resin is deposited in the pores of the wood to act as a consolidant. Alternatively PVA can be used on some pieces. The resins consolidate the wood, but more importantly, they seal it off so that it is not as subject to warping due to changes in the relative humidity.

This method has proved to very successful, producing a very natural looking, light (weight & color) wood. It is only economically feasible for the treatment of small objects. The alcohols and especially the ether are highly flammable and extreme caution should taken. The dehydration process can be very effective, but the alcohols and ether must be water free. For many objects, a dehydration of only alcohol and acetone is effective.

Camphor-Alcohol Method

This treatment is analogous to the alcohol-ether method. The success of this treatment depends on replacing all the water with a water miscible alcohol, and then replacing the alcohol with camphor, which results in all the cavities and cell walls being filled with camphor. The camphor 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, light weight and light colored wood. The camphor can be dissolved in any of the alcohols. In essence, this treatment is a dehydration method, as describe above, but with a temporary bulking agent added until it sublimates.

The following procedure is recommended:

1. Wash object thoroughly and with care.
2. Dehydrate the specimen in a series of alcohol baths. Start with a 50% alcohol, 50% water bath (50%/50%), then 75%/25%, 90%/10%, and finally 100% alcohol. This is the most conservative procedure and, in practice, the exact strength of the alcohol baths can vary. The dehydration process depends on the condition of the object to be treated. As originally described, the wood was dehydrated in methanol (cumulative poison) so either ethanol or isopropanol can be substituted.
3. Immerse the object in a 95% alcohol/5% camphor solution. Accurately weigh the object after it has been dehydrated. Leave the specimen in the 5% camphor solution until the piece stops gaining weight. Check the progress by weighing daily. Each time the weight levels off, add 5% camphor to the solution. Make 5% increments until a concentration of 75-80% camphor is achieved. The 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 the crystallized camphor in the cell walls. Over a period of months the camphor will vaporize by sublimation, exerting no surface tension on the cell walls. 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. This method comes very highly recommended, but like the alcohol-ether method, it is only economically feasible for treating small specimens. Also, it is highly flammable.

Freeze Drying of Waterlogged Wood

Freeze drying is used with some regularity of small pieces of wood, but the only limitation is access to the proper size freeze drying container Ambrose 1970, 1975; Rosenquist 1975, Watson 1982; McCawley, Grattan and Cook 1982). In the past the main problems that presented themselves was the tendency for the surface of the wood to check and crack. This is caused by the water freezing, and the ice crystals expand and expand and damage the cell walls. Ambrose (1970) found that if the wood was pre-treated by soaking it in a 10% solution of PEG 400, until it was saturated, then it the formation of ice crystals is essentially eliminated. In more recent years, pre-treating in 10% PEG 400 before freezing the wood has become a standard part of freeze drying wood, just as it has become for leather also. More recently, Watson (1987:274-275) soaking in 20% PEG 400, "rather than the 10% recommended by Ambrose in order to prevent bacterial slime from forming in the soaking bath. At concentrations above 20% micro-organisms are dehydrated by osmosis and cannot survive." If you use a PEG solution of less than 20%, a fungicide such as 1% borax/boric acid or Dowicide 1, or other fungicide should be mixed with the PEG solution to stop any slime or mold from growing in the solution during the soaking.

The addition of PEG, in addition to inhibiting the size of the ice crystals that form during the freezing, act as a humicant after treatment and prevents the wood from undergoing excessive shrinkage. Watson (1987) goes on to recommend using 20% PEG 400 for little degraded wood, 10% PEG 400 + 15% PEG 4000 for more degraded pieces, and for more degraded pieces the PEG 4000 can be increased to as high as 25%, but the treatment time is increased when PEG 4000 is used. After absorbing all the PEG solution, the wood is then frozen in a domestic freezer. After freezing, it is best to place the wood in a freeze-drying chamber at a temperature of -32° to -40° C and a vacuum is applied after the temperature of the wood reaches -25° C. During the process the frozen ice crystal 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 %. Freeze drying as described here and in the leather section 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 acetone with dry ice (frozen CO_2) in it. Some acceptable results has been had using non-vacuum freeze drying in a domestic freezer chest, especially the frost free freezers. When a domestic freezer is used, the wood is place in the freezer, after pre-treating in the appropriate PEG solution and left there until it is dried. In this non-vacuum process, the treatment time is much longer, in terms of months, as opposed to weeks in the vacuum freezer driers (McCawley, Grattan, and Cook 1982).

Of the treatments discussed here, freeze-drying is the most expensive. The cheapest freeze drier on the market is right at $5000.00 and with that you have the capacity to treat a hand size object. The only chemical costs is for the PEG 400 used to pretreat the wood and the amount required to treat a hand-size artifacts is negligible. Because of the size limitations, 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

For the past three years, Dr. C. Wayne Smith of the Conservation 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. We have successfully conserved waterlogged wood, glass, leather, woven basketry, cork and notably, artifacts such as corn cobs, which have been nearly impossible to conserve maintaining the diagnostic features of the samples. We have also had great success in conserving animal hides, biological tissues, archaeological and histological bone samples, as well as a range of applications that are useful for medical and forensic investigations. Electron microscopic and chemical analysis of organic samples that 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 other universities as well as in museum and artifact conservation, archival work and in industrial applications.

The use of polymerized silicone oils for the stabilization and consolidation of anatomical and biological specimens has nearly unlimited possibilities. Organic samples conserved using siloxane polymers suffer less cellular damage and structural disfigurement than samples stored in formalin, formaldehyde and alcohol. These same samples are more durable, and the absence of noxious chemicals makes them more attractive and safe for hands-on study. Acquiring microtome sections of silicone bulked specimens for microscopic analysis is easier for most organic specimens since the stabile nature of polymer treated specimens ensures that there is less stress and distortion caused by the sectioning process.

The goals of research at CRL have expanded to include continuing research on the development of areas of application for silicone bulking as well as defining new areas of application and research. Currently, Our silicone bulking processes have immediate applications in laboratories and facilities at Texas A&M University as well as other major educational and scientific institutions.

In all cases, the long-term best interest of an artifact should be the main concern when considering a conservation strategy. Too often, however, the diagnostic attributes of artifacts are compromised and lost because a conservator is forced to choose a less-than satisfactory process, due to cost constraints or lack of experience. More artifacts are lost due to these short-falls than all other reasons. Neglect also claims many artifacts. Failure to design adequate conservation strategies takes its toll amongst inexperienced conservators and adherence to dogmatic ideals can also place stresses on the well being of an artifact assemblage. In recent years, I have seen situations where conservators have insisted on using traditional processes to conserve glass beads that yielded poor results, simply because they believed that the issue of reversibility was more important than successfully conserving what has become a nearly depleted assemblage. Common sense appears to be one of the missing ingredients from the conservator's tool kit.

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. To the best of my knowledge, it is absolutely 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, making complete removal of this polymer impossible. In addition to chemically bonding, additional PEG will simply be trapped in cellular voids, and therefore, remain in the wood. Clearly, even the best of processes in

treating wood with PEG causes intracellular damage during treatment. In essence, the process of conserving the wood can 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 retreating heavily waterlogged damaged timbers causes more damage than should be desirable. Too often, the theoretical state of reversibility of an artifact outweighs important issues including the real potential for successful 100% reversibility, degree of degradation, effects of attempted treatment reversal and best interest of the artifact. In contrast, our new processes for treating even heavily waterlogged damaged wood do not cause the cellular distortion that has been associated with PEG treatments. Notably, 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, we have shown that to some degree or another, silicone and polymer treatment processes are reversible. In reality however, we consider the potential for loss of diagnostic attributes to be too high, suggesting that a great deal of research needs to be completed in the development and 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 addresses 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. It has become common knowledge that over time, PEG treated timbers and other artifacts tend to warp and become unstable as the water miscibility of PEG allows the intra-cellular flow of PEG to distort and eventually, escape to the surfaces of the artifact. Simply put, even in very controlled environment, PEG breaks down. Our research has helped us understand new ways to remove a portion of the unstable PEG and re-constitute the remaining bonded PEG into a more stable bulking material. The technology we use for this processing is polymer technology - without the polymer.

Addressing the issues of life expectancy of treated artifacts is another area in which the benefits of conventional processes have been overstated. 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.

Longevity of silicone and polymer processes is not an issue. Through extensive testing and nearly twenty-five years of data collected by the silicone and polymer industries, we know that the minimum half life of the polymers we use in conservation is at least two hundred 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 site (1300BC) is approximately twenty minutes. Once completed, the beads require only a few hours of uninterrupted curation 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. Our current ability to rework PEG in waterlogged wood is one such example. Research into the use of silicones and polymers for the preservation of archaeological materials is a reality. So too are the new technologies that we can foresee in the near future. We are not suggesting that silicones are the panacea for all conservation needs. We are suggesting 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 simply an additional set of tools in the conservator's tool kit. Our own research has indicated that the following decades will hold exciting new

advances in the science of archaeological conservation. Conservation sciences we feel, have a responsibility to seek out, define and refine tomorrow's technologies.

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

1. Take waterlogged wood and place directly in a bath of ethanol and hold under a vacuum for approximately one hour.
2. Place the dried wood into a bath of acetone and hold under vacuum for approximately one hour.
3. Remove wood and place it in SFD-1 silicone oil that has had 4% Isobutyltrimethoxysilane added to it. The isobutyltrimethoxysilane is a cross-linker that sets the silicone oil up for curing in the nest steps. Keep wood submerged in this mixture under vacuum over night.
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 over 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 FASCAST and the vapors causes the silicone oil to cure in the wood, stabilizing it.

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 that some other treated woods do. Still, it must be kept in mind that this treatment is not reversible, but for that matter most of the other treatment are not either.

CONCLUSION

There are several other treatments that can be used for treating waterlogged wood, such as bulking with paraffin in a solution of hexane, but they are not extensively used. What is important to know, is that the problems of conserving waterlogged wood can be overcome with a number of treatments. The decision on what treatment is selected might be entirely a matter of aesthetics, in that the treatment results in a certain color wood, a light colored wood, it enhances the wood grain, it is glueable, it is flexible, it is rigid, it is part of a compound wood-metal artifact, it is not sensitive to fluctuations of humidity and can stand storage in adverse conditions. All of these are considerations, and there are ways of treating waterlogged wood that results in each of these considerations. All the treatments are applicable in given situations and all are acceptable alternatives.

LEATHER CONSERVATION

PRELIMINARY CLEANING

When conserving leather it is often safer to select a treatment that least affects the leather. As for all porous material, it is necessary to remove the bulk of the soluble salts which will be resent. The procedure is the same as described for bone and ceramics.

All archaeological leather conservation is preceded by washing to remove any ingrained dirt. First try washing in water alone. If this is not successful, try alternative methods. Leather may require a variety of mechanical cleaning techniques, depending on the condition of the leather and the particular cleaning problem. Soft brushes, water jets, ultrasonic cleaners and a Cavitron, an ultrasonic dental tool, may be required. If chemical cleaning is necessary to remove ingrained dirt, a small amount of non-ionic detergent (about a 1% solution) or sodium hexametaphosphate can be used. If Calgon, a commercial water softener, is used, make sure the pH is 3-5; the addition of additives may make it unsafe to use on leather. Rinse well after washing. Do not use any chemicals that will damage the collagen fibers of the leather.

A safe storage solution for waterlogged leather, or any organic material for that matter, can be made by taking 90% of a stock solution of 50% water/50% ethanol. To the 90% solution add 10% glycerin and 2-3 drops of formaldehyde. A 50% mix of ethanol and water is also an effective storage medium for many materials.

One must always remember, that it is often better to leave stains on the leather in order to prevent the damage caused by trying to remove them. Some metal stains are stable. For stain removal, particularly iron staining, 3-5% ammonium citrate or ethylene-diamine-tetraacetic acid (disodium EDTA) is used. Commercial trades names for EDTA are Titriplex III and Disodium Deterate. Soak for 2-3 hours, monitor closely. Rinse 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 complete removal of the chemicals. Always keep in mind that chemicals used to clean rusts and mineral concretions (oxalic acid, EDTA) may produce further hydrolysis of the proteinaceous collagen fibers, leather's main constituent, and that they can remove tanning, coloring agents, painted decorations and other attributes that are part of the diagnostic attributes of the leather object. Diagnostic attributes should never be removed. Caution should be exercised when using any of these chemicals on leather.

For waterlogged leather, freeze drying and solvent dehydration are often selected, quite often without adding any additional lubricant. Very good success have been achieved conserving bog bodies with freeze drying using 15% PEG 400 as a lubricant to minimize skin and bone shrinkage during drying. The drying behavior of any piece of leather 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, manufacture or tanning method used, and finally, the leather object's history.

TREATMENT OF BRITTLE and/or DESICCATED LEATHER

The following treatments, involving 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 humicant for the leather.

Smithsonian Glycerin Treatment

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

OR

25% glycerin
75% 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 glycerine is hygroscopic and can support mold growth. In spite of this the treatment has been widely used in the past successfully. The process went out of favor for a while, but recently (Jenssen, in Pearson 1987) interest in the treatment has been revived. As in the case with all organic conservation methods, this treatment should be used cautiously.

Waterlogged leather recovered from excavations by The Museum of London is conserved by placing it in a solution of 30% glycerol, 70% Alcohol (ethanol) for 2 weeks. The leather is then dried by 3 baths of acetone, 3 hours long each. Glycerol is not soluble in acetone. Basic success can be achieved using a glycerol treatment by using 10-40% glycerol mixed in 90-60% alcohol or water. Avoid using concentrated glycerol. While the solutions in alcohol can remove tanning agents, alcohol speeds up the process. In alcohol solutions, the leather has more overall strength during treatment. In other words, the alcohol allows the leather to support itself better than does a water solution.

The treatment has also been applied to basketry, matting, sandals, etc. to restore pliability; quite often with disastrous results. Always remember, 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 glycerol, such as basketry, remove the glycerol 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 di-ethyl ether, B.P. 60-80 F or 330 ml of hexane

Mix the first three by heating and then pour the molten liquid into the ether or hexane. Allow to cool while constantly stirring. Take extreme precautions!!! Ether and hexane are flammable liquids. Rub mixture well into the leather, but use sparingly; a little bit goes a long way. Apply, wait two days, then polish the treated leather with a soft cloth. Beeswax can be omitted; its function is to act as a polish. Very hard leather can be soaked in BML diluted to 1 part BML, 3 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 in any form is generally detrimental to leather.

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

As mentioned above there are several types of PEG and each has its own characteristics. PEG 540 Blend (equal parts of PEG 1450 and 300) is slightly hygroscopic and becomes moist at high humidity; for this reason the surface of the leather is sometimes sealed with a hard wax, i.e., a mixture of 100 gm. micro wax and 25 gm. polyethylene wax. PEG 3250 is very hard and is not very hygroscopic. Its main disadvantage (in some cases an 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 seems to give consistently good results. The various PEG treatments are more commonly used for the conservation of dry leather. 15% PEG 400 is commonly used as a pretreatment when the leather is to be freeze dried.

PEG treated leather can be hygroscopic, greasy, dark and there is the danger of the PEG migrating out of the leather.

Bavon

Bavon ASAK 5205 is an emulsion that is water soluble. Bavon ASAK ABP is solvent soluble. 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. When applied as a leather dressing it lubricates the leather, resulting in a pliable, natural brown leather.

The emulsion form of Bavon (ASAK 5205) can be used in the same way as described below except that there is no need to dehydrate the leather since the treatment starts with waterlogged leather. Many conservators report unsatisfactory results with the emulsion form of Bavon. Some conservators report too much shrinkage while others report good results. Personally, I have had better results with solvent soluble Bavon.

When it was first introduced, Bavon, was widely accepted and used. Many conservators are now abandoning treatments using Bavon. Glycerol and PEG treatments are used.

Very hard, desiccated leather has been successfully softened by soaking in a concentrated Bavon leather dressing consisting of 6 parts Bavon ASAK ABP to 4 parts 1:1:1 trichloroethane (Bavon is described below). 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) and the difficulties in conserving it so that it looks natural and will not suffer from the chemical added has long been known (Jenssen 1983). The best review of the current treatment commonly in use is presented by Jenssen (1987). The most relevant treatments are discussed. below.

Prior to Treatment, waterlogged leather should be stored in water with 0.1% Dowicide 1. If the leather is to be treated in an organic solvent, the leather can be stored in 50% H_2O/50% ethanol or straight ethanol and a fungicide is not required. Treated leather should not be stored at a relative humidity higher than 63%.

PEG TREATMENTS FOR WATERLOGGED LEATHER

Treat with PEG 400, 540 Blend, 600, 1450 and 3350 and proceed as described above for desiccated leather. It is recommended that you start with a dilute solution (1-10%) of PEG and gradually increase the concentration through evaporation of the solvent or by adding PEG up to 30%-100%. This allows the water to evaporate as equal amounts of PEG replaces the water.

Aqueous solutions of PEG are slower processes, but less expensive. Solvent solutions are much faster and considerably more costly. They however, produce a lighter leather with more uniform shrinkage. Some conservators prefer alcohol treatments, while others think that alcohol treatments cause the leather to shrink more than comparable aqueous treatments. All the PEG treatments can be satisfactory by themselves, but the treatments are considerably enhanced if taken through a freeze drying as the final step. The steps are identical to those described under 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% solution of Lissapol; never use commercial detergents on leather as they may extract tanning materials. Use castile soap, soft soap or saddle soap.
2. To remove iron stains place leather in 3-10% Disodium EDTA (pH 4) or ammonium citrate (pH 5) for a maximum of an hour; shorter if possible. Tap water can be used. The H_2O may yellow from the EDTA dissolving iron tannate. Note: EDTA has been reported to damage fibers of leather, but is relatively safe if used selectively and cautiously. A 3-5% ammonium citrate (pH 5) can also be used and, in fact, is recommended over Disodium EDTA by the Canadian Conservation Institute. This step is necessary only if iron stains are present.
3. If necessary, place in 2% HCL for up to one hour to dissolve calcareous material.
4. Rinse very thoroughly in running water for 30 minutes to lower the pH to 3-6 or to the pH of the rinse water.
5. Dehydrate in acetone. Use two or more baths; for example, four successive baths of one hour each.
6. Air dry until the "leather feels like leather", then place between absorbent tissue and glass to dry for 24 hours.
7. Apply Bavon Leather dressing with a brush. Flex and manipulate leather during the application of the Bavon.

<u>Bavon Leather Dressing</u>

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

GLYCEROL TREATMENT

Waterlogged leather recovered from excavations by The Museum of London is conserved by placing it in a solution of 30% glycerol, 70% Alcohol (ethanol) for 2 weeks. The leather is then dried by 3 baths of acetone, 3 hours long each. Glycerol is not miscible in acetone and is thus not removed in the acetone baths. Good results can be achieved using a glycerol treatment by using 10-40% glycerol mixed in 90-60% alcohol or water. Avoid using concentrated glycerol. While the solutions in alcohol can remove tanning agents, alcohol speeds up the process. In alcohol solutions, the leather has more overall strength during treatment. In other words, the alcohol allows the leather to support itself better than does a water solution, because the alcohol keeps the leather fibers stiff. removed by air drying and sometimes with the use of vacuum.

FREEZE DRYING

Freeze drying works the best as a means of conserving leather. In freeze dying the leather is first immersed in a 15% solution of PEG 400 which acts as a humicant, preventing excessive shrinkage. A fungicide, such as 1% borax/boric acid, or other fungicide should be mixed with the PEG solution. After immersion, the object is then frozen at -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 dry chamber under vacuum for a period of 2-4 weeks. Some acceptable results has been had using non-vacuum freeze drying in a freezer chest --the frost free freezers work best and are faster.

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 are used, e.g., a series of baths of x% H^2O - x% of isopropanol, a bath of 100% isopropanol, a bath of 100% ethanol or methanol followed by 100% methyl ethyl ketone, then 100% acetone and finally 100% 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.

Waterlogged Leather Treatment described by Plenderleith & Werner (1971:34)

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

In this treatment method, leather drys out in a flexible condition without undue shrinkage

Personally, I recommend the solvent drying treatments followed by the application of a leather dressing. 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. Others prefer freeze-drying with a pretreatment of PEG 400. The major costs involved are the organic solvents for drying and the cost of the freeze-drier for freeze-drying. These are the two most common treatments, and both give acceptable results.

TEXTILE CONSERVATION

The term "textiles" is applied to woven objects and also to those fabrics which are products of other kinds of interlacing of yarns of comparable structures such as braiding, looping, knitting, lace making, 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. The term "textile" is used to describe the fibers and also yarns, twines, cords, and ropes produced by spinning, twining and the rope-making process. The words "ancient textiles" refers to those materials that are made of natural fibers and are found in archaeological sites from past centuries.

This short 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 are primarily made of protein and are more resistant to decay than the vegetable fibers which are composed primarily of cellulose. For instance flax and cotton 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 singularly or together cause considerable loss of tensile strength and pliability. The oxygen in the atmosphere affects all organic substances to varying degrees. Textiles are very prone to aging and deterioration from exposure to the atmosphere. Prolonged exposure to normal atmospheric conditions will cause textiles to weaken and disintegrate. The speed of the deterioration varies according to the nature of the fibers and existing local conditions. 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 the contact of the material with vegetable matter. Attack by destructive insects may also be encountered.
2. Physical - Excessive heat causes desiccation and embrittlement, whereas exposure to ultra-violet light causes a type of deterioration known as tendering and photochemical degradation of susceptible dyes.
3. Chemical - Exposure to noxious gases 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 the experts. However, many archaeological specimens can be treated by the novice. The identity of the fibers composing a fabric should be known before any treatment is undertaken; particularly if stain removal is required. Physical tests such as burning quickly identifies 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 be readily identified by microscopic examination. For instance many animal hairs can be identified by their characteristic cuticle patterns and medullar cross-sections. Simple staining tests enable the conservator to distinguish the different kinds of fibers.

Textile materials encountered most often in archaeological sites are linen, cotton, wool, and silk.

Linen - A vegetable based fiber derived from flax stalks and branches that have been spun and woven. Linen fibers lie close together and are sturdy. They withstands moderate alkaline conditions because of their cellulose content, but are easily affected by acids. Moisture easily passes through the fibers of linen which causes it 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.

Cotton - 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, in a processed state, it is very absorbent. It is this absorbent characteristic which allows it to take dyes well. Cotton has a very characteristic clockwise twist and for this reason it is commonly spun in a "z" twist.

Wool consists of protein fibers. The majority of the amino acids in the protein of the wool are keratin which contains sulfur. This attracts insects that thrive on wool. Wool fibers absorb more moisture than vegetable fibers and wool has a physicochemical nature that causes its fibers to accept dyes better than any other natural fiber. Wool is not a strong fiber and weakens considerably when wet.

Silk - 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. Silk 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 to support fragile textiles during rinsing, treatment, and drying. Treatment involves: 1. documentation, 2. cleaning, 3. re-enforcing, 4. sterilization, 5. proper storage and protection from environmental dangers.

Documentation

A thorough documentation of the specimen, both photographically and written, is made to record all pertinent information about the item. The various features and properties to look for are:

1. the nature of the fibers
2. the spin of the yarn ("Z" or "S" twist)
3. the number of wefts and warps per inch (or centimeter)
4. the type of weaving, the type 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 simply by washing in water. Since water is the best solvent for ordinary dirt, cleaning can be as simple as washing in tap or deionized (D.I.) water. Where possible, D.I. water is always preferred. Add 0.4% to 1% ammonium hydroxide (0.4% for animal fiber, 1% for vegetal fibers) to the D.I. water for greater cleansing power. If necessary add 1% neutral non-ionic detergent, such as Lissapol N, to reduce the surface tension of the water to get out more stubborn soil. During the washing and cleaning process, the fabric can usually be bleached in a 4% hydrogen peroxide/4% ammonia solution. Soak in one of the following solutions to remove more stubborn stains:

1 liters D.I. water
60 ml 30% hydrogen peroxide
2.5g sodium silicate dissolved in 100ml hot .D.I. water

For more stubborn stains:

1 liter D.I. water
300 ml. 30% 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 it in a closed bag to oxidize.

Sodium silicate and metasilicate are stabilizers that are added to control the decomposition of H_2O_2 to H_2O. Where possible, just hydrogen peroxide and possibly a stabilizer is recommended, because as the hydrogen peroxide loses oxygen, it bleaches, and converts to water. Therefore, there is no danger of continuing chemical action. It can be used on all vegetable fibers and its bleaching effect is permanent. Do not use on hair or any fiber that was not white when 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.

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

1. The solvent does not soften textile fibers as water does therefore, there is less risk of shrinkage and loss of shape.
2. Dyes which are 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. A solution of 20% lanolin in toluene can be applied to fibers that have a tendency to shred or lint.

REMOVAL OF STAINS

Iron rust:

1. 5% hydrochloric acid [muriatic acid (HCL)]. 2. 5% oxalic acid $(COOH)_2$
2. 10% hydrofluoric acid (HF)
3. 5% EDTA, disodium
4. 5% acetic acid (CH_3COOH)
5. 5% Formic acid (HCOOH)
6. 2-10% ammonium citrate.

All these chemicals can be used in 2-10% solutions-a 5% solution is most common. From my personal experience I have found that oxalic acid (toxic) and hydrofluoric acid (very, very dangerous) are the most effective for removing iron stains. EDTA disodium (pH 3) and ammonium citrate are both often recommended because their higher pH's, potentially, do less damage to fibers. The latter two solutions can be effective, but they are rather slow.

Cotton fibers can be damaged when solution pH levels are low, e.g. 2.5 or lower. Oxalic has a pH of 1.0, hydrochloric acid has a pH of 0.7 and hydrofluoric acid has a pH of 2.2. Be careful and monitor the process closely.

Black sulfide stains, organic stains, mildew and mold can be removed by using hydrogen peroxide, see above. If necessary stronger solutions may be used. For copper corrosion stains, use 1-5% 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% solution of sodium thiosulfate.

After using any chemicals, rinse the textile in neutralized D.I. water intensively to remove all residue which may adversely affect the fibers over time.

REINFORCING FRAGILE TEXTILES

Quite often the only means of reinforcing fragile textiles is to fasten them to a synthetic mesh of terylene, light cotton fabric, fiber glass, or other substances. Mounting between sheets of plastic or glass is sometimes done when there is no other good method of treating a particularly fragile textile. In most instances a heat sealable adhesive such as PVA, PVAl, Acryloid B-72 and emulsions of these are used to coat the backing which is then ironed (heat sealed) onto the fabric.

In other cases, various synthetic resins are used to consolidate and reinforce fragile textiles. The most often recommended are:

1. polyvinyl alcohol, water soluble, dries clear with minimum shrinkage.
2. polyvinyl acetate (V7) - shrinkage can distort fibers.
3. ethulose (ethyl-hydroethyl cellulose) is water soluble, very pliable.
4. polymethacrylate.
5. Acryloid B-715% in toluene

Since water softens and makes textile fibers pliable, the emulsions and water soluble resins are preferred for many jobs. Of course water base adhesives gives the conservator more working time.

A mixture of 0.15% ethyl-hydroethyl cellulose, 0.6% polyethylene glycol (PEG) 400 and 0.2% fungicide has been used to consolidate fragile fabrics and to restore moisture to dry, brittle fibers. 1% Ethulose and 5% PEG 400 is used as a pretreatment prior to freeze drying.

During conservation 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.

STERILIZATION

Sterilization may have been achieved in the conservation process. 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% Lysol solution. This treatment will remedy most problems. If this becomes necessary, check the storage conditions. Carbon disulfide can also be used as a fumigation agent.

"Lysol" Disinfectant Spray Formulation can be mixed in the lab. Mix 0.1% Dowicide 1 (ortho-phenylphenol), 68% ethanol, and 30% D.I. water. A 0.05% solution of the above mix is lethal to most bacteria, fungal spores and surface mildews. Keep in mind that the fungicide is a topical treatment and is

not long lasting. The alcohol itself is an effective fungicide and bacterial deterrent. Dowicide 1 has a maximum solubility of 0.1% in water and a maximum solubility of 46-58% in different alcohols, 58% in ethanol. Alternatively, a solution of 2% Dowicide A and sodium ortho-phenylphenate can be used. Dowicide A has a maximum solubility of 120% in water and a maximum solubility of about 350% in alcohol. In most cases store bought Lysol Disinfectant Spray will suffice. Lysol Spray consists of 0.1% Dowicide 1, 79% ethanol, 8% n-alkyl, and 0.035 n-ethyl morpholinium ethylsulfates (deodorizers and scents).

CONSERVATION OF WATERLOGGED CANVAS AND ROPE

After a series of tests by the Conservation Division of the Western Australia Museum on canvas and rope recovered from a ship sunk in 1803, the following sequence of treatment is proposed for the conservation of canvas (and other similar fabrics) and rope. Steps not applicable are skipped.

1. Immerse in 10% hydrochloric acid to remove adhering encrustation and some iron corrosion and stains.
2. Rinse in running water. Watch for any dyes that may be adversely affected.
3. Soak in acetone to remove any tar, pitch, tallow or other acetone soluble substances. Watch for any dyes that may be removed.
4. Soak in 5% oxalic acid to remove the bulk, if not all of the iron stains. Time will vary from a couple of hours to a couple of days.
5. Immerse in 5% EDTA disodium to remove any remaining iron stains. Soaking time will vary from a couple of hours to up to 3 days. Both steps 4 & 5 may be required for particularly stubborn iron stains. At other times either 4 &/or 5 may be used.
6. Bleach in a hydrogen peroxide solution. Particularly stubborn stains may be treated for short periods in a stronger H_2O_2 solution (10-20%). Use only for cloth, canvas, and textiles that were white. Should not be necessary for rope. Of course, never use hydrogen peroxide on hair.
7. Rinse thoroughly in D.I. or distilled water, especially if fine fabrics are being treated.
8. Dehydrate in acetone and air dry.
9. If necessary, consolidate with a suitable synthetic resin, and in some instance, the fabric may have to be treated with either heat sealable resin and dry mounted or heat sealed to a backing of another fabric, such as light cotton or a synthetic mesh.

PROPER STORAGE

Store under proper conditions, keeping the artifact away from atmospheric pollutants and limit exposure to ultra-violet light. Relative humidity should be kept at a maximum of 68% (below 70%, which is the RH at which mold can grow). Ideally, textiles should be stored in a dark place with a low temperature of 10° C (50^oF) and a low relative humidity of 50% or less. This will help prevent bio-deterioration of the cellulose of vegetal fibers by micro-organism. In addition, moths and other insects should be deterred by keeping moth balls (paradichlorobenzene) in the storage area. Such care is especially true for wool. Paradichlorobenzene is a volatile insecticide that offers the most protection from insect attack. If mold is ever detected, treat by spraying the fabric with Dowicide 1 and correct the problem in the storage environment. Commercial Lysol Disinfectant Spray would be just as effective, but if there is doubt about some of the chemicals that may be in Lysol, make your own "Lysol Spray" by the formula given earlier.

METAL CONSERVATION

Archeological material from marine sites presents some of the most difficult problems confronted by the conservator. The techniques of preserving this material have been carefully studied and a variety of techniques developed. The following sections describe the most applicable and useful approaches and conservation techniques that can be utilized to process and document the archeological material from shipwrecks.Only the conservation of metals is discussed in this section. Successful treatment of any object requires that the conservator be familiar with the deterioration and corrosion processes, as well as the physical and chemical properties, of the specimen. Sections on metal corrosion, preliminary steps; documentation, storage, and mechanical cleaning; conservation of ferrous metals; conservation of nonferrous metals; casting and molding; are includedDuring 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 utilized with consistent regularity to manufacture tools, weapons, ornaments, hardware and other paraphernalia. Each of these 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 effectively used. Consequently, corrosion is briefly covered. 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, and more to point, is to look at the corrosion resulting from the interacting effects of wet, dry, aerobic, and anaerobic environments, i.e., the presence of oxygen and moisture. In any environment moisture is a critical variable and since aquatic environments, especially sea water, are the topic of interest in this paper, 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, such as chloride in the water, determine the rates and types of corrosion.

Salt water corrosion on the metals of antiquity is stressed here, with emphasis on marine archeological material. For clarity, however, other environmental conditions are briefly considered. The corrosion of iron, cupreous metals, silver, and silver alloys, tin, lead and lead alloys, and gold and gold alloys are included.

IRON

FERROUS METAL CORROSION

Iron is usually the most prevalent metal in archeological sites. Of all the metals of antiquity this one presents the conservator with the most ponderable problems because of the variety of conditions and environments under which corrosion can occur and the number and complexities of the corrosion products. Moreover, corrosion processes are applicable to other metals and make iron a useful introduction to all metallic corrosion. It is discussed in more detail and is used to introduce and define electrochemical corrosion. The following relies heavily on Evans (1961), Potter (1956), Pourbaix (1966), Hamilton (1976), and Pearson 1987a).

Electrochemical Corrosion

Iron buried in the soils or lying on the ground surface exposed only to ground and air moisture corrodes essentially by an electrochemical process. The corrosion of iron in sea water proceeds in somewhat the same manner but is greatly accelerated because normally water becomes more corrosive as the salt content increases. For example, iron corrodes five times faster in sea water than in soil and ten times faster in sea water than in air (Cornet 1970:439).

For iron artifacts buried in the ground, pitting is generally a prominent feature of the corrosion process, and this environment tends to be chemically reducing, forming 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 which results 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 because they form 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 water, or in the soil, a very conductive solution is formed and electrochemical corrosion is accelerated.In electrochemical corrosion a galvanic cell can be 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.

The corrosion of metals submerged in salt water, as is the case with most shipwrecks, is a complex process. It has often been explained in terms of a large galvanic cell (Peterson 1969:30; 1972:244) which is based on the electromotive series of metals. Stated in general terms, all the 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 the metals (Table 1). The least active metals are at the top and the most active ones are at the bottom. The more negative the electrode potential is, the more active the metal is, and there is a greater 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 having the more negative reduction electrode potential in the electromotive series becomes the anode. It loses electrons and forms positive ions which go into solution. The more noble or positive metal in the cell forms the cathode and is given cathodic protection, while the anodic metal is preferentially corroded in any resulting electrochemical reaction.

As a blanket explanation for the corrosion of different metals in a shipwreck in salt water, the large galvanic cell concept and the electromotive position of the metals have been overplayed and are not completely understood. The large mass of different metals in a shipwreck in salt water, the large galvanic cell concept and the electromotive position of the metals have been overplayed and are not completely understood. The large mass of different metals associated with a sunken ship in salt water consists of thousands of independent galvanic cells and does not form a single gigantic battery. Each galvanic cell is formed between two metals having different electrode potentials. In order to establish a

galvanic cell the metals have to be in very close proximity or in contact. This requirement necessarily limits the metals that can form a galvanic couple to a single encrustation. Even then, different variables such as conductivity of the electrolyte, aggressive ion concentration, and mass transport can come into play and alter or interfere with the expected theoretical or laboratory reactions.

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

$$2H_2O + 2e \rightarrow H_2 + 2(OH)^-$$
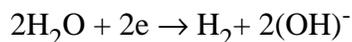
The hydroxides combine with the sodium ion in thesolution to form sodium hydroxide as the cathodic produce.

$$Na^+ + OH^- \rightarrow NaOH$$
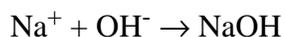
Table 1
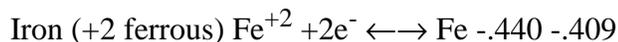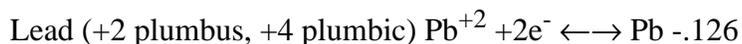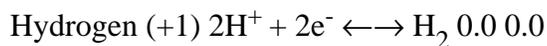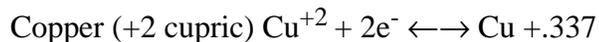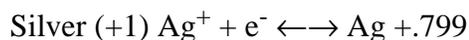Electromotive Series of the Metal of Antiquity
Standard Reduction Potentials in Salt Solutions
of Normal Ionic Activity, 20°C, pH 0

Noble End (Cathodic) Ionic Reaction Electrode Potential*
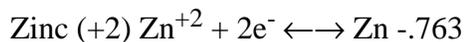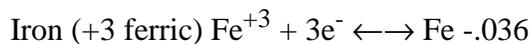
Gold (+1 aurous, +3 auric) $Au^{+3} + 3e^- \longleftrightarrow Au$ +1.50

Silver (+1) $Ag^+ + e^- \longleftrightarrow Ag$ +.799

Copper (+1 cuprous) $Cu^+ + e^- \longleftrightarrow Cu$ +.552

Copper (+2 cupric) $Cu^{+2} + 2e^- \longleftrightarrow Cu$ +.337

Hydrogen (+1) $2H^+ + 2e^- \longleftrightarrow H_2$ 0.0 0.0

Lead (+2 plumbus, +4 plumbic) $Pb^{+2} + 2e^- \longleftrightarrow Pb$ -.126

Tin (+2 stannous, +4 stannic) $Sn^{+2} + 2e^- \longleftrightarrow Sn$ -.136

Iron (+2 ferrous) $Fe^{+2} + 2e^- \longleftrightarrow Fe$ -.440 -.409

Iron (+3 ferric) $Fe^{+3} + 3e^- \longleftrightarrow Fe$ -.036

Zinc (+2) $Zn^{+2} + 2e^- \longleftrightarrow Zn$ -.763

Base End (Anodic)
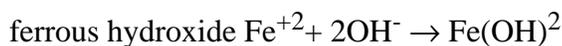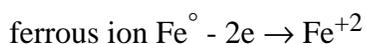
At the anode the reaction is the production of ferrous ions, $Fe^+ - 2e \rightarrow F^{+2}$ which in turn combines with chloride in the salt water to form ferrous chloride as the anodic product.

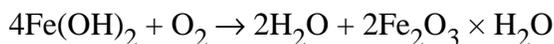$$Fe^{+2} + 2Cl^- \rightarrow FeCl^2$$

On exposure to air or solutions containing dissolved oxygen, the ferrous chloride oxidizes to ferric chloride and ferric oxide. Sodium hydroxide, ferrous chloride, and ferric chloride are freely soluble and may yield ferrous hydroxide where they meet.

$$FeCl^2 + 2NaOH \rightarrow Fe(OH)^2 + 2NaCl$$
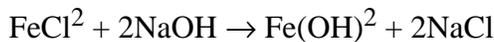
In solutions containing dissolved oxygen a secondary reaction oxidizes the ferrous hydroxide to a ferric state. In the presence of hydroxyl ions in a neutral or slightly alkaline solution, this hydrated ferric hydroxide (any form of ferric oxide with internal water, i.e., common rust) is precipitated on or about 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 $Fe^{\circ} - 2e \rightarrow Fe^{+2}$

ferrous hydroxide $Fe^{+2} + 2OH^- \rightarrow Fe(OH)^2$

hydrated ferric hydroxide (red-brown rust)

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3 \times H_2O$$

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 when the supply of oxygen is restricted as in stagnant water or in the soil. Intermediate oxidation products of ferrous hydroxide such as hydrated magnetite and black magnetite are formed (Evans 1963:28-29, 75; Potter 1956:236-237).

$$6Fe(OH)_2 + O_2 \rightarrow 4H_2O + 2Fe_3O_4 \times H_2O$$
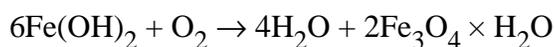
(green hydrated magnetite)

$$Fe_3O_4 \times H_2O \rightarrow H_2O + Fe_3O_4$$
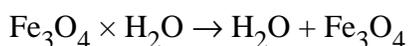
(black magnetite)

Depending on the environment, the corrosion products can take on a variety of physical forms, state of division, and hydration. It is common to find corroded iron 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.

$Fe_3O_4/2Fe_3O_4 \rightarrow H_2O/2Fe_2O_3 \times H_2O$
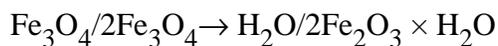
In the explanation of an electrochemical cell, it was stated that the electrodes could consist of two different pieces of the same metal, or different parts of the same object. This needs clarification.

Only exceptionally are metals pure, so that a metallic surface is almost certain to contain inclusions of more noble metals. 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. For example, iron fastings that are bent during the wrecking and sinking 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 to the above, just the effects of different oxygen concentration, temperature, and pH at a metal surface will cause corrosion.
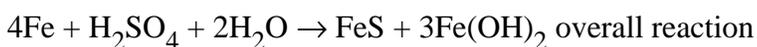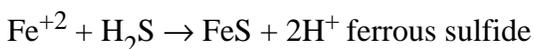
It is easy to see how two different areas of the same metal object can become anodic and cathodic to form an electrolytic cell. Electrons flow from the anodic area to the cathodic area causing the metal to corrode by forming soluble positive ions at the anode. Millions of these cells over the surface 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.According to the principles of electrochemistry, iron oxidizes preferentially in a galvanic cell with iron as one electrode and copper or silver as the other electrode. I have observed many instances where a number of silver coins, encrusted less than one-fourth of an inch from a large iron mass such as a wrought iron anchor, were badly corroded or even completely converted to an oxidized state. On the other hand, silver coins in what appeared to be less favorable locations were in good condition. Many variables, such as surface area, electrolyte and mass transport, play a role in the corrosion process, and all have to be considered when a shipwreck with a great array of organic and metallic material is deposited in salt water.A major factor to be considered is that, as the 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 and the corrosion products--especially ferrous hydroxide, ferrous sulfide, and magnetite--intermix with sand and marine life 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. The encrustation will actually separate two metal pieces that were initially touching each other and prevent galvanic corrosion. In fact, I have seen silver coins once obviously in contact with each other become insulated from each other by a thin layer of encrustation consisting primarily of silver sulfide mineral products and calcium carbonate. It has been my observation while processing artifacts from a number of shipwrecks that it is indeed a rare occurrence to ever find any two metal objects actually touching each other. They are always separated by a layer of encrustation. Such encrustation effectively separates the metals from each other and destroys the electrochemical cell by cutting off the current flow and/or oxygen supply.

Anaerobic Corrosion

Despite the fact that the corrosion processes are impeded by the formation of the surrounding encrustation, the deterioration continues because of 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 and buried in the soil under anaerobic conditions (Evans 1963:224; Leigh 1973:205; Pearson 1972a:35). It is now generally acknowledged that the various species of these bacteria play a large part in the chemical corrosion of iron in waterlogged anaerobic environments. In fact, as much as 60% of the corrosion of iron in salt water can be attributed to bacterial action (Pearson 1972a:35). It accounts for most of the rapid corrosion of buried iron and steel pipelines in waterlogged clay soils in England (Farrer, et al. 1953:80). 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. The decaying organic material consumes oxygen and creates localized anaerobic environments. Sea water has a large supply of sulfates and under aerobic conditions these bacteria utilize hydrogen to reduce the sulfates $(SO_4)^{-2}$ to sulfides (S^{-2}) as a metabolic by-product according to the reaction:

$$H_2SO_4 + 8H \rightarrow H_2S + 4H_2O$$
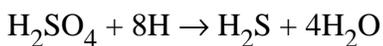
In this process the hydrogen that accumulates on the iron as a cathodic product polarizes the cathode in an oxygen-free environment. The polarization of the cathode ordinarily halts the electrochemical corrosion process. However, the utilization of hydrogen in the metabolism of the bacteria depolarizes the cathodic areas of the cell and allows the corrosion to continue unabated. In addition, the hydrogen sulfide formed as a metabolic by-product reacts not only with iron, but all 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:

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

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

_____

$$4Fe + H_2SO_4 + 2H_2O \rightarrow FeS + 3Fe(OH)_2 \text{ overall reaction}$$

The life cycle of the sulfate-reducing bacteria stimulates both the cathodic and anodic reactions of the electro-chemical 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 effectively inhibited.

Ferrous Alloys

It has been found (Evans 1963:93) that there is comparatively little difference in the corrosion of mild steel, wrought iron, and numerous low alloy steels. Even cast iron oxides 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 in the iron and the cathodic graphite flakes 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 deformation has to result because the graphite framework is not capable of supporting the object by itself.

Summary

In summary, it is apparent that 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 with 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 expected iron corrosion products are:

$Fe(OH)_2$ ferrous hydroxide

$FeO(OH)$ ferro-hydroxide

$FeCl_2$ ferrous chloride, anhydrous

$FeCl_2 \cdot x \, H_2O$ ferrous chloride, hydrated

FeS ferrous sulfide

Fe_3O_4 or $FeO \cdot Fe_2O_3$ ferro-ferrous oxide (magnetite)

$2Fe_3O_4 \cdot H_2O$ magnetite, hydrated

$2Fe_2O_3 \cdot 3H_2O$ ferric hydroxide (common rust)

Fe_2O_3 ferric oxide

$FeCl_3$ ferric chloride, anhydrous

$FeCl_3 \, x \, H_2O$ ferric chloride, hydrated

On the metal objects from shipwreck, 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. Others completely mineralize to a massive oxide, magnetite, but retain their structural integrity and surface detail. Others 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 Fe_3O_4 in buried encrustations and the prevalence of FeO(OH) and Fe_2O_3 in encrustations exposed to open seawater (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 they be properly stored in an inhibitive solution to prevent further corrosion. If the iron in an encrustation is exposed to the air or an uninhibited solution, the ferrous compounds can oxidize to a ferric state which occupy a greater volume and scale off the surface. Just this process can disfigure a piece and eventually destroy it. Without exception, it is much better to conserve iron artifacts with ferrous corrosion products than iron with ferric corrosion products, which disfigure the object. 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:

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

which in turn oxidizes to ferric chloride and ferric oxide in the general reaction:
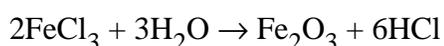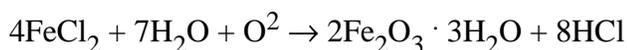
$$6FeCl_2 + 3O_2 \rightarrow 2FeCl_3 + 2Fe_2O_3$$
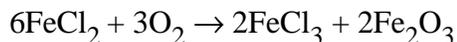
Both of these reactions are gross oversimplifications, but the reaction proposed by Eriksen and Thegel (1966:90):

$$Fe + 2NaCl + 2H_2O \rightarrow FeCl_2 + 2NaOH + H_2$$
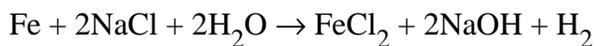
is not thermodynamically feasible. Regardless of the exact equation, both the ferrous chloride and ferric chloride combine with water to form hydrates:

$FeCl_2$ .x H2O, and$FeCl_3$. x H_2O, where x is normally 2, 4 or 6

It is these hydrated chlorides that cause the trouble. On exposure to moisture and oxygen they hydrolyze to form ferric oxide or ferric hydroxide and hydrochloric acid. The hydrochloric acid in turn oxidizes the uncorroded 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:

$$Fe° - 2e \rightarrow Fe^{+2}$$

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

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

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

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

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

$$FeO + 2HCl \rightarrow FeCl_2 + H2$$

$$4FeO + 3O_2 + 12HCl \rightarrow 4FeCl_3 + 6H_2O$$
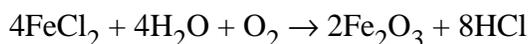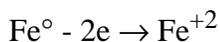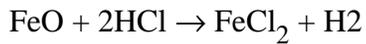
Of the above corrosion products, it is possible by electrolytic reduction to reduce the ferrous compounds $Fe(OH)_2$, $FeCl_2$, FeS and the ferrous oxide portion of Fe3O4, which probably exists as $FeO \cdot Fe_2O_3$. It is not possible to reduce the ferric compounds in an aqueous solution. This problem is discussed under the Electrode Potential section of electrolytic cleaning iron

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. 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. The hydrogen sulfide that forms as a metabolic by-product of the bacteria reacts with the metal and accelerates the corrosion process, forming various metal sulfides. This corrosion reaction is most evident on iron, silver and lead in direct contact with wood. An early paper on the major corrosion products of the different metals can be found in Gettens (1963 & 1964), and by far, the most detailed discussion of 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 archeological 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, at least in a general way. It is regrettable that a lot of the extant literature on the conservation of iron and other metals from salt water has either been neglected or oversimplified, or is misleading as to alternative procedures, cost, time involved and problems encountered. See for example Peterson (1964, 1969, 1972); Marx (1971); Townsend (1964, 1972); Eriksen and Thegel (1966); and 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, but all the conservation procedures used on them can be applied equally to metals from other archeological environments. The absence of marine encrustation and excessive chloride contamination considerably reduces the length of time required to process and stabilize nonmarine objects. If the conservator understands the corrosion and preservation problems of artifacts from a salt water environment and is familiar with the alternative procedures that can be utilized, he can cope with metal artifacts from any other archeological context.Whatever conservation technique(s) is 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. storage or exhibition, can be heuristically conceived in terms of a flow diagram which incorporates a number of possible sequential steps and alternative procedures. The major steps are:

I. Conservation: preliminary steps
    A. Initial documentation
    B. Storage prior to treatment
    C. Mechanical cleaning
    D. Preliminary evaluation
II. Conservation: treatment
III. Conservation: 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 archeological 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 utilized. 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. All records should be well organized in a filing system so the data will be readily accessible.

Proper records will include all the pertinent archaeological data, identifications, descriptions, and the complete conservation procedures each artifact underwent.The conservation data records the treatment history of every specimen, thereby accumulating valuable research records on the evaluation of particular conservation techniques. If any specimen needs retreatment in the future the card provides valuable information on why the original treatment failed and how to reverse the process. Considerable archeological 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 archeological data necessary to reconstruct details of ship life, trade and commerce.

STORAGE OF IRON PRIOR TO TREATMENT

The following emphasizes metals recovered from sea water but is equally applicable to other kinds of artifacts recovered from other kinds of 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. Within any one encrustation there may be objects of a variety of materials including metal, wood, bone and fiber. In order to prevent further corrosion, disintegration, breakdown or collapse, these materials must be kept wet between recovery and treatment. It is necessary therefore to select a storage solution in which all can be safely housed. Since iron artifacts, many quite large, are likely to be the most common, solutions which provide good protection for this metal but do not adversely affect other metals and materials should be selected. Some of the problems can be eliminated by leaving the encrustation intact. The encrustation forms an excellent protective coating which retards corrosion, prevents the chemical conversion of the corrosion products already present, protects the artifacts from additional deterioration, and preserves the associations until they can be adequately 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.

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

Alkaline Inhibitive Solutions

The most common alkaline inhibitors generally 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) by the formation of an oxide film on the metal. Generally speaking, iron can be passivated in a solution with a pH above 8, if it is free of chloride. (See Hamilton (1976:21-25) for a more thorough discussion of storage environments) Below a pH of 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 free from oxidizing agents. Thus, if iron is stored in an alkaline solution with the pH maintained between 11 and 13, the iron will remain passified and will not corrode (Figure 2).
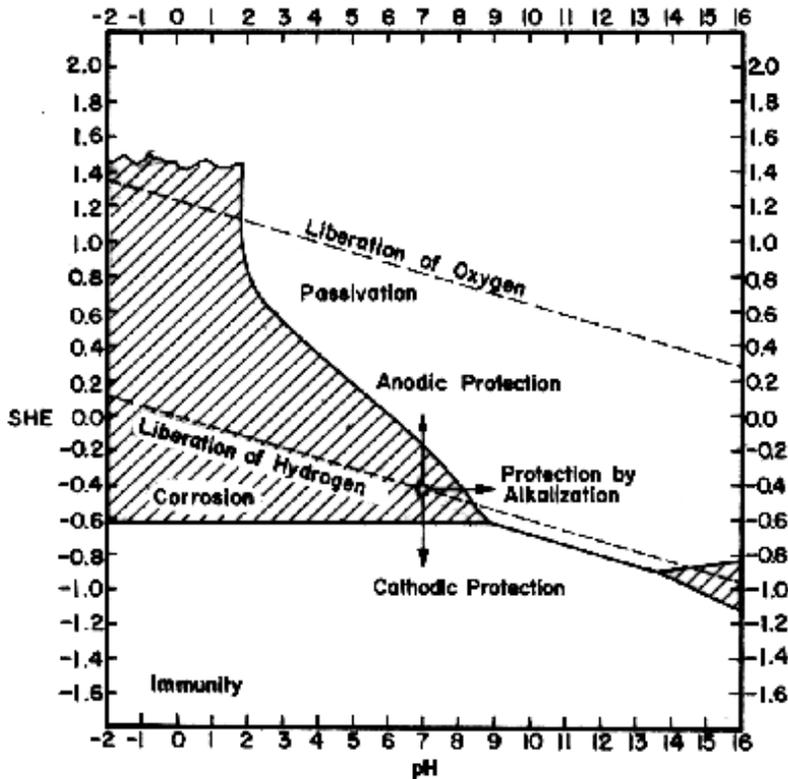
Figure 2: Corrosion, passivation, and immunity domains of pure iron

Five percent sodium carbonate (pH 11.5) and 5% sodium sesquicarbonate (pH 9.7) storage solutions are 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 of other temporary laboratory storage.

Oxidizing Solution

If long term storage is required, an inhibited solution containing oxidizing agents can be used, but the difficulties in properly disposing of these chemical prohibit them from being generally used. It is safer, environmentally speaking, to just 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 the alkaline inhibitors as long as the concentration, and especially the pH is maintained at safe levels. It is known that chromate solutions prevent corrosion by forming a very thin passivating film of ferric oxide and chromic oxide on the metal surface (Pearson 1972a:14).

This oxidizing solution creates an environment where a much wide range of pH's and electrode potentials of the surface of the metal is in the Passivation range of the metal (Pourbaix 1966:74). See Figure 3. It must be emphasized, however, that the solution must be alkaline. The natural alkalinity of chromate, pH 9.1 to 9.3, is an important factor in passivating iron. Dichromate is much more acidic (pH less than 7) 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 break down at too low a pH. Should this occur the chromate can stimulate intense localized attack and create pits covered with a membranous blister of iron hydroxide. The iron hydroxide shields the chromate from the area and allows the anodic reaction $Fe° \rightarrow Fe^{+2}$ to take place (Evans 1963:141; Kranz 1969:20). Because of this it is necessary that the pH be maintained in a range of 9.0 to 9.5, otherwise the corrosion attack will be worse than if no inhibitors were used. As long as there is free hexavalent chrome (Cr^{+6}), however, the concentration of chloride is not a critical factor as they are in alkaline inhibitors (Worth Carlin 1975, personal communication). For these reasons chromate solutions are particularly suited for the storage of iron from chloride-contaminated environments.

The pH of the chromate solution needs to be regularly checked as some of the chromate in the solution is reduced and the solution becomes acidic. When 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 when ingested and inhaled. They are strong irritants and some are a dangerous fire risk in contact with organic material. A chromate solution should not be discharged into city sewage lines or natural drainages since it kills the desirable bacteria. Most cities have regulations concerning the disposal of solutions with chrome IV of this nature and a conservation laboratory
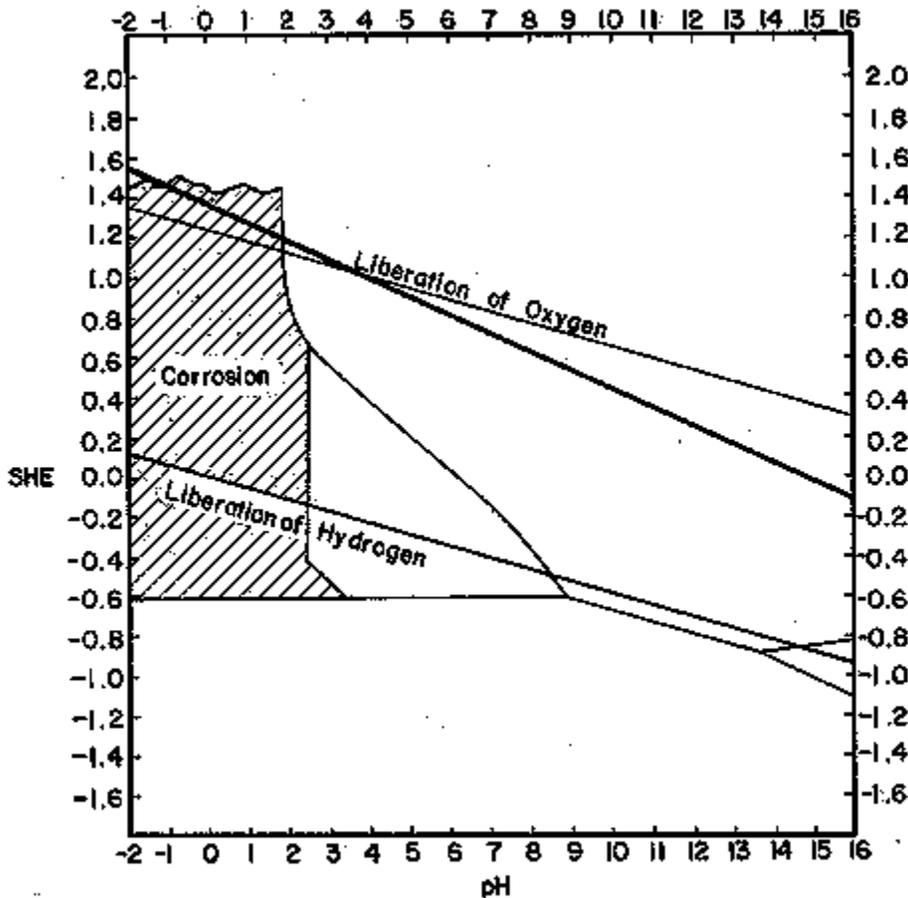
Figure 3. Stability Conditions of Pure Iron in a Chromate Solution.

must, of course, comply with them. If proper disposal cannot be arranged, chromate solutions should not be used. For these reasons, even thought excellent, safe, long-term storage of iron can be afforded in chromate solutions they are not generally used.If chromate solutions are used, they must be disposed of safely. There are several ways of treating a chromate solution for disposal. One way 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% 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.

I have successfully used a .1N solution of potassium dichromate ($K_2Cr_2O_7$) and added sodium hydroxide to it. Many wrought iron artifacts recovered from the 16th-century Spanish ships have been stored in this solution for more than three years with no apparent corrosion. Still, sodium chromate is a cheaper compound and sodium hydroxide does not have to be added unless the solution becomes acidic as the chrome is reduced. Periodically the pH may have to be adjusted to and maintained at 9.0 to 9.5 by the addition of sodium hydroxide.

Use of Deionized Water

Normally the literature on conservation will recommend that all storage solutions be prepared with distilled or deionized water. The exception to this general rule occurs when the material contains more chloride than is present in the local tap or well water.In this case there is no advantage to mixing up a solution with expensive distilled or deionized water only to have it contaminated with chloride well in excess of the local water supply. Tap water should continue to be used for all storage solutions and electrolytes until the chloride level is less than that of the tap water. Using rain water in electrolytes between tap water and D.I. water will consdiderably reduce cost. Following this procedure will result in great financial savings when a large number of chloride-contaminated materials are to be processed.

Occasionally just deionized or distilled water is recommended as a storage solution for metal artifacts. Unaltered deionized or distilled water should never be used. They are generally slightly acidic and hence highly corrosive. Likewise, when used for rinsing or as a bath for detecting chlorides, the duration should be kept to a minimum and adequate precautions taken.

ENCRUSTATION REMOVAL

On delivery to the conservation laboratory, marine archeological 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 encrustation, large industrial x-rays machine such as a 260 KVP water cooled Picker Industrial X-ray has to be used. Small to medium size encrustations up to approximately 4 x 4 feet 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 (24" x 24" is an ideal size film). On the overlay all the discernible artifacts are traced. Any specimens not detectable on the radiographs can be drawn in and their correct provenience located 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 have been found to be 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 removed, it is much safer to leave a thin layer of encrustation on the surface of the metal where the original surface can not be determined. When the object is placed in electrolysis, the evolution of hydrogen bubble at the surface of the metal will loosen the encrustation and mechanically remove any encrustation 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 as much of the encrustation as you can by hand. The encrusted bores of cannons present a special problem. Tube drills are ideal but each different

caliber gun requires a different size 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. Then a sandblaster can be employed 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 actually 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 HCl, attack the metal oxide as readily as the encrustation and so, are too damaging to consider. Even if successful, chemical techniques pose problems in recording association, observation, and measurements and in 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, reported as "deganquing" 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 on 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 therefore is to stabilize the artifact by diffusing the soluble chlorides out 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 the treatment begin.

IRON CONSERVATION

The processes by which any metal artifact is cleaned is determined by the preliminary evaluation and only then can the appropriate conservation measures be taken. The conservation treatments accorded an object of iron will be discussed under the five main categories:

1. Electrochemical cleaning
    a. Galvanic cleaning
    b. Electrolytic reduction
2. Alkaline Sulfite
3. Chemical cleaning
4. Annealing
5. Water diffusion in alkaline solutions

ELECTROCHEMICAL CLEANING

The corrosion of metal, as explained earlier, is an electrochemical reaction. In turn, electrochemical and electrolytic reduction cleaning processes are the most common techniques utilized to halt, stabilize, and even reverse the oxidation of the metal. See Hamilton (1976:30-49) and North (1987:223-227) for a detailed discussion of electrolytic reduction. In the conservation literature, but not in the field of electrochemistry, it has been the general practice to distinguish between electrochemical and electrolytic cleaning. Both techniques, in fact, are electrochemical reactions based on the couple of two metals occupying different positions on the galvanic or electromotive series of the metals without an externally applied electromotive force (EMF) and the latter is an electrochemical reaction maintained by an externally applied EMF or electric current. Breaking with the convention established in the conservation literature, this publication distinguishes the two by the terms galvanic cleaning and electrolytic reduction or electrolysis. Both cleaning techniques are described in the literature. Plenderleith (1956) is a source often cited. While useful information is provided by Plenderleith and Torraca (1968) and Plenderleith and Werner (1971), a more thorough coverage is desirable to realize the maximum potential and benefits of these techniques.

GALVANIC CLEANING

This technique is the one most often described in the literature on the conservation of shipwreck material. For example, in two frequently cited works (Marx 1971:125; Peterson 1969:83-84) on underwater archeology, it is the only technique recommended. For marine-recovered iron artifacts which are severely chloride-contaminated, electrochemical cleaning is not a desirable alternative. Even for metals from terrestrial sites, where chlorides present no real problems, it is often not desirable. I need only to repeat Noël Hume's (1969:276) comment: "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."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. 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 much 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 metal. The chlorides are removed and reduced metal is left by the reaction. 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 two metals and by the electrolyte;

unfortunately, it cannot be manipulated.The simplest form of galvanic cleaning consists of wrapping the object loosely in aluminum foil and placing it in a glass beaker of 10% sodium hydroxide, NaOH (caustic soda), or a 10 to 20% solution of sodium carbonate, Na_2CO_3 (soda ash). Noël Hume (1969:283) suggests using an electrolyte of baking soda (sodium bicarbonate, $NaHCO_3$) but tests in our laboratory using this solution have not been effective. 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 form of galvanic reduction differs from the above only in that granulated zinc or aluminum granules are used to cover the object and a 10 to 20% solution of sodium hydroxide is employed (Plenderleith and Torraca 1968:241; Plenderleith and Werner 1971:194-197). Since heating accelerates the process, metal pans, or heat resistant glassware, are recommended. Ideally the solution is heated to boiling, 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 diminishes. The process is repeated with fresh or cleaned zinc and fresh caustic soda until all the materials are reduced and all traces of chlorides have been eliminated. (See section on qualitative test for chloride described later.) If high levels of chlorides are allowed to remain, future outbreaks of corrosion are inevitable.The 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 considerably 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) or melted in a ladle under a reducing flame and re-granulated by slowly pouring into water (Organ 1973:193). In the latter, the reducing flame is going to have to be very good to remove oxychloride and carbonate and 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 and it is not possible to follow visually its progress. Even under ideal conditions the process requires constant supervision and is messy. The fumes produced are obnoxious and are irritating to the skin, the eyes, and the throat. Also, it is often difficult to provide simultaneously adequate ventilation and adequate heat. Any large artifact, especially chloride-contaminated ones, require a long processing time and a prohibitive amount of zinc, which has to be constantly recleaned and replenished. For example, just the technical grade mossy zinc needed to clean a large iron object would be well in excess of $1,000. The caustic soda and, most importantly, the labor, would easily triple this figure.

In sum, 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 lot of iron artifacts, especially if they are very large.

ELECTROLYTIC REDUCTION CLEANING

The ease of setting up, maintaining and long-run economy of an electrolytic unit along with the versatility of electrolytic cleaning makes it one of the conservator's most valuable tools. It can be selected exclusively for its mechanical cleaning action of the evolved hydrogen, for the reduction process or, as usually is the case, a combination of the two. It can be used for most metal objects. Efficient electrolytic reduction, however, involves more than wiring up artifacts for electrolysis. A knowledge of corrosion processes and electrochemical thermodynamics is essential. One must be

familiar with electrode potentials and pH, and 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 a good knowledge 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 containing a suitable electrically conducting solution called the electrolyte. An electric current from an external direct current 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 externally applied electromotive force (EMF), or electric current, provides the conservator with considerable flexibility. It allows him to control the current density. 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. Likewise a high current density can be selected so that the evolved hydrogen will mechanically remove completely oxidized crust. When using electrolytic reduction cleaning, the procedural factors to be consideredare 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

D.C. Power Supplies

The regulated D.C. 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. For example, the 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 D.C. power supplies have an output current with less than 0.1% ripple. The larger power supplies, battery chargers, have 0.5% or more ripple. For well-controlled reduction, the low ripple power

supplies are recommended, however a little ripple is not harmful. The choice of a power supple depends upon the desired control, the size of the artifact, the number of artifacts on any one unit, the amount of current controls and an amperage meter. These 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 the object and the electrolyte decreases. The IR (current resistance) 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 regulating 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 utilized in electrolysis it is usually necessary to remove timers, relays and charging rate devices to make them serviceable. Anyone with a basic knowledge of electrical circuits can easily alter most direct current battery chargers for electrolytic cleaning of metal artifacts.

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 line and variable rheostats or line resistors on the outgoing direct current negative terminals serve this purpose well. Anyone with a basic knowledge of electronics can successfully modify battery chargers and other D.C. power supplies can be modified easily for the purposes of conservation. Over the years, I have modified a number of large 220V, three-phase airplane battery chargers that were obtained through government surplus into serviceable electrolytic reduction power supplies. The easiest procedure is to add a variable autotransformer to the input-alternating current circuit. This allows the full amperage range of the unit, from 0 to 200 amps, to be used.

Terminal Wires and Clips

For most objects 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. The wire is quite flexible and easy to use. One strand of the wire is used for the negative connection, the other one for the positive connection; or they can be joined at the terminal ends to make one pole connection if a larger size wire is required. For larger artifacts needing more current, No. 2 to No. 0 AWG multistrand wire is required. In all cases multistrand copper wire is recommended because it has a larger current capacity than comparable size solid wire and is more flexible and easier to manipulate. 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 during electrolysis the wire should not heat up; if it does, the wire is not heavy enough.To attach the terminal leads to the artifact and the anode, it is suggested that steel alligator test and battery clips (Mueller clips) be used. Appropriate size 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 placement of attachments. Mueller clips Nos. 25, 27, 48 and 85 are the most useful sizes and should be kept in stock. Steel clips usually are cadmium or zinc-plated and should be stripped of this plating by a quick bath in a dilute solution of hydrochloric acid. If left too long in the acid, the tempered steel spring is weakened and breaks 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 plates onto the cathode. In order to prevent the anodic dissolution, the exposed copper wire should be coated with an acrylic, polyvinyl acetate or silicone rubber.

Anode Material

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

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. Therefore, 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 needs to be selected; particularly serviceable is type 316 stainless steel, which is composed of 16 to 18% chromium and 10 to 14% nickel and 2-3% molybdenum.

Only type 316 stainless steel resists Cl^- corrosion and is a good alternative to mild steel anodes in an alkaline electrolyte. All the other stainless steel anodes present problems, some considerably greater than that of mild steel. The expanded stainless steel mesh, like the expanded mild steel, is preferable. Stainless steel is very expensive and its use as anode material for large objects is usually prohibitive. Because of the expense, it is impractical to cut and form-fit it to clean a single artifact; therefore, certain setup alternatives described below, for treating a number of artifacts at one time is the most practical way to use stainless steel anodes.

As long as the hydroxyl ion concentration in the electrolyte is kept high, one will get better service from mild steel anodes than stainless steel. In any case, when either is used, 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. Regardless of whether stainless steel or mild steel anodes are used, the electrolyte should be regularly replaced, using a chloride-monitoring system as a guide.

Vats

A wide variety of containers can be used in an electrolytic setup. Many kinds of nonconductive vats of various caustic and acid-resistant plastics such as polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE) are also widely used. Also PVC plastic pipes with the ends sealed up make excellent vats for long slim artifacts such as rifle barrels. Fiber-resistant plastics (FRP), unless one knows

positively that they are alkali-resistant, should be avoided. Many FRP vats are not alkali-resistant and will break down. Even wooden vats or frames lined with sheets of PVC plastic can be quite serviceable as long as care is taken not to puncture the plastic. Glass containers are also often used. The variety and range of potentially satisfactory vats are obviously broad. With a little improvisation a number of containers for electrolysis can be readily and inexpensively obtained. For small artifacts, a common coffee can, with the can used as the vat and the anode, is as effective as anything much more elaborate and costing considerably more money.In addition to nonconducting containers, conducting mild steel vats have a definite place in electrolyte cleaning. The metal vat serves as all or part of the anode and may be substituted for any of the electrolytic setups described in a section which follows. As an example of what can be done, we have constructed a two-piece 15 foot-long mild steel vat designed to be used to clean anchors and other very large specimens. 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 near the top surface to achieve a better distribution of current. Separated, the two are employed to clean an assortment of large iron artifacts. After all of these objects were cleaned, the two vats were bolted together, placed on a "T" arrangement of stoves to rinse the guns, other breechblocks, and an anchor in alternate boiling-cooling deionized water. The water was drained and replaced with microcrystalline wax for the final sealant. It was not necessary to dry the artifacts before heating up the wax, for the temperature of the wax is taken to over 300° F which is well above the boiling point of water; thus all residual moisture is vaporized in the wax impregnation step.Mild steel vats can be constructed in various gauges and are surprisingly durable and versatile, even in the lighter gauges. However, for maximum life, use a gauge that provides the strength required, and does not increase the weight beyond your ability to handle it. 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. Metal vats 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.

For large artifacts, such as anchors, cannon, and many other artifacts, welded mild steel vat work quite well. They can be constructed very economically, and will last for years. My laboratory has several welded mild steel vats that have been in use for over 10 years with only minor repair of minor leaks. Several anchors and canons have been treated in them over the years, and in every instance the mild steel vat was used as the anode. In contrast, North (1987:225) states, "If mild steel tanks are being used on no account should these be made the anode, in the presence of Cl^- ions, this causes corrosion particularly at weld lines and bends in the metal." I agree that when corrosion takes place it is going be at the stress points such as weld seams and bends. After about 6 years, one welded mild steel vat, developed a series of leaks along the seams. I repaired it easily several time, and eventually gave it to another lab, who continued to use if for several more years. I am presently using several welded mild steel vats that are more than 10 years old. Considering the cost of acquiring a comparable vat made of stainless steel vat (which has the same problem as mild steel in the presence of Cl^- ions, as discussed above under anode material.) or of even various plastic vats, and rubberized liners, welded metal vats are clearly the better choice. In my opinion, if a mild steel vat self destructs in 10 year from using it as the anode, it can be easily replace many times and still save money over the alternatives. I can only speak from experience and I have been successfully using welded mild steel vats as the container and as the anode for nearly 20 years with great success and I recommend them to any one looking for a cheap, dependable vat. For the same reason, I also use and recommend to others the use of 55 gallon steel drums or barrels, and even coffee can or paint cans, for use in electrolysis. Thus North's recommendation should be ignored, but the precautions of not using a sodium carbonate electrolyte and using 5% sodium hydroxide instead of 2% sodium hydroxide for the first 2 or 3 baths when cleaning a large steel object with high chloride content should be taken.In addition, it is difficult to understand how

a metal vat can be isolated from the anodes, and even if it is done, the Cl⁻ ions are still present which will still attack the metal vat, but if the vat is not hooked up as the anode, it is not anodically passivated which affords it some protection. The recommendation by North is totally disregarded by most conservator responsible for treating large iron artifacts from marine sites. Care must be taken to insure that the 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% sodium hydroxide electrolyte is used until the chloride levels decrease or the current density can be increased to keep the anode passive. A few comments should be made concerning the safety of using metal vats as the container and the anode. Most direct current 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 utilized is only 3 to 6 volts. At this voltage there is little personal danger in using metal vats. A good rule of thumb is that less than 32 volts is not hazardous because the IR (current resistance) drop in the human body is such that little or no current would pass. Care should be taken, however, to avoid shorting the two terminals of the higher voltage power supplies against each other.

CHLORIDE MONITORING

Crucial to the efficiency and success of electrolytic reduction of seabed antiquities is a system to monitor quantitatively the chloride concentration in the electrolyte. Several such tests exist. The Mohr method and ion specific electrode are often used, but the mercuric nitrate titration method is suggested because of 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 repeatable results. The following procedure is a modification of the "Compleximetric Titration of Chloride" as described in Volume 1 of Standard Chemical Analysis, edited by N. Howell Furman (1962: 331-332).

Equipment

1. Two 25 ml. burets; preferably one automatic.
2. Two small amber bottles with droppers.
3. 250 ml. beakers.
4. A magnetic stirrer.
5. Teflon-coated stirring bars.
6. Two 500 ml. amber plastic bottles.

Chemicals

1. Diphenylcarbazone-bromophenol blue indicator (keep a supply of No. 1 and No. 2 in amber dropper bottles).
2. .02N mercuric nitrate solution.
3. 18N sulfuric acid (keep a supply of No. 3 and No. 4 in amber plastic bottles to refill each buret).
4. Nitric acid to clean the stirring bars.

Procedure:

1. Take a 20 ml. sample of electrolyte or solution to be tested, and place it in a 250 ml. 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 NaOH electrolyte, 9N for sodium carbonate electrolyte, or 4.5N for water solutions) from the buret or with an eye dropper until an acid end point is reached. The acid end point is indicated by a color change form blue to clear. The amount of sulfuric acid does not need to be measured, it only acidifies the sample for the next step.
6. Titrate .02N mercuric nitrate, drop by drop, from the automatic buret until the sample 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. Additional drops make the color more intense, but do not change it.
7. Note the amount of mercuric nitrate titrated to reach the end point.
8. The concentration of chloride or sodium chloride in parts per million is calculated by the following formulas.

$$\frac{T \times N \times .05846 \times 1,000,000}{20} = T \times N \times 2923 = ppm \ NaCl$$

$$\frac{T \times N \times .03545 \times 1,000,000}{20} = T \times N \times 1772.5 = ppm \ Cl^-$$

T = amount of mercuric nitrate titrated.
N = normality of mercuric nitrate

The sensitivity of the titration can be increase by using a smaller normality solution or decreased by using a larger normality solution of mercuric nitrate. Adjustments can also be made for larger or smallersample sizes. After mixing the new solutions, they should be calibrated against a known standard. In order to facilitate the calculations a table, such as the example below, can be established using the formula above, and save much time in the future.

Amount of Mercuric Nitrate Titrated	ppm NaCl	ppm Cl⁻
.1	5.8	3.5
.2	11.7	7.0
.3	17.5	10.6
.4	23.4	14.0
1.0	58.5	35.0
10.0	585.0	350.0

etc. etc. etc.The NaCl readings are used to check the reagents against a known solution of sodium chloride.

The test gives the total amount of Cl⁻ or NaCl in the electrolyte. However, the unused alkaline electrolyte has a certain amount of chlorides in it. What needs to be measuredare the chlorides expelled from the artifact. To do this, the same test is run on a sample of unused electrolyte. This provides a blank which is subtracted from the sample from the electrolytic bath.Example:If a sample takes 4 ml. of mercuric nitrate to reach the end point, then 23.4 ppm Cl⁻ is present; if the blank is 17.5 (as in our lab) then the amount of chlorides derived from the artifact is 5.8.

Since the reagents are unstable they should be tested weekly against a known sodium chloride solution to assure consistency.

Comments on the Mercuric Nitrate Test

In taking the electrolyte samples, separate clean beakers should be used for each sample or the beakers should be rinsed with deionized water between each sample. Different stirring rods should be used with each sample or rinsed between samples. The stirring rods become stained purple but can be cleaned by putting them in dilute solution of nitric acid. Through this whole process, it should always be kept in mind that the glassware must be kept clean and uncontaminated at all times. After thoroughly washing the glassware, they should be rinsed with deionized water to avoid any cross contamination.

Two notes should be added in regard to the chloride testing procedure. First, the diphenylcarbazone - bromophenol end point is to some degree subjective, but most individual are consistent about their end point. Therefore, more reliable and consistent results are obtained if only one individuals familiar with it should the tests. All the chemicals at the exact concentration required for the chloride test can be purchased from a chemical supply house. Considerable expense can be saved, 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 deionized water. Slowly add the acid to the water, never the water to the acid. Extreme heat is generated. Let cool.

.02N Mercuric Nitrate Solution, $Hg(NO_3)_2 \cdot H_2O$

Dissolve 3.42 grams of reagent grade mercuric nitrate to 1 liter of distilled or deionized water.

Diphenylcarbazone-bromophenol blue indicator

Dissolve .5 grams of reagent grade crystalline diphenylcarbazone and .05 grams of crystalline bromophenol blue in 100 milliliters of 95% ethanol. While this may be mixed, the weight are so small, that I always purchase it already prepared.

1000 ppm Sodium Chloride Solution to test reagents

Dissolve 1 gram of reagent grade sodium chloride in 1 liter of distilled or deionized water. Dilute in half for 500 ppm NaCl, dilute a second time for 250 ppm, etc.

It is possible to determine how the chloride removal is progressing by quantitatively measuring the chloride concentration in parts per million in a sample of the electrolyte, or any other solution. The chloride level should be regularly and frequently (at least once a week) calculated and recorded. These

data can be used to make a graph that visually depicts at a glance the cleaning progress of an artifact. This will save much valuable time and enable the conservator to determine when to change a chloride-contaminated electrolyte and when all the detectable soluble chlorides have been removed from the object. Systematic chloride monitoring assures that each artifact remains in electrolysis the minimum amount of time. Chloride monitoring is an essential aid in evaluating the efficiency of chloride removal from the artifact during treatment. It measures the chlorides going into solution from the artifact and is used to determine when this process is completed. Chloride monitoring cannot 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 4 presents the progress of a typical iron artifact recovered from a marine environment. It clearly depicts the high initial rise in the chlorides coming from the guns and the subsequent decreases 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 was when the guns were taken out of electrolysis 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. Perhaps this is 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.
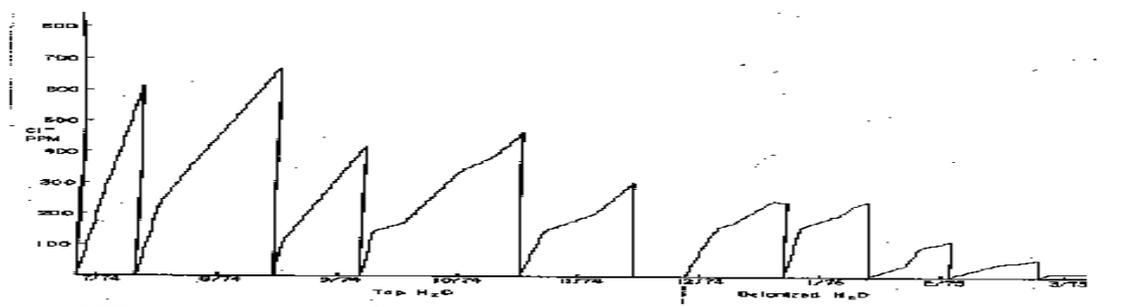

Figure 4. Graph Depicting the Diffusion of Chlorides into Solution During Electrolysis.

EXPERIMENTAL VARIABLES

Types of Electrolytic Setups

The manner in which artifacts are set up for electrolysis is dependent upon 1) the size and condition of the specimens, 2) the backlog of artifacts waiting to be processed, 3) the number of available regulated direct current power supplies, 4) the current capacities of these units, and 5) the number, size and nature of the vats. Each alternative has its disadvantages and advantages (Hamilton 1973. 1976).

The "Ideal" electrolytic setup (Figure. 5, A) consists of one artifact, surrounded by a close, form-fitted anode that is equidistant from all surfaces of the artifact, in one vat and on one regulated direct current power supply. With this setup a conservator is able to control precisely the current to the artifact and to maintain a predetermined electrode potential conducive to metal reduction on the surface of the specimen. The setup also allows one to monitor the chloride level in the electrolyte as it comes out of a single artifact. This option is selected when it is important to the optimum conditions to preserve those artifacts that are especially significant and need to be conserved as carefully as possible. Because a separate power supply is necessary for each artifact, this setup is not used for processing the average artifact.

The Type 2 electrolytic setup (Figure 5, B) has several artifacts in one vat, but each is surrounded by its own close, form-fitted anode, and each is on a separate direct current 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 5, B.) With this setup the current flow to each artifact can be carefully controlled and the correct electrode potential maintained. Since the chlorides present in the electrolyte come from all the artifacts in the vat, it is not possible to determine exactly when any one is free of chlorides. The chloride test, however, does tell the conservator when to change a chloride-contaminated electrolyte and when all specimens have been cleaned.

If a specimen requires close supervision, for example, to consolidate the 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 less importance.

There are any number of ways of connecting multiple artifacts to a single power supply and some form of this setup is the one most commonly used in electrolytic reduction. Regardless of how it is done, Type 3 electrolytic setups (Figure 5, C-D) are the least desirable from the standpoint of control, but they have the advantage of processing a number of objects at one time on one power supply in one vat. In one variety (Figure 5, C), 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.

The most popular variety of this same setup (Figure 5, D) is to suspend artifacts from a brass cathode rod conductor, with adjustable vertical anode sheets hung to either side, and preferably another anode along the bottom of the vat. This setup is sometimes referred to as the "sandwich setup". The oxygen evolved off the bottom anode sheet assures that the solution is continually mixed, thus 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 strongly oxidizing, acidic hypochlorite from forming at the anode.

The Type 3B setup (Figure 5, D) is the one most ommonly described in the literature (Plenderleith 1956:194-196; Plenderleith and Torraca 1968:243; Plenderleith and Werner 1971:198). This setup has all the disadvantages discussed above. In addition to the varied resistance of each artifact, 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. If one uses this setup, it can be improved by regularly repositioning the artifacts so that for the duration of the treatment, each object receives an average current. This alternative has the advantage of making it possible to process a number When of specimens on one power supply in one vat. This consideration is important when limited facilities are available to clean a great many 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 at the top to adjust for differences 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 assures that the solution is continually mixed, thus preventing the tendency for molecular chlorides and hypochlorite to concentrate along the bottom or at the anodes.
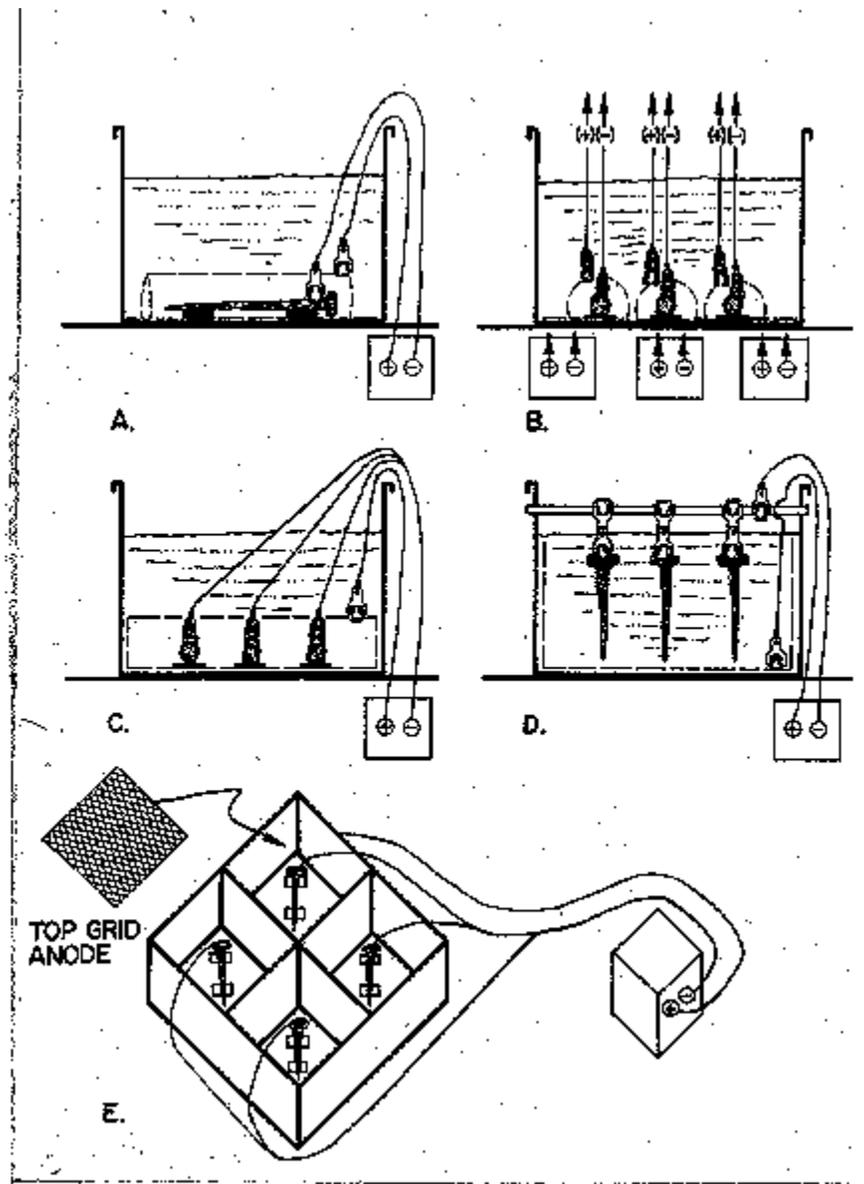
Figure 5. Electrolytic Reduction Setups.

Other refinements can be made to improve this work-horse alternative setup for electrolytic cleaning. Most descriptions (Plenderleith 1956:195) recommend that three brass rods be suspended across the top of the vat, vertical sheets of steel be hung by copper wire from the side rods, and artifacts be 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.

Utilizing the technique of suspending the artifacts by copper wire wrapped around then and the cathode rod is not effective. Inevitably, at some point electrical contact will be lost. It is more desirable (at least for most small specimens) to attach them 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 assure maintenance of a secure contact on the cathode rod and on the artifacts. With wrapped copper wire, a good contact is difficult to maintain. The clips also facilitate attaching and removing artifacts without unnecessary difficulty.

All of these varieties have the disadvantage of being unable to regulate the current to each artifact. Therefore, since the electrode potential or the current density cannot be controlled, the possibility of reducing the appropriate corrosion compounds back to a metallic state is considerably lessened. It is also impossible to monitor the chloride loss from any one artifact.

There is also a number of setups that involve a number of different artifacts, each in its own vat, but all connected to a single power supply. In Figure 5, E 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 direct current power supply for several artifacts. It also enables the conservator to determine exactly when each object is cleansed of chlorides, thus keeping the length of treatment of any one to a minimum. When an artifact is completed, any compartment can be taken down and set up without disturbing the electrolytic treatment in the other cells.

Another variation, being used by a number of conservation laboratories, is a single power supply hooked to a control panel consisting of a number of amperage gauges and rheostats. Each artifact is placed in a separate vat, and the current to it from the single power supply is regulated by means of the rheostat wired in line to it. Each artifact or vat has a gage that shows the amperage going to it. This particular setup can be used to regulate the current to a number of artifact from a single power supply and it has no particular disadvantages if the number of artifacts being treated is kept reasonable. However, a number of laboratories have adopted a practice of treating a number of marine iron (20 or more) from a power supply that can only put out 20 amps. The current to each artifact is in the milliamp range. The result is that is largely cosmetic; a lot of artifacts ar put into treatment at the same time, but the time to finished a single artifact is dramatically increased. In fact the situation or question arises of whether or not all the chlorides can actually be removed during this exclusively low current density electrolysis. I strongly recommend, from a multitude of experience, that whatever setup is utilized, that a range of current densities be used, and at some point in the treatment, it necessary to have a steady evolution of hydrogen from the artifact. Otherwise, this setup is a waste of time. See the discussion on current densities.

ELECTROLYTES

The only two electrolytes commonly used in conservation for treatment of iron objects are alkaline solutions of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), the most alkaline electrolyte one can get. In all cases it should be kept in mind that the alkalies (and acids) used in conservation should be concentrated enough to do the required job, but no stronger. This avoids over cleaning the specimen and helps keep the operating cost as low as possible. In recent years there has been a switch from a general use of sodium hydroxide to sodium carbonate. In his first description of electrolytic reduction, Plenderleith (1956:194) recommended a 5% solution of sodium hydroxide, but in the recent revision of the book, Plenderleith and Werner (1971:198), only a 5% sodium carbonate solution is recommended. No discussion is presented as to the advantages and disadvantages of each electrolyte and under what circumstances one is preferable over the other. In proper conservation procedures, both electrolytes have their uses and the conservator needs to know when to choose the one best suited for the object at hand.

Sodium Carbonate

Generally speaking, a 5% sodium carbonate electrolyte with a pH of 11.5 will suffice for the electrolytic cleaning of most iron artifacts if maximum reduction is not the objective. In terms of safety, it is much less caustic than sodium hydroxide and is much safer to handle. It is less conductive than sodium hydroxide and has to be used in stronger concentrations, 5 to 10% versus 2 to 5%. It is less soluble, which makes it more difficult to mix, but it does not generate the extreme heat of sodium hydroxide when mixed in concentrated solutions. When expense is considered, the stronger percentages of sodium carbonate are only slightly less costly, and sodium carbonate is usually easier to obtain from chemical supply houses than sodium hydroxide.

Preliminary experiments comparing 5% sodium carbonate electrolyte to 2% sodium hydroxide produced some interesting data. One set of experiments (Locke, ms) compared artifacts treated in 5% sodium carbonate mixed in tap and deionized water and 2% sodium hydroxide mixed in tap and deionized water. In all cases chlorides seem to diffuse out of the artifacts and reach higher Cl^- concentration in the sodium carbonate electrolyte more quickly than comparable artifacts in sodium hydroxide electrolyte. The major problem encountered with the sodium carbonate is the cathodic precipitates of insoluble carbonate on artifacts. The carbonate precipitates from the electrolyte and is more apt to happen at high current densities and when certain tap water is used to mix the electrolyte.

The marked carbonate deposit on the artifacts treated in 5% Na_2CO_3 is much more prevalent if the tap water has a large amount of carbonate in it. Artifacts from salt water, 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 possibly magnesium carbonate. Once an article is plated with a carbonate deposit, it can seal off the surface and chlorides can be trapped inside, misleading the conservator as to when treatment of the artifact has been completed.

If a white, insoluble carbonate precipitate occurs when using sodium carbonate as the electrolyte, then gluconic acid, sodium gluconate or sodium glucoheptanate can be added as a sequestering agent to the electrolyte. With the addition of gluconic acid there was a decrease in the deposit, but it was still very apparent on iron objects in Na_2CO_3 in tap water, and slightly noticeable in Na_2CO_3 in deionized water. By adding 2% of the weight of the sodium carbonate in the electrolyte as gluconic acid or sodium gluconate, the tendency to deposit carbonate is reduced but not always eliminated. For maximum effectiveness gluconic acid or sodium gluconate require an excess of a free base (hydroxide). The pH of 5% sodium carbonate (11.5) is too low for maximum effectiveness. Tests with sodium glucoheptanate as a sequesterant appears to eliminate the carbonate deposit. If the tap water in an ares contributed to the formation on the precipitate, then only deionized water should be used with Na_2CO_3. In the precipitate is not noticed, then there is no reason to go to the trouble of adding a sequesterent to the electrolyte.

If a carbonate deposit does precipitate on an object it is usually impossible to brush off or remove by electrolysis. The carbonate deposit can, however, be eliminated by soaking several days in a 5% 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).

Another major problem commonly encountered with a sodium carbonate electrolyte is that the pH and conductivity of the solution are not adequate to keep the mild steel anodes passive in the presence of high chloride levels. In sodium carbonate (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 than when NaOH, with its surplus of hydroxyl ions, is used. To avoid this the mild steel anodes must be cleaned and replaced more often than in sodium hydroxide, especially if the electrolyte is not circulated. It has also been noted that takes longer to rinse out all residue of a sodium carbonate electrolyte 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 a ferrous corrosion compound is possible using 2% to 5% NaOH with a pH of 12.9 than 5% Na_2CO_3 with a pH of 11.5. More details in regard to this are discussed subsequently under electrode potentials. In general, sodium carbonate can be used as an electrolyte if reduction is not the objective, but when it come to treating metals from marine site, sodium hydroxide is preferred.

Sodium Hydroxide

The shortcomings of 5% Na_2CO_3 are overcome by using 2 to 5% NaOH with its higher pH. However, this electrolyte being much more caustic, constantly presents a potential hazard to those working with it. Caution has to be exercised, and adequate safety equipment such as gloves, eye shields, eye washes, and safety showers should be available. In spite of these problems, a 2% solution of NaOH is the only option is the objective is to reduce corrosion products. In most laboratories that treat iron recovered from marine sites, it the standard electrolyte.

As a precautionary measure, gluconic acid, sodium gluconate, or sodium glucoheptanate in the amount of 2% 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 (which come from residue of the encrustation and/or the electrolyte) onto the objects being electrolytically cleaned is a problem. In our operations 50% aqueous sodium glucoheptonate has been found to be the superior sequesterent in both NaOH and Na_2CO_3 and can be stored for longer periods than 50% aqueous gluconic acid. In addition to preventing undesirable deposits on the cathode, the gluconate ions act as rust inhibitors which keep the steel anodes clean by sequestering dissolved ferric ions which would ordinarily precipitate as ferric hydroxide or oxide. They also prevent the specimens from rusting during rinsing and drying. More enduring protection is suspected but not substantiated.

EFFECTS OF ELECTROLYTES ON METAL VATS

When iron objects from the sea are cleaned there is a very large buildup of chlorides in the electrolyte for the first few baths. The high level of chloride (2,000 to 18,000 ppm) and lack of external circulation can cause the anode (the metal vat) to corrode extensively through anodic dissolution. The problem is worse with 5% Na_2CO_3 so it should not be used in vats that are not easily replaced. Corrosion is still encountered with 2% NaOH even with its higher pH of 12.9. By using a 5% NaOH electrolyte with its surplus of hydroxyl ions, anodic dissolution is more easily prevented. After the chloride levels drop below 1000 ppm, 2% NaOH can be safely used.

WATER IN ELECTROLYTES

It is common to see the statement that only distilled or deionized water is to be employed in all electrolytes. The exception to this general rule occurs when the objects to be cleaned are heavily contaminated with chloride. It is more economical and safer to use tap water in the electrolyte until the

chloride level approximates the level of the local tap water. Then deionized water is substituted. The use of tap water in the first electrolytic baths may actually reduce the electrolysis time. Our preliminary experiments indicate that chlorides are removed more rapidly when tap water rather than deionized water is used in the electrolyte, Na_2CO_3 or NaOH. While there was a problem of selecting truly comparable artifacts for the experiments, the same conclusions have been derived from four tests on eight apparently analogous specimens.

In summary, when sea-recovered artifacts are cleaned by electrolytic reduction, it is recommended that the artifact be started in 2 to 5% NaOH in tap water. During this early period, at low current density, the reduction of ferrous compounds is attempted and high levels of chloride are removed. Reduction is continued in the tap water electrolyte until the chloride measurements approximate the level found in the tap water. Tap water is then replaced by deionized water, electrolysis is continued with 5% NaOH or lowered to 2% NaOH. A low current density is maintained until the electrolyte is again changed, then a medium current density is used.

The higher pH of NaOH is preferable when the objective 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 archeological sites, but this generalization should not be carried out too far. There will almost always be some ferrous compounds that can be successfully reduced.

CURRENT DENSITY

The current density used in electrolytic reduction is expressed as the number of amperes per unit of square area, introduced in the electrolytic cell by external D.C. power supply, such as one ampere per square centimeter (1 amp/cm2). Any given current density should have a given objective, but in the literature these objectives, if any are intended, generally are not stated. Current densities from .001 to 1 amp/cm2 have been proposed in the literature (Plenderleith 1956:195; Plenderleith and Torraca 1968:242; Plenderleith and Werner 1971:198; Townsend 1972:252; Pearson 1972a:12), but guides to their use are seldom given.

Plenderleith and Werner (1971:198) suggested approximately 10 amps per square decimeter (1 amp/cm2) of cathode area so as to give a steady, vigorous evolution of hydrogen. They say, however, that this density is not critical for iron and steel artifacts. This statement is misleading. If the artifact is solid, well-consolidated metal, or has only ferric corrosion compounds, the current rate is not critical. If the object has ferrous corrosion compounds, an initial high current density 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. By using a low current density in the early stages these problems can be avoided. Even more important, it is possible to reclaim enough of the metal through a reduction process to consolidate the metal oxide interface and thus preserve a closer approximation of the object's actual dimensions. This is true even of wrought iron objects whose corrosion layers are often nonadherent.

In Hamilton (1976:41) I proposed the following current densities and objectives:

1. Low current density .001-.005 amp/cm2 attempts to approximate the reduction range of ferrous corrosion compounds.
2. Moderate current density, .05 amp/cm2 attempts to approximate the optimum conditions for chloride removal without undue evolution of hydrogen.

3. High current density of .1 amp/cm2 has as its major goal the vigorous evolution of hydrogen for mechanical cleaning.

These were recommended as rough guidelines for treating most iron artifacts from under the sea. These current 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. They do work as rough guidelines. 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, 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 current density and medium current density the marine encrustation, some corrosion products and scale 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 insures the complete removal of any remaining marine encrustation and loose corrosion layers or scale, as well as any remaining chlorides. When high current density electrolysis is used only in the last state of electrolysis, the metal corrosion products that are capable of being reduced have been reduced and it is less likely that they will be removed by the vigorous evolution hydrogen. While the above densities serve as useful guidelines, they cannot be adhered to rigidly. The conservator should respond to the individual peculiarities of the objects and to the facilities available. Thus, in the case of very large objects, these calculations might require current in excess of the maximum capacity of an available or practical power supply.

Anyone who has used current densities knows the difficulty of determining the square area of many metal artifacts because of their irregular shapes. Although it is seldom stated, the calculated area should be concerned only with the cathode area that is exposed opposite an anode. The total area of the cathode is used only when an anode is form-fitted around all sides of the cathode; otherwise, only that area exposed to an anode is used. It must be understood that any given current density determines the electrode potential established between the electrodes and the electrolyte and the rate of hydrogen evolution at the cathode. For reduction of metallic corrosion compounds, the establishment of a certain electrode potential on the cathode is essential. Since there is not a one-to-one relationship between a given current density and a corresponding electrode potential on differentially corroded iron artifacts and different iron alloys, current density alone is not the ultimate guide. Calculated current densities are simply not a fine enough tool for precision treatment.

For these reasons, North (1987:226) recommends starting electrolysis off at an applied voltage of 1.8 volts D.C. and to continue treating the artifact at this voltage for at least one week. This voltage is usually not sufficient to cause hydrogen to be evolved, but it does reduce the more reactive specie present in the artifact and sets up the artifact so that a hydrogen potential graph can be developed for that particular artifact. After the first week of electrolysis the point, as indicated by voltage, is found where the current, as indicated by amperage starts to increase rapidly. The chart is made starting with points much lower than the point of hydrogen evolution and increasing the voltage well above the point of hydrogen evolution. By graphing the intersection points, with amperage as the x-axis and volts as the y-axis, it is easy to see where the voltage that corresponds to the point at which the amperage starts to increase rapidly. This is the hydrogen evolution voltage. The electrolysis is then conducted at this voltage. By using this technique, some of the difficulties of using current densities are eliminated, and it use is recommended.

In practice, I discovered years ago, that neither measuring current densities or establishing hydrogen evolution voltage is necessary for most artifact. One can merely "eye ball" the artifact. Start the electrolysis off by slowly increasing the voltage or amperage, until you first began to observe a few bubbles of hydrogen evolving. In theory, for metal reduction you do not need any hydrogen evolution at

all, but the irregular evolution of hydrogen from the surface of the metal gives one a visual indicator that the current is flowing. By this technique, neither voltage or amperage is the indicator, it is the evolution of very first evidence of hydrogen evolution. Run the artifact at this setting. However, after a short time, one will observe the evolution of hydrogen increases as the resistance of the artifact is broken down and there is some reduction of the corrosion products in the metal. So, you usually have to decrease the setting back to the point where hydrogen first starts to evolve. After going through this low hydrogen evolution, where the objective is to reduce as much of the corrosion products as possible, the current is increase so that there is a steady, not vigorous, evolution of hydrogen. This is necessary if one wants to remove the maximum amount of chlorides within a reasonable length of time. Maintaining a very low current density current will only prolong the process an unacceptably long time and not contribute any other benefit. As an option, one may choose to run the artifact for a few hours or days at a high current density that is for maximum mechanical cleaning. In general, I have found that surfaces of the artifacts that might come off at this point during the high current density treatment, have little change of staying intact as you carry it through the rest of the treatments. This process is a simplification over that proposed by North (1987:226) for it depends on: 1) visual evolution o slow, irregular evolution of hydrogen for maximum reduction, 2) visual evidence of a steady evolution, not vigorous, of hydrogen for the much longer process of chloride removal, and optionally, 3) a vigorous evolution of hydrogen for final mechanical cleaning to remove any last remaining encrustation or loose corrosion products. In practice, this is how most of the experiences conservators determine the current density at which to treat iron artifacts, as well as artifacts of other metals and works well for most artifacts.

At times, a more precise alternative, than that proposed by North, or that just described above is required for treating those one of a kind artifacts, for which there is no room of guessing. In those cases, it may be necessary to actually measure the electrode potential established at the surface of the artifact being treated. By treating taking a series of carefully measured artifacts at different voltage/amperage rate and measuring the resultant electrode potential is how I derived the current densities I recommended in 1976. Over a period of time, I found, and electrode potential measurement validated it, that all that was necessary was a visual indicator of the rate of hydrogen evolution through treatment. I will briefly discuss electrode potential measurements, for the objective of current densities, hydrogen evolution potential, and visual observation of rate of hydrogen evolution is to establish at the metal surface and corrosion layer the voltage necessary to reduce the corrosion products present. In the case of iron, most of the corrosion products, if they can be reduced, are reduced to magnetite. It has not been shown that any of the corrosion products actually reduce back to metal, as in the non-ferrous metals. By considering electrode potential, it also clearly shows why one electrolyte is preferred over another, when maximum reduction is the objective.

ELECTRODE POTENTIALS

The normal electrode potential, or relative activity, of each metal is ranked in an electromotive series based on the hydrogen scale (Table 1). The normal electrode potential of each metal is in comparison to a normal hydrogen electrode since there is no practical means of measuring a single electrode potential without reference to another single electrode potential. 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 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, a potential more positive than the equilibrium value must be established. For cathodic reduction a more negative potential must be created. Cathodic reduction of iron becomes pronounced only if the potential is made considerably more negative than the equilibrium value. Dissolution of the anode becomes significant when the potential is made considerably more positive.

The potentials of the 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 volt for a monovalent ion, or 0.029 volt 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).

> 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).

From the Electromotive Series in Table 1 it can be seen that the reduction reaction of ferrous ions, $Fe^{+2} \rightarrow Fe°$ - 2e, occurs at -.409 volts to -.440 volts at a pH of 0. The reduction potential increases -.029 volts for each pH increase. The reduction of ferric ions, $Fe^{+3} \rightarrow Fe°$ -3e, occurs at -.036 and increases -.019 volts per pH increase. The hydrogen discharge potential $2H^+ \rightarrow H_2$ -2e occurs at a voltage potential of 0 and increases -.058 volts per unit pH increase. The reduction potential of ferrous, ferric and hydrogen ions at different pH's and standard temperature of 20° C. are graphically presented in Figure 6. Utilizing this graph it is possible to determine the theoretical electrode potential voltage necessary for reduction of iron oxides for any given pH.

In electrolytic cleaning of iron the cathode electrode potential is critical because as the hydrogen discharge potential is reached, hydrogen ions are formed, which are utilized to reduce adjacent ferrous compounds. At more negative potentials molecular hydrogen is formed so rapidly that the molecules combine with each other and evolve as hydrogen gas. Any hydrogen evolved as a gas does not reduce oxide compounds. Rather, it acts as a mechanical cleaning agent that physically removes any unconsolidated corrosion layers. The theoretical point for the electrolytic reduction of ferrous ion corrosion compounds is at the intersection of the hydrogen discharge line and the ferrous ion reduction line (Figure 6). Using the formula $Fe^{+2} + 2e \rightarrow Fe°$ and substituting values for the Fe^{+2} reduction potential and the correction for pH (-.409 -.029 pH) the intersection appears at a pH of 14.1 and an electrode potential of -.82. This potential is reached just prior to the evolution of hydrogen. It is possible to establish or at least approach a maximum pH of 14 on the surface of a cathode in dilute aqueous caustic soda. At low current density electrolysis, little or no hydrogen is evident; however, the objective is to establish the electrode potential of the intersection of the discharge potential of hydrogen and the reduction potential of ferrous ions or immediately to the left of this intersection on the cathode surface. It is then theoretically possible to obtain maximum reduction and/or consolidation of the ferrous corrosion compounds.

It has already been stated several times that it is thermodynamically impossible to reduce ferric oxide and other ferric iron corrosion compounds in an aqueous solution. This point is graphically depicted in Figure 6. The reduction electrode potential is well out of the range possible for electrolytic reduction in an aqueous alkaline electrolyte and an external EMF. By measuring electrode potentials it is possible to insure that a desired electrochemical reaction will occur on a metallic surface in contact with an electrolyte of known pH and ion content. Controlling the electrode potential is the main objective and advantage of electrolytic reduction of metal artifacts. The procedure for measuring electrode potentials is described in Hamilton (1976:103-105).

By using electrode potentials it is possible to determine what current density in an electrolyte of known pH is required to establish the condition most conducive to the reduction of ferrous compounds on the metal. Figure 7 gives the measured potentials of an artifact in an electrolyte of 2% NaOH 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 IR of the electrolyte had dropped, and the resistance of the artifact was broken down. After a period of 20 minutes, and throughout the 11-day test period, the measurements fell within a rather narrow range. Utilizing the data presented in Figure 6, the potential range for ferrous ion reduction at a pH range of 13 to 14 can be determined as -.79 to -.85 volts. On Figure 7 this potential range is achieved at a current density below and up to .005 amps/cm2, which is barely within the capability range of 2% NaOH. As can be seen in Figure 8, which compares the potentials of the same artifact in 2% NaOH and 5% Na_2CO_3, the sodium hydroxide is in the more favorable position. 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. Electrode potentials are affected by temperature, pH value and electrolyte composition. In the conservation of iron it is the pH that is most important. There are several ways of measuring the pH of the electrolyte, but no simple way of determining the pH at the surface of the electrodes. 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 the remaining electrolyte. In order to arrive at a reasonable estimation of the prevailing pH at the cathode, the pH of the electrolyte was taken and a maximum increase of one pH for each electrolyte was assumed, for a maximum pH of 14 for NaOH and 12.5 for Na_2CO_3. This approach is imprecise, but no other means was perceived for ascertaining the pH. These adjusted pH ranges are those shown in Figures 6, 7 and 8.

Once an electrode potential has been established on the surface of the cathode, periodic measurements and adjustments have to be made in the direct current to maintain that potential. 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 (M-H) bond is established and the surface becomes saturated with hydrogen, followed by the evolution of hydrogen. Until the metal surface becomes saturated with hydrogen the potential shifts. Once equilibrium is established the potentials even out. After establishing an electrode potential on an artifact, daily adjustment may be necessary to maintain the potential as the IR of the electrolyte drops with the addition of dissolved salts and the resistance of the metal and its corrosion products are altered. Before adjusting back to the predetermined potential, one has to be sure that any shift is due to changes in the cathode, and not due to the transport system, i.e., the electrolyte through lack of circulation. In Figure 7 the six series of tests were taken over an 11-day period without circulating the electrolyte. On the last day the electrolyte was air-lanced and the test run again. It can be seen that there are negligible differences in the potential readings in the last two tests except for the
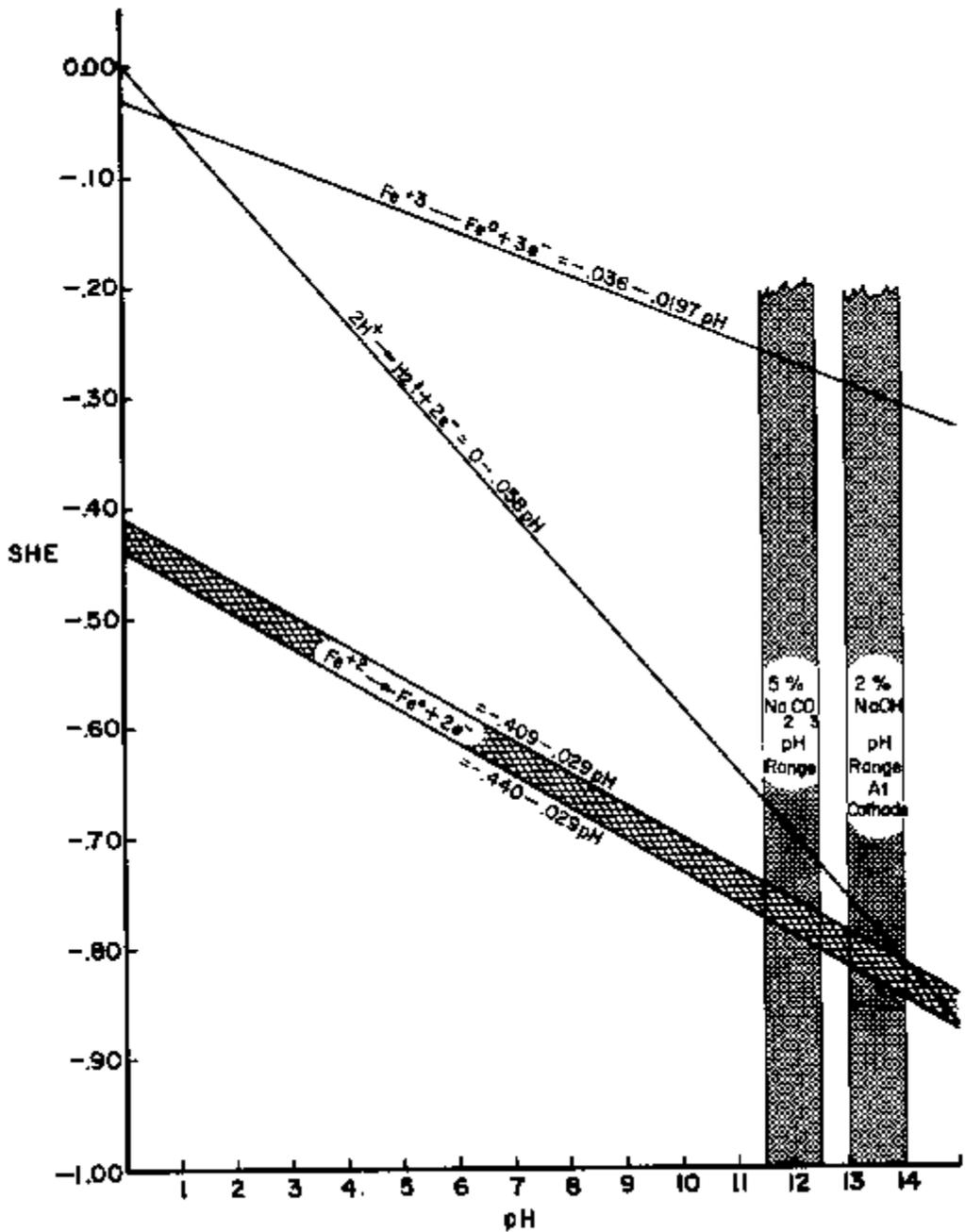
Figure 6. Reduction Potentials of Ferric, Ferrous, and Hydrogen Ions at Different pH's and Standard Temperature of 20°C. The pH Range of a 5% Na_2CO_3 and a 2% NaOH Electrolyte are shaded.
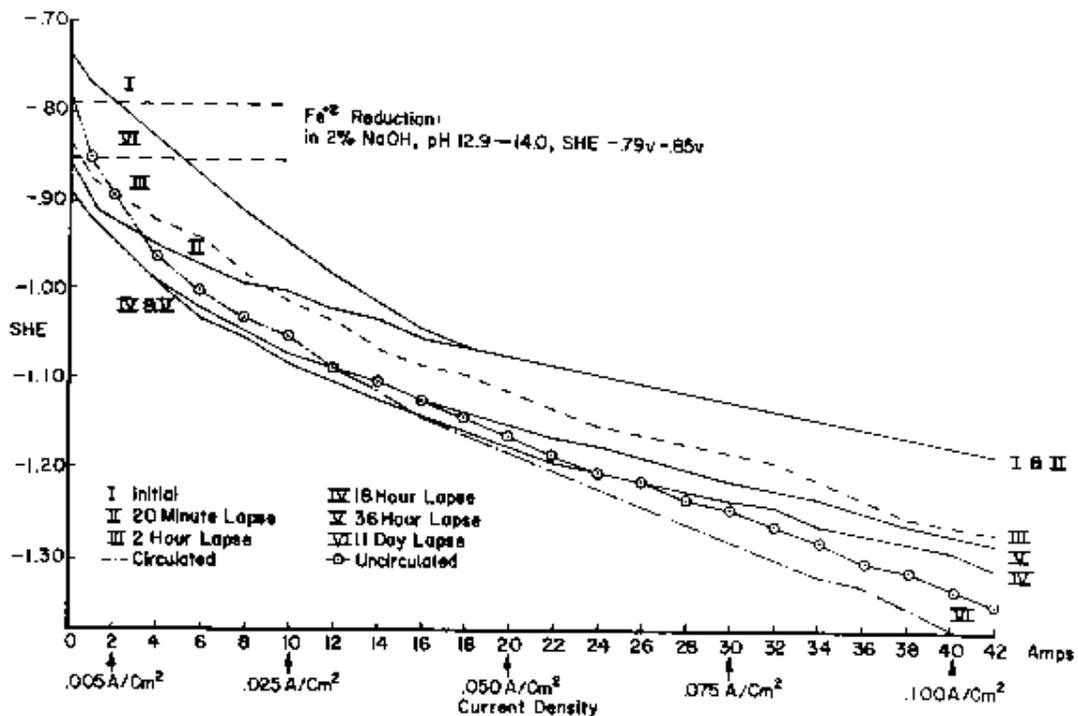
Figure 7. Reduction Potentials at the Surface of an Iron Cathode during Electrolysis in a 2% NaOH Electrolyte at Different Current Densities over an 11 Day Test Period.
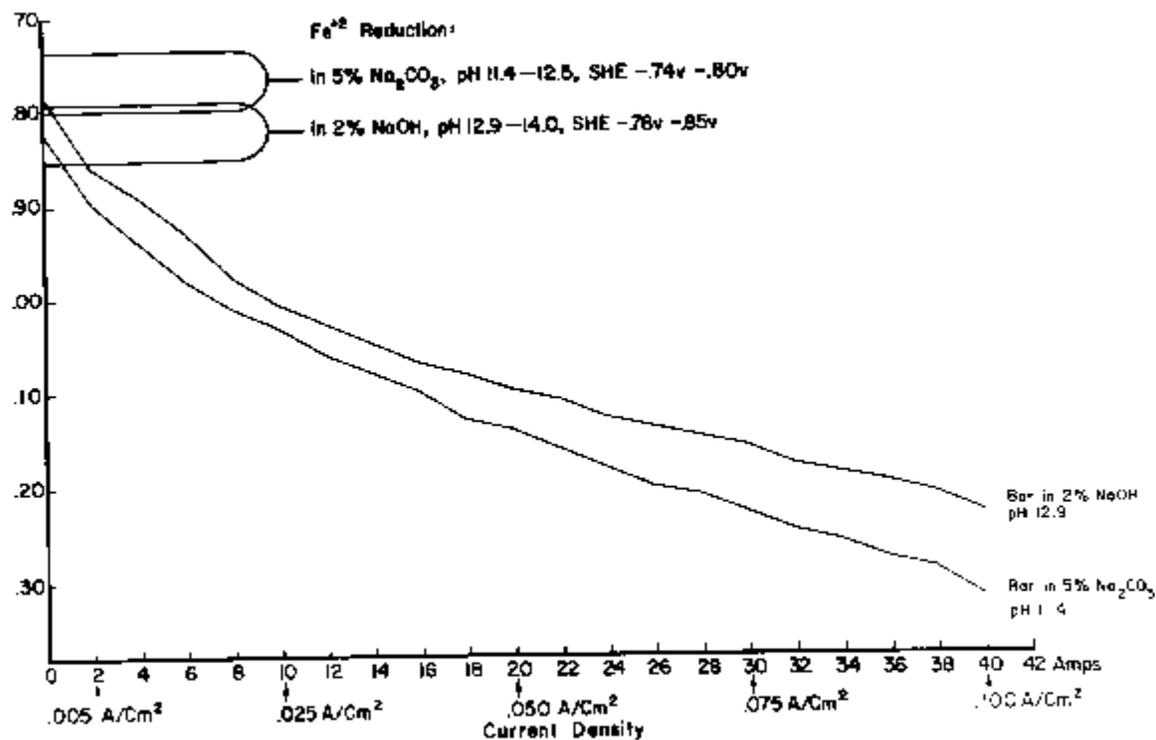
Figure 8. Comparison of the Reduction Electrode Potential on the Surface of the Same Iron Cathode in a 5% Na_2CO_3 and a 2% NaOH Electrolyte.

potentials at high current densities.The transport system is still adequate, especially at the reduction potentials of ferrous compounds. If any changes occur in the transport system it will become visually apparent at the anode. Even though an alkaline electrolyte is used, acidic areas can form at the anode. In these areas chloride ions react with the positively charged anode to form hypochlorite ions (ClO^-) or hypochlorous acid (HClO) which oxidizes 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 is altered, however. 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 will be reflected in the electrode potentials, making it possible for the conservator to identify those areas requiring more extensive reduction and a way to measure the progress of the electrolyte reduction. The data acquired from electrode potential measurements was used to arrive at realistic current densities that established the approximate electrode potentials for the bulk of the iron artifacts that will require treatment but do not warrant the close supervision or the time required for taking potential measurements. Still, there is the difficulty of arriving at current densities for given artifacts, especially irregular shaped artifacts and differentially corroded artifacts. For these reasons, except for those special artifacts, using either hydrogen evolution potential voltage or merely visually observing the rate of hydrogen evolution is sufficient.

OUTDOOR ELECTROLYSIS

Any electrochemical reduction cleaning process results in irritating caustic vapors and hydrogen gas, which have to 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, or the electrolytic vats can be placed outside. In practice, most laboratories will utilizes 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 year-round in outside vats made of mild steel or plastic.

Working outdoors overcomes the problems of expensive air exhaust systems. The solutions are changed often enough so that any air-blown dirt and sand present no problems. Rain is of no concern, unless it is heavy enough to dilute the solution substantially. This problem can be determined easily 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 deionized 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 (safe from human traffic) and has adequate utilities, it is strongly recommended that outdoor electrolytic reduction be seriously considered. The power supplies must be kept out of the weather, but sheds over the vats are optional. Although lower winter temperatures do not decrease the chemical activity significantly, there can be an IR drop in the electrolyte that will increase the cell voltage. In my laboratory, at Texas A&M University, by far, the majority of electrolysis is carried out in various metal vats place outside.

GENERAL OBSERVATIONS ON CLEANING IRON OBJECTS ELECTROLYTICALLY

These observations are directed primarily toward large iron objects, but are not restricted to them. Recommendations for the improving the procedure and reducing the time in electrolysis are given.

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

The earliest attempt to clean electrolytically 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:

1. Failure to remove the wooden undercarriage shielded a large portion of the cannon and prevented an even distribution of the current.
2. Treatment was too brief to remove the chlorides. It lasted 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 assure an even distribution of current.
4. After the brief electrolytic treatment, the wooden undercarriage was swabbed with hydrochloric acid to neutralize the 1% 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 clean a large cast-iron cannon. In 1963 two guns from a ship sunk in 1790 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% Na_2CO_3 electrolyte. They were run at a rate of 20 amperes at 4 volts (current density ca. .027 amps/cm2) for one month and a rate of 150 amperes at 4 volts (current density ca. .2 amps/cm2) for five months.

Not enough details on all aspects of the electrolytic treatment are presented to evaluate adequately the methods used, but after being displayed outdoors for two years the treatment of the wet gun was judged to be successful, although the dry gun continued to deteriorate as rapidly as before electrolysis. Regardless, the treatment appears to have been successful, for the wet cannon continues to be stable. Perhaps the main reason for the successful treatment of one gun is that is was kept wet, preventing further corrosion, and the six months of electrolysis assured the complete removal of the chlorides in the metal.

The preliminary conclusion of Patoharju is that wet cast-iron objects coming directly from the sea can be conserved by electrolysis in a liquid phase. If the object is allowed to dry out before treatment the specimen will undergo further oxidation and any conservation attempt may be futile. A similar problem has been noted in my work. A couple of large breechblocks had been successfully treated, leaving the majority of the corrosion layer intact on the specimens. A month after completion of the treatment it was decided to put them back into treatment in order to darken the surfaces. The wax was melted off in an oven, which probably caused increased conversions of FeO to Fe_2O_3 on the breechblocks, and they were put back into electrolysis. In both cases the corrosion layer completely detached, leaving a badly disfigured surface. These examples suggest that if there are thick layers of corrosion, the treatment must be successful the first time. Wrought iron corrosion layers are nonadherent and after the water is

removed from the corrosion layers during the drying and sealant steps, they 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. Perhaps this can be alleviated by soaking the object in electrolyte for a long time to re-establish the electrical couple prior to any further electrolysis.

Pearson (1972a, 1972b) reports the conservation of six cast-iron cannons and other relics jettisoned in 1770 by Captain Cook on Endeavor Reef off the Australian coast. Pearson's very thorough and detailed report on the conservation of the cannon is summarized here.

Upon arrival at the laboratory the cannons were stored in 2% solution of sodium hydroxide and each cannon placed in an epoxy-coated wooden support cradle especially constructed to handle it throughout preservation. The coral encrustation was mechanically removed with hammers and the cannon surfaces carefully scrubbed with water to remove the loose black corrosion products. Each cannon and its support cradle was then set in a fiberglass-lined wooden tank to be electrolytically cleaned in a 2% NaOH electrolyte. The 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 (.001 amps/cm2) was applied. Three cannons were simultaneously treated in separate vats hooked up in series on one power supply, analogous to the type 4 setup described earlier. 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. In this way 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 required six to eight weeks of electrolysis for each cannon.

A current density of .001 amps/cm2 was chosen by Pearson because through experiments, it proved to be the optimum 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 to remove chlorides. More importantly, this current density is within the range most efficient for the reduction of ferrous iron compounds. A series of experiments (Hamilton 1976:40-46) on wrought iron indicate that .001 amps/cm to .005 amps/cm2 is theoretically most efficient for metal reduction (as is shown in Figures 9 and 10), .05 amps/cm2 to .1 amps/cm2 is most efficient for chloride removal and the vigorous evolution of hydrogen produced by a density of .1 amps/cm2 and above is used for mechanical cleaning.

EXPOSURE TO ANODE SURFACE

When Pearson (1972a) cleaned Captain Cook's cannons, he used 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 assume 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 has occurred at these two support points because the cannons were not rotated sufficiently during the treatment. We have found similar occurrences at support points and even on small surface areas covered with plastic identification tape. From these examples it is clear that no portion can be covered throughout electrolysis, for even a small piece of narrow tape can shield the area beneath sufficiently to prevent complete removal of the corrosive chlorides. To avoid this, cannons should be rotated frequently and the position of movable supports, such as bricks, should be shifted each time the electrolyte is changed. When numbered plastic tape is placed on artifacts for purposes of identification, the position of the tape should be moved at least once during electrolysis.

More than any one factor, it is unfortunate that the conservation literature has failed to emphasize the importance of form-fitted anodes when electrolytically cleaning artifacts. Anodes placed to assure an even current density over all the surface of the artifact improves the over-all efficiency of the process. Now by form-fitted, I do not mean that there is an exact distance maintained between the artifact and the anode. This is nearly impossible for irregular shaped artifacts. I simply mean for artifact, especially irregular shaped artifacts, bend and shape the anode so that is some what evenly distanced form the anode. North (1987:225) states that the use of form-fitted anodes has been suggested, citing Hamilton (1976) but he goes on to state that these have been shown to be unnecessary as long as the artifact-anode distance is between 20-80 cm a satisfactory current distribution will be achieved. However, in support of my recommendation he then goes on to say that when a rod is used as the anode in the barrel of a cannon, this does not apply, for the current will be concentrated in the bore because of the small distance between the rod and the cannon. Then while discussing the establishment of hydrogen evolution potential voltage (North 1987:226) he states that if the hydrogen gas evolution is coming from only one area of the artifact, that there is either a poor electrical contact at this point or **that the anode is too close to the artifact at that point** (emphasis mine). Obviously, my recommendation stands; a anode shaped to conform to the shape of the artifact is recommended even if we do not do it in everyday conservation, usually placing artifacts between two anodes. In any case a form-fitted anode, if I may call it that, will maximize iron reduction and chloride removal, and will cut down on the electrolytic time. Since all areas of the objects should be exposed to anode surface, immovable supports, lifting frames, and such things as wooden undercarriages on cannons should be avoided.

DURATION OF ELECTROLYSIS

Another disturbing aspect of the preservation of Cook's cannons was the short electrolysis time, six to eight weeks, and the long rinse period, up to five months. The latter indicates that the full potential of electrolysis was not achieved. If time had permitted a longer electrolysis period, it is probable that the rinsing time could have been substantially cut.

Ora Patoharju (1964) reported an electrolysis time of six months to clean two cannons recovered from a 1790 wreck. This is similar to our experience, as every wrought iron object approaching the size of a cannon has required between six and twelve months of electrolysis. As an example of the length of time required for large wrought iron objects, one fully armed swivel cannon, 6'7" (198 cm) long, required 20 days to remove all the encrustation and to dismantle the component parts, 251 days of electrolytic cleaning at 20 to 50 amps, seven days of rinsing in several changes of alternate boiling and cold deionized water, 15 days dehydrating in alcohol, and one and a half days submerged in molten microcrystalline wax. Three hooped barrel cannons processed together in one vat required 480 days of electrolysis, three months of rinsing (rinsing period was prolonged while awaiting delivery of microcrystalline wax), five days of dehydration in alcohol, and five days submerged in microcrystalline wax. Even small wrought iron artifacts such as spikes often require 60 to 90 days of electrolysis.

Reducing Electrolysis Time

It is clear that when artifacts are electrolytically cleaned in small vats with a low volume 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. It follows that more frequent changes of the electrolyte will considerably speed up the process also.

Several aspects of shortening the length of electrolytic treatment have been worked out. It has been concluded that the problem of reducing the chloride (Cl$^-$) level in the electrolyte below 50 to 100 ppm

Cl⁻ requires the greatest amount of electrolytic time. Below 100 ppm Cl⁻ the artifact is presumably in the final stages of cleaning. There are at least two explanations for this long electrolytic time: 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 equation.

The Donnan 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 as 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 is higher or equal to the Cl⁻ level in the artifact. This results, according to the Donnan theory, because Cl1 = Cl2, i.e., the chloride ion concentration of two solutions in contact will equalize. As a result, chloride tests can be misleading under equilibrium conditions. Negligible or no increase in the chloride reading in the electrolyte over several days may lead the conservator to believe that the chloride removal has been accomplished and terminate electrolysis, leaving deep-seated chlorides in the artifact.

For optimum efficiency in electrolysis, the chloride level of the electrolyte should be less than the chloride level of the artifact. When the Cl⁻ content in the electrolyte maintains a steady level in a controlled constant volume of electrolyte, it is apparent that: 1) Equilibrium conditions have been obtained and unless the electrolyte is renewed to lower the Cl⁻ concentration, little or no Cl⁻ removal from the artifact can be achieved. 2) The chloride removal process has been completed. By changing the electrolyte this can be easily validated. By frequently changing the electrolyte and using as large a vat as possible, principles of the Donnan equilibrium equation can be used to the conservator's advantage. The lower the Cl⁻ level in the electrolyte, the greater the driving force for Cl⁻ removal, which translates as Time and Efficiency.

For example, with more frequent changes of electrolyte, one wrought iron anchor required six months of electrolysis in contrast to 11 months for the first anchor cleaned. Three wrought iron cannons required 16 months of electrolysis at 100 to 150 amperes and three volts to remove the chlorides. A second group of three hooped barrel cannons were completed in 11 months. Similar decreases in required electrolytic time have been achieved with other specimens treated in larger volumes of electrolyte and when the electrolyte is changed often. Crucial to the electrolytic process is a satisfactory quantitative chloride-monitoring test. The chloride tests allow the conservator to determine the rate and efficiency of the chloride removal.

SODIUM SULFITE TREATMENT

The alkaline sulfite treatment was developed by North and Pearson (1975) to stabilize marine cast iron, but 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 they must have a metallic core. Otherwise, the iron object breaks up in treatment. The procedure is as follows:

1. Once the objects have been mechanically cleaned, they are 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. Tap water can be used for the first one or two baths but deionized or distilled water

should be used in the final baths. The container should be filled as full as possible and sealed to prevent any access to air. The solution is mixed and the object placed in it as quickly as possible to avoid any oxidation of the solution. The container is placed in an oven and kept heated to a temperature of 60 degrees C. The object is processed through several baths until chlorides are eliminated; this may take from a week to several months and numerous 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 where they are discarded with each bath change. The objects come 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 objects are washed for one or more hours in several baths of deionized 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 deionized water following the alkaline sulfite stabilization, the barium hydroxide baths can be eliminated -- thus it is optional.

The alkaline treatment has been very effective for conserving iron recovered from a marine environment. The main drawbacks of the treatment are that it has to be carried out in an air tight container and the solution should be kept heated.

CHEMICAL CLEANING

A number of chemical cleaning procedures are used for iron artifacts from non-marine environments with negligible chlorides present. The most common chemicals are oxalic acid, citric acid, phosphoric acid, ethylenediamine tetra-acetic acid (EDTA), and other complexing agents. Because of the problems of chlorides in iron from the sea, the exclusive use of any of these 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 from salt water. Details concerning the use of these and other chemicals are described by Plenderleith and Werner (1971).

Two chemicals, phosphoric acid, along with 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 in a possible 2,000 year-old Roman tannery in England were found to be in an excellent state of preservation (Farrer, Beck and Wormwell 1953). Before either chemical can be used, however, the chlorides must be removed by electrolytic reduction, alkaline sulfite, 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 a phosphate-coating. Solutions of hydrolysable tannins such as chestnut, myroblans, or valonea extracts 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 to high of a pH, phosphoric acid should be added to bring it down to a pH of 2.4. I have found that it is important that the right tannic acid be selected as many are not effective. Tannic acid sold by Baker Chemical has a pH of 2.5 to 3 and has been found to be the most effective (Hamilton 1976:50). See Argo (1981) for a discussion of the requirements and benefits of tannic acid solutions. Tannic acid solutions (Baker

reagent tannic acid, $C_{76}H_{52}O_{46}$) with a pH of 2.5-3.0 provide good, weather-resistant tannate films. Tannic acid solutions are a standard part of the conservation of all iron artifacts in most conservation laboratories. Although some use the tannic acid coating as the final step, I recommend that an additional sealant, such as microcrystalline wax, be applied over the oxidized tannate film for maximum protection.

For maximum protection, several coats of 20 tannin solution (200 g. tannin, 1 liter water, 150 ml. ethanol) is applied with a stiff brush. A brushed-on film provides better protection than a dipped or sprayed application because the brushing assures that the solution has access to the metal in areas of loose rust and eliminates the polarization of cathodic areas by the formation of hydrogen (Pelikan 1966:112). Nevertheless, cast iron cannon balls have been successfully treated by vacuum-impregnating with a tannin solution. After applying, the object is allowed to completely air-oxidize between each application of the tannic acid. Allow it to dry one to two days after the final application.

The tannin solution reacts with the iron or iron oxide to form a ferrous tannate with oxidizes to a mechanically strong, compact blue-black colored ferric tannate. In order to assure a continuous film. Knowles and White (1958) recommend that all the iron oxide be removed, otherwise, they contend, 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, for Pelikan (1966:110-111) found that tannin solutions react directly with the metal base and with the rust if the solution is sufficiently acid, 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% solution of phosphoric acid (H_3PO_4). Impregnation under a vacuum is recommended to assure complete penetration into all the 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. Rees-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 removing the chlorides by water diffusion. Similar results is 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 and it appreciably improves the corrosion resistance of a phosphate film. One hundred milliliters of 80-85% phosphoric acid solution is added to the 20% tannin solution and several coats are brushed on the artifact, then at least four coats of the standard 20% tannin solution is brushed on the object. Following the treatment of an object with the mixed solution, phosphoric acid or tannin, a final sealant should be applied to seal off the tannate or phosphate film. I do not generally use this phosphoric acid/tannic acid solution because it does not form the dense black coloration that Baker Chemical tannic acid does by itself.

More recently, Logan (1989) recommends mixing up 1 liter of a 10% tannic acid solution of tannic acid (100 g. tannic acid, 50 ml ethanol, 900 ml deionized water) and if necessary, add sufficient concentrated phosphoric acid so that the solution has a pH of at least 2.4. She also cautions that different brands of tannic acid react differently and recommends BHD Chemical tannic acid as working consistently well. She differs primarily in that she states that a 10% solution of tannic acid is much too concentrated and recommends that several coats of diluted 2-3% tannic acid be brushed on the object. She differs also in that she does not recommend using a sealant over the tannic acid, but instead recommends controlled storage.

For the past 20 years, I have used only the 20% mixture of tannic acid on marine iron that has been treated, and I have had consistently good results. I have never found this concentration to be too concentrated. However, I have never attempted to use a 2-3% solution of tannic acid on marine iron, and it may well be that this strength works quite well. Otherwise, we agree on the advantages of the treatment. I still recommend that a sealant, such as microcrystalline wax be applied over the ferric tannate film formed over the object, The wax will provide a vapor barrier, which the ferric tannate film does not, and will also contribute some strength to corrosion layers on the metal. Regardless, of the exact procedure, I consider the application of tannic acid to be an inherent part of the treatment of any piece of iron, and especially iron recovered from marine environments.

ANNEALING

Oxidizing Atmosphere

Treating sea-recovered iron objects by heating 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 inactive anhydrous ferrous chloride. It should be noted, however, that just leaving chlorides in an anhydrous state will not prevent subsequent corrosion. Both ferrous and ferric chloride are deliquescent, capable of absorbing water from the atmosphere and reinitiating the corrosion process unless a perfect airtight, atmosphere-proof coating is applied. The success of annealing in the air is probably 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 since some of the cast iron guns were treated in this manner is testimony to its success. Notwithstanding, considerable sacrifices have to be made:

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, leaving 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, making it 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 by sublimation the corrosive chloride compounds.

The iron to be treated is placed in a hydrogen furnace and heated in the presence of hydrogen gas. The temperature is slowly elevated to 1060° C. over a period of one week. At this elevated temperature, all the moisture is driven off and all 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.

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 the technique are the lack of hydrogen kilns sizeable enough to treat large objects and the expense of the equipment even for small objects. Presently, a few conservation laboratories use annealing to treat very numerous, small artifacts, such as cannon balls, with a minimum amount of hands-on handling. One drawback to the treatment is the large amount of HCl produces when the chlorides are driven off and which attack any exposed metal in the kilns or furnaces. When one, some companies who owned industrial furnaces allowed archaeologists to use these furnaces to treat cannons, the detrimental effect the HCl fumes on the metal hardware has discouraged most from volunteering their furnaces.

Generally speaking, objects ranging in size up to about 10 inches by 4 feet is the size of object usually treated by this technique, because most laboratories can only afford the smaller size furnace, which have to be changed all too often. Cannons and other similar size artifacts have been preserved by this process and in most instances they remain stable, even though in most cases they have been annealed in an oxidizing furnace and the surface are badly oxidizing. In general I am not a proponent of this treatment and do not recommend it. Considerable interest has been manifested in objects that have been annealed in a reducing atmosphere. Still, there remains some controversy over possible side effects the heating and cooling have on the surface corrosion layers and the morphology of the metal.

Over the years the temperature to which the hydrogen oven is taken to has been decreased. As recently as 1978, objects undergoing hydrogen reduction were placed in a special furnace with 100% dry hydrogen gas, or a mixture of hydrogen and nitrogen, and heated to a temperature of 300° C and over a period of days taken to 1000° C (Barkman 1978:155-166). During the treatment, all the moisture is driven out of the artifact and the chloride corrosion compounds are volatilized. The hydrogen reduces the iron corrosion compounds back to a lower oxidation state or metal. Hydrogen also combines with oxygen in the corrosion products, forming water which is driven off by the heat. This treatment, while successful, has several drawbacks. First it requires rather expensive and sophisticated equipment that is outside the financial capabilities of most laboratories. Also the larger the object, the more expensive the treatment. Second, there is the problem of the changes in the metallurgical characteristics in the metal when heated to high temperatures. Recent information by Tylecote and Black (1980:95) reports:

> The loss of information by the treatment of totally rusted marine cast iron at 800 degrees C will not be great and there seems to be little objection to the use of the hydrogen reduction process at 800 degrees 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 degrees 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 degrees C the treatment time must exceed 60 hours.

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

HYDROGEN PLASMA REDUCTION

Hydrogen plasma reduction is a new technique being experimented with in a number of laboratories (Patscheider & Vep_ek 1986). In this treatment, iron artifacts, as well as those of copper and silver, have been conserved by placing them in a quartz discharge tube surrounded by hydrogen gas under a low pressure which is ionized into plasma by the introduction of high frequency radio waves. In the process iron is in the center of the hydrogen plasma and the magnetite and ferric oxide on the piece 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.

The primary disadvantage of this conservation technique, although preliminary results have been encouraging, 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. A unit capable of treating a single artifact in a chamber about 30 cm X 10 cm. costs in the neighborhood of $15,000.00. Thus far, the technique has not seen use in most conservation laboratories.

WATER DIFFUSION

In any archaeological excavation of a ship, there will always be some artifacts that can not be conserved by any the treatments discussed above. Any electrochemical or chemical treatment would considerably alter the form of the object. Little or no metal may remain. Three main choices are possible. 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. The last-named choice is discussed under Casting and Molding.

The only way 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 the overall form and dimensions of the object are to remain intact, the only alternative is to remove the soluble chlorides in 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. However, for all intent and purpose, water diffusion is not an option when it comes to treating iron recovered from a marine environment. It just does not remove the chlorides within in any accepted time frame when any other option is available. It is only a consideration, when one is attempting to conserve an artifact that is so badly corroded that it chances of being destroyed if it were cleared by electrolytic reduction or by the alkaline sulfite treatment discussed elsewhere.

Since water diffusion requires a long time, the water must be inhibited to prevent the metal from rusting. Alkaline chemicals, such as a 5% sodium sesquicarbonate, 5% sodium carbonate, or 2% sodium hydroxide solution, serve only as inhibitors to prevent rusting; it is the water that removes the soluble chlorides. For chloride-contaminated iron, the solution is made with tap water until the maximum chloride level approximates that of the tap water; then deionized water is substituted. Uninhibited deionized water should not be used in water diffusion because it is very corrosive.

Alternating hot and cold temperatures, suggested by Organ (1955) is said to speed up chloride removal by alternately expanding and contracting the capillaries in the metal and the corrosion layer, causing a flushing action of expelling and drawing in fresh water. From a standpoint of coefficients of thermal expansion, however, the alternate heating and cooling probably 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 at room temperature and at ca. 50° C. for both iron and bronze. The alternated heating/cooling cycle may facilitate the treatment, 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 need to 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 all the chemical residues through an 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 removed and rinsed thoroughly in several changes of alternate boiling and cold deionized water to get rid of any residual electrolyte and chlorides. By rinsing in boiling water the surface of the metal oxidizes to a flat black color that provides a pleasing appearance. Since large objects may require two to four weeks of rinsing, the iron may rust in the deionized water. This can be prevented by adding gluconic acid, sodium gluconate or sodium glucoheptanate, The gluconates act as rust inhibitors during any washing and continue to serve in this capacity during solvent dehydration, heat-drying or air drying. Still, in practice, these are not commonly used unless there is some problem. Pearson (1972a:13-14) prevented Captain Cook's cannons from rusting during the rinse process by washing with a potassium chromate solution (1000 ppm chromate) with a pH not lower than 8.5. But the strict disposal requirement of chromate solutions prevents their being used on a large scale. Neither the gluconates or chromate solutions are used widely, and satisfactory results are achieved without them. Still, it is worth know of the protection that they can provide, when and if their use is required.

The artifact is allowed to 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 .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, however, many of the objects treated by water diffusion are in very fragile condition, they may not be able to stand the mechanical action of boiling water. The rinse water, if heated, is kept below the boiling point. Sodium glucoheptanate is 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 deionized water for a few hours or overnight. A 10 to 20 milliliter sample of the solution is placed in a test tube and acidified with a few drops of dilute nitric acid (ca. 10%). The solution is mixed and five drops of .2 N silver nitrate (17 grams 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 chloride.

Drying

After rinsing, the moisture absorbed by the artifact must be removed before any sealant, except 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. Contact with air should be minimized until tannic acid can be applied to the surface, if the black coloration is desired, or the final sealant or insulating coating is applied to the artifact in order to prevent superficial rust that quickly forms. Some exposure to air is inevitable and it is particularly troublesome when drying by heat (ovens or infra-red lamps) or vacuum desiccation. (Using gluconate rinses could be helpful here to prevent rust). Also, 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 nontoxic, has a higher flash point, and does not have an obnoxious odor. Ethanol, and acetone are as effective, or even more effective, but suffer from one or more of the above disadvantages. Each of these solvents surmounts the problems of rusting when exposed to air and can be used on objects of any size. For objects with little metal remaining, drying in an oxygen-free environment, such as provided by alcohols, is necessary to 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 while the objects are still in the alcohol. Artifacts also can be held indefinitely or stored in alcohol until it is convenient to process them.

Upon completion of the water-rinsing, an artifact is removed while the water is hot and wiped with rags. This allows most of the water to evaporate before giving it a preliminary rinse in alcohol that has been previously used for drying wet objects to remove the bulk of the remaining surface water. It is then submerged in the water free isopropanol to dehydrate for a minimum of 24 hours. By taking these precautions the water content of the alcohol bath is kept low and it can be used for long periods. When the water content 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 shortages and high prices.

Sealant and Consolidation

After treatment of sea-recovered iron objects it is imperative that their surfaces be covered with a protective coating to insulate the metal from the effects of moisture, chemically active vapors, and gases. It is highly important to choose the right sealant or coating 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 craze, peel, are irreversible, or have a high degree of permeability to water vapor. No one sealant is completely successful and all have some disadvantages, but microcrystalline waxes best satisfy the requirements of conservation. Most importantly, they are the least permeable to water vapor of any of the sealants commonly used (Rudniewski and Tworek 1963:212). They have a high melting point and are relatively hard waxes. Besides sealing the surface of the artifact from the atmosphere and moisture, they provide considerable

stability and strength to artifacts and are excellent for consolidating fragile objects. I recommend and have been using microcrystaline wax on both cast iron and wrought iron that is to be stored and displayed indoors. In contrast, some laboratories (North 1987:230) use microcrystaline wax as the final coat only on cast iron artifacts.

Cosmoloid 80H is the most often-recommended microcrystalline wax seen in much of the conservation literature, but it is not available in the United States. At various time over the past 20 years I have used Gulf 75 Micro-wax, but for the last 15 years I have relied exclusively on Witco 180M microcrystalline wax. Both melt at approximately 180° F. and have been satisfactory, although Gulf 75 is a little harder and more brittle. There are other satisfactory substitutes both here in the United States and other countries.

In some instances it may be advisable to dewater, dry or dehydrated 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. The wax is heated to 350° F. (176° C.) to 400° F., well above the boiling point of water. Therefore, it is possible to take the artifact directly out of the water rinse and place it in melted wax. As the temperature of the wax rises, any water in the artifact is vaporized. The object must be kept in the wax long enough and at a high enough temperature to completely vaporize the water. Since the water boils out of the artifact, this alternative should not be used on fragile objects or objects with a loose oxide layer. These fragile specimens should be dried by one of the methods mentioned above. With this exception, combining the water removal and the sealant steps remain a very satisfactory approach. Time and expense are saved and good results are achieved.

If the object is in fragile condition, all the alcohol must be evaporated; otherwise, the vaporization of the alcohol in the corrosion layers by the hot wax can damage the specimen. The object is left in the wax until all bubbles stop evolving from the artifact. This may require several days for large artifacts. After complete penetration the wax is cooled to 200° to 225° F. (93° to 107° C.), the artifact is removed and the excess wax is promptly wiped off with rags.

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 the wax runs off. After cooling, if any excess wax should remain, it can be removed with a torch, a hot air gun, or by scraping lightly with a knife. The last-named 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 various other coatings must be used. There have been experiments with chromate paints, lacquers, clear epoxies, linseed oil, and polyurethane. In general, all but polyurethane were found to be ineffective. Over a period of months they crazed, peeled, and became permeable to moisture. The opaque coatings hid 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 was too glossy and was irreversible, causing further damage to a few specimens which had 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, hard, flexible coatings with excellent adhesion that are highly resistant to moisture, salt water, acids, alkalis, abrasion, impact, 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. A number of years back, I processed a large 18-pound Civil War cast iron siege cannon recovered from Galveston Island on the Gulf Coast. After cleaning, a sealant had to be applied, but the cannon was larger than any of the wax vats in the laboratory. It was decided to paint the surface of the cannon with a 20% tannin solution to form a corrosion-resistant ferric tannate film on the surface of the cannon. The painted surface was allowed to air oxidize for two days, changing the gray surface color of the cannon to a more pleasing blue-black color. 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. 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 (Hamilton 1976::55; North and Pearson 1975:177; North 1987:230)

Success has also been had with using Rustolium, a fish oil based paint, but it has a only 10 years, as opposed to 20 years for polyurethane (North 1987:230).

For wrought iron artifacts to be displayed indoors, North (1987:231 recommends, after drying with commercial dewatering fluids , using clear drying zinc phosphate-based anti-corrosion primer as the first coat, followed by up to 6 sprays of high durability, clear, acrylic lacquer, and finished off with a final coat of Krylon Mat Spray Finish (North and Pearson 1975:177, North 1987:230).

With the exception of microcrystaline wax, which is easily removed by placing the artifact in a vat of boiling water, all the others present some problems. Polyurethane has to be sandblasted off, and the Rustolium has to be place in sodium hydroxide to remove the paint. For ease of application, resistance to water vapor, the presence of chloride, transparency, ability to strengthen the surface of the artifact, microcrystaline wax stands out for use on both cast iron and wrought iron that are stored and displayed indoors. In an object is to be displayed outdoors, or if it can not be treated with microcrystaline wax, then polyurethane based paints is recommended.

For large objects to be displayed outdoors Townsend (1972a:253) suggests using a coating made up to three parts zinc silicate powder mixed with 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 more than three years.

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 preservation of antiquities should produce objects that are chemically stable with an aesthetically acceptable appearance. Treatment should be reversible in the event the object should require additional preservation; after an artifact has been completely processed it can deteriorate. Only if stored or displayed under optimum conditions can this be prevented. Atmospheric pollutants, sulfur dioxide, hydrogen sulfide, sodium chloride, dust, and soot, to name the more common, are detrimental, ubiquitous, and difficult to control even inside a reasonably tight building. Even more critical is the relative humidity in which an artifact is stored. The moisture level at which corrosion appreciably accelerates is called the critical humidity and is considered to be 60% for iron and steel (Cornet 1970:443). If iron still contains chlorides (theoretically it remains doubtful that all can be removed), a humidity as low as 50% may have to be maintained. Below this critical humidity, subsequent corrosion sometime in the future is inevitable. 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 inspection, 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 assure one of an object preserved in perpetuity. At our present stage of knowledge, perhaps it is most realistic to say that the objective of antiquities conservation is to delay by proper storage reprocessing 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 our present state, there are a number of procedures that successfully contend with the majority of problems encountered when conserving iron.

SUMMARY

Based on my own experience, and the experiences of others as reflected in the published literature, the majority of the iron recovered from marine sites is treated by electrolytic reduction. This treatment consistently produces stable artifacts with a minimum of equipment, less costly equipment, chemicals and less, hand on treatment time. For a number of problem artifacts, the alkaline sulfite treatment is commonly used. Less common, but still utilized by a few laboratories is hydrogen reduction of iron, but cost of the equipment prohibits it more general use, and the same applies to hydrogen plasma reduction. 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. Equipment includes: various regulated D.C. power supplies, plastic vats, metal vats, anode material, wire, clips, fume hoods, tap water supply, D.I. water, sodium hydroxide, sodium carbonate, tannic acid, sodium sulfite, pneumatic chisels, air compressor, microcrystaline wax, polyurethane, fork-lift if heavy artifacts are to be treated, source for heating the rinses and wax, mercuric nitrate, silver nitrate, nitric acid, sulfuric acid, expanded scale, pH meter, x-ray machine, epoxies and materials for casting are the more essential items. All are easily secured at reasonable expense, and much of the equipment can be secured through federal surplus.

CONSERVATION OF NONFERROUS METALS

It is not uncommon to find nonferrous metals, copper, silver, lead, tin, gold, and their alloys, in archeological sites. These metals were 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 iron specimens. Perhaps it is for this reason that considerable attention has been given to their preservation and many conservation procedures have been developed for them. Nevertheless, the corrosion problems of each metal varies in different environments. Only those techniques applicable to the problems of sea-recovered metals are considered here.

As has already been observed, sea-recovered materials are often encapsulated by encrustation. However, when present on nonferrous metals, it is much thinner that what is found on iron. Of course, artifacts of these metals are often found encapsulated in the encrustation surrounding 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 some detail.

STORAGE OF NONFERROUS METALS

A variety of metal artifacts made of different metals are often found encrusted together in marine sites. In those 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 in association. Since iron artifacts are the most commonly found metal, the storage conditions discussed under iron are most often utilized. However, gold, silver, pewter, brass, bronze, copper and lead artifacts; as well as ceramics, stone, glass, bone, cloth, seeds and wood are often all found together in various combination. In some cases, the best storage might be simply in fresh water. Once the different material are removed, then they are placed in the most appropriate storage environment for that material. While iron artifacts, as discussed earlier, should at a minimum be stored in an alkaline solution shielded from light, this solution is not necessary or even recommended for artifacts made of other metals. Copper is corroded by oxidizing solutions and in strong alkaline solutions. In neutral or slightly alkaline solutions the copper is passivated, the corrosion being checked by an oxide film that is formed on the surface. A 5% solution of sodium sesquicarbonate or sodium carbonate is recommended. A 5% solution of sodium carbonate with a pH of 11.5 will protect copper and silver. Silver is stable in aqueous solutions of any pH value and in the atmosphere, so long as these environments are free from oxidizing substances. Since chlorides do not affect lead or silver, once the encrustation has been removed, they do not need to be placed in an aqueous solution and can be stored dry. However, prior to the removal of adhering encrustation, it is best to house them in an appropriate solution to keep the encrustation from becoming harder and difficult to remove. It is quite safe to store silver objects in either a 5% sodium sesquicarbonate or sodium carbonate solution, along with iron artifacts. When silver is stored in a chromate solution, a film of brown Ag_2O forms, which can be removed during the conservation, but for this reason, it is not recommended for the storage of singular silver artifacts. On occasion, it may be necessary for silver to be place in a chromate solution, when it is encrusted to an iron object.Lead, tin and pewter are more easily stored. All are often stored dry, but as mentioned above, when the encrustation on metals is allowed to dry out, it becomes much harder to remove. For this reason, they are stored in aqueous solution. Lead is corroded by aqueous solutions free from passivating substances, especially soft water, deionized water, or distilled water. Thus, lead should never be stored in either deionized water, or distilled water, both of which are slightly acidic and lack any passivating substances in them. However since lead is corrosion resistant in hard, bicarbonate water because the bicarbonate is

passivating, 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. Both lead and pewter can be place in sodium carbonate, which has a ph of 11.5, but this pH is borderline to the corrosion domain of tin, so it should not be used for the storage of tin. Tin will resist corrosion in slightly alkaline solution free from oxidizing agents but will react adversely to strongly alkaline solutions. So any alkaline solution above 10 is potentially dangerous. Generally speaking tin can be safely stored in tap water. Lead, tin, and their alloys such as pewter should not be stored in a chromate solution because of its oxidizing effect which forms an orange chromate film on their surfaces, that is difficult to remove. In the absence of passivating substances, an oxidizing agent such as chromate can damage the specimen.

COPPER AND COPPER ALLOYS

CUPREOUS METAL CORROSION

The term cupreous metals is used to designate all the metals that consist of copper or copper alloys that contain copper as the predominant metal 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 submersion in salt water, that often completely oxidize iron. They 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. However, the mineral alterations in the copper alloys, bronze and brass, can be more complex than those of just 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.

$$Cu° - e \rightarrow Cu^+$$

$$Cu^+ + Cl^- \rightarrow CuCl$$
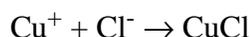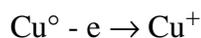
Cuprous chlorides are very unstable mineral compounds. Once cuprous objects are recovered and exposed to air, they inevitably continue to corrode chemically by a process commonly referred to as bronze disease. In this, cuprous chloride in the presence of moisture and oxygen are hydrolyzed to form hydrochloric acid and basic cupric chloride (Oddy and Hughes 1970:188).

$$4CuCl + 4H_2O + O_2 \rightarrow CuCl2 \cdot 3Cu(OH)_2 + 2HCl$$

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

$$2Cu + 2HCl \rightarrow 2CuCl + H_2$$
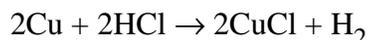
The reactions continue until no metal remains. Any conservation of chloride-contaminated cupreous objects requires that the chemical action of the chlorides be prevented by removing the cuprous chlorides or converting them to harmless cuprous oxide. Otherwise, the artifact will self-destruct over time.

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 sulfide to undergo subsequent oxidation to a higher oxidation state, i.e., cupric sulfide. The whole chemical reaction generally proceeds along the same lines as described for iron.

On removal from the 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, however, the corrosion process will create a pitted surface, but this is more common on the cupreous alloys where the tin or zinc is corroded preferentially, leaving the surface pits. The copper sulfide layer does not adversely affect the object after recovery from the sea like the copper chlorides do; they are primarily just disfiguring and may affect the shape and size of the object. The sulfide corrosion is easily removed and does not present the conservator with any major problems. See North and MacLeod (1987) for a detailed discussion of the corrosion of copper, bronze and brass in a marine environment.

CUPREOUS METALS

Here the nonspecific term cupreous metals is used for copper and the alloys such as brass and bronze where copper predominates because of the difficulty of distinguishing copper, brass, and bronze objects from each other without analytical tests. In general it matters little what the specific alloy is, for they are usually treated in the same way. Care needs to be taken only when there is a high percentage of lead or tin, both of which are amphoteric metals and dissolve in alkaline solutions. There are a considerable number of chemical treatments for copper, bronze and brass, and most are not satisfactory for cupreous metals from marine sites. Consult the bibliography for further information.

In a marine environment the two most commonly encountered copper corrosion products are cuprous chloride and cuprous sulfide. However, the mineral alterations in the copper alloys are more complex than those of just copper. Once any cupreous object is recovered and exposed to the air, it continues to corrode by a process referred to as bronze disease. In bronze disease the cuprous chlorides in the metal in the presence of moisture and oxygen are very unstable. They hydrolyzed to form hydrochloric acid and basic cupric chloride. The hydrochloric acid in turn attacks the uncorroded metal to form more cuprous chloride. The reaction continues until no metal remains. Any conservation of chloride contaminated cupreous objects requires that 1) the cuprous chlorides be removed, 2) the cuprous chlorides be converted to harmless cuprous oxide, or 3) the chemical action of the chlorides be prevented.

Neither cuprous chloride or cuprous sulfide imparts a pleasing patina on the surface of the metals there is no reason to preserve them. In fact, most copper, bronze, and brass are darkly colored by sulfide, which often imparts a lead or pewter-like appearance to the metal. The stable 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.In some instances, it is necessary to remove mechanically the gross encrustation and corrosion products down to the preserved surface of the metal. This step is facilitated for sea-recovered cupreous objects because the marine encrustation forms a cleavage line between the original surface and the encrustation. When the artifacts are removed from gross encrustation, superficial encrustation is often deliberately left adhering to the surface because of the artifacts' fragility or to avoid marring the surface. Careful mechanical cleaning and rinsing in water may be all that is required to remove this remaining residue. In other cases, all adhering encrustation is removed by soaking in 5 to 10% citric acid with 1-4% thiourea added as an inhibitor to prevent etching

of the metal (Plenderleith and Torraca 1968:246; Pearson 1974:301; North 1987:233) Care must be taken as citric acid can dissolve cupric and cuprous compounds. The artifact is left 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 drastic. In these cases, the artifact can be soaked in a 5 to 15% solution of sodium hexametaphosphate (Plenderleith and Werner 1971:255) to convert the insoluble calcium and magnesium salts to soluble salts which can be 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
   4. chemical cleaning
      a. sodium sesquicarbonate
      b. sodium carbonate
      c. benzotriazole

The first three techniques can remove cuprous chloride (CuCl) 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, both will restore the object to a stable condition and maintain a form approximating its original uncorroded appearance. If misapplied they can strip the corrosion layer down to bare metal. Jedrzejewska (1963:135) draws attention to the fact that stripping, especially by electrolysis, may destroy significant archeological data such as tool marks, engraved lines, and decorative elements, as well as altering 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 them *in situ* through very controlled electrolytic reduction or alkaline dithionite. The two chemical techniques described do not strip the corrosion layer. Rinsing in a sodium sesquicarbonate solution removes the chlorides, 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. Since I regard it as an obsolete technique, except under certain circumstances already mentioned, there is no point to further discussion.

ELECTROLYTIC REDUCTION CLEANING

Electrolytic reduction of cupreous metals is also carried out in the same manner as described for iron. Either 2% sodium hydroxide or 5% sodium carbonate can be used for the electrolyte. The latter is used most often although acceptable results have been achieved using 5% formic acid as the electrolyte as

described below for treating silver. 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 are used.

The duration of electrolysis is shorter than for comparable chloride-contaminated iron objects. For example, small pieces such as coins require only a couple of hours while larger specimens such as cannons may require several months. Precise data concerning the current density are not available. Plenderleith and Werner (1971:198) state the current density should not be allowed to fall below .02 amps per square centimeter in order to prevent the deposition of a salmon-pink film of copper on specimens. Keel (1963:24) states that a current density above .01 amps per square centimeter will damage the specimens. Along these same lines Pearson (1974:301-302) correctly warns that care must be taken with mineralized bronze from under the sea when electrolytically cleaned in order to prevent damage to the surfaces by the evolution of hydrogen gas. Current densities within these given ranges and well in excess are commonly utilized on different objects. North (1987:238) recommends using the hydrogen evolution voltage techniques described for iron. In general the same procedure described for iron applies. The main difference being the much shorter time required to treat cupreous metals.Following electrolytic and chemical cleaning, cupreous metals are put through a series of hot rinses in deionized water. Because copper tarnishes in water, Pearson (1974:302) recommends washing in several baths of denatured ethanol. If a water rinse is used the rinsing can be followed by cleaning the tarnish with 5% formic acid or polishing with a paste of sodium bicarbonate.

After rinsing, the copper objects are dehydrated in acetone and are coated with a protective sealant such as clear acrylic. The commercially available Krylon Clear Acrylic Spray No. 1301 is recommended for ease of application, durability, and availability. Pearson's (1974:302) procedure of mixing 3% benzotriazole in the ethanol wash as an inhibitor against "bronze disease" followed by a clear acrylic lacquer containing the benzotriazole inhibitor (Incralac) is a good procedure to follow. The same protective sealant can be prepared by adding 3% benzotriazole to a solution of polyvinyl acetate (V15) in ethanol.

ALKALINE DITHIONITE

This treatment was devised for consolidating mineralized silver. Since then, it has been found to be effective on cupreous objects. See a complete description under Silver. The treatment destroys the patina, but it effectively removes the bulk of the total chlorides in the shortest period of time as well as reduce some of the copper corrosion products back to metal.

CHEMICAL TREATMENTS

Many cupreous specimens with chloride contamination, such as well-patinated bronzes with bronze disease, extensively mineralized bronzes with or without cuprous chloride, bronzes without a substantial metallic core, and bronzes with mineralized decorative features, cannot be treated by either of the reduction techniques. For these objects, three procedures are used to stabilize the artifacts while leaving the corrosion layers intact. They are: treatment with 1. sodium sesquicarbonate, 2. sodium carbonate, and 3. 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% solution of sodium sesquicarbonate, the hydroxyl ions of the alkaline solution react chemically with the insoluble cuprous

chloride 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 deionized 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% sodium sesquicarbonate, mixed with tap water in the initial baths, followed by deionized water in the subsequent baths. If the chloride contamination is extensive, tap water can be used until the Cl$^-$ increase in the solution approximates the Cl- level in the tap water. Then deionized water in substituted. This procedure is very economical when processing objects that require months of treatment.

In the beginning the baths are changed weekly; later the interval in extended. Monitoring the chloride level by the quantitative mercuric nitrate test, described under iron, enables the conservator to determine precisely how often to change the solution. In lieu of a quantitative chloride test, the qualitative silver nitrate test, previously described, 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.

Immersion in sesquicarbonate is followed by rinsing in several changes of distilled or deionized water until the pH of the last bath is neutral. The object is then dehydrated in acetone or a water-miscible alcohol, and coated with clear acrylic lacquer or microcrystalline wax. For increased corrosion protection, benzotriazole can be added to the drying alcohol and even added to lacquer.

The sodium sesquicarbonate method is often selected because, unlike other cleaning treatments, it does not remove the green patina of copper objects. Side effects, however, such as the formation of blue-green malachite deposits on the surface of the objects, can intensify the color of the patina. If this occurs, the object needs to be removed from the solution and the deposit brushed off. On some bronze pieces, there is considerable blackening of the surfaces, which obscures the original green patina and is difficult to remove. This blackening is attributed to the formation of black copper oxide and seems to be inherent in some cupreous alloys.

Sodium Carbonate Rinses

Sodium sesquicarbonate rinses, as described above, have been the standard treatment for fragile cupreous artifacts with chloride contamination and for artifacts that have a patina that is desirable to preserve. However, in practice, conservators found that it often enhanced the patina, making it much bluer in appearance. In other examples, it considerably darkened or blackened the patina.Recently, Weisser (1987:106) stated:

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.and Weiser (1987:108) concluded:

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. Weiser suggests that if previous treatments with BTA have not been successful, then treat with 5% w/v of 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 part of any conservation treatment of a cupreous metal, following any stabilization process and preceding any final sealant. In some cases, it can be a single treatment unto itself, but when marine cupreous objects are conserved, it usually used as a final step in addition to some other treatment such as electrolytic reduction, or alkaline rinses which remove the bulk of the chlorides. In this method of cleaning (Madsen 1967; Plenderleith and Werner 1971:254) 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 that causes bronze disease. The treatment does not remove the cuprous chloride from the artifact, it merely forms a barrier between the cuprous chloride and moisture of the atmosphere.

The process consists of immersing an object in 1-3% benzotriazole dissolved in ethanol or water. For artifacts from a freshwater site, it may be the only treatment required; it being used to prevent any future corrosion or discoloration of the patina. The BTA is usually dissolved in water, but ethanol can be used. See Green (1975), Hamilton (1976), Merk (1981), Sease (1978) and Walker (1979) for additional information. BTA forms an insoluble, complex compound with cupric ions. Precipitation of this insoluble complex over the cuprous chloride forms a barrier against any moisture that could activate the cuprous chlorides responsible for bronze disease. It has been found that if the artifact is left in BTA for at least 24 hours, 1% BTA mixed with D.I. water works as well as the stronger solutions. For shorter treatment, 3% BTA mixed in either water or ethanol in recommended. The main advantage of the ethanol, if there is one, is that it penetrates cracks and crevices better than water. In some cases ethanol is preferred when the BTA treatment is of short duration. In most situation the best results are achieved if the specimen is impregnated with the solution under a vacuum for 24 hours. On removing the object it is wiped off with a rag saturated in ethanol to remove excess benzotriazole. The artifact then is exposed to the air. If any fresh corrosion appears, the process is repeated until no adverse reaction occurs. 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 benzotriazole may fail because of the widespread distribution of cuprous chloride CuCl in the corrosion layers. It has been found by any number or conservator that when cupreous artifacts from marine sites are treated, better long-term stability is achieved, if the bulk of chlorides are removed by either sodium sesquicarbonate rinses or sodium carbonate rinse and then BTA is applied and a final sealant, such as Krylon Clear Acrylic 1301 is applied.It has to be emphasized that the BTA treatment does not remove the cuprous chloride from the

artifact, but 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 copper/brass/bronze objects, the treatment may have to be combined with one of the processes described above. Treatment by this method alone is not always successful but it is now a standard part of any treatment of copper or copper bearing alloys, in addition to any other treatment. 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 deionized water. Because copper tarnishes in water, Pearson (1974:302), recommends washing in several baths of denatured ethanol. If a water rinse is used any tarnish can be removed with 5% formic acid or by polishing with a wet paste of sodium bicarbonate (baking soda).

After rinsing, copper objects should polished to any degree desired, treated with BTA, dehydrated in acetone and sprayed with a protective coating of clear acrylic. Krylon Clear Acrylic Spray #1301, which is Acryloid B-66 in toluene, is recommended for ease of application, durability, and availability. For additional protection BTA can be mixed with Acryloid B-72 or polyvinyl acetate and brushed on the artifact. 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 containing copper. Each is effective in its own way and is the preferred treatment for given artifacts. Of the conservation alternatives considered in this section, electrolytic reduction, alkaline dithionite, 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, 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 on the surface of the alloyed metal. In some cases, as in the case of cupreous specimens from the sea, this is a small price to pay for a chemically stable artifact. My experience and the apparently successful application of electrolytic reduction to large number of copper and bronze artifacts clearly demonstrates that electrolysis is the quickest, the most effective, and the most 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 the sodium carbonate or sodium sesquicarbonate treatment discourages its use. A preliminary treatment of sodium carbonate, followed by treating with benzotriazole, may provide satisfactory results, but more experiments need to be reported before a final judgement can be made. Although preliminary, good result are being had with the use of alkaline dithionite solution treating cupreous alloys. It, like electrolytic reduction, has the ability to reduce copper corrosion products back to a metallic state and like the alkaline rinses, remove the soluble chlorides. This treatment may prove to be as useful for treating cupreous artifacts as silver artifact, for which it was originally developed.Regardless, of the mode of treatment, an application of BTA is an inherent part of the treatment of any cupreous metal artifacts. In most cases, if the artifact is effectively treated with any of the treatments discussed above, treated with BTA, sealed with an acrylic such as Krylon 1301 Clear Acrylic, and stored in the right environment, the artifact 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. Furthermore, it is not attacked appreciably by dry or moist air when the air 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 most evidenced by tarnish on silver objects when exposed to sulfur in any form, but especially hydrogen sulfide and also 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 the available sulfate 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.

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$
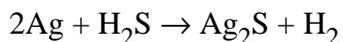
In anaerobic marine environments silver sulfide (Ag_2S) is by far the most common mineral alteration compound of silver (North and MacLeod 1987:94). It is commonly reported from shipwrecks in the Caribbean and Australia and constitutes the most prevalent corrosion compound on the silver pieces from marine sites. In fact, a large percentage of the silver artifacts are completely converted to sulfide. Others have minimal metal remaining. Most have a thin sulfide surface layer which has removed some surface detail such as inscriptions, marks and stamps.In aerobic seawater the most commonly encountered corrosion products on silver and silver alloys are silver chloride (AgCl), and silver bromide (AgBr), with varying amounts of silver sulfide (Ag_2S) (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. I have observed only a few instances where silver chloride appeared to be present on some silver artifacts I have treated. 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, silver sulfide (Ag_2S) and silver chloride (AgCl) predominate. In the case of base silver alloys with significant amounts of copper, the copper corrodes preferentially, forming cuprous oxide, cupric carbonate, and cuprous chloride. In base silver alloys with copper, the copper corrodes preferentially and forms cuprous chloride which continues to corrode the copper component of the silver. In these cases the silver is 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 from further corrosion to the metal. They also often provide an aesthetically pleasing patina which is often desirable and is 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, the marine encrustation is removed mechanically and in some cases by immersion in 10 to 30% formic acid solution. The conservation alternatives for cleaning silver and silver alloys are: 1) galvanic cleaning, 2) electrolytic reduction, 3) alkaline dithionite, 4) chemical cleaning, and 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% formic acid (Plenderleith and Torraca 1968:241-246; Plenderleith and Werner 1971:197 and 221). After treatment, the metal goes through an intensive rinsing, is dehydrated in a water-miscible solvent and is covered with clear acrylic lacquer. Galvanic cleaning is effective but has nothing 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 positive 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. Organ (1956) refers to the two as normal reduction and consolidative reduction. Normal electrolytic reduction uses a fully rectified direct current power supply. Consolidative reduction employs a partially rectified (asymmetrical) alternating current power supply. Both techniques require that a metal core be present in the object. Our laboratory has been concerned primarily with the normal reduction process in 5% 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. Five to 30% HCOOH and 2 to 15% NaOH in deionized water have been proposed (Organ 1956:129; Plenderleith and Werner 1971:222; Pearson 1974:299). Either a 5% HCOOH or a 2% NaOH solution has been used as the electrolyte for cleaning silver.

Current Density

A current density of .01 amp per square centimeter, the same as proposed by Organ (1956:129), with good results. Plenderleith and Werner (1971:198) state that the current density should not be allowed to fall below .02 amps per square centimeter in order to prevent a film of salmon-pink copper from the corrosion crust, cathode screen, or copper leads from being deposited on the artifacts. 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. In a series of experiments Organ (1956:134) found that a current density of 30 to 50 milliamperes/dm2 (.3 to .5 milliamperes/cm2) reduced more silver. However, North (1987:240) notes ". . . that the voltage applied during electrolysis does not appear to be critical, good results being obtained with a wide range of applied voltage." This just points out the obvious fact that silver is easily reduced in electrolysis, regardless of the voltage or setup. Still, in most cases a very low current density in the range proposed by Organ is best for maximum metal reduction.

Anode Material

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

Cathode Contact

One often wants to avoid attaching a clip to small silver pieces in order not to scratch the surface. This is especially true for coins and delicate pieces of jewelry. Direct, individual connections can be eliminated by using a cathode conductor screen made of copper mesh (Figure 9. The specimen to be cleaned makes an electrical contact to the negative terminal through the cathode screen which is connected to the negative terminal. The areas of the screen not used for making contact with the specimen should be covered with silicone rubber. The rubber keeps the objects separated and cuts down on the exposed copper, thus reducing the problem of copper plating on the silver. The electrolytic cell can be set up in any of the alternatives described for iron. As for iron, the setup where artifacts are attached with clips to a cathode rod and sandwiched between two suspended anodes (Figure 5-D) is the most used. This electrolytic setup is useful for numerous pieces and can be used for coins and other small pieces.

Procedural Description

After the objects have been removed from the encrustation with a small pneumatic chisel, preferably using radiographs as a guide, they are thoroughly rinsed and are then ready to be cleaned electrolytically. Small specimens can be set up as shown in Figure 9. This setup is designed to clean coins, but is applicable to any small objects of silver or other nonferrous metals. The setup uses a glass container, a copper mesh cathode conductor screen, a wooden support frame for the anode, and an expanded platinized titanium anode attached to a mild steel rod. The rod is covered with silicone rubber to prevent its reacting, and insuring that only the inert platinized titanium anode acts as the anode. Alternatively, stainless steel No. 316 can be used as the anode. The specimens are placed on the cathode screen, the current applied, and the 5% formic acid electrolyte added. The current is never turned off while the coins are in the electrolyte in order to prevent any of the salts in the electrolyte from plating on the coin. This precaution will reduce considerably the problem of copper plating on the silver. Periodically the coins are removed, while the current is on, to be brushed under deionized water and dipped in a .2N solution of silver nitrate to remove any plated copper and superficial sulfide. They are then put back in electrolysis with the opposite side up. Electrolysis is continued until each side has a uniform appearance as determined by visual inspection, and hydrogen is fully evolving from the surface. Generally, small objects require only a few hours of electrolysis. Large silver objects or irregularly shaped pieces can be cleaned in the same way as described above, except that a cathode conductor screen is not used. The object is connected to the negative terminal with a clip. Due to cost factors, expanded stainless steel No. 316 mesh is more commonly used as the anode material than platinized titanium.
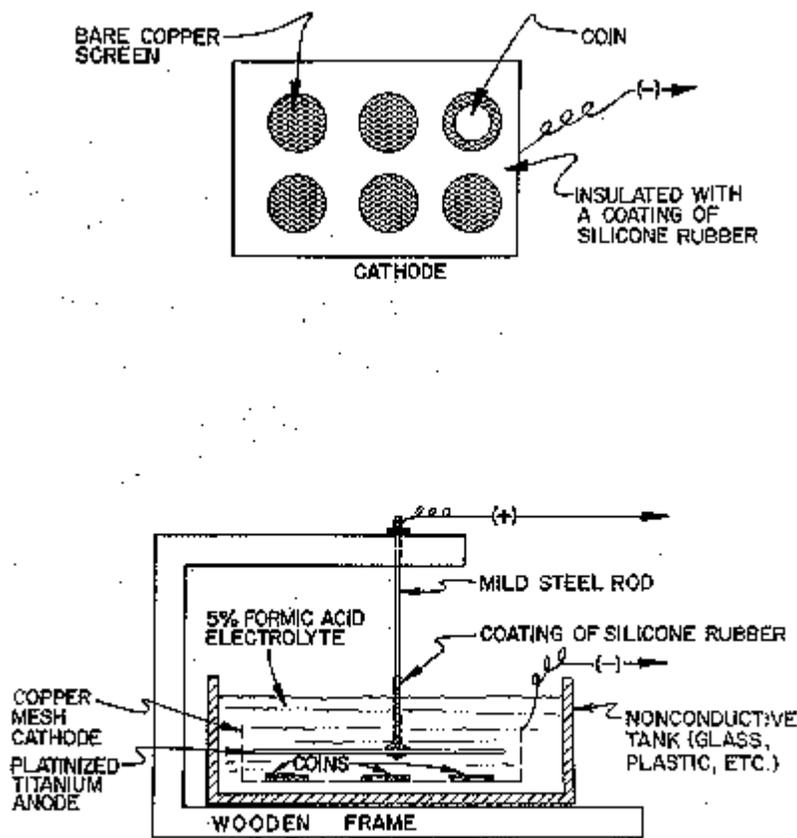
Reduction in Formic Acid

Figure 9. Electrolytic Setup for Cleaning Silver Coins or Other Small Artifacts.

Organ (1956) conducted several detailed experiments on silver reduction techniques and alternatives. He notes that standard electrolytic reduction in 30% aqueous formic acid has been favored because it is a volatile acid that has no detrimental effect on silver and requires minimum washing after reduction. He found that when formic acid electrolyte is used at a current density of 1 amp/cm2 the reduced layer of transferred material external to the original surface delaminates, i.e., readily detaches along the original surface, revealing it. For this reason, treatment in a formic acid electrolyte is ideal for silver with the original surface preserved in the corrosion layer as long as a substantive metallic silver core remains. 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 metal core. Clear acrylic lacquer is then applied to secure the layers in place on the surface to preserve the detail of the specimen. Being particulate, the reduced metal is dark, brittle, and not ductile, but the method of electrolysis in HCOOH results in a darkened silver that is stable, cleansed of corrosion products, and yet still looks old. 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% aqueous solution of sodium hydroxide at a low current density (10 to 50 milliamps/dm2) is said (Organ 1956:135) to result in firm, hard, metallic silver capable of being polished. The regenerated silver retains the detail and texture of the original laminated corrosion surface but it is full of voids and is not ductile. More recent tests have shown that more thorough reduction is achieved in a NaOH electrolyte.

Consolidative Reduction

Fully rectified direct currents have been used in conservation, electroplating and battery charging, but it was discovered some years ago 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.

Reduction of
hydrogen or
metal at cathode

Dissolution of
cathode

A.

Reduction of
hydrogen at
cathode

B.

Reduction of
hydrogen or
metal at cathode

Dissolution of
cathode

C.

Figure 10. Electrical Sine Wave Forms.

reverse current (current flow from positive to negative); therefore, it has a symmetrical sine wave form. If anartifact is undergoing electrolysis, hooked up to alternating current, metal and hydrogen are deposited and metal is reduced from the corrosion compounds during the forward half of the cycle. In the subsequent reverse half of the cycle the metal and hydrogen deposited or reduced are dissolved. No progress in reduction takes place.

Direct current flows only in a forward direction, therefore only reduction and deposition reactions take place at the cathode (Figure 10-B). In normal reduction using direct current, 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. This provides for uneven metal deposition and microscopic voids in the newly reduced metal. In consolidative reduction 10-20% reverse current and 80-90% forward current is usually used. During electrolysis the net effect is a rapid succession of reduction and dissolution cycles (Figure 10-C). During the 90% forward half of the

cycle, reduction of metal in the corrosion compound and deposition of metal dissolved in the previous reverse current half cycle takes place. During the 10% reverse half cycle there is a partial dissolution of the previously reduced or deposited metal; however, the 90% forward current puts the emphasis on reduction and deposition over dissolution as the current reverses 120 times a second. In the process the extent of polarization of the cathode is reduced.Organ (1956) used asymmetrical alternating current in a sodium hydroxide electrolyte to regenerate the silver on the Ur lyre that was completely mineralized to silver chloride to massive metallic silver while preserving the surface details of the corrosion layers. The reduced silver was ductile and more homogeneous than the silver reduced by normal reduction techniques using fully rectified direct current. He used a 3% NaOH electrolyte, a carbon rod anode, and a very low current density of 10 milliamps/dm2 (.1 ma/cm2) to reduce the silver and to prevent the rapid evolution of hydrogen that would tend to disturb the reduced silver.

For badly or completely corroded specimens, more complete reduction is achieved if the cathode wire is laid against one side of the silver and the exposed wire covered with wax or polymethacrylate. This insures that the current passes through the corroded metal in flowing from the electrolyte to the cathode. The hydrogen discharges at the surface of the mineralized metal and reduces it. Organ (1956) resorted to this technique in order to make an electrical contact with the nonmetallic, poor-conducting silver chloride on completely mineralized silver. The arrangement is advantageous even when a thin core of metallic silver remains. During the process, the corrosion layers external to the original surface are reduced in place, preserving all the details present on this surface. The treatment usually requires weeks. Since this technique preserves all the outer corrosion surface, it should not be used on specimens with an original surface preserved within the corrosion crust. Following reduction the piece is rinsed in cold deionized water to remove all the alkali and then coated with any suitable sealant.

Additional details concerning the development and application of consolidative reduction are to be found in Organ (1956:137-144), in summary form in Plenderleith and Werner (1971:223-226), and additional research presented in Charalambous and Oddy (1975). The description of the circuit for the partially rectified current is provided in both sources. Asymmetrical alternating current seems to have some advantages over straight direct current, and may prove to be superior when used to treat any metal artifact, even iron objects. More experimentation is needed, but in general, even though this option of using asymmetrical current seems to have some advantages, it has never been adopted very widely by conservation laboratories since reduction of silver corrosion products back to metallic silver can be achieved with very low current densities using straight D.C. current and a NaOH electrolyte.

ALKALINE DITHIONITE

The alkaline dithionite treatment is similar to that of alkaline sulfite described for iron. Is a relatively cheap, simple and rapid method of consistently reducing silver corrosion product to metallic silver (MacLeod and North 1979). The steps in the processing of silver by this method are:

1. Immerse the object in 10-12% hydrochloric acid to remove the encrustation layer that may consist of sand, shell, calcium carbonate, and copper and iron corrosion compounds. This requires from 12 hours to a week or until all cleaning action ceases and no more gas bubbles evolve. During this step it is necessary to make sure that the solution remains acidic. If necessary, concentrated hydrochloric acid is added to the solution to maintain a working strength.
2. Rinse thoroughly in tap water to remove all residual encrustation and mechanically remove any stubborn spots.
3. Immerse in a solution of alkaline dithionite. Mix up a solution of sodium hydroxide (40 g. sodium hydroxide per liter of water). Once the sodium hydroxide dissolves add 59 g. of sodium hydrosulfite and then immerse the silver quickly to eliminate oxidation of the solution in the container. The container should be completely full of solution and have an air tight seal. The

amount of sodium hydrosulfite is not critical -- so any thing in the 55-65 gram range will be effective.
4. For one week agitate and turn the container daily to keep the solution mixed and to expose all surfaces of the specimens to the solution.
5. After one week remove and rinse the specimens 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 effectively reduce copper corrosion compounds on badly corroded copper and bronze objects and reform the original surfaces. It has been used successfully on all cupreous artifacts, converting copper corrosion products back to metallic copper.

To dispose of the used solution, allow it to air-oxidize for several days to oxidize the sulfites to sulfates. Then neutralize it with the left-over Hcl. It can then be safely disposed in the drain; however, by using electrolyitc reduction, it is possible to extract all the silver from the soultion -- by plating it on a cathode. The money recived from the sell of the silver anc come close to paying for the treatment.

RINSE AND SEALANT

Following electrolysis, the specimen is rinsed with deionized water. If an alkaline electrolyte is used the rinsing should be quite intensive, otherwise, a white precipitae can form. The silver is dried with hot air or dehydrated in acetone and then coated with clear acrylic lacquer such as Krylon 1301.

CHEMICAL CLEANING

The majority of silver objects recovered from archeological 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 can be prepared that consists of 5% thiourea and 1% non-ionic detergent in distilled water. A solution of 15% ammonium thiosulfate in distilled water with 1% 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 it dissolves silver chloride and will substantially weaken badly corroded silver. Formic acid in a 5 to 30% aqueous (deionized water) solution is effective for dissolving copper compounds without affecting silver chloride. Formic acid also can be used to brighten silver that has been cleaned with some other chemical or other technique. Silver nitrate solution is used for removing films of metallic copper. Often just simple washing in soapy water or rubbing with a mild polishing abrasive is sufficient.

STABILIZATION AND CONSOLIDATION

Since silver sulfide and silver chloride are stable compounds, corroded silver pieces do not need to be stabilized. Consolidation, however, is often required. Many of the silver coins and other small silver pieces likely to be found within an encrustation have completely converted to silver sulfide. In some cases all that remains of the silver is a wet slush without form or structural integrity. 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. In many instances these data can be preserved by making a case of the impression.

Where the object is nearly or completely converted to a compact, cohesive silver sulfide, the form and all the details and marks of the original specimen are retained. All that may remain of some coins is 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 would destroy the coin or at least destroy all the markings and details preserved only in the mineralized sulfide layer. In some instance it may be possible to conserve the in the alkaline dithionite solution described above. In other instance, the only alternative is to consolidate the sulfide. This is easily accomplished by placing the sulfide coin in acetone to dehydrate it. The coin is then placed in a dilute solution of polyvinyl acetate (PVA) and acetone. It is left in the solution until bubbles cease to rise; then the coin is removed, allowed to partially dry and the process in then repeated two or three times. The repeated immersions and drying assures that a maximum amount of the acetate is absorbed. Upon drying thoroughly, the treatment is completed. The PVA consolidates the sulfide layers, although the coin remains fragile and can be easily broken. Any number of other consolidants such at butyl acetate, various polymethacrylates, or even wax, can be used.

SUMMARY

Since the corrosion products of silver are stable, the treatment accorded silver artifacts is less critical. In some instance, however, when treating base silver with a significant amount of copper, it is the copper and its corrosion products that create the problem, and in these case, the artifact should be treated as copper. In many instance silver may be treated exclusively by mechanical means or by various chemical treatments. Because of silver's susceptibility to corrosion in anaerobic environments so 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, then only electrolytic reduction and the alkaline dithionite treatments are applicable, and for this reason, 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 is base on the particular set up 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 archeological sites. This metal is found more often used in various alloys, especially in combination with copper for bronze and with copper and/or tin for pewter. Gettens (1964:560) notes that tin seldom survives because of the transformation of tin by direct intercrystalline oxidation to mixed stannous and stannic oxide (SnO and SnO_2) or by allotropic modification to a loose powdery gray tin, commonly referred to as "tin pest." The alteration compounds of tin in a marine environment have not been adequately studied; it is known, however, that sodium chloride also stimulates the corrosion of tin. Off the coast of Turkey George Bass (1961) found probable ingots of tin completely oxidized to tin oxide. Although not often mentioned in literature, stannous sulfide can be expected to be found where sulfate-reducing bacteria are active in anaerobic environments.

Lead is commonly found in shipwrecks where it was used for weights, cannonballs, sheeting, and stripping. Lead is a stable metal in neutral or alkaline solution free from oxidizing agents especially if carbonates are present in the water (Pourbaix 1966:488-489). During prolonged exposure under most archeological conditions where there is exposure to the atmosphere, basic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$) and lead oxides (PbO & PbO_2) are formed. The gray lead carbonate and lead oxide generally form a protective layer 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 common.

Gettens (1964:558) noted that few occurrences of lead sulfide have been reported, but more recent research (North & MacLeod 1987:89) report that the main lead corrosion products in anaerobic marine environments is lead sulfide, while in aerobic seawater it is lead sulfate, as would be expected. In marine environments, it is not unusual to find the remains of lead straps that have been completely converted to a black slush. The bulk of the corrosion is probably lead sulfide which results from the action of sulphate-reducing bacteria, as explained for iron. Possibly some intermediate forms of the lead oxides (PbO & PbO_2) are formed, and oxysulfides are present. Lead often exhibits extensive corrosion attack when it is in contact with wood. For instance, I have seen lead strips that were nailed onto a ship's keel that were very badly deteriorated. Evidently the oxygen-consuming, decaying wood and the marine encrustation that forms over the lead created the anaerobic conditions conducive for the metabolism of the sulfate-reducing bacteria and the decaying wood provides nourishment for the bacteria. Most of the lead corrosion products, except white lead ($Pb_3(CO_3)_2(OH)^2$), which has not been found on lead artifacts form marine sites, do not adversely affect the artifact after recovery. They may be unsightly or even disfiguring, but they do not take part in chemical reactions that attack the remaining metal. The objects need to be cleaned for aesthetic reasons and possibly to reveal surface details under or in the corrosion layers. The corrosion products themselves are stable.

Lead alloys such as old pewter, which was formerly an alloy of tin and lead, oxidizes to the same compounds as the two parent metals. In archeological sites the condition of different pewter pieces varies widely, primarily because of different local conditions and varying percentages of tin to lead. In marine environments leaded pewter always survives in better shape than does lead free pewter, probably because of the formations of a protective lead sulfate ($PbSO_4$) Lead free pewter suffers extensive corrosive attack in aerobic seawater; in fact pewter is commonly completely mineralized as stannic

oxide (SnO_2), lead sulfide (PbS) and various very brittle, mineralized antimony, tin (SbSn) compounds are formed. In contrast, in anaerobic environments, both leaded and lead-free pewter survives in good condition through the protective formation of lead and tin sulfide films (North and MacLeod 1989:90-91). In fact the only corrosion 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 need to be cleaned only for aesthetic reasons and to reveal surface details under the corrosion layers. Old pewter, being an alloy of lead and tin needs to be treated as tin, which is the more anodic and chemically sensitive metal. Therefore, no acids, or sodium hydroxide should be use, 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 treatment for lead from any archaeological environment is the acid treatment described by Caley (1955). The same treatment can be used on tin or pewter. The lead is immersed in 10% hydrochloric acid which removes the adhering marine encrustation, along with lead carbonates, lead monoxide, lead sulfide, calcium carbonate, and ferric oxide. If lead dioxide is present, it is removed by soaking the object in 10% ammonium acetate. The ammonium acetate also acts as a buffer to protect the lead from the action of any hydrochloric acid that may remain. Lead, if placed in ammonium acetate, should be left in the solution only as long as necessary, as the solution can etch the metal. For most lead objects, the ammonium acetate step is not required. 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. However, for the general cleaning of lead, without a lot of hands-on labor, it remains a much used and acceptable technique provided that all residue of the HCL is removed by rinsing in tap water, so that there is no contamination of any chloride sensitive material that it may be stored with.After using the HCL treatment on lead, one can still has the option to use electrolytic reduction to reduce any corrosion layer that are still in place back to a metallic state.In the objective is to completely remove all the lead corrosion products from a lead object, then a 5% solution of ethylenediaminetetraacacetic acid (EDTA) disodium salt is most effective. After complete immersion in the EDTA solution for 2-3 hours, or in some cases up to 24 hours for larger pieces, the object is then rinsed in tap water.

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, but since tin is an allotropic metal that is slightly soluble in NaOH, heating should be avoided and the duration limited. 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 consider using galvanic cleaning for any object of lead, tin, or their alloys.

In general, galvanic cleaning does not play much of a role in a properly equipped conservation laboratory.

In cases of badly oxidized tin objects, the only alternative is to consolidate in microcrystalline wax, or embed in a plastic material. Slow, extended diffusion of chlorides in alkaline solution are not a consideration because of the solvent action of the solutions.

ELECTROLYTIC REDUCTION CLEANING

The ability to control the reaction speed through current controls in electrolytic reduction makes it especially useful for lead coins and medals - 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 can be cleaned by the normal reduction process using 5% sodium hydroxide, anodes of mild steel or stainless steel, and a current density of 2 to 5 amps/dm2. Very satisfactory results are achieved by this technique, but 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 it 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 it should be supported well enough to insure that the electrical contact is maintained. An initial high current density will remove the lead corrosion layers; therefore, when a low current density should be used to consolidate the corrosion layers through reduction. Since lead, tin and pewter are susceptible to attack by strong alkalies, a sodium carbonate electrolyte is safer to use. For instance, if the electricity were to go off and the lead or tin object, or alloy were in NaOH, it would be attacked. If sodium carbonate was being used as the electrolyte, a passivating film of carbonate would form and the 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 those special artifacts where there is some reason to try to achieve that absolute maximum amount of corrosion products reduced back to metal. For example where there are inscriptions or marks that are preserved in the corrosion layer, then, sodium hydroxide should be used as the electrolyte. For the cleaning of well preserved lead, sodium carbonate is effective. This applies to either normal reduction or consolidative reduction.

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/dm2. In the process, 5% sodium

hydroxide electrolyte with stainless steel anodes is recommended. In consolidative reduction, which utilizes very low current densities, mild steel anodes can not be used because the current flow is so low that there is no way to keep the anodes passivated and they quickly disintegrate through a process called anodic dissolution. The procedure described by Plenderleith and Werner (1971:268-269) using a 10% solution of sulfuric acid with a lead anode is not used that often, because of the difficulties of handling sulfuric acid and the deposition of lead from the anodes on the artifacts being treated. In addition, more recent research has shown that there is more thorough reduction 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, but as discussed under silver, the use of asymmetrical A.C. current is not widely used since low current density electrolysis using straight D.C. current effectively reduces lead corrosion products back to metallic lead, especially when sodium hydroxide is used as the electrolyte. The use of asymmetrical A.C. current does not seem to increase the degree of reduction (Lane 1975; 1979). The important thing to remember is make sure that a cathodic protection is maintained by a flow of electrons to the lead or tin metal is being treated at all time.

Rinsing Procedure Following Electrolytic Reduction

The NaOH residues of the electrolyte cannot be removed completely from lead by rinsing in water alone; and a more complex procedure must by followed (Plenderleith and Werner 1971:269-270). The object is submerged in a dilute solution of sulfuric acid (15 drops of concentrated H_2SO_4 per liter of tap water) with a pH of 3 to 3.5 which neutralized the alkalinity of the electrolyte and also forms a protective coast of lead sulfate on the surface of lead objects. The artifact is taken through a succession of H_2SO_4 baths until the pH ceases to rise from the alkali diffusing from the lead. After the removal and neutralization of the alkali the lead is left acidic. The residual acidity is removed by immersion 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 lead is then strengthened as well as 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 proceeds rapidly. To be safe, lead should by stored in sealed containers or polyethylene bags.

Old pewter, being an alloy of tin and lead, can be treated by any of the methods described for lead. Electrolytic reduction is particularly recommended in order to reveal or preserve surface details, maker's marks, and designs. For well-preserved lead, cleaning with HCL or EDTA are effective. Of the metals recovered from marine sites, they preserve the best and are one of the easier to treat, in most circumstances.

Like silver, because the corrosion products of lead artifacts recovered from marine environments are stable, the exact mode of treatment is less critical. For this reason, treatment with hydrochloric acid (Caley's Method) is often employed because of its simplicity and effectiveness. For the same reason EDTA, disodium salt, is also effective for clean lead, as well as reasonably well preserved tin and pewter. However, still electrolytic reduction is the treatment most often employed because of the

possibility of reducing some of the lead, tin, pewter corrosion products back to a metallic state. The exact mode of treatment depends on the condition of the artifact, the laboratory and the decision of the conservator. Each of the treatments are effective and are selected with some regularity.

GOLD AND GOLD ALLOY CONSERVATION

GOLD CORROSION

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

GOLD CONSERVATION

Pure gold and high gold alloys do not require any treatment. All the gold objects that I have seen 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. 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 about silver and copper conservation are made under those headings.
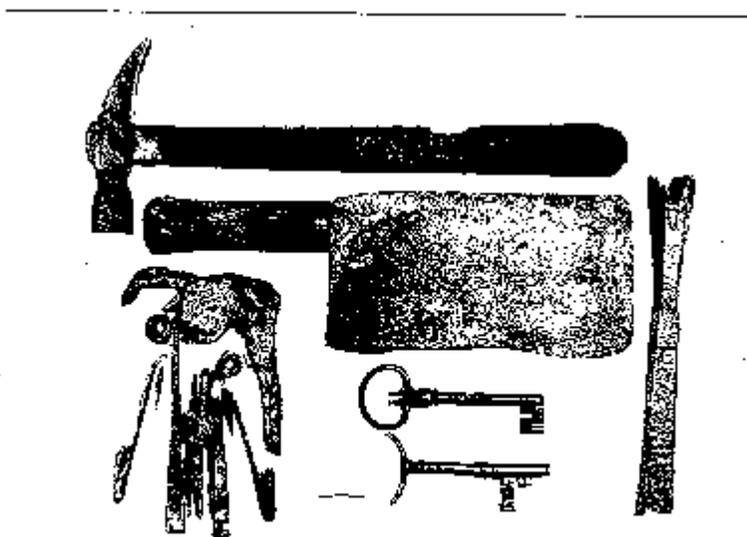
Figure 11. Epoxy casts of iron tools from the submerged town of Port Royal, Jamaica. From top to bottom and left to right: a hammer with the original wood handle, a cleaver with the original wood handle. a door lock, two keys, and a socketed chisel.

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), Frazier (1974), Rigby and Clark (1965), and Hamilton (1976).In the conservation of marine archeological specimens, casting is resorted to when the artifact itself cannot be treated. In some cases, only through casting can the object be saved or its form determined. As explained earlier, 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, forming a mold and preserving details of the original form as well as marks or stamps on the surface. Quite often, the encrustation is more informative than the deteriorated or badly oxidized object. Several ways of retrieving artifactual data are discussed.A number of different casting materials from many different manufacturers can be used. Through the use of many, we have come to rely on just a few. The materials include Dow 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. However, I have used these extensively and know that they work well.

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). Utilizing a lapidary saw, they sectioned small encrustations containing natural molds left by oxidized Byzantine iron tools. Some specimens required only one cut, other more complicated objects required several cuts. The corrosion residue was removed from the natural molds and a piece of cardboard or plastic made to fit between the sawn halves to compensate for the material removed by the saw blade. 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. These rubber casts are not permanent nor long lasting, but 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 keep them from stretching and losing their form. If a permanent epoxy cast is needed, then a mold has to be made of the polysulfide rubber cast, and then this mold cast in epoxy.

After casting several molds sectioned with a lapidary saw, we noticed several disadvantages. The technique is limited to small encrustations 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 saw 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. The radiographs reveal the shape of the object and extent of the corrosion. In certain encrustations it is possible to use a pneumatic air chisel to cut openings into distal ends or key points of an object. Through these holes, the corrosion residue can be washed out and the rubber 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 encrustations are easily opened and cast this way. I do not recommend using a lapidary saw to open natural molds in encrustation, it is much more effective to break them open and cast the void with epoxy.

On most marine sites, the only way to recover a number of the smaller, thin, iron artifacts is to cast the natural mold left inside the encrustation after they have corroded to a slush. The corrosion residue can be remove, sometimes as simply as washing it out with water, and other time it take a considerable amount of picking. After it is removed, the void is filled with epoxy, which eliminates the problems presented with the polysulfide rubber molds. After setting, the encrustation can be removed with a pneumatic chisel, revealing a perfect replica of the original iron objects. By this technique we have been able to cast in epoxy the corroded hammer heads directly onto the original wooden handle, as well as iron cleaver hafted onto the original wooden handle, a variety of iron keys, and several door locks (Figure 11). See Hamilton (1976:72-85) , North (1987:231-232), and Muncher (1988) for a more complete discussion of the techniques of casting and it value when applied to the material from marine sites. It can be emphatically stated, that is casting techniques are not being utilized, a significant amount of data is

going to be lost.Natural molds of disintegrated metal objects are often encountered in a very large encrustation, where they cannot be detected on radiographs even if they could be X-rayed. To avoid destroying possible valuable information, close observation is required when the encrustations are being taken apart with the air chisels to detect the molds before they are destroyed. Because of the presences of these natural molds in large encrusted metal objects, the use of acids or even electrolysis to remove encrustation (Montlucon 1986, 1987) is not recommended for general use. When molds are found, it is possible to open a small area on one side, clean it out, and fill it with epoxy. This opportunity is lost, if "deganguing" were used without some discretion. The casting examples discussed above involved iron artifacts, however, similar casting procedure are often employed on silver artifacts which often corrodes extensively in anaerobic marine environments. Casting techniques also have been extremely useful in recovering stamps from corroded silver specimens. From two 16th-century Spanish shipwrecks there were a number of silver discs which are usually sand cast, circular, and plano-convex in cross section. On the flat surface of the silver discs are usually one or more stamps indicating ownership, mines, and tax marks. Frequently the stamps are obliterated in the corrosion process. The encrustation, however, forms a perfect mold of the original surface of the silver and a reverse impression of the stamps remains 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 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 recovered many otherwise lost stamps through this procedure and it is routinely incorporated into our conservation of encrusted silver discs in order to preserve this valuable data. Few historians or archaeologists would deny that the salvage of the stamps is historically more significant than the silver with its stamps obliterated.

Out of many casting problems encountered the examples discussed above unquestionably present a 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 archeological material. They emphasize the reasons why marine shipwreck material should be processed by personnel

familiar with the material culture and the alternative techniques of salvaging and preserving the maximum amount of data. There are many ways of utilizing casting techniques during the conservation of shipwreck material. The important thing is that some knowledge of the procedures be had and the necessary supplies and casting compounds be kept ready for use.

CONCLUDING REMARKS

This paper has attempted to present the current state of conservation of archaeological material from marine environments. Various requirements, equipment, chemicals, and procedures have been discussed, but many more were not. There are many minor variations, optional steps, and tricks that are used and learned by each practitioner. Time and space did not allow a thorough discussion of each technique and the variations within the different techniques; therefore, there is no way around consulting the original, more exhaustive published sources. Individuals interested in archeological 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. Just because an object has been successfully conserved, does not mean it will not deteriorate in the future. Only if stored or displayed under optimum conditions can stability be assured. Metal artifacts, as well as those made of organic or siliceous material can become chemically unstable from a myriad of causes and require periodic inspection and evaluation, as well as

possible retreatment. At our present stage of knowledge, perhaps it is most realistic to say that the objective of archeological conservation is to delay reprocessing as long as possible by proper storage and to make any necessary retreatment simple and brief. It is obvious that the conservation laboratory can play a major role in archeology, if the objective is to produce the maximum amount of archeological data from the excavation of waterlogged and underwater sites. Conserving the recovered artifacts is just one of the steps.During the course of this discussion a clear idea of the facilities required, the treatments available, chemicals utilized, and various insights on conservation have been presented which 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 shipwreck sites. Estimating the costs involved is more complicated. Still with a knowledge of what is needed, it is just a matter of determining for each facility, the equipment required to start off with, the level or volume expected of the laboratory, the variety of treatments to be done and the figures fall into place.All the treatments discussed are used to conserve material from marine sites. With most, it is not a question or matter of which is preferred or which is better than another. The fact is that a one of every treatment discussed here would be the preferred means of treatment of a given artifact. For that reason, a conservation laboratory has to have a conservator familiar with the various treatments, know on what occasions and situations they are the most appropriated, and have the facilities, equipment, and chemicals to carry out the treatments.

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When a conservator writes a conservation reports such as this, much of the data is in his head and from personal applications, thus common procedures that are used extensively are so ingrained, that when writing, the original reference or even a reference might be left out. In some instance, one can not even remember where various information came from. To help alleviate any problems that this might create, in addition to the cited references, a more intensive bibliography, separated by major materials, is included here.

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CCI, *Canadian Conservation Institute Publications and Notes*

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