CONSERVATION OF METAL OBJECTS FROM UNDERWATER SITES: A STUDY IN METHODS

BY D. L. HAMILTON

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By Donny Leon Hamilton

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D. L. Hamilton

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Abstract

The role of conservation in underwater archeology and the methods of conserving metal artifacts from salt water environments are presented.

When cultural material is recovered from a marine environment, it is commonly encrusted with corrosion products and precipitates from the sea which must be removed. The corrosion processes and products of iron, copper, silver, tin, lead, gold, and their alloys are detailed and preliminary conservation steps—initial documentation, storage, encrustation removal, and artifact evaluation—outlined.

The conservation of metal artifacts is discussed in terms of ferrous and nonferrous metals. All aspects of electrolytic reduction, including equipment and experimental variables, are examined and assessed. Electrode potential measurements, which allow one to derive the maximum effectiveness from electrolytic reduction, are introduced as a conservation technique. Final conservation steps, rinsing, drying, and sealing, are appraised.

Techniques of casting and molding are described, not for replication, but as a means of salvaging and preserving specimens and data not recoverable by any other means.

The relationship of conservation to marine archeology is an intimate and essential one. Conservation can involve more than just preserving artifacts; in some cases it can contribute basic archeological data. Specific examples of encrusted shipwreck material from a 1554 Spanish ship recovered in the Gulf of Mexico are used to demonstrate the potential of this relationship. It is concluded that conservation with a sensitivity to the nature of archeological associations and the scientific value of artifacts is indispensable to marine archeology.
INTRODUCTION

HISTORICAL PERSPECTIVE

Within the field of archeology in the United States the treatment of cultural material beyond initial washing and cataloging is rarely emphasized. As a result, many invaluable artifacts and considerable data are lost. Some of the blame for the lack of proper treatment must be leveled at the curatorial staffs of museums and repositories of archeological material that have a responsibility to care for the specimens in their possession; initially, however, the blame lies with project archeologists. It is their responsibility to see that the material which they recover is treated and stored so that it will be available for research long after the field work has been completed and reports have been written. Although an awareness of the need for specimen conservation subsequent to field recovery was stated as early as 1910 (Hodge 1959: 305-306), little helpful information has appeared in the professional archeological literature. More recent field manuals and papers have only cursorily treated the problem (see for example Heizer and Graham 1967). Keel's (1963) publication remains the single inclusive, but rather general, work on conservation published in the anthropological archeology literature. This lack of interest by archeologists is surprising considering that artifacts are one of the basic units of analysis, but some reorientation is occurring.

In the past two decades there has been a considerable increase in interest in the conservation of cultural property, such as portable works of art, books, manuscripts, and other objects of artistic, historic, or archeological origin, including scientific collections, as well as architectural monuments (Daifuku 1968: 19). Within this 20-year period all the major international conservation bodies have been founded, including The International Institute for Conservation of Historic and Artistic Works (IIC), which publishes Studies in Conservation, the major technical journal in conservation, established in London in 1952; and The International Centre for the Study of the Preservation and the Restoration of Cultural Property, founded in Rome in 1969 by the United Nations Educational, Scientific, and Cultural Organization (UNESCO). A major reference book, The Conservation of Antiquities and Works of Art by H. J. Plenderleith, came out in 1956.

This recognition of the significance of cultural property and its conservation is having an impact on anthropological archeology. Now, at a few universities in the United States, courses in conservation are being offered by archeology/anthropology departments. As a result, there is an increasing appreciation of the value of conservation training and the responsibility of the arche-
ologist to see that recovered material is properly curated.

At present, however, many archeologists do not have the necessary experience or training to handle conservation problems commonly encountered in the field. To compound the problem, few archeology programs or laboratories have adequately trained staffs, properly equipped laboratories, or sufficient funds and time available. If the material warrants excavation, it warrants treatment to insure its continued stability. Before field work is initiated conservation problems should be anticipated and appropriate plans made. A field laboratory often satisfies all the requirements; in other cases a better equipped conservation laboratory is required.

One apparent reason for the lack of attention by archeologists in the United States to the conservation of archeological collections is the fact that in the past, most materials from archeological sites did not require extensive treatment in order to be identified and analyzed for a report. Minimal processing, such as washing and brushing, usually satisfied the demands for analysis. Perishable or singularly spectacular items were sometimes given additional treatment and placed on display. With the increasing attention to investigation of historic sites and particularly underwater historic sites, collections are being recovered containing specimens such as iron, where a lack of concern can lead to irreversible deterioration and even complete destruction.

There remains the problem of having access to a conservation laboratory willing to process archeological material. In the past 10 years a great many institutionally affiliated conservation laboratories have been established throughout the world. The vast majority, however, do not accept outside material. Many focus on unique or spectacular items from archeological sites or collections. Others are concerned with paintings, frescos, textiles, and other material not often found in archeological sites. Little concern is given to the more mundane, commonly found items.

**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. In addition, all treatments should be reversible. 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 conservation of marine archeological material is a perfect example of the intimate relationship that can exist between archeology and conservation.

This publication, which is concerned with conservation in marine archeology, contends that conservation is not important only because it preserves the material remains of the past, 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 archeologically 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 associations. 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. 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 archeologists.” 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, archeologists are always concerned with these interrelationships, whatever broader interests they may have, and these interrelationships are the special business of archeology. (Speulding 1890: 438).

These definitions serve to differentiate archeology, which is a scientific investigation, from uncontrolled salvage and “treasure hunting,” which are oriented toward relic collecting.

The kinds of underwater archeological sites, in salt or fresh water, include 1) sunken 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 material—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 archeologists 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. Archaeological excavation in sites of this period provides additional details to fill the missing pages of history and to correct the misinterpretations. Underwater archeology also can play an important part in interpreting history; the analysis of the sixteenth century Spanish shipwrecks off the Texas coast along with the information from the Spanish archives, will add considerable insight into this era.

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 conservation 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, drawings, 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 intrasite problems can be considered.

When artifacts are recovered from the sea 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" is used here to refer to any of 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 of many different kinds of materials. The investigation of 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.
THE INVOLVEMENT OF TARL IN MARINE ARTIFACT CONSERVATION

In the fall of 1969 the Texas Archeological Research Laboratory (TARL) at The University of Texas at Austin was introduced to the complex problems of preserving antiquities recovered from the sea. A large and invaluable collection from at least one ship of the 1554 Spanish plate fleet, believed to be the ship Santa Maria de Iciar (Carl Clausen 1975, personal communication), was recovered off Padre Island on the Texas coast by Platoro, Inc., a treasure hunting firm from Gary, Indiana. Their activities initiated an extended legal controversy concerning ownership of the material. Pending the settlement of the litigation between the state of Texas and Platoro, the 28th Judicial District Court of Texas of Kenedy County, Texas ordered on September 24, 1969 that the objects in dispute in Cause No. 81 before that court, be placed in the temporary custody of TARL, specifying that the laboratory was:

...authorized, empowered, and directed to do all things necessary to restore and process all artifacts which may require treatment and said Research Laboratory is further authorized and empowered to fully study, describe, photograph and analyze all said artifacts with a view to a full preservation of all of the data which may be accumulated as concerns such artifacts.

At the time the collection was received, TARL had no experience in the conservation of materials recovered from a sea environment. A great deal of time has been spent developing the necessary facilities and skills to carry out the court’s directive.

Since this material was recovered by a treasure hunting company, provenience data were not available. Subsequently, similar material from a wreck of the same 1554 fleet was recovered in a scientific project carried out by the Texas Antiquities Committee. This site, No. 41 KN 10, is believed to be remains of the ship San Esteban, and it was excavated with particular care taken in maintaining careful controls and plotting the provenience of all encrusted material.

Throughout the Texas Antiquities Committee’s marine archeology program, committee members have realized the need for and value of conservation and have wisely budgeted for it. Through interagency contracts between the Antiquities Committee and TARL, all the recovered material has been processed.

A wide variety of artifacts is represented in the materials from the two 16th century shipwrecks processed in the laboratory. Included among the metal specimens are a large number of wrought iron objects: anchors, crossbows, breech-loading guns with their associated breechblocks, breech wedges, and cannon balls of both wrought iron and cast iron, as well as many spikes, straps, chains, and assorted tools. In addition to the ferrous materials there are nearly 2,000 silver coins and a number of silver discs. The lead artifacts include cannon balls, straps, weights, bars, and much lead sheeting. Less numerous are specimens of pewter, brass, bronze, and copper. The few cuprous artifacts consist of one small breechblock, a few coins, a weight cup, three navigational astrolabes, shipfittings, tacks, straight pins, buckles, fragments of chain mail, and miscellaneous small pieces. There are only four gold objects: a crucifix, a gold-bound wooden cross, and two ingots. Numerous organic specimens are included in the collections: a large section of the keel; fragments of planks, boxes, barrels, and hooped barrel gun undercarriages; crossbow stocks; breechblock plugs; anchor stocks; pieces of rope, cloth, rawhide, olive pits, almond shells, hazelnuts, animal bones; and even cockroach exoskeletons and egg cases. Most of these objects were intimately associated within the sea-encrusted conglomerations.

The magnitude, diversity, and size of the iron objects in particular have presented many problems not adequately covered by the literature on antiquities preservation. We were forced to embark on a learning program which has involved considerable experimentation and numerous consultations with experts in conservation and related fields. As a result of this conservation program, we have developed considerable expertise in dealing with marine shipwreck material.
SUMMARY

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. As will be shown in Chapter VII, significant relationships have been maintained over the centuries in the 1554 San Esteban shipwreck. 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 the young science of marine archeology.

The interest in marine archeology and the problem of conservation is manifested by: recent establishment of The Council of Nautical Archeology and its publication The International Journal of Nautical Archeology and Underwater Exploration; the UNESCO book, Underwater Archaeology: A Nascent Discipline; the International Council of Museums' committee to study the conservation problems of archeological material from the seas; and the emphasis on the conservation of metals from the sea in the International Congress of the IIC held in Stockholm in June, 1975. The preprints of the 1975 Congress papers were published as Conservation in Archaeology and the Applied Arts (1975).

Archeological material from marine sites presents some of the most difficult problems confronted by the conservation laboratory. The techniques of preserving this material are coming under close scrutiny and people working in this field are obligated to contribute to the science of conservation. Hopefully, the following chapters on the approach and conservation techniques utilized by TARL to process and document the archeological material from two mid-16th century shipwrecks will be useful contributions.

Only the conservation of metals is discussed in this publication. 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. Since only the treatment of metals is considered, the discussion is initiated with a chapter (III) on metal corrosion. This is followed by chapters on preliminary steps: documentation, storage, and mechanical cleaning; conservation of ferrous metals; conservation of nonferrous metals; casting and molding; application of conservation as an archeological technique; and by four appendices.
METAL CORROSION

During most of the history of metallurgy only a relatively 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 zinc, 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 considered here in some detail.

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, cuprous metals, silver, and silver alloys, tin, lead and lead alloys, and gold and gold alloys are included.
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), and Pourbaix (1966).

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, 1973: 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 poten-
tial 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 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:

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

The hydroxides combine with the sodium ion in the solution to form sodium hydroxide as the cathodic produce.

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

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

$$Fe^0 - 2e \rightarrow Fe^{+2}$$

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 (1966: 236) is:

$$\text{ferrous ion } Fe^0 - 2e \rightarrow Fe^{+2}$$

$$\text{fer, hydroxide } Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$$

hydrated ferric hydroxide (red-brown rust)

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_3O_3 \cdot H_2O$$

The primary anodic reaction of electrochemical corrosion of iron is the production of ferrous ions. The secondary stage, the oxidation of the ferrous ion compounds to a ferric state, is modified 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).
### TABLE 1

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

<table>
<thead>
<tr>
<th>Noble End (Cathodic)</th>
<th>Ionic Reaction</th>
<th>Electrode Potential*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>Au⁺³ + 3e⁻ ↔ Au</td>
<td>+ 1.50</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag⁺ + e⁻ ↔ Ag</td>
<td>+ .799</td>
</tr>
<tr>
<td>Copper (cuprous)</td>
<td>Cu⁺ + e⁻ ↔ Cu</td>
<td>—</td>
</tr>
<tr>
<td>Copper (cupric)</td>
<td>Cu⁺² + 2e⁻ ↔ Cu</td>
<td>+ .337</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2H⁺ + 2e⁻ ↔ H₂</td>
<td>0</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb⁺² + 2e⁻ ↔ Pb</td>
<td>— .126</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn⁺² + 2e⁻ ↔ Sn</td>
<td>— .136</td>
</tr>
<tr>
<td>Iron (ferrous)</td>
<td>Fe⁺² + 2e⁻ ↔ Fe</td>
<td>— .440</td>
</tr>
<tr>
<td>Iron (ferric)</td>
<td>Fe⁺³ + 3e⁻ ↔ Fe</td>
<td>— — .036</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn⁺² + 2e⁻ ↔ Zn</td>
<td>— .763</td>
</tr>
</tbody>
</table>

Base End (anodic)

---

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

\[
6\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 4\text{H}_2\text{O} + 2\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O} \\
\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{Fe}_3\text{O}_4
\]

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.

\[
\text{Fe}_3\text{O}_4 / 2\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O} / 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}
\]

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. 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 concentrations, 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 mid-16th century Spanish shipwreck material 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:

\[ \text{H}_2\text{SO}_4 + 8\text{H} \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} \]

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:

\[ \text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+ \text{ fer. sulfide} \]

\[ 3\text{Fe}^{2+} + 6\text{OH} \rightarrow 3\text{Fe(OH)}_2 \text{ fer. hydroxide} \]

\[ 4\text{Fe} + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{FeS} + 3\text{Fe(OH)}_2 \text{ overall reaction} \]

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 oxidizes by the same processes including the action of sulfate-reducing bacteria. In addition, when cast iron is submerged in salt water, it undergoes a corrosion process called graphitization (Patoharju 1964: 316, 1973: 3; Pearson 1972a: 10). In this reaction the salt water conducts a current between the anodic pearlite 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:

- \text{Fe(OH)}_2 \quad \text{ferrous hydroxide}
- 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \quad \text{ferric hydroxide (common rust)}
- \text{Fe}_3\text{O}_4 \text{ or } \text{FeO} \cdot \text{Fe}_2\text{O}_3 \quad \text{ferro-ferrous oxide (magnetite)}
- 2\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O} \quad \text{magnetite, hydrated}
- \text{Fe}_3\text{O}_4 \quad \text{ferric oxide}
- \text{FeCl}_2 \quad \text{ferrous chloride, anhydrous}
- \text{FeCl}_2 \cdot x\text{H}_2\text{O} \quad \text{ferrous chloride, hydrated}
- \text{FeCl}_3 \quad \text{ferric chloride, anhydrous}
- \text{FeCl}_3 \cdot x\text{H}_2\text{O} \quad \text{ferric chloride, hydrated}
- \text{FeS} \quad \text{ferrous sulfide}

On the Spanish shipwreck material that TARL has been processing for the past five
years, the most prevalent iron corrosion products are ferrous sulfide, magnetite, ferrous hydroxide, and iron chlorides. Many of the iron objects have completely converted to ferrous sulfide, leaving only a loose slush within a natural mold of encrustation. Others are completely mineralized to a massive oxide, magnetite, but retain their structural integrity and surface detail. Others have also 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.

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 uninhibitive 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. The greatest damage, however, 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):

\[
Fe + 2NaCl + 2H_2O \rightarrow FeCl_2 + 2NaOH + H_2 \uparrow
\]

is not thermodynamically feasible. Regardless of the exact equation, both the ferrous chloride and ferric chloride combine with water to form hydrates:

\[
FeCl_2 \cdot xH_2O, \text{ and } FeCl_3 \cdot xH_2O, \text{ where } x = \text{is normally } 2, 4, \text{ or } 6
\]

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:

\[
Fe^0 - 2e \rightarrow Fe^{+2}
\]

\[
Fe^{+2} + 2Cl^- \rightarrow FeCl_2
\]

\[
4FeCl_2 + 4H_2O + O_2 \rightarrow 2Fe_2O_3 + 8HCl
\]

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

\[
2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl
\]

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

\[
Fe^0 + 2HCl \rightarrow FeCl_2 + H_2 \uparrow
\]

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

Of the above corrosion products, it is possible by electrolytic reduction to convert the ferrous compounds Fe(OH)_2, FeCl_2, FeS and the ferrous oxide portion of Fe_3O_4, which probably exists as FeO \cdot Fe_2O_3, back to a metallic state in an aqueous solution. The reduction of the ferric compounds is limited by thermodynamic consideration. This problem is discussed under the Electrode Potential section of electrolytic cleaning of iron.
NONFERROUS METAL CORROSION

Cuprous Metal Corrosion

The term cuprous 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 cuprous 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 (CuCl₂), cuprous oxide (Cu₂O) and the aesthetically pleasing green and blue colored cupric carbonates, malachite [Cu₂(OH)₂CO₃], and azurite [Cu₃(OH)₂(CO₃)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.

\[ \text{Cu}^0 - e \rightarrow \text{Cu}^+ \]
\[ \text{Cu}^+ + \text{Cl}^- \rightarrow \text{CuCl} \]

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).

\[ 4\text{CuCl} + 4\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{CuCl}_2 \cdot 3\text{Cu(OH)}_2 + 2\text{HCl} \]

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

\[ 2\text{Cu} + 2\text{HCl} \rightarrow 2\text{CuCl} + \text{H}_2 \uparrow \]

The reactions continue until no metal remains. Any conservation of chloride-contaminated cuprous objects requires that the chemical action of the chlorides be prevented by removing the cuprous chlorides or converting them to harmless cuprous oxide.

Copper objects in sea water are also converted to cuprous and cupric sulfide (Cu₂S and CuS). Gettens (1964: 555-556) refers to some copper coins and fittings recovered from marine shipwrecks that were altered to cuprous sulfide. He attributed the source of the sulfide to the presence of sulfate-reducing bacteria. No mention of cuprous sulfide is made in the literature, but, since the copper objects would be in anaerobic environments, it is reasonable to expect the copper sulfide products to be originally in the lowest oxidation state as are the ferrous sulfides and silver sulfides. After recovery and exposure to oxygen, it might be possible for 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. Although qualitative tests have not been made, it appears that cuprous sulfide is a major corrosion product on most of the cuprous artifacts from 41 KN 10 and the Platoro Collection. On removal from the marine encrustation they 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 cuprous 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.
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. When corrosion does occur, few mineral alteration products are produced. In the case of relatively pure silver, silver sulfide, Ag₂S, and silver chloride, AgCl, are formed. 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 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.

\[ 2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H}_2 \uparrow \]

Silver sulfide is by far the most common mineral alteration compound of silver recovered from sea water. It is commonly reported from Spanish shipwrecks in the Caribbean, and constitutes the most prevalent corrosion compound on the silver pieces recovered from 41 KN 10 and the Platoro Collection. In fact, a large percentage of the silver coins and even small silver discs 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.

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 coins; but it is clear from the silver nitrate test that chlorides are present.

Regardless of whether the corrosion products are silver chloride or silver sulfide, both are stable and do not take part in any further corrosive reaction with the remaining silver. In fact, the two minerals 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. It is only when the corrosion products are disfiguring and hide underlying detail that there is any reason to treat silver artifacts with these two corrosion compounds or patinas.

Tin, Lead, and Lead Alloy Corrosion

Tin articles were seldom made; this metal was used most often in various alloys, especially in combination with copper for bronze. Gettens (1964: 560) notes that tin seldom survives because of the transformation of the tin by direct intercrystalline oxidation to mixed stannous and stannic oxide (SnO and SnO₂) 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 mentioned in any literature, stannous sulfide can be expected to be found where sulfate-reducing bacteria are active in anaerobic conditions similar to the material recovered off Padre Island, Texas. No identifiable tin objects have been recovered from 41 KN 10 or the Platoro Collection.

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, basic lead carbonate (\(2\text{PbCO}_3 \cdot \text{Pb(OH)}_2\)) and lead oxides (\(\text{PbO}\), \(\text{PbO}_2\)) 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 (\(\text{PbCl}_2\)) and lead sulfide (\(\text{PbS}\)) are also common.

Gettens (1964: 558) notes that few occurrences of lead sulfide have been reported. Although qualitative tests have not been run on samples at TARL, it is believed that this mineral constitutes the bulk of the corrosion present on lead objects that have been processed. 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 sulfate-reducing bacteria, as explained for iron. Possibly some intermediate forms of the lead oxides (\(\text{PbO}\), \(\text{PbO}_2\)) are formed, and oxy sulfide are present. Loose lead corrosion products are especially noticeable on a large section of the ship's keel from 41 KN 10. Along the seams of each outer plank a lead strip was nailed. All the lead was completely converted. 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.

Most of the lead corrosion products, except white lead (\(\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2\)), 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 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. Various combinations of lead carbonate, lead oxide, lead sulfide, lead chloride, and tin oxide are possible. Old pewter objects often have wartlike blisters on the surface of the metal which possibly result from localized contaminations of salts (Plenderleith and Werner 1971: 278).

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.

Summary

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 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. A detailed paper on the major corrosion products of the different metal can be found in Gettens (1963 & 1964).
III

PRELIMINARY STEPS: DOCUMENTATION, STORAGE, AND MECHANICAL CLEANING

The Conservation of Antiquities and Works of Art (Plenderleith and Werner 1971) is the single most valuable reference for the conservation of archeological material from any environment. While it contains only a few direct references to the objects recovered by marine archeologists, all the basic conservation techniques are discussed, at least in a general way. It is regrettable that most 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). It is with this in mind that the following discussions on the treatment of metals are presented. Hopefully, they will fill some of the gaps in the literature.

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 conservation laboratory operation, from the time any metal specimen is received to its final storage or exhibition, can be heuristicly conceived in terms of a flow diagram which incorporates a number of possible sequential steps and alternative procedures. The diagram presented in Figure 1 concerns the treatment of iron from a marine environment, but it exemplifies the steps and decisions that must be made when conserving any metal. 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
   D. Sealant
   D. Storage
   E. Periodic inspection
Figure 1.—Flow diagram of basic processes of treating iron from a marine environment.
INITIAL DOCUMENTATION

TARL's basic approach to conservation is 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 descriptions, radiographs, 4 x 5 black and white photographs, 35 mm 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. Each negative should be stored in a glassine envelope and in an opaque paper envelope. All records should be well organized in a filing system so the data will be readily accessible. The recording system used at TARL has worked well and is described below.

An Encrustation Record Form (Fig. 2), an 8½ x 11-inch card, is completed as soon as possible after the object reaches the laboratory. On this card, the site number, site name, encrustation identification number, and preliminary descriptive data are recorded. A black and white photograph of the encrustation is attached and a sketch is often drawn on the back of the card. A complete photographic record of color, black and white, and

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**Figure 2.—Encrustation record card**
X-rays is kept on the card for quick reference. Space is provided for any mechanical or chemical treatment accorded, and for a listing of artifacts in the encrustation. Each artifact is given a sequential subnumber of the encrustation accession number, and a specimen record card (Fig. 3), another 8 1/2 x 11-inch card, is completed. More specific artifact identification data are recorded on this card along with a photographic record which lists the number of each color, black and white photograph, or radiograph, taken of the specimen in its encrusted form, after removal and before treatment, during processing and after treatment. On the back a scaled drawing is usually made. It is especially important to have a scaled drawing and a photograph before treatment because the treatment may result in alterations in form and the dimension of the specimen. For badly deteriorated objects the changes may be significant.

On the left side of the specimen record (Fig. 3) space is provided to document major aspects of chemical, electrochemical, or electrolytic reduction treatment. Since a large number of metal artifacts can be expected to occur in any shipwreck collection, the card is set up to facilitate the recording of electrolytic reduction data, such as surface area of the artifact, current density, electrolyte, and anode material. The length of time in electrolysis, amperage/volts ratio, electrolyte chloride content in parts per million, and frequency of electrolyte changes are the types of pertinent data that are maintained. In the upper left hand corner of both the Encrustation and the Specimen Record cards is a small square. Shorthand symbols, such as an “X”
for processing completed, or a "D" for specimen discarded, are recorded for quick reference. This eliminates the necessity to refer to the notes to see whether or not the treatment or documentation is completed. 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. Usually accompanying the two basic forms, the En-

**STORAGE 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.

**Storage of Iron**

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 alkali 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 (Fig. 4) in a solution with a pH above 8, if it is free of chloride. 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, rela-
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.

If the aqueous solution contains aggressive anions (i.e., any negatively charged ion that readily reacts with iron such as chlorides or sulfates) the passivation boundaries are altered and a higher pH is required to prevent corrosion. Pearson (1972a: 7) considered a 2% solution of sodium hydroxide with a pH of 12.6 to be adequate for the storage of Captain Cook’s cast iron cannons. He felt that insufficient chlorides would go into solution from the cannon to extend the corrosion zone into the vicinity of pH 12.6.

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 SOLUTIONS

If long term storage is required, an inhibited solution containing oxidizing agents should be used. 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 effect maintains the electrode potential of the surface of the metal in the passivation range of the metal (Pourbaix 1966: 74). It should 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. Therefore, when Kranz (1969: 20) states that tests have determined that a 0.01 to 0.1% solution of potassium dichromate is sufficient to inhibit the corrosion of steel, it must be remembered that sodium hydroxide has to be added.

Figure 4 depicts the corrosion domains of pure iron along with the theoretical corrosion, immunity, and passivation domains of iron. Figure 5 represents the stability conditions formed by the reduction of a 0.1 N chromate inhibitor solution. This figure, however, is somewhat misleading. As stated, chromates have a limited pH range of 9.1 to 9.3,

![Graph](image-url)
while dichromates have a pH of less than 7. This figure combines both dichromates and chromates. A vertical line drawn in at pH 9.1 to 9.3 represents a true chromate solution. The hatched sections of Figure 4 show the theoretical domains of corrosion in the absence of chlorides. The thick line in Figure 5 represents the potential gradient below which the chromate inhibitor can be reduced, while the hatched areas represent the remaining corrosion domain of iron (Pourbaix 1966: 75).

It must be emphasized that Figures 4 and 5 represent the behavior of pure iron, not alloys, in solutions not containing any substances which can form soluble complexes or insoluble salts. In the presence of aggressive anions, such as chloride, the passivating film is porous and localized pitting can occur. The addition of oxidizing agents such as chromates apparently provides cathodic protection to iron. Hydrogen evolution at the surface of a steel cathode reduces chrome VI ions to chrome III. Chrome III is relatively inert and forms a protective chrome III oxide (Cr$_2$O$_3$) film on the surface which prevents additional corrosion. The Cr$_2$O$_3$ film forms a passivating surface that has such a high overpotential that electrochemical corrosion and the reaction with aggressive ions is decreased (Worth Carlin 1975, personal communication).

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$^+$ → 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. The chromates as CrO$_4$ in parts per million can be determined by a chromate titration test and additional chromate added as required. A chromate test is given in Appendix II.

Chromate solutions also 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 must, of course, comply with them. If proper disposal cannot be arranged, chromate solutions should not be used.

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.

Alternatively, the chromate solution can be acidified to a pH of 3 to 4 by bubbling sulfur dioxide (SO$_2$) through the solution to reduce the hexavalent chrome to trivalent chrome, i.e., chrome oxide (Cr$_2$O), which is very insoluble. Sodium hydroxide is then added to precipitate the chrome oxides. The solution is drained and the precipitate is gathered and disposed in a chemical dump (Worth Carlin 1975, personal communication).

For the past four years TARL has utilized a .1N solution of potassium dichromate (K$_2$Cr$_2$O$_7$) 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.

Storage of Nonferrous Metals

At TARL, all the encrusted shipwreck material from the 16th century shipwrecks has been stored in a potassium dichromate solution. Iron is the most common metal, but gold, silver, pewter, brass, bronze, copper, and lead artifacts are present, as well as ceramics, stone, glass, bone, cloth, seeds, and wood. All this material has been stored safely in the storage solution, while both in the encrusted form and even after removal from the encrustation with no apparent harm to any specimen.

While iron artifacts are always stored in a chromate solution after removal from the encrustation, this solution is not necessary or even recommended for artifacts made of other metals. The following discussion on safe storage conditions for the nonferrous metal relies heavily on data from Pourbaix (1966).

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. Silver is stable in aqueous solutions of any pH value and in the atmosphere, so long as these environments are free from oxidizing substances. If oxidizing agents, such as chromates, are present silver covers itself with a film of brown Ag₂O.

Tin will resist corrosion in slightly alkaline solution free from oxidizing agents but will react adversely to strongly alkaline solutions. Moderately alkaline solutions are passivating if they contain oxidizing solutions capable of raising the potential. Lead is corroded by aqueous solutions free from passivating substances, especially soft water, deionized water, or distilled water. It is, however, corrosion resistant in hard, bicarbonate water because the bicarbonate is passivating. In the absence of passivating substances, an oxidizing agent such as chromate can damage the specimen.

Copper, copper alloys, silver, and tin can be affected adversely by oxidizing solutions, hence on removal from the encrustation they should be stored in alkaline solutions. A 5% solution of sodium sesquicarbonate with a pH of 9.7 is adequate for each. A 5% solution of sodium carbonate with a pH of 11.5 will protect copper and silver but is borderline to corrosion for tin, which can be stored in tap water or a chromate solution. Lead needs only to be stored in tap water, with the pH adjusted to a range of 8 to 10 by the addition of sodium sesquicarbonate. Pewter also can be stored in sodium sesquicarbonate. Lead and its alloys should not be stored in a chromate solution because of its oxidizing effect which forms an orange film of lead chromate that is difficult to remove. 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 hard and difficult to remove.

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. 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. TARL has a 260 KVP Picker Industrial X-ray that is capable of X-raying most of the encrustations. The 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 the very large conglomerates—those containing cannons, anchors, breechblocks, wooden planking, and the like—the procedure developed at TARL has been to remove carefully the encrustation from the anchor or cannon in the largest possible sections. The location of each of these fragments is accurately plotted onto a photograph. Each section is then X-rayed, an overlay drawing made, and the smaller enclosed artifacts removed. Then, from assembled overlays, a scaled drawing showing all the associations is constructed.

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.

The encrusted bores of cannons and breechblocks 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 and 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. Muzzle-loading guns and breechblocks can be cleaned the same way, but it is more difficult.

The use of acids is generally a slow, ineffective process. Acids 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 associations, observations, and measurements and in making casts from molds of completely oxidized 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.
IV

CONSERVATION OF FERROUS METALS

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 five main categories:

1) Galvanic cleaning
2) Electrolytic reduction
3) Chemical cleaning
4) Annealing
5) Water diffusion

Since TARL has had considerable experience with a wide variety of wrought iron objects, each of the conservation alternatives for cleaning this metal will be explained in greatest detail. Much of what is covered is fully applicable to the preservation of other metals. Consequently, the discussion of nonferrous artifacts can be brief.

ELECTROCHEMICAL CLEANING

The corrosion of metal (Chapter II) is a chemical and an electrochemical reaction. Electrochemical and electrolytic reduction cleaning processes are the most common techniques utilized to halt, stabilize, and even reverse the oxidation of the metal. 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 (1966) is the source most 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 Electrochemical 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 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, Na₂CO₃ (soda ash). Hume (1969: 283) suggests using an electrolyte of baking soda (sodium bicarbonate, NaHCO₃) 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 minerals are reduced and all traces of chlorides have been eliminated. (See section on qualitative test for chloride described later in this chapter.) If any chloride is 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 oxycarbonate 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 regranulated by slowly pouring into water (Organ 1973: 193). In the latter, the reducing flame is going to have to be very good to remove oxycarbonate 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 reclined and replenished. For example, just the technical grade mossy zinc needed to clean a wrought iron bombardetta cannon tube, 222 cm. long, 18 cm. diameter, would cost approximately $1,000 to $1,500. 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.

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 considered are the equipment and the experimental variables.

1) Equipment
   a) Power supplies
   b) Terminal wires and clips
   c) Anode material
   d) Chloride monitoring
   e) Vats

2) Experimental variables
   a) Types of electrolytic setups
   b) Electrolytes
   c) Current densities
   d) Electrode potentials
EQUIPMENT

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 at TARL 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.

<table>
<thead>
<tr>
<th>A.C. VOLTAGE</th>
<th>D.C. VOLTAGE</th>
<th>D.C. AMPERAGE</th>
<th>EXAMPLE MODELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 110V 1φ</td>
<td>6/12</td>
<td>0–20</td>
<td>Eico, ATR, Kapco</td>
</tr>
<tr>
<td>2. 110V 1φ</td>
<td>24–32</td>
<td>0–50</td>
<td>Gates, Kapco, modified</td>
</tr>
<tr>
<td>3. 220V 3φ</td>
<td>32</td>
<td>0–200</td>
<td>Aerotronic Controls Inc. airplane battery chargers</td>
</tr>
<tr>
<td>4. 220V 3φ</td>
<td>28</td>
<td>0–300</td>
<td>Rapid Electronic Co. metal rectifiers</td>
</tr>
</tbody>
</table>

The small power supplies, Kapco, Gates, ATR, 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. The choice of a power supply 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 regulated power supplies it is not surprising that many conservation laboratories build their own power units. Foley (1967) and Organ (1988: 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.

TARL has successfully modified a number of varying size battery chargers. The alterations made to large 220V, three-phase airplane battery chargers exemplify what can be done to transform these units to serviceable 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. Variable autotransformers for 220 volt three-phase chargers, however, are very expensive and could not be provided for all of the units. It was found that each unit had built-in low and high current line resistors, but the resistance these provided was not sufficient to keep the unit from operating at too high an amperage. This problem was solved by replacing the low current resistors with the high current ones from other power units. By employing the different resistant current taps, it is possible to maintain fixed amperage rates of 100 to 200 amperes. The 0 to 100 amperage range was eliminated, but this range is not important when cleaning large objects such as anchors, cannons, or a number of breechblocks. In practice only those artifacts whose calculated current density requirements exceed the maximum output of the power supply are cleaned with these resistor regulated power supplies.

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.

**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 multi-strand 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. For larger artifacts needing more current, No. 2 to No. 0 AWG multi-strand wire is required. In all cases multi-strand copper wire is recommended because it has a larger current capacity than comparable size solid wire and is more flexible and easier to manipulate.

**ANODE MATERIAL**

For electrolytic cleaning of iron, 16-gauge expanded mild steel mesh with half-inch openings is an inexpensive but efficient anode material. This steel mesh is 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 a small addition of magnesium.

Data provided to me by Worth Carlin of PPG Industries, Corpus Christi, Texas indicate that only type 316 stainless steel resists C1 – corrosion and is a good alternative to mild steel in an alkaline electrolyte. All the other stainless steel anodes present problems. 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, such as type 3, described below, for treating a number of artifacts at one time with permanent anodes is the most practical way to use stainless steel anodes.

Organ (1973: 193) correctly states that at a low current density stainless steel anodes may corrode because of a deficient evolution of oxygen at the anode, which prevents the anode from becoming passive. Organ recommends that the problem be corrected by reducing the total area of the anode and distributing the lesser area as smaller anodes all around the object. The use of half-inch expanded stainless steel would alleviate this problem more efficiently. However, by decreasing the anode area the current density is increased, which, in essence, eliminates the passivation of the anode caused by dissolution which gives a chrome-oxide type anode. When the total area of the anode is reduced, the current density is increased, which probably increases the overall anode corrosion over an extended period.

Organ (1973: 193) also says that since a stainless steel anode is usually unreactive, the chlorides from the artifact do not react with the anode and build up in the electrolyte; so the electrolyte has to be replaced more frequently. Seemingly, Organ implies but does not state that the chlorides react with the mild steel anodes and the electrolyte does not need to be changed as often. If, however, the hydroxyl ion concentration is kept up, one will get better service from mild steel anodes than stainless steel. In any case, it is much simpler and more economical to change the electrolyte before the chlorides build up to such an extent that they indirectly 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.

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. This test is described in detail in Appendix I.

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 6 presents the progress of two wrought iron hooped barrel guns. 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.

**VATS**

A wide variety of containers can be used in an electrolytic setup. Many kinds of non-conductive vats of various caustic and acid-

![Figure 6.—Graph depicting the diffusion of chlorides into solution during electrolytic cleaning.](image-url)
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-reinforced 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 PCV 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.

In addition to nonconducting containers, conducting mild steel vats have a definite place in electrolytic 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. These can be bolted together with a teflon gasket for a watertight seal or used separately by bolting a plate on each open end. When the parts were joined, the vat was used to clean anchors in a type 1 electrolytic setup, with auxiliary sheets of expanded mild steel near the top surface. Separated, the two were employed to clean two wrought iron hooped barrel guns, a smaller gun, and two breechblocks in a type 3 setup. 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 stoves were cut off, the vat drained and filled with alcohol to dehydrate the large objects. The alcohol was drained and replaced with microcrystalline wax for the final sealant.

Mild steel vats can be constructed in various gauges and are surprisingly durable and versatile, even in the lighter gauges. Mild steel 55-gallon drums, cut lengthwise, 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.

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.

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.

**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).

The *Type 1 electrolytic setup* (Fig. 7, A) is the ideal setup. It 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.
Figure 7.—Setup alternatives for electrolytic cleaning:

A. Type 1 setup.
B. Type 2 setup.
C. Type 3A setup.
D. Type 3B setup.
E. Type 4 setup.
on the surface of the specimen. The setup also allows one to monitor the chloride level in the electrolyte.

*The Type 2 electrolytic setup* (Fig. 7, 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 of current. (*This point is not graphically depicted in Figure 7, 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.

*The Type 3 electrolytic setups* (Fig. 7, 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 (Fig. 7, 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.

Yet another variety of the same setup (Fig. 7, D) is to suspend artifacts from a cathode rod conductor, with adjustable vertical anode sheets hung to either side, and preferably another anode along the bottom of the vat. 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.

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.

The Type 3B setup (Fig. 7, D) is the one most commonly described in the literature (Plenderleith 1956: 194-196; Plenderleith and Toracca 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 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.

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 disconnects from the clip, which is a common occurrence on anode connections submerged in the electrolyte.

Instead of suspending the artifacts by copper wire wrapped around the cathode rod and the artifact, 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 boiling 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.

The Type 4 electrolytic setup (Fig. 7, E) uses 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.

**ELECTROLYTES**

The only two electrolytes commonly used in conservation for treatment of iron objects are alkaline solutions of sodium carbonate (Na₂CO₃) and sodium hydroxide (NaOH), the most alkaline electrolyte one can get. In all cases it should be kept in mind that the alcalies (and acids) used in conservation should be concentrated enough to do the required job, but no stronger. This avoids overcleaning 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 will suffice for the electrolytic cleaning of most iron artifacts. 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. It is also much easier to rinse out of the metal than is sodium hydroxide, which cuts down on the time required for the final rinse. 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 by TARL personnel 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\textsuperscript{–} 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.

The marked carbonate deposit on the artifacts treated in 5% Na\textsubscript{2}CO\textsubscript{3} mixed with tap water can be explained by the fact that the city of Austin water supply is derived from a limestone area and contains calcium bicarbonate which reacts with hydroxyl ions to form calcium carbonate. 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.

In our experiments the deposit was significant in an electrolyte of sodium carbonate mixed with tap water, and noticeable even when mixed with deionized water. To prevent this, gluconic acid was 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\textsubscript{2}CO\textsubscript{3} in tap water, and slightly noticeable in Na\textsubscript{2}CO\textsubscript{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, however. Preliminary tests with sodium glucoheptanate as a sequesterant appears to eliminate the carbonate deposit but generally only deionized water should be used with Na\textsubscript{2}CO\textsubscript{3}.

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 (Calgon). 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\textsuperscript{–}) ions discharge as oxygen at the anode more readily than the dissociation products of carbonate ions (CO\textsubscript{3}\textsuperscript{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.

The most important disadvantage of Na\textsubscript{2}CO\textsubscript{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\textsubscript{2}CO\textsubscript{3} with a pH of 11.5. More details in regard to this are discussed subsequently under electrode potentials.

**SODIUM HYDROXIDE**

The shortcomings of 5% Na\textsubscript{2}CO\textsubscript{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 used as the standard electrolyte at TARL.

As a precautionary measure, gluconic acid, sodium gluconate, or sodium glucoheptanate in the amount of 2% of the NaOH or Na\textsubscript{2}CO\textsubscript{3} in the electrolyte is 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. In our operations 50% aqueous sodium glucoheptonate has been found to be the superior sequesterant in both NaOH and Na\textsubscript{2}CO\textsubscript{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% Na₂CO₃ 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 NaOH is used and 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, Na₂CO₃ 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. At the next electrolyte change, 5% Na₂CO₃ is substituted and continued until all the chlorides have been removed. Toward the end of the electrolytic treatment and as a final step, a high current density is used to clean the object mechanically. By substituting Na₂CO₃ after reduction in NaOH, there is a more efficient removal of chlorides and the rinsing process at the end of electrolysis is facilitated.

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 for the first days or weeks. If the corrosion products are in a ferric state, there is no advantage in using NaOH, and Na₂CO₃ 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 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 Torracca 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 non-adherent.

Current densities used at TARL and their objectives are:

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 are recommended as rough guidelines for treating most iron artifacts from under the sea. 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 of 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 oxides back to a metallic state, 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. At times, a more precise alternative is required, such as measuring the electrode potential established at the surface of the artifact.

**ELECTRODE POTENTIALS**

The normal electrode potential, or relative activity, of each metal is placed in an electro motive 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$^{2+}$ → Fe$^{0}$ − 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$^{3+}$ → Fe$^{0}$ − 3e, occurs at −.036 and increases −.019 volts per pH increase. The hydrogen discharge potential 2H$^{+}$ → 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 8. 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 iron corrosion compounds is at the intersection of the hydrogen discharge line and the ferrous ion reduction line (Fig. 8). Using the formula Fe$^{2+}$ + 2e → Fe$^{0}$ and substituting the 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 ion 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 8. 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 electro-
Figure 8.—Reduction potentials of ferric, ferrous, and hydrogen ions at different pH's, and standard temperature of 20° C. The pH range of a 5% Na₂CO₃ electrolyte and a 2% NaOH electrolyte are shaded.

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 9 gives the measured potentials of an artifact in an electrolyte of 2% NaOH with a pH

chemical 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 Appendix IV.
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 8, 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 9 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 10, which compares the potentials of the same artifact in 2% NaOH and 5% Na₂CO₃, 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 Na₂CO₃. This approach is imprecise, but no other means was perceived for ascertaining the pH. These adjusted pH ranges are those shown in Figures 8, 9, and 10.

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 9 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 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 re-
Figure 9.—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 10.—Comparison of the reduction electrode potential on the surface of the same iron cathode in a 5% \( \text{Na}_2\text{CO}_3 \) and a 2% NaOH electrolyte.
duction. The data acquired from electrode potential measurements can in turn be used to arrive at realistic current densities that will establish 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.

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. TARL utilizes 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.

GENERAL OBSERVATIONS ON CLEANING IRON OBJECTS ELECTROLYTICALLY

These observations are directed primarily toward large iron objects, but are not restricted to them. Recommendations for 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, including the few published descriptions and representative examples from TARL. The artifacts processed by TARL are from 41 KN 10 and the Platoro Collection.

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% Na2CO3 electrolyte. They were run at a rate of 20 amperes at 4 volts (current density ca. 0.027 amps/cm²) for one month and a rate of 150 amperes at 4 volts (current density ca. 0.2 amps/cm²) for five months.

Not enough details on all aspects of the electrolytic treatment 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 it 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 conversion of FeO to Fe₂O₃ 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.

Most recently Pearson (1972a, 1972b) reports the conservation of six cast-iron cannons and other relics jettisoned in 1770 by Captain Cook on Endeavour Reef off the Australian coast. Pearson's report is by far the most thorough and complete description to date. It is a report well worth emulating and warrants summary 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 5% 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 value 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. The experiments at TARL on wrought iron indicate that .001 amps/cm² 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 fails 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 so placed assure an even current density over all the surface of the artifacts. This 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 became quite apparent from the TARL experience 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 H2 evolution.

2) The Cl− concentration in the electrolyte is governed by the Donnan equilibrium equation.

The Donnan theory pertains to the unequal distribution of ions on two sides of a membrane (Kunin 1968: 14-16). Although no membrane exists between the artifact and the electrolyte, the interface between the solid and liquid phases may be considered a membrane. An exchange of Cl ions continues until the concentration ratios are equal in both phases. The lower the Cl− ratio in the electrolyte, the more effective the diffusion of the Cl− ions from the artifact to the electrolyte. Using the Donnan equilibrium theory, it can be generalized that the rate of Cl− transfer from the artifact to the electrolyte is negated despite the electrolytic field when the Cl− content of the electrolyte 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 hooped barrel 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.
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 Pledgerleith 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 or water diffusion in an aqueous 5% sodium sesquicarbonate solution.

A phosphate film is formed on iron objects by impregnating them with a 20% solution of phosphoric acid (H₃PO₄). 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 can be expected on wrought iron or steel.

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). Tannic acid solutions (Baker reagent tannic acid, C₃₆H₅₂O₄₆) with a pH of 2.5–3.0 provide good, weather-resistant tannate films. Tannic acid solutions are generally used by TARL. For maximum protection, several coats of 20 to 25% 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 air-oxidize one to two days.

The tannin solution is believed to react with the iron or iron oxide to form a ferrous tannate which 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 color to iron.

Tentative 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 in the tannate or phosphate film.

ANNEALING

Oxidizing Atmosphere

Treating sea-recovered iron objects by heating to a temperature of 850° C. was first attempted in Denmark in 1965 (Eriksen and Theggen 1990). 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 the 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 sublimes 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 crumple, 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 metalurgical microstructure of the metal, making it useless for future metallographic examinations.

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

Reducing Atmosphere

More recent 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. As yet,
only wrought iron fittings and cast iron cannon balls have been processed. The maximum size of any object to be cleaned in this way is about 10 inches by 4 feet (Pearson 1972a: 26). No cannons or objects of similar size have been preserved by this process despite the widespread interest and enthusiastic endorsement. Considerable interest will be manifested in the results when a cannon has been successfully treated by annealing in a reducing atmosphere. What, if any, side effects the heating and cooling will have on the surface corrosion layers and the morphology of the metal are unknown.

STABILIZATION AND CONSOLIDATION

Stabilization and consolidation treatments are reserved for artifacts that are so badly oxidized that any chemical, galvanic, or electrolytic reduction 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 in Chapter VI, Casting and Molding.

Water Diffusion

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 (Appendix I and below).

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 approaches 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 c. 50° C., for both iron and bronze. The alternated heating/cooling cycle may facilitate the treatment, however, when significant levels of chlorides 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 or heat-drying. Pearson (1971a: 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.

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 chlorides. 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 AgNO₃/1 liter of H₂O) 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, 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 dessication, 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 the final sealant or insulating coating is applied to the artifact in order to prevent superficial rust. Some exposure to air is inevitable and it is particularly troublesome when drying by heat (ovens or infra-red lamps) or vacuum dessication. Also, infra-red lamps are not very effective on dense objects and it is expensive to obtain ovens or vacuum cham-
bers 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, methanol, 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, acrylics, acetates, epoxies, paints, oils, lacquers, and other sealants have been used in the past, but few have withstood the test of time. They all 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. Cosmoloid 80H is the most often-recommended microcrystalline wax, but it is not available in the United States. At TARL we have used Gulf 75 Micro wax and presently rely 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.

After the artifact has been dried or dehydrated in alcohol, it is placed in a vat of melted microcrystalline wax and heated to 350° F. (176° C.). At this temperature the viscosity of the wax is considerably decreased and more efficient penetration is assured. Graphite can be added as a pigment to enhance the appearance of badly corroded objects. 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 tem-
perature 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.

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. 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, the water 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.

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. TARL has experimented 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 coatings are a relatively new thermoplastic polymer 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.

Recently TARL 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 large specimens to be displayed outside or in areas of high humidity and salt vapor in the air.

For large objects to be displayed outdoors Townsend (1972: 263) suggests using a coating made up of 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. At this time, TARL has had no experience with this coating.

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. 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.
CONSERVATION OF NONFERROUS METALS

It is not uncommon to find nonferrous metals, copper, silver, lead, tin, gold, and their alloys, in archaeological 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 therefore, 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 vary 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 usually encapsulated by encrustation. Prior to any treatment of the metal artifacts, preliminary conservation steps (Chapter III) 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., cuprous metals, silver and its alloys, tin, lead and their alloys, and gold and its alloys, is discussed in some detail.

CUPREOUS METALS

The use of the nonspecific term cuprous metals for copper and the alloys where copper predominates is desirable because of the difficulty of distinguishing copper, brass, and bronze objects from each other without analytical tests. 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 alkalis.

The most commonly encountered corrosion products on cuprous metals are cuprous chloride and cuprous sulfide. Since neither 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. Copper chlorides are very unstable, reacting with the atmosphere and continuing to corrode the metal by a process referred to as bronze disease. 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.

Preparing the Specimen for Cleaning

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 cuprous 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. On other specimens it may be necessary to remove residue by soaking in 2 to 15% citric acid with 4% thiourea added as an inhibitor to prevent etching of the metal (Plenderleith and Torraca 1968: 246; Pearson 1974: 301) or 5 to 30% formic acid with no inhibitor (Organ 1963b: 109; Dowman 1970: 143-144). Care must be taken as both acids dissolve cupric and cuprous compounds. Formic acid is preferred over citric acid because, unlike citric acid, it is volatile and completely vaporizes after use, leaving no residue.

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), known by the trade name Calgon, to convert the insoluble calcium and magnesium salts to soluble salts which can be washed away.

**Treatment of Chloride-Contaminated Specimens**

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, or 3) sealing the cuprous chloride in the specimen from the atmosphere. The possible treatment alternatives include:

1) galvanic cleaning
2) electrolytic reduction cleaning
3) chemical cleaning
   a) sodium sesquicarbonate
   b) benzotriazole
   c) silver oxide

The first two techniques remove cuprous chloride (CuCl) by reduction; they can, however, be used only on objects with a sound metallic core. If carefully applied, both will restore the object to a stable condition and maintain a form approximating its original uncorroded appearance. They have the disadvantage that they often 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. The three chemical cleaning 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. At TARL the latter is used most often although comparable 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: 193) 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 amp 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. Ultimately, electrode potential measurement experiments will provide the necessary data to arrive at current density rates most conducive for metal reduction and chloride removal.

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. 1303 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 (Gelva V15) in ethanol.

Chemical Cleaning

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) benzotriazole, and 3) silver oxide.

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.

In practice, the superficial corrosion products are mechanically removed from the metal objects prior to putting the 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 is 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 is extended. Monitoring the chloride level by the quantitative mercuric nitrate test (see Appendix I) 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 the 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 cuprous alloys.

**Silver Oxide**

This conservation approach is similar to the benzo triazole treatment in that it does not remove the cuprous chlorides which cause bronze disease. It merely seals the chlorides from the atmosphere. While benzo triazole could be used to treat the entire surface of an object, silver oxide is used only on isolated spots of bronze disease. The high cost of silver oxide prohibits extensive application even though very little of the chemical is required. It cannot be used on weak, thin, or mineralized pieces incapable of safely supporting the oxide layer.

The process (Organ 1961b, 1963: 110; Plenderleith and Werner 1971: 253) requires that spots and cavities of bronze disease be excavated down to a fresh surface of the wax-like cuprous chloride with a needle or dental pick under low power magnification. A paste of silver oxide moistened with ethanol is then rubbed into the exposed areas with a pointed stick. The specimen is next placed in an enclosed space such as a plastic bag, with a tray containing a slurry of photographic hypo (sodium thiosulfate) in distilled water. This creates an atmosphere with a relative humidity of 78%. Under these conditions the cuprous chloride reacts with the silver oxide to form cuprous oxide and silver chloride. Both of these compounds form stable salts which establish a barrier between the cuprous chloride and moisture that is required for further corrosion.

If within 24 hours after treatment, a green efflorescence of basic cupric chloride appears on the object (treated or untreated areas) while in the high humidity environment, the specimen is thoroughly dried, re-treated with silver oxide in the active areas, and exposure to a high humidity environment is repeated. This process is continued until the object shows no signs of active corrosion when exposed to the high relative humidity. In most instances, no more than two treatments are required.

**Summary**

Of the conservation alternatives considered in this section, galvanic, electrolytic reduction and sodium sesquicarbonate are the only ones which actually remove the cuprous chlorides.
For this reason they promise the most enduring protection. While TARL has not had to contend with any large bronze pieces, a number of small brass objects and a bronze breechblock have been processed.

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 cuprous 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 bronze statuary by the Tamil Nadu Government Museum, Madras India (Thangavelu 1972) indicate that electrolysis is the quickest, the most effective, and the most enduring means of processing large brass or bronze objects such as cannons from a salt water environment.

The extremely long time required for the sodium sesquicarbonate treatment discourages its use. A preliminary treatment of sodium sesquicarbonate, followed by treating with benzotriazole, may provide satisfactory results, but more experiments need to be reported before a final judgment can be made. The silver oxide treatment is reserved for localized treatment.

SILVER AND SILVER ALLOYS

In a marine environment the most commonly encountered corrosion products on silver and silver alloys are silver sulfide and silver chloride. Both compounds are stable mineral forms and do not take part in any further corrosive action with the remaining silver. It is only for aesthetic reasons and to uncover underlying detail that there is any cause to treat silver. In base silver alloys with copper, the copper corrodes preferentially and forms cuprous chloride which can continue to corrode the copper component of the silver. 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) chemical, and 4) stabilization and consolidation.

Galvanic Cleaning

Treating silver galvancally 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 (Pledgerleith and Torraca 1968: 241-246; Pledgerleith 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 in the conservation laboratory.

Electrolytic Reduction Cleaning

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

Two methods of electrolytic reduction cleaning have been described in the conservation literature. 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 Pledgerleith and Werner (1971: 222). Both techniques are discussed below.
NORMAL ELECTROLYTIC REDUCTION

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). TARL uses a 5% HCOOH electrolyte for most artifacts. A 2% NaOH solution has been used as an alternate electrolyte.

CURRENT DENSITY

TARL employs 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/cm² (.3 to .5 milliamperes/cm²) reduced more silver. In all cases a very low current density in the range proposed by Organ is required for maximum metal reduction. To settle the question of what current density to employ, electrode potential experiments need to be conducted to determine the most efficient reduction current density and whether an alkaline or acid electrolyte is best.

ANODE MATERIAL

When treating silver, inert anodes such as expanded platinized titanium, stainless steel No. 316, or carbon anodes are preferable. 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. 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 in Chapter IV for iron. The type 3B 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 11. 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 the 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. At TARL large silver objects or irregularly
shaped pieces are 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 rather than platinized titanium is used as the anode.

**REDUCTION IN FORMIC ACID**

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 (Fig. 12). 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.

**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.

There are three possible kinds of induced electromotive currents: alternating current, direct current, and asymmetrical alternating current (Fig. 13). In every cycle of alternating current there is an equal amount of forward current (current flow from negative to positive as in direct current) and reverse current (current flow from positive to negative); therefore, it has a symmetrical sine waveform (Fig. 13A). If an artifact 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 (Fig. 13B). 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.

At TAIL a small experimental, partially rectified power supply was constructed with variable controls to change from alternating current to direct current. The unit is being tested utilizing 10% reverse current and 90% forward current. During electrolysis the net effect is a rapid succession of reduction and dissolution cycles (Fig. 13C). During the 90% forward half of the cycle, reduction of metal
Figure 12.—Sixteenth century Spanish silver four-real Carlos and Johanna coins and a small silver disc, with four stamps on the top surface, processed by electrolytic reduction in formic acid and coated with clear acrylic lacquer.
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 milliamperes/cm² (0.1 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 this technique while treating the Ur lyre are to be found in Organ (1956: 137-144) and in summary form in Plenderleith and Werner (1971: 223-228). The description of the circuit for the partially rectified current is provided in both sources. Asymmetrical alternating current has several advantages over straight direct current, and should prove to be superior when used to treat any metal artifact, even iron objects. More experimentation is needed.

**RINSE AND SEALANT**

Following electrolysis, the specimen is rinsed with deionized water. If an alkaline electrolyte is used the rinsing should be quite intensive. The silver is dried with hot air or dehydrated in acetone and then coated with clear acrylic lacquer such as Krylon.
A PROPOSED PROCEDURE TO DETERMINE
THE POSSIBILITY OF REDUCING SILVER SULFIDE

Consolidative reduction was developed by Organ (1956) to treat silver largely converted to silver chloride. The applicability of the technique to silver converted to silver sulfide is not confirmed. The two compounds are quite different. It remains to be seen if the sulfide components of the silver corrosion products can be removed and the silver reduced in place while preserving the original surface detail. The reduction achieved in 5% formic acid at low current density and fully rectified direct current is encouraging. The problem of silver sulfide corrosion products was not considered by Organ but comparable results should be possible using low current densities on objects with extensive silver sulfide corrosion compounds. In our experiments, if all the adhering encrustation was not removed from the surface, disfiguring lumps of hard metallic silver were reduced in situ on the surface of the silver under the encrustation. The reduced silver is very hard and can be difficult to remove. Evidently the reduction results from the pressure of the adhering encrustation which holds the sulfide corrosion layer tightly against the metallic silver. It is possible that this reduction of silver can be used to the advantage of the conservator if the cathode potential can be controlled so that the reduced silver retains the original details and does not disfigure the surface. For example, many silver coins are found encrusted singularly or in groups and have the appearance of thick black cookies. The condition of the coins within the encrustations can vary from very good to nearly, or completely converted to silver sulfide. Radiographs of the coins readily confirm their condition. If little or no metallic silver remains there is no use in removing the encrustation. It is possible, however, that the sulfide remains of the coins can be reduced in situ within the encrustation.

Silver sulfide is a conductor of electricity and the black encrustation which surrounds a converted coin probably contains enough silver sulfide to make it conductive. The encrustation forms at the original surface of the coin and seals the sulfide remains of the coin tightly in place. It should be possible to insert a silver or stainless steel needle through the encrustation and make contact with silver core of a largely converted sulfide coin. The extruding portion of the needle could be attached to the negative terminal of a direct current or asymmetrical alternating current power supply and all exposed metal contacts sealed with wax. This would ensure that the current flows through the mineralized metal. The encrusted piece could be surrounded with a stainless steel anode, electrolyte added, and a very low current density, just below the range of H₂ evolution, applied. Enough of the sulfide remains should be reduced to a metallic state to strengthen it structurally. Before-and-after X-rays would be able to confirm the results.

Confirmation experiments have not been attempted at TARL. The idea outlined above developed after encountering tenacious reduced metallic silver deposits, capable of taking on a metallic polish under the adhering encrustation on the surface of sound metal coins. Additional experiments will have to be conducted using both the normal and consolidative technique to determine whether the 5% formic acid electrolyte most commonly used at TARL for cleaning silver or the 3% sodium hydroxide used by Organ (1956) in his consolidative reduction process is preferable. As shown earlier for ferrous compounds, there is a pH and electrode potential range that is theoretically most efficient for reducing silver sulfide to metallic silver. It remains to be established whether or not the texture of the reduced silver formed in the above manner will preserve the original surface details after the sulfide components of the corrosion products are eliminated.

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 (Pledgerleith 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% nonionic detergent in distilled water. A solution of 15% ammonium thiosulfate in distilled water with 1% nonionic 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 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 (de-ionized 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 (see Chapter VI).

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. 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 is 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 as butyl acetate, various polymethacrylates, or even wax, can be used.

TIN, LEAD, AND LEAD ALLOYS

Tin

As stated in Chapter II, articles of tin are seldom encountered in archeological sites. Any solid object of tin can be cleaned galvanically or by electrolytic reduction in the same way as described in Chapter IV.

Normally, in galvanic cleaning, the vat with the electrolyte, anodic metal, and specimen is heated to speed the reaction, but since tin is an amphoteric metal that is slightly soluble in NaOH, heating should be avoided and the duration limited. Tin coins do 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 1963). 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 eliminated because of the solvent action of the solutions.

Lead and Lead Alloys

In my experience, based on processing the material from 41 KN 10 and the Platoro Collection, most lead objects are weights, sheets, stripping, ingots, scrap, and lead-covered cannon balls.

The more massive objects are usually in good condition. Thin strips or plates of lead,
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 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, iron, or lead anodes can be used. The procedure described by Plenderleith and Werner (1971: 268-269) using a 10% solution of sulfuric acid with a lead anode gives the best results, and is especially recommended, but it requires more time than the alkaline electrolyte process. As described by Organ (1963a), a controlled direct current source is used. Plenderleith and Werner (1971: 269) suggest using a partially rectified alternating current source, which provides a “bumping” effect, for better results.

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 be followed (Plenderleith and Werner 1971: 269-270). The object is submerged in a dilute solution of sulfuric acid (15 drops H₂SO₄ per liter of water) with a pH of 3 to 3.5. It is then placed in a succession of H₂SO₄ 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. Objects reduced in sulfuric acid only need to be rinsed in the distilled water.

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.

CHEMICAL TREATMENT

Because of the ease of application and the availability of the necessary chemicals, the most widely used treatment for lead from any archeological environment is the acid treatment described by Caley (1955). The corroded objects are soaked in a 10% hydrochloric acid, which gets rid of the lead carbonates and lead monoxide by converting them to lead chloride which dissolves in the solution. Calcium carbonate, hydrated ferric oxide, and lead sulfide are also dissolved. If lead dioxide is present, it is removed by soaking in 10% solution of ammonium acetate. The acetate also acts as a buffer to protect the lead from the action of any hydrochloric acid that may remain. Lead treated by this method has a pleasing appearance, but the retention of surface design varies with a degree of corrosion. This treatment is especially good for lightly corroded specimens. The procedure is satisfactory if carefully monitored, but in practice it has generally been superseded by electrolytic reduction.

ION EXCHANGE RESIN

The use of ion exchange resin to remove lead carbonate and chloride is an innovative method developed in the British Museum Research Laboratory by Organ (1953) and described in detail by Plenderleith and Werner (1971: 271) to remove basic lead carbonate corrosion products. The process is extremely easy to carry out on a small scale. The specimen is prepared for treatment by mechanically removing the gross carbonate corrosion in order to speed up the process and to prevent the solvent action of the distilled water on the lead. The corroded lead specimen is then placed in a beaker or other suitable container, surrounded by granules of a cation exchange resin such as Amberlite IR 120, covered with deionized water, and heated. In the process the lead ions in the basic lead carbonate are taken up by the cation resin in exchange for hydrogen, and carbon dioxide is evolved from the hot liquid. The object is kept in the resin until the white carbonate encrustation is removed, changing the resin if necessary. The metallic lead is unaffected. The ion exchange resin treatment can be used only if the carbonate corrosion is superficial; otherwise consolidative reduction is used. The ion exchange resin method is favored because no chemicals which have to be removed are used on the objects; therefore, the lead does not require washing after the treatment. The technique is especially suited for small objects such as coins, medals, and weights. The treatment is followed by dehydration in a water-miscible solvent and sealing in microcrystalline wax.

The initial cost for cation exchange resin is very expensive but it can be regenerated for a time after using by treatment with nitric acid to dissolve the absorbed lead. It is then rinsed in distilled water until it has a neutral pH. There is an average resin loss of 2% to 8% each time it is used; so it cannot be regenerated indefinitely.

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 oaken cabinets or drawers. If so, even small concentrations or vapors of these acids can initiate corrosion, which proceeds rapidly. To be safe, lead should be 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 and the ion exchange process are particularly recommended in order to reveal or preserve surface details, maker's marks, and designs.
GOLD AND GOLD ALLOYS

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.
VI

CASTING AND MOLDING

The techniques of casting and molding are often used to restore and replicate specimens. 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), and especially Rigby and Clark (1965).

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. Occasionally, therefore, the encrustation is more informative than the deteriorated or badly oxidized object. Several ways of retrieving artifactual data are discussed, along with the materials used.

MATERIALS

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. These materials and their manufacturers are introduced at the beginning of the chapter so the reader can follow the examples described later in the text. The materials include Smooth-On polysulfide rubber, Surgident Neo-Plex Rubber, Peramold Latex, Hysol Epoxy, plaster of Paris, and Coecal plaster. Many similar products could be substituted for those recommended here. However, we have used these extensively and know that they work well. We have found these to be quite useful and compare favorably with products recommended by others.

In many cases those recommended here are the most economical products.

Smooth-On FMC-100 and 200 are two-component polysulfide compounds used to make flexible rubber molds or casts. The base component is mixed with the curing agent just prior to pouring and then cured at room temperature with no shrinkage. The flexible molds can be used to make gypsum, Hysol, Smooth-On, or other casts. Smooth-On is available from Smooth-On, Inc., 1000 Valley Road, Gillette, New Jersey 07933.

Surgident Neo-Plex Rubber Base Impression Material No. 56067 is a polysulfide pro-
duct utilized by dentists to make impressions for inlays, crowns, or bridges but is very useful in conservation. The rubber and catalyst are thoroughly mixed until the material loses its stickiness. It is then pressed into an open mold or impression where it cures in approximately three to four minutes. This substance replicates detail well and saves considerable time. It is, however, suitable only for small objects. This material is available from Warner Lambert Company, Lactona Products Division, 201 Tabor Road, Morris Plains, N. J. 07950.

Permamold Latex Molding Compound is for making permanent latex rubber molds and peels. It is applied by dipping or brushing on successive thin coats. It can be thinned with water and dries at room temperature. Permamold Latex is available from Polymer Chemical Company, 111 Barron Drive, Cincinnati, Ohio 45215.

Hysol Epoxy Laminating and Casting Compounds include a number of casting and laminating products to make rigid, permanent molds or casts. They consist of a base and a curing agent. Casting compounds TC9-4351 and TC9-4353 are particularly good. TC9-4351 is a general purpose aluminum-colored casting compound for molds and structurally sound casts that can be tooled. TC9-4353 is a steel black, wear-resistant, low viscosity metal-forming compound. The laminating compounds include TC8-6328, a white general purpose surface coat, or TC9-4341, a steel black wear-resistant surface coat, which are used in combination with a body coat such as TC8-6329. Hysol products and technical data are available from Hysol Division, the Dexter Corporation, 4151 Price Street, Olean, New York 14760.

Plaster of Paris, or ordinary gypsum plaster employed by builders, is adequate for making mother molds to support flexible molds and casts. It is often used to make the first cast from a newly made mold to clean the mold of any adhering debris. It is commonly available in drug stores and lumber yards.

Coecal is a fine grade casting plaster used by dentists. It is considerably more expensive than the builder's plaster, but it gives better detail. Coecal is available from dental supply houses or Coe Laboratories, Inc., 3737 West 127 Street, Alsip, Illinois 60658.

CASTING TECHNIQUES IN MARINE ARTIFACT CONSERVATION

The only published account of casting in marine conservation as a means of retrieving completely oxidized artifacts is that reported by Katsev and 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.

Any number of casting products can be used, but Katsev and Doorninck (1966: 140) recommended using Smooth-On FMC-100 for small narrow objects and Smooth-On FMC-300, or a combination of No. 100 and No. 300, for larger and more complex objects. FMC-300 apparently is no longer produced by the company.

After casting several molds sectioned with a lapidary saw, we noticed several disadvantages. The technique is limited to small en-
crustations and to uncomplicated shapes which require only a few cuts. A problem also arises in correctly aligning the two halves and the cardboard gasket. 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. The procedure, as shown in Figures 14 and 15, exemplify the technique as described. An encrustation with the mold of a spike sawn in half, the cardboard gasket, and the resulting Smooth-On FMC-200 rubber cast are shown.

At TARL we use Smooth-On FMC-100 and FMC-200. The light tan color of the No. 100 compound does not produce a natural appearing cast of a metal object, but is useful for making flexible molds and peels. Smooth-On FMC-200 is a black, medium viscosity, polysulfide compound that is more viscous and stronger than FMC-100. The carbon black filler in FMC-200 makes it less expensive per unit volume and has served the bulk of the casting needs of TARL. It is durable, replicates detail well, and produces a black, natural-looking cast.

If X-ray facilities are readily 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.
Figure 15.—Casting the mold of a spike cut with a lapidary saw (continued):

A. Pouring Smooth-on FMC 200 into the mold after securing the two halves of the mold with plaster and forming a clay sprue.
B. The rubber cast of the mold after separating the two halves of the mold.
C. Cutting the rubber flashing formed along the seams of the mold from the cast of the spike.
D. Two casts of the spike after removing the rubber flashing and one cast with flashing left on it.
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 en-
crustation. 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 as shown by Figures 16 and 17. The
X-ray of one such encrustation revealed an
oxidized circular iron washer. The encrusta-
tion was inscribed and cracked open with a
chisel. The corrosion residue was removed,
a sprue hole was made, and breaks in the en-
crustation filled with clay. The natural mold
was filled with Smooth-On FMC-200 to make
a cast of a wrought iron washer.

More complicated encrustations (Figs.
18, 19) with more than one mold can be
cast in the same way. The radiograph of the
encrustation (Fig. 18B) shows a cannon ball,
two planking spikes, and a spike shank, all
completely oxidized. The encrustation was in-
scribed around the center so that all the ob-
jects would be broken in half. In addition, the
distal end of one spike was opened. The ends
of the other two were already open. The cor-
rosion residue was removed with running
water and wire probes. The natural molds and
the encrustation were thoroughly dried in al-
cohol. The molds were filled with Smooth-On
200 and the broken irregular halves fitted
back without fear of misaligning or slipping
or the addition of a gasket. The irregular
breaks acted as "keys." After the rubber had
cured, the encrustation was chiseled off with

Figure 16.—Casting the mold of an iron washer:

A. Encrustation containing the mold,
B. Inscribing a line around the circumference of the encrustation with a pneumatic air scribe to
facilitate breaking it in half in a predetermined manner.
C. The two halves of the mold in the encrustation.
Figure 17.—Casting the mold of an iron washer (continued):

A. Repairing the breaks in the encrustation with clay.
B. Pouring Smooth-on FMC 200 through a clay sprue into the mold held together with plaster.
C. The two halves of the mold, a rubber cast with the flashing cut off and a cast with the flashing left on it.
the pneumatic chisel, as there was no need to used the encrustation mold again. If additional specimens or a rigid cast are required, a mold can be made from the rubber casts. The excess rubber and flashings are cut off with scissors or knives (Fig. 18B) and the superfluous encrustation removed. Figure 19C shows the rubber cast of the four specimens. A layer of oxide can be seen on the surface of the casts, imparting a natural appearance to them.

The examples of casting cited above are restricted to small encrustations with simple-shaped objects that were completely oxidized. Large encrustations or encrustations with artifacts that have areas of solid iron remaining cannot be cut with a lapidary saw because of their size and/or the presence of the solid iron. An example is provided by a large encrustation (Fig. 20) which was revealed by an X-ray to contain a badly oxidized rudder gudgeon. From the radiograph it could be de-

Figure 18.—Casting the molds of three spikes and a cannonball in an encrustation:

A. The encrustation.
B. X-ray of the encrustation showing the location and oxidized condition of each object.
C. Removing the encrustation with a pneumatic air scribe after filling the cleaned-out molds with Smooth-on FMX 200.
terminated that only the distal ends of the gudgeon straps and the pindle bearing contained a solid metal core. It was decided to break the strap ends of the encrustation close to the circular bearing. Through the open breaks the corrosion residue was flushed out with running water and wires. After drying the mold interior with alcohol, the oxidized sections were replaced with Smooth-On 200 and the broken pieces of the encrustation reattached with plaster. Once cured, the rubber connected the pieces together. The encasing encrustation then was removed with an air chisel. Wood fragments of the stern post and lead seam straps in situ on the gudgeon were removed, treated, and saved to be positioned on the finished cast. Once the casting was removed from the encrustation, clay was added to smooth out the corroded areas and irregularities (Fig. 20B). The gudgeon was correctly positioned, with the aid of the radiographs and work drawings and a Smooth-On 200 mold was made of the gudgeon (Fig. 20C). The rubber mold then was cast in Coecal (dental plaster) and painted black. The wood fragments and lead straps were placed on the cast in the same position they occupied on the original (Fig. 20D). The reconstructed gudgeon enables the archeologist to obtain measurements and an object that otherwise might not have been recovered.

Encrusted, complex artifacts present more difficult problems. One such small encrustation from the Platoro Collection contained a goat’s foot lever, a cocking device for a crossbow (Figs. 21, 22). The encrustation was broken apart before it was X-rayed and we found it was completely oxidized. The molds

Figure 19.—Casting the molds of three spikes and a cannonball in an encrustation (continued):

A. The rubber casts connected by rubber flashing after removal from the encrustation.
B. Cutting off the rubber flashings.
C. Completed casts of the three spikes and the cannonball.

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Figure 20.—Casting a badly oxidized wrought-iron gudgeon:

A. The encrustation containing the gudgeon.
B. The remains of the gudgeon with the midsections of the straps joined with Smooth-on FMC 200 and the oxidized areas filled with clay.
C. Making the Smooth-on FMC 200 mold of the gudgeon. The bottom half of the mold has been completed and is sitting in a plaster mother mold.
D. The plaster cast of the gudgeon painted black with the lead straps and wood fragments placed in position.

were cleaned out, cast with dental wax, and the parts fitted together (Fig. 22A). The wax cast had an irregular surface and several inaccuracies where the mold had not been thoroughly cleaned. Because of the inferior quality of the first cast it was decided that a more exact and more durable cast of this interesting specimen was needed. The pieces of the encrustation were carefully reclined and painstakingly glued together. Several pieces could not be joined, but all the distal ends were present, and in the few areas where parts of the mold were absent on one side, they were present on the other side. Clay was used to model in the gaps and the pieces were reinforced with plaster (Fig. 22B, C). All the molds and voids were filled with Smooth-On 200 and allowed to cure. The encrustation was broken off, the excess rubber cut off, and the different sections of the lever cut apart. A Smooth-On 200 mold was made of each rubber part after they were correctly positioned. Plaster casts were made from these molds, and the parts were sanded and filled with additional plaster to smooth out the casting irregularities. Following this, a second series of Smooth-On 200 molds were made of the plaster casts. The second set of molds were filled with Hysol TC9-4363. The individual Hysol casts were assembled into a working
Because of the complex nature of the goat's foot lever, its mold could not have been cut with a lapidary saw. Accurate casts of comparably complex specimens with thin sections can be made if the form of the objects and the extent of corrosion is first determined by radiographs. The mold then can be broken at key points, cleaned, tightly reassembled, and cast with much less difficulty and more accuracy.

Up to now, only casts made from the molds in small encrustations that could be easily X-rayed have been discussed. Nevertheless, 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. When some molds are found, it is possible to open a small area on one side, clean it out, and fill it with a flexible casting compound. In other cases, the encrustation along one side of the mold can be removed, leaving a two-dimensional mold. Two-dimensional molds can be filled with Smooth-On, or for speed, Neo-Plex Impression Material can be mixed up and firmly pressed in the mold. The latter sets up in three to four minutes, after which time it can be removed and the excess material cut off. A two-dimensional mold of a goat's foot lever hook (Fig. 23A) was cast with Neo-Plex. The excess rubber was cut away from one hook to more clearly show its form. The retrieval of this hook may not appear to be significant, but it is the only evidence of a goat's foot lever, or for that matter, a crossbow, at 41 KN 10.

Often, small diagnostic or decorative parts of otherwise substantial pieces may be completely oxidized. Details are preserved in the mold of the encrustation. A wrought iron, hooped barrel bombardetta cannon tube alongside two anchors was in fair condition except that the front sight and part of the muzzle were completely oxidized. The encrustation in the muzzle area was removed in several pieces, reassembled, and cast with Smooth-On 200. The rubber cast of the upper third of the muzzle and sight made it possible to reconstruct the muzzle of the gun (Fig. 23B).
Another example of the value of casting is demonstrated by the treatment of a fragmentary pair of wrought iron pincers. The pincers were so badly oxidized that they could be safely treated only by water diffusion in a sodium sesquicarbonate solution. Any other chemical or electrochemical treatment would have completely disfigured the specimen. Since the jaws of the pincers were completely oxidized, it is doubtful that they could have been removed successfully from the supporting encrustation which was left on the specimen. A Smooth-On mold was made of the pincers and was cast in plaster. The partially encrusted pincers, the Smooth-On mold in a plaster mother mold, a cast from the mold, and a cast of the pincers, with the plaster cut off so only the pincers remain, are depicted in Figure 23C. Similarly, a two-dimensional Smooth-On 200 mold of a “sickle-shaped” artifact was made after it was determined that the sharp cutting edge was completely oxidized and would crumble if removed from the encrustation. A plaster cast was made from the mold. Contrast the treated artifact with the cast (Fig. 23D).
All the casting examples discussed above involved iron artifacts. Casting techniques also have been extremely useful in recovering stamps from corroded silver specimens. From these mid-16th century Spanish shipwrecks have come 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 en-

Figure 23.—Miscellaneous molds and casts:

A. Mold of a goat's foot lever hook (center) with a Neo-Plex cast of the mold (left) and a Neo-Plex cast with the excess rubber cut off (right).
B. The muzzle of a hooped barrel gun showing the badly oxidized condition (left). A Smooth-on FMC 200 cast of the gun sight and the front of the muzzle (center). Reconstruction drawing of the muzzle made possible by the cast.
C. Smooth-on FMC 200 mold in a plaster mother mold (top) made of a badly oxidized pair of pincers (bottom left). Coarse plaster cast made from the mold (bottom center) and a plaster cast with the excess plaster cut away (bottom right).
D. Smooth-on FMC 200 mold in a plaster mother mold of a "sickle-shaped" object (left). Plaster cast of the object. The original object after treatment. Note the irregular edge of the treated specimen.
crusted 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. The results of this casting procedure are shown in Figure 24. Depicted are an encrusted silver disc (Fig. 24A), the disc after removal from the encrustation, along with the part of the encrustation with the silver stamps, the latex peel of the encrustation’s interior surface and the plaster cast of the stamps (Fig. 24B), and the line drawing of the two stamps (Fig. 24C).

This same procedure has been used on silver disc stamps and coin impressions found within the large encrustations, as well as singularly encrusted specimens. Alternatively, the Neo-Plex rubber base impression material can be used. Success depends on careful observation while breaking down the encrustation and the deliberate attempt to preserve the en-

Figure 24.—Cast and molds of silver stamp:
A. Encrusted silver disc.
B. Part of the interior surface of the encrustation containing the impressions of the silver stamps (upper left), corroded silver disc (lower left), and the latex peel (upper right) made from the interior surface of the encrustation and the plaster of Paris cast made from the peel with the stamps lined with pencil (lower left).
C. Drawing made of the two stamps recovered by casting.
crustation around any silver artifact. We have 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 archeologists 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.
VII

APPLICATION OF CONSERVATION AS AN ARCHEOLOGICAL TECHNIQUE

THE ROLE OF THE CONSERVATOR

The relationship of conservation to marine archeology has been stressed here as both intimate and essential. Throughout this paper it has been emphasized that conservation can and should be more than preserving artifacts. When the conservator is trained as an archeologist as well, he is qualified, indeed obligated, to contribute basic archeological data. The benefits of this complementary approach cannot be overemphasized.

Curtiss Peterson, conservator of the Research and Preservation Laboratory in Florida, has defined this role:

The potential of archeological conservation is finite. Its principal function is to salvage such data as are available in an object or set of objects by salvaging the objects themselves, by documenting a history of changes that have taken place within the objects and why these changes have happened. Conservation provides a name, an analysis: what it is, how it was made, what has happened to it; and it provides a face: an object can be stabilized in its present condition so it will deteriorate no further (a strange state at best) but will bear the signs of its experience. It can be restored; certain changes can be undone, missing pieces added and the item can, in many instances, be made to appear as it may have once appeared when in use. And of course there is the reconstruction, the manufacturing of an object to match a case or impression of what once was but is no more. (1974: 64)

That the benefits of archeological conservation are finite and that the standard conservation procedures outlined above are valid contributions is agreed, but the statement ignores the potential of other types of retrievable archeological data from these contexts. Peterson fails to point out that the conservator is in a position to document associations and make pertinent observations as he removes objects from each encrustation. In conservation, the documentation and excavation controls initiated in the field must be continued in the laboratory. Even with adequate documentation, excavation is a destructive process that destroys the cultural context in the site and within each encrustation. Shortcomings in either field documentation or in laboratory conservation can diminish the potential mutual contribution.

A prime concern of archeology is maximum retrieval of cultural data to solve problems; therefore, conservators dealing with encrusted marine archeological material have equal responsibilities that have to be met. When material is recovered by uncontrolled salvage operations, it represents a collection of artifacts with poor cultural context. Although close documentation of associations within encrustations is less meaningful in these cases, it still can be valuable. For example, the Platoro Collection lacks field documentation and good cultural context, but the conservation laboratory was able to provide some data on associations. The bulk of the information, however, is in the artifacts themselves (Olds, manuscript). The material from 41 KN 10 was recovered in a controlled ar-
archaeological excavation with each encrustation, all structural parts, and ballast distribution plotted on a site map. Accordingly, the details on the association of the artifacts within each encrustation will significantly supplement the field data.

As previously stated, the underlying premise when we begin to process encrustations from a shipwreck is that the overall associations of the artifacts within each encrustation and among encrustations is potentially culturally significant and is capable of contributing to the study of cultural behavior. In order to make these contributions, conservation begins during field excavation.

FIELD RECOMMENDATIONS

The protective encrustation covering the artifacts should not be removed in the field. As discussed earlier, without proper treatment and storage the specimens will corrode, warp, crack, fall apart, and even completely deteriorate. Also, considerable data represented by molds and impressions in the encrustation can easily be lost; artifacts can be damaged and meaningful association can be overlooked.

Divers working on one of the Spanish sites off the coast of Texas often complained that all they did was plot, bring up, and attach numbered tags to encrustations; they seldom saw the actual artifacts. One can sympathize with the diver, but the field is not the place to tackle the complex problems presented by encrusted shipwreck material. Field recovery involves one set of archeological techniques and requirements; conservation involves another set. The data from the two sets come together to produce an archeological reconstruction in the best tradition of controlled, scientific archeology.

Once raised, the encrusted material should be kept wet and sent to the conservation laboratory as soon as possible. The conservation laboratory personnel will record the context of each artifact within each encrustation and then will treat each artifact. In a conservation laboratory precise documentation is possible in the form of photographic and radiographic records. These basic archeological records are turned over to the investigating archeologist. From these data it may be possible to reconstruct remains of the ship and to determine the different activity areas, the functional relationships of the parts of the ship and the way the ship broke up.

As a conservator who has worked with considerable shipwreck material, my recommendations concerning procedures in the field are simple:

1) Make arrangements for conservation before beginning excavation. If conservation cannot be assured, excavation should not be undertaken.

2) Accurately record the precise position and orientation of every object—ship timbers, encrustations, individual artifacts—and number each item, so that there will be no confusion as to how each object lay and what surface was resting on the seabed, after the material has been delivered to the laboratory for processing.

3) Do not remove the encrustation from any of the material; it provides a protective, corrosion-preventive layer around the material and preserves associations. Also, considerable data can exist in the form of impressions and molds in the encrustation, data easily lost or overlooked in the field.

4) Keep all material wet at all times, either in sea water or, preferably, in water with the pH adjusted to a reading of 10 to 12 with sodium hydroxide.
The soundness of the advice given above is easily validated by the examples of the processing of just two encrustations out of the many processed by our laboratory. These examples illustrate the documentation procedures and requirements, and the distributional data that enables the archeologist to reconstruct the cultural system of which this shipwreck is a subsystem.

Encrustation No. 5

This small but very complex and interesting encrustation (Fig. 25A) was X-rayed and the individual radiograph plates assembled. A tracing was made of the plates, drawing in every detectable object. The procedure then was to remove the encrustation, revealing and extracting the artifacts with a small pneumatic chisel while using the radiographs and the tracing as a guide (Fig. 25B). Some of the artifacts could not be seen on the X-rays, but they could be accurately drawn on the tracing of the radiographs by using the detectable artifacts as reference points. As each artifact was removed, it was given a unique number which was recorded on the work sheet and on its specimen record card. Photographs were taken of the encrustation at successive stages of mechanical cleaning (Fig. 26A-C). A scaled drawing of each object, even those completely oxidized, was made on the specimen card and on the work plan. Each specimen capable of being cleaned was processed and reassembled in a reconstruction (Fig. 27B). The inventory of recovered artifacts from this encrustation included copper and silver coins, a silver disc, a brass pin, a copper-covered iron key, an auger bit, several barrel straps, and a number of iron spikes. The most interesting specimen in the encrustation was a polished iron pyrite half-sphere, which may have been an aboriginal Mesoamerican mirror.

The final scaled drawing (Fig. 27A) of all the specimens, including all the unrecoverable artifacts, were drafted from the work sheet. This drawing, along with the record cards, photographs, work sheet, and artifacts, constitute the data concerning this encrustation that are given to the marine archeologist to be incorporated into his records.

Encrustation No. 81

The associations in the large encrustations have to be recorded differently because it is impossible to obtain usable radiographs of encrustations such as No. 81 which are two to three feet thick and contain numerous ballast stones. The only alternative is to break off the encrustation in large pieces and X-ray them individually. Encrustation No. 81 (Fig. 28) contained a large wrought iron anchor with one arm broken off, two hooped barrel breechblocks, and 114 other specimens. It exemplifies the procedure adopted to process large encrustations. Vertical, side, and oblique photographs were taken before the processing began in order to show the horizontal and vertical relationships within the encrustation.

As the pieces of encrustation were broken off, the placement of each was drawn directly onto the black and white photographs and then placed onto a measured drawing of the anchor. Each piece of the encrustation was individually X-rayed and a tracing made of its outline and the detectable objects. The individual pieces then were processed in the manner described for Encrustation No. 5. The photographs, tracings, and work notes were used to draw scaled drawings of the associations which were used to make the final drawing of the overall associations within the encrustation (Fig. 29).

Some interesting relationships were still preserved in Encrustation No. 81 after more than 420 years on the sea floor. The remains of four white oak barrel staves with iron barrel hoop fragments still circling over and under the staves were lying across the arm of the anchor. On the interior surfaces of the staves and in the area around the staves were a large number of silver coins, a silver disc, two small pieces of silver, an English pewter porringer, potsherds, a brass weight cup, brass pins, and a number of miscellaneous specimens includ-
Figure 25.—Processing encrustation No. 5:

A. Encrustation No. 5.
B. Removing the encrustation from No. 5 with a pneumatic chisel and the aid of assembled X-ray plates.
ing the exoskeleton of a cockroach, *Periplaneta americana*, and an articulated pig's foot. It seems probable that the barrel contained most of these specimens and broke up on the arm of the anchor. Along the bottom edge of the anchor shank were a number of small wrought iron cannon balls, lead-covered cannon balls with square wrought iron cores, and a stone cannon ball. At the anchor ring were two large hooped barrel breechblocks.

Figure 26.—Processing encrustation No. 5 (continued): A–C. Three successive stages of encrustation removal and artifact extraction.
SIGNIFICANCE OF DISTRIBUTIONAL STUDIES

It is known from historic documents (Cas- taneda 1936: 140-156) that the 1554 Spanish fleet was carrying silver for the coffers of King Charles of Spain, cargo, and a large number of passengers—conquistadores, settlers, merchants and their families—with their possessions and worldly wealth back to Spain from Mexico when they wrecked on the beaches of Padre Island. An analysis of the ship’s material in the wreck, the oldest documented shipwreck yet located in North America, can provide facts about the material culture of the mid-16th century, what types of items were being shipped from Mexico to Spain, the kinds of food carried on board, and the kinds of tools used. Even events such as the introduction and distribution of Old World insects and vermin to the New World and vice versa may be documented.

If there is good distributional documentation, it is possible that individual chests, boxes, and barrels with their contents can be discerned, then more specific cultural problems can be considered. The example in Encrustation No. 81 is just one of several chests or barrels at 41 KN 10 with discrete clustering of artifacts. These associations indicate the kind and range of goods being taken to Spain by the passengers and the crown-controlled trade.

From the number of coins and amount of silver in these containers, it is possible to make assumptions about the amount of wealth accumulated by individuals and carried back to Spain. The range of assayers on the coins indicate how long coins remained in circulation. The number of coin die varieties of each assayer provides information about mint technology and the number of coins produced by a given die. The mining, tax, and ownership stamps on the silver discs provide information about operation of the mines, and the taxation and assaying of precious metals and the king’s share of the silver. Analysis of the silver enables one to talk about mining technology.

The presence of English pewter utensils, Spanish majolica, and Cologne stoneware flagons are indicative of status wares brought to Mexico and being taken back to Spain by the higher social classes of the period. The origin point of the wares and the extent of their distribution can be studied.

The kind and number of ship artillery and hand arms are indicative of the armament policy and probable conditions prevailing in Europe. For example, no cast iron guns, only wrought iron guns were found on the ships of this fleet; and wrought iron guns were practically obsolete in Europe by 1554. Their presence at that time suggests that the older, obsolete artillery was being sent to the New World where there was less need of the more modern cast iron and bronze muzzle-loading guns and cannons.

Other matters to be considered from Site 41 KN 10 are the presence of wrought iron shot and the absence of cast iron shot, the covariation of brass pins with coins in several of the encrustations, the weight system represented by the brass weight cup, and the several aboriginal objects, possible souvenirs, such as the polished iron pyrite half-sphere in Encrustation No. 5.

All these considerations are just a few of many cultural and individual behavioral problems that can be derived from an analysis of the material from just the two examples, Encrustations No. 5 and No. 81, discussed earlier. Some of the data can be obtained by studying the material without regard to its distribution, but more specific problems can be considered if all the specimens are contrasted with each other and the discrete clusterings analyzed. Distributional and associational data are of immeasurable value when the objective is to study the full range of human behavior and cultural systems. With careful analysis and interpretations of the various subsystems represented in the ship, it is possible to arrive at a partial reconstruction of the culture of which the subsystems are a part.
CONSERVATION CONSIDERATIONS

Clearly, detailed information can be lost if an attempt is made to process marine encrustation in the field. Many of the specimens are completely converted to corrosion compounds. Although these specimens are not ever recoverable in the lab, their proveniences can be recorded, measurements taken in situ, and locations shown in all drawings. Their presence is just as important as the artifacts which survive intact. Additional information is recovered by casting the natural molds and impressions from obliterated silver stamps, letters on the blade of a sword, and other disintegrated objects. Occasionally, the only possible documentation is in the form of in situ photographs and measurements from which reconstructions can be made. At times, recorded observations have to suffice.

Much more is contributed by the conservation laboratory than simply individual objects which have been stabilized. The conservation laboratory documents the associations, documents and photographs and artifacts, makes scaled drawings, makes preliminary identifications, arranges or conducts various analytical tests, has wood samples, bones, and other faunal material identified, and makes casts of artifacts in addition to cleaning and stabilizing the material.

The role of the conservation laboratory is usually considered to be completed after the services are performed. The conservation data are ready to be integrated with the field and archival data. It remains, however, for a trained conservator, who knows what the tell-tale signs of corrosion or deterioration are, to periodically check the processed specimens to insure their continued stability. Any artifact evidencing signs of deterioration must be reprocessed. No conservation process can be assured to last indefinitely and depending on storage or display environment, some will have to be retreated at some time in the future. The objective of any conservation technique is to delay this reprocessing as long as possible and to make any necessary retreatment brief.

Most archeological specimens can be successfully treated by one of the methods previously described. At the present state of knowledge, electrolytic reduction is the most versatile tool available to the conservator for cleaning metals from any environment, especially a marine environment. In comparison to galvanic cleaning, chemical treatments, and water diffusion, it is the most economical and thorough. The good results reported from annealing iron objects in an inert atmosphere are encouraging and warrant further investigation. The initial expense, however, for the kiln or furnace is prohibitive for many conservation laboratories.

The expenses involved in conservation forces some hard decisions. With the continuing increases in the cost of utilities, equipment, chemicals, and labor, it is not economically feasible to treat every artifact from a site. Large objects pose special problems because of the equipment required to process them and the great expense inevitably involved. The decision as to what to treat or not to treat must be worked out with the investigating archeologist. Factors such as budget, facilities, and time are important considerations. In lieu of total conservation, photographs and scaled drawings will have to suffice for the more common specimens and even for some of the less ordinary pieces.

As one learns the various basic conservation techniques, reads the textbook descriptions, and processes artifacts, it becomes necessary to improvise continuously. Occasionally the most appropriate equipment or facilities are not available and it is up to the conservator to manipulate what is at hand to fulfill the necessary requirements. In the process, the skills of a conservator, as normally defined, must also include the qualities of an administrator, an electrician, a chemist, a carpenter, a mechanic, a welder, and particularly, an archeologist. It is this last role, that of the archeologist, that has much too long been neglected or disregarded. The archeologist brings to the field of conservation an outlook and an appreciation of the archeological record and material culture that may not be considered by the art historian or science-trained conservator. In marine archeology it is easier to train an archeologist to be a diver than to train a diver to be an archeologist. The same reason-
Figure 27.—Processing encrustation No. 5 (continued):

A. Scaled drawing of the overall associations in encrustation No. 5 made from laboratory notes, photographs, and drawings.
B. Recreation of artifact provenience with the treated specimens.
Figure 28 (above)—Encrustation No. 81.

Figure 29 (left)—Drawing of the overall associations in encrustation No. 81.
ing may be applicable to the conservation of archeological material.

Most conservation laboratories are not archeologically oriented, i.e., concerned with processing material in all of its exotic and mundane forms with a primary objective of providing basic archeological data. It has been our practice to consider conservation as an archeological technique and to interpret the data with an anthropological viewpoint. The results and recovered data have been significant. Hopefully, more conservation laboratories will be established taking into account the potential of an anthropological perspective and taking an active role in recovering archeological data that can be used to reconstruct past human behavior.

INTERACTION OF CONSERVATION AND ARCHEOLOGY

Archeology and conservation have a symbiotic relationship. Conservation provides archeology with archeological data, and archeology contributes material to be processed which also can be used for research and experimentation in conservation. Treating of archeological specimens makes it possible for the conservation laboratory to contribute valuable information to the technology of conservation. In addition to utilizing established preservation techniques, new procedures can be tried on unimportant or numerous objects and the more successful ones can then be applied to museum and art collections. The detailed records on treatment maintained on specimen record cards make it possible to evaluate the treatment of each object over a long period of time. Much of the preservation data presented earlier on metals was developed while processing archeological material by different procedures and then evaluating the results immediately after treatment, and after a lapse of several years. Through these procedures more realistic evaluations could be made and more insights obtained.

In addition to contributing data to archeology and conservation, the conservation laboratory affords an opportunity for first-hand training of students in both fields. Part and full-time employment opportunities often are available; courses on conservation can be taught in the laboratory and even incorporated into the academic training program of archeologists. In the process, considerable historical, archeological, and ethnographic material will be saved and available for research and study by students in the future.

Nevertheless, conservation cannot be considered an independent discipline; there must be continuous interaction between it and archeology. The operations of the conservation laboratory should be included in the research design and the budgeting of archeological excavation projects. Scheduling also is important. The conservation laboratory has to have time to process the material to coincide with the report schedule. For example, our laboratory is set up to process large volumes of material, but it requires two to three years to process what the marine archeologist recovers in a three or four-month excavation season. From the time the processing begins, the laboratory has a continuous input, providing data to be incorporated in the report. There is a continuing interplay of ideas between the conservator and the archeologist throughout the processing, and the final report must await final conservation.

From the earlier presentations it is obvious that excavation of marine shipwrecks is not good archeology unless the recovered material is processed by a conservation laboratory whose trained personnel have an archeological perspective, a familiarity with material culture, and awareness of the problems and complexities of marine archeological conservation. Archeological conservation should be considered an indispensable archeological technique where marine archeology is concerned.

In more general terms, conservation should be carried out in other kinds of archeological projects as well. Proper conservation should be anticipated and planned at any site where metal artifacts are found and in any site in
arid or specialized environments where perishable materials are recovered. The material from most terrestrial sites in the United States do not require conservation, thus not necessitating a close association with a conservation laboratory. In some instances there may be exceptional finds that cannot be anticipated, and the services of a conservation laboratory can suddenly be required.

It is obvious from the data presented that the conservation laboratory can play a major role in archeology. Cooperation between the Texas Antiquities Committee’s underwater archeology program and the Texas Archeological Research Laboratory of The University of Texas at Austin has been highly productive of archeological data and conservation technology. When a similar relationship is established between other archeological projects and conservation laboratories, increased productivity from archeology, especially marine archeology, can be expected.
APPENDIX I

CHLORIDE DETERMINATION BY THE MERCURIC NITRATE METHOD

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

Procedure

1. Take a 20 ml. sample of the electrolyte from an artifact in electrolysis.
2. Put the sample in a 250 ml. beaker.
3. Place the beaker on the magnetic stirrer and put a stirring bar in the beaker.
4. Adjust stirrer until the liquid is in a steady swirl.
5. Add four drops of methyl orange indicator.
6. Add the sulfuric acid from the buret drop by drop until the methyl orange end point is reached. The color changes from orange to a pink. The amount of sulfuric acid does not need to be measured. Its purpose is to acidify the sample.
7. Add five drops of diphenylcarbazone-bromphenol indicator.
8. Titrate .02N mercuric nitrate drop by drop from the automatic buret until the sample reaches a violet end point. The color changes gradually from lavender to a violet. Toward the end point each drop will show a flash of color. Continue until no color flash is observed in the solution and it is an even violet. Additional drops make the color more intense, but do not change it.
9. Note the amount of mercuric nitrate titrated to reach the end point.
10. The concentration of chloride or sodium chloride in parts per million is calculated by the following formulas in which:

\[
T = \text{amount of mercuric nitrate titrated.}
\]
\[
N = \text{normality of the mercuric nitrate.}
\]
In order to facilitate the calculations, a table, such as the example given below, can be established using the formulas shown above, and save much time in the future. Example:

| .1 | 5.8 ppm NaCl | 3.5 ppm Cl⁻ |
| .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 | 335.0 |
| 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 measured are 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**

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.

Two notes should be added in regard to the chloride testing procedure. First, the diphenylcarbazone-bromophenol end point is to some degree subjective. For this reason, more reliable and consistent results are obtained if only one person runs the tests. Second, some artifacts coming from a chromate storage solution have a chemical reaction with the electrolyte that changes the color of the electrolyte to a light green for the first couple of baths. When this occurs the chloride test cannot be run because of reaction with chromate ions. The problem is usually remedied by the second or third electrolyte change.

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:

**Methyl Orange Indicator**

1 gram of methyl orange to 1 liter of distilled or deionized water.

**18N Sulfuric Acid, H₂SO₄**

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. Excessive heat is generated. Let cool.

**.02N Mercuric Nitrate Solution, Hg(NO₃)₂·H₂O**

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

**Diphenylcarbazone-bromophenol blue indicator**

Dissolve .6 grams of reagent grade crystalline diphenylcarbazone and .05 grams of crystalline bromophenol blue in 100 milliliters of 95% ethanol.

**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 600 ppm NaCl, dilute a second time for 250 ppm, etc.
APPENDIX II

CHROMATE TEST OF STORAGE SOLUTION

When metals are stored in a chromate solution, free hexavalent chrome must be available. During prolonged storage some of the chromate is converted to dichromate; therefore, the solution needs to be checked periodically. The following test, adapted from "Chromate Test Procedure," made available by Betz Laboratories, Inc., Trevose, Pennsylvania 19047, provides a means of determining the amount of chrome, as CrO₄²⁻, in a range of 100 to 1500 ppm (Anonymous 1967).

Equipment

1. 25 ml. automatic buret,
2. 250 ml. beakers.
3. 50 ml. graduated cylinder.
5. Teflon-coated stirring bars.
6. Brass measuring dipper, supplied by Betz with starfamic indicator and iodide crystals.
7. Plastic measuring dipper, supplied by Betz with sulfamic acid.

Chemicals

1. .1N sodium thiosulfate.
2. Iodide crystals.
3. Starfamic indicator.
4. Sulfamic acid.

Procedure

1. Take 50 ml. of the storage solution and place in a 250 ml. beaker.
2. Place the beaker on the magnetic stirrer and put a stirring bar in the beaker.
3. Adjust stirrer until the liquid is in a steady swirl.
4. Use the plastic dipper to add two dipperfuls (ca. 2 grams) of dry sulfamic acid.
5. Wait for two minutes to eliminate any nitrite interference.
6. Use the brass dipper to add two dipperfuls (ca. ½ gram) of iodide crystals.
7. Wait for two minutes.
8. Titrate the sample with .1N sodium thiosulfate until the yellow-brown color of iodine has almost disappeared.
9. Add one brass dipperful (ca. ¾ gram) of dry starfamic indicator. All the indicator may not dissolve and may create a slight haze in the sample.
10. Continue to titrate with .1N sodium thiosulfate until the blue color which developed upon the addition of the indicator first disappears. Disregard any reappearance of the blue color. Record the ml. of the sodium thiosulfate used.
11. Using a 50 ml. sample, the chromate in parts per million as CrO₄²⁻ is equal to the ml. of .1N sodium thiosulfate required multiplied by 77.4. For example: T x 77.4 = ppm CrO₄²⁻
    .1 ml. x 77.4 = 7.74 ppm CrO₄²⁻
    1.0 = 774.0
APPENDIX III

ELECTROCHEMICAL REACTIONS THAT OCCUR AT AN IRON CATHODE AND ANODE IN AN ELECTROLYTIC CELL

Seven variables (power supply, current density, anode material, terminal wires and clips, electrolyte, chloride-monitoring, and setup alternatives) have been considered in the text. Each of the variables discussed plays a direct role in the results achieved in electrolytic cleaning. Summarized here are the ionic reactions that occur in the operating electrolytic cell.

The objective of electrolytic cleaning is to reverse the oxidation reactions initiated by electrochemical corrosion by taking advantage of the reduction reactions that occur at the cathode when connected to an external D.C. power supply. When the current is turned on the positively charged ions are attracted to the cathode and reduced, while the negatively charged ions are attracted to the anode and oxidized. It is often difficult, however, to predict what products or reactions will result when a direct current is passed through an aqueous electrolyte containing the ions of the electrolyte and the water molecules. Each of these may participate in various chemical reactions along with the reactions of the anode and cathode.

Ion Sources

The ions present in a dilute aqueous alkaline electrolyte (NaOH or Na₂CO₃) are derived from the water, alkali, cathode, and anode. From the water in the solution, hydrogen ions (H⁺), oxygen ions (O⁻) and hydroxyl ions (OH⁻) are obtained through electrolysis. At the cathode, water is reduced with the production of diatomic gaseous hydrogen and hydroxyl ions which make the surrounding electrolyte more alkaline.

\[ 2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \]

or

\[ 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \uparrow \]

At the anode, water is oxidized by the loss of electrons and produces diatomic gaseous oxygen molecule and hydrogen ions which make the electrolyte in the vicinity more acidic.

\[ 2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2 \uparrow + 4\text{H}^+ \]

The overall reaction is:

\[ 6\text{H}_2\text{O} \xrightarrow{\text{D.C.}} 2\text{H}_2 \uparrow + \text{O}_2 \uparrow + 4\text{H}^+ + 4\text{OH}^- \]

Sodium ions (Na⁺), hydroxyl ions (OH⁻), and carbonate ions (CO₃⁻) are derived from the electrolytes. What is significant, however, are the reactions resulting from the electrolysis of water. For clarity the sodium, hydroxyl, and carbonate ion reactions are not considered.

Along with the ions resulting from the electrolysis of water, the ions from the iron cathode and anode are important. Ferrous ions (Fe²⁺) are derived from the anode. The corrosion products of the iron cathode supplies additional ferrous and ferric ions (Fe²⁺, Fe³⁺), oxygen ions (O⁻), chloride ions (Cl⁻), and
sulfide ions \((S^{2-})\) from the ferrous and ferric oxides \((Fe(OH)_2, Fe_2O_3, Fe_3O_4)\), the ferrous and ferric chlorides \((FeCl_2, FeCl_3)\) and ferrous sulfides \((FeS)\). Carbonate ions \((CO_3^{2-})\) from ferric carbonate \((FeCO_3)\) and carbonate ions and calcium ions \((Ca^{2+})\) from the calcium carbonate \((CaCO_3)\) are not discussed. The ions whose reactions in the electrolytic cell of the most interests are:

1. \(H^+\)
2. \(O^-\)
3. \(Fe^{2+}\)
4. \(Fe^{3+}\)
5. \(S^{2-}\)
6. \(Cl^-\)

**Ferrous and Ferric Ions**

In an aqueous solution, hydrogen ions \((H^+)\) are attracted to the cathode, where they are discharged by gaining an electron and become highly reactive absorbed atomic hydrogen. The absorbed atomic hydrogen combines with the insoluble oxides or hydroxides to form water and reduced iron.

\[
FeO + 2H_{(ads)} \rightarrow Fe^0 + H_2O
\]

It is impossible to identify all the reduced states, but some are stable iron metal. If no iron oxides are present to be reduced the atomic hydrogen combines to form diatomic gaseous hydrogen which is evolved off the cathode surface.

When ferrous ions are present, the basic reaction is:

\[
Fe^{2+} - 2e \rightarrow Fe^0
\]

How the \(Fe^{2+}\) exists, oxides, hydroxides, or chlorides, makes no difference. What is important is that at a very low current density in an aqueous electrolyte the reduction potential of \(Fe^{2+}\), where no \(H_2\) is formed, can be established so that the positively charged ferrous ions gain electrons flowing to the cathodes from the external regulated D.C. power supply and are converted to a metallic state in a straight reduction reaction. In this process the ferrous compounds are reduced, reclaiming the metal at the interface. Above the \(H_2\) discharge potential the reduction of the ferrous ions is less efficient because it occurs along with the reduction and evolution of hydrogen.

In an aqueous electrolyte it is not possible to reduce the ferric ions. Therefore, the reduction of ferric oxide \((Fe_2O_3)\), hydrated ferric oxide \((Fe(OH)_3)\), and magnetite \((Fe_3O_4)\) are limited by thermodynamic considerations. The hydrogen may combine with them to form water and hydroxyls, but the ferric ions are not reduced to a metallic state. These corrosion products are removed by the evolution of hydrogen. It is possible, however, that the FeO portion of magnetite, which probably exists as FeO- \(Fe_2O_3\) can be reduced and will consolidate this corrosion product in situ.

At the mild steel anode some of the iron can be oxidized and go into solution as ferrous ions. The bulk of the iron going into solution results from the oxidizing reaction of hypochlorite \((ClO^-)\), chlorite \((ClO_2^-)\) or hypochlorous acid \((HClO)\) on the anode. In a salt-free solution very little iron dissolution of the anode occurs. The ferrous ions from the anode are attracted to the negatively charged cathode where they are reduced and may plate on the cathode where they possibly provide additional stability to the reduced metal oxides—anode reaction \(Fe^0 - 2e \rightarrow Fe^{2+}\), cathode reaction \(Fe^{2+} + 2e \rightarrow Fe\). Instead of being attracted to the cathode, the ferrous ions may combine with the negatively charged hydroxyl ions to form ferrous hydroxide which coats the anode or sinks to the bottom of the vat.

\[
Fe^0 + 2OH^- - 2e \rightarrow Fe(OH)_2
\]

**Oxygen Ions**

Oxygen ions \((O^{2-})\) resulting from electrolysis of water, water of hydration, by-products of the reduction of metal oxides by hydrogen and of the hydroxides discharged at the anode, are attracted to the anode. At this point they discharge by giving up two electrons forming oxygen atoms which combine with other oxygen atoms and evolve from the anode as molecules of gaseous oxygen.

\[
2O^{2-} - 4e \rightarrow O_2 \uparrow
\]

The evolution of oxygen maintains the anode in a passive domain as long as the pH remains around 9. If the anode becomes acidic by the
accumulation of hydrogen from the oxygen evolution reaction, \( 2\text{OH}^- \rightarrow 4e^- + \text{O}_2 \uparrow + 2\text{H}^+ \), anodic dissolution occurs. The presence of Cl\(^-\) ions accelerate the dissolution.

Sulfide Ions

A common corrosion product of iron from a sea environment is ferrous sulfide (FeS). In electrolysis the sulfide breaks its bond with the iron and accumulates in the solution as sulfide which is oxidized to sulfate at the anode.

\[
\text{FeS} + 2e^- \rightarrow \text{Fe}^{0} + \text{S}^{2-} \quad \text{(cathode reaction)}
\]
\[
\text{S}^{2-} + 4\text{O}_2 \rightarrow \text{SO}_4^{2-} + 4\text{O}^- \quad \text{(simplified an. reac.)}
\]

The ferrous ions are reduced to a metallic state while the sulfide ions go through several oxidation steps before forming a sulfate.

Chloride Ions

In the corrosion layers of the cathode are the iron salts—ferrous chloride (FeCl\(_2\)), ferric chloride, anhydrous (FeCl\(_3\)) and ferric chloride, hydrated (FeCl\(_3\) \cdot x\text{H}_2\text{O})—that results from prolonged immersion in salt water. The negatively charged soluble chloride ions go into solution and are attracted to the anode where they may discharge to form chlorine. This atomic chlorine combines with other chlorine atoms to form molecular chlorine which builds up in the solution or combines with the corrosion products from the anode. The probability of the evolution of chlorine gas is very slight, if possible at all, in an alkaline electrolyte. The water of hydration in the hydrated iron chloride can be electrolyzed into \( \text{H}^+ \) and \( \text{OH}^- \) ions by electrolysis. The positively charged ferrous ions can be reduced as explained earlier. The ferric compounds are sloughed off by the evolution of hydrogen.

Oxygen derivatives of chlorine, such as hypochlorite (ClO\(^-\)), chlorite (ClO\(_2\)^-), and hypochlorous acid (HClO), have strong oxidizing properties and can be obtained by the electrolytic reduction of alkaline solutions of chloride (Pourbaix 1966: 599-603). The formation of these are responsible for the heavy attack on and the dissolution of mild steel anodes. The discharge of oxygen at the anode is accompanied by the formation of \( \text{H}^+ \) which tends to create small areas of acidity at the anode. Since hypochlorite is unstable in acid conditions, it decomposes to chlorites, converts to sodium chloride, or it forms hypochlorous acid which attacks the anode to form a mixture of ferrous chloride and ferrous hydroxide. The formation of the acidic areas causes the attack by hypochlorite; otherwise, in the presence of sufficient alkali, the hypochlorites form NaClO\(_3\). If alkaline conditions are maintained at the anode, the NaClO\(_3\) will not attack the anode. This attack can be prevented by circulating the electrolyte, either by air-lancing or by using a small circulating pump to maintain the alkalinity at the anode.
APPENDIX IV

ELECTRODE POTENTIAL MEASUREMENTS

In Chapter IV electrode measurements were described as a valuable conservation tool to control the reduction of metal corrosion species back to a metallic state. The required equipment and procedure are described below:

**Equipment**

1. Electrolytic cell with anode, cathode, electrolyte, and regulated D.C. power supply.
2. Silver/silver chloride (Ag/AgCl) reference electrode.
3. High impedance (10 mgh.) voltmeter, preferably with a digital readout capable of registering three decimal places.
4. Luggin capillary probe with a .3 mm. to .5 mm. diameter. The smaller diameter is recommended.
5. Open top separatory funnel with teflon stopcock.
6. Rubber stopper with center hole the same diameter as the top of the reference electrode (the stopper fits into the funnel and the reference electrode fits into the center hole of the stopper).
7. Surgical tubing to connect separatory funnel to the Luggin probe.
8. Support stand and clamps.

**Procedure for Measuring Cathode Potentials**

The equipment as set up as shown in Figure 30 A-B represents the minimum apparatus for measuring electrode potentials. The procedure is as follows:

1. Affix the separatory funnel to the support stand, elevated above the level of the electrolyte in the working cell.
2. Connect the surgical tubing to the bottom of the funnel and to the Luggin probe to form a salt bridge.
3. Fill the funnel with the same electrolyte solution as in the working cell.
4. Place the reference electrode in the center of the rubber stopper and place in the top of the separatory funnel.
5. Attach the reference electrode lead to the negative terminal of the voltmeter.
6. Attach the positive terminal of the voltmeter to the negative lead-in wire of the D.C. power supply to measure cathode potentials.
7. Open the stopcock of the salt bridge slightly to allow a minimum flow of electrolyte through the tip of the Luggin probe. Make sure that all the air bubbles are out of the hose. Actually, no measurable flow is required if there are no bubbles present, but a minimum flow is allowed to insure that the electrolyte from the salt bridge maintains an electrical contact with the cathode and does not back off from the tip of the probe.
8. Record the electrode potential voltage on the voltmeter at each spot on the cathode where the probe is placed. These observed volt readings are in ref-
Figure 30.—Measuring electrode potentials in an electrolytic cell.
A. Equipment setup.
B. Schematic drawing of equipment setup.
9. Record the current density of the operating electrolytic cell.

10. Convert the Ag/AgCl readings to the Standard Hydrogen Electrode Scale (SHE).

11. Plot the SHE potential on the X axis and the current density on the Y axis of a graph.

Comments

The most important variable on measuring electrode potentials is current density. In addition, electrode potentials are affected by temperature, pH, differences in electrode material, and electrolyte composition, but since we are comparing units operating under the same conditions, these variables need not be considered. We need only to measure the difference between two half cells, where the Ag/AgCl reference electrode with a known value of \( +0.22 \text{ (AgCl} + e^+ + \text{Cl}^- = +0.2223) \) is one half cell, and the cathode with an unknown value is the other half cell. If the test cells are maintained at an approximate temperature of 25°C, all components are at unit activity, the digital voltmeter has a high impedance and there is minimum flow of solution through the salt bridge, there is negligible internal resistance (IR) drop; therefore, adjustments for these do not need to be made. The electrode potentials thus measured at the cathode are in reference to the Ag/AgCl electrode and result from the formula:

\[
E_{\text{C observed}} = E_{\text{C observed}} - E_{\text{refer. Ag/AgCl}} = -0.660 \text{ v.} - (-0.22 \text{ v.)} = -0.440 \text{ v. vs. Ag/AgCl}
\]

This value is converted to the SHE Scale since most electrochemical series potentials are listed as SHE potentials. The conversion is made by adding the value of the reference electrode to the observed value.

\[
E_{\text{C vs SHE}} = E_{\text{C observed}} + E_{\text{refer. Ag/AgCl}} = -0.660 + 0.22 = -0.440 \text{ volts}
\]

The potential measurements can be taken by placing the Luggin probe on one given spot on the cathode at a given current density, or different current densities. Alternatively, measurements can be taken at different spots on the cathode at a given current density or varying current densities. It is possible to determine the efficiency and evenness of the current distribution or to determine and control the theoretical direction of the electrochemical reactions occurring at any given or desired electrode potential being established by any given current density. It is therefore possible to adjust the current density until the theoretical potential for the reduction of metal in an aqueous solution of known pH is established. It allows a precise method to determine the efficiency or effectiveness of a given current density on a specimen undergoing electrolytic reduction.

Anode Potentials

Electrode potentials are measured at the anode by connecting the positive terminal of the voltmeter to the positive lead-in wire of the D.C. power supply and placing the Luggin probe against the anode surface. Anode potential measurements are useful for determining the current density conducive for anode passivation and to determine conditions under which anodic dissolution occurs. The voltmeter readings are converted to the SHE Scale by the formula:

\[
E_{\text{a vs SHE}} = E_{\text{a observed}} + E_{\text{refer. Ag/AgCl}} = +1.30 + 0.22 = +1.52 \text{ volts}
\]
REFERENCES CITED


REES-JONES, S. G., 1972. “Some Aspects of the Conserva-


Other Texas Memorial Museum publications include *Bulletins*, the *Pearce-Sellards Series*, *Museum Notes*, and mimeographed information circulars. A complete list will be sent on request. Others in this, the *Miscellaneous Papers series*, are:

*Bonfire Shelter: A Stratified Bison Kill Site, Val Verde County, Texas*, by D. S. Dibble and Dessamae Lorrain, 1968; 138 pp., 64 figures, $3.00.

*Falcon Dam and the Lost Towns of Zapata*, by Patsy J. Byfield, 1971; 69 pp., illustrated, $1.25.
