Conservation of Archaeological Metal Artifacts - Emphasizing on Copper/Bronze

Ambika Bipin Patel¹

¹. Department of Museology, Faculty of Fine Arts, The Maharaja Sayajirao University of Baroda, Vadodara – 390 002, Gujarat, India (Email: ambikamsu@yahoo.com)

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Abstract: Collections acquired through archaeological excavations need utmost care since they are vulnerable to the surrounding. As they vary in nature from organic, inorganic to composite materials (from stone to bone; metal to ceramics); soon after the removal from the buried context, start showing effects of the new environments they are exposed to. Out of the unearthed collections, especially metal artifacts are prone to deterioration and corrosion. This paper is an attempt to discuss the conservation measures to be taken up for metal artifacts. The present paper also discusses the conservation measures undertaken for about 150 copper/bronze artifacts from the Museum of Archaeology collection.

Keywords: Copper Alloys, Corrosion, Investigative Cleaning, Stabilization, Restoration, Preventive Coating, Microclimate

Introduction

From Field to Museum - Unearthed Metal Artifacts: In India, numerous excavations carried out till date by various organizations namely Archaeological Survey of India, the State Archaeology departments and archaeology departments of various universities revealed huge quantum of material assemblages/artifacts collection to fit in to various cultural periods. The unearthed artifacts (movable and immovable objects) are very significant in reconstructing past human cultures hence, conservation and preservation of them are equally important unless much of the archaeological data may be lost.

The excavations carried out in the early years of archaeology as a discipline were targeted to discover and recover artifacts. Conservation and preservation of the discovered artifacts remained secondary and conservation of those times was limited to basic repairing and maintaining the anatomy of the object. The unearthed materials finally became assets of nation, state, university or department and as a result became part of museum collections.

Significance of collaborative efforts by archaeologists and museum professionals were raised and discussed at length during conferences at Athens in 1931, at Madrid in 1934,
and at Cairo in 1937. The International Museums Office League of Nations in 1949, established the necessity for close interrelations between excavation and museum work. Progress of application of systematic criteria to resolve questions related to the objects such as provenience, manufacturing techniques, materials and techniques led to the introduction of chemical analysis of ancient objects (Caldararo 1987). Of late, museums focused on ensuring proper care of artifacts by cataloguing, documenting and reporting, storing and so on. Standards for proper treatment including documentation, in the field and the laboratory, can increase the percentage of artifact retrieval and sustainability which had been reiterated by scholars namely, Ford (1977); Christenson (1980) and Stanley-Price (1984) through their publications.

Metallic elements encompass the largest proportion of the materials that makeup the mother earth and the basic ores from which metals are obtained. Due to their reactivity, metals normally occur as minerals in combination with other elements notably oxygen and sulphur, rather than in the elemental metallic state (Craddock 1995). Metals which are known for their luster, strength, thermal and electrical properties are extracted from the ores. Since ancient times metals played a major role in the technological and economic development of mankind so much that, two important eras of human cultural development were identified as Bronze Age and Iron Age. Metals have been extensively used for various applications; for making functional objects, applications in architecture, decorative arts, fine arts etc. Metal elements are frequently combined (melting the metal and adding other metals in to it) in order to modify their properties is known as alloying (Nayak 1982). In general, the unearthed metal objects are mainly of copper, iron, gold, silver, lead, tin, zinc, nickel and aluminum; alloys of copper (bronze/brass) and iron (depending on the chronological setting of the site/area from where they were discovered).

The stability of metals depends upon retention of their normal metallic properties. Instability can be recognized by the presence of spots, weals or gross mineral incrustations on the metal which frequently occurs in the form of localized patches marking areas where active corrosion is taking place (Plenderleith and Torraca 1979). Metallic corrosion denotes the chemical and electro chemical changes that take place when metals revert to minerals (from which the metals were originally extracted through smelting (Gettens 1963).

Metals in general conditions of exposure get affected by gaseous actions (that of oxygen sulphur etc.) and in buried circumstances; the metals are susceptible to intensified deterioration due to the presence of soluble salts in the soil. The salts in the presence of moisture initiate galvanic actions and as a result metals become emaciated (Plenderleith and Torraca 1979), same is the case with museum objects. In any case, all metals except gold undergo some degree of corrosion while buried. By investigating the environment of the artifact in which it was buried, one can explore the factors behind its deterioration/weathering. The examination of the state of deterioration will enable in choosing the appropriate methods of conservation. Analysis of soil can be
done to assess the buried condition of the object (wet or dry; saline or alkaline) and also the characteristics of the soil (e.g. the chlorine content of the soil provides exuberant information for designing further conservation strategies). In order to control the progression of corrosion after unearthing a metal artifact, it is vital to identify the cause of deterioration and eliminate as many causative factors as possible. Unearthed archaeological artifacts of metal are subjected to scientific investigations relating to their structure, material and undergo conservation treatments before being displayed in public or put in storage (Cronyn 2001).

**Onsite First Aids**

Often metal artifacts are in an advanced stage of corrosion or deterioration and any attempts to remove them intact can result in damage to its morphology. During excavation, metal artifacts which have remained relatively sturdy can be removed without any special measures however with due care. Fragile objects need support and it can vary from application of simple to elaborate techniques depending on the nature of the discovery. Utmost care should be provided to prevent any sort of damage while lifting up the artifacts from the context i.e., from *insitu* position. Special care must be taken when performing on-site cleaning of artifacts which have heavy siliceous and encrusted deposits and there is a possibility that the soil around it may contain textiles or other organic artifacts. A similar situation is observed during the present case study on copper spear heads from the site of Bagasra which had some fabric impressions and small bone pieces sticking on the surface along with incrustation perhaps indicative of the remains of a bone cover/handle. Two bone handle knives were also removed from the *insitu* context at the site with utmost care. Hard urethane foam was used as support for the removal of fragile metallic artifacts and similar measures can be taken at any site. When the artifact is too fragile and broken into many fragments, several sheets of finely cut up wire gauze are pasted together and backed with resin can be used as support material prior to the removal of artifact. The metallic artifacts could be brushed with alcohol to remove sand and soil on the surface to some degree to which it is possible. When drying is not possible, water soluble acrylic resin may be used for treatment, or hard urethane foam may be utilized to cut out the artifact along with the surrounding soil and wrap it for removal. Though plaster of paris was often used in the past for the removal of fragile artifacts, it is laborious and time-consuming to remove the plaster afterwards. Hence, it is advisable to avoid the use of plaster. On-site cleaning should be kept to a minimum to avoid any loss of information that the artifact may hold. Thus the onsite conservation enable archaeologists to understand how and why materials decay in buried environments which in turn can assist in designing better cleaning and stabilization treatments (Cronyn 2001).

**Documentation at the Site**

Documentation of the excavation of metal objects is vital in establishing their proper care and conservation at the outset of their new ‘lives.’ The first set of information should be based on providing a description from the onset of discovery and *insitu*
photography of the same. The type of soil and the environmental circumstances of the objects in situ should be recorded with the condition of the objects. A simple rule to be followed at the site is to record who, what, why, where, when, how? of any situation or change. Block-lifting procedures should be recorded along with any first-aid treatments that are applied during excavation or immediately afterwards. Thus a brief report of the condition and the nature of the deposition along with insitu photographs will be the basic documentation records of the life of the object at the time of the discovery.

**Care and Cure in the Lab**

Documentation along with a condition report should be generated for the metal object that has been brought into the laboratory for conservation prior to having any treatment. Observations and thoughts about any technological and art historical information that is uncovered in the course of examination should also be documented (Dolley 1996). In the condition report the environment and storage conditions in which the object is kept should also be recorded along with the recommended ideal conditions (Collins 1995). A plan for conservation treatment should be drawn up after a condition report has been completed. Based both on the condition report and on what the curator or archaeologist, acting as the client, desires for the object as expressed in the request for conservation.

The plan can detail the problems that the object has and how they might be corrected by specific conservation procedures; the expected results of the procedures should be noted as a justification of the chosen methods. The date and the name of the conservator who proposed the treatment should be recorded in the report along with an estimate of the time needed to complete treatment. Additional documentation on the condition of the object should be recorded at every stage of treatment as well as at the completion of conservation cure. Any type of conservation treatment that is done on an object also should be recorded in a detailed manner. Materials used for fills, adhesives and consolidants should be written down completely along with materials and methods used during conservation processes such as ultrasonic treatment and electrolysis. Thus, recording of all conservation processes should be completely done no matter how insignificant they could be along with date and sequence of the treatment. Any mistakes or failures in a conservation treatment should also be noted in the treatment report as it will be easier to deal with the mistake if it is known rather than covered up (Dowman 1970).

**Copper and Copper Alloys**

Copper and Copper Alloys were among the first metals to be widely used by mankind. The Bronze Age of the three Age system indicates inferences about the use of copper and its alloys for various utilitarian purposes. Properties of metals such as appearance, strength, malleability and chemical reactivity can be altered by alloying with other metals bronze (alloy of copper and tin) and brass (alloy of copper and zinc) are used for making objects of various functions with improved qualities.
Understanding Corrosion

Metals being thermodynamically unstable tend to liberate free energy to achieve stable state. This leads to alterations on their surface by reacting with various environmental agencies, widely known as corrosion. Corrosion is a chemical or electro chemical process in which a metal is converted to its mineral form. Corrosion is a never ending phenomenon, the rate depending upon the nature of the metal and the severity of the reacting agencies and for conservators corrosion is an undesirable deterioration of metal. It is a rapid and severe process of deterioration in humid climate, because most chemical reactions get accelerated due to the presence of moisture (Agrawal 1987).

Under the favourable conditions, during the process of corrosion an incrustation of mineral substances may be formed that seals up the surface, protecting the underlying metal from further attack and establishing a condition of equilibrium. However, once the copper artifacts in that case once removed from its environment, i.e., upon excavation, get exposed to a fresh series of influences-variations of heat, moisture and atmospheric gases; corrosion may well break out again and changes in appearance, shape and metallic content are the results. (Plenderleith and Torraca 1979).

Copper is the first member of the group 1B of the periodic table having atomic number 29 (2, 8, 18, 1). Not being chemically very active it oxidizes very slowly in air. Corrosion of copper is basically aqueous in nature stir by electrochemical mechanism of anodic (oxidation) and cathodic (reduction) reactions (Lal et al. 2012). The element in its metallic form is the most reduced state whereas in solution it is in its oxidized form. The problem of corrosion is severe in unearthed copper artifacts as cuprous ions get oxidise to cupric very fast though the formation of Cu+ and Cu++ depends on various factors. The mechanism is:

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

Most often, unearthed copper and copper alloys have patina or encrustation of chlorides and oxides on the surface. Such encrustations/crusts are brittle and readily get cracked through mechanical shock and the cracks become loci of active corrosion and provide platform for oxygen and moisture to penetrate to the residual metallic core. Tropical conditions of damp heat furnish a serious threat to the stability of copper and copper alloys and intensify the corrosion (Lal et al 2012).

Out of the unearthed collections, especially metal artifacts are prone to deterioration by corrosion while buried and pose problems for conservation. In concern with unearthed copper and copper alloys, Scott (1991) opines, the typical treatment for archaeological bronzes from 1880-1970 was the chemical or electrolytic removal of corrosion products either by local application or by complete immersion of the object. Also, the rationale for this kind of treatment was to remove dangerous compounds within the corrosion crust. Such cure methods frequently altered the appearance of the objects quite drastically and the historical and aesthetic issues were never properly debated within the conservation profession at that time.
Some copper/bronze archaeological objects require some form of treatment to avoid the risk of bronze disease, but it appears that no testing was done to ascertain if the treatment was really necessary?. Objects not at a risk were subjected to the same treatment along with those with chronic problem and as a result healthy bronzes were needlessly stripped off. Their conservation starts from the field/site, with the first aid, i.e., the application of the basic elements of preventive conservation.

Conservation of Copper Artifacts from the Collection of Museum of Archaeology

The copper artifacts from Harappan and Regional Chalcolithic sites from the state of Gujarat namely Nagwada, Shikarpur and Bagasra constitute a major part of the collection of Museum of Archaeology at The Maharaja Sayajirao University of Baroda. On the basis of excavated material assemblages from various sites of Indus realm, it appears that, copper and copper alloys were extensively used for making a variety of artifact types such as tools/implements (knives, blades, saws; spears, arrow heads); ornaments such as beads, rings and bangles; house hold materials (vessels), objects of religious importance (parasu); items of economic significance such as scale pans, tablets etc. by the Indus crafts people (Kenoyer 1998; Vidale 2000; Vidale and Miller 2000).

Condition of the Objects

All details of the objects recovered from the site are recorded manually in antiquity register. These hand written registers were converted digitally into an Excel file. Objects are photographed and measurements (length, breadth, weight and other standard dimensions) are recorded. Some of the very small objects, fragmentary prills and unidentified objects were scanned in group (Fig. 1).

Due to prolonged burial condition, majority of the copper artifacts recovered were corroded with heavy incrustation leaving almost no core. Corrosion of chloride trapped in calcareous concretions noticed in the copper based artifacts from Nagwada, Bagasra and Shikarpur, all from the state of Gujarat during the case study. Majority of the artifacts were heavily corroded and a very small percentage of the whole collection have copper artifacts with core left out.

Some of the objects indicated pockets/spots of pale green powder as corrosion products. The corrosion products observed on the artifacts were thick encrustations of copper carbonate in bulky green and areas of copper oxide in reddish and brown colour. More than 50 objects were treated.

Investigative Cleaning

To avoid any sort of future problems, as part of the present conservation work, the researcher documented every minute activities carried out. The copper artifacts were first gently brushed for removing the dust and dirt. Appearance of the surface and its features are photographed. The surface investigation for understanding extent of corrosion, unusual corrosion features, mineralized remains etc. was done before actual
cleaning. The condition report for each of the artifact was generated so as to preserve the history of treatments done for the future reference.

Figure 1: Prills and Unidentified Fragments (scanned and documented)

Due to difficulties in controlling reactions during chemical treatments, mechanical cleaning is preferred for copper/bronze artifacts. After the general surface observation, each one of them underwent investigative cleaning under the microscope under magnification of x10 to x40 (Fig. 2). The object is illuminated by a fiber optic light source attached on the microscope to avoid undue heating of it during cleaning. Differential levels of corrosion removal was adopted, artifacts with less corrosion have given minimal cleaning, while those with heavy calcareous deposit and encrustations were cleaned with utmost care. The objects were cleaned with soft brush to remove the dirt and dust. To expose the surface details, it was found necessary to remove the heavy siliceous and calcareous encrustations. Ethnol is applied on the surface to moisten and soften the calcareous and siliceous encrustations so as to facilitate their easy removal. The fine tools such as fiber brushes, paint brushes, dental picks, metallic scalpels, points, needles, tools fashioned in wood or sticks etc. were used. This treatment was applied to objects like knives, blades, nails, daggers, rods and rings.
The present investigative cleaning under microscope proved to be very useful to the collection, as it revealed some interesting features of embedded fabric/vegetation impression on the surface of the spear heads (towards the tapering end), knife blades and a celt. As organic residues or preserved fibers are very significant for the socio-economic and cultural understanding and interpretation such locations were left untreated so as to retain and preserve them. The rest areas of the objects were cleaned mechanically under the microscope with utmost care. The impressions were preserved by giving a coating of 2% B72. Mechanically removed corrosion products from the surface of the artifacts were collected, properly documented with description of the area and the artifact from which it has been removed and stored properly for corrosion studies in future.

The copper vessel/pot from Bagasra was treated with 5% sodium hexa-meta phosphate (calgon) for the removal of calcareous encrustations by applying the solution soaked cotton on it. To reduce the damage of the patina, (basic copper carbonate) sodium tripoly sulphate (STPP) which is less reactive with patina was used for cleaning the calcareous encrustation further. Cotton pads soaked with solution of sodium try poly phosphate were left in contact with the object for half an hour followed by mechanical cleaning of the surface accretions with the help of sharp scalpel and blunt knife, needle etc. For removing the ingrained accretions freshly prepared carboxyl methyl cellulose paste with 2.5% STTP in distilled water was applied on the affected part and left to dry for a day. The dried CMC film was then removed carefully with forceps. After removal of incrustations from the surface, the deposits of STTP were removed from the cracks, depressions and uneven areas. The object was cleaned with hot distilled water and dried in an oven.

**Stabilization**

Among the entire collection, all of them which had shown patches and spots of bronze disease (the light green powdery eruption) were mechanically removed by pointed needle under the magnifying glass. The objects which have seen active corrosion areas were treated separately and carefully for stabilization. Those with structural damages were also underwent structural stabilization treatment. The spots of bronze disease areas were cleaned under the magnifying lens mechanically (Fig. 3).

Active corrosion areas were cleaned minutely and treated with corrosion inhibitor Benzotriazole (1-3% solution is prepared with isopropanol). A bath of BTA solution is specially prepared in a glass trough for the copper vessel and is kept in the bath overnight so as to allow its all bent/curved inner areas get stabilized where bronze disease was severely affected. The object was removed from the bath and BTA solution was applied on it at preferential areas where severe bronze disease was observed. The application of BTA with cotton was done at every half an hour during the day time repeatedly for three days. White powdery deposit of BTA was cleaned by using isopropanol and cotton swab. BTA works by forming a thin, insoluble and invisible film, and the effectiveness of BTA depends on how well the film can form. It
is observed in the copper vessel at some local spots due to acidity, BTA film forming is not occurred properly and demanded preferential stabilization treatments.

**Figure 2:** Investigative Cleaning of Copper Artifacts Under Microscope

**Figure 3:** Removal of Bronze Disease Spots Under the Magnifying Lense

**Restoration**

Some of the structurally fragmentary artifacts were restored / joined by using 5% B48 acrylic resin so as to make them structurally stable and also ready for display as and when required. The bigger fragments were joined easily and the smaller ones were joined one by one carefully to reconstruct the shape/ morphology of the object. The figure (Fig. 4) illustrates the restoration done on *Parasu* razor to make it structurally stable.

**Figure 4:** The *Parasu*/Razor Before and After Restoration
Preventive Coating

The Paraloid B72, popularly known as Acryloid B72, is a co-polymer of ethyl methacrylate and methyl methacrylate has been extensively used in bronze conservation work both as adhesive and also as preservative coating. 3% of the B72 was used for coating so as to avoid shining appearance of the surface of the artifact. In some cases, a swab dampened with acetone was used to remove (extra coating) shining from the surface.

Storage and Maintenance

To slow down the process of deterioration, metal objects should be housed below 35% relative humidity in a microclimate storage box. A microenvironment is an enclosed space with an airtight seal that controls RH with desiccants such as silica gel or montmorillonite clay. These remove excess RH from the enclosed space. Polypropylene (PP) or Polyethylene (PE) storage container with silicon gasket should only use as box for creating microclimate (Senge 2011).

Figure 5: Microclimate Box Storage

The objects were prepared to keep in the microclimate box (Fig. 5). They were provided proper housing with the help of ethfoam sheets of various thicknesses as the base for support. Small objects were kept in zip lock bags padded with polythene sheets. For bigger and heavy objects, the foam sheet used was thicker and the shapes of the objects were cut into it. The objects were placed in the cut shapes so as to avoid movement/shaking of the object. After keeping the object inside the ethfoam, another thin sheet was kept on top and tied by cotton ribbons or twill tape ties. Drawing of the object and the accession number was written on the upper surface of the cover foam.
sheet so as to identify the object inside without opening the cover and thus avoid frequent handling to make the object more sustainable. Thus a microclimate was provided to all the treated and untreated artifacts by keeping silica gel and storing them in transparent airtight plastic containers.

The transparent containers were kept in bigger containers and stored them properly in metallic racks. The polyethylene or polypropylene storage container with a silicon gasket is moisture permeable and humidity slowly leaks through the seal over time. The desiccant will absorb that moisture and regulate the environment and the effectiveness drops with time. The amount of time is dependent on the amount of moisture present in the local climate. The humidity indicator card provides a visual signal that the RH has increased. Monitoring and checking the microclimatic environments were done at regular intervals on a quarterly basis. The desiccant may need to be reconditioned or replaced on an annual basis. To sum up, conservation activities must continue at various levels as per the requirement, as long as it is decided that, the excavated assemblage/collection is to be retained (Cronyn 2001).

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