Conservation of Metals in Humid Climate

(Ed) O.P. Agrawal



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Conservation of Metals in Humid Climate

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CONSERVATION OF METALS--PROBLEMS AND PROSPECTS

O. P. AGRAWAL

INTRODUCTION

A LL metal objects corrode due to interaction with its surroundings, whether it be ground, waer or air. Corrosion is a never-ending phenomenon, the rate depending upon the nature of the metal and the severity of the reacting agencies. This is also a fact that corrosion is much more rapid and severe in humid climate, because most chemical reactions take place with the help of moisture.

The corrosion phenomenon has been studied in great detail by a large number of scientists; not only in relation to cultural property but also in relation to metals used in the industry and for other purposes. An attempt has to be made to understand how corrosion takes place and how can it be prevented. In the industry, the effort is to produce a metal which would resist corrosion under different conditions. As far as cultural heritage is concerned, the objects are already available and therefore, there is no question of producing a new artifact with the latest types of metals.

In the conservation field, the basic steps are :---

- 1. Analysis of metals.
- 2. Examination of corrosion products.
- 3. Conservation treatment of objects.
- 4. Application of protective coatings.
- 5. Safe storage and display of objects.

ANALYSIS

For analysis of metal objects, very sophisticated and advanced analytical techniques are available today. For chemical analysis of components, besides the classical standard method of wet-analysis, the technique of atomic absorption spectrophotometry has come to be used a great deal.(1). This technique of analysis is very quick and precise, needing a very small sample from the object.

X-ray fluorescence spectrometry has also been used a great deal for analysis of archaeological and art objects. (2-7). It goes without saying that non-destructive types of analytical methods are extremely useful for analysis of art objects. X-ray fluorescence spectrometer, for that reason, is a very useful tool for this purpose. There have been advancements in the use of the technique. Earlier, the objects had to be brought to a specialised laboratory where the equipment was placed. However, now portable units are also available which can be taken to the place where the object is kept. Cesareo *et al.* performed a series of experiments to test the efficacy of this technique for analysis of antiquities(8).

Although, this technique of analysis has often been used, because of various limitations, it is difficult to say how accurate or precise it is, to give the required information. There is no doubt that by itself it is an accurate technique, but because the measurement is done on the surface of the objects, rather than on a sample from in-depth, the results may sometimes he misleading. Writing on this subject, Jedrzejewska cautioned that the whole matter needed a thorough re-consideration of relevant factors. In her opinion, the main point lies not in *measuring* but on the proper interpretation of *what was measured*.(9)

For mineralogical identification of corrosion products, X-ray diffraction technique is to be used. X-ray diffraction also takes a very small sample for accurate determination of composition of materials, particularly of corrosion products on metals.

Although. X-rav diffraction is extremely useful for identification of corrosion products, its use on a regular basis for routine qualitative analysis becomes very costly and cumbersome. A simple qualitative test for common iron corrosion products, using normal laboratory equipment has been suggested by James Argo.(10).

The test is based upon the differential solubility of the minerals in pure acetyl acetone and on the colour of the product formed. It is found that different iron minerals produce different colours. However, this method of identification is not applicable when a mixture of two or more of the minerals are present together in an artifact and in that case the X-ray diffraction technique is the only answer.

There are several other techniques of analysis, like the X-ray photoelectron spectrography and Mossbauer spectroscopy, which have been used for analysis of metal objects and their corrosion products. Infra-red spectrography has been used for distinguishing different naturally occurring isomers of basic copper chloride, namely botallackite, paratacamite and atacamite(11). The intention here is not to give a list of all the analytical tools but only to point out a few which have found the widest use.

Analysis of metal objects can be done from several points of view, one of them certainly is to understand the technical history of the alloys, metals and to understand the fabrication techniques. This type of examination is basically an archaeo-metallurgical exercise which throws light on the development of cultures in a particular region, it does not have much relationship with conservation, except in an oblique manner.

Another aim of analysis is to know the composition of the metal with a view to deciding the process of conservation. The analysis also takes into account the composition of the corrosion products and of the metal composition and then correlate it with the solutions that are to be used for treatment. Metallographic examination is helpful in deciding the strength of the solutions and their likely effect on the objects.(12).

In fact, metallographic studies give an insight into the micro-structure of metals. While there have been a large number of studies on the archaeo-metallurgical understanding, much work does not seem to have been done on the other aspect, namely inter-relationship with corrosion and conservation, which is of a direct relevance to us.

Therefore, I believe that for conservators it will be of relevance to take up a project for the study of various types of metals in different regions and the mineral composition of the corrosion products, in order to understand the phenomenon of corrosion. This project could further be enlarged to include the study of the effect of varying humidity conditions on corrosion of metals particularly high humidity, and short of airconditioning, how could it be prevented and controlled.

Precautions for sampling

Before analysis of metal is undertaken, it should be ensured that the sampling procedures are of a correct type. Their choice will depend on the method of analysis, their limitations and the type of information which is required. According to Jedrzejewska, it should be ensured that the corrosion products are included in the sample for general analysis of an ancient alloy(13). During the process of corrosion, preferential corrosion of metals and their alloys takes place, thereby leaving the remaining alloy enriched in the more stable components. It is, therefore, necessary that analysis is done before the cleaning of corrosion products.

Writing on the subject Jedrzejewska summarizes four principles of testing, as follows (14) :---

- 1. A representative number of samples should be taken in every case of investigation, and sufficient evidence brought to prove the correctness of every sample. This is strictly necessary, even if only for methodological reasons. The size and position of the sample, the structure of the object, the methods of testing, should all be clearly stated in the report.
- 2. Objects whose treatment after excavation has not been fully recorded are not to be used for reliable examination.
 - 3. Premature and hasty cleaning should be recognized as the worst danger to the accumulation of knowledge.
 - 4. The analyst should state in his report to what extent his samples are representative of the whole object, and should not extend his conclusions beyond this point.

In the opinion of R. M. Organ who analyzed thoroughly the above statement showed that the present composition of the corroded portion of a metallic antiquity does represent its original composition and thus neither the heterogeneity of the metallic structure, nor the presence of mineralization, nor products of improper cleaning can render unrepresentative, results of an analysis made on a sample obtained from the object, provided the sample, is obtained with care(15).

Corrosion Products

Much work seems to have been done for the identification of corrosion products on metals. Gettens reviewed the knowledge of reported alteration products and presented the list at the first IIC Conference held in Rome in 1960(16). Since then further studies have been done and we have a better understanding of the subject. Mentioned below are some of the studies.

Copper

Probably, the most widely occuring alteration products present on ancient copper and its alloys is cuprite, Cu₂O cuprous oxide. Most of the time, it remains hidden under the green basic salts of copper. Black cupric oxide, CuO is seldom found.

The other two most widely occuring corrosion products of copper objects are the two basic copper carbonates of copper, namely malachite and azurite. These minerals are presumably tound when the object comes in contact with the soil, water or water having carbon dioxide. It is observed that malachite occurs more than azurite does.

Gettens and Frondel reported a new corrosion product of copper, namely chalconatronite (17). This mineral was identified by them on some copper artifacts from Egypt. Another mineral which is extremely important in the process of deterioration is atacamite, the basic chloride of copper. This mineral is found when the object remains in long contact with the salty soils.

Copper sulphate was observed on copper roofs and bronze statues in cities where pollution level is high. Sulphides have seldom been reported.

Iron

The main corrosion products of iron are Goethite, FeO(OH) or Limonite, FeO(OH). nH₂O, oxide of iron. Magnetite, Fe, Fe_2O_4 has also been reported. (18).

Gilberg and Seeley have done a critical review of the identity of compounds carrying chloride ions in marine iron corrosion products (19). The role of these compounds in corrosion promotion has been evaluated by them with a view to throw some light on the selection of the conservation techniques.

North has carried out extensive studies to determine the corrosion products of iron found under sea water. He has given a detailed list in his article on corrosion products in marine iron.(20).

Turgoose has studied the corrosion products of iron objects found from excavation on land. (21). He also studied the changes that take place in iron antiquities after excavation, and during their storage. He showed that these changes were identical to those occuring during the oxidation of ferrous ions in the presence of chloride. He also showed that these reactions occur even at a relative humidity as low as 20%. (22).

North and Pearson reported that iron oxychloride, FeOCI was the predominant chloridecontaining corrosion product of iron found in sea water (23, 24).

Argo studied the nature of ferrous corrosion products on marine iron. He found the main products to be the hydrated iron oxide as well as oxide. He did not locate the ferric oxychloride found by North and Pearson (25).

Silver

Silver sulphide and silver chloride are the two most familiar alteration products of silver. While silver sulphide is found due to the action of polluted atmosphere, the silver chloride forms in salty soils.

In some cases silver bromide was found to be the dominant corrosion product of silver. (26). The presence of silver bromide was reported by Hedges as a corrosion product of silver in some objects excavated from the ground as well as from the sea. The most likely explanation of the formation of silver bromide is the produce of the natural bromide in the ground.

Lead

Normally lead carbonate, cerussite, is the most commonly occuring alteration product of lead. Various oxides of lead, like Massicot (Yellow lead mono-oxide), Litharge (Orange lead monooxide), Plattnerite (Lead dioxide) have been reported to be present in lead corrosion products. The presence of lead sulphide has also been reported. (27). There is no report of the occurence of lead sulphide.(28).

CONSERVATION TREATMENT

Various methods for the conservation treatment of metal object have been in use. Some of these methods may be termed as classical and have been used for a long time. As a result of constant research, there are several advances in the methods of conservation of various types of metals. Some of these advances will be discussed here.

Gold

Gold is a very durable material and does not corrode. It hardly needs any treatment except general cleaning with a detergent. Although gold is a stable metal, the gold alloys do deteriorate. It has been the subject matter of a study by David Scott. He has described different ways in which gold alloys can deteriorate.(29). He has also examined the various procedures that can be applied for the treatment of gold-copper alloys. Thus, he showed that alloys of gold with silver may tarnish due to formation of silver sulphide. He also indicates that gold-copper, goldsilver and gold-copper-silver alloys, as well as gilded surfaces, are liable to corrode during burial in soil.

Silver

Silver is also a noble metal but when buried underground or under sea it corrodes to form corrosion products, the main of which are silver chloride and silver sulphide. When it is alloyed with other materials like copper in appreciable amounts, corrosion products of the alloying metal are also present.

The usual methods for treatment of silver are electro-chemical reduction with aluminium and caustic soda or zinc and formic acid or caustic sode. Silver objects are also reduced electrolytically. (30). Silver-dip is the recommended treatment for removal of tarnish.

A comparatively new method for removal of tarnished corrosive products from silver is the use of thiourea. The formula contains thiourea, hydrochloric acid, and a detergent diluted with water.(31). Stambolov while treating a copper/silver alloy bowl with this method came across a difficulty. He found that the periphery of the treated areas became covered by black precipitate of silver sulphide, possibly because of the preferential absorption of sulphide ions at the interface, liquid-air-metal. To overcome this difficulty, Stambolov made some modification in the method. A stream of air was blown in the solution containing sulphide ions to oxidise them to thio-sulphates and sulphates.

A method for chemical reduction of the silver corrosion products to metallic silver was developed by MacLeod and North(32). In this method alkaline dithionite solution in the absence of atmospheric oxygen is used to reduce the silver corrosion products. It is claimed by the authors that the results obtained were superior to those using other methods.

The alkaline dithionite solution is prepared in an air-tight sealable container by first adding 40 gms of caustic soda per litre of water, mixing thoroughly and then quickly adding 50 gms sodium dithionite, per litre of solution. The silver objects are kept in the container quickly and the container is sealed. Sodium dithionite powder must be kept dry as it is inflammable. Therefore, it should be handled with care and the container must be filled completely with solution to exclude oxygen as much as possible. The container is kept closed for one week and the objects are then taken out and cleaned in water with brush.

In this treatment a great disadvantage is that the treatment has to be done in a closed container and there are no means to keep a check on the progress of treatment. Secondly, sodium dithionite can be a dangerous chemical if not handled carefully.

Sometimes, combination of methods has to be used for treatment of a single silver object. For instance, during the treatment of a silver visceral vessel belonging to the beginning of the 17th century, two different cleaning methods were used to remove silver chloride corrosion and silver encrustations from its different areas.(33). The vessel was covered with a black layer of corrosion products with patches of green. Black and grey deposits were present over the whole surface of the vessel. It was found by the restorers that the inner part of the object was smooth and black. Analysis showed that silver sulphide was the main corrosion product. The treatment therefore was done with a solution of thio-urea and formic acid after cleaning in 1% solution of non-ionic detergent. After this treatment, most of the vessel was cleaned except some black encurstations remained.

Analysis with atomic absorption spectrography showed that the material of the vessel was silver with 6.1 to 6.3% copper. The corrosion products were identified as silver chloride by x-ray diffraction.

For cleaning, an alkaline solution of dilute sodium salt of EDTA is used. After about an hour, most of the encrustations had been removed. However, treatment even for 12 hrs did not remove one of the big stains and therefore electrolytic reduction in 5% formic acid was used.

It is well known that certain ancient silver objects with time become exceedingly brittle. Silver coins also often become brittle. Thompson and Chatterji have studied this phenomenon in some detail (34). They examined the coins metallographically and came to the conclusion that neither the silver content of the alloys nor the temperature of the striking nor severity of corrousing a Hilger medium quartz spectroscope showed that in the metal of the brittle coins, without exception, copper and lead were found in appreciable quantities, and no other elements, except in copper-lead system and came to the conclusion that the brittleness of the coins is mainly due to the influence of the super-saturated solution in the original ingots or to the reheating and sudden cooling involved in hot striking. Aging at ordinary temperature may be very slow but in semitropical conditions and if the material has been subjected to fire the embrittlement would be

As far as the removal of this brittleness is concerned, it has been shown that reheating to temperatures of about 200 to 250° C will strengthen the silver with lead alloying. The silver-copper-lead alloys possibly need a temperature of around 500° C

A need often arises for testing materials which have a potential to tarnish silver by evolution of hydrogen sulphide. These materials could be, wood for example in cupboards and boxes, tissue paper used for wrapping silver objects, cloth lining used for storage of boxes, etc. Daniels and Ward have suggested a rapid test for the detection of sulphur which will tarnish silver. The test is based on the decomposition of a sodium azideindine solution by sulphur containing groups to evolve nitrogen bubbles, (35-36). This test is also used for detection of pigments having sulphide group as the principal ingredient.(37).

Copper

Copper objects easily corrode, particularly when burried in salty surroundings. Copper oxide, carbonates, chlorides, etc. are the main corrosion products. The presence of chloride poses an acute problem, because an unstable cuprous chloride is formed as a corrosion product that reacts with moisture and a progressive corrosion takes place. The treatment, therefore, attempts mainly to remove cuprous chloride.

The usual treatment methods for copper are, alkaline Rochelle salts, alkaline glycerol, sodium sesquicarbonate, Calgon, etc. Silver oxide is used to form a stable seal of silver chloride on the exposed cuprous chloride.(38). This method of treatment was first of all suggested by Organ.(39).

In all the methods of treatment, corrosion products covering the cuprous chloride are removed and then the chloride layer is stripped. The removal of all corrosion products may not be permissible in certain circumstances when it is desirable to retain the patina.

The treatment of objects in sodium sesquicarbonate converts harmful cuprous chloride into the harmless cuprous oxide. The treatment, however, is for very long periods. The methods of silver oxide is used to cover the active bronze disease. In this method the areas where bronze disease is expected is excavated with pointed needle or knife and silver oxide is filled into it to protect the spots from atmosphere. (40).

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Use of sodium sesquicarbonate is a standard method for the removal of soluble chloride from corroded copper and iron objects. Oddy and Hughes took up investigations to determine the optimum conditions for its use.(41). On the basis of this experiment, it was suggested that weekly changes of solution are not necessary for cleaning bronze objects, except when a secondary green malachite deposit on objects begins to form. Soluble copper salts within the corrosion layers produce a blue-green colour in the sesquicarbonate solution and quite often this results in a deposit of basic cupric carbonate. When this type of deposit starts forming, the solution should be changed and the object brushed to remove the deposit. Therefore, normally infrequent changes of liquor are enough, unless the solution becomes very blue due to the copper concentration getting too high.

Oddy and Hughes' study also showed that there was no evidence to suggest that the application of ultrasonic vibration speeds up the removal of chlorides. However, he found that with ultrasonic vibrations considerable amounts of colloidal material was released from the objects into the liquid.

It was a also significant conclusion that washing in a hot solution of sodium sesquicarbonate did not increase the rate of chloride removal.

Mechanical cleaning of an object before starting the washing in sesquicarbonate solution was helpful in speeding the chloride removal from bronze objects. Mechanical cleaning during washing to remove any secondary deposit of basic copper carbonate increases the rate of the washing process.(42).

The use of benzotriazole for stabilization of bronze disease has proved to be an epoch making method, first of all suggested by Medsen.(43). Before this time, benzotriazole was being used in the industry in preventing the corrosion of copper even in polluted atmosphere. Medsen treated a number of objects having bronze disease from different countries with benzotriazole. He found that after treatment all of them became completely stable.

Since then, we have come a long way and benzotriazole as a standard method of treatment of bronzes has been in use in almost all countries. One of the disadvantages is that it is costly and it is reported that in many a case it is not so effective, particularly in the high humid climate.

Benzotriazole is a white or slightly tan odourless crystalline compound, melting at 98—100°C It has been found that it forms stable metallic salts. It is soluble in alcohol and reasonably soluble in water. Studies done by Cotton indicate that the benzotriazole complex of copper is thermally stable upto about 25°C. (44, 45). The protective film which is found on the copper surface by reaction with benzotriazole is very thin, less than 50 A.

Benzotriazole has been used for protection of cleaned uncorroded copper or copper alloys, and for stabilization of corroded bronze artifacts. Normally, bronzes are treated with 3% solution of benzotriazole dissolved in alcohol. Impregnation is done under vacuum. If the object is heavily chloride-attacked, small amounts of benzotriazole will not give satisfactory protection, but by using 30% by weight of benzotriazole, dissolved in alcohol and treating the object under vacuum and by applying heat, a good protection is obtained. (46, 47).

A very ambitious project of treating numerous Thai bronzes was undertaken in 1977 with the help of JDR III Fund. The bronze objects were treated mainly using benzotriazole. The experience gained during this project should be of great value of us. (48).

While using benzotriazole, precautions should be taken to ensure that it does not pose a health hazard. It is necessary that the benzotriazole powder is not inhaled and it should not come in contact with skin or eyes. (49).

It was reported that possibly benzotriazole is carcinogenic. Examining this question Oddy in his note has observed that the toxicity of benzotriazole is uncertain. He observes that there seems to be no evidence of damage in humans although tests on animals suggest that damage may be possible.(50).

Benzotriazole has been found to be an invaluable chemical for the treatment of copper antiquities. An excellent review article on the use of benzotriazole has been published by Catherine Sease(51). Surveying the available literature till 1978, she has dealt with the chemistry of benzotriazole, its reaction with copper, mechanism of inhibition due to benzotriazole application of benzotriazole and its toxicity. A comprehensive bibliography citing 47 references has been given at the end of the article.

Several reagents are used for cleaning bronze and copper objects. It is necessary that these chemicals, while removing the corrosion products should not affect the metal. Very little work has been done on understanding the interaction between such chemicals and metal alloys. Fransworth studied the effect of Calgon on metal and came to the conclusion that it has no effect on any remaining metal core (52). A study was undertaken by Linda Merk for ascertaining the extent to which stripping agents used to remove corrosion products from bronzes may attack the metal.(53). The cleaning agents tested by her were alkaline glycerol, alkaline Rochelle salt. Calgon and citric acid. Merk used metallographic technique and monitoring of pH for testing the effect of the chemicals. She found that the samples of bronze alloys underwent etching in all these stripping solutions even before the recommended treatment time had clapsed. With alkaline Rochelle salt the depth and rate of etching was considerably less than with alkaline glycerol while treating tin bronze samples. However, in the case of the lead-tin-bronze, in the absence of corrosion product, the speed and extent of etching was more than with alkaline glycerol. On the other hand, when the corrosion products were present the speed of etching was slightly less. In conclusion it can be said that the use of these stripping solutions should be carefully controlled, to avoid the etching of exposed metal while removing unwanted corrosion products.

Similar work for testing some of the methods of archaeological bronze conservation was done by Angelucci *et al.* (54). These authors used a procedure to reproduce the structure and composition of original patina of bronzes so that testing can be done in as near original circumstances as possible. The most common methods of treatment, namely benzotriazole in alcohol solution, in water solution and sodium sesquicarbonate were tested. On the basis of their experimentation, they came to the conclusion that the treatment with benzotriazole is the most suitable for the conservation of copper and bronze archaeological artifacts.

Potasium sodium tartarate solutions, either alone or alkaline do not effect the copper present in the metal alloy (bronze) and do not attack copper oxides which are still present in the patina. This reagent therefore can be safely used for the cleaning of gilded bronzes. (55).

The effect of treatment solution on exposed metal has been a matter of concern. Several inhibiting chemicals in cleaning solutions have been in use to save the metals from being attacked. Benzotriazole was found to be effective to inhibit the corrosive behaviour of cleaning solutions. (56). Tests were done by adding benzotriazole to alkaline Rochelle salt, alkaline glycerol and Calgon. Benzotriazole, however, does not reduce the corrosive behaviour of citric acid.

The problem of desalination mechanism of corroded copper alloys has been studied by MacLeod.(57). His study of more than 12000 objects recovered from sea and ground indicate that there are several parameters that determine the rate of release of chloride ions during conservation treatment. MacLeod showed that factors such as metallographic structure, salinated surroundings and dissolved oxygen levels during burial give rise to a series of characteristic chloride release rates that enable treatment times to be calculated.

A comparison of various methods for stabilising corroded copper alloy artifact was done by MacLeod(58). He used objects of various types, both marine and from ground. His studies indicate that alkaline dithionite which was first of all used for treatment of corroded silver was most effective for removal of chlorides from objects. The inhibited citric acid solutions give the second fastest release rates. Thiourea is used as the inhibiting agent.

The next best for removal of chlorides was a solution of 5% sodium sesquicarbonate which was more effective than 1% solution of benzotriazole in ethyl alcohol. Next in order was 50% solution of acetonitrile. The rate of removal of chloride with 1% sodium sesquicarbonate was still less and more or less the same as deionized water.

MacLeod also came to the conclusion that sodium dithionite, citric acid, thiourea, 5% sodium sesquicarbonate and benzotriazole generally produced residual chloride at a level below that theoretically required for "active bronze disease", whereas the aqueous acetonitrile. 1% sesquicarbonate and deionised water leave higher amounts of chloride in the artifacts.

For cleaning of an object the most difficult problem is to decide how much to clean. Very often the metallic carvings and designs are fully corroded, and if removed during the process of cleaning the object will be reduced to a lump of metal with no archaeological or historical signifinance. For this reason, it is very necessary to examine the object very thoroughly making sure that none of the corrosion products which are important from the point of view of designs are removed. Quite often such a situation can be achieved only by mechanical means because chemicals may take away all the corrosion products.(59).

For progress of 'bronze disease', humidity is very necessary and therefore control of humidity would be one of the methods for its control.

R. M. Organ studied the various aspects of bronze patina and has described some methods to maintain the object in a dry atmosphere in a relative humidity condition not exceeding 50%. 40% relative humidity will be still safer. Under such dry conditions, cuprous chloride is stable. However, such dry conditions are not practical to have in all museums particularly in the humid climate. There is therefore, need for other methods.(60).

In this respect, protective coatings could play a positive role. Protective coatings could also save the objects from pollution effect. Smith and Beale undertook experiments to evaluate the effectiveness of various plastic and wax coatings in protecting out-door bronze sculptures exposed to acid deposition. Their experiments are still continuing but the preliminary conclusions drawn by them show that both the plastics and waxes tested are measurably effective in protecting bronzes exposed to acid deposition. (61).

Covering the object with an oxide layer has also been applied with great success. (62). The column of King Sigismundus-III Waze, a unique work of art in Warsaw, Poland, was erected in 1644. During the World War-II, the column was completely in ruins; some parts were totally destroyed and some were lost. In 1948-49, the column was restored and missing parts were completed. All metal parts were mechanically cleaned and their surfaces were covered with a thin layer of sulphide. Later, it was found that the metal parts of the monuments were seriously affected by corrosion. On examination it was found that corrosion was occuring below the sulphide layer also and therefore, total removal of the corrosion products was necessary. The problem was studied in great detail and it was then decided to form a layer of copper oxide, first cuprous and then cupric.

The conservators used a mixture of potassium sodium tartrate, EDTA and sodium hydroxide to remove the corrosion products. A thickening agent was added to make a paste. After the corrosion products were removed, the column was washed with running water, rinsing was done with a 5% solution of citric acid. Oxidation layers were formed by using hot solution of alkalies with the addition of oxidizing agents. Finally all the bronze elements were coated with microcrystaline wax, using a 5% solution in xylene.

The question of protective coatings for metals is an area having great significance. Nevertheless, it is true that this is an aspect in which much work has not been done and should be undertaken with all seriousness. It is of greater relevance to humid climates where the corrosion is very fast.

Many of us do not realize that metal objects are also affected by microbial deterioration, for example, it is well known that copper objects found in damp soil are often covered by a black layer of copper sulphide. It is observed that this copper sulphide is produced by the hydrogen-sulphide obtained by sulphate-reducing microorganisms under anaerobic conditions in waterlog-ged soil.(63).

Several instances have been quoted in literature giving observations of this phenomenon.(64). This has been dealt with in more detail by Dr. Shashi Dhawan.

Iron

Objects of iron corrode and rust very quickly in humid conditions.

For treatment of iron objects, reduction methods, electro-chemical as well as electrolytic are the standard practices, whenever there is a good core of metal present (65).

Boiling with solution of caustic soda and treatment with sodium-sesquicarbonate are other normal procedures. (66).

Electrolytic treatment cannot be given to all types of objects. Only such objects which have enough solid metal left and have a shape can be cleaned by reduction. Those objects which have a considerable corroded layer and are not very strong when treated with electrolytic reduction process can be reduced to a lump of metal and therefore are not fit to be treated with this technique. Corrosion products are best removed mechanically using small chisels, knife, wire brush, etc.

Those objects which are very fragile and have no metal are also treated mechanically in a way that the original shape remains, even though in a corroded form. Local shaping after removing powdery corrosion dirt, etc. can be done.

A protective coating of micro crystalline wax has been recommended for impregnation of iron objects. A coating of graphite can be applied to give a black, slightly metallic appearance, somewhat similar to that of a wrought iron finish(67).

Electrolytic reduction has been a standard method of archaeological metallic objects. A technique developed by Aldaz *et al.* used local reduction of corrosion. In this technique the object is made the cathode and the electrolyte is a solution of sodium hydroxide. A plastic cylinder contains the electrolytic solution within which there is a cylindrical bar of carbon or other materials that act as the anode. A porous tip is placed at one end of the tube. A drop of solution is placed on the area of the object to be treated which has already been made the cathode. The porous tip is put in contact with this area. Thus the electrolytic contact is made and the reduction of the corrosion products proceeds normally.(68).

Rust from iron objects can also be removed with thioglycolic acid. Stambolov and Van Rheeden reported that rust on iron can be removed in minutes with organic compounds containing one or more thiol (-SH) groups (69). This report was based on U.S. Patent filed by Krockhow in 1966. The most suitable thiol compound for rust removal was ofund to be thioglycolic acid. The derusting takes less than an hour to be completed. Thioglycolic acid mixed in an inert thickening matter such as CMC, glue or gum can also be used for local application.

A method for the removal of rust from iron object is based on the action of sodium salt of ethylenediamine tetra-acetic acid (EDTA). This is a very reliable method but slow (70).

Sodium gluconate is also very effective in derusting, however, when the rust is thick and contaminated with clay and calcareous deposit, its action is slow.

North and Pearson have suggested treating iron objects in a hot alkaline sulphite solution. Basically, it is a reduction process and is said to be very quick and effective. (71).

Girberg and Seeley have studied the alkaline sodium sulphite reduction process for archaeological iron and they came to the conclusion that the effectiveness with which the alkaline sedium sulphite reduction method extracts chlorides from marine cast iron artifacts is maximum when the concretion layer is not allowed to dry and undergo oxidation prior to treatment. They are of the opinion that the method would be most effective if applied immediately upon excavation of the artifacts, thereby inhibiting the transformation of ferrous compounds and amorphous material present to ferric oxyhydroxides, which would then not be capable of undergoing reduction to magnetite. However, fragile iron artifacts treated in this manner may disintegrate because of the evolution of hydrogen gas causing concretion layer to disintegrate.(72).

The mechanism of corrosion of archaeological iron during its burial underground and later treatment has been the subject of a study by Turgoose. He has also examined the question whether corrosion of iron continues during washing in sodium hydroxide solution. He came to the conclusion that corrosion may continue in sodium hydroxide solution. (73).

Removal of chloride from deteriorated iron objects is considered to be extremely important for their stabilization. A statistical method was used by Keen and Orton to determine whether chloride removal treatment had been effective. Their conclusion is that objects which had been treated, using desalination methods, corrode less than untreated objects. It is therefore, necessary to evolve better methods of removal of chlorides. (74).

The mechanism by which chloride are removed from iron objects found under sea during washing methods have been the subject of investigation by several laboratories. North and Pearson compared the decomposition rates of FeOCl and the chemical extraction rates and concluded that under most conditions, the chloride removal process is diffusion controlled.(75).

A method of removing chloride from iron objects consists of heating the object at a sufficiently high temperature to about 860°C. The chloride volatilises at this temperature and the object is stabilised. A modification was introduced by Arrhenius et al. who used a hydrogenated atmosphere at 800 to 1000°C to overcome the difficulty of surface sealing.

In order to study the effect of heat on the metallurgical structures of various types of cast and wrought iron, experiments were conducted by North *et al.* It was shown by them that the original metallurgical structures can generally be preserved through heating if the maximum treatment temperature does not exceed 400° C.(76).

This question was further examined by North and Pearson when they determined the thermal decomposition reactions of prepared FeOCl in inert, oxidising and reducing atmospheres. Pure dry hydrogen was found to be the best atmosphere for use in thermal stabilisation treatment. But to achieve complete chloride removal, the required treatment temperature will be much above the limit of metallurgical stability.(77).

The effect of heating on the metallurgical structure of iron object was also studied by Tylecote and Black.(78). They studied the effects of heating and cooling in ferrous materials in different atmospheres. The effect of hydrogen and nitrogen on the mechanical properties of iron were also studied. On the basis of these studies they came to the conclusion that hydrogen reduction process should not be used on an artifact whose structure is unknown. As an example if there are some objects containing iron and steel in a decorative fashion hydrogen reduction process will completely ruin the decorations. If we are first of all to find out the types of the object the whole advantage of the hydrogen reduction process, which is the speed, will be lost. They, therefore, recommended that the use of hydrogen reduction process should be confined to those objects whose composition is accurately known. The need seems to be to perfect a process and its structure in any manner.(79).

A method based on the application of low pressure hydrogen plasma has been experimented upon for the restoration of iron artifacts. The method efficiently removes chlorides and thus prevents any significant corrosion of objects afterwards. The treatment has to be carried out in a quartz discharge tube which is surrounded by external water-cooled electrode made of copper. The method depends on reduction of iron artifacts in hydrogen at an elevated temperature. Patscheider and Veprek have developed a technique in which the treatment temperature is less than 400°C. This temperature does not introduce any irreversible changes in the wrought iron, preserving its original composition, structure, inclusions and morphology, which contain important information on the origin and manufacturing methods of the artifacts. It is claimed by the authors that the method is simple, safe and significantly faster than the conventional washing. (80).

A washing process for archaeological iron using Soxhlet extractor has been described by Scott and Seeley.(81). Highly deteriorated iron objects cannot be treated in strongly reducing solutions, such as alkaline sulphite because it is likely that the object might completely disintegrate. Only washing cannot remove chloride ions completely. Washing in hot water, or in many changes of distilled water, removal of chloride with solutions are the standard practices for cleaning iron objects. However, since water and oxygen are always present in the process, rusting and oxidation also continue simultaneously. In the Soxhlet washing process, the object is completely engulfed in the container and the air in the container is replaced by an inert gas such as nitrogen. In Soxhlet washing, water contained in the flask is heated to boiling and the vapour is condensed by the reflex condenser which slowly fills the Soxhlet container with freshly distilled water, until the level of the syphon is reached when the liquid is returned by the syphon to the flask. The water in the flask boils and so the cycle is repeated. Pure nitrogen is introduced in the flask through which it passes to the container, and thus washing is done in an inert atmosphere of nitrogen.

Preservation of iron objects recovered from the sea presents special problems. Objects recovered from sea are almost always encrusted with coral, shells, hard soil and other concretions. These encrustations are removed with the help of chisel, drills, knife, etc. as far as possible and thereafter chlorides are removed with the help of normal procedures. Electrolytic treatment is also applied to objects having solid metal. (82, 83).

A problem often faced by the conservator is the prediction of the extent upto which iron objects are mineralized. It was shown by Watkinson that the weight/volume ratio of iron work can be used with a reasonable degree of accuracy to predict whether an artifact is totally mineralized or not. He determined the ratio weight/volume of iron work from four archaeological sites. From

his experiments, it was interesting to note that total mineralized iron objects generally contained much less chloride than do iron objects retaining a metallic core.(84).

Coatings for Iron objects

It goes without saying that cleaned and treated iron objects should be protected against further corrosion. Different types of waxes, resin solutions, varnishes, grease, and oils have been used as protective coatings for iron objects. However, most of these coatings have limitations. It is necessary that these coatings form a continuous and unbreaking layer to be really effective. Quite often, this is difficult to achieve. Moreover, most of the coatings change in nature and in appearance and therefore, have an effect on the preservation of iron objects.

Several methods have been suggested for the treatment of the metal itself thus changing its surface composition which is passive to the effect of water vapour.

Pelikan suggested a method for protecting iron objects by creating amorphous phosphate coating. (85). According to Pelikan these coatings fulfil the high demands of both corrosion resistance and aesthetic appearance. Amorphous phosphate layers have the same corrosion resistance as the crystalline phosphates. The formation of crystalline phosphate produces an undesirable colour on iron. On the other hand, amorphous phosphate layers form coating of light grey colour which is almost invisible on metal surface.

The method first of all appeared in a British Patent suggesting the use of suitably adjusted solutions of molecularly dehydrated phosphates, particularly sodium hexa metaphosphate. Pelikan carried out detailed investigations and determined the optimum conditions for the composition of solutions, its pH, temperature and time required for the formation of a suitable coating. A pH of 5.6 was found to be the most effective in the formation of corrosion-resistant amorphous coatings of phosphate. The thoroughly cleaned object is suspended in the bath and connected to the positive pole of the source of voltage. A carbon electrode is made the cathode. About 10—20 minutes are required for the formation of a phosphate layer. The current required is 2mA/sq. cm of the area to be protected.

After the phosphate treatment, the object is washed in running water and dried at 110°C. After the object is dried, it is coated with an acrylic solution of vaseline or micro crystalline wax.(86).

For protecting iron, tannins have also been used. In some archaeological excavations, it was found that iron objects which remained in cortact with some types of tannins remained in excellent condition. To preserve the objects having a light rust, the object is first of all thoroughly cleaned and while it is still wet, it is rubbed over with a tannin solution, prepared by dissolving 200 gms of tannins in a litre of distilled water and 115 c.c. of methylated spirit.

Tannins may also be used on objects having thick layers of rust, which with the application of the tannin solution are converted to a powdery material which is easily removed mechanically by brushing.

This method is best suited for objects combined with some organic material like wood. After cleaning of the iron parts, tannin solution is applied on the surface.(87).

Lead

Normally the corrosion products on lead objects are lead oxide and lead carbonate.(88).

Examination of a lead paten belonging to the 11th century showed that the chief corrosion products on the paten were lead carbonate, lead dioxide. lead oxide and lead sulphide. Analysis was done by X-ray diffraction.

The generally used method of treating lead objects is reduction. Besides, electrochemical or electrolytic reduction, a method of consolidative reduction has been described by Organ while treating the wholly mineralized silver. (89). In this method partly rectified, very low density curvent is used for reducing the objects. Platinized titanium is used as the anode while the object becomes the cathode. The lead paten was treated with this method for 3 months using a 5 percent solution of sodium hydroxide at a current density of 100 mA/cm². After conservation the lead content of the plate rose to 95% as compared to the original 13%.(90).

Caley has presented some studies on the examination and cleaning of several lead objects discovered in the excavation of Agora at Athens in 1937(91). He has reported that all the objects were corroded by various agencies, some superficially, most of them moderately, and one severely. Examination of corrosion products showed that lead carbonate was the principal lead corrosion compound present in all the coatings and encrustations. Another compound identified by Caley was lead dioxide, Plattnerite. This is always found next to, or very close to, uncorroded metal in the form of an extensive thin layer, or in the form of very thin isolated patches. Such layers or patches were dark brown in colour and when present on the surface of the metal gave the appearance of a film of dark brown paint. Lead monoxide, Massicot or red lead are the composition of lead dioxide.

For the treatment of lead objects, Rathgen as early as 1924, recommended their electrochemical reduction using zinc granules and nitric acid. (92). This treatment has been criticised on the ground that much or most of the lead during electrolysis of lead solution will go to the anode and deposit there as lead dioxide and therefore, the process will not be a success. Most probably the lead carbonate was removed by the action of the nitric acid. However, nitric acid is a very good solvent for the metal itself.

Lucas used dilute acetic acid for treating lead. Nevertheless, acetic acid also dissolves some lead. (93). Sulphuric acid was also used but it is not much effective for removing the corrosion products because basic lead carbonate is converted into insoluble lead sulphate.

Caley used cold dilute hydrochloric acid for treating lead objects. Hydrochloric acid was diluted one part by volume of concentrated reagent grade of specific gravity 1.19 with 10 percent by volume with, distilled water. The object was kept in the dilute acid until all the carbonate was dissolved. The objects were then washed in hot distilled water. The object was treated with about 25 times by volume of warm 10 percent ammonium acetate solution. The object was kept in this solution till no more corrosion products were visible on the surface of the lead. Afterwards, the object was washed atleast 4 times with cold air-free distilled water. Washing is to be done carefully and the object is soaked in water amounting to about 100 times of the object. A 10 minute period of soaking was allowed for each portion of water. After taking out the object, it is allowed to dry spontaneously at room temperature, or first soaking for a few minutes in about 15 times its volume of 95 percent alcohol. After removing from the alcohol the object is allowed to dry spontaneously at room temperature.(94).

Tin

Not much literature is available on the technique of conservation of objects of tin. In fact, objects of tin are to be found rarely, however, for some countries like Malaysia, it is a very important metal.

Plenderleith and Organ have studied the problem of the decay and conservation of museum objects of tin. According to them, the stability of metallic tin is such that it can be used as a protective coating for less stable metals. Normally, tin remains bright and untarnished for long periods. However, when it is buried in the ground for long periods, it becomes grey and eventually almost white, as the surface film of stannous oxide is converted to the stannic condition.

Two types of decay have been noticed on tin objects : one which is described as a local kind of chemical decay appearing in the form of disfiguring, eruption of oxides, rather hard to the touch, and the second, known as the "Tin Pest", which is similar in appearance, but in this case the spots are soft and powdery and in time spread and puncture the metal. Studies indicate that these two types of decay are due to different causes; the first, because of chemical or electrochemical action in the ground and the second by continued exposure to conditions of extreme cold which cause a change of crystal structure, resulting in the loss of lustre and weakening of the metal. The corrosion products in tin objects are mainly stannic oxide and some quantities of stannous oxide.

The treatment of tin corrosion is the usual method of electrochemical reduction. (95).

The question of tin disease has been studied in some details by Lihl. He examined a number of tin sarcophagi. The corrosion products were found to be oxides of tin. In this particular case the most important measure for preserving the sarcophagi consisted in a reduction of the relative humidity of the atmosphere. (96).

CONCLUSION

Mentioned above is a review of only some of the significant developments which seem to be of some relevance. In fact, much more work needs to be done in all the areas. It is necessary to develop simple methods of analysis and examination. They should be non-destructive and reliable. It is not possible for most laboratories in Asia to have costly advanced equipment.

Analysis of a large number of metal objects found in various Asian countries also is essential. Very little information seems to be available. In this type of study not only the metal components but corrosion products should also be included.

Mechanism of the corrosion and rusting of iron is still not fully understood. Studies should be done for understanding this mechanism, only then we can know what is to be done for treatment.

As will be seen from the above description it would be evident that a large number of different processes of treatment have been devised, many of them actually used. In fact, it is almost baffling, as which one to choose from them; some of them need costly and elaborate equipment which may be out of reach of most of our conservation laboratories. Therefore, another very important research area to my mind is the comparative study of various methods of treatment of different types of metals—silver, copper, iron, lead, zinc, tin and their alloys.

Inspite of so much research and advancement in the field of protection of iron, suitable protection coatings which would protect rusted iron objects from further rusting are still not available. High humidity plays a role in accelerating rusting and scaling of rust layers. How can it be prevented, is still a question mark. A programme of study for developing techniques of providing protective coatings to rusted iron objects is also a great necessity.

Work has also been done on developing corrosion inhibitors for various metals like copper, iron and silver which corrode very rapidly in the atmosphere, even after treatment. Can there be a coating or some other technique by which further corrosion can be prevented? Some work has been taken up at the NRLC for the study of some natural products for prevention of corrosion of brass and bronzes. More intensive work needs to be done in this area as well.

I am sure there are more areas which need to be researched upon. The need, I feel, is to evolve and pursue collaborative programmes.

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METHODS OF TREATMENT OF IRON OBJECTS

V. C. SHARMA

INTRODUCTION

RON is thermodynamically unstable in the presence of moisture and is most susceptible to rusting. Fine rust that appears on museum objects creates favourable conditions for rusting to continue and, in the process, objects are progressively destroyed. Contaminated iron objects deteriorate at much faster rate depending upon the amount and composition of electrolyte. Moreover, the iron objects deteriorate even at low humidity than generally expected, if infected with salts. Also, corrosion products, particularly the chlorides in excavated iron objects, react with the humidity in the presence of atmospheric oxygen. Droplets of a yellow solution, the so called ferric chloride, appear on iron objects that exfoliate and crack after excavation.

Iron objects for chemical treatment can broadly be categorised into two groups (i) museum objects with thin rust layer and (ii) archaeological objects from soil or marine environment with thick rust layers. Light rust on museum objects needs to be removed to stop further rusting of metal iron whereas archaeological iron objects necessitate the elimination of chloride for stabiliza-

The aim of the paper is to describe different methods for the removal of thin rust layer from museum objects and elimination of chlorides from archaeological objects. Before various methods are described, it is felt necessary to emphasise that rust promotes rusting, iron objects deteriorate at low humidity, metal iron corrodes at accelerated rate in the presence of salts, and objects of iron after excavation coming in contact with air crack and eyfoliate.

Deterioration of Iron at Low Humidity in Museum Environment

Iron in the presence of atmospheric oxygen and water gets converted into a hydrated form of iron oxide i.e., rust. The hydrated rust is mainly limonite, FeO.OH. It being amorphous, cannot protect the metal underneath. The porous limonite serves as a reservoir for humidity in humid environment, and once rust has formed, even briefly in a contaminated environment, rusting takes place even at very low humidity than generally expected. That is why, it is most difficult to preserve iron objects in museum environment. It is expected that iron in contact with ferrous chloride would corrode at a humidity of 55% and above. However, laboratory experiments(2) corroborate the known observation that iron objects rust at very low humidity in muesum environment. It has been shown that between 20-44% R.H. iron in the presence of ferrous chloride (FeCl₂.4H₂O.) reacts with the formation of FeO.OH. The mechanism of reaction occuring in the range of 20-44% is uncertain but it is possible that β FeO.OH is initially produced at the point of contact of FECl₂4H₂O crystals and iron and that this β FeO.OH is hygroscopic . In this case, a thin film of adsorbed water may exist below 44% R.H. thus producing the necessary aqueous for corrosion.

Corrosion of Iron and Seeel in the Presence of Salts

The overall corrosion reaction for the iron can simply be explained by the following two reactions :

 $4Fe \rightarrow 4Fe^2+$ 2e(anodic reaction) 20₂+4H₂O+8e \rightarrow 8OH (cathodic reaction) or $4Fe+2O_2+4H_2O \rightarrow 4Fe(OH)_2$

In the presence of oxygen, the ferrous hydroxide will be converted to rust, Fe₂O₃.H₂O

 $Fe(OH)_2$ is soluble (0.9%) in pure water, but slight oxidation renders it appreciably less soluble. Thus, in the presence of water and oxygen alone, the corrosion product may be formed in close contact with the metal and attack is stiffied. In the presence of an electrolyte, such as sodium chloride, however, anodic and cathodic reactions are modified, ferrous chloride being formed at the anode and sodium hydroxide at the cathode. These two compounds are very

soluble and not easily oxidised, so that they diffuse away from the sites of formation and react at a distance from the metal surface, to form ferrous hydroxide, or a basic salt, which then combines with oxygen to form rust with regeneration of sodium chloride(3).

$$F_{c}C1_{2}+2NaOH \rightarrow F_{c}(OH)_{2}+2NaC1$$

$$4F_{c}(OH)_{2}\rightarrow 2F_{c}O_{2}H_{2}O+2H_{2}O$$

Consequently, rust is formed at a distance from the metal and stiffing can not occur, and bare metal surface continues to corrode unprotected.

Stability of Excavated Iron objects

Excavated iron objects, containing ferrous chloride on exposure to moist air outside, react with atmospheric oxygen and humidity. The overall reaction may be represented as follows : (4).

$$4Fc^2 + O_2 + 6H_2O \rightarrow 4F_cOOH + 8H +$$

The acid produced will cause the pH to drop, until the solubility of FeO.OH becomes significant and then ferric ions will remain in solution, giving rise to the 'weeping' of objects. If the sites of FeOOH precipitation are localized, the formation of solid may give rise to local stresses which could eventually cause fracture. Also the acid produced will cause the dissolution of other corrosion products such as magnetite, thus assisting the propagation of cracks and aid in the disintegration of objects.

In the objects that do not possess a metallic core, the only ferrous ions that can take part in the above reaction, are those which were present at the time of excavation. Their concentration would be expected to be low in totally mineralized objects, unless corrosion has only just proceeded to completion. Therefore, a consequence of the above explanation for the deterioration of objects is that objects with no remaining metal should be much more stable than those with a metallic core.

Chemical Cleaning of Museum Iron objects

Rust is the number one enemy, especially, having chloride salts. If left unchecked, the chloride ions will pit the metal and eventually destroy the object. Overtreatment is the number two enemy. Leave the object alone unless you know what you want to do and are certain that you want to remove the surface layer.

I will briefly review the various methods of treatment of iron objects.

1. Light uniform rust from swords, daggers, firearms, etc. can be removed by diluting commercial thioglycolic acid to 28.4% to which sufficient ammonia has been added to make pH-7(5). Iron object is immersed in the solution until complete removal of rust. Occasional brushing off of the loosend rust accelerates cleaning. Since, thioglycolic acid readily attacks exposed iron surfaces causing considerable damage this method finds application to remove uniform layers of rust as long as the progress of the treatment is monitored. The method is not widely used.

Oxalic and citric acid are also used as stripping solutions for iron. Although solution of oxalic acid is useful for removing iron stains, in practice, it removes rust layers very slowly and is therefore not recommended(6). 3.5% solution citric acid is used to remove magnetite. pH is adjusted to 3.5 with ammonia.

- 2. 250-500 gm. phosphoric acid, 5-20 gm. sodium carbonate, 3-10 gm. zinc oxide or manganese oxide, 0.5-2 gm. non-ionic detergent and 500-700 gm. water is another useful formulation for removing rust from historical museum objects(8). This however leaves a thin grey protective film on the cleaned metal. Therefore, this method for cleaning is only to be opted when the object has to be painted afterwards.
 - 3. The most common sequestering agent used for stripping iron is ethylene diamine-tertraacetic acid (EDTA). Since EDTA is only slightly soluble in water, it is modified with sodium hydroxide for use as a stripping agent. In removing rust from iron objects, 5% aqueous solution of EDTA disodium salt which has a pH of 4.5 is used though the optimum pH for EDTA to complex Fe II and III are 5 and 1 respectively.
 - 4. Commercial rust removers are generally quite powerful in their action. But their use is not recommended because the nature of their constituents is generally not known.

Stabilization of Excavated Iron Objects

The main aim of the stabilization process for excavated iron is to remove the chlorides from the corrosion products. If these are not removed they catalyse the corrosion of the artifacts rapidly causing serious damage and object crack and exfoliate.

All the treatment described below involve the extraction of the chloride ions into a wash solution. It is essential to monitor the chloride ion concentration in the wash solution so that the progress of the extraction can be followed. In all these processes, the rate of chloride released from the artifact is controlled solely by the chloride diffusion rate in the corrosion product. Consequently, any operation which increases the chloride diffusion rate will improve the treatment efficiency and reduce treatment time.

Sodium Sesquicarbonate Method

This method of application involves immersing the objects in 5% W/V solution of sodium sesquicarbonate which is changed frequently in the beginning and once a week afterwards, until the objects are free from chloride and the extraction of chloride is significantly slow(11).

Sodium Hydroxide Method

Artifact is cleaned of accretions and immersed in a 2% aqueous solution of NaOH. The chloride content of the solution is monitored and the NaOH solution is changed as necessary until the chloride extraction is finished. Generally sodium hydroxide solution is changed daily for a week to remove large amounts of chloride. Afterwards the solution is changed once a week, till such time chloride extraction is finished. Treatment is presumed to be over, if the chloride level remains unchanged for four weeks in the treatment bath. If the level has risen, say, by 10 ppm, weekly washing is continued till extraction of chloride is over.

Sulphite Method

The alkaline sulphite method(12) is based on the fact that the iron corrosion products are more dense when reduced. The main corrosion products, iron oxyhydroxide, FeOOH; sp. gr. =2.4-3.6 g cm⁻³ and iron oxychloride, FeOCl, sp. gr. =3.1 g c³m⁻³ are reduced appreciably to magnetite Fe₃O₄, sp. gr. =5.2 g cm⁻³. Hence the increase in the porosity of corrosion layer and consequently, rise in the diffusion co-efficient. The increase in diffusion coefficient with this method may be as high as by a factor of 500 but will depend on the initial composition of each sample. While this method does appear to satisfactorily stabilize the artifacts, there are problems in removing the residual reactants. They do not seem to injure the artifacts, but they can produce unsightly white crystals on the surface.

This method was originally developed to treat iron objects salvaged from sea. But, it has been found suitable also for the treatment of archaeological objects, dug out from soil covered with a thick reddish-brown corrosion layer, and iron with a thin blackish corrosion layer has been stabilized using this method(13).

The method of treatment is to immerse the objects in a solution made up of 20 g/l sodium hydroxide (NaOH) and 252 g/l sodium sulphite (Na₂SO₃.7H₂O) in sealed containers maintained at 60°C for one week. During this period the solution may develop a brownish colour. After one week the objects are removed from the solution and then placed in a fresh bath of the alkaline sulphite solution in closed container maintained at 60°C. The solution is changed weekly until no colour can be observed at the end of the immersion period. Even after there is no colouration in the alkaline sulphite solution, atleast two solution-changes should still be carried out (i.e. a total of three one-week immersions). The solution does not attack any residual metal so there is no danger in giving too many immersions.

When these stabilization treatments are complete, the objects must be washed. This can be done by completely immersing them for one hour in baths of distilled or deionised water (twice) and then in 0.1 M (32g/1) barium hydroxide Ba(OH)_{2.8H2}O.

Some white deposits may be observed on the object after it has been removed from the barium hydroxide solution, especially in cracks and crevices but these are quite easily removed with a needle or a brush.

The object should be washed again by immersion in distilled water or deionised water for one hour and then dried. Immersion in a solvent such as acctone or industrial methylated spirit would assist rapid drying.

A suitable finishing process such as wax or lacquering depending on the nature of the object, may be carried out if necessary(14).

Lithium Hydroxide Method

This method is based on the fact that LiCl is easily soluble in alcohol whilst LiOH is only sparingly soluble, as can be seen from the Table.

Ethanol	Isopropanol	
1 ·8 gm/l	Traces	
	Ethanol 1 •8 gm/l	

During the process, the chloride ions of the corrosion are exchanged with hydroxide ions and lithium chloride is dissolved in the alcohol according to the process.

$LiOH + Cl \rightarrow LiCl + OH$

The great advantage of the LiOH method is that it is a much less violent treatment than almost all other methods available for conserving iron ore.

Objects are carefully cleaned and totally dehydrated in a mixture of equal volumes of methanol and isopropanol and under vigorous stirring in repeated changes of liquid. Total dehydration is important, because even a small residue of water may invalidate the following processes.

Thereafter the objects are placed in equal volumes of pure anhydrous methanol and isopropanol, to which is added 2 gms of LiOH analytical grade per litre solution delivered as a 33% solution in pure ethanol. The washing out of chlorides takes place under automatic stirring in a tightly scaled glass tank. It is continued until no change of the chloride concentration can be measured; sometimes the whole process taking several weeks to complete.

The objects are then impregnated either with micro-crystalline was or clear lacquer.

Electrolysis

This method (15) is mainly for treating marine iron. The method is very similar to sodium sulphite method except that the ferric compound reduction is achieved by electrical means, instead of chemical. This reduction produces a decrease in volume occupied by the iron compounds and a corresponding increase in the porosity of the corrosion products. As the porosity increases, so does the rate of chloride diffusion through the corrosion product into the wash solution. During electrolysis, no reduction of iron oxides to metallic iron occurs. In case of wrought iron objects a rapid evolution of hydrogen is deliberately produced during electrolysis as this removes residual accretions and loose corrosion product from the metal. Electrolysis works best for those wrought iron artifacts which have a solid metal core but retention of the surface corrosion product is not possible. With care, electrolysis can also be used for cast iron artifacts, provided solid metal core remains. Electrolysis should not be used for completely corroded artifacts.

Due to difficulties in determining surface area and current densities through a corroded artifact, it is better to use voltage, rather than current control. A voltage of 4 volts, which causes vigorous hydrogen evolution, is used for wrought iron. With cast iron, 2 volts is applied for initial 48 hours then the voltage is increased until H_2 evolution just commences (generally between 2.3 to 2.5 volts). Rapid evolution of hydrogen from cast iron must be avoided, as this will cause blistering of the graphitized zone. Anodes of mild steel, must have large surface should not be closer than 20 cm to the artifact. An exception to this rule is the case of cannon barrels. In this case, a mild steel anode rod inserted into the barrel, during the first 8 weeks of electrolysis is only to ensure the reduction of the interior barrel surface with cast iron artifacts. Once the ferric compounds initially present are reduced to magnetite, the continued passage of an electric 4--643 NRLC/88 current has very little effect on the rate of chloride release from the artifact. Consequently, a repeated treatment cycle of 4 weeks on and 8 weeks off, has proved just as effective for cast iron, as continuous electrolysis.

The bulk of accretion must be removed before commencing electrolysis. It is essential to obtain good electrical contact to the metal of the artifact. With wrought iron this can be achieved by wire-brushing an area to remove corrosion products and then clamping the electrical leads on this area. For cast iron artifacts it may be necessary to drill a small hole through the graphitized zone into the metal core to obtain a good electrical contact.

Care must be taken to ensure that the entire surface of the artifact is treated. Small objects should be suspended from wires and large objects which need supporting stands, must be rotated The chloride concentrations in the electrolysis solution must be monitored.

Soxhlet Washing Process

This method (16) has been recently reported for fragile excavated iron objects, which cannot withstand treatment in strongly reducing solutions, such as alkaline sulphite. In the ordinary washing methods, hot water or changes of distilled/deionised water, were employed by many laboratories to remove chloride ions, fragile objects continue to rust and oxidise. In the use of soxhlet washing process, the objects are treated in enclosed space, this allows air in the system to be replaced by the inert gas, such as nitrogen, thereby ensuring that apparatus is oxygen-free. This important distinction exists between simple hot-washing and washing with soxhlet technique under nitrogen. In the soxhlet washing technique, chloride ions are removed from fragile and mineralised objects in the absence of oxygen and iron objects remain free from corrosion and oxidation.

For this treatment, very fragile or fragmented material should be carefully wrapped in fine nylon netting to prevent the accumulation of debris in the base of the extractor. The base of the extractor can also be cushioned with glass wool. Having introduced the objects, nitrogen is then admitted to the apparatus and the soxhlet heating mantle is switched on. 10 to 15 cycles of the soxhlet have been found to be sufficient to remove most of the water soluble chloride content. The provision of the stopcock at the base of the soxhlet allows small samples of wash water to be removed at any stage in the process for monitoring chloride content, whilst the total amount of chloride ion removed can be checked by testing a sample of the water contained in the flask itself. If the washing cycle has to be interrupted, it is better to stop the process, whilst the soxhlet chamber is full of water to prevent partial exposure of objects.

Anion Exchange Resin Method

To develop an improved method over the existing methods and easy in operation, experiments were conducted at NRLC, using anion-exchange resin for the removal of water soluble chloride from archaeological excavated iron objects. The method has been found to be quite useful. As treatment bath is alwavs free from chloride ion, the treatment is rapid, particularly for the objects having metal core. The objects during treatment need minimum attention. Objects during treatment are not contaminated with any chemical and hence, do not require any washing, once the treatment is over. Lastly, because the resin can be regenerated and used again and again, the process is economical.

CONCLUSION

Various methods have been outlined in this paper for the cleaning of rust and stabilization of chloride infected iron objects. Also, various problems encountered in the preservation of iron objects have been elucidated so that the urgency and necessity of treatment is appreciated by those who are responsible to treat them. Full details of these treatments can be found in the papers referred in the text. Provided right treatment is choosen, methods give consistently acceptable results.

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TREATMENT OF CORRODED COPPER COINS

D. C. MEHROTRA

INTRODUCTION

A hoard of 65 ancient copper coins from the village Ballhari. District Banda, (U.P.) was brought to the chemical laboratory of the State Museum, Lucknow for treatment. Almost all the coins were highly corroded and completely covered with green and black salts of copper. Nothing was visible on them and the legends were covered with corrosion products.

Preliminary Examination

Before proceeding to the chemical treatment, these coins were examined for giving proper treatment. For this, a small portion of the incrustation, i.e., the corrosion product was detached from some coins and was chemically tested.

The acid redicals were found to be mostly chloride and partially carbonate; the metal was copper.

Treatment

- 1. Washing with hot water to remove earthy matter and the soluble salts.
- 2. The coins were dipped in a 10 percent solution of sodium sesquicarbonate. The solution was found to turn blue after a few hours. The next morning, the coins were thoroughly washed under tap water and were replaced in the solution. The solution was changed after every third or fourth day and at the same time brushing and the mechanical cleaning was also done. The process continued for about six weeks and the solution was changed at intervals for removal of chloride ions. The amount of chloride was found to be progressively lower until at the last stages, only a few traces could be noticed.

Subsequently, the coins were thoroughly washed under running tap water for about 4 to 6 hours and finally with distilled water, until the washing showed no trace of soluble salts.

Finally the coins were thoroughly dried and coated with 1% solution of polyvinyl acetate to protect against harmful atmospheric agents.

Result of Treatment

All the hidden inscriptions on coins were visible in their natural copper colour.

These coins were treated in April 1986 and are kept under observation and no adverse effect has been noticed.

(24)

OBSERVATIONS ON CORROSION OF BRONZES ACQUIRED FROM TREASURE TROVES AND THEIR CONDITION AFTER TREATMENT IN THE GOVERNMENT MUSEUM, MADRAS

N. HARINARAYANA

HE Government Museum, Madras has the largest collection of South Indian bronzes which are the toast of art connoissuers everywhere. The bulk of the bronzes in the collection has been acquired through treasure trove finds in the State. According to the existing Treasure Trove Act, any chance find of objects made by digging, belongs to the Government and is ultimately deposited in a central repository for each state. For Tamil Nadu, the Government Museum, Madras is the central repository. There is a constant inflow of such finds in this Museum ranging from bronzes and coins to jewellery and pottery. After being received in the Museum, these finds are duly catalogued, given preservatory or restoratory treatment and put on display or in the reserve, depending on the uniqueness or otherwise of the find.

Having been under the earth for quite a large number of years, possibly for hundreds of years, these objects, when discoverd, are covered with layers of earthy matter as well as products of corrosion. The materials of the objects must have been interacting with the moist earthy matter around and salts present in it. Quite often, the objects, especially the smaller ones like coins or jewellery, are found kept in metal containers, but this safe-keeping inside containers had not made them proof against chemical reaction with the moisture and the salts around. Quite often, coins are discovered lumped together, into a hard mass of metal, corrosion product and earthy matter. There have been bronzes which even when received in the Museum had heavy incrustations on their surface.

It is to be expected that the interaction between the material of the object and the earthy matter around it would depend on the chemical composition of the material of the object, the condition of the surface of the object, the composition of the earthy matter surrounding the object and the pressure of the earth above it (i.e. the depth at which the object is found). It should be possible to relate all these factors to establish why the surface deterioration has happened in the way it has actually happened and to derive some conclusions about the mechanism of corrosion under the earth on objects of metal. Considering the unique set of conditions in which the objects had been lying inside the earth for a long span of time and the difficulty of reproducing such conditions exactly in the laboratory, studies of these objects, their corrosion products, and surface encrustations and surrounding soil could be rich source of knowledge about deterioration of materials under the earth.

But one snag about treasure trove finds undermines these possibilities. Treasure troves are chance finds, brought to light by non-scientific people who, in their eagerness to know what they have uncovered, disturb the digging area and possibly carry out some rough-and-ready cleaning of the objects discovered. From the find spot, the objects are taken to the nearest Revenue Department Office and then to the Collector's Office and only lastly to the Museum. All this takes a few months and even a year or two, and in the course of these passages, the surface encrustations fall off or are cleaned away. Therefore, what comes to the Museum ultimately is only a watered-down crust that may have lost some of its components. This is true of bronzes especially since they exercise greater interest on account of their iconographical features.

Inspite of this surface disturbance, a study of the crusts on bronzes is revealing. It has been found that the crusts on bronzes are divisible into three types. One is the covering of the bronze surface 'with a thick non-translucent crust which is rough and obscures the decorative details. This crust may be hard and compact. Removal of the crust may leave a bronze surface rough and pitted. The second type of corrosion crust contains light green patches which are moist. This corrosion occurs along with the other types and is very deleterious to the bronze because it has a tendency to spread all over the surface of the bronze. If unchecked the smallest patch can spoil the surface of the entire object. The third type is a thin translucent coat of minerals of pleasing colour. This coating also enhances the appearance of the bronze. Since it developes uniformly over the surface, it acts as a protective coating also. The mechanism of formation of this coating has not been adequately investigated, and artificial coatings attempted never attain the perfection of the coatings developed naturally under the earth. Of these three types of corrosion, it is generally noticed that the first type predominates. Even after the rough cleaning which might have been done immediately after the finding of the bronzes as treasure trove objects, there is sufficient amount of crust left which is an indication of the extent of corrosion taking place under the earth. The surface of the crust is generally coarse with visible siliceous or clayey particles seen here and there. Below the rough layer, there is a compact and smooth layer of clayey soil intertwined with products of corrosion. Normally, the colour of this layer is brown with patches of dull green. With mechanical cleaning, it is possible to break up the upper layers of coarse crust, but the closely knit clayey soil layer is harder to remove through mechanical means. It is also noticed that this crust remains stable even after exposure to the atmosphere. However, since this is quite a thick layer, it hides details of workmanship on the bronze. Ben Johnson in his report on 'Some South Indian Bronzes in the Los Angeles County Museum' has reported that the thickness of the crust is as much as 3 mm(1). A magnified photograph of the crust shows clayey soil and resinous crystals closely intertwined. The presence of the resinous crystals has been explained by the fact that they are air-borne particles resulting from very routine burning of resins over long periods of time.

Sometimes on these layers of coarse crusts, malignant patina is seen in the form of greenish white patches of powdery and moist salt crystals. The process of corrosion in such cases continues, and in course of time, the greenish white patches of salt spread all over the bronze. Mere mechanical cleaning does not remove these layers of salt because the salt gets settled in pores on the bronze and causes corrosion in humid conditions. It is only cleaning with chemicals or through electrolysis that enables the salt to be removed completely. It is also noticed that after treatment the bronze surface tends to show pitting wherever there had been patches of malignant patina. There was one case, of a set of bronzes of Rama, Sita and Lakshmana belonging to the Vijayanagar period, in which the surface was so porous that even after electrolytic treatment, there was recurrence of malignant patina. Such was the virulence of the salt formation that it became moist and drops of liquid formed at the points of corrosion. This set of objects had to be given intensive washing with alternate baths of cold and hot distilled water before recurrence of corrosion could be controlled.

Another interesting observation was the formation of malignant patina occurring in the case of a big musical instrument made of bronze called '*panchamukha vadyam*'. This instrument was a five-faceted drum and consisted of a bronze vessel with a covered top on which there were five tubular projections of different sizes. These open-ended projections were covered with tightly stretched skins, constituting thus the five drums of varying tonal values. In the Museum, breakages in two places on the body of the vessel had been repaired by soldering the detached pieces to the body of the vessel. It was noticed that there was break of greenish white patches of salt at the junction of the solder and the bronze of the surface. This was locally treated with zinc and sulphuric acid and the patches of salt removed. After treatment, a coating of polyvinyl acetate was given. There has been no further recurrence of corrosion for the past 20 years.

In this connection, the remarks of Dr. Paramasivan on the composition of corrosion products on bronzes are illuminating(2). He gives an analysis of typical corrosion products from a bronze belonging to the 9th century A.D. as follows :

Electrolytic Restoration of Bronze Statue Chemical Analysis (percent)

an a				 					Bronze	patina
Copper					address to the sec		4	•	83.39	76.16
Tin									16.61	15.09
Lead						100 10			Tr	Tr
Arsenic				100	19.9	a Made	1.00	a legiture i	Tr	
Iron									Tr	0.09
Water		101-								1.23
Carbon dioxid	e									1.75
Sulphuric anhy	drid	le, SO	2					Ster Ile		Tr
Chlorine								111		Tr
Oxygen										5.52
Lime CaO						-		-		0.14
										and the second se

He says, 'In some of the bronze statues, the patina invariably holds a large proportion of sand through long burial in the earth. Thus the corroding agents ever present in moist soil have converted the copper and tin into mineral compounds such as oxides, chlorides, sulphates and carbonates (malchite and azurite). With the Madras Museum specimens, the corrosion has not gone deep and there is still sufficient metal left'.

Another observation made from a study of metal objects from treasure troves is that objects of thin metal tend to get deformed. This is noticeable especially in the case of containers. Bronzes being solid escape deformation. However, in the case of one image of Nataraja from Melperum-pallam, Ihanjavur District, there is a break in the right arm. This seems to be a hollow bronze since through the broken portion, a core of earthy matter is noticed.

II was after a thorough study of the corrosion of these bronzes and their safe removal without affecting the artistic workmanship on the figures that the electrolytic process was selected as the best means of 'restoring' the bronzes. Specially designed equipment was installed for the purpose, and the treatment of bronzes has been carrid out for the past 50 years in the Chemical Conservation Laboratory of the Government Museum, Madras. A study of the bronzes so treated and an assessment of the efficacy of the method was made and the observations published in a paper in CONSERVATION OF CULTURAL PROPERTY IN INDIA Vol. XIV and XV(3). In this paper, a survey of bronzes treated from 1946 was made. On the basis of this survey of treated bronzes, it has been found that only 10% showed recurrence of corrosion. In a few cases in which corrosion recurred, it was found that intensive washing helped to remove the causes of corrosion. One particular case was that of a set of three bronzes of Rama, Sita and Lakshmana from the Vijayanagar period. The surface of these bronzes is very rough and pitted. It is surmised that the recurrence of corrosion was due to the pores on the surface holding chloride salts. In all other cases, the surface of the bronze has remained free of corrosion and the details of artistic workmanship have become visible.

CONCLUSION

Not all facets of the corrosion of treasure trove bronzes have been adequately investigated, and there is still good scope for a wide range of researchers on this problem. The composition of the bronzes and the product of corrosion may be determined in a representative selection of bronzes and, if possible, may be linked with the composition of the soil from which they were dug up. Particularly, research may be done on bronzes containing malignant patina to establish the detailed mechanism of such corrosion and its recurrence in certain cases with reference to the texture of the surface of the bronze. Such work may give new insight into the corrosion of bronzes and its prevention.

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COMPARISON OF ANALYSIS OF SURFACE AND INTERIOR OF METAL OBJECTS BY X-RAY FLUORESCENCE SPECTROMETRY AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

U. S. LAL & K. K. NARANG

INTRODUCTION

THE composition of ancient metal object has always interested conservators and archaeologists and has been determined by various techniques. W.T. Chase has suitability of analytical techniques and arranged them in decreasing order as :-

AAS, MS, XRF, wet chemical, ES, POL, NA.(1).

Our efforts are to employ non-destructive methods of analysis as much as possible thereby avoiding any damage to the objects. X-ray fluorescence spectrometry is one such technique used at NRLC. XRF technique has been used by several workers for the analysis of excavated metal objects, coins, museum, objects, etc. (2, 3, 4). But this does not solve the problem fully. Other than the limitations of sample size, sensitivity, preparation of standards, cost of instrumentation, etc., the technique of XRF provides the analysis of surfaces only. The depth reached by this technique is of the order of a few microns only. As the surfaces of ancient metal objects undergo alterations in the course of time, their superficial composition is often quite different from that of the interior. The thickness of altered surface layer is usually much more than the depths reached by XRF method. The unaltered metal usually resides in the interior and the analysis of this part can give the actual or original composition of the object.

Another very accurate technique is the atomic absorption spectrophotometry. This has been widely used for the analysis of ancient metal objects. A very little amount of sample, of the order of few milligrames is required for the analysis by this technique. Except for the fact that this technique consumes few milligrams of sample, it is free from all sorts of problems.

In this study, we have analysed some objects of three different types of alloys by both the techniques of XRF and AAS. The aim was :

(i) to study the extent of differences between the surface and interior composition.

(ii) to study the suitability of XRF technique for the analysis of ancient metal objects of different alloys.

The material taken for the present work was;

(a) Silver-Copper alloy :

- (i) Victoria coin (1880 AD);
- (ii) Silver coin (Shah Alam II);
- (iii) Alloy ring-period VII-Medieval (site-Atranjikhera).
- (b) Copper-Tin alloy :
 - (i) Dagger handle (site-Mahurjhari).
 - (ii) A metal piece (site-Khairadih).
- (c) Copper-Zinc alloy :
 - (i) A nail (site-Khairadih);
 - (ii) A copper object (site-Atranjikhera).

EXPERIMENTAL

X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectrometer (Model-PHILIPS-PW 1410-semi automatic) was used for the surface analysis of the objects. The objects have been so selected that these should fit into the sample holder (dia 51 mm) of spectrometer. Wherever necessary suitable masks were used. Bronze discs, pressed pellets of mixture of metal powders of different compositions and pure silver sheet were used as standards. Pressed pellets of metal powders were also used as standards by Padfield(5). Silver coins were used without cleaning as they appeared in good condition but in case of copper-tin and copper-zinc objects, gentle rubbing was done for obtaining suitable surfaces. Firstly, objects were analysed qualitatively and subsequently analytical conditions were set for quantitative estimation of Cu, Zn, Ag and Sn. Background corrections were made for all the measurements. Instrumental parameters are shown in Table 1.

Atomic Absorption Spectrophotometry (AAS)

The interior of the objects was analysed by taking a few milligrams of sample from them by drilling. Drilling was done by a very fine drill bit of tungsten carbide (dia 0.5 mm). The initial drillings were discarded and pure metal was taken for analysis. About 5-7 mg. of sample was dissolved in HNO₃ (in case of Ag-Cu and Co-Zn alloy) and in HNO₃+HCI (in case of Cu-Sn alloy) and the volume made upto 25 ml. From these solutions Cu, Ag, Zn, Sn, Pb, Fe and Ni were quantitatively analysed by Atomic Absorption Spectrophotometer (Model Perkin Elmer 2380). Air-acetylene flame was used for all the elements except for Sn. for which nitrous oxide-acetylene flame was used. Various parameters of the instruments were set as per the standard conditions for each element given in the instruction manual of the instrument. The standards for XRF were also analysed by AAS and the results were found to be in good agreement.

The results of analysis by XRF and AAS are shown in Table 2.

RESULTS AND DISCUSSION

The lower values for copper and higher values for silver in case of XRF analysis indicate the enrichment of silver and depletion of copper on the surface. The possible mechanism for the above results may be :

- 1. Due to higher solubility of copper in contact with soluble salts and humidity and also due to the good solubility in water of some copper corrosion products, preferential electrochemical corrosion of copper takes place.
- 2. Due to the electrochemical corrosion of silver-copper alloy with a re-deposition of silver on the surface.

Out of the three objects of this alloy, both the silver coins show marked difference between the values of copper content measured by the two techniques. This may be due to the fact that coins change hands quite often and are, therefore, more vulnerable to alteration,

Objects of Copper-Tin and copper-Zinc alloys

The results for copper-tin alloy objects (Table-2) show the enrichment of tin on the surface. This seems to be connected with the fact that migration of oxidation products of tin to the surroundings is difficult in comparison to the oxidation products of copper. The special feature of copper-zinc alloy is that it is one phase alloy (homogeneous). The alteration of these alloys is essentially superficial. Hence, the difference between the surface and interior composition is least in case of copper-zinc alloy objects. The oxidation products of zinc formed on the surface are easily transferred to surroundings in comparison to the oxidation products of copperalso a possibility of redeposition of copper from the corrosion products of copper-zinc alloy. Both these factors may be responsible for the lower percentage of zinc on the surface than the interior percentage.

CONCLUSION

The changes suffered by ancient metal objects in course of time have repurcussion on the result of superficial analysis. The difference between surface and interior composition is least in case of Cu-Zn alloy objects as compared to Ag-Cu and Cu-Sn alloys. Scouring may be required 5-643 NRLC/88

to remove the altered layer if one wishes to obtain a percentage close to the interior percentage by XRF for silver-copper and copper-tin alloy objects.

TABLE 1

Instrumental Conditions (XRF)

Target		Chromiu	m anode
kV, mA		. 60, 30	
Counters		Flow/Sci	ntillation detector
Measuring ime		. 20 secon	ds
Collimator		. Fine	
Crystals		. LiF-200	, LiF-220
Medium		. Air	
Detector gas	1.00	. B-10 (Ar	gon/Methane)

TABLE—2

Analysis of Surface and Interior of Metal Objects

Description of Objects		Major	Elements	Trace Elements Percentage (By AAS only)		
A. Silver-Copper alloy	Cu	%	Ag	%		
	XRF	AAS	XRF	AAS		
1. Victoria Coin	4.20	8.27	95.10	90.62	Pb (0.06) Zn (0.02) ; Fe (0.02)	
2. Silver Coin	4.70	12.03	95·20	86.28	Pb (0.29) ; Zn (0.05) ; Fe (0.02)	
3. Ring	42.46	48.70	55.15	49.70	$Pb(1 \cdot 10); Zn(0 \cdot 07); Fe(; 0 \cdot 10)$	
B. Copper-Tin alloy	Cu	%	Sn %			
	XRF	AAS	XRF	AAS		
4. Dagger handle	85.86	87.00	13.80	11 .20	Pb(0.88); $Z_n(0.06)$; Ni(0.03) Fe(0.20); Ag(0.02)	
5. Metal piece	75.80	78.45	23.15	19.70	Pb(0.18); Zn, Ni, Fe(0.20)each	
C. Copper-Zinc alloy	Cu	%	Zn	0/	· // / · · · · · · · · · · · · · · · ·	
	XRF	AAS	XRF	AAS		
6. Nail	82.10	80.20	15.46	16.40	Pb(0.45); Ni(0.10); Fe(0.53)	
7. Copper object	80.20	76.40	18 . 20	20.60	Pb(3.5); Ni(0.02); Fe(0.86)	

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A NOTE ON THE PROBLEMS OF METAL OBJECTS WITH SPECIAL REFERENCE TO INDIAN MUSEUM COLLECTIONS

R. K. MUKHOPADHYAY

INTRODUCTION

INDIAN Museum, Calcutta, is the oldest museum in the country having a wide range of unique objects in its collection. Metal objects in the form of beautiful sculptures, ornaments, weapons, smoking devices, domestic utensils, coins, etc. constitute an important part thereto. Moreover, a good number of metal antiquities are added to the collections through excavation, exploration, donation, single acquisition or purchase of private collections. Some of these specimens are exhibited in different galleries in a systematic fashion and the rest are kept as reserve collection in a more than century old building.

Of all the ancient artifacts that have passed down to us, objects composed of metals are the most numerous. A study of these objects not only gives us fine ornamental details, carrying inscriptions and legends (in case of coin and metal plates) but also provide valuable evidence about the art, history and socio-economic condition of the society. Any loss to such a material is irreplaceable.

In a tropical climate like Calcutta, metal antiquities (which are very seldom found in original state) are very much susceptible to deterioration due to variety of reasons. As a result, the metal antiquity requires frequent treatment for its maintenance and proper upkeep. Very often metal objects are found to undergo chemical as well as physical changes which lead to their decay and sometimes total destruction also. Adverse climatic condition, environmental pollution and corrosion reactions (internal & external) are considered to be most hazardous to them.

Metal objects in Tropical Climatic Conditions

It is quite obvious that metal objects are badly affected with the alteration of temperature and variation in relative humidity in a particular place. On this consideration, temperature and relative humidity are determined regularly in different galleries of the Indian Museum where certain fluctuations in temperature and relative humidity are always there in different seasons (like summer, rainy and winter) as shown below.

Season record for one week						Ave	rage Temperature ⁰ C	Average Relative Humidity (R/H)%		
Summer										
29/5/86 to 5/6/86							34-35	6080		
Rainy										
23/7/86 to 30/7/86							31—32	94—98		
Winter										
14/1/87 to 21/1/87							24—25	50—55		

TABLE I

Presence of excess moisture often causes detrimental egects more rapidly and temperature changes affect the metal antiquities with dimensional change. The ultimate result is slow but steady physical breakdown of the object.

Besides climatic condition, environmental pollution is always a threat to the survival of cultural heritage. Metal objects are prone to attack by the pollutants prevalent in the atmosphere. An environmental study was conducted by NEERI (Regional Centre) in Calcutta and Howrah the result of which is shown in Table II, III and IV.

TABLE II

Pollutants					Pollutants in Metric Ton (from different sources/per day)						
		Industry	Transport	Thermal Plant	Total	Present in					
Particulate Matte	rs				335(208)	16(8)	61(40)	557(419)	43		
Sulphur dioxide					44(29)	52(26)	11(6)	122(76)	1		
Carbon dioxide					164(68)	239(176)	50(33)	448(280) 35		
Hydrocarbon					52(43)	28(18)	21(19)	101(81)	, 55		
Nitrogen dioxide			•		13(11)	31(13)	7(4)	70(47)	5		

Air Pollutants & Emissions in Calcutta/Howrah

1 Metric Ton=0.9842 ton=1000 Kilogram.

(Conducted by National Environmental Engineering Research Institute).

TABLE III

Ambient Air quality standard (as notified by Central Pollution Control Board, New Delhi)

			Concentration—Microgramme per meter bube							
Area	Category		S.P.M.	SO-SO ₂	СО	NO ₂				
A. Ind	ustrial & Mixed yuse	•	500	120	5000	20				
B. Resi	idential & Rural		200	80	2000	80				
C. Sens	sitive		100	30	1000	30				

TABLE IV

Air quality of a particular traffic junction near the Indian Museum Building, Calcutta

Traffic Junction	SO3	NO ₂	NO	Total Oxidants (TO)	CO (ppm)	No. of vehicles/ min.
	m	icrogramme	re			
Jawahar Lal Nehru Road	230	354	198	213	50	40
& S.N. Banerjee Road	230	173	258	514	100	36
Junction	560	551	226	486	100	43

In the recent years with the taking up of Metro-Rail in the Chowringhee area, accumulation of dust in the galleries of the Indian Museum posed a great problem. An attempt was made for determining the amount of dust/dirt particles in a particular gallery. The result is given below :

1.2-1.4 mg/100 sq. cm. per day (when the gallery is closed for the whole day)

1.6-2.0 mg/100 sq. cm. per day (at the time of opening the gallery).

It is quite clear from the above data that the high pollution zone and adverse effect of particulate matter in and around the Indian Museum building definitely have adverse effect on the metal artifacts (directly or indirectly) either by chemical action or by abrasion effect. Due to regular deposition of dust, dirt and sooty particles on metal artifacts, an atmosphere is generally formed where acidic oxides in the environment followed by humidity have a continuous damaging ecect on the objects. The position of the Indian Museum building being by the side of the main road, damaging effect of the pollutants and hostile climatic condition always go against easy preservation and proper keeping of the antiquities including metal objects in good condition.

Causes of Deterioration of Metal Objects

Most of the metal artifacts are composed of more than one metal and sometimes more and the presence of impurities like arsenic, antimony, lead, iron, nickel, sulphur, phosphorous, berylium are also reported which facilitate casting of different types of metal objects. Generally, corrosion of metal objects take place because "in natural environment most metals are not inherently stable and tend to be converted into more stable compounds (e.g. metallic ores). Natural phenomena always favour the formation of stable compounds. Since the products of metal corrosion are more stable than the metal themselves, it follows that corrosion is a perfectly natural thing to expect.

The chemical reaction taking place during corrosion can be expressed by general equation :

Metal+Environment -> Stable metal compound—Energy.

In man-made metallurgical processes, this natural sequence is turned about-face through the local application of large amount of energy and the metals with their invaluable properties become available for human use.



But this is only a temporary situation, nature takes its inexorable course and the process of corrosion re-establishes the natural equilibrium. All man can hope to do is to halt, or rather show down corrosion for longer or shorter periods.'

The form of corrosion encountered in metal objects (in tropical climate) is complex in nature because the various metals and alloys of which they are made and the varied environmental condition in which they have survived. Sometimes, corrosion of metals is caused by direct chemical action from the soluble salts from the ground and of different deleterious ingredients present in the atmosphere. In other cases, metal objects are corroded due to complex electrolytic process and the presence of impurities present (sometimes deliberately added) in them which often accelerate these corrosion processes.

It is quite evident that metal artifacts can often form a natural electric cell (artifacts containing two or more metals) where nobler metal is well preserved at the expense of weaker metal in presence of an electrolyte like sodium chloride. Corrosion products are found to be deposited on the nobler metal.

Principles of Cleaning of Metal Objects

Different types of corrosion products are reported (through extensive study and research) for metal artifacts. Corrosion products like Cu₂O (Red); CuO (Grey to black); Cu₂ (OH)₂CO (Darkgreen); Cu₃ (OH)₂ (CO₃)₂ (Bright blue to red indigo); Na₂Cu (CO₂)₂' $3H_2O$ (Blue green); Cu₃(OH)₃ C1 (Emerald to black green); Cu₂(OH)₃ Cl, H₂O(Green blue); CuCl (Pale grey); CuSO₄ (OH)₆ (Green); CuSO₄ (OH)₄ (Green); Cu₁₉ SO₄ Cl₄ (OH)₃₂, $3H_2O$ (Bright blue); Cu₂S (Black); CuFeS₂ (Brass yellow); CuS (Indigo blue); Cu₉S₅ (Blue to black)

are infested with metal artifacts made of copper and its alloys. Irregular heavy incrustation like AgCl (Grey) and Ag₂S (Black) are known to be present on silver objects. Lead antiquities are generally having corrosion products like PbO (Yellow); PbO₂ (Brown to black); PbCO(Grey); Pb₃ (CO₃)₂(OH)₂ (White); PbS (Grey).Rust Fe_3O_4 (Brown) are the main corrosion products for the iron objects. A good number of chemical and physico-chemical mthods are in use for removal of corrosion products from metal artifacts which are found in good, moderate and fragile condition. Very often, corrosion on the surface appears to be irregular and erratic, leading to changed composition of the metal object.

For the purpose of removal of loose accretions/incrustations from the metal object suitable mild chemical agents are used to dissolve the same. Objects which had suffered from hard incrustation, reduction method by using zinc and alkali/acid gives good result. In extreme cases electrolytic method (by using a suitable anode and object as cathode) are found to be more useful in order to get clear idea about the artistic detail and hidden carvings of the object. Mechanical methods (by using knife, needle, chisel, air-abrasion unit) ultrasonic cleaning method (with the help of a machine producing high frequency vibration) are considered necessary with a few metallic artifacts having hard incrustation and suitable metallic core.

Corrosion products are generally identified in the laboratory by applying classical chemical methods and spot tests (in the absence of X-ray diffraction machine) in order to detect the harm-ful ingredients infesting the object. Preventive, curative and sometime restorative measures are undertaken by the Conservation Laboratory for the affected antiquities from time to time by following standard methods and techniques as recommended in the literature/journal, results of which are found to be quite satisfactory.

DISCUSSION

It is now well-established that moisture with the change of temperature in presence of degenerating agencies present in the atmosphere often play active role in disintegration of metal object. From Vernon's laboratory experiments in air containing moisture and trace of sulphur dioxide, it is observed that metal remains bright when the humidity is gradually increased from zero. At about 60% RH, a critical point occurs and corrosion occurs faster, at 80% RH, a second critical point occurs and corrosion becomes more rapid.

A comparison of iron, zinc and copper in presence of small amount of sulphur dioxide is studied under condition in increasing humidity.

A series of quantitative experiments conducted by Vernon sometime on copper indicates that sulphur dioxide or moisture has little effect on copper when acted upon singly but copper undergoes, serious alteration when both were present.

The corrosion o copper containing 10% sulphur dioxide and moisture provides an instructive example of critical humidity. As long as the RH of the atmosphere was less than 63% there was little action except slight darkening even at high sulphur dioxide concentration.

But when the RH is raised to about 75%, the corrosion becomes very sharp and increases with the weight of sulphur dioxide. The absorbed sulphur dioxide can collect water sufficiently for catalytic oxidation to sulphuric acid which in presence of oxygen attacks copper easily. When the moisture content was kept constant whilst the sulphur dioxide was varied, Vernon found that 0.9% SO₂ produced less corrosion on copper than either higher or lower content.

Among the art objects manufactured from different metals, artifacts made of copper and its alloys are huge in number in comparison with many other metals and alloys. So the problems of preservation lying with the copper objects are worth mentioning. Copper alloys are normally covered by a protective oxide film of Copper (1) & Copper (II). Very often chloride ions are involved in the fundamental nature of corrosion process, either exerting an influence on the kinetics of the oxidation process or assisting through the formation of corrosion products. Generally, the mobilisation of copper as Cu Cl₂ at the concentration of chloride ion about 10,000 p.p.m. is thermodynamically favourable and accelerated corrosion sets in within the object causing bronze disease. So the process of cleaning involves mainly the removal of chloride ions as well as other products also. 5% aqueous sodium sesquicarbonate; 5% citric acid with 1% thiourea; 3% benzotriazole; 5% sodium dithionate; 15% Rochelle salt with 5% sodium hydroxide, 50% aqueous acetonitrile, 10% EDTA, etc. are the common reagents used for treatment of copepr alloy which remove all the corrosion product or reduction of corrosion product to metallic state or substitution of chloride ion with inert anion.

Aqueous sodium sesquicarbonate (5%) is most suitably used to stabilise the copper object with the removal of chloride ion. But the rate of release of chloride ion is very slow with this reaction which takes much time (sometimes 6 months) to complete the treatment. It is reported that sometimes chloride ions remain inside the patina even after long treatment causing harm to the object.

Aqueous alkaline Rochelle salt (5% NaOH and 15% Rochelle salt) reacts only with copper **(II)** corrosion products forming a soluble complex but the remaining oxide layer and copper **(I)** layer are not affected with the reaction.

In thiourea inhibited citric acid reaction (5% citric acid and 1% thiourea), citric acid first reacts with copper (II) corrosion product forming soluble complex where Cu₂O and CuO are also dissolved by this acid. Thiourea reacts subsequently with CuCl and Cu₂O yielding soluble copper (I) thiourea complex but complexity of this reaction process arises when copper (II) thiourea complex produced during the reaction (small amount) oxidised thiourea forming a yellow-brown tarlike film deposit.

Acetonitrile (50% aqueous solution) reacts with copper (I) corrosion products forming a copper (I) soluble complex and releasing the chloride ion but it has no action on copper (II) salts and oxides.

. Alkaline sodium dithionate (4% NaOH & 5% sodium dithionate) is a strong chemical reducing agent which reduces both copper (I) and copper (II). All the chloride ions present in corrosion products go into solution at a very fast rate.

Of all the methods mentioned above, alkaline dithionate method is the most effective method for removal of chloride ions from copper alloys as observed by Ian Donald Macleod through series of experiments conducted by him during the last six years.

Corrosion reaction associated with metal artifacts other than copper are not extensively studied. Only traditional methods of treatment are followed in those cases.

CONCLUSION

It is well known that active corrosion of a metal or alloy occurs, when its surface is sufficiently heterogeneous (rather than homogeneous) in contact with an electrolyte. The first and foremost principle of arresting corrosion is to ensure stability to the object by physicochemical means. Sometimes treated objects require further chemical treatment if proper environmental conditions are not provided to them. A new concept of using vapour phase corrosion inhibitor (with certain limitations) for metal object could solve this problem to a great extent which will not only prevent deterioration but also ensure stability to the metal object. Satisfactory results are reported to have been obtained by different laboratories by using specific (vapour phase inhibitor) chemicals or a particular type of object. It is now high time to find out new techniques and new materials (like vapour phase inhibitor) through extensive research programme for metal object being preserved in humid climate.

In recent years with the advancement of science, sophisticated equipments are now being used by different laboratories to perform physicochemical study on metal objects and their corrosion products which often help the conservator to diagnose the disease of the ancient metal object. In near future, it is expected that conservation laboratory of the Indian Museum would be in a position to procure a few such mordern scientific equipment in order to enable the conservator to timely defect the disease of the concrned object more efficiently and expeditiously.

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CORROSION INHIBITORS IN CONSERVATION

V. C. SHARMA

THE corrosion inhibitors may be defined as "any substance which, when added in small amounts to the corrosive environment of a metal or alloy effectively decreases the corrosion rate."

Inhibitors are in use in industry for application on clean metal surfaces but in some cases their inhibitive properties have ben expolitd for corroded metals in conservation. There are, however, some problems in the use of inhibitors in cases of corroded metal artifacts. Some of these are :

- 1. The presence of corrosion products restricts access of the inhibitor to the surface of the artifact thus making the inhibition difficult.
- 2. For long term preservation, corrosion prevention is necessary, rather than simply a reduction in corrosion rate.
- 3. The appearance of treated object is very important and this generally rules out the possibility of incorporating inhibitors into multi coat paint systems or other such opaque coating.

Types of corrosion inhibitors

The corrosion of metals is electrochemical and the anodic and cathodic reactions may occur at different places on the object.

The anodic dissolution (1) must obviously occur at the metal surface. This need not be true of the cathodic reaction, which is generally oxygen reduction (2) or hydrogen evolution (3) in acid solutions.

$M - M^{n-} + ne -$	(1)
$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$	(2)
$2H_{+} + 2e_{$	(3)

The cathodic reaction can occur on the surface of any electronic conductor that is connected to the corroding metal such as another metal or graphite in the case of cast iron or conducting corrosion product such as magnetite on iron.

Chemicals that retard the anodic reaction are called as anodic inhibitors and chemicals which retard the cathodic reaction are, similarly, called 'cathodic' inhibitors. For an inhibitor to be effective as anodic inhibitor it must reach the metal surface or rather all parts of the surface. *Cathodic inhibitors*, on the other hand, only need to reach those places to which the cathodic reactants can diffuse, and this may be easier. Inhibitors may be further classified as adsorbents or film-forming, according to whether they function by causing general precipitation of insoluble products e.g. insoluble organo-metallic complex (Cu-BTA.) on the surface of copper metal. In general the chosen inhibitors for near neutral and alkaline solutions would be of the film forming type, whereas adsorption inhibitors are generally, used in acid solutions, although in both cases there are exceptions. Another class of inhibitor, vapour phase inhibitors (VPs) protect metal against corrosion in the presence of moisture and oxygen, through the emission of vapours from a against corrosion in the presence of moisture and oxygen through the emission of vapours from a inhibitor supply is not necessary. Two important features of VPIs make them of special interest to conservators. Corrosion protection is maintained as long as the VPI supply is sufficient, vet there is no permanent adsorption, thereby eliminating the problem of removing the protective substance from the object at a later date.

Inhibitors for neutral and alkaline solution

The mechanism of action of anodic and cathodic inhibitors shows that corrosion layer over metal artifacts may restrict the effectiveness of the inhibitors. The anodic ones function by formation of insoluble compounds with the metal ions at the anodic areas and these precipitates may

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either assist in the maintenance of an oxide film on the metal surface or may themselves protect it. The factors that influence the effectiveness of such inhibitors are :---

- 1. The metal composition, since metal salts must be formed.
- 2. Inhibitors concentration.
- 3. Dissolved oxygen concentration.
- 4. The presence of other anions, such as chloride.
- 5. The solution pH.

In 2-5 the relevant conditions are those at the anodic areas, i.e. the metal surface, and the presence of corrosion products may prevent these from being under the control of the operator since it will not be directly related to the bulk solution concentration and pH.

Cathodic inhibitor

Cathodic inhibitors generally function by virtue of their reaction with cathodically produced hydroxide ions and the consequent deposition of an insoluble product on the cathode surface. This film may restrict oxygen access to the cathode and lower the overall corrosion rate, since this is usually determined by the rate at which oxygen can be reduced. Unlike anodic inhibitors, access to the metal surface is not always necessary and the chemical nature of the cathode surface is often unimportant. Like 'anodic inhibitors, the efficiency of cathodic inhibitors depends on pH, since precipitation of a film must occur with only a small pH rise.

Another important difference between anodic and cathodic inhibitors is the effect when the concentration of inhibitors is too low to give complete protection. As corrosion rate is generally under cathodic control, any film formation on cathode surface will lead to a reduction in this rate. However, anodic inhibitors present in amounts too small to give complete protection do not reduce the corrosion rate at all, although some, particularly oxidising agents such as chromate & nitrite, may cause metal loss to be localised at small areas, with consequent deep pitting.

In acid solutions, adsorption inhibitors are generally used, partly because oxide films are soluble under such conditions and partly because one of the major applications is in the removal of oxide scale from metals & film formation would retared this process. These inhibitors are often nitrogen or sulphur containing organic molecules which bind to the metal surface via these atoms and retard either or both electrode reactions. Even the most efficient inhibitors do not usually totally prevent corrosion, but reduction in rate can be considerable and the problem of inhibitor access to the metal surface does not occur, since treatment removes the corrosion products.

Inhibitor use in Conservation

1. Benzotriazole

BTA has over 30 years, been successfully employed as corrosion inhibitor for copper and copper alloys to prevent corrosion during packing, storage and transport. It has since 1967 been adopted for the treatment of 'bronze disease' infected antiquities of copper and copper alloys. 'Bronze disease' infected copper objects after excavation in coming in contact with oxygen in presence of moist air oxidise, resulting in the formation of atacamite of paratacamite with loss of details and destruction of metal. BTA has been employed to stop the outbreak of bronze disease and thus to stabilise the antiquities.

Benzotriazole $C_6H_5N_3$ a white to light tan odourless powder with melting point of 95 C is a heterocyclic compound. When BTA is in contact with copper and copper allovs it is considered to form a thin, chemically bonded complex, cuprous benzotriazole, on the surface, where it reinforces the protection already afforded by the naturally occuring oxide film. It has been shown that this process is rapid on a cuprous oxide layer but very slow on a cupric surface.

The thickness of Cu-BTA film has been given as $40-140A^{\circ}$ although values of up to 5000A^{\circ} have been reported. The surface film produced may be a multilaver consisting of Cu-Cu₂0- chemisorbed cuprous benzotriazole/anodic corrosion product cuprous benzotriazole. Two possibilities are proposed for the linking of these molecules :

1. The cuprous benzotriazole complex on the surface consists of polymeric chains.

2. A cupric benzotriazole complex has possibly a network structure. Several studies suggest that the cuprous complex is the more probable. There have been a considerable number of studies on the inhibition of copper corrosion by BIA in neutral and acidic chloride solutions. BIA adsorbs onto copper and its oxide surfaces trom chloride solutions to form a surface nim. Studies snow that corrosion of copper is necessary for cuprous ions to participate in the formation of the protective him. The thickness of the him increases with the BIA concentration, and concentration of BIA has to be high enough to reduce the dissolution rate of Cu-BIA film and repair any crack in the film. The corrosion rate decreases with increasing film thickness.

This suggests that film formed on copper in the presence of BTA produces a barrier to the corrosion environment.

Method

Objects are carefully cleaned with equal parts of acctone and toluence and then immersed in a 3% by weight solution of BfA in alcohol. The immersed objects are placed in a vaccum until no more bubbles emerge from it. After this treatment, the whole procedure is repeated, until after one week no further visible signs of corrosion were found. The object after BTA treatment is given a coat of lacquer.

The BTA treatment is a relatively inexpensive and simple treatment, the effect of which may be readily assessed in the humidity chamber. The treatment has proved to be very effective and has been used widely for both historic and recent bronzes with great success.

Vapour phase inhibitors

The first vapour phase inhibitors were developed during world war II in order to extend the shelf lite of terrous products by impregnation of packing materials with an inhibitor. The effectiveness of VPIs on clean metal surface is well known. Yet on the basis of most existing research it is not known whether the VP1 will inhibit the further corrosion of corroded or patinated museum artifacts. They have rarely been used in conservation. They possess sufficient vapour pressure to move in the vapour phase and no can reach all parts of an artifact surface without the need of immersion treatment. Studies have shown that dissociated cations and anions of the vapour phase inhibitor molecule are concentrated at the cathodic & anodic areas respectively. Typical volatile inhibitors are; dibenzylamine nitrite and dicyclohexylamine chromate. Amine group probably buffer the pH, whilst the nitrite or chromate probably act as oxidising agent promoting metal passivity. Beyond this elementary consensus, there are conflicting opion to as to whether dissociation occurs in the vapour phase or within the moisture layer on the metal surface and as to how the passivation of reactive metallic sites is achieved. Several sources charac-terise the mechanism of VPI adsorption as a combination of chemisorption which is highly specific & more or less irreversible and physical adsorption which is nonspecific & reversible. Yet the chemisorbed layer cannot be considered as a permanent protective film since the bond between the adsorbed inhibitor and the metal surface is not strong enough to prevent the inhibitor from leaving freely, as it does, from the metal surface. Thus once the source of vapours is depleted or removed, no protection is accorded to the metal.

Cyclohexylamine carbamate in protection of firearms

Cyclohexylamine carbamate (CHC) proved effective in protecting firearms in the Norwegian Army Museum against corrosion in storage where relative humidity was 80 percent or more. The process of application included cleaning of weapons after which they were placed in plastic bags containing 2 grams of inhibitor. This was effective for periods up to 10 years.

Fire engines & other machinery under lubricated conditions has been kept with corrosion free vapour spaces for 5 years using this inhibitor.

Following mechanism has been put forward to explain the protection provided by CHC in a sodium chloride environment :

- 1. Settling of amine part of the molecule on the C1 ion and.
- 2. Settling of the carbon dioxide fraction on the Na⁺ ion.

Inhibitors in acidic solution for cleaning of corrosion products

Inhibitor for these solution are almost exclusively of the adsorption type and rarely give complete protection, which must be remembered when their use is considered. For inorganic acid solutions (e.g. sulphuric & hydrochloric acids) they are usually nitrogen or sulphur-containing organic molecules, such as quinoline and thiourea and their derivatives and their effectiveness depends an the metal composition and the nature of acid used. These factors mean that it is difficult to predict the effectiveness of a corrosion inhibitor in one stripping solution from results obtained in another, especially if the metal composition is also different. The problem can be illustrated by reference to the use of benzotriazole in the stripping of copper alloys. In sulphuric acid it is more effective for copper than for brass. Also, dissolution of tin from tin-bronzes is inhibited in alkaline solution such as tartrate & glycerol but not in citric acid. Thus the inhibitors must be tested under different test conditions before their effectiveness can be guaranteed.

The efficacy of BTA and thiourea in sulphuric acid or hydrochloric acid for stripping of iron has been compared with the more commonly used citric & phosphoric acids. It was found that although metal corrosion rates were slightly higher in inhibited sulphuric acid than in citric acid this was compensated for by the shorter treatment times involved and the amount of metal loss during stripping was less in the case of sulphuric acid. This suggests that there is a considerable potential use for inhibitors when stripping is required.

Corrosion inhibitors in solution treatments of iron objects

Washing of iron objects is done in water/hot water/deionised water to remove soluble salts, mainly chlorides. The ions such as hydroxide, chromate and nitrite claim to have inhibitive effects when used in wash solutions. These are anodic and are perfectly good for clean iron. But it is doubtful whether these will exert any inhibitive action on corroded iron artifacts. There are several reasons :

- 1. Access of inhibitors to all parts of the metal surface is probably impossible. Because of the very slow liberation of chloride between metal surface and bulk solution there is no reason to suppose that inhibitive anions will move through the corrosion product layers with any greater ease.
- 2. High chloride levels that will initially exist at the metal surface will make inhibition more difficult.
- 3. The pH at the metal surface is initially quite low and this must be raised before the inhibitors will be effective. The overall effect of these difficulties is to make it extremely unlikely that anodic inhibitors will have any beneficial effects in washing unless they arise simply from chemical reactions of the substance. In this context it may well be that the lack of visible deterioration in artifacts treated in sodium hydro-xide solution is due to the prevention of acidity, which would otherwise build up due to reaction :

$4Fe^{2+}+O_2+6H_2O$ \rightarrow $4FeO.OH+8H^+$

An alternative would be to use cathodic inhibitors as it is not necessary for them to reach metal surface but only to those places, to which oxygen can diffuse. If the cathodic areas are at an appreciable distance from the metal surface, as often appears to be the case with iron, this may be much easier. Also even if there is no inhibitor access to all parts of the cathodic areas, some corrosion rate reduction may be obtained.

Cathodic inhibitors are widely in use in acidic solutions but their use for neutral and alkaline solutions have hardly been studied. Washing of iron objects is generally done in plain water or 2% sodium hydroxide. So, it is doubtful whether cathodic inhibitors employed in acidic solution would provide complete protection. But other methods to limit corrosion of iron objects in solution treatments are possible. It is not experimentally difficult as long as sealed containers are available and one washing solution already in use (alkaline sulphite) does remove oxygen from the solution. However; oxygen removal can be easily accomplished in less extreme conditions by use of dilute, approximately neutral sulphite solutions. If corrosion is preceived as a major problem in washing, then this course, oxygen removal, would seem to be a better way of preventing it than the use of inhibitors, but the latter are perhaps easier to use.

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METALLOGRAPHIC TECHNIQUE AS AN AID FOR THE CONSERVATION OF METALLIC ARTIFACTS

INTRODUCTION

HARI NARAIN

METALLOGRAPHY is a very useful tool for the conservator for studying the microstructure, mature of the metal, and detecting types and depth of corrosion present(1), in metal and strains caused due to the development of corrosion with the passage of time. This technique was applied during the conservation of a copper vessel with the following aims.

- (i) Whether the metal core is present or not in the vessel.
- (ii) What type of corrosion was present in the metal and how much it had penetrated into the metal.
- (iii) Selection of optimum condition of cleaning agents (water, alcohol along with benzotriazole).

The copper vessel belonging to the 3rd century B.C. was received from Sringverpura excavation site (near Allahabad, U.F.) for conservation treatment and examination in the National Research Laboratory for Conservation. The vessel was covered with an extremely distiguring crust of deposited clay and corrosion products. Top and middle portions were more or less in good shape, whereas its bottom portion was in a fragile condition. Antique copper and bronzes are usually covered with thick uneven crust of different deposits on parts of metal put together with solder, glue, rivetts, etc. This situation poses difficulties during their cleaning, so before starting the cleaning of the vessel visual examination was conducted which revealed that it had three main portions; (i) neck, (ii) middle (main body) and (iii) bottom. The neck was joined with the middle portion (main body) by overlapping the metal sheets, and the middle portion was joined with rivetts to the bottom portion, which was now in fragile condition and could easily fall to pieces under any kind of shock or blow during cleaning(2). Cleaning is a major and most common operation in conservation and gives the object a better appearance, protects it from further decay and also helps conservators to detect the details present underneath the deposit. It is an irreversible process hence any type of cleaning needs caution, restraint and practical experience. Mostly cleaning operations are mechanical or chemical (chemical, electrolytic or electrochemical). Sometimes ultrasonic methods can also be applied by a conservator as per the condition of the artifact. By way of treatment, the thick deposits were reduced mechanically and some preliminary tests were performed to see how the metal responds to a particular operation before starting conservation.

Preliminary Examination

The copper vessel was very fragile and sampling for metallographic examination was also a problem, so it was decided to use the impregnated micro drill (hollow) fixed in hand operated machine. Samples were taken from two different zones i.e. middle and bottom part of the vessel. The samples were cut lengthwise into two pieces by isomet low speed saw (Buehler Ltd., U.S.A.). All the cut portions of the samples were mounted in transparent thermoplastic resin, polished on Buehler flat abrasive paper, grit no. 240, 320, 400 and 600. During grinding they were rotated 90° between each grinding after rinsing them in running water to remove any abrasive particle sticking on the surface. Polishing was done on a revolving velvet cloth wheel, sprayed with 0.05 micron alumina emulsion powder unit, a scratch free mirror-like finish was attained. All the sections were washed with distilled water, alcohol and dried with hot air and examined under metallurgical microscope before and after etching. Examination at low magnification (50X) revealed that the metal remaining in the vessel (middle part (zone-a) and bottom part (zone-b) was full of corrosion pits and cavities(3). Micro examination at 250X indicated the presence of intergrannular corrosion in bottom part i.e. zone (b), where as middle portion (zone-a) was having very little attack of intergrannular corrosion. Documentation of the penetration of corrosion and its cleaning operation in the sections were done at 125X and 500X with Leitz-orthoplan microscope on cut-film size 9×6.5 cms and speed 400 ASA (27 DIN).

Choice of Treatment Method

The remaining second half of cut portion drawn from the sample of middle part (zone-a) and bottom part (zone-b) were polished as described above. The experiments were conducted

by immersing the sample in 1% BTA (5) in water, 1% and 3% in BTA in alcohol(6) and 1 percent and 3 percent in mixture of 25 per cent, 50 percent and 75 percent alcohol in water at room temperature(7). The effect of 1% BTA in water at 50 per cent was also studied separately. The specimens were also dipped in 0.2 per cent, 1 per cent BTA in water at room temperature for five hours. The effect of these solutions was studied on the specimen one by one. After each experiment the samples were taken out of the BTA solution, washed thoroughly with distilled water, alcohol and dried with hot air, examined under the microscope until etching became apparent and tolerable removal of the corrosion products was achieved.

CONCLUSION

The above observations led to the conclusion that the concentrated solution started attacking the metal after 5 hours and the mixture of water and alcohol solution also could not produce satisfactory result. Fruitful results were achieved by 1% BTA in water (50° C) and 3% BTA in alcohol at room temperature, but 1% BTA in water at 50°C was preferred as it was cheaper and less time consuming. Copper vessel showed no observable etching after treatment.

FORMS OF CORROSION

1. General corrosion

The type of corrosion involving almost uniform decrease in volume of metal by chemical action is known as uniform corrosion (general corrosion).

2. Pitting

The type of corrosion which is localised and produces fine pits at various locations on a metal surface is known as pitting. Mainly halide salts are well known pit producers.

3. Galvanic or two metal corrosion

A type of electrochemical corrosion which involves setting up of glavanic cells because of two dissimilar metals in contact under favourable environment, is known as galvanic or two metal corrosion.

4. Concentration cell corrosion

A type of electrochemical corrosion which involves setting up of a concentration cell because of the concentration of the electrolyte in contact with the metal being not homogeneous, is known as concentration cell corrosion. Metals corroded due to the accumulation of dirt on the surfaces are mainly due to this type of corrosion.

5. Selective corrosion or dezincification

In alloys of two or more metals, one component can sometimes be removed selectively, leaving behind the others with the help of a corrosion medium. The process in that case is known as selective corrosion.

Brasses having high zinc percentage generally suffer due to this corrosion.

6. Erosion corrosion

A type of corrosion which takes place in the presence of moving environment that causes both erosion and corrosion of the metal is called erosion corrosion.

7. Intergranular corrosion or grain boundary corrosion

A type of electrochemical corrosion, which takes place along the grain boundaries of a metal piece is kiwn as integranular corrosion or grain boundary corrosion. This type of corrosion usually begins at the surface where there can be contact with an electrolyte. It may rapidly progress inwards so that the damage may be largely internal and initial disintegration of metal component may take place.

8. Stress corrosion

A type of electrochemical corrosion occurring in internally stressed metal components being used in corrosive environment, is known as stress corrosion. This type of corrosion occurs predominantly in metal components having internal stresses, caused due to cold working, etc.

9. Transgranular or transcrystalling corrosion

Corrosion proceeding along the grains of the crystalline structure.

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GENERAL TECHNIQUE OF METAL CASTING

SUWARCHA PAL

INTRODUCTION

T HE classification of historical periods according to metal is a very old practice probably of Iranian origin. The modern distinction in copper, bronzes and iron ages has been proposed on the basis of early European history. Excavations in the near east have yielded the same chronological sequence in regard to the use of different metals and alloys, whereas on the Indian subcontinent the development of metallurgy was dicerent as tin was not available. This resulted in limited utilization of bronze (an alloy of copper and tin). Thus during the Indus civilization most likely bronze casters were made after obtaining tin from Khorasan and the Karadagh mines near the Caspian sea. It was with the establishment of trade relations between India and South East Asia that supply of this became more simpler. Therefore, the classification used for Europe and the near East regarding metallurgical sequence can be used only in a limited sense.

The first metals with which early man came in contact were surface finds in the form of ores. These chance discoveries included raw ingots of gold, silver and copper and in rare cases also meteorite iron. It was the irregular formation and colour which must have attracted the attention of our ancessors. These were at first used in every day activities in the same manner as the more common stone. During the course of evolution different appropriate methods were gradually developed for the better implementation of these strange 'stones'. The initial methods for their use included the hammering, heating, cutting and grinding of these raw hammered metal which was inclined towards brittleness. Later, heat was applied which reduced the brittleness of the metal and increased its malleability. This led to the age of metal but the real science of metallurgy began only when the discovery of reduction of ores combined with the preception that metal can be melted and cast into forms was experimented.

The real development was achieved when this realization was made that several metals can be mixed into alloys, having a multiple of varying properties, large stability as well as a lower melting point, which facilitated the smelting process.

Casting technique can be classified into three categories corresponding to the time periods when they were introduced.

- 1. Open forms.
- 2. Closed forms.
- 3. Lost forms.

Open Forms

The most natural and simple method of casting employed at the beginning was the pouring of molten metal into a cavity consisting of one piece in the required shape. Moulds used were made by heat resistant stone. Fire proof clay moulds were also used. In order to facilitate the slow and uniform cooling of metal, the moulds could be preheated and also vocered after casting. This method of employing one piece moulds was only suited for the manufacture of simple shaped implements such as axes, arrow heads, etc. The ultimate advantage of this method was that such moulds could be reused at any time. The flat axes discovered during the excavations at Harappa in the Indus Valley represent the oldest known Indian objects manufactured of metal and were cast in open forms sometimes in the period between 2500 and 1800 B.C.

Multiple Forms

The next development in the ancient metallurgy was the discovery that objects with a more complicated shape could not be cast in a single unit mould. For them a cast with two or more joinable part moulds had to be used, each consisting, of stone or fire proof clay. These part moulds could be affixed to each other by the use of pegs and grooves. This technique helped in making intricately shaped utensils and the moulds could still be reused. This method led to the use of airvents and pouring channels. Through the pouring channel the liquid metal would be directed into the preheated mould while the air vent enabled the melted metal to circulate freely. This also led to hollow casting. In this technique the mould was spun around, shortly after the infusion of the molten metal at precisely the right moment when only a portion of the liquid metal had solidified along the inner surface of the mould. The remaining fluid metal would come out, thus resulting in a hollow casting.

In India, pointed harpoons and axe blades discovered at Gungeria are made by this method.

Lost Forms or 'Cire Perdue'

From time immemorial the most wide-spread method of casting has been referred to as cire-perdue or lost wax. In this method the shape of the desired objects is modelled in wax which is then given a coating of clay all over, except for the mouth of the pouring channel. After the clay mould drys, the wax is melted out and replaced with molten metal poured into the cavity. After the metal is sufficiently cooled, the clay mould is broken off in order to reveal the cast image. The main difference of the *cire perdue* method is the open and multiple forms, which enabled the reuse of the casting moulds. In this method each mould could only be used once, because it had to be broken during the course of casting and was, therefore, lost. The irony is that the only substance which is not lost is the molten wax which could be collected in a container filled with water and subsequently used again and again. Thus the term lost form is used by scholars in place of *cire perdue* or lost wax.

Literary References on Bronze Casting

The process of casting has been compared with the embryonic stage of man in two texts.

The fourteenth book of the Mahabharata 'Asvamedhi Ka Parva' describes the horse sacrifice of Yudhishthira 'As liquid iron being poured out assumes the form of the image, such you must know is the entrance of soul into the foetus'.

In the Caraka Samhita, in the third chapter of 'Sarirasthana dating back to the 2nd or 3rd century A.D. 'In whatever womb the impregnating conditions occur, of viviparous and eggborn creatures, in that womb they take shape accordingly, as when gold, silver, copper, tin and lead are poured into various wax moulds.

'If images are to be cast in metal, the wax has first to be melted in fire and all defects left by the artist are to be removed with a cloth'. 'When a image is to be made of earth, one should fire rod inside, if it is to be first made of wax'.

Many other literary traditions describe the casting. Due to religious belief, solid casting is recommended rather than hollow casting.

'Whether he makes a moveable or stationary statue, the artist who wants to attain blessedness by it must not make any of them with a hollow body, be it out of gold, iron or any other materials. 'If a statue is made with a hollow body, there will be as a consequence, strife and quarrelling and the loss of possessions; soon there will be famine, trade and traffic will subside and the king will be ousted'.

Literary References to Repairing or Disposing of Damaged images

'When an image is slightly damaged, it should never be discarded, but when its arms, heads, feet and legs are severed, when it is broken, split up or when it gets disfigured it is usually to be discarded. If its fingers, etc., are cut up (or broken) the sages recommende binding (repairing) them'. These Sanskrit texts have detailed instruction on replacement of damaged statues. Agni-puranam 'Patimamanalaksanam and Atroyatilaka give detailed accounts of the damaged images restoration.' In Tibet, they have special shrines set apart to house damaged manuscripts, paintings and statues.

Himachal Metal Casting Technique

Himachal metal icons are usually cast by the lost wax technique and may consist of three basic alloys, 'bronze, brass or copper'. By the lost wax technique the icon is first either fully fashioned in wax or to have metal if the icon is large, modelled in wax on a core of light clav, which is grossly shaped in the general outline of the icon. We come across both methods in Himachal but since the icons are rather small, the plain lost wax technique prevails.

When complete, the wax model is covered with successive layers of clay mixed with straw to obtain a mould. When dried the mould is heated and the molten wax evacuated through channels, provided at the base of the mould, thus leaving the hollow matrice of the icon which is then filled with the molten alloy. After cooling, the mould is broken and an exact metal replica of the wax original is obtained which is polished.

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The lost wax technique thus generally implies an unique specimen, although very frequently parts of the icon may have been separately cast in wax or imprinted in standardized moulds and then assembled. Sometimes, the wax model of a relatively simple, small and flattend iron was 'edited' by way of a mould in several copies, combining these two wax imprinting and moulding techniques from matrices obtained from an original icon is the usual way fakers use to make copies which they sell as genuine antique. In most cases, a trained eye can quickly detect traces of joints between the parts and such imperfections as inaccuracy in finish and polishing. More seldom, however a fake may be taken for a genuine piece, until either the original icon or another faked specimen turns up.

As for the main alloys—bronze, brass or copper-bronze, which consists mainly of copper (80 to 95%) and tin (20 to 50%) and is either brownish or yellowish in colour, is very rarely found in Himachal where tin had to be imported. However, it could have been used in an early period (fifth to seventh century) but it is difficult to state whether bronze icons were imported from south and north-eastern India or were of local workmanship. Pure copper, which is reddish or brown, is practically never encountered.

As a rule, brass has been largely and commonly used in Himachal and is easily recognizeable by its bright yellow colour, when not altered by a dark-greyish green patina. It consists mainly of copper and a variable amount of zinc.

As in the case of stone and earlier wooden sculpture and architecture, metal icons of Himachal consist mainly of two stylistic varieties, one classical, mostly imported and a later traditional or local 'Folk' style which evolved from the first.

A very curious feature occurs on the frontal element of the crown where the big cabochon was substituted for another ornamental part on the wax model itself. This is evident if one looks at the rear, where a hole was first cut in the wax before the casting process, as if there was a deviation from a former decision to fit a real cabochon on the final brass model.

Generally, the back of both the Uttar Pradesh and Eastern Himachal Pradesh brass icons are rough in workmanship, whereas those from north-western India and western Himachal Pradesh are, although void of details, smoothly and neatly finished. The rear surface of the former is not only unpolished but often the backs of the *prabha* and figures bear finger prints of the caster and pegs and cross bars are crudely fashioned to ensure a stronger rear structure.

There are embossed *mohras* (masks) also found in Himachal Pradesh especially in Kulu and Mandi fairs, only few of them are ancient, most of them being of the 18th, 19th and 20th centuries, as older ones are frequently melted to make new ones.

Large numbers of fake bronzes are also found in Himachal Pradesh. Lost wax technique makes it possible to produce an unique specimen but a copy of work already cast, like a mohru (mask) can also be quite easily produced by imprinting it in plaster or clay, which in turn will be used as a permanent mould from which wax specimen can be reproduced and cast. It is difficult to fake brass icons of eastern Himachal; they are too elaborate to allow such a process, they may show similarities but they are all different. When two brasses are identical one is often a genuine original from which a mould of its different parts has been made, the faked specimen can only be detected by thorough examination that would bring to light some minor misunderstood features. Embossed works could be edited with a wooden nucleus on which a thin sheet of metal is beaten into shape.

These bronzes are so successfully created that they are bought as 'genuine antiques'. Even 'genuine' looking black patinas can be obtained by a sulphur heating process or a green, copper patina by burying a fake brass or bronze in earth mixed with grass. To alter a too bright and modern appearance icons are even submitted to a buffing process which gives them the appearance of having been used for worship for centuries. Fake of Himachal brass icons and *mohras* are far more in number than people believe.

Himachal Pradesh has peculiar problem of preservation of these bronzes. At some places like in Shimla, Dharmshala the humidity remains generally high, ranging between 60 to 95%. Bronze disease is also common in museums.

But most of the bronzes are found in temples and with small village *deotas*. They are subiected to lot of *puia* rituals so they get rubbed off and many a time corroded. But now there is a genuine attempt to preserve them and they are being regularly inspected and cleaned by the expert.

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CORROSION OF METALS

V. M. BHANDARI

CORROSION or oxidation of metals is an irreversible process in which thermodynamic property entropy of the system increases and further spontaneous change decreases. The increase of entropy in the universe is continuous and when it does not increase that will be a dooms day. Corrosion for museologists or conservators is the undesirable deterioration of metal, constituting the antiquity. It is of great interest to know that in 'iron antiquities iron oxidises to hydrated ferric oxide, which is loosely bound and does not form a protective layer, whereas in copper/copper alloys antiquities oxidation results in the formation of bronchantite which in turn forms a protective coating and isolates the metal from atmosphere.

Process of Oxidation

The metal/element reacts with the atmosphere and from its reduced state goes to oxidised state. (Dry corrosion).

 $M \rightarrow M^{n+}$ ne M=Metal M^{n+} is interstial ion ne is interstial electron.

These interstial ions occupy MnII cation vacancy where as ne II is a positive hole. These interfaces are anodes and cathodes respectively. Whereas in wet corrosion the half reaction is :

 $M^{n+} + ne + H_2O \rightarrow M^n$ aqueous $O_2 + H_2O + 4e \rightarrow 4(OH)$ $O_2 + 4H + 4e \rightarrow 2H_2O$

So we can see that in dry corrosion the direct ionisation of oxygen occurs.

Whereas in wet corrosion metal ions are hydrated and ionisation of oxygen to hydroxyl must involve the hydronium ion. So in humid climates or as in India, dry and wet corrosion of museum exhibits is a usual phenomenon.

Copper, Iron and alloys were used in antiquities and their use has been discovered by archaeologilst from periods where fables and truths are inseparately blended. Copper was known in 8000 B.C. and was used in Babylon even earlier to iron which came in existence in 6500 B.C. whereas bronze was discovered in 3500 B.C. Great work in constructing history on the use of metals before Christ was done by archaeologists. Notably among them are Max Muller and in India, Dr. Satya Prakash.

The task before conservator is to check the deterioration of metallic antiquities and stabilize the same for future generations. There are various techniques for protecting metals but for museum and archaeological objects the following three are of great interest.

1. Cathodic or anodic protection.—As in famous iron pillar of Delhi (India), which is 23 feet 8 inches long, 22 feet vertically above the ground, upper dia $12\frac{1}{2}$ inch, lower dia $16\frac{1}{2}$, is a cathodic protection in which sacrificial anode is being used.

2. Use of protective/decorative coatings by using chelates. It is the technique which most of us are using in museum bronzes (PVA and 1, 1, 1, Benzotriazole). The use of coatings is allowed without disturbing the aesthetic value of the object.

3. Conditioning of environment.

Chemistry of corrosion of bronzes

Before understanding the corrosion which is undesirable deterioration of the metal or an alloy one should know the constituents of a bronze. Bronze is an alloy of copper and tin whereas brass is an alloy of copper and zinc. The oxidation of copper alloys can only be understood if chemistry of copper is known. Copper is the first member of the group 1B of the periodic table (coinage metals) having atomic number 29 (2, 8, 18, 1). It is not very active chemically and oxidises very slowly in air, does not place/displace hydrogen even from acid solution because in the electro-chemical series it lies near the noble end. The copper alloys are liable to undergo a selective type of corrosion in certain circumstances i.e. dezincification of brass.

The corrosion of copper and its alloys is different from other metals like iron in which rust $(Fe_2O_3H_2O)$ is loosely bound with the metal and does not slow further oxidation, the process continues till the whole metal is consumed, whereas in copper, green patina corresponding to basic $CuSO_4.3Cu(OH)_2$ being a protective film, isolates the metal from the atmosphere and checks its further oxidation.

Ore is the most stable form of any metal and every metal has the tendency to go to the lowest energy level, this is what oxidation does. The element in its metallic form is the most reduced state whereas in solution it is in its oxidised form. In a bronze, metallic copper reacts with CO_2 and moisture in the air giving rise to greenish layer or film. The greyish green basic carbonate formed under these conditions is called verdigris and is derived from vert-de-gris greyish green. The museum objects are liable to develop a disease called *rogina* or *caries* (bronze disease) and is like pest or plague for museum objects. The copper and bronze antiquities found in the earth or graves are also covered with green or blue crust called *aerugonobilis* or patina. This noble patina formation is completed in about 70 years, which is soothing to eye and acts as a protective layer from further deterioration of the object (in seventy years basicity of the oxidation product reaches to its maximum).

The outer greenish crust of the patina on the object is mainly basic copper carbonate, below it is reddish coloured copper oxide and then comes the metal core. The patina may contain (i) Malachite—Basic $CuCO_3(OH)_2$ (ii) Azurite—Basic $2CuCO_3Cu(OH)_2$ (iii) Attacamite—Basic Cu Cl₂ 3Cu (OH)₂ mixed with corellite CuS and some other salts depending upon its burial environments.

This basic copper sulphate is identical with mineral brochantite (Ore;). In some, basic carbonate $CuCO_3Cu(OH)_2$ (malachite) and basic chloride $CuCl_2$ $3Cu(OH)_2$ (atacamite) is also present.

Artifically patina is deposited by keeping the object in salty water atmosphere and charging it with air and carbon dioxide. This artifically prepared patina is oxychloride analogous to mineral atacamite, 3CuO,CuCl₂3H₂O which is not basic in character and can be easily distinguished from naturally developed patina.

The other way of preparing artificial patina is to keep the object in aqueous solution of bleaching powder. (In this reaction oxygen is also evolved). Verman W. H. J vide his publication in Trans Faraday Soc. 27 p. 255, 582 (1931) communicated that when R.H. is less than 63% there is no corrosion of copper and its allovs even in the presence of SO_2 whereas it reached alarming proportions when R.H. is raised to 75%. This formed the basic concept of care of bronze object in museums but every museum is not conditioned. The other good preservative 1, 1, 1 Benzotriazole was found by J. B. Cotton, Corrosion Sci 3, p 69 (1963) but being carcinogene in nature, museum staff resists its application on the bronze objects. This has developed my interest for the search of a new stabilizing agent, in collaboration with N.R.L.C. under a joint research project. The material may be chelate or cation exchange resin, etc. and will be applied with varnish/plastics/lacquering on the object. The copper allovs with suitable chemicals will be dropped into solution and cmf. so developed as Nearest Equation will be measured by potentiometer against S.C.E. The other electro-chemical behaviour of copper metal will also be recorded while selecting the best material. The emf of measurements will form any basic studies as copper electrode potential, which will measure its oxidation and by varying protective cation exchange resins/coatings, a suitable preservative will be introduced sooner or later.

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CONSERVATION OF METAL OBJECTS IN THAILAND

KULPANTHADA JANPOSRI

INTRODUCTION

T HAILAND is rich in cultural properties of all types, including metal objects. There are many metallic objects belonging to both prehistoric and historic periods. Many bronze and iron artifacts excavated from archaeological and historic sites are in very bad condition. These objects are related to art and archaeology. The majority of archaeological objects are bronzes and iron objects. In the past 30 years, bronze objects, including the important pieces in Thailand have been threatened by bronze disease in the form of recurring corrosion, because of improper cleaning or treatment, before being exhibited or stored, after recovery from the site. In 1974, the Thai Bronze Project, a joint project of JDR 3rd Fund in New York, the Freer Gallery of Art in Washington and the Department of Fine Arts, Bangkok, was carried out and it succeeded in finding out the best method to conserve bronze objects in Thailand. Besides, the other metallic objects are of iron, silver, gold, tin, lead, copper, brass and silver plate. The problems of metallic objects are mostly on bronze and on iron objects, particularly those which are form excavated sites.

General Conditions

The condition of an object depends mainly on two aspects :

- (i) Climate, and
- (ii) Composition of metallic objects.

Thailand has a tropical climate, which is characterized by hot and humid conditions. The prevailing humidity in Thailand is generally quite high. The average humidity is more than 80% in April and around 70% in January, whereas the temperature is about 28-34°C. Besides the chlorides contained in ground water, high temperature and high humidity contributes to the substantial incidence of corrosive salt on metallic objects found under the ground.

Copper, Brass and Bronze Objects

Objects made of copper and its alloys, such as bronze are in various forms, most of them being related to religion and some to archaeological excavations. The chemical composition of copper alloys is particularly variable, especially in the objects of ancient times, which can be differentiated by corrosion products or the patina on the objects. The examples of chemical composition of bronzes are given in Table I.

Elements		Budha h.	47 cm, 11-1	4 Cent.	Budha Dyarayadi	Budha Ayudhya	Satu Avudhya	Object Bangkok	
			Upper arm	lower arm	Body	style h. 109Cm 6-11Cen	style . 15-18Cent t	style 15-18Ce	style nt 18Cent to present
Cu		 	82.46	80.20	85.33	81.00	83.78	82.84	85.03
Sn			14.07	15.30	13.35	13.55	15.40	_	10.68
Pb			2.75	3.77	0.40	5.12	trace	. 1	trace
Zn			0.25	0.19	0.15	0.05	0.68	15.18	4.07
Sb			0.35	0.16	0.04	0.18		-	
Fe			0.12	0.38	0.64	0.10	0.14	trace	0.22
Ag	•		trace	trace	trace	trace			

TABLE 1

NOTE : Sample was drilled out with twist drills and analysed by Atomic Absorption Spectrophotometer at the Department of Mineral Resources.

The problem of copper and copper alloys for the conservation is common due to chloride of copper, which is called "bronze disease". In this paper, bronze objects will represent the objects made of copper and its alloys.

More than 50% of bronze objects recovered from the archaeological sites, of both prehistory and history, and kept in the National Museums were threatened by 'bronze disease', because they were sent directly to the museums to be displayed without proper cleaning or treatment. These bronze objects are in 34 provincial museums and the Bangkok National Museum. Because of high humidity in Thailand, 'bronze disease' occurs quickly and causes damage to the objects. On the other hand, the climate in Thailand accelerates 'bronze disease' to attack and corrode bronze itself. Besides, the different chemical composition of bronze and condition of surrounding will give the different rate of corrosive reaction. For example, bronze containing more lead will promote more activity of bronze disease because lead makes the structure of bronze more porous which allows the oxygen, humidity and salt penetration easy and causes corrosion.

The other problem of bronze objects is the concretion of corrosion products on the surface of bronze which always disfigures and conceals the details on the objects.

There were more than 50% of bronzes in Thailand which were threatened by bronze disease in the past 30 years but now this number is minimized.

CONSERVATION OF BRONZES

The conservation of bronzes in Thailand is carried out into two aspects, namely preventive conservation and conservation treatment.

Preventive Conservation

As we know, bronze disease can further proceed at high relative humidity, in the presence of oxygen, so that it is better to keep the bronze objects in dry condition, in low relative humidity. This can be done by air-conditioning or by various atmospheric dryers. The normal relative humidity in Thailand is so great and the ceilings of the buildings also so high, that this approach is rather difficult. The relative humidity should be kept below 70% RH and preferably in the range of 40-50% RH. In the exhibition, an object was placed in a sealed case with silica gel as dryer, which gives marked difference between the humidity inside and outside the case, with the humidity inside the case being much lower than that prevailing outside the case. With this experiment, bronze object even if it is afflicted with bronze disease will remain in a stable condition without further corrosion.

The measurement of relative humidity showed that an air-tight show-case made of wood, with glass door will give nearly constant relative humidity or even lower than outside the showcase. Another experiment was made to reduce the relative humidity in the sealed showcase by using silica-gel in the suitable amount, which can reduce the humidity and keep the humidity constant at the required level. We tried to use other materials such as wood, cotton but the reuslt was not as satisfactory as with silica-gel.

The conclusion is that for preservation one can keep bronze objects containing bronze disease in dry atmosphere or in lower relative humidity, under 70% RH or preferably in the range of 40-50% RH without further accelerating the activity of bronze disease. The simple way is the use of silica-gel sealed show-case, or even in a sealed plastic sac for bronze objects recovered from the excavated site to avoid further corrosion.

Treatment of Bronze Objects

The conservation problems of ancient bronze objects are 'bronze disease' and its encrustation which disfigures the object and conceals the details on the object. The procedures or methods used in order to overcome these problems are as follows :

1. Mechanical Cleaning

Mechanical cleaning is very useful for all types of objects prior to other treatments. Simple needles, sharp knife or blade and the dentist tool with the help of binocular microscope are very useful for mechanical cleaning. The advantage of mechanical cleaning is the control on how far the cleaning should go without damaging the object.

2. Chemical Treatment of Bronze Disease

2.1 Stabilization with benzotriazole

'Bronze-disease' which occurs on the object can be stopped by stabilizing 'bronze-disease' with benzotriazole which we found in Thai Bronze Project in 1975 that it is the best chemical to treat 'bronze-disease', because it can stop the activity of 'bronze-disease' and at the same time the other green patina still remains.

Benzotriazole is a strong complexing agent for copper which makes it impossible for chloride to attack the copper further. The procedure is simply by immersion of the bronze object after mechanical cleaning in the benzotriazole solution for a short time then removing it and allowing it to dry. Any excess benzotriazole is wiped off with alcohol. For the more porous object, immersion in a solution of benzotriazole in ethyl alcohol under vacuum will give more and deeper penetration of benzotriazole.

In some cases for big objects, the treatment can also be done by wrapping the object with cotton wool soaked with benzotriazole. The object is put in a sealed plastic bag.

2.2 Stabilisation by immobilizing the copper or chloride ions.

The individual spots of bronze disease on the object can be treated by using silver oxide. This method is quite practical and satisfactory on some objects. It does not change the green patina. The individual spots of bronze disease are excavated and filled with silver oxide in ethyl alcohol applied as a paste.

Silver oxide will react with the chloride in the patina to form silver chloride. When bronze is exposed to high relative humidity, the silver chloride forms an imperveous layer at the bottom of the excavated pit, preventing further access of water vapor, thus stabilizing the bronze.

2.3 Stabilization by removal of chloride ions.

There are many methods used to remove chloride ions; such as sodium sesquicarbonate, alkaline Rochelle Salt, electrochemical and electrolytic reduction. These methods can remove chloride ions completely and the objects will be stable but green patina disappears, so that they are not recommended for conservation of bronze objects.

From 1975 up to present, the number of bronze objects treated with benzotriazole and which are still in good condition are about 50% of the total amount of objects with us which are 6,500 in number.

IRON OBJECTS

Iron objects have been found since prehistoric period. They are in various forms upon which the civilization has been built. They are in different sizes, some are small and some are very big.

Iron is readily attacked by oxygen in the presence of moisture, to form rust. Without oxygen and moisture it is relatively stable.

The rust or corrosion product is the mixture of ferrous and ferric hydroxide and also hydrated ferric oxide.

In the presence of aggressive salts such as sea water or water under the ground, iron chlorides are formed. Iron corrosion products are not protective and tend to accelerate corrosion of the metal by forming localised corrosion cells. The sign of corrosion activity is brown droplet of moisture. Iron corrodes easily in humid climate, easier than copper alloys do. Corrosion of iron or rust can be very destructive, therefore prevention of rust should be attempted.

Iron objects from excavated sites are always covered with rust and are deformed. When objects were brought to the museum in the past, they were not examined whether corrosive salts were contained in them or not, and were not treated properly, so that many iron objects were destroyed. But now they are examined to determine the extent of deterioration also whether the corrosion is still active before the objects are stored or displayed.

The conservation treatment of iron objects always consists in using mechanical cleaning and treatment of corrosive salts with alkali solution.

The protective coating of microcrystalline wax is always used for protection of iron from moisture. Other lacquers, such as Paraloid B72, Incralac and Polyvinyl acetate are also used in some cases.

The iron objects are kept dry, wrapped with acid free tissue paper, then put in plastic bag or plastic boxes containing silica-gel as dessicant.

LEAD AND PEWTER

Lead is a soft metal while pewter is an alloy of lead and tin. Objects made of these two types of metals are found mostly in historic period. The main corrosion product on lead and powter is white/grey basic lead carbonate. This provides a protective patina to the metal surface which should not be removed.

Conservation Treatment

Conservation treatment of lead and pewter is always carried out by cleaning method. Object can be cleaned with warm water and non-ionic detergent such as Lissapol by using a soft tooth brush. The object should then be dried by using cotton swabs of industrial methylated spirit. After cleaning and drying, a protective coating with acrylic lacquer, such as Incralac or Frigilene is applied on the surface.

Lead and lead alloys can be attacked by organic acid vapour emitted from wooden containers or cabinet or adhesive based on polyvinyl acetate which have been used as glue for making cabinet or container. Metal shelves, cabinets and drawers are used for storage of lead and lead alloy objects. Objects are wrapped in acid-free tissue paper and stored in polyethylene bags or polyethylene boxes before storage in suitable cabinets.

SILVER OBJECTS

Silver is a soft and white lustrous metal. It has been used for many centuries and does not readily corrode. It has been used in particular for jewellery and coinage. In Thailand, silver coins were found in historic period since Dvaravadi period which is 6th–11th century. Silver objects were quite often found near bronze objects, so that the corrosion product of bronze will cover silver coins.

Corrosion products on silver are white-grey silver chloride and black silver sulphide. Silver utensils, such as bowls, vases, and other containers are also found in museums. These silver objects can develop a black tarnish on the surface, as a result of the action on the metal of sulphide gases present in the atmosphere. Sulphur present in rubber, bakelite, certain plastic paints, some pigments and moulding materials can also tarnish silver objects.

Conservation Treatment

Black tarnish on the surface of silver objects is not harmful to the object and seems to form a beautiful thin layer as the protective film on the surface of the object. It takes quite a long time to develop such a beautiful black patina on the surface of the object. It shows the age and the decorative value of the object. Artificial patina cannot be produced in the same appearance as the original one. Decision should be made carefully before cleaning off the black patina.

The conservation treatment of silver objects is not a serious problem in Thailand. Most of silver objects need only cleaning because of the black tarnish from the sulphur present in the atmosphere. There are different kinds of commercial silver cleaning products in the market, such as Duragrit and Wright. These two types of commercial products give good results in cleaning and polishing of silver objects. Soft cloth is always used on the final polishing of the surface of the object. Polishing the surface of silver objects very often is avoided since this action will remove away the metal as well as its corrosion products.

After cleaning the object, a protective coating such as Frigiline, Incralac or Paraloid B 72 should be applied on its surface by brushing or spraying.

For restoration of broken parts, HMG adhesive (cellulose nitrate) can be used. In some cases, super-glue or cyanoacrylate adhesive may be used.

For storage, silver objects should be wrapped with soft acid-free tissue paper and anti-tarnish paper for the second wrapping. For display purpose, silver object should be displayed in an air-tight show-case to avoid the tarnish action from the sulphur gases present in the atmosphere.

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TIN AND TIN ALLOYS

Tin is a soft white metal. It is quite stable, although it reacts slowly with the atmosphere to form grey stannous oxide and finally white stannic oxide. Many museum objects made of tin or its alloys are covered with a dull-grey corrosion product. It forms a protective patina which should be retained, if possible.

The conservation problem of tin objects is not a serious problem in Thailand. Most of them are cleaned mechanically. After cleaning, a protective coating like Frigiline or Paraloid B-72 is applied.

For storage, the objects are wrapped in soft and acid-free tissue paper before placing in cabinet or drawer.

They are displayed in an air-tight show-case.

GOLD OBJECTS

Gold is soft, yellow, lustrous and the most malleable and ductile of all metals. As it is a rare metal, it has been used for jewellery and coinage since ancient times. It is often applied as a decorative surface coating in the form of gold leaves for manuscript illumination and on paintings. Very often, it is alloyed with copper and silver to improve its mechanical properties.

Gold is a noble metal, very resistant to corrosion. Therefore, gold objects do not have many problems of conservation. Only there may be deformation of gold object because of softness.

Gold objects are found very often not to be made of pure gold but alloyed with copper or silver. Very often some gold objects are concreted with green corrosion product. Besides, gold objects burried under the ground are dirty because of concretion on surface due to the condition of surroundings.

Conservation Treatment

The conservation treatment of gold objects is very simple, not very complicated, since the problem is less than that for other metallic objects. The concretion on the surface of gold objects can be removed easily by using citric acid or formic acid with the help of mechanical cleaning with soft wood stick. Dirt on the gold surface can be cleaned simply with cotton-wool swabs of distilled water, with non-ionic detergent such as Lissapol. Grease on the surface can be removed by using industrial methyl spirit or acetone. Chamois leather or soft cloth is recommended to be used for polishing a gold object.

The restoration of broken part and distorted objects is carried out carefully. HMG adhesive (cellulose nitrate) is used for joining broken pieces together. Super glue or cyanocrylate adhesive is also needed in some cases.

SPECIAL CATEGORIES

There are certain types of metallic objects with decorations on the surface. Sometimes there are combinations of many metals. Therefore, such objects need special care. Also the normal rules for handling and storage of these objects are recommended.

Enamelled objects also need special care. Some types of enamels are easily affected by a moist climate. Special care in handling of enamel objects is, therefore, necessary. They must be stored on padded shelves or shallow padded drawers.

Ms. Kulpanthada Janposri, Division of National Museums, Fine Arts Department, Bangkok (Thailand).

CONSERVATION OF COPPER AND BRONZE METAL ANTIQUITIES IN PAKISTAN

GHULAM MUSTAFA

LARGE scale conservation of copper and bronze antiquities in Pakistan is carried out mostly in two conservation laboratories of the Department of Archaeology and Museums of Pakistan situated in Old Fort Lahore and the National Museum of Pakistan. The latter has, in addition, an excellent paper documents conservation unit. The Department's third laboratory which is at Archaeological Site Museum, Moenjodaro, is a water and soil investigation laboratory.

The Department of Archaeology and Museums of Pakistan looks after 356 Archaeological sites and monuments protected under the Antiquities Act. 1975. There are about 30 unprotected sites, out of which six are placed on World Cultural Heritage list—viz. Moenjodaro, Taxila, Takti-Bahi, Thatta monuments, Lahore Fort and Shalimar Garden, Lahore. The Department controls 20 museums. About 30 other museums are controlled by Provinces and local bodies and other agencies. The Department's conservation laboratories are doing the chemical conservation for the above sites and museums of the country. Only Lahore Museum has a separate laboratory for conservation of objects.

The Department of Archaeology and Museums of Pakistan has under consideration plans to establish one Monuments Research and Analytical Laboratory at Lahore and one Dating Laboratory for C-14, Thermoluminescence and Fission track dating technique for determining the age of antiquities.

About 9500 years ago, small native globules of copper were found first at Catal Huyuk near Ankara (Turkey), and at Sandak in the province of Baluchistan (Pakistan), where huge deposits of copper are existing not very far from Mehrgarh and Moenjodaro archaeological sites. Copper ore smelting to copper metal as well as copper/tin-ores smelting to bronze was discovered by the camp fire of our ancestors. Bronze antiquities of prehistoric chalcolithic (bronze age) from Mehrgarh phase III date back to 6500 years. Indus valley civilization (Moenjodaro and Harappa, Hakara River settlements at cholistan), Gandhara art, Budhist objects from Taxila and Swat date back to 5000 years. There are abundant Hindu rulers period copper/bronze coins and antiquities. Muslim period coins and antiquities date from 8th century A.D. (Banbore and Mansura) onward. From 17th and 18th century, Sikhs and British period copper/bronze coins and antiquities are also abundant in Pakistan.

As metals are mostly extracted from their ores, through appropriate metallurgical processes, when metals and their alloys are fashioned into implements, the reverse process of corrosion starts to convert them into ores. It is the task of conservation experts to delay their inevitable decay and protect them from further deterioration by applying effective measures of preservation and restoration to enable future generations to see and examine these antiquities and metal objects.

Copper and bronze antiquities, though resistant to corrosion, still during long burial in saltladen soil or exposed to environmental conditions develop corrosion products and incrustion. Usually in my country, a thin layer of black cupric oxide (CuO) is formed first, which is not destructive, but in polluted air black cupric sulphide (CuS), and reddish cuprous oxide (Cu₂O) is formed. Sometimes white powdery tin-oxide (SnO₂) is also visible in these antiquities. Basic cupric sulphate (CuSO₄ .3 Cu(OH), is formed when the bronze antiquities are exposed on church roofs top. When bronzes are buried for a long period in salt-laden soil, basic cupric carbonate CuCO₃ Cu (OH)₂, known as malachite is formed, which is dark green in colour, and when bronze antiquities are exposed to the salt laden air the famous 'bronze disease', basic cupric chloride, CuCl₂ Cu(OH)₂, para-atacamite, which is light green powdery material, is formed and the metal antiquities are converted to their ores. These later two products malachite and paraatacamite are common in Moenjodaro, Harappan and Ghandara—Taxila bronzes. Swat Museum bronzes have very stable green patina and are in a very good state of preservation. Moreover, the bronze antiquities displayed in the Harappa Museum are in a very good state of preservation. Moreover, while the same type of objects in Moenjodaro are in bad state. Those displayed in the National Museum, Karachi have very little metal core, and they are virtually converted into their ores due to exposure to salt-laden sea-winds and polluted air. Recently I treated four door handles each weighing 33 kg. Door handles were made of a bronze disc with Kulic inscription, riveted with a central late Gupta period distorted human figurine of eighth century A.D. found during exacavation of Manusra in upper Sind, Pakistan.

We examine corrosion with naked eye, magnifying glass, microscope, X-ray radiography. Recently X-ray radiography has been successfully, employed to observe thickness of corrosion layer and to find decorative inlay-work underneath the corrosion layer, and to reveal the method of casting and rivetting of the bronze antiquities. Moenjodaro hoard of copper objects, found in the recent salvage excavation of Moenjodaro, having antique bronze bangles, carnelium ornaments in a bronze pitcher were studied by me radiographically. The pitcher was made by rivetting two bronze parts together. After employing these modes of examination, the copper/bronze antiquities are treated in our laboratories by these techniques :

- (a) With mechanical methods by tools like vibrotools, by mimi air-abrasive machine, using alumina powder under microscope. Small antiquities and coins are cleaned with vibrotool to remove calcareous incrustations.
- (b) Stabilizing the patina of bronzes by dipping in 5% solution of sodium-sesquicarbonate for a long period in glass containers, until the chloride test with silver nitrate is negative, the extensive washing of bronze objects with running water and finally with distilled water and drying them under infrared light and then lacquering the antiquities with 'Frigile' lacquer.
- (c) 'Bronze-disease' (para-atacmite) is removed mechanically by a blunt scalpel blade digging to the metal core and applying a slurry of silver oxide in industrial alcohol (methanol) in the cavity. After two weeks, the effectiveness of the method is tested by placing the bronze qutiquity in high humidity.
- (d) Benzotriazole method—The bronze antiquities are first mechanically cleaned, then dipped in 3% benzotriazole solution in industrial alcohol (methanol) for several hours in fume-cupboard in vacuum, and finally washed with industrial alcohol. The effectiveness of this method was tested on Taxila rivetted bronze pitchers and on many other bronze antiquities with high humidity for a long time. The method gave excellent results, but this method has serious health hazards, as benzotriazole is suspected to be carcinogenic.
- (e) Alkaline Rochelle salt solution is also used to remove corrosion rom bronze antiquities and coins. The solution has following ratio :

Sodium hydroxide	40 grams
Sodium potasium tartarate	150 grams
Distilled water	1 litre

(f) Sodium hexa-mataphosphate 5% solution in distilled water at 40°C is used to strip off corrosion mineral and calcareous material rom antiquities. This method needs strict control (Calagon method).

Other treatment techniques for removal of incrustation, like alkaline glycerol, 3% formic acid solution, electro-chemical and electrolytic reduction are also used whenever required.

Restoration of missing parts and lacunae-filling of copper/bronze antiquity is done with plaster of Paris or 'Tecknovit' paste, or with epoxy resin.

Finally drying of copper bronze antiquities under infrared lamps, sometime an impermeable layer of coatings by impregnation in molten wax, or a thin coating of Incralac, benzotriazole based Frigiline or diluted Bedycryl 122-X to save the bronze antiquities from atmospheric effects have proved fruitful. I prefer to keep the antiquities in wax-impregnated wrapper after lacquering. I have seen that this simple precauation reduces the impact of humidity on antiquities.

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CONSERVATION OF METAL OBJECTS IN MALAYSIA

OTHMAN BIN MOHD. YATIM

INTRODUCTION

A LL of us agree that conservation is an important aspect of museums work. In fact, conservation is one of the main activities of any museum. It is not exaggerating to say that conservation is the nerve centre of museums. Indeed, it plays the role of preserving museum objects and also in slowing the process of deterioration of objects as well as making them presentable when displayed. However, as far as National Museum in Malaysia is concerned, conservation is still lacking behind, both in terms of facilities and trained staff, as compared to our neighbouring countries such as Thailand and the Philippines. This is due to the fact that our conservation laboratory was destroyed by fire in 1985, caused by an electrical short-circuit. We are yet to recover from this tragic incident.

Types of Metal Objects in our Collection

Metal objects in our collection comprise of archaeological as well as ethnographical materials :

- (i) Iron.
- (ii) Silver.
- (iii) Gold.
- (iv) Pewter.
- (v) Copper alloys.
- (vi) Lead.

Major Problems

As in other humid climate countries, our metal objects face the problems of rusting, tarnishing and corroding.

Conservation Facilities

We have a very small conservation laboratory. It was built after the fire in 1985. This small laboratory is equipped with very basic equipments such as :

- 1 —**O**ven.
- 2 —Ultrasonic tank for cleaning.
- 3 —Hair drier.
- 4 -- Some basic chemicals, such as :
 - (i) Caustic soda.
 - (ii) Rust remover.
 - (iii) Silver dip.
 - (iv) Hydrogen peroxide.
 - (v) Rust inhibitor.

In our expansion programme, special attention has been given to up-grade our conservation facilities. A new conservation laboratory with modern facilities will be established very soon. *Treatment methods used*

In conserving our metal objects, we have applied both traditional and western methods. Since archaeological works in our country are not frequently conducted, thus archaeological artefacts discovered are very small in numbers. From our archaeological sites, we usually discovered copper coins, ceramics and beads. All these evidences indicate that Malaysia was an important entrepot in the past.

We have very small numbers, in fact, a handful of religious statues made of bronze. Most of them were discovered at the turn of this century. When they were handed over to us, they had been properly preserved and our duty now is to service them from time to time.

With the less number of archaeological and historical objects, ethnographic materials mainly of silver and bronze are the main metal objects in our collection. They form 50% of the whole collection of our museum.

The traditional method we employ in cleaning our tranished bronze objects is by soaking (usually overnight) the objects in the tamarind liquid, locally known as *assam java*, or botanically known as *tamarindus indicus*.

The western techniques or methods that we use are by employing commercial chemicals especially on iron objects, the same methods used by other conservation laboratories in this region.

Training Facilities

Most of our staff had their training in conservation of museums objects mainly from ICCROM, Italy; Institute of Archaeology, London; NRLC, Lucknow (India) and in Thailand.

They are not only stationed at our National Museum but also in some of the State museums.

With all the limitations and short-comings, we are unable to provide training for conservators except to those from our own country. However, the types of training that we could offer are very basic.

CONCLUSION

Although we at the moment lacking in advanced conservation facilities, we have very good arrangements for dating and determining composition of metal objects. The Malaysian PUSPATI (National Atomic Research Centre) possess the facility which can supplement our needs. With their collaboration some of our metal objects are tested. We have a number of trained chemists in our local universities who are ever-willing to assist us in our conservation work.

Last, but not least I think regular meetings such as this, are very important for the future. It gives us ample opportunities to discuss and share our experience in term of conservation for the benefit of our respective museums.

Othman Bin Mohd. Yatim, Senior Curator (Research), National Museum, Kuala Lumpur (Malaysia).

TRAINING IN METAL CONSERVATION

H. K. NAITHANI AND S. K. BHATIA

INTRODUCTION

T HE first attempt at conservation in India was made in the latter half of the nineteenth century when some monuments were repaired and made structurally stable by applying the techniques of civil engineering. Apart from this, no attempt was made during this century for the protection and conservation of antiquities and works of art such as paintings, bronzes, manuscripts, sculptures, coins, etc.

The first attempt at preserving paintings was made during 1872-85 when Griffiths laid varnish on paintings in the Ajanta caves. The disasorus effcet of varnish on these paintings was apparent and was noticed when Maindron visited the caves in 1884. The varnish was found to have flaked, carrying with it the painting, the fragments of which were lying on the ground. Since Griffiths was not a trained conservator, results are not difficult to explain.

This episode highlighted the need for conservation training in India. With the arrival of Lord Curzon in India in 1889, the conservation of cultural property came to be recognised as an important function of the Govt. of India. In the words of Lord Curzon, "not merely are beautiful and famous buildings crumbling to decay but there is neither principle nor unity in conservation or repair".

The Archaeological Survey of India (ASI) came into existence in 1861 in the present form. At that time, majority of scientists and conservators received their training in laboratories in Europe and America. The first conservation laboratory for the preservation of antiquities came into being in the second decade of the present century when a laboratory was set up by ASI at Calcutta. This laboratory functioned under a trained and qualified chemist who got his training at the British Museum Research Laboratory.

The earliest attempt at conservation training was made by Sir Mortimer Wheeler, formely Director-General of ASI in 1940 to train young and budding Archaeologists at the Taxla School of Archaeology. At this school, training in the cleaning of antiquities, consolidation treatment, etc. was provided.

Since then, conservation has made big progress and it has developed along the scientific lines. A need has always been felt for evolving broad-based training programmes in conservation so that the trained conservators could man our conservation laboratories and undertake conservation work in a more systematic and scientific manner. At a Seminar on 'Conservation Planning in India' held in 1983 at the NRLC, the participating directors from different museums and institutions opined that 'For any conservation laboratory trained staff is absolutely essential.'

The theme of the present paper is mainly concerned with the training in metal conservation. Metal artifacts are one of the major collections in Indian museums. Archaeology department and museums have metal artifacts in the form of sculptures, coins, bells, lamps, arms, implements, etc. These may be made of pure metals or may be in the form of alloys. The important metals and alloys used have been, gold, silver, iron, copper, lead, brass, bronze and bidriware. Techniques of fabrication of metal objects in ancient India were quite advanced. Steel-making has been found to exist in the Southern India as far back as 1000 B.C. This has been revealed by metal-lographic studies carried out in the NRLC on metal artifacts found at the excavated site of *Tadakanhalli* in Karnataka.

Some institutions which are imparting training in metal conservation cover the following aspects in brief :

- 1. Types of metal and its alloys.
- 2. Causes of deterioration.
- 3. Removal of corrosion products.
- 4. Strengthening and consolidation.
- 5. Preservative coatings/stabilization.
- 6. Effect of climate.

However, at the NRLC, the following additional aspects on metal conservation are also covered :

- 1. Fundamentals of metallurgy.
- 2. Analysis of metals.
- 3. Storage designing.
- 4. Techniques of display.
- 5. Transportation.

View-Point on Training in Metal Conservation

An attempt has been made to design a 2 years specialized course on metals for science graduates (chemistry as one of the subject) keeping in mind the types of metal artifacts generally received for treatment. Metal artifacts are usually found in either of the following conditions:

- 1. Fully corroded and mineralized with no metal core.
- 2. Artifacts having sufficient metal core and covered with noble patina.
- 3. Artifacts having sufficient metal core and covered with malignant patina.
- 4. Broken metal artifacts, etc.

Following topics should be covered :

I. History of Metals and Ancient Metallurgy in India

- (a) History of metals.
- (b) Ancient metallurgy.
- (c) Alloying of metals in Ancient India and their properties (copper alloy, silver alloy, iron alloy, etc.)
- (d) Ancient and modern furnaces.
- (e) Knowledge of ancient casting, molding, welding methods to fabricate the artifacts.
- (f) Modern metallurgical sources.
- (g) Phase development of iron and steel.
- (h) Technique of Damascus swords.
- (i) Punchmarked coins.
- (i) Techniques of wootz, steel, etc.
- (k) Silver filgiri work.
- (1) Bidri work.

- 1. Study of techniques of fabrication under the microscope.
- 2. Wet analysis of metal samples.
- 3. Use and application of modern equipment in analysis, such as Emission Spectroscopy, Atomic Absorption Spectrometer, etc.
- 4. Study of impurities and their importance in conservation.
- 5. Sampling technique for conducting various studies.
- 6. Corrosion study by metallographic examination.
- 7. Study of corrosion products through X-ray flurescence, X-ray diffraction and spectrographic analysis.
- 8. Visit to the mines.
- 9. Visit to the cultural sites.
- 10. Visit to the metallurgical and casting sites.
- 11. Practical on actual casting (various methods).
- 12. Case studies.

III. Causes of Deterioration

- 1. Introduction of corrosion products on different metal artifacts.
- 2. Effect of Environment.
- 3. Atmospheric corrosion.
- 4. Corrosion in salty environment.
- 5. Corrosion on soil environment.
- 6. Electrochemical phenomenon.
- 7. Electrolytical phenomenon.
- 8. Anodic and Cathodic corrosion phenomenon.

IV. Treatment Procedure

- History sheet of each object.
- Chemical cleaning.
- Mechanical cleaning.
- Electrolytic method for cleaning.
- Use of Ultrasonic cleaning system to treat special types of objects.
- --- Electroplating/Patination.
- Washing/Drying. This will include the use of pH meter.
- -- Consolidation/joining/repair/welding/filling of gaps, etc.
- Judicious use of corrosion inhibitor/coatings.
- --- Stabilization and observation.
- --- Photography in conservation.
- Case studies.

Actual samples from different types of objects having different problems may be studied with the help of the above referred techniques of examination. The aim of such studies is to acquaint the students in order to study, detect the corrosion products, composition, fabrication technique, structure, etc.

Each case study will be covering various aspects, such as, history, fabrication techniques, metallurgical information, compositon, nature of corrosion prducts and its behaviour, method of treatments to be employed giving full details of steps and stages of conservation, actual conservation work done, coating/consolidation, etc. Observation and results are to be compiled in the shape of dissertation/thesis. In keeping with the recent advancements in science, it would be worthwhile to include various sophisticated instrumental techniques mentioned above for examination and conservation of metal objects. Metallography is the study of metal structure under the metallurgical microscope. Besides giving an insight into the fabrication techniques employed by the ancient metal workers, it is also an important aid in the study of corrosion process and to plan conservation treatment accordingly. It can help us show the progressive stages of corrosion in cross-sections of the metal. In the dark field, microstructure may not be so well-defined but the corrosion products are in their true colours. Under the microscope, we can classify different types of corrosion e.g. uniform surface corrosion, pitting, galvanic action, dezincification. etc.

By metallographic examination, it is possible to know whether the object has voids inside and is porous. Besides, it indicates what salts are present as corrosion products, by seeing them under the polarised light and how deep is their penetration. It is possible to know whether there is any metal core left or the object is completely mineralized. The conservation treatment is different in all such cases. For example in the case of a completely mineralized bronze object, it is not desirable to subject it to chemical or intensive cleaning; only a little mechanical cleaning will be sufficient. Similarly, if there are crevices present, mechanical cleaning is not advisable as the removal of corrosion products from the surface exposes more corrosion products underneath making an ugly appearance.

Similarly, for iron objects, conservation treatment depends upon the extent of corrosion scen under the microscope. In the case of heavily corroded objects, only wet brushing mechanically to remove the crusts is required to be done. It is desirable to subject the object to electrolytic **reduction, treatment with NaOH**, etc. only if a metal core is sufficiently present. Besides, metallographic examination can show us whether the object is made of cast iron or wrought iron and whether any impurities are present. Presence of lead can also be ascertained by seeing the sample under the microscope where it appears as black globular particles. Presence of lead warrants different conservation treatment.

Radiography is also an important tool of help reveal the existence of a cavity, corroding away of metal pores, casting defects and cracks inside the structure. It may also help us to find out whether any decorative in-lay may be hidden under corrosion layers since the presence of such an in-lay may have an important bearing on the choice of treatment method.

X-ray fluorescance spectroscopy is particularly useful for precious objects, coins and small-size objects as no sample is required. Determination of corrosion products or patinas can be done by X-ray diffraction. Spectrographic analysis helps us to find out the cations present.

CONCLUSION

It can be seen that the conservation training should be both theoretical and practical and it should cover all aspects of metal conservation e.g., history, techniques of fabrication, deterioration factors, corrosion products and conservation treatment. The application of modern scientific equipment besides the traditional analytical method should be given due emphasis in order to determine the exact nature of the materials and damage caused to the objects. The training programme should also lay more stress on the practical demonstrations and actual conservation work so that the person who gets the training is able to handle and conserve the deteriorated objects independently later on.

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EXPERIMENTS ON THE USE OF 2-COUMARINYL BENZIMIDAZOLE (CBI) TO CONTROL BRONZE DISEASE

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INTRODUCTION

THERE have been numerous experiments to treat bronze-disease. Such experiments have given the keys to arrest the chloride ion activity by complexation. The investigations by the authors using the ligand 2-coumarinyl benzimidazole have opened the path for stabilising chloride ion in a non-aqueous medium. 2-Coumarinyl benzimidazole (CBI) forms stable complexes with Cu(II) and Cu (I) ions and imparts effective protection. The composition and stability of complexes formed were studied in detail.

(a) Bronze disease

The pulverulent green mineral which is the mark of bronze desease is basic cupric chloride (paratacamite) which is formed from cuprous chloride in the presence of moisture and atmospheric oxygen. It is observed on bronzes after long contact with saline soils. Corrosion of bronzes can occur in both aerobic and anaerobic environments where chloride ions are involved in the corrosion process.

(b) Methods for controlling chloride ion activity-a brief review

Two types of techniques are followed for controlling chloride ion activity and thus curing bronze disease. (i) stripping methods (ii) stabilising methods :

(i) Stripping methods.—Corrosion products may be in various degrees of stability and can be the sources of secondary corrosive processes. Their removal seems the best way to ensure the stability of the bronzes. This can be done by chemical or electrochemical means.

(ii) Stabilising methods.—In this case the cuprous chloride may not be removed. It is either converted into an innocuous compound or protected by some means from the reaction with moisture or oxygen or both.

Ian Donald MacLeod(1) has given a comparison of new and traditional methods for removing chloride ions from bronzes. He has established that release of chloride ions in alkaline dithionite citric acid 5 wt% sesquicarbonate, 1 wt% of benzotriazole, 50 vol% acetonitrile water; 1 wt% sesquicarbonate deionised water. But stripping method cannot be adopted for all the bronzes since patina is disturbed.

Benzotriazole impregnation is a method that enjoys a good deal of popularity because of the remarkable corrosion-resistance it imparts to the bronze. E.L. Merk (2) has studied the effectiveness of benzotriazole in forming Cu(I) and Cu(II) complexes. But it is reported that benzotriazole is carcinogenic and should be handled with extreme care.

USE OF 2-COUMARINYL BENZIMIDAZOLE

Scientists are in search of an ideal ligand capable of complexing with Cu(II) and Cu(I) ions without altering the other minerals of the patina. Synthesis of 2-Coumarinyl benzimidazole offered interesting possibilities of using it as a neutral ligand in non-aqueous medium.



2-Caumarirnyl Benzimidazole

CBI is amphoteric. It can act as a base by accepting a proton at N_8 and as an acid by deprotonation at N_1 . The possibility of coordination is enhanced by the presence of the coumarinyl group at the 2-position. CBI can be made to behave as a mono, bi or tridentate ligand by a proper choice of the complexing conditions.

(i) Preparation of the ligand (CBI)

CBI was prepared according to the procedure suggested by Sarpeskar(3). O-Phenylenediamine (1 mole) and ethylcoumarin-3-carboxylate (1 mole) were heated for four hours at 175°C in polyphosphoric acid. The product was poured into crushed ice. The dark solid obtained was separated by filtration and reslurried with 5% sodium carbonate solution. The CBI obtained as an yellow solid was washed free of soluble impurities and further purified by soxhlet, using benzene as solvent (mp 247°C).

(ii) Method for stabilising chloride

The affected bronze is impregnated in a 1% solution of CBI in 1:1 benzene/methanol for about 2-3 days. Addition of ammonium thiocynate (to a conc. of 0.5%) enhances the effectiveness. The treatment converts chlorides of copper to complexes of CBI. After the treatment the bronze is taken out, washed free of CBI, using benzene-methanol mixture (1:1) and dried. Localised treatment can also be given with a conc, solution containing 1 gm of CBI in 30 ml. of 1:1 methanol and benzene, containing 0.5 gms of ammonium thiocynate.

(iii) Nature of protection/stabilisation

Chemical analysis showed that the protection offered by CBI is due to complexation. Chemical analysis showed that $Cu(CBI)_2Cl_2$ and Cu(CBI)NCS are formed as a result of the treatment. The brown layer of the complex coating formed is insoluble in water, benzene, etc. and is non-hygroscopic. The following studies were undertaken to understand the nature of the protection and the stability of the complexes formed.

(iv) IR Spectra

IR spectra were recorded on a Perkin Elmer 397 spectrophotometer (KBr). Table 1 gives important 1R spectral bands of CBI along with $Cu(CBI)_2 Cl_2$ and Cu(CBI) NCS. Lowering of the C=O frequency of CBI by 30 cm⁻¹ (1710 to 1680) in Cu(CBI)₂ Cl₂ and 40 cm⁻¹ (1710 to 1670) in Cu (CBI) NCS indicates the participation of C=O group in complexation.

(v) Magnetic behaviour

Magnetic susceptibilities were measured by Gouy method. The Cu(CBI) NCS was found to be diamagnetic, indicating a d^{10} configuration without any unpaired electrons. For Cu(CBI)₂ Cl₂ gave the following results :

Molar susceptibility $M \times 10^6$ cgs units .				720
Diamagnetic correction D \times 10 ⁶ cgs units				320
Corrected molar susceptibility $m \times 10^6$.				1035
eff in BM 301 \pm 22° K .				1 .62

Under conditions of magnetic dilution Cu(II) ions gives a moment close to the spin only value of 1.73 BM expected for one-unpaired electron of d^{9} configuration.

TABLE 1

Important spectral bands and tentative assignments

CBI	Cu (CB	I) ₂ Cl_2	Cu (CBI) NCS	S Assignment			
3400 m	3260 m		3300 s	N-H			
3320 m			3270 m				
3240 m							
3000 m	2850 m		2900 m	СЧ			
1710	1600 (1	(9)	1(70 (.)	Сп			
1710	1000 (V	.3.)	16/0 (s)	C=0			
1620 m	1620 (a)	\ \	1(30(-)	(—unsatura	ted lactones)		
1565 m	1020 (8))	1620 (s)	C=0			
1305 m 1450 m	1570 m		1580 m				
1400 m	1445 \$		1420 m	Skelatal impla	ane vibration		
1400 m	1425 m		1240				
1310 m	1320 w		1340 w				
1280 m	1280 m		1300 m	C-C			
1120 s	1260 m		1240 m				
	1140 m		1220 (s)	C-0			
1040 m	1050		1140 (m)				
940 m	1050 m		1050 m	C-O-C			
850	850 W		950 W	benzene ring			
780 w	760 m		770 m	Implane ring deformation			
760 w	740 s		760 m	C L defer			
740 w	700 m		740 s	C-n delon	C-H deformation.		
680 w							
		TAI	BLE 2				
		Thermoan	alytical data				
Complex	D.T.A. in air Peaks °C	Dec. temp ranges	TG in air stability range	DTA in nitrogen peaks	Decomposi- tion range		
Cu (CBI) ₂ Cl ₂	290 w endo 410 hm exo 510 bs exo	275-300 300-450 450-530	Ambient up to 280°C	290 m endo	270-305		
Cu (CBI) NCS	550 s exo	470-600	Ambient upto 250	260 bw endo	220-280		
V. s. very strong s. strong m. medium	w. b. endo. exo.	weak broad endother exother	ermic mic	bw—broad wea bm—broad medi	k ium		

The data gives an idea about the stability of the complexes i.e. temperature ranges of stability and decomposition peak temperatures. For Cu (CBI)₂ Cl₂ the data in air gives an endothermic peak at 29° and two exothermic peaks at 41°C and 51°C. In N₂ it shows only one peak. The TG shows that complex is stable upto 28°C. It starts decomposing at 28°C and decomposition to complete at 34°C. Similarly TG of Cu (CBI) NCS shows that the complex is stable upto 25°C. First stage of decomposition is 25°C to 35°C and second stage is from 42° to 505°C.

(vii) Test for effectiveness

Effectiveness of the treatment was tested by placing the treated bronze in a sealed bag at 100% RH for a few weeks, to see if green spots appear on the surface. It was found that by increasing the duration of treatment and also by increasing temperature upto 60° C the cure can be complete.

(viii) Advantages and disadvantages of the method

Bronzes which are not in sound metallic conditions can also be treated through this method since non-aqueous methods are followed. Technological characteristics of the object, its past nistory are not affected by this method since this treatment neither introduces any new metallic ion, nor removes any metallic ion. CBI complexes are found to be very stable upto 25°C. On the whole CBI will preserve the actual state of objects without introducing any chemical change other than complexation. It also does not disturb the naturally established equilibria considerably.

The main disadvantage of this method is the use of benzene : methanol solvents which are toxic and inflammable.

CONCLUSION

The experiments have opened a new route to stabilise chloride ion activity in bronzes forming complexes with 2-coumarinyl benzimidazole. The impregnation of the bronzes in solution of the ligand in benzene and methanol offers effective protective treatment. The duration of the impregnation can be reduced by increasing the temperature. Physical and chemical analysis data confirms complexation and shows that the complexes are very stable.

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STUDY OF COPPER FROM RAMAPURAM EXCAVATIONS

S. SUBBARAMAN and SREELATHA RAO

INTRODUCTION

The study of the composition and mode of fabrication of a metal artifact has great relevance in the context also of its conservation, besides the other fields of application of such a study because it is axiomatic that proper conservation of any material is possible only though a full understanding of its nature and properties.

Metal artifacts are often alloys of two or more metals and a knowledge of their exact composition helps to understand their physical and chemical properties including the different types of deterioration that they may undergo due to environmental as well as inherent factors. In other words, analysis of an object leads to a knowledge of its exact state of preservation and hence enables us to devise the correct method for its conservation.

Metal artifacts also contain a number of minor elements in trace quantities. The knowledge of the trace-element-patterns helps in the "finger-printing" of objects and correlation with the patterns of other known objects may lead to the establishment of the provenance and the authenticity or otherwise of an object.

MATERIALS AND METHODS

One hundred and nine copper objects from the excavations at Ramapuram, Kurnool District, Andhra Pradesh, formed the material for this study. The copper objects which were not subjected to any prior treatment for preservation, were however, free from incrustation. The material for analysis amounting to a few milligrames was collected by gently rubbing a corner of the object with a medium file. A small aliquot of the powder was mixed, homogenised and brought into solution. The following elements were anlysed by the use of 2380 Perkin Elmer Atomic Absorption Spectrophotometer : Cu, Zn, Pb, Fe, Sb, Ni, Au, Ag, and Cr(1). Sn was analysed by conventional wet procedures (2). The data obtained is shown in Table 1.

DISCUSSION

An in-depth study of the data of chemical analysis revealed the following features :

Copper was the principal constituent of all the objects falling in the range of 73-92%. Only one object contained Cu-7.02% and had iron as the major constituent-91.80% (namely Bell Torques ASI No. 8). The presence of Zn upto 11.96% (in copper ring ASI No. 30) was noteworthy, because the composition follows Cu-Zn-Pb-Sn alloying system. This is similar to gear bronzes, but differs in stoichiometric proportions. Copper locket (ASI No. 49) follows Cu-Sn-Pb-Sb-Fe-Ni pattern which has similar composition of bronzes, i.e. Cu-Sn-Pb (of 1000 BC-500 BC transition) and Sb-Fe association with addition of Ni. Not much comparison can be made on analysis of one object, and hence a definite conclusion cannot be derived.

In general, the analysis can be classified into three types and comparisons with the Ramapuram copper objects can be extrapolated thereof :

(a)	Babitt Metal	•	Sn 85%	Sb 10%	Cu 5%	
(b)	Gun Metal	•	Cu 88 %	Sn 10%	Zn 2%	
(c)	Bronzes	. (Cu 85%	Sn 5%	Zn 5%	Pb 5%
Sn is present in nearly all the objects and is completely absent in 5 objects. An examinasion of Table 2 reveals that Cu/Sn predominates the entire alloying system. The addition of Sn to Cu was only to increase the hardness of the alloy. The composition here differs from any of the conventional metal frameworks made for coinage or jewellery. The other elements Fe—Pb and Sb are added in minor quantities. In case where the Sn is absent, the alloying system follows the Cu—Fe—Sb pattern of composition.

The Cu-Fe-Sb alloying system is peculiar in that the following compositions were prevalent in ancient times :

Sample particulars	C	omposition o	of	(After)	Zyi
	Cu	Fe	Pb	S Goffer	r (3)
Early Indus Valley . Civilisation	96 • 7	0.03	0.02	0 •98	
Early Mesopotanian (Pre 3500 BC)	98 •8	0 •98	-	-	
Roman Coins (Ist century CE)	99.6	0.04	Trace	-	

Composition of Cu% from Wady Arabah

		and the second sec			
1.	89	9.7	0.8	0.05	
2.	92	5.0	0.7	_	
3.	89	7.2	1.2		
4.	90	9.0	0.2		

It is suggested that the presence of Fe is mainly due to its association with the Sb component. Though Sb is brittle and powdery, its alloys are corrosion-resistant and anti-frictional. The alliance of Fe in Cu alloys are seen in Delta metal, Phosphor Bronzes and cld Roman coins. The probable role of Fe $^{3+}$ would be in adding red-yellow colour to the object to make it look like gold.

The presence of Pb in the objects is due to its easy machinability and self lubricating soft greasy character. The Pb content in these copper objects is, however, small and its role in these objects is unclear despite its workability for carving.

The presence of Ag and Au is primarily due to their association with the Pb component in the copper objects (Table 3).

The presence of Au in the artifacts is consistent as a minor element ranging from 0.01-1.3%. The absence of Pb and Ag and presence of Au upto 1.3% in the copper wire (ASI No. 48) is indicative of the association of Au with the Cu component in the artifact. Both Ag and Au are present together in only 17 objects, but are completely absent in 27 copper objects.

Ni is present in 40 copper objects and absent in the rest of the artifacts. It is present in the range of 0.01—0.074% as a minor element. Since its presence is in varied composition, it is assumed that strichiometric were not adhered to strictly and homogenity was not obtained on addition of Ni to the alloying mixtures.

The presence of Cr from 0.01% - 0.08% suggests that it is mainly a trace element that has been carried into the alloying system with the Fe component. It may, however, be added that Ni & Cr are usually added to Fe in combination to refine the structure and increase the strength and hardness without impairing the machinability.

The trace elemental composition of these copper objects has not been looked for. It is important that such an analysis be carried out to provide valuable information leading to the fingerprinting and authenticity of these copper objects.

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TABLE I

Ramapuram Copper Objects

Al.	Wt. of sampl taken	f % of e Cu	% of Pb	Fe	Ni	Zn	Au	Ag	Cr Sb	Со
		2		5		7	0	0	10	
1		3	4	5	0	1	0	9	10	
3.	4 ·0	77 .5	0.15	0.25	0.17	0.02	0.15		- NO	
4.	6.6	81.8	0.18	0.86	0 -	0.05	0.01		0.03	
5.	2.4	76.66	1.13	1.48	0.60	0.04	0.27	-	- 101 - 10- h	
6.	5.9	80.30	0.38	0.60	0.19	0.03	0.03	0.02	10 To 10	
7.	8.6	61 • 161	0.12	0.41	0.02	0.03	0 00	0.01	0.01	
8.	2.5	7.48	0.28	91.8		0.14	-	0.02	10-07 70-01	
9.	4.6	66 ·02	0.39	0.12	0.14	0.09	11 -12		10 20	
10.	3.2	78.12	0.19	1.27		0.05	1 1 2	0.02	3 2 12	
11.	11.7	81.08	0.35	0.39	0.08	0.03		0.01		
12.	6.7	63.05	0.13	0.16	-0	0.05	0.15	0.01	0.01	
13.	9.8	74.23		0.13		0.01	_		0.01	
14.	9.8	73.75		0.14	L []	0.05		0.02	0.02	100
15.	7.8	65.38	0.17	0.37		0.04		0.04		
16.	11.9	78.99	0.11	0.44	0.16	0.01	0.02	0.03	-	
17.	2.0	55.60	0.73	2.27	0.25	0.12	0.49	0.10	0.03	
18.	5.4	70.59	0.17	0.25	-0	0.05	-0 -0	0.02	10.3 45	- 25
19.	2.6	66.35	0.04	2.10		0.02		-	In The na	.00
20.	14.9	81.71	0.65	0.09	0.05	0.08	0 2	0.02	_	
21.	4.5	48.04	1.03	0.10	- 11	0.07			0.02	
22.	11.1	11.10	0.65	0.10	h	0.03	0.04	10 -10	-124 - 45X	
23.	4.5	61.66	0.16	0.00	0 -00	0.08	×0. –18	0 0	0.01	
24.	7.3	83.21	0.05	0.22	0.15	0.05		0.01	0.01	
25.	3.1	01.21	0.95	0.70	0.00	0.09		0.01	0 00	
26.	7.0	74.40	0.01	1.23	0.08	0.07	0 02	0.02	0.02	35
27.	1.0	00.20	0.15	0.20	0 (2	0.07	0.02	0.02	0.01	
28.	4.0	05.95	0.13	0.25	0.02	0.11		0.02	0.01	
29.	2.0	50.80	2.10	0.49	0.11	11.06	0.20	0.02	0.02	
30. 21	5.6	70.75	0.27	0.22	0.44	0.04	0.04	0.02	0.01	
21.	1.0	47.50	0.27	0.23	- 0	0.35	0.04	0.02	0.01	
32.	2.7	75.00	0.22	0.20		0.11	0 10	0.04	(2) <u>- (</u>	
24	5.3	69.09	4.74	0.20	0.22	0.03	-0 <u>-</u> M	0 04	0.01	
25	4.4	82.39	0.56	0.02	0 22	0.08	0.27		0.01	
35. 26	7.0	88.37	0.15	0.63	0.15	0.01	0 21		0.01	
30.	2.2	63.32	0.41	2.15		0.16	- 11	-0		
37.	1.8	87.77	0.92	2.19	_	0.08			0.02	
30.	3.0	66.66	0.62	1.30		0.10		0.11		
40	3.7	79.73	1.53	1.24		0.11		-	0.05	
41	2.0	72.5	1.50	0.70	_	0.12		0.06	-	
42	4.4	71.86	0.34	0.41		0.07		0.02	0.01	
43.	5.7	75.21	0.22	0.65	0.07	0.09	0.18			
44.	1.8	58.33	1.42	2.16	-	0.14	0.27		0.06	
45.	0.9	81.88	0.55	3 .66	0 -20	0.11	-	0.03	0.06	

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TABLE	1-contd.
TUDLU	1-comu.

1	2	3	4	5	6	7	8	9	10	
46.	6.9	63 ·21	0.36	0.22	0.16	0.03		0.03	0.01	
47.	3.3	65.15	0.92	0.48	0.11	0.04	-	_	0.03	
48.	1.3	88.46		2.30	1.03	0.23	1.30	0.04	0.04	
49.	2.5	66.00	2.96	1.26	0.74	0.14	0.02	0.03	0.02	
50.	4 ∙0	78.75	0.24	0.10		0.14	0.11	0.04	0.01	
51.	4.3	57.56	1.46	1.36		0.05	-	-	-	
52.		-	-							
53.	3.5	66 . 43	0.76	0.20	0.02	0.06			0.03	
54.	3.6	67.00	0.51	0.32		0.04	_		0.01	
55.	4.8	68 ·48	0.31	_	0.08	0.08	0.16	0.07	0.01	
56.	9.8	72.61	0.60	0.26	0.16	0.02	_	0.01		
57.	4.8	71.88	0.30	0.92	_	0.05	0.23	0.03	0.01	
58.	10 · 0	79 · 25		0.33	0.06	0.01	0.01	_	0.01	
59.	4.6	66.85	0.20	0.74	0.03			0.02	0.01	
60.	3.2	65 ·21	0.52	0.09		0.22	0.11	-		
61.	2.7	72.22	0.28	0.24	_	0.15	20 <u>-</u> 20		0.02	
62.	4.7	68 ·09	0.34	0.43	-	0.04	-	0.03	-01-5-	
63.	4.6	70.91	0.19	0.23	-	0.06	_	0.01	_	
64	6.5	83.08	0.29	0.22		0.05	0.01	_	0.02	
65	1.2	-		1.54		0.17	0.62	0.08		
66.	2.1	60 · 71	0.55	0.50	0.40	0.09	_	0.05		
67.	4 .1	82.93	0.61	0.30		0.10				
68.	10.3	66 . 99	0.06	0.13		0.03	-	0.02	11 -	
69.	10.3	71.35	0.19	0.14	0.01	0.04	_	0.02	0.01	
70.	8.2	69 · 35	0.27	0.20		0.03	0.08	0.01		
71.	3.3	73.09	0.47	1.27	0.77	0.09	10 _0	-1	-	
72.	12.0	65 ·21	0.25	0.12		0.03		0.02	0.01	
73.	3.2	73 ·03	0.61	0.23	0.06	0.06	0.08	0.02		
74.	4.3	71 . 79	0.40	0.53	_	0.05			0.01	
75.	6.3	70.83	0.19	0.21		0.05	0.08			
76.	2.9	65 · 52	0.29	0.52	0.16	0.22	-	-	0.02	
77.	3.7	70.26	1.02	1.05	0.11	0.03		-	0.02	
78.	5.5	70.91	0.27	0.12	-	0.04			0.01	
79.	7.6	74.5	0.43	0.40	-	0.03	0.03		0.04	
80.	15 • 4	91·55	0.15	0.13	-	0.02	-	-	- 0	
81.	2.6	71.15	0.90	0.46		0.10		9 -	-073	
82.	6.4	62 . 89	0.30	0.48	0.28	0.06			- U - U	
83.	5.3	67 • 20	0.34	0.66	0.09	0.06	-	0.08	- 11	
84.	9.9	62.37	0.13	0.21		0.03	_	0.05	-	
85.	3.0	78.33	0.53	0.61	-	0.10		0.16		
86.	6.5	69 • 42	0.30	0.19		0.01		0.08	0.01	
87.	5.2	63 . 54	0.67	0.42	0.25	0.08	-	-		
88.	2.7	82.41	1.57	1.60		0.07	0.30			
89.	7.5	78.83	0.57	0.61		0.02		0.02	0.02	
90.	5.6	64.50	0.75	0.76	0.05	0.04	0.03	0.06	0.01	
91.	5.6	64.29	0.16	0.26		0.06		0.00	0.02	
92.	6.4	62.96	0.15	0.34	0.06	0.03	_	0.03		
93.	0.0	69.13	0.11	0.44		0.04	0.04	0.04	0.01	
94.	1.9	01.84	0.09	1.30		0.05	-	0.03		
93.	11.0	87.17	0.07	0.18	0.03	0.02	-	0.11		

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		125								
1	2	3	4	5	6	7	8	9	10	OKLER C
96.	2.7	75.93	0.11	0.18	0.53	0.09				
97.	9.6	75 ·00	0.12	0.33		0.01	0.01	0.09	-	
98.	2.2	51.70	0.72	1.20	0.93	0.02	0.38		_	
99.	1.9	53.95	0.63	0.52		0.26	-	0.05	0.05	
100.	6.3	77.38	0.33	0.08		0.04	0.01	0.40	0.008	
101.	3.7	75.32	0.28	0.39		0.05		0.08		
102.	3.3	67 ·03	0.11	0.18		0.04	0.03	-	-	
103.	5.8	71.33	0.34	0.25		0.04	0.04	0.02	0.008	
104.	7.9	74.68	0.27	0.58		0.02	-	0.006	0.006	
105.	6.2	85·27	0.38	0.41		0.07		0.02	0.03	
106.	11.5	86.19	0.01	1 .49		0.03		_	_	
107.	3.0	77.9	0.12	1.20	0.68	0.01		0.01	-	
108.	15.7	87.74	0.05	0.05		0.02	0.04	0.63	-	
109.	9.1	82.27	0.52	0.19		0.04	0.06	0.005		

TABLE 1-concld.

TABLE 2

Showing relative enrichment ratios of elements with Cu in their upper and lower limits

	 Cu/Sn	Cu/Fe	Cu/Sb	Cu/Pb	Au/Cu	x10-4 Ag/Cu	x10-2 Au/Pb	Ag/Pb	Sb/Fe
Lower	6 ·45	0 ·08	1 ·21	8 ·35	1 ·04	1 ·03	0 ·23	0 ·45	4 ·4x10-3
Upper	157	1902	2403	9511	138	42	115	125	33 ·4

TABLE 3

Showing presence and absence of Ag, Au Ag+Au, and Pb in the copper objects:

Particulars	Au	Ag	Ag+Au	Pb
Absence in number of copper objects	69	46	27	5
objects	37	60	17	101

CONSERVATION OF METALLIC CULTURAL PROPERTY UNDER HIGH HUMIDITY IN JAPAN

INTRODUCTION

SHIGEO AOKI

J APAN is surrounded by sea on all sides, lying along from northeast toward southwest. thus, there is a large difference in meterological conditions between the north end and noticeable differences in environment between the Pacific coast and the Japan, we can see the mountains rising behind each other as borderline. And the inland areas are also quite different from the above two in meteorological conditions. In discussing the subject chiefly in Kanto, Tokai and Kinki districts with population and cultural properties assets consentrating in them, the following meteorological features are to be pointed out in general :

- 1. For its latitude (average : 35 degrees), Japan has rather cold winter (monthly average : 4 degrees) whereas it has considerably hot summer (monthly average : 27 degrees).
- 2. There is plentiful annual rainfall of about 2,000 mm. In particular, it tends to rain more heavily from June, the early-summer rainy season, through September, the autumn rainy season. Humidity is more at the time of heavy rainfall. The inland areas have quite a heavy snowfall from December to March.

Such characteristic climate of Japan is due to its geographical situation. In general, Japan is located among the subtropical zones or in the mesothermal climate.

The sequence of the seasons is recognizable by plotting the relative humidities on the horizontal axis and the temperatures on the vertical axis after their daily averages are taken every month, and then connecting them. With a view to grasping more clearly the climatic feature of our country, the climates of four principal cities in Europe and the United States are also written in. In compiling Figure 1, however, for individual cities separate methods of obtaining the mean values were taken up. Although it has not helped us with exact comparison among one another, a general trend may be understandable from this.

Noteworthy features of the climate in Tokyo are high temperature and high humidity in summer, and low temperature and low humidity in winter. High temperature and high humidity are apt to deteriorate cultural properties in quality. As shown in Figure 1 four months of the year are in the domain of slanting lines, *i.e.*, the season of mould growth. Vermin begin to move about actively, when temperature rises more than that in April and May. Thus, it is readily presumable that under such humid environment, metal surface goes from bad to worse, caused by condensation on it. Low humidity in winter will rarely result in its mechanical damage, but an unstable climate in the period of high temperature will be more liable for its damage. Nevertheless, high humid phenomenon caused by drastic temperature fall is very harmful to conservation of metals.

Viewed from the aspect of relative humidity, Japan is not among the countries of excessive high humidity. The mean annual relative humidity in Tokyo is higher than that of Washington, but not than those of London and Paris. In European countries, high humidity often occurs at the time of low temperature, thereby, doing little harm on account of organic life.

Table 1 shows average daily maximum and minimum temperatures per month and average monthly temperatures and humidities in Tokyo from 1951 to 1980, which has been taken from the meteorological data.

According to Figure 2, humidity change influenced by temperature variation is larger at the time of low temperature than at the time of high temperature. Average daily temperature variation in August marks 7.2°C while daily relative humidity change then is no less than 30%. In the meantime, average daily temperature variation in January is 9.0°C while daily relative humidity change at that time is similarly around 30%. As a matter of fact, it may safely be said that cultural assets would be subject to the daily relative numidity change of at least 30% under natural climate. In addition, the data suggests that water is made to condense, nom which it is made known that meteorological environment in Japan is by no means good for conservation of metallic cultural poperty assets.

History of conservation circumstances

Ever since the Yayoi period (ca. 3rd century B. C.—ca. 3rd century A. D.), it has been customary in Japan to preserve the grain on an elevated floor where humidity from the ground can have no effect.

At "Shosoin" (a wooden building), we see treasures, which have come over through the so-called Silk Road, stored in the double wooden boxes, which are lacquered by way of the prevention of external temperature and humidity from coming in. Thanks to this method, we can see the treasures retain their brilliant colors even today even after the long passage of more than one thousand years.

Table 3 shows average annual maximum and minimum temperatures and humidities both in the external atmosphere and inside "Shosoin". Table—3 shows average daily changes of temperatures and humidities recorded in the external atmosphere and further inside the wooden boxes placed there. The characteristic of such conservation circumstances is that the temperature inside "Shosoin" is nearly identical to that in the external atmosphere. The humidity change inside is half of that in the external atmosphere. The daily temeparture variation inside the box is one-tenth of that in the external atmosphere while the daily humidity change inside the box is extremely small, that is less than one hundredth of that in the external atmosphere. The daily temperature variation inside the box is one tenth of that in the external atmosphere. The daily temperature variation inside the box is one tenth of that in the external atmosphere. This implies that such storage method where things are kept in the combination of the wooden built "Shosoin" and the wooden boxes which are placed inside the building can minimize the influence of temperature and humidity which the treasures are to undergo.

Besides such elevated floor type of storehouse as "Shosoin" there is another type of storehouse called "Dozo" which had been in frequent use in the Edo Period (1603—1867), starting in the Kamakura Period (1192—1333). It is built of wood, which is coated with mud, several tens of times on it to resultantly make the mud wall of about 30 cm in thickness. The "Dozo" is also rather small in daily humidity change just as the "Shosoin". Furthermore, it is usual that the things stored here are kept in the wooden boxes, whose humidity change is nearly invariable.

It is commonly recognized that most of the Japanese wooden and mud buildings are apt to show little daily humidity change. From this, it can be presumed that the wood and the mud work for moderating the humidity change, by properly absorbing and/or emitting the moisture in the air.

Moreover, as for the treatment directly connected to the objects themselves, "Shosoin" has the custom of 'airing' which has been taken over since early times. It has been held during the time of comfortable fine weather, some time from mid October to late-November, when they carry out inspection and airing of the treasures, and replacement of insecticides on schedule. This practice has been followed by many shrines and temples. Conventionally speaking, it may be called hanging things to 'air' or 'airing'. They sometime air clothes and works of pictorial art and calligraphy at the time of stable and hottest summer, after the rainy season is over. It means the work of removing the moisture which has been absorbed into the goods caused by the rainy season. Needless to say, this is a wisdom quite naturally worked out by the native folks who have to undergo high temperature and high humidity environment in summer.

Burial environment

Japan is generally situated under the subtropical zones or in the mesothermal climate. Its annual rainfall is plentiful as about 2,000 mm. A greater part of Japan is of acid soil, though it is rather difficult to define the country as having a certain specific soil type owing to its complicated topography and a great influence of volcanic ashes since it is a volcanc country. The organic matter decomposed by microorganism and the soluble salts is readily soluble in water and is apt to be washed away by rain. Therefore, it is out of question for us to experience in Japan the action of line accumulation and that of salts accumulation like alkali soil which are seen under the arid or semi-arid climatic circumstances of a light rainfall just as in China and the Middle and Near East countries. That is why, the archaeological objects in Japan are rarely damaged by deposits of soluble salts, unlike the case of the objects which have been excavated from arid areas. Here, we see no breakage of earthenware caused by salty deposits. As for the metallic objects so far unearthed, however, some of them are seen suffering from bronze disease affected by the chemical reaction of salts, while lying underground.

First aid of excavated metallic objects

Archaeologists must be held responsible for the safe keeping of the archaeological objects. The control over the process from their excavation up to their conservation and restoration treatments, and the aftercare management of their belongings are now left in the charge of these archaeologists and the curators of museums. We give them proper directions, drawing up a guideline for conservation management on the objects covering all the procedures.

Following is the guideline on metallic objects : Metallic objects must be kept in dry circumstances in principle. In order to prevent corrosion from generating after excavation, these objects must be put in the dry place of 15% or less relative humidity. It is necessary to prepare 1 kg silica gel per 1 m to keep the inside of the sealed receptacle at 15% or less relative humidity. Checking the humidity all the time is essential by putting a humidity indication card inside the box. If it marks 25% or more humidity, replacement or reproduction of silica gel is required. The use of an electronic drying storehouse and a tent-type drying chamber is also applicable. It is desirable to put free-oxygen absorber in these receptacles. The free-oxygen absorber will be able to remove oxygen which is the cause of metal corrosion by absorbing the oxygen existing inside the receptacle.

1. Iron objects

Iron objects must be kept in dry environments. Removing the rust ridge, if any, is desirable for fear of possible lurk of moisture inside. The mud adhering to the object must be wiped out as best as it can be.

2. Copper and copper alloy objects

Just as iron objects, copper and copper alloy obejcts must be kept in dry circumstances. Care should be taken of the completely mineralized objects due to their fragileness.

3. Silver objects

They must also be kept in dry circumstances just as the other metals. Be careful about handling the completely mineralized objects due to their fraglieness. Gold and silver alloy objects, or the objects overlaid with gold, are so fragile that they must be kept in the receptacle with packing placed inside.

4. Organic matter adhering metallic objects

They must be conserved in a free of place solar radiation under the humidity-controlled circumstances by using humidity-controlled silica gel. Be watchful about the mould generation when the goods have to be kept under high humidity. If mould occurs or the necessity for settling relative humidity arises, the conservator must be consulted about it because the quality or material and the degree of deterioration vary with different types of objects.

Materials for Conservation.

- 1. Plastic sealed receptacle : Use polyethylene or polypropylene material.
- 2. Zippered polyethylene bag : Avoid the use of vinyl chloride material.
- 3. Packing paper : Use acid free paper, avoiding the use of newspaper which contains a lot of harmful substances.
- 4. Polyester cotton.
- 5. Silica gel as drying agent.

- 6. Silica gel for humidity-control safekeeping.
- 7. Humidity indication card.
- 8. Electronic drying storehouse.
- 9. Free-oxygen absorber : This is an agent which absorbs oxygen, the cause of oxidation. The agents adopted by us are of iron oxide for both the use of normal humidity and high humidity. We always pick up the optimal sort of free-oxygen absorber just fit for the humid environment which is required by individual objects. The free-oxygen absorber, if necessary, is used together with the oxygen monitor.

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Shigeo Aoki, Tokyo National Research Institute for Protection of Cultural Properties, Tokyo (Japan).

					Av	erage Da	ily Maxi	TA mum and	d Minimu	im Tempe	erature P	er Each N	Aonth				
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Humidities TABLE 2 . TABLE 2 .	Temperatures	•	•	•		4.7	5.4	8 -4	13.9	18 •4	21.5	25.2	26.7	22.9	17.3	12.3	7.4
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25.7 25. 2 21.4 6.0 11.5 16.0 2.3 TEMPERATUERS 2.9 INSIDE SHOSOIN 75 77 78 74 69 74 74 71 76 HUMIDITIES

-0-

FIGURE 3

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EXTERNAL ATNOSPHERE TEMPERATURS INSIDE SHOSOIN TEMPERATURES

EXTERNAL ATMOSPHERE RELATIVE HUMIDITIES INSIDE SHOSOIN RELATIVE HUMIDITIES

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AVERAGE ANNUAL TEMPERATURES AND HUMIDITY IN THE EXTERNAL ATMOSPHERE AND INSIDE SHOSOIN.

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CONSERVATION OF METALS-SOME RATHER IGNORED ASPECTS

C. P. UNIYAL

I N my paper I wish to discuss about some rather ignored aspects of conservation of metallic artifacts. When I say ignored aspects, I mean those dangers to which metallic artifacts, particularly decorative metal wares are constantly exposed in our day to day activities. These dangers may be in their display, in storage, in packing or transportation. No worthwhile work has been done on the testing of materials which are used in various processes of construction of show cases, storage boxes, packing cases, dressing materials, and so on.

This situation needs particular study in tropical climates where high humidities and high temperatures and their fluctuations accelerate the different deteriorating reaction. And more so when we do not have a technical control on the commercial products used in construction of showcases, packing and storage boxes, etc. We use commercially available synthetic woods, adhesives. dressing materials, packing materials, etc. about whose side effects on delicate decorative metal wares of silver, copper and lead (particularly coins), we do not have suitable evolved test procedures.

The corrosion of metals due to these factors may not be very rapid, as compared to other agencies of decay, but it does affect slowly and constantly. This becomes particularly important in art museums which have large collections of decorative metal wares and where other problems of metallic corrosion are not so alarming.

Types of affected objects

Prominent types of objects which are affected are decorative metal wares of silver, copper and its alloys and other types having inlayed decorations, Niello decoration of silver and some gilded objects are the most affected metallic artifacts.

The other group of objects affected is of embroidered textiles which have silver wire as part of their decoration. Yet, another type of objects are paintings in which metals like silver have been used in leaf and powder form as part of their painting process.

The decay or deterioration in these types of objects due to the factors being discussed here is mostly tarnishing and related corrosion reactions.

Types of corrosive materials

Broadly, various types of materials used in display, storage, packing, etc. can be put into four categories :

- (1) Materials of construction of showcases, cupboards, packing and storage boxes, etc. These include woods, both natural and synthetic, plastics and other related materials.
- (2) Paints and varnishes used in various formulations for different purposes on different types of works including wood preservatives and insecticidal chemicals.
- (3) Adhesives used for different purposes. Most of them are synthetic polymers or resins and their derivatives in different formulations.
- (4) Different types of packing, dressing and lining materials like textiles, cotton, wool, etc.

Until a few years back, teak and other natural timbers were the basic raw materials of museum furniture but in recent years the widespread use of synthetic woods like chipboard and plywoods have created many problems. These synthetic woods are made by using large amounts of adhesives, many of which may give off vapours which are harmful to museum objects. The most difficult problem with these synthetic woods is that manufactures often change their formulations.

Similarly, the increasing use of synthetic plastics in the construction materials may be problematic, particularly in the tropical climate. Some tests on strips of plastic 'dust excluder' for use along the edge of sliding glass doors, have shown that vapours given off by the plastic at 60°C tarnish copper.

As a matter of fact there is a difficulty with compiling information about plastic construction materials because of the changes the manufacturers make from time to time to improve certain physical characteristics of the material. Such changes, for example, an alteration in the type of plasticizer may result in a particular product becoming corrosive to metals.

Coming to another category of materials like paints and varnishes, it is well known that sulphur base paints are the sources of tarnishing of metals. Now with the availability of synthetic enamels, plastic and other emulsions, these need a careful testing so as to observe their effects on different types of metals susceptible to tarnishing. The sources of trouble in this category may be again the various constituents of paints like the use of changing plastizers or emulsifying agents. Particularly 'Vinyl' paints should be regarded as harmful to lead objects until they are tested and found suitable.

Similarly, use of wood preservatives and insecticidal chemicals has to be taken up after careful study of their side effects on the metals to be kept near treated structures. As a general precaution artifacts should not be placed in freshly painted or varnished showcases until the smell of paint is detectable.

Yet, another prominent group of materials which may prove corrosive to metals is of the adhesives. Adhesives Hand Book (2) has classified adhesives into about 85 different chemical types, manufactured by several companies. Therefore, it could be realized that the number of different adhesives in use may run into several hundred. However, many of these adhesives are very specialized in their uses and would not normally be used in showcase construction and dressing.

On the basis of some tests conducted at the British Museum Research Laboratory, London (3), it has come to notice that polyvinyl acetate emulsions are corrosive to lead. The amount of tarnishing produced depends upon the plasticizer employed in a particular brand. For absolute safety the use of a urea/formaldehyde type of glue for building showcases has been suggested.

Some rubbery adhesive and acrylic emulsions containing ammonia may be harmful to lead, silver and especially copper. Some epoxy adhesives have also been found to be corrosive. In this case, it is almost certainly due to incorrect mixing of the two constituent parts of the adhesive and careful weighing of the two components should eliminate this problem. Experimental works of Oddy (4) and others at the British Museum Research Laboratory, London established that both cellulose acetate and cellulose nitrate adhesives, which are widely used for repair of antiquities are safe on copper, silver and lead.

Other types of materials like plasticine and putty like substances used to fix or hold the art object in show-cases also need testing. This is because some brands are reported to be safe whereas others have shown corrosive action.

Another group of materials is that of textiles and other lining or dressing materials in show-cases or packing cases. Besides, paint, textiles and paper are the usual materials for lining showcases. On the whole, paper would be expected to be harmless unless it contains soluble salts as a result of the process of manufacture, or unless it has been coloured with dyes containing sulphur. However, some poor quality paper and cardboard have been shown to be harmful to lead. For any long term display purposes, therefore, 'acid free' paper should be used. Coloured/ dyed textiles, fetts, fire-proof textiles, etc. may also have tarnishing effect on silver, lead or copper because of presence in them of chemicals and dyes. These, therefore should be selected after proper testing.

Selection of correct materials

Whatever has been said so far will be certainly sufficient to sound an alarm about the use of different materials in show cases, storage boxes and packing cases. It does not necessarily need an abrupt stoppage of the use of all the commercially available products. Then, what has to be done? How to test the materials? What are the parameters to be set for the use of different materials? To answer all these questions, a careful testing of different brands of various types of materials is needed and then a well organised information system on available materials thought of. However, undertaking precaution measures to counter threats of tarnishing have to be a regular practice. Testing of materials like wood, textiles, adhesives and resins, which are to be used in construction of showcases has been initiated at the British Museum Research Laboratory, London (5). It consists of placing the suspect material inside a flask or test tube with a test piece of copper, lead or silver. Addition of a few drops of water or moist cotton wool is a later modification in the test to make it more relevant to real conditions.

The normal suggested duration of this test is 28 days, during which period flasks are maintained at a temperature of $60 \cdot C$. Any material which have not caused corrosion during the course of this test may be regarded as safe, as far as copper, silver and lead are concerned. However, the test is quite severe, particularly high temperature of $60^{\circ}C$, which is sufficient to cause some thermal degradation of organic materials. This may be, therefore, suitably modified having more relevance to the environmental conditions of the museum of area or region for which the testing of materials is required.

Another interesting test for the detection of substances which may tarnish silver has also been devised at the British Museum Research Laboratory, London (6). It it based on the principle that a sodium azide based solution decomposes when in contact with materials which have the potential to tarnish silver by evolution of hydrogen sulphide. The rate of evolution of nitrogen from the reagent has been used to assess the severity of tarnishing. The test is microchemical and takes only few minutes to perform.

Other tests like optical, thermal and chemical accelerated ageing tests could also be devised to test the stability and corrosive nature of various materials on the basis of tests of various materials and their different brands could be classified into different categories, namely :—

- 1. Highly corrosive
- 2. Moderately corrosive, and
- 3. Slightly or negligibly corrosive.

Different brands of materials generally available for various uses may then be selected for their uses in show-cases, storage boxes and packing cases, etc.

However, the normal precautionary measures to counter the harmful effects of tarnishing vapours should be undertaken. Some generally used measures are the use of anti-tarnish papers. Devising some inert absorbent materials capable of absorbing acidic harmful vapours by chemisorption process could also be an effective method.

The problem of not getting required technical information about commercial products, particularly of changes in their components, could also be gradually solved if there is a better communication between conservators and manufactures and their dealers. Communication could be by way of circulation of published technical literature or by associating them in conferences, workshops, seminars, etc.

A system of collecting technical information regularly about products available in each country, or region on the basis of their regular testing, and above all a well-balanced planning keping these aspects in view could considerably slow down the process of decay of precious decorative metal wares and other artifacts.

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INTRODUCTION

T HERE are reports of damage to the material of cultural property from Europe caused by lichens. Etching of glass used in windows of churches and also of marble forming part of various buildings by lichens has been a serious problem in preservation of ancient cultural property. But there seems to be no serious attempt to go deeper into this problem for suggesting the remedial measures. A few years back I had the occasion to hear talk by Dr. Mason E. Hale of Smithsonian Institution during his visit to Lucknow about the assignment allotted to him by the Mexican Government. He was to suggest ways and means to eradicate lichens growing on the recently discovered monuments of the Mays Civilization that lay hidden for centuries under the thick tropical forest cover. The study at the time of the lecture was at a preliminary stage. I am, however, not aware of its outcome.

Our country too, suffers from the lack of knowledge in this regard, despite the fact that branch of lichenology is fairly well established in India and as far as the material of cultural property is concerned, we have no dearth of it. India has the distinction of being associated with one of the most ancient civilizations of the world and has ever since remained under diverse cultural influences resulting in varied types of historical monuments spread all over the country. This material represents our cultural heritage and is our invaluable and proud possession. It is our prime duty to preserve it for posterity. Due to wide expanse of our country and with its varied types of terrain, diverse types of climatic conditions are encountered and each type presents its own set of problems to be faced for preservation of monuments. Perhaps, no other country has such an assortment of climatic conditions met within its political boundaries. We find alpine and temperate conditions in the Himalayas, tropical conditions in the Western Ghats and the eastern states and again from extremely wet situations in the Western Ghats and Eastern Himalayas to extremely dry conditions prevailing in the hot Thar desert of Rajasthan, or the cold desert of Laddakh. Remaining parts of India enjoy intermediate types of climate between these extremes.

In India, the historical monuments are built of different kinds of stones. The lichens or other groups of plants do not discriminate for their colonization between monuments and the natural rocks as both of them present the same kind of substratum for their growth. They present same ecological conditions for these plants and also sustain same type of damage caused by their growth on them.

The rock surface is generally devoid of life sustaining factors necessary for vital activities as it is exposed to more or less total periodical dessication and is subjected to extreme temperature conditions. Lichens by virtue of their peculiar structural and physio-logical qualities are able to overcome these harsh conditions presented by this habitat. They are thus quite at home in this inhospitable substratum.

NATURE OF LICHENS

Before probing into different ways by which the lichens affect their substratum, it is necessary to understand their nature and their morphological as well as physiological details.

Lichens as we understand, represent a symbiotic association in which two groups of plants, fungi and algae pass their life in a mutually beneficial relationship. It has proved to be a highly successful relationship and consequently the lichens are considered as the best examples of symbiosis in nature. The dual nature of lichens was first recognized by Schwendener (1). It is supposed that a close nutritional relationship has developed between the two symbionts. The fungal symbiont, called the mycobiont produces haustoria or appresoria within the cells of the algal symbiont, termed as phycobiont, but the cells of the latter show no sign of injury, which otherwise is quite obvious in a host-parasite relationship. Another obvious point regarding the success of this relationship is that both the symbionts are obligate symbionts, i.e. they (especially the mycobiont) cannot grow in isolation, or even if they do so, they cannot thrive for long. It seems that they have become totally dependent on each other for nutrition as well as growth factors. This symbiotic association has brought about changes in the morphology of the thallus, which by and large is quite different from thalli of the two symbionts. Not only this, the lichen thallus seems to have undergone evolution in more than one direction. The process of lichenization has provided added advantage to both the symbionts, that is longevity, which while growing separately have a short span of life, especially the fungal partner. Moreover, the lichen thallus can withstand extremely harsh climatic conditions, which the two symbionts growing separately will hardly find fit for their survival.

For a long time the lichens were considered by many as a separate entity, while others, did not agree with this view, and included lichens within the group of fungi, notwithstanding their different mode of nutrition. In other fungi the mode of nutrition is either saprophytic or parasitic. As per our current knowledge, the latter view seems to be nearer to the truth. It would be interesting to note that the life style of lichens has been so successful that the majority of inoperculate ascomycetous fungi that constitute the largest groups among overall fungi have undergone lichenization during the long course of evolution.

TYPES OF LICHENS

According to habit, lichens can broadly be classified as crustose, foliose and fruticose, though many intermediate forms are also seen. The crustose lichens form a crust on the substratum that may be superficial or may penetrate deep, up to a few mm in it. The foliose ones also are close along the surface but their attachment to the substratum is loose and they can easily be separated from it. The organs of attachment are groups of fastigiate hyphae called rhizinae. The fruticose lichens are bushy and have a single point of attachment with the substratum. They may be erect or hanging.

For the growth of lichens, a fair amount of moisture and pollution-free atmosphere is required. Lichens are autotrophic plants, i.e. they are able to manufacture their own food. Water and minerals they obtain form the atmosphere. The substratum thus is needed to serve as a foothold only. This is the reason that a good number of lichens species are able to grow on a variety of substrates. The majority of the species, however, have a restricted range in this regard. Such an aspect is perhaps due to ecological factors rather than nutritional. In accordance with the nature of substratum the lichens inhabit, they have been classified as terricolous growing on soil, saxicolous-rocks inhabiting species, corticolous bark lichens, follicolous those found on leaves and omnicolous found on a variety of substratum. In addition there are a number of substrata for lichen growth. They are iron poles, wooden planks, glass, animal shells, bones, leather, inorganic building materials, nonferrous metals, etc. As a matter of fact all objects that are of permanent nature can act as foothold for lichens.

Action of Lichens

For long, lichens have been considered as the pioneers in land plant succession. They have been attributed the ability of disintegrating rocks on which they grow gradually converting them to soil, creating favourable conditions for other groups of plants to invade and establish in that area, this leads ultimately to the establishment of rich forests. Though the pedogenetic quality of lichens causing biological weathering of rocks to the large scale as mentioned above seems to be a myth, yet the action of lichens on rock surface on which they grow and bring about certain changes to it cannot be denied. Ascaso *et al* (2) worked on pedogenic action of *Parmelia conspersa*, *Rhizocarpon geographicum* and *Umbilicaria pustulosa* and found out that these lichens are able to induce both chemical and morphological changes in rocks as well as their mineral contents. Biological weathering of rocks by lichens has thus two aspects, physical and chemical. These two aspects do not work in isolation but they act simultaneously and help each other in corroding the rock surface. Regarding weathering of rocks by lichens, Syers and Iskandar(3) suggested the following mechanisms:

1. Physical weathering of rocks

It takes place in three ways :

(a) Penetration of rhizinae

Rhizinae in lichens are organs of attachment of thallus to the substratum, they are found in the majority of foliose lichens, arising form the ventral surface of the thallus. It is a known fact that rhizinae penetrate the rock surface and cause its mechanical disintegration. The rhizinae are not hard enough to penetrate, the rock surface. Their penetration is through cracks and crevices on the surface that the rhizinae gain their entry. The physical as well as chemical composition of the rock also perhaps decides the extent to which rhizinae can penetrate. For example, the rhizinae have an easier passage to deeper layers of the rock containing calcium chloride as compared to rocks consisting of other minerals.

Crustose lichens form a considerable part of the overall lichen cover of the rock surface. They have no rhizinae but their medullary hyphae are in direct contact with the rock surface. In case of limestone the lichen thalli are completely or partly endolithic. In such cases the medullary hyphae may penetrate the substratum down up to 1.5 cm. Mechanical action of rhizinae is quite effective. It can cause disintegration of granite.

Rhizinae of lichens have been reported to cause mechanical disintegration of glass surface(4).

(b) Heptera detachment.

The thallus of Collema (a highly gelationus lichen genus), Xanthoria parietina and some other foliose lichens have heptera as organs of attachment to the substratum, which are much thicker than rhizinae. The distal end of heptera consists of tuft of loose gelatious hyphae and thus constitutes efficient organs of attachment. Due to more contraction in the upper cortex on drying, the thallus slightly curls upwards causing a pulling strain on heptera. The heptera while remaining firmly attached to the substrum either get broken from the thallus or they may detatch from the substratum, carrying with them either small particles or a very thin film of the latter. On the glass substratum too, this phenomenon takes <u>place</u>. On the return of moist conditions the thallus straightens against and the heptera reattach themselves to the substratum, by means of hyphae that circumvent the detached substratum particles.

(c) Expansion and contraction of thallus

In crustose lichens the lower cortex is generally absent and the medullary zone of the thallus forms the lowermost layer. Its hyphae are attached directly to the substratum. Endolithic thalli may not be subjected to contraction and expansion appreciably on drying and wetting respectively as they are wholly embedded in the rock material. In epilithic forms, however, the upper surface (i.e., the upper cortex) of thallus is more prone to changes caused by atmospheric humidity. As observed in foliose lichens, the upper cortex is crustose thalli too, shows greater contraction when dry, as compared to medulla. It thus exerts a pulling strain on the medullary hyphae, which is more pronounced at the margins of the thallus. If the thallus is thin, it is not able to withstand the pulling strain and is thus torn along the margin. But in species with more robust thalli the medullary hyphae are torn from the substratum and in this process they dislodge and pull along minute rock particles. On wetting, the thallus regains its former posture, it straightens and the medullary hyphae once more attach themselves to the substratum, but the detatched rock particles are lost to the substratum for ever. At the central part of the thallus also, disintegration of the substratum constantly goes on. Lichen thalli have considerable proportion of gelatinous or mucilagenous substances, which expand and contract under wet and dry conditions respectively. This action loosens the substratum particles, which in many cases get incorporated in the lichen thallus. Such a process is better discernible below the highly gelatinous apothecia. Fry(5) in his studies of mechanical action of crustose lichens on their substrate demonstrated this phenomenon in the case of shale substratum. Shale is a clay rock that splits readily into thin laminae along the bedding planes.

Fry(5) and some others consider that physical disintegration of rocks by biological agents is quantitatively more as compared to the biochemical weathering, but it is difficult to make a correct assessment of such a comparison. Syers and Iskandar (3) think that the process of physical disintegration perhaps increases the surface area of the rock, rendering it more susceptable to biochemical weathering of the substratum.

2. Chemical weathering of rocks

Chemical reactions take place in solution. Nature has provided water as the most abundant and widespread solvent for a wide variety of chemical substances. Lichens absorb and retain water in their thalli to the extent that when fully saturated, their water content may be 100 to 300% of their dry weight. The medulla, which consists of loosely arranged hyphae act, as water reservoir of thallus. In crustose forms, this water reservoir (medulla) is in direct contact with the substratum. It greatly increases the possibility of the substratum being corroded by certain chemicals dissolved in this water. As lichen thalli are able to retain moisture, the surface of substratum covered by them remains moist for a longer period than the surface devoid of lichen cover, the chemical weathering process thus continues for a longer period in the former case. 12-643NRLC/88 Chemical weathering of rocks may be on account of the following :

(a) Biogenic production of carbon dioxide.

Carbon dioxide is produced by lichen thallus in respiration. As the rate of photosynthesis is very much lower in lichens than in other green plants, lesser amount of this gas is utilized in the latter process or conversely, greater amount of it remains untapped and the surplus is available for other chemical reactions. It is dissolved in water contained in the thallus providing H^+ ions, which may take part in chemical reactions with minerals of the substratum causing their decomposition. The solubility of carbonate minerals is dependent on H^+ concentration (pH). The extent to which this CO₂ in dissolved state affects chemical weathering of rocks is not known exactly but it does not seem to be to an appreciable degree.

(b) Oxalic acid formation by mycobiont of lichens

The fungal hyphae in the lichen thallus of many species produce oxalic acid as excretory substance. When dissolved in water it reacts with calcium of the substrate producing calcium oxalate. This product is insoluble in water and is deposited as extracellular compound inside the lichens thallus. Lichens growing on limestones have greater deposit of calcium oxalate crystals in their thalli. When rocks are moist, the water flowing over their surface contains a good percentage of calcium salts as they are easily soluble in water. If a minute fraction of calcium dissolved in this water is converted into calcium oxalate, it hardly makes any difference in the overall calcium level of the substratum.

(c) Chelation or complexing action of lichen acids

There has been a general belief that lichen acids are insoluble in water. But the antimicrobial activity of many lichen substances within an aqueous medium indicates to the contrary. Many lichen substances show solubility, ranging from 7 to 75 mg in one litre of water. It has also been demonstrated that lichen substances in aqueous solution show chelating action on metals. Soluble metal complexes have been obtained in the laboratory when lichen compounds were allowed to react with minerals and rocks. In the field as well, chemical and mineralogical changes on the surface of the substratum covered by lichen thalli have been observed. Iskandar and Syers(6) showed that significant amounts of Ca, Mg, Fe and Al were complexed by lichen compounds using iron chelaton as a measure of biological weathering of rocks. Willaims and Rudolph(7) studied rock lichens and fungi isolated from the same rock surface. Squamatic acid Seshadri and Subramanian extracted from lichen Cledonia squamosa chelated iron in solution. (8) carried out chemical investigations and reported a high percentages (20.3%) of lecanoric acid and a small amount of atravorin from *Parmellia tectona* a sample of Buddhist monument of Borbudur central Java. The chemical constituents of this species form India, published by Murthy and Venkateshwarlu(9) show in two collections the presence of atravorin (1.2%) and (0.6%) and lacanoric acid (4.8%) and (3.0%) and in one collection that of atravorin (1.3%). lecanoric acid (3.8%) and norstictic acid (1.1%). According to Seshadri and Subramanian(8) this sufficiently strong acid is water soluble and can be reckoned with affecting soft particularly calcareous structure. With such a high percentage, the damage caused to the monument would be considerable. Chemical weathering by lecanoric acid, a substance commonly found in a num-ber of lichens, is well known. Chelating properties of some lichen substances thus seem to play important role in chemical weathering of rocks.

CONCLUSION

Based on observations on the biological weathering of rocks in nature it is logical to assume that such a phenomenon must also be occurring on historical monuments, for the basic material they are made of, is the same. Lichens are important weathering agents that induce both chemical and morphological changes in the rock as well as in its mineral contents. The sculptures and sculptured panels get defaced and their details are obscured. Because of neglect in this aspect of study we have remained ignorant about the role of lichens in damaging the historical monuments in India. There is thus an urgent need to undertake the study and survey of the lichenflora confined to this substratum so as to gain knowledge of the morphology and chemistry of different species. It will go a long way in suggesting proper methods for assessing the extent of damage caused by them and also for their eradication form the surface of the monuments. This study will open a new field of work in the Indian lichenology which has remained restricted so far to the areas of taxonomy and to a lesser extent to chemistry.

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PROTECTIVE COATING IN CONSERVATION OF METALL IC ANTIQUITY

KHATIBUL HUDA

INTRODUCTION

H UMIDITY plays a vital role to corrode and deteriorate metallic artifacts mainly made of iron and copper. In presence of water, iron changes to Fe_2O_3 , $Fe(OH)_3$, FeO_4 Copper and its alloys deteriorate to basic copper carbonate i.e. $Cu(OH)_2CuCO_3$, in humid condition moreover the presence of pollutant hydrogen sulphide, sulphurdioxide, chlorine, hydrogen and chloride in atmosphere also damage the metallic antiquity. Acetic acid vapour released by wood and paper board used in museum's showcases accelerates the deterioration of metallic artifact. After treating corroded artifact, conservator generally applies a protective coating on the metallic object. Several commercially available protective coatings e.g. Ercalene, Incralac, Frigiline are being used for this purpose. But till today, a suitable protective coating has not been found which can stop the penetration of water vapour and pollutant.

The Bangladesh National Museum, situated in Dhaka, the capital of Bangladesh, has a good number of different metallic artifacts made of copper, iron, copper alloys and silver. Relative humidity and temperature of Dhaka varies from 45%—98% and 14°-38°C respectively. Moreover city atmosphere possesses the pollutants like SO₂, SO₃, H₂S, Cl₂, HCl, CH₃ COOH, dust, carbonaceous matter coming up from waste product of mills and factories, automobiles and woodburning, coal-burning, vulcanization of rubber, etc. So the artifacts made of metal are always susceptible to attack by the above pollutants and water vapour. Though the rate of corrosion is slow, but prolonged action creates a problem. The rate of corrosion is also accelerated at elevated temperature. In this environment a good metal protective coating can reduce the corrosion rate of the metallic antiquity at least to some extent. There are mainly two types of metal protective coating, one is inorganic and other is organic. Inorganic coatings are mainly metallic. On antiquity this type of protective coatings are not permitted because it reduces the aesthetic beauty of the artifact. Another type of natural inorganic protective coating is also a product of corrosion but sometime it acts as a protective for the underlying metal.

It is generally agreed that metals may be corroded by direct chemical attack or by an electrochemical mechanism. Reactions of dry chlorine, hydrogen sulfide, oxygen and other gases with dry metals are examples of direct chemical attack. On the other hand, it is now well established that in most cases the attack on metals and alloys by moist air, water vapour or aqueous solutions proceed by an electrochemical mechanism. The film of corrosion which is produced by electrochemical mechanism tends to stiffe the corrosion process by increasing anodic polarization, cathodic polarization or the resistance between anodic and cathodic areas. If the metal oxide has a lower specific volume than of the metal, the oxide film shrinks and cracks causing entrance of oxygen and thereby further deterioration occurs. When the oxide has a higher specific volume than of the metal and has thickness of a few molecular layer then this film acts as a protective coating. Presence of chloride ion will cause the film to break down and accelerate corrosion. This protective coating is natural. This type of inorganic protective coating can also be produced artificially by the action of oxidizing agent on metal carefully.

On the other hand, there are organic protective coatings which are used universally throughout the world. To find out or choose a good protective organic coating for conservation of metallic antiquity is a difficult task, because more or less all the polymeric macromolecules have a tendency to absorb water vapour. Some polymers and waxes were subjected to accelerated ageing test and the qualitative results observed are discussed in this article. Before choosing a polymer as coating we have to consider the following points :

- (i) Coating must be clear and transparent.
- (ii) Must be elastic in nature.
- (iii) Adequate bonding to underlying metal surface to avoid peeling or flaking.
- (iv) Resistance to water and polluted gaseous matter.

- (v) Stable to oxygen, heat and light.
- (vi) Soluble in common solvents.
- (vii) If materials are used in molten condition, melting point should not be too high.
 - (ix) Considerable shrinkage property.
 - (x) And finally reversible in nature so that coating may be withdrawn by applying solvent from the surface of artifacts if a necessity arises.

Following polymers and waxes were selected for experimental work to find out their feasibility as a protective coating on metallic antiquities :

- (i) Ercalene lacquer.
- (ii) Cellulose nitrate.
- (iii) Polystyrene.
- (iv) Paralloid B-72.
- (v) Polymethylmethacrylate.
- (vi) Polyvinyl acetate.
- (vii) Soluble Nylon.
- (viii) Bees wax.
- (ix) Microcrystalline cosmolloid wax.
- (x) Incralac lacquer.

Experimental

MOISTURE ABSORPTION TEST :

Procedure : A definite dimension of polymer was taken. Polymer was weighed (W_1 gms) and dried in oven at almost 50°C for 24 hrs. to constant weight. After cooling in a desiccator and reweighing (W_2 gms), each was placed in a separate dish and covered with distilled water. The temperature was maintained at 25-30°C for 24 hrs. The samples were then removed, surface dried and reweighed immediately (W_3 gms). The specimens were redried using the same time and temperature as before and again cooled and weighed (W_4 gms).

mersion

Calculation :	(a) Percentage of moisture originally
	$= \frac{W_1 - W_2}{100} \times 100$
	W1
	(b) Percentage of water absorbed during in
	$(W_3 - W_2) + (W_2 - W_4) \times 100$
	(c) Percentage of water soluble matter
	$- W_2 - W_4 - \times 100$
	W2
Data No. 1	

Name of polymer		Pe	rcenta	tage of water absorption in 24 hours	
1. Cellulose nitrate			•	. 1.5	
2. Polystyrene				. 0.05	
3. Potymethylmethacrylate				. 0.3	
4. Paralloid B-72				. 0.4	
5. Cellulose acetate				. 2.8	
6. Nylon				. 1.4	
7. Polyvinyl acetate				. 0.8	

From the above data we can say that cellulose acetate has the highest water absorption property whereas polystyrene has the lowest absorption property. We can arrange the above polymers in order of decreasing moisture absorption.

Cellulose acetate, Cellulose nitrate, Nylon, Polyvinyl acetate, Paralloid B-72.

Polymethylmethacrylate, Polystyrenc.

Chemical Resistance Test

Generally chemical resistance may be expressed as loss or gain in weight. Qualitative terms are normally used. Effect of weak acids were expressed denoting the letter E, F, G. U.

Note : E=Excellent, G=Good, F=Fair, U=Unsuitable

Data No. 2

Name of polymer		C		Dil. Hcl	Dil.H ₂ SO ₄	Dil. HNO3
1. Cellulose nitrate	۰.			U	U	U
2. Cellulose acetate				U	U	U
3. Polystyrene .				E	E	F
4. Polyvinyl acetate				U	U	U
5. Polymethylmethacrylate				E	Е	F
6. Paralloid B-72				E	G	G
7. Nylon .				U	U	U

If we mark arbitarily E=4, G=3, F=2, and U=1, then total marks of individual plymer obtained is as follows:

1.	Cellulose nitrate			3
2.	Cellulose acetate			3
3.	Polystyrene .			10
4.	Polyvinyl acetate			3
5.	Polymethylmethacrylate			10
6.	Paralloid B-72			10
7.	Nylon .			3

If we arrange all the polymer in order of decreasing resistance to acids then we can write.

PolystyreneCellulose nitrate, cellulose acetate, Polyvinyl acetate,PolymethylmethacrylateNylonParalloid B-72

Accelerated ageing test No. 1

Sample preparation : Copper, brass strips of 10 cm, 4 cm, 3 mm size were taken. The strips were cleaned with fine grade of emery paper. Then they were washed with running water, followed by distilled water and dried in oven at 60°C for 2-4 hrs. Metal strips were taken out from oven, cooled and washed with pure acetone and left to dry in atmosphere. After that they were kept in a desiccator to avoid direct contact of water vapour.

Apparatus : (a) A large desiccator without silica gel. (b) Four 250. Ratt IR lamps (c) A mercury thermometer (d) Surface thermometer (e) Evaporating dish.

Chemical: (a) Sulphur dioxide solution (5% w/v) (b) 0.1 N acetic acid solution in water. (c) 1 N hydrochloric acid in water (d) 1% sodium chloride sol. in water.

Procedure: (a) Desiccator was cleaned thoroughly. One litre of 1% solution of sodium chloride was poured into the desiccator. About 50-100 c.c. of SO₂ solution, acetic acid, hydrochloric acid solution were poured in separate evaporating dishes. They were then placed in lower part of desiccator. Some pieces of broken glass rod were put on each of the evaporating

dish so as to keep the dishes always vertical. The desiccator disk was placed on the desiccator properly. A small mercury thermometer was inserted inside the desiccator.

(b) Brass and copper strips which were earlier cleaned and kept in desiccator were taken out. Now the metal strips were heated with hot air blower for a few minutes, cooled and then polymer/wax solution applied on them. Six coats were applied with soft small brush on one side and then dried by hot air blower. This operation was repeated on six sides of metal strips. Specific gravity of the polymer solution was always kept within 0.9—1.1. Too much thick solution was avoided so that coating on metal surface was uniform.

(c) After completing operations (a) and (b) the metal strips were inserted into the desiccator with proper marking to identify the polymer/wax material used. Then the lid of the desiccator was closed airtight. Later, desiccator was heated using four 250 watts infrared lamps. The inside temperature was observed from time to time by a mercury thermometer and surface temperature of the desiccator by surface thermometer. The whole apparatus and lamps were placed in a closed cabinet to minimize the loss of heat generated from IR lamps. Temperature was more or less maintained at 60°C for eight hours and then slowly cooled to 15°C. Alternate heating and cooling continued for six weeks. Strips of copper and brass, without coating, were also placed inside for comparison.

(d) Water inside the desiccator was maintained at 100% RH throughout the experiment. After six weeks the experiment was over. The metal strips were taken out and examined carefully.

Accelerated ageing test No. 2

This test was carried out on iron only. The sample was prepared like accelerated ageing test no. (1). Caution was taken that there was no sign of corrosion or oxide film on the experimental iron strips.

Apparatus : (a) A cabinet type desiccator of size $24'' \times 18'' \times 15''$ (b) mercury thermometer. (c) Four 250 watt IR lamps (d) Evaporating dish (e) Hydrometer.

Chemical: (a) 1N Hydrochloric acid.

Procedure: Four evaporating dishes full of water and one full of 1N hydrochloric acid were placed inside a desiccator cabinet. A plastic net was placed over it. Plastic net was used to avoid any contamination with iron strips to be tested. Now the iron strips with different kinds of coatings and a piece without coating were inserted in the desiccator, and kept on the plastic net. A mercury thermometer was placed in the cabinet. Coatings on iron strips were applied as in the previous experiment. Specific gravities of polymer solution were maintained within the range of 0.9-1.1 by using hydrometer. After that the desiccator was closed well to avoid any leakage of moisture or HC1 vapour from it. It was then heated by four IR lamps upto 60°C for eight hours and then slowly cooled to 15°C. Alternate operation of heating and cooling continued for six weeks. Change of temperature was noticed by the thermometer inside the cabinet. The whole apparatus and the lamps were placed in a closed cabinet to avoid loss of heat generated from IR lamps. After that the desiccator cabinet was opened and the iron strips were examined.

Accelerated ageing test No. 3

This was the same type of test as the test carried out on iron strips. But here hydrochloric acid was excluded and iron nail of 4 inches length was choosen in place of iron strips. In this experiment iron nails were coated with different polymers and wax. Half of each nail was immersed in 1% sodium chloride solution in water in a test tube. The remaining part of each nail was left in atmosphere. Later they were sealed in a desiccator cabinet at a temperature of 60°C for eight hours and cooled down to 15°C. Heating and cooling was carried out alternatively. This operation continued for six weeks.

Accelerated ageing test No. 4

This test was carried out on copper and brass only. Sample preparation and experimental procedure was the same as or the accelerated ageing test no. 1 but here no other chemical was used except 1N acetic acid solution in water. Humidity was maintained within 98%—100%. Corrosion induced by acetic vapour was examined. A sample without coating also was subjected to the experiment.

Accelerated ageing test No. 5

This test was done on copper, brass and iron strips, covered with different types of protective coatings. Preparation of samples and application of coating was as in the previous method.

Procedure: 500 cc. of water was saturated with H₂S gas and diluted six times. About 1000 c.c. of this solution was poured in a desiccator and iron, copper and brass strips were placed inside it. Then the desiccator was sealed. Alternate heating and cooling continued as before. After six weeks the desiccator was opened and diffcernt metal strips were examined. A sample without coating was also subjected to the experiment.

Precaution: (i) Cation was taken to ensure that there was no sign of corrosion before the experiment began. (ii) A sample without coating was subjected to each experiment for comparison. (iii) Humidity maintained within was 98%-100%. (iv) Care was taken to have a uniform coating on metal surface. (v) Any contamination (NaC1) from hand was minimized by using hand gloves.

Discussion : Several polymers and waxes were selected, some experiments were carried out with them. From the results of the experiments, we can recommend some polymer/wax for protection of metallic antiquity. It has been observed that more or less all the polymers permit water vapour or pollutant to pass through them. So it is unwise to expect an absolute imper-vious polymer material. The only possibility is to compare to find out better ones among them.

The first point to be considered is the transparency of the protective film. Polymer/wax which were subjected to testing are more or less colourless or transparent in solid state as well as in solution or molten condition. One of the coating material 'Ercalene' is very light yellow in colour. Though in bulk it looks light yellow, in film it is more or less colourless, (Data No. 4) but it was noticed that it has a tendency of yellowing. So from the point of transparency there may be some hesitation to use 'Ercalene'.

Bees wax, and microcrystalline wax also give very light yellow colour in molten condition, but they do not affect metallic object at all. From the Data No. 3 and 4 it was seen that all the polymers which were selected for testing are soluble in common solvents thus fulfilling an important criterion of conservation.

Mainly water is responsible for corrosion of metallic antiquity. We have therefore to choose a polymer whose water absorption is less. In this regard if we look at Data No. 1, we can say that cellulose acetate has the highest and polystyrene has the lowest water absorption property. On this account polystyrene, polymethylmethacrylate and paralloid B-72. may be recommended. PVA and Nylon may be the second choice due to their turbid nature in thick solutions.

Three types of acid vapours namely HC1, H₂SO₄, HNO₃ are found in atmosphere. Sulphuric acid and nitric acid form in nature according to the following equations :

- SO₂ (in atmosphere)=HSO₃⁻⁺+H⁺ HSO₃^{-++ $\frac{1}{2}$ O2=H⁺ +SO₄²⁻ N+0 Thundering NO $\frac{1}{2}$ 02 N} (i)
- H₂O HNO₂+HNO₃ NO₂ (ii)

Hydrochloric acid forms by reaction between water and chlorine gas coming from waste products of mills and factories. From Data No. 2 we can say that polymethylmethacrylate, poly-styrene and paralloid B-72 are more or less resistant to acid vapour in comparison to other polymers.

Accelerated ageing test No. 1 was carried out on two types of metals namely brass and copper. They were subjected to a drastic action of sulphur dioxide solution, acetic acid vapour, hydrochloric acid vapour in presence of 100% RH. It we go through the data obtained by this experiment we can see that polystyrene. paralloid B-72, 'Incralac', polymethylmethacrylate gave more or less good results in protecting the above metal from corrosion. Cellulose acetate, cellulose nitrate have the least protection capacity. From the Data No. 1 we know that cellulose based polymer has the highest water absorption property and is unsatisfactory to acid resistance. In this experiment it was observed that water, acetic acid, Hcl and SO₂ solutions attack those metal plates which were coated with cellulose base polymer. Another problem arises from cellulose acetate which deteriorates by the action of temperature and humidity giving out acetic acid vanour. 'Ercalene' shows a result of moderate tolerance with copper only but it has a tendency of yellowing on ageing. Therefore, it is better to use polystyrene, paralloid B-72, polymethylmethacrylate

coatings. Ready-made lacquer 'Incralac' also shows a good result on copper and its alloys. In fact it is an acrylic based lacquer having some benzotriazol. BTA helps to stabilize copper object and acrylic polymer protects the metal artifact to a considerable extent from corrosion.

From Data No. 7, it observed that more or less all the polymers fail to stop the corrosion of iron in presence of hydrochloric acid vapour or chlorine, but microcrystalline cosmolliod wax and bees wax have given somewhat satisfactory results.

Data No. 8 show that though iron was subjected to saline environment, but in the absence of hydrochloric acid vapour, not only the waxes give good result, but also polystyrene, polymethyl-methacrylate and paralloid B-72 in acetone give good results.

Acetic acid is one of the corroding agents of metallic antiquity mainly made of copper, copper alloys and lead. It is known that wood and paper-board which are used in manufacturing museum show-cases are source of acetic acid vapour. Accelerated ageing test No. 4 was carried out only on copper and brass. Data No. 9 shows that 'Ercalene', polystyrene polymethylmethacrylate, intethacrylate and paralloid B-72 in acetone give good results.

Hydrogen sulphie gas is found in industrial cities and it corrods metallic objects in two ways First it converts the metal to metal sulfide and secondly it shows protonic characteristic also, so it can break the protective film of polymer.

 $H_2O+H_2S-H_3O^++HS^ HS^-+H_2O-H_3O^++S_2^-$

Data no. 10 tells us that actually no polymer is absolutely helpful in hindering sulfide corrosion. But to some extent we can choose Ercalene, Incralac, polystyrene and paralloid B-72.

Conclusion

Summing up all the data and findings we can say that protective coatings manufactured from polystyrene, polymethylmethacrylate, paralloid B-72 and Incralac lacquer are more or less good for conservation of metallic antiquity made of copper and brass, but in case of iron. microcrystalline cosmolloid wax is rather more acceptable. In some cases though, cellulose base material and Ercalene have a considerable good performance but their heat-resistance and light sensitivey (data No. 5) are so poor that it is wise to avoid them. As we know, no protective coating is completely impervious to the slow diffusion of salts, moisture and pollutants which results in further corrosion, therefore, I have to draw attention to the most fundamental point of conservation that object must be stored or displayed in ideal condition of humidity and temperature i.e. 33% - 40% RH and 25-30°C.

SOLUBILITY AND SOLVENT

SI. No.	Polymer/wax	Constituency	Solvent
1.	Ercalene	. Viscous liquid C . solid, colourless to slight whitish	Contains amyl acetate as solvent. Amyl acetate, acetone.
3.	Cellulose Acetate	. Solid, colourless more or less transparent.	Acetone
4.	Paralloid B-72	. Solid, colourless transparent.	Acetone, Toluene
5	Polymethylmethacrylate	Solid, colourless transparent	Xylene
6	Polystyrene	. Solid, colourless transparent	Toluene
7.	Polyvinyl acetate	. Solid, colourless slight whitish in bulk.	Toluene
8	Soluble Nylon	, Solid, whitish	Hot methanol
9. 10.	Bees wax Microcrystalline	. Yellowish white Solid, whitish	Light yellow liquid when melted Toluene
11.	Incralac	. Viscous liquid colourless.	X

Thet	BT.	- 7
Data	NO .	3

13-643 NRLC/88

Data No. 4

SI. No.	Polymer/wax	Solvent	Sp. Gr. of solvent	Sp. Gr. of polymer/ wax	Colour of polymer solution/wax	Nature of film on metal surface
1.	Ercalene .	Amyl acetate	0.870	X	Light yellow	Colourless, trans- parent film, non-
2.	Cellulose nitrate	Amyl acetate, Acetone	0 ·870 0 ·700	1.3	Colourless transparent.	Transparent, Non-sticky sur-
3.	Cellulose acetate	Acetone	0.700	1 •2	Colourless with slight turbidity	face. Transparent when coating is thin but too much thick coat makes the film translucent. Non sticky surface
4.	Paralloid B-72	Toluene Acetone	0.855 0.700	1 •25	Colourless and transparent when toluene was used as solvent. Acetone made the solution slightly turbid	Transparent film if toluene is used as solvent. Acetone made the film trans- lucent; sticky upto 2-3 brs then non-
5.	Polymethyl-	Xvlene	0.860	1.2	Highly transparent	sticky surface.
	methacrylate		0 000	1 2	like glass.	sticky surface.
6.	Polystyrene	Toluene	0.855	1 • 1	Highly transparent like glass.	Transparent, non- sticky surface
7.	Polyvinyl acetate	Toluene	0.855	1.15	Colourless, slight turbid.	Transparent, non- sticky surface-
8.	Soluble nylon	Hot.Methanol	0 • 700	1.5	Colourless, slight turbid.	More or less tran parent if coating thin. Non-stic surface
9.	Bees wax	Х	Х		Very light yellow in molten condition.	Transparent; if thin layer is applied.
10.	Microcrystallin cosmolloid way	e Toluene	0.855	Х	Colourless	Transparent if thin layer is applied,
11.	Incralac		-	Х	Colourless	Transparent, non- sticky surface.

Data No. 5

SI. No	Polymer		Heat resistance ^o C	Light Sensitivity
1.	Polystyrene .		(70—100)	Nil
2.	Polymethylmethacrylate		(70—100)	Nil
3.	Cellulose nitrate .	• •	(55—90)	Tendency of decomposition in presence of water.
4.	Cellulose acetate	• • •	(55—90)	Decompose, yellowing, vapour of acetic acid evolved.
5.	Paralloid B-72		(72—90)	Not noticed.
6.	Soluble nylon .		(135-149)	Not noticed.
7.	Polyvinyl acetate.	• •	(100—120)	Yellowing.

Khatibul Huda, Conservation Chemist, National Museum, Dacca (Bangladesh),

ACCELERATED AGEING TEST NO. 1

Data No. 6

	Ercaler	le C	Cellulc nitrate aceton	se P in i	olysty. n tolue	rene I ene. B a	Paralloi 1-72 in Icetone	d Pol me in 1	ymeth thacry kylene	lyl- I vlate E . to	Paralle 3-72 in oluene	oid Pc 1 ac	olyvin etate i tolue	yl- y sne	Cellulo acetate acetor	se N in r	lylon i nethar	n W lol c	/ithout oating	In	cralac	
Observation	C	Br	C	Br	ပိ	Br	CC	Br	CoB	Sr	Co I	3r	Co	Br (Co Bi	5	Co E	r (Co Br	Ö	0 Bi	ц
Cuprite	0	0	0	-	0	0	0	0	0	-	0	0	7	5	-	2	0	0	2	5	0	0
Tarnish	-	1	2	0	0	c	0	0	0	0	0	0	-	0	0	0	0	3	0	0	0	0
Green incrustation by naked eye.		-	1	0	0	0	0	0	0	0	0	0	-	0	-	-	7	0	4	4	0	0
Green incrustation und	er																					
scope • •	•	5	2	0	0	0	0	0	0	0	0	0	7	0	1		5	0	4	4	0	0
Flaking of coating	•	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7	#	*	0	0
Cracking of coating	0 .	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		7	*	*	0	0
Roughness of surface	0 .	5	3	0	0	0	0	0	0	0	0	0		2	1	7	1	1	*	*	0	0
Note . Co-means	duno	r and	Br n	Sugar	hrace						-						=					_
Note . Comment	sitive r	espon.	se u		01400.																	
1-Very sn	nall po	sitive	respo	nse																		
2-Small p	ositive	respo	onse																			
3-Fairly 1	ositive	e resp	onse																			
4Highly	positiv	e resp	onse.																			

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Data No. 7

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NO.	
TEST	
AGEING	
CCELERATED	

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Data No. 8

	Ercale	ne	Cellulos nitrate i acetone	e c	Polystyr in tolue	ene	Paralloi B-72 in acetone	T	Polymeth methacry in toluen	nyl- late e	Paral B. 72 tolue	lloid in ne	PV acetat in toluen	le.
Observation	Lower U part p	pper Lo art	ower part	Upper part	Lower	Upper part	Lower U part pi	pper art	Lower part	Upper part	Lower part	Upper part	Lower L part	Jpper
Black corrosion .	0	0	2	0	0	0 0	0 0	0 0	_ <	0 0		- 0	n (1	
Brownish corrosion	1 0	0 0	0 5	0 13	00	0 0	0 0	0 0	00	0	00	, 0	1 7	-
Corrosion is non-	60	0	7	5	0	0	0	0	1	0		1	0	0
riter of continue	C	C	0	0	0	0	0	0	0	0	0	0	0	0
Flaking of coating	0 0	0	0	0	0	0	0	0	0	0	0	0	_ •	
Roughness of surface	0	0	2	2	0	0	0	0	0	0	-	0	7	-
	Cellulos acetate i acetone	eu	Nylc meth	n in 1anol	Witho Coati	ut bg.	Microcry: alline cos molloid w (molten)	ax	Bees w (molte	ax n)	Microcr line cost loid wax toluene	ystal- nol in	Incrala	IC
Observation .	Lower	Upper	Lower	Upper part	Lower	Upper part	Lower	Upper part	Lower	Upper part	Lower part	Upper part	Lower L part	Jpp part
Black corrosion .	2	1	2	2	4	4	0	0	0	0		0	- -	- <
Brownish corrosion .	0	0	-	0	0	0	0	0	0 0	0 0	0 0	0 0	- 0	
Corrosion is uniform	5	2	2	7	3	e	0	0	0	Ð	0	>	>	>
Corrosion is non- uniform	0	0	0	0	0	0	0	0	0	0	- 0	0 0		C
Flaking of coating	0	0	0	0	0	0	0	0 0	0 0	0 0				
Cracking of coating	0	0		1	0	0	0	0	0 0				> -	
Roughness of surface	2	5	2	1	0	0	0	0	0				-	

ACCELERATED AGEING TEST NO. 4

DATA NO. 9

ithout	Br	1	3	6 M M 1		
ac w	Co		4	A N N I	4	
ncral	Br	0	1	1 4 0 0		
ys- Ir	C	00	-	-000	>	
icrocr lline ssmoll ax in uene	Br	00	Ţ	- 0 0 0		
ta Wu control	C	00		-000		
lulos ate	Br	0 -	0	0000		
te Cel e acet in acet	Co	0 -		-000	= = =	
Aceta toluen	Br	0 0	0	0000		
in	S	50	-	1000		
alloid 72 in tene	Br	00	-	1000		
- Par B-G	ပိ	00	-	1000		
nethyl hacry- in ne	Br	0	0	0000		
Polyr met late xyle	ပိ	0	1	1000		
lloid 2 in one	Br	0 0		0 0 0		
Para B-7 acet	S	0 0	-	1000		
luene	Br	1	0	0000		
Polyst in to	°	1	0	0000		
ose te in one	Br	0	0	0000		
Cellul nitra aceto	C	0 0	-	1 0 0 1		
ne	Br	0 -	0	0000	•	
Grcale	Co	1	0	0000		
ł			rustation under	f coating . of coating . s of coating .	CoCopper BrBrass	
Observa		Cuprite Tarnish Green inc	naked eye Green inc metalloor	scope Flaking o Cracking Roughnes	Note :	

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ACCELERATED AGEING TEST NO. 5

DATA NO. 10

	Ercalene	Cellulose nitrate in acetone	Polystyrene in toluene	Paralloid B-72 in acetone	Polymethyl- methacry- late in xylene	Paralloid B-72 in toluene	PV Acetat in toluen	e Cellulose e acetate in acetone	Without coating	Microcrys- Ir talline cosmolloid wax in toluene	cralac
bservation	Co Br In	Co Br In	Co Br In C	o Br In	Co Br In C	o Nr in	Co Br In	Co Br In	Co Br In	Co Br In Co	Br In
Tarnish	2 1 1	1 2 0	1 0 0 2	0 0	2 0 0 2	0 0 2	5 0	2 1 0	4 0	2 1 0 1	1 0
Black incrustation of sulphide	0 0 1	0 0 3	0 0 2	0 0 1	0 0 2 0	0 2	0 0 2	0 0 2	0 0 4	0 0 3 0	0 1
Flaking of coating	0 0 0	0 0 0	0 0 0	0 0 0 0 0 2	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 5	0 0 2 0 2	0 0 2		0 0 3 0	0 1
Cracking of coaung . Roughness of surface .	0 0 1	0 0 2	0 0 1	0 0 2	2 0 2 0	0 2	0 0 2	0 0 2	x x x	0 0 3 0	0 2
Note : Co-Copp Br-Brass	er										

In-Iron

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ROLE OF MICRO-ORGANISMS IN CORROSION OF METALS--A LITERATURE SURVEY

SHASHI DHAWAN

INTRODUCTION

T HE first indication that micro-organisms may be involved in metallic corrosion processes appeared in the work of 'Gaines (1), when he concluded that the corrosion of underground iron and steel structures was in part due to bacterial activity. The iron bacterium (Gallionella ferruginea) was infact isolated from corrosion products on burried steel conduit and high concentration of sulphur and organic matter indicating the presence of sulphur bacteria.

The role of microbes in the corrosion of metals is due to the chemical activities (metabolism) associated with microbial growth and reproduction(2). As the growth of microbes is very fast, the onset of changes may be sudden, and even when apparently suppressed by mechanical or chemical cleaning often returns because a residual low number of living organisms rapidly grow again when favourable conditions are resorted. These are the typical characters of biodeterioration of materials caused by microbes, of which corrosion is a special case.

According to Miller(3) microbial corrosion may perhaps be defined as metal loss cause or accelerated by microbial action at one or both of the two sites controlling electrochemical corrosion, namely the anode and the cathode.

Recently Daldrff(4) while descriing the corrosion of museum iron objects believed that corrosion caused by micro-organisms is not easy to measure and has no distinct separation from galvanic corrosion caused by inorganic salts. To deny or neglect their presence is dangerous but easy.

Classes of Corrosive Microbes

The role of microbes in corrosion processes is not always clear, the mechanisms are not completely understood, and even today much controversy and conflicting data exist. Korbin(5). reported as follows:

- 1. Produce acids inorganic such as sulphuric, as well as organic such as formic and acetic.
- 2. Destroy protective coatings.
- 3. Create corrosion cells/differential aeration (oxygen) and iron concentration cells are notable example.
- 4. Produce hydrogen sulphide.
- 5. Concentrate anions and cations.
- 6. Oxidize metal ions.
- 7. Depolarise cathodic sites by consumption of hydrogen.
- 8. Foul equipment, cooling towers, water lines, heat exchanger, etc.

He further classified corrosive microbes in six groups :

- 1. Acid producers—Some microbes can oxidize sulphur compounds to sulphuric acid, a pH as low as two has been recorded where sulphur oxidizing microbes are active. Others can produce organic acids from organisms.
- 2. Mold growers-These are primarily fungi.
- 3. Slime formers—Certain algae, yeast_bacteria and fungi fit in this class. The deposits they form created concentration cells and foul equipment.
- 4. Sulphate reducers—Perhaps the most publicized class of corrosive microbes. They reduce sulphates to sulfides and depolarize cathodic sites on metal surfaces by consuming hydrogen.

- 5. Hydrocarbon feeders-Virtually all microbes feed on hydrocarbones, but those of specific concern to corrosion engineers disbond or destroy organic coatings and linings.
 - 6. Metal ion concentraters/oxidizers-Iron and manganese bacteria are important examples of this class. They generally form thick bulky deposits which create concentration cells or harbor other corrosive microbes.

Microbes may be aerobic which thrive in air and actually need air to survive or anaerobic which can exist and multiply in the absence of air.

There is a considerable overlap within these class of microbes, for examples, certain mould growers also produce acids and form slimes. The general microbiological corrosion of metals have been reviewed by a few scientists (3) (5-11) while most scientist have concentrated on corrosion due to a particular type of micro-organism.

Sulphuric Acid Corrosion

Acid Production by Thiobacillus

There are several species in the genus Thiobacillus (Pseudomondals) of which all but one are strict autotrops. The ability of thiobacilli to oxidize sulphur and its compounds under aerobic conditions to higher states of oxidation leading often to sulphuric acid is well known. Costello(13), Miller and Tiller(14), Miller(3), Vishniac and Santer(15) have reviewed the thiobacilli and discussed their isolation, cultivation and metabolism. Important species for corrosion are Thiobacillus thiooxidans, T. thioparus and T. concretivorus.

T. thio-oxidans and T. concretivous are capable of oxidising sulphur via sulphite, thiosulphate and tetrathinate to free sulphuric acid(16). Sulphite, thiosulphate and tetrathionates may be used in place of sulphur as starting points for the oxidation. The oxidation of these reduced sulphur compounds results in a net gain in energy for the organism which is thus able to grow autotrophically. Hydrogen sulphide can also be oxidised by these organisms, but only when pre-sent in low concentration i.e. below 200 ppm(16). High final concentration (10-12%) of free sulphuric acid may be developed by these organisms(10).

Horvath(17), has shown the importance of microbiological oxidation of reduced sulphur compounds to the corrosion of burried metals and has indicated the weight loss data in laboratory cultures of *ihiobacilli* and polarisation curves that the oxidation of reduced inorganic sulphur compounds by these organisms can greatly increase corrosion rates by lowering pH values and removing protective films from the metal surface. Beakwith(18) has discussed how thiobacilli may, in alternating aerobic and anaerobic conditions form a corrosive situation where sulphate reducing anaerobes have been active.

Corrosion due to acid production by Ferrobacillus species

Ferrobacillus ferro-oxidans utilises the energy of oxidation in aerobic environments to support its autotrophic metabolism. The ferric salts thus produced oxidize reduced sulphur compounds to sulphuric acid.

The frequently called Ferrobacillus ferro-oxidans now regarded by most authorities as belonging to the genus Thiobacillus. Thiobacillus-ferro oxidans is important economically because of its ability to leach metal ores, i.e. to solubilize them so that the metal can be recovered without recourse to smelting. Le Roux(19) have given an important reaction.

 $4\text{FeS}_2 + 150_2 + 2\text{H}_2\text{O} = 2\text{Fe}_2 (\text{SO}_4)_3 2\text{H}_2\text{SO}_4$

In this reaction the organisms clearly oxidizes the sulphur as well as the ferrous iron in the substrate showing the affinity with other thiobacilli. In nature, the organism is often associated with the oxidation of pyritic deposits (20-22). Millions of tons of sulphuric acid was contributed annually due to the oxidation of pyritic deposits in the mines of western Pennsylvania(21), Acid waters thus produced in mines have been shown corrosive to pumping machinery Postgate(10).

Corrosion due to organic acid production by micro-organisms

Corrosion of iron, copper and aluminium due to organic acids associated with mould growth have been reported (10, 23, 24) and Staffeldt and Calderon (25), that the mechanical properties of steel, copper and aluminium wires may be adversly affected by acids produced by moulds. They have shown in screening tests that organic acids have greater corrosive effect than enzymes.

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Coles and Davis (26), Coles *et al* (27), have demonstrated that corrosion of underground lead coaled with tar impregnated wrapping materials is due to the production of low molecular weight organic acids by bacterial decomposition cellulosic wrappings.

Allen *et al* (28) have elaborated corrosion of steel in a beet suger factory due to acids produced by the growth of *lactobacilli of the Lactobacillus delbruckii* type. Hughes (2) explained that paper and synthetic rubber coatings for insulation cables may also be attacked. Under strong aerobic conditions CO_2 , is the end product of the oxidation of organic materials and lead carbonate has been detected as a corrosion product of lead coated underground cables. Under semianaerobic conditions organic acids accumulate and these may lead to simple acid corrosion or alternatively may accelerate corrosion by chelation of passive layers on metal.

Besides bacteria, moulds and yests may accumulate organic acids even under aerobic conditions and in some cases may synthesise complex secondary metalobites some of which although only weakly acidic, are powerful chelating agents. These may be of special significance when microbial slimes accumulate on metal surfaces, as relatively high concentrations of potentially correceive products may be trapped in them, and corrosion pit results. Thomas and Hill (29) found that Aspergillus funigatus, causes corrosion of aluminium alloy. It was found that corrosion accelerated in the presence of its growth when compared with the corrosion that occurred in sterile control. It was further noticed that corrosion caused by the fungus appeared to be correlated with its growth medium. They explained that corrosion in the presence of fungus may be due to the combined action of organic acids produced during metabolism and galvanic cells formed, where its mycelium adheres to the metal, whereas corrosion in the sterile controls was probably electrochemical.

Hedrick *et al.* (30) demonstrated that there is a predominance of pittings in corrosion caused by chemical action whereas, microbial corrosion causes blistering, intergranular corrosion and only some pitting in areas in contact with the water phase and fuel water inter phase.

Hendey (31), Crum et al (32) and Parbery (33) found the major contaminant of subsonic air craft fuel was *Cladosporium resinae* causes intergranular corrosion, loss in weight and drop in pH. Churchill (34) compiled the following list of microbes reported to be present in significant amounts in aircrafts. *Pseudomonas, Aerobacter, Sphaerotilus, Closiridium, Bacillus, Desulfovirrio, Micrococcus spicaria, Fusarium, Aspergillus, Penicillium* and *Cladosporium*. Eventually it was realised that corrosion of aluminium alloys under mcrobial deposits characterized particularly by pitting. Exfoliation, and inter-granular attack was caused by some way by microbes.

Salvarezza and Videla (35) from Argentina studied the electrochemical behaviour of aluminium and its alloy in *Cladosporium resinae* cultures by conventional electrochemical technique complement with SEM and EDAX (Energy dispersive x-ray analysis). It was suggested that localized corrosion of metal is produced by a local increase in proton concentration derived from (a) organic acid production (b) the yet non-identified metabolics (c) a decrease in the inhibitor concentrations. These different factors enhance the action of chloride anions already present in electrolyte. The whole process seems to be narrowly related to the enzymatic activity of the micro-organisms and depends in a complex manner in culture composition.

Stranger-Johannessen (36) of Central Institute for Industrial Research, Norway, demonstrated unusually rapid appearance of severe pitting corrosion in the holds of ship. A sample of the corroded steel was investigated for micro-biological deterioration. On incubation on mineral salt agar, fungal growth development from the corrosion product was observed. Corrosion and pitting could be reproduced with two of the isolated strains on sound steel plates after inoculation and incubation for two weeks. The steel surface in the holds had been protected by painting and corresponding paint was found to support growth of these fungi. On incubation of the painted inoculated steel plates, fungal mycelium spread over the surface within a few days and caused blistering and debonding of the paint film. Subsequently, pitting corrosion occurred underneath the blisters. The deteriorgenic fungi was *Scopulariopsis brevicaulis*. Acid production was checked from the deteriogenic fungi S. *brevicaulis* and two other forms (unidentified). It was observed that deteriorating fungi caused no change to the pH. However, the other nondeteriorating fungi lowered the pH. Thus acids produced by fungi may not be the only reason for the corrosion attack on steel.

Corrosion due to the action of sulphate reducing bacteria

Sulphate reducers are found all over the world in soils and waters. They are of anaerobic habit and the use of sulphate or some other oxidised form of sulphur as terminal electron acceptor in respiration. Much valuable information on science and art of the cultivation has been reviewed
by Postgate (37). The nutrition, hydrogen metabolism and other biochemical aspects of the sulphate reducing bacteria has been reviewed by Le Gall and Postgate (38), Postgate (39), and Cragnolino and Tiovinen (40).

The first description of a sulphate reducing organism was of *Spirillum desulfuricans* (now known as *Desulfovibro, desulfuricans*) by Beijerinck (41). Since that time, large number of sulphate reducing bacteria have been isolated, differing in biochemical behaviour, preferred environmental characteristics and resistance to inhibitors, Campbell and Postgate(42) had proposed :

- 1. Desulfotomaculum (Containing all spore forming sulphate reducters).
- 2. Desulfovibrio (Containing all non-spore formers) are recognised.

Desulfotomaculum includes the species D. nigrificans formerly widely known as Clostridium nigrificans a thermophillic species (optimum temp, 55°C).

Nature and Extent of Corrosion by Sulphate Reducing Bacteria

Pipelines and other objects burried in the ground frequently show sulphide corrosion. Such corroded objects if examined immediately after removal from the soil have some characteristics which are as below :

- (1) The pits generally filled with black corrosion product (Sulphide) which when treated with HCl liberates hydrogen sulphide (43).
- (2) Metal surface beneath the corrosion products are often bright and active (Anodic area (44).
- (3) Pits are round at the outer surface and conical in cross-section with concentric rings inside the pits(45).

Mechanism of Corrosion in the Presence of Sulphate Reducing Bacteria

Kuhr and Vlught (46) explained that cathodic depolarisation was considered to be an essential step in the corrosion mechanism. In the absence of oxygen, the cathode reaction on the corroding metal surface would be hydrogen evolution and since the activation overpotential for hydrogen would be too high to be supplied by corrosion cell, the cathodic areas would be covered by a layer of atomic hydrogen and corrosion would cease. They consider that the role of sulphate reducing bacteria was to remove the atomic hydrogen from the metal surface by the reaction of the type—

$$SO_4^{2-} + 8H^+ = S + 4H_2O$$

The corrosion product formation being given by :

 $Fe^{++} + S^{2-} = FeS$ $3Fe^{++} + 60H = 3Fe (OH)_2$

The overall corrosion reaction would then be

$$4F_e + SO_4^{2-} + 4H_2O = F_eS + 3F_e(OH)_2 + 2OH^{-1}$$

If the overall reaction is correct, the composition of the corrosion product should be such that the ratio of total iron and corroded iron as sulphide, would have the value of 4. From time to time various calculations of this ratio have been made for actual corrosion products. Kuhr and Vlught (46) found an average value of 2.9 for the case of corroded cast iron. Low values of this ratio have usually been ascribed to the presence of excess sulphide from decomposition of sulphur containing organic matter. (Starkey(47) found support for the Kuhr mechanism in the quantitative data of Stephenson and Sfickland(48). These authors found that sulphate reducing bacteria perform the reduction of sulphate, quantitatively as follows :

$$H_2SO_4 + 4H_2 = H_2S + 4H_2O$$

If the iron were reduced to FeS by such a system, the value of 4 would be realised.

Wanklyn and Spruit (49) found that the value of the ratio varied between very wide limits, values ranging from 0.9 to 48 being recorded. Thus corrosion product composition data do not seem to provide sufficient evidence for the mechanism proposed by Kuhr and Vlught.

Electrochemical data have similarly given rise to conflict over mechanisms. Hadley(7) measuring changes in potential of mild steel in culture of sulphate reducing bacteria found that during active growth, potentials fell to more negative and considered that this negative shift indicated cathode depolarisation. Wanklyn and Spruit(49) challenged the view that negative shifts indicated cathode depolarisation, indicated on the basis of the Evans-type corrosion diagram, that such negative shifts indicated anodic depolarisation. These authors concluded that sulphide pioduced by bacteria and not the presence of bacteria themselves was the most important factor in this type of corrosion. Hoar and Farrer(50) in studies of the anodic characteristics of mild steel in the presence of sulphate reducing bacteria found that in the presence of bacteria of small amounts of sulphide high corrosion rates could be expected as anodic stimulation took place.

The main body of electrochemical experimental work on corrosion due to sulphate reducing bacteria is due to two groups of workers. Booth and Co-workers in England and Horvath and Co-workers in Hungary. Horvath and Solti(51) were the first to use polarisation techniques in studying this type of corrosion. They found that in the presence of cultures of sulphate reducing bacteria, depolarisation as diagnosed by reduction of slopes of polarisation curves took place in both cathodic and anodic plots, and that this apparent depolarisation effect diminished with the age of the culture.

Booth and Tiller (52, 53) investigated the influence of a number of types of sulphate reducing bacteria on polarisation curves of mild steel, emphasising the importance of using pure culture of organisms. These authors found that strains of sulphate reducing bacteria containing hydrogen as enzyme were capable of causing anodic and cathodic depolarization (Fig. 1, 2.). This work was done in a cell in a separate anode and cathode compartments, one containing sterile medium, the other inoculated with the strain to be studied. They found also that hydrogenase negative organisms caused anodic depolarisation only (Fig. 3, 4).

Booth *et al* (54) found later on, that the semiprotective sulphide films became detached after 20-30 weeks exposure to bacterial action and the corrosion rates increased significantly. The direct correlation between corrosion and hydrogenase activity, which is one of the basic assumptions of the cathodic depolarization theory, became doubtful.

Booth et al (55) also observed that the addition of high Fe $^{2+}$ concentration to the culture medium gave rise to a very high corrosion rate, comparable to those measured in field, because ferrous ion reacted with sulphide produced by bacterial action and thus prevented the formation of a semiprotective sulphide film. Under such conditions, a complete unprotective and loose mass of corrosion products, consisting of iron sulphide and ferrous carbonate was formed.

King and Wakerley (56), King et al (57, 58), showed that different iron sulphides can lead to accelerated corrosion of mild steel, indicating that the action of sulphate reducing bacteria is exercised through formation of fresh iron sulphides. Smith and Miller (59) reviewed the properties of different iron sulphides and their corrosive effects. On the basis of work conducted at the Corrosion and Protection Centre, UMISI (UK) Miller (3) suggested that all iron sulphides are cathodic towards iron.

A different view has been proposed by Costello(60). He measured cathodic polarization curves of mild steel in cultures of *D. vulgaries* and *Desulfovibrio* at pH 6.5 and compared the results obtained in the presence of $0.01M-H_2S$ at the same pH. It was concluded that cathodic depolarization in cultures of sulphate reducing bacteria may be attributed to the cathodic activity of dissolved hydrogen sulphide produced by micro-organisms. The specific role of biogenic H₂S was clearly demonstrated by Togono *et al* (61). A correlation was established indicating that corrosion rate was proportional to the instantaneous concentrations of H₂S produced by bacteria, although the influence of H₂S became complicated because of formation of sulphide films. He later claimed that the accelerating effect of H₂S was greater on the anodic reaction than on the cathodic reaction.

Iverson (62, 63) reported the addition to hydrogen sulphide, sulphate reducing bacteria, produce a highly corrosive substance, possibly a soluble compound containing phosphorus which enhances the dissolution of iron under aerobic conditions at a neutral pH. He emphasized that enhanced corrosion can be expected only when the substance comes in contact with iron, before

Iron film formation takes place. Otherwise, corrosion is stiffled although the subsequent breakdown of the film could result in a further increase of the corrosion rate.

Corrosion of other metals by sulphate reducing bacteria :

Very little work has appeared on metals other than iron and steel. Gilbert (64) found severe corrosion of copper pipes in a moist clay soil; sulphate reducers were detected in large numbers and the corrosion product contained sulphide.

Wan (65) studied the effect of semicontinous cultures of sulphate reducing bacteria of a few months duration on specimens of a copper nickel alloy. Weight was negligible and an apparently protective sulphide film formed, however some pitting was found under it. Hedrick (66) surveyed the possible role of sulphate reducers in causing corrosion of aircraft aluminium alloys.

Hjelem Hansen (67) reported that prehistoric bronze objects found in bogs are often covered by a black layer of copper sulphide. This hydrogen sulphide produced by sulphate reducing micro-organisms under anaerobic conditions in bogs and water-logged soil.

Brinch Madsen (68) drew attention to a hitherto unnoticed form of sulphide formation on bronze items which occurs in museums. This was a black spot of copper sulphide with a crystal structure which when magnified looks like a small bush. A very typical example was an arm ring from prehistoric well. The sulphide corrosion has however been produced while the ring has been in the care of the National Museum, Denmark.

Brinch had pointed out the phenomenon, this type of corrosion was observed in many parts of the world. He further suggested that the phenomenon might be a micro-biological attack on the bronze. Subsequently, Brinch Madsen and Hjelm Hansen (69, 70) and Oddy (71) pointed out that the phenomenon may be explained by the chemical attack of hydrogen sulphide or other forms of reduced sulphur.

From India Garg et al (72) of H.B. Technology Institute Kanpur have also studied the microbiological corrosion of metals of sulphate reducing bacteria (*D. sulfuricans*). Increased corrosion (expressed as percentage) in inoculated media over sterile values was in the following decreasing order : Aluminium, mild steel, zinc, brass, copper, stainless steel.

Prevention and Control of Corrosion Due to Micro-organisms

Since it is not possible to develop microbeproof boundaries, we therefore have to be content with controlling microbial growth to an acceptable level. Oxygen is the cheapest and most effective inhibitor of sulphate reducers. Thus oxygenation could be done.

Miller and Tiller (14) classify methods of prevention or retarding underground corrosion. it can be applied to aqueous situations where appropriate.

1. Using non-corrodable materials.

2. Using corrodable materials.

2.1 In a non-aggressive environment.

2.2.1 By giving the installation a non-aggressive surrounding.

2.2.1.1. By arranging that the environment contains nothing that will accept electrons or cations.

2.2.1.2. By using a biocide in the environment to prevent the growth of sulphate reducing bacteria.

2.2.2. By making the metal sufficiently negative with respect to its environment to prevent cations escaping into it.

2.2.3. By arranging a barrier, impervious to cations and for electrons between the metal and its environment.

Use of Biocides

Reports on the use of inhibitors of sulphate reducing bacteria have been made by Lewis (73), Tehle (74) and Wachs *et al* (75). It is of importance to note that acridine dyes used by Rogers (76, 77) as inhibitors for sulphate reducing bacteria are also useful corrosion inhibitors Putilova *et al* (78). Chromates, used by Drummond and Postgate (79) are common corrosion

inhibitors and quartenary ammonium surfactants shown by Saleh et al (80) to be useful inhibitors of sulphate reducing bacteria, have also been successful in inhibiting aqueous metallic corrosion.

Evans (81) mentioned quite interesting phenomenon that good conditions obtain for buried iron objects over many centuries in soil containing tannin. This was tentatively attributed to the inhibition of bacterial growth by tannin and hopes may have been aroused that small quantities of tannin could provide a cheap means of combating microbiological corrosion. He reported bactericide, Di-chlorophenol Methane.

Bennett (82) tested seventeen diethylene triamine compounds and one diprophylene triamine compounds for their antimicrobial properties in metal working fluids against mixed flora of bacteria and fungi, 1, 4, 7 trimethyl diethylene triamine was found to have the best antimicrobial activity. Hirsch (83) has found that Diethylene triamine have no inhibitory activity against tubercle bacilli, however, it was inhibitory for yeast (84). Others have noted that compounds such as N- (2, 4, 5-trimethyl benzyl) diethylene triamine (Merianos and Adams, 85, 86), N-(pentachlorophenyle) diethylene triamine (87), N-(Pentachlorobiphenyl) diethylene triamine, Npolyalkylene-N-polyoctyle diethylene triamine *et al* (88) and a diethylene triamine triarylborane derivative, (89), all exhibit antimicrobial activity. Diethylene has been employed in combination with dithiocarbamates as fungicide (90).

Costello (13) reported Hibitane (Bis-p-chlorophenyl diguanidoheane diacetate) as a successful bactericide for backfills.

Hjelm-Hansen (67) reported techniques for conservation of antiquities containing sulphide corrosion products and recommended 1-amino-lycanoethylene 2, 2, -di (Sodium thiolate) for dissolving the sulphide layer. For the long term protection the treatment with benzotriozole followed by lacquering is recommended.

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CURRENT DENSITY MA Cm-2 Fig. 1

Anodic and cathodic polarisation curves for mild steel at 30°C. Anode compartment for mild steel at 30°C. Anode compartment sterile; cathode compartment inoculated with inoculated with Dv. desulfuricans (Hilden-Dv. desulfuricans (Hildenborough).

Anodic and cathedic polarisation curves borough); cathode compartment sterile

3 days incubation; —after 10 days incubation cubation, \triangle after 10 days incubation (Booth (Booth and Tiller, 1960).

. initially; \times after 2 days incubation; \times -initially; -after 2 days incubation; -after . after 3 days incubation; - after 7 days inand Tiller, 1960)





CURRENT DENSITY, LLA Cm2



Fig. 3

Anodic and cathodic polarisation curves for mild steel at 30°C. Anodic compartment sterile; Cathode Compartment inoculated with *Dm. orientis* (Singapore).

. initially; \times after 2 days incubation; after 10 days incubation (Booth and Tiller, 1960).

Anodic and cathodic polarisation curves for mild steel at 30°C, Anode compartment inculated with *Dm. orientis* (Singapore); cathode compartment sterile.

initially; \times after 2 days incubation; \square after 7 days incubation; \triangle after 10 days incubation (Booth and Tiller, 1960).

(hydrogen scale)

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Fig. 4

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RECOMMENDATIONS

1. It is felt that testing of materials used for the construction of showcases, storage boxes, packing cases, etc. is extremely important. No material should be used for this purpose unless it has been tested for its properties. A working group may be constituted to study the problem.

In this connection paper and board manufacturers may be requested to prepare good quality paper, suitable for museum work.

- 2. The suggested use of 2-coumarinyl benzimidazole to control bronze disease was considered of great significance. Further experiments should continue on this subject. Various institutions may collaborate in this programme.
- 3. High or too low humidity is considered dangerous for museum objects. Studies should be undertaken to devise suitable means for maintenance of constant relative humidity inside showcases and galleries.
- 4. The question of protective coatings should be further studied in order to find out the best protective coating for metals.
- 5. A publication describing techniques for arresting decay of metal objects should be prepared which can act as a guide to museum curators and archaeologists.
- 6. In order that there be a better communication between various institutions in terms of flow of technical know-how about different materials, particularly about standard materials suitable for museum work, there should be a quarterly newsletter.
- 7. It was interesting to note that there was influence of light on the phenomenon of corrosion of metals. Studies should be undertaken to understand its mechanism.
- 8. The importance of corrosion inhibitors was emphasized. It was therefore felt that new and better corrosion inhibitors should be evolved. A working group should be formed for this subject as well.
- 9. Biodeterioration of metal objects is comparatively a new aspect of metal corrosion and all efforts should be made to study the subject further.
- 10. It is essential to lay down criteria defining the extent of removal of alteration products or deposits from metal objects. A working group may be constituted to look into this aspect.
- 11. Study of composition of bronzes and corrosion products is essential for improving methods of conservation of metal objects. A working group for this should also be constituted.
- 12. There should be a proper training course of a minimum duration of 2 years leading to B.Sc. Degree in Conservation.
- 13. It was felt by all the participants that the present Seminar was extremely useful in focusing attention on the various problems of metal conservation in the region. It was felt desirable that there be a periodical seminar once in 3 years to review the progress of work on the subject.

17-643NRLC/83

PROGRAMME

Monday 7 Dec. 1987	exore ne	
Chairman : Dr. T.Y. Lee	10.00. A.M.—10.45 A.M e	I. Registration of participants.
	10 ·45 A.M.—11 ·45 A.M	I. Welcome and key paper Conservation of metals—Problems & Prospects. O. P. Agrawal
	11 .45 A.M12 .00 Noc	on Tea
	12 ·00 Noon—1 ·00 P.M.	Observation on corrosion of bronzes acquired from treasure troves and their condition after treatment in the Govt. Museum, Madras. —N. Harinarayana
	1.00 P.M2.00 P.M.	Lunch
Chairman : Dr. Tej Singh	Service The July Service	
	2.00 P.M.—3.15 P.M.	Application of Metallurgy in Conservation. —Hari Narain
		Experiments on the use of 2-coumarinyl benzimidazole to control bronze disease. —M.V. Nair & O. P. Agrawal
	3.15 P.M3.30 P.M.	Tea
	3 ·30 P.M.—5 ·30 P.M.	Visit to special exhibition on metals and the NRLC facilities.
Tuesday, 8 Dec. 1987		
Chairman : Mr. N. Harina	arayana	
	10.00 A.M.—10.30 A.M	Dr. Gamil Hamdy, UNDP Resident Representative in India to address the participants.
	10.30 A.M.—11.30A.M	Conservation of bronzes in Thailand. —K. Janposri
		Comparison of analysis of surface and interior of metal objects by XRF and AAS.
		Conservation of metalssome rather ignored factsC.P. Uniyal
	11 ·30 A.M.—11 ·45 A.M.	Tea
	11 ·45 A.M.—1 ·15 P.M.	Practical demonstration in Analytical Laboratory.
	1 ·15 A.M.—2 ·30 P.M.	Lunch
:	2·30 P.M4·00 P.M.	Practical demonstration in Analytical Laboratory.
	4·00 P.M.—5·00 P.M.	Visit INTACH Conservation Centre.

Wednesday 19 Dec. 1987

Chairman : Mrs. Kulpanthada Janposri 10.00 A.M.-11.30 A.M. Methods of treatment of iron objects -V.C. Sharma A note on the problems of decay of metal objects. -R.K. Mukhopadhyay corroded copper coins Treatment of -D.C. Mehrotra 11.30 A.M.-11.45 A.M. Tea 11.45 A.M.-1.00 P.M. Corrosion -V.M. Bhandari Use of inhibitors and surface coatings in preservation of metal objects. -Kamta Prasad 1.00 P.M.-2.00 P.M. Lunch Mr. Ghulam Mustafa Effect of light on the corrosion of Chairman : 2.00 P.M -- 3.30 P.M. iron objects contaminated with chloride ion. -T.Y. Lee. Training in metal conservation -H. K. Naithani & S.K. Bhatia General technique of metal casting -Suwarcha Paul Conservation of metallic cultural property under high humidity in Japan-S. Aoki 3.30 P.M.-5.00 P.M. Visit to State Museum. Thursday 10 Dec. 1987 Chairman : Mr. S. Aoki 10.00 A.M.-11.30 A.M. Microbial deterioration of metals. -Shashi Dhawan Effect of lichens on cultural property-A need for further study -Ajay Singh Protective coatings in conservation of -K. Huda metal Antiquity. 11.30 A.M.-11.45 A.M. Tea 11.45 A.M.-1.00 P.M. Corrosion inhibitors. --- V.C. Sharma Chemist & Restoration of bronze objects

—B. Samal Study of copper objects from Ramapuram, Distt. Kurnool, Andhra Pradesh

-S. Subbaraman & Sreelatha Rao Lunch

1 ·00 P.M.—2 ·00 P.M. 2 ·00 P.M.—5 ·00 P.M.

Practical demonstration in metal conservation Laboratory

Friday 11 Dec. 1987 Chairman : Dr. Othman Bin Yatim

10.00 AM-11.30 A.M.

Country paper Conservation of copper and bronze metal antiquities in Pakistan -Ghulam Mustafa Metal conservation in Bangladesh -K. Huda Conservation of metals in Thailand. -K. Janposri Conservation of excavated metal objects in Japan-Shigeo Aoki Country report -- Malaysia Country reports ---Othman Yatim N. Harinarayana V.M. Bhandari Subbaraman Kamta Prasad

11 JU A.WI. 11 45 A.WI. 16a	
11.45 A.M1.00 P.M. Country Papers	
1.00 P.M2.00 P.M. Lunch	
2.00 P.M4.00 P.M. Visit Lucknow monumen	ts
4.00 P.M5.30 P.M. Visit State Archives	

Saturday 12 Dec. 1987

10.00 A.M.—11.30 A.M. General discussions on questionnaire of metals.
11.30 A.M.—11.45 P.M. Tea
11.45 A.M.—1.00 P.M. General discussions on questionnaire of metals.

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