# ELECTROLYTIC RESTORATION OF BRONZE STATUES AND INSCRIBED COPPER-PLATES

By S. Paramasivan

(*Archæological Chemist, Government Museum, Madras*)

Received December 5, 1940

## 1. *Introduction*

The electrolytic process for the restoration of ancient bronzes, which is the reversal of the process of corrosion,[1] was first suggested by Finkener,[2] Ch. Frisch,[3] François Margival[4] and Francesco Rocchi.[5] But these suggestions were not put to much practical use. It was Colin G. Fink,[6] who worked out the experimental details for the first time and recommended its adoption on an extensive scale for the restoration of ancient bronzes in the Metropolitan Museum of Art of New York in preference to the older chemical methods advocated by Dr. Alexander Scott[7] of the British Museum. The electrolytic method was so startling in its effects that the Field Museum of Natural History,[8] Chicago, Museum of the University of Pennsylvania,[9] Fogg Art Museum of the Harvard University, Cambridge, Mass., and other American Museums have been regularly adopting it.

But the electrolytic restoration of Bronzes was popular only in America, and has been exclusively confined to the treatment of small bronze objects measuring about one foot at the most in extreme cases. Recently, the process has been extended in the Madras Government Museum for the restoration of ancient bronze statues which measure about 4 feet in height. Thus these bronzes are much larger than the ones ever treated elsewhere. The process has also been successfully adopted for the restoration of inscribed and heavily corroded copper-plates, probably for the first time.

## 2. *Ancient Bronzes in Madras Museum*

The Madras Government Museum has the richest collection of ancient bronzes in India. They are of wonderful artistic workmanship and some of them are the largest and the most famous throughout the world. Many of them are treasure trove finds. Through long burial in the earth, they have become covered with thick crusts which are composed of the products of corrosion. The crust not only hides the details of artistic workmanship, but frequently eats into the bronze, thereby causing considerable damage to it. Thus the main problems with these bronzes are, (1) to remove the disfiguring incrustations which conceal the decorative details, (2) to restore to the object its original appearance and (3) to eliminate the corrosive substances which cause rapid disintegration and thus to assure the permanence of the valuable exhibit. These have been effected by the electrolytic process.

### 3. *Chemical Composition of the Bronzes*

The collection of bronze statues in the Madras Museum date from about the ninth century A.D. down to modern times. Bronzes belonging to various periods were selected at random and drillings taken from their pedestals or other unimportant portions were analysed. The results of analysis were as follows:—

*Chemical Analyses* (*Per cent.*)

| | 10–11th century A.D. | 13th century A.D. | 15th century A.D. | 17th century A.D. |
|---|---|---|---|---|
| Cu .. | 86·88 | 91·05 | 96·29 | 91·25 |
| Sn .. | 10·44 | 2·86 | 2·58 | 6·66 |
| As .. | Tr | Tr | Tr | Tr |
| Pb .. | 1·48 | 6·09 | 1·09 | 2·02 |
| Fe .. | 1·19 | Tr | 0·06 | 0·07 |

The results of chemical analysis clearly show that Indian bronzes are rich in copper and that tin has been specially added to harden the alloy. In the case of the thirteenth century bronze, lead* has been purposely added, probably with the object of hardening the alloy. The same is true of iron in the tenth-eleventh century bronze.

### 4. *Composition of Corrosion Products*

The composition of the corrosion products of museum exhibits have been fully discussed by Rathgen.[10] It is not, however, an easy matter to collect samples of corrosion products from the valuable bronze collections of various periods exhibited in the Madras Museum, for purposes of analysis. Even if they are available, the results of analysis are not of importance for comparison, especially when corrosion has not taken place under identical conditions. The following however are the results of analysis of typical corrosion products from a bronze belonging to the ninth century A.D.:—

* Lead occurs also in early Babylonian and Egyptian bronzes.

*Chemical Analysis (Per cent.)*

| | Bronze | Patina |
|---|---|---|
| Copper .. .. .. | 83·39 | 76·16 |
| Tin .. .. .. | 16·61 | 15·09 |
| Lead .. .. .. | Tr | Tr |
| Arsenic .. .. .. | Tr | — |
| Iron .. .. .. | Tr | 0·09 |
| Water .. .. .. | | 1·23 |
| Carbon dioxide .. .. | | 1·75 |
| Sulphuric anhydride, $SO_3$ .. | | Tr |
| Chlorine .. .. .. | | Tr |
| Oxygen .. .. .. | | 5·52 |
| Lime, CaO .. .. | | 0·14 |

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 soils have converted the copper and tin into mineral compounds such as oxides, chlorides, sulphates and carbonates (malachite and azurite). With the Madras Museum specimens, the corrosion has not gone deep and there is still sufficient metal left.

The bronze statues in the Madras Museum have been subjected to different degrees of disintegration. The crusts thus formed as a result of corrosion can be classified thus:—

*Corrosion Product*

- Edel Patina
- Corrosive crust
  - Normal (without deformation) (with or without metal core)
  - Botryoidal mass
  - Deformed crust
- Malignant Patina

(*i*) A few of the bronzes are covered with a thin transparent coat of minerals of pleasing colour and of enamel-like appearance, which gives an air of antiquity to the bronze. This coating is called *Edel patina*.[11] The metal surface under it is quite smooth. The *Edel patina* does not obscure the details of workmanship. On the other hand, it protects it.

(*ii*) In some cases, the surface of the bronze is covered with a thick non-translucent crust, which is rough and obscures the decorative details. The crust might be quite normal, or it might be a botryoidal mass of malachite and azurite or it might be outwardly deformed. When the crust is normal, the metal under it is perfect. At times it might be roughened and pitted. When the crust is of a botryoidal mass, the surface under it is always roughened and pitted. Some of the bronzes are heavily encrusted and outwardly deformed, the latter being confined to the crust alone. Ordinarily bronze statues seem to resist the distorting forces as the excess material, in the form of oxidation products, migrates outwards and is deposited on the outer crust.

In all the cases, where the surface of the bronze is not roughened or pitted, the oxide of copper which replaces the original metal surface retains the details of that surface.

(*iii*) Some of the bronzes have *Malignant patina* on them. If unchecked, the smallest patch of it will destroy the entire bronze. It is erratic in its action. A patch of it, not larger than a pin's head, may remain passive for years and then, for no apparent reason, suddenly become active. *Malignant patina* is due to the presence of copper salts[12] such as the chloride or the sulphate which adheres to the surface and is occluded in the pores of the corroded bronze. They continue the destructive action indefinitely even after the bronze has been removed from the primary source of trouble.

### 5. *Process of Corrosion*

The crusts or the products of corrosion of a bronze are due to electrochemical action[13] which in turn, depends upon various factors such as the amount of moisture and the salinity of the soil in which the statues have long buried. It is also influenced by the duplex structure of the copper alloy which contains very slight impurities of more or less noble metals. These impurities set up many local miniature electrolytic cells on the metallic surface. The salts in the ground water serve as electrolytes. Inequalities in the concentration of the salts and the amount of oxygen present in it give rise to differences in the electrolytic potentials. They result in the transport of the metallic ions from one local area to another. On some of these local areas (anodic), the copper is attacked by the salt and a soluble copper salt is formed. On other areas, which are cathodic, alkali accumulates, and the copper is little affected. The action of the salt and oxygen can be properly expressed thus:—

$$Cu + 2\,NaCl + H_2O + O \rightarrow \underset{\text{Anodic}}{CuCl_2} + \underset{\text{Cathodic}}{2\,NaOH}$$

This reaction takes place only when conditions are such as will tend to cause a difference of potential between closely adjacent local areas on the surface of copper. A similar local electrolytic action gives rise to pitting on the surface of the bronze. Such differences of potential between the different parts of the metal might be as much due to physical or chemical variations in the metal itself, *viz.*, local strains, segregations of impurities, presence of second metal phase, as to variations external to the metal, such as differences of oxygen or metal ion concentration.[14]

The actual rate of corrosion in any particular case is determined by various factors in the soil, the interaction of which makes the subject exceedingly complicated. Some of the factors which operate on the bronzes while lying buried under the earth are as follows:—

*Relating to metal*

1. Electrode potential.
2. State of aggregation.
3. Presence of internal stresses.
4. Overpotential.
5. Nature of concentration of metals in solid solutions.
6. Nature, amount and distribution of second phase.
7. Chemical reactivity.

*Relating to external conditions*

8. Temperature.
9. Pressure of oxygen.
10. Rate of supply and distribution of oxygen.
11. H-ion concentration.
12. Nature and distribution of corrosion products.
13. Conductivity of the liquid.
14. Metal ion concentration.
15. Specific nature of ions present.

With treasure trove finds which have been lying buried in moist soils containing water alone or salt solution, (12) becomes very important since the films and mounds of corrosion products might form at the metal surface and affect other factors in a complicated manner.

### 6. *Electrolytic Restoration*

Without any preliminary treatment, the corroded bronze statue is placed in an iron tank or cell and insulated from it by porcelain insulators. The cell contains a 2% solution of sodium hydroxide. A current of electricity is allowed to pass through the cell, the bronze acting as the cathode and the iron tank as the anode. The process consists in the electrolytic decomposition of the sodium hydroxide and the evolution of hydrogen at the cathode, which reduces the crust to finely devided or spongy copper, which can be brushed off, with the result that the decorative details are exposed.

Before starting the electrolytic reduction of specially valuable and heavily corroded bronzes, radiographs of them are taken in order to find out the extent of the corrosion, the nature of the precautions to be taken in the course of electrolytic reduction and the final result to be expected.

### 7. *Apparatus at the Madras Museum*

The apparatus used for the electrolytic restoration of heavy bronzes is not unlike that used for electroplating on a large scale. It consists of a 7 kilowatt motor generator set capable of generating up to 60 amps. at any voltage ranging from 0 to 110. In addition, there are means of measuring and controlling voltage and the current supply. There are also electrolytic cells to conduct the reduction in.

*Current Supply.*—The motor generator set is fed by 440 volts D.C. power. Its output is a direct current, which may be regulated up to 110 volts or 60 amps., provided its maximum capacity of 7 kilowatts is not exceeded. The voltage is regulated by a rheostat in the field winding of the generator. All the controls for the motor and the generator are on a marble-panelled switch board.

There are three parallel circuits leading from the control switch board to a separate room in which the electrolytic cells are housed. The electrolytic reactions in the cells can be independently controlled from the switch board. The current in the first circuit can be varied from 0 to 60 amps. by a control rheostat joined in series. The current passing through the second and the third circuits can be similarly varied from 0 to 20 amps. and 0 to 5 amps. respectively by suitable rheostats. In this equipment, the output under constant load does not fluctuate, except when the voltage is low, namely 0 to 30 volts. If the generator is to supply current at low voltage, the field rheostat is to be constantly adjusted to maintain the same current strength.

There are other sources of current supply such as utilising the 220 volts D.C. power line with suitable resistance lamps to reduce the voltage. In view of the experiences of American museums even with small bronzes, such equipments were found to be quite unsuitable for the restoration of large objects. Even storage cells were unsuitable. The motor generator has been found to be more useful from the point of view of its ease of operation and control and freedom from trouble.

*Current Control.*—The control panel has three ammeters respectively in the 0–60 amps., 0–20 amps., and 0–5 amps. circuits. In the first, readings can be adjusted correct to 1 amp. from 20–60 amps. This circuit is operated only when the objects which require more than 20 amps. are to be restored. In the second circuit, the current strength can be adjusted correct to 0·5 amps. from 5–20 amps. This circuit is intended for the restoration of those objects which require more than 5 amps. In the third circuit, the amperage can be adjusted correct to 0·05 amp. and from 1–5 amps. and is specially used for the restoration of objects requiring more than 1 amp. It is only very rarely that objects requiring less than 1 amp. have to be restored. In such cases, readings correct to 0·05 amp. from 0–1 amp. can be obtained with another rheostat having a maximum resistance of 2000 ohms, and a current rating of 1 amp. A double throw knife switch is introduced in the 0–5 amps. circuit by which connection can be made either with the 0–5 amps. circuit or with a fourth circuit in which the current can be varied from 0–1 amp. To guard against damage from short circuits, fuses for the different circuits are provided in the switch board itself.

*Measuring Instruments.*—The effectiveness of the treatment and the safety of the specimens depend upon accurate knowledge and control of the current strength during electrolysis. For this purpose, well calibrated ammeters and voltmeters are provided in the switch board. The instruments are permanently in circuit. The voltage at the electrodes in the cells is determined by a separate portable Weston-type voltmeter.

The computation of the proper current strength to be used with each object is very important. Too heavy a current might result in too much gassing at the electrodes which might blast away the corrosive crust, thereby damaging the bronzes. It has been estimated that the current density at the cathode should always be from 1–5 amps. per sq. ft. With many objects, it is about 2 amps. per sq. ft. Where there is too much gassing at the cathode, the current density is even less. The voltage is kept low, preferably at about 10 volts. But if the crust offers resistance to the passage of current, the voltage is much higher, going up to about 110 volts in the initial stages.

The computation of the area of the cathode surface in order to determine the necessary current strength is an easy matter.[13]

*Electrolytic Cells.*—The weight and the size of the specimens preclude the use of electrolytic cells of glass or earthenware as in American museums. In the early stages of the eletrolytic work in the Madras Museum, paraffined wooden cells were used with an iron wire-gauze closely touching the inner walls acting as the anode. On account of troubles through leakage, they have now been discontinued. At present cylindrical iron tanks with welded joints have been substituted with success. Nothing that has been tinned, galvanised, soldered or brazed can be used because of the secondary electrolytic action through formation of miniature cells.

*Electrolyte.*—The electrolyte used is a 2% solution of caustic soda. Commercial grade of caustic soda in flakes has been used. The avidity with which the substance absorbs moisture and carbon dioxide from air makes it necessary to observe certain precautions when storing or handling the substance. It is purchased in 1 and 5 lbs. tin containers. If the caustic soda is damp or in lumps, it is rejected lest the carbonate present in it should damage the valuable bronze.

For preparing the 2% solution of caustic soda, the following procedure is adopted. The cell is filled with water so as just to cover the top of the statue placed in it, and the level of the water marked. The statue is taken out of the cell and the level of water marked again. From the internal dimensions of the cylindrical cell and the difference in the two water levels, the volume is calculated in c.c.'s and this is numerically equivalent to the weight of water in grams. The amount of caustic soda needed will be just 2% of this.

The statue is now placed in the cell and insulated from it by porcelain cable insulators. After making the necessary electrical contacts, the cell is now filled with water so that only about four-fifths of the bronze is immersed in it. The requisite quantity of caustic soda is quickly weighed and separately dissolved in minimum quantity of water and poured into the cell, and the contents stirred. Water is then added to the cell till the bronze is just immersed. The specific gravity of this solution is 1·0207. As the commercial grade of caustic soda is not pure, the solution is slightly understrength, which does not affect the result. But if the strength is kept above 2%, damage will result to the bronzes during electrolysis.

*Electrodes.*—Formerly when wooden cells were used, anodes were cut out of wire-gauze and laid against the inner vertical wall of the cell, and then clamped. At present, the iron tank, insulated from the ground and from the bronze (cathode) by porcelain cable insulators, acts as the anode. It has a binding block of brass permanently clamped to the rim through which electrical connections are made from the switch board. These iron cells can be used over and over again. The cells in the Madras Museum have been in regular use for the last seven years, and are likely to last for many years more.

It has been found that the farther the anode is from the cathode, the more regular is the electrolytic reduction. This fact is always borne in mind when arranging the cathode in the cell. The bronze statue which stands upright in the cell acts as the cathode and is clamped to a special stand through which proper electrical contacts are maintained. The weight of the entire bronze pressing upon the brass stand aids the maintenance of proper electrical contacts.

Objects in almost identical state of corrosion and measuring alike are clamped together and restored simultaneously in the same cell.

In the case of inscribed copper-plates, they are suspended in the electrolyte with two anodes (iron wire-gauze) suspended on either side of it. The anodes exactly resemble the cathode in shape.

A serious difficulty is encountered in the restoration of the inner walls of the base of the pedestal. The base always encloses air and is not filled with the electrolyte. Further the base of the brass stand completely covers the base of the pedestal, thereby preventing the electroyltic reduction. In such cases, a hole is drilled through the top of the pedestal which enables the enclosed air to escape and the electrolyte to fill the hollow. Further, a circle measuring about 4 inches in diameter is cut through the base of the stand, whereby the electrolytic action between the inner wall of the pedestal acting as the cathode and the bottom of the cell acting as the anode is not prevented.

In the case of heavily corroded bronzes, which are mostly small, the electrical connections are made by wrapping an annealed copper wire around the specimen in a close coil of three to six turns. When the specimen is entirely composed of earthy matter with high resistance, the wire is attached in the usual way and is carried in a loose spiral over the entire length of the specimen for the purpose of providing a larger contact surface. When the crust is thick it may happen that the crumbling of the coating during the treatment may release specimens which are mere shapeless concretions under such conditions, they are wrapped and tied with the wire much as a parcel is tied with a string.

*Duration of Treatment.*—The reduction of a thin crust 2 to 3 mm. in thickness usually requires 3 or 4 days. Bronzes with crusts varying from 3 to 6 mm. in thickness usually require 3 to 6 months of electrolytic treatment. The use of too strong an electrolyte or too high a current density or voltage causes excessive gassing at the electrode, and this gives rise to warping and disintegration, unless there is a strong metallic core. Thus with extremely corroded bronzes, where there is gassing even at low current density, the strength of the current has to be lowered still, in which case, the duration of treatment is correspondingly increased.

The metal compounds in the crust are slowly reduced back to metal and on further electrolysis, the finely divided metal becomes more and more compact. If this stage is desired, then the duration of treatment is correspondingly increased.

In the Madras Museum, the electrolytic plant is in operation for six hours a day and for 6 days in the week. The completion of the treatment is indicated by the gassing at the cathode even at low current density.

*Results of Electrolytic Treatment.*—The results of the electrolytic treatment of bronze statues can be set down thus:—

| Nature of the crust | Results of treatment |
|---|---|
| 1. Edel Patina | No treatment except when associated with destructive salts like the chloride or the sulphate. Where the surface under the patina is roughened or pitted by corrosive salts, the surface cannot be improved by treatment. |
| 2. Malignant Patina | Good results. |
| 3. Thick crusts obscuring details:— | |
| (*a*) Normal (with or without metal core) | Good results. |
| (*b*) Botryoidal Mass | Surface appears badly corroded after treatment. |
| (*c*) Deformed crust | Good results if the specimen is not very thin. |

*Record of Results.*—The results of the electrolytic treatment are recorded as follows:—

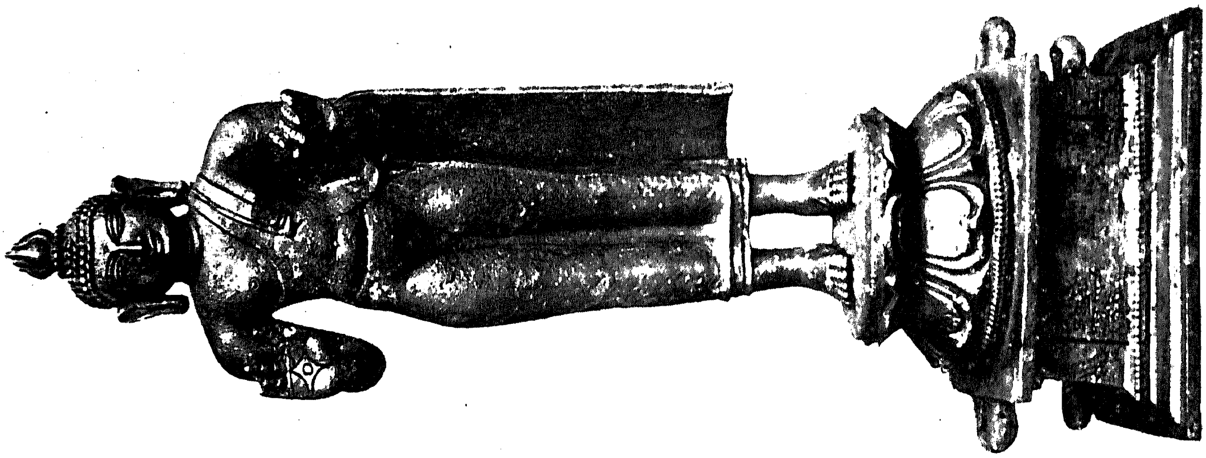
TABLE I

| 1 Serial No. | 2 Catalogue No. | 3 Dimensions | 4 Weight | | 5 Appearance | | 6 Surface (area) | 7 Voltage |
|---|---|---|---|---|---|---|---|---|
| | | | Before | After | Before | After | | |
| | | | | | | | | |

| 8 Amperage | 9 Strength of Electrolyte | | 10 Duration of treatment | 11 Energy consumed | 12 REMARKS |
|---|---|---|---|---|---|
| | Before | After | | | |
| | | | | | |

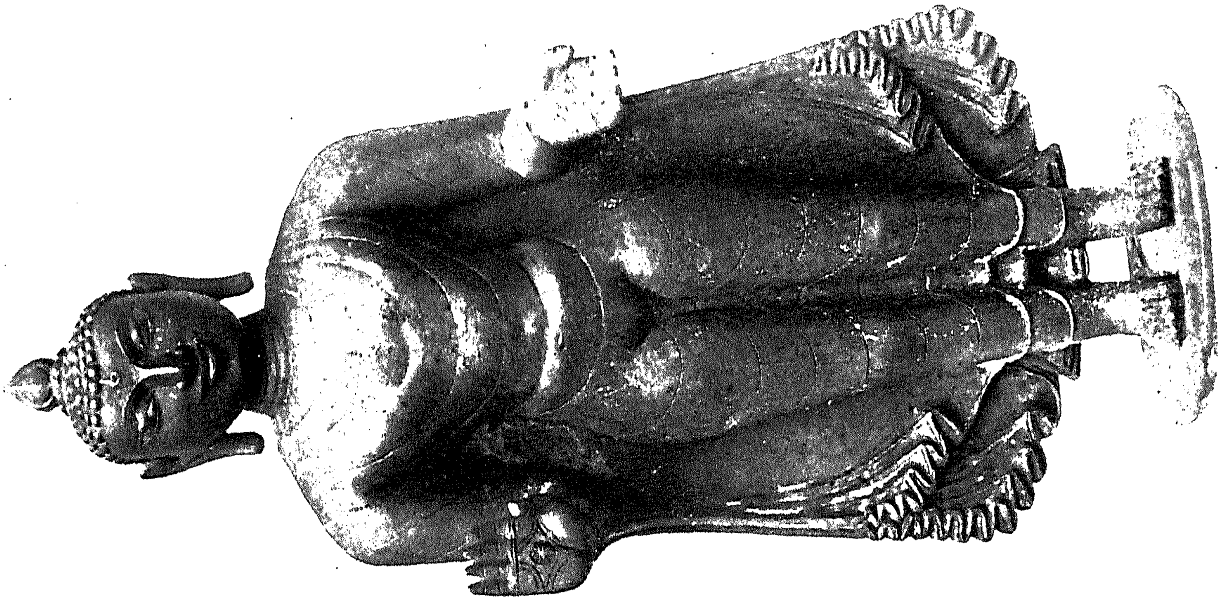
After

Before



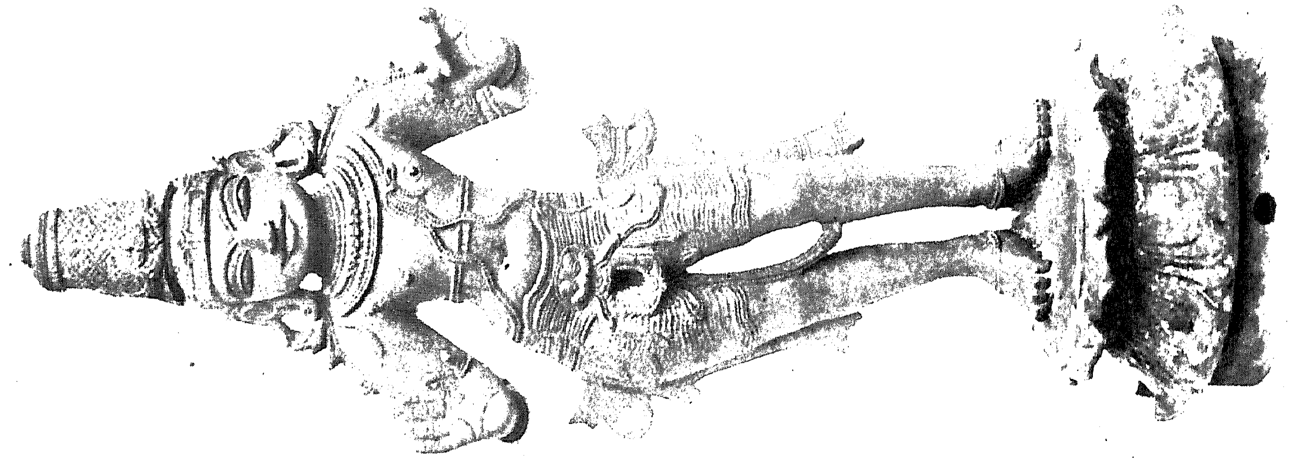
After

Before



After

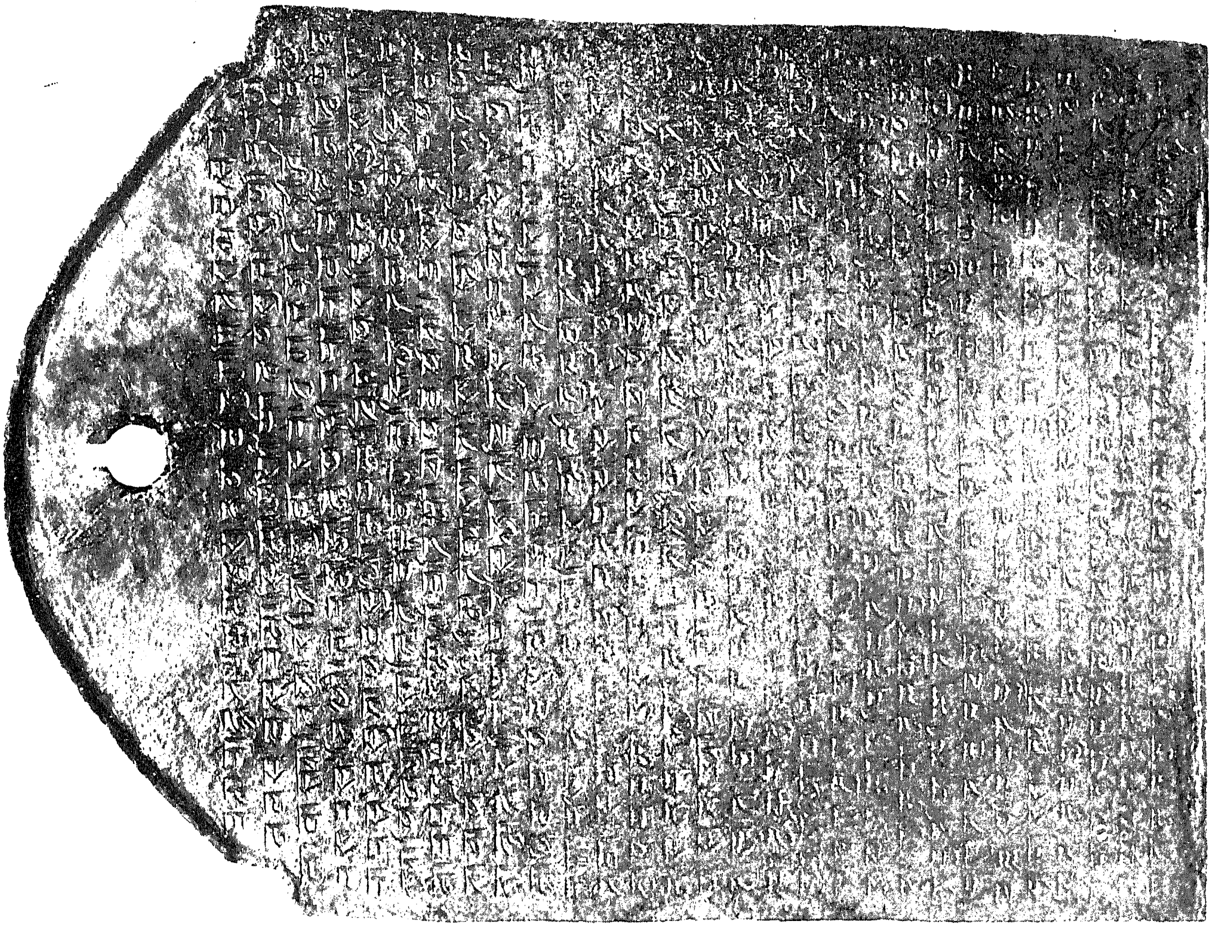
Before



After

Before

INSCRIBED COPPER PLATES BEFORE AND AFTER TREATMENT


After

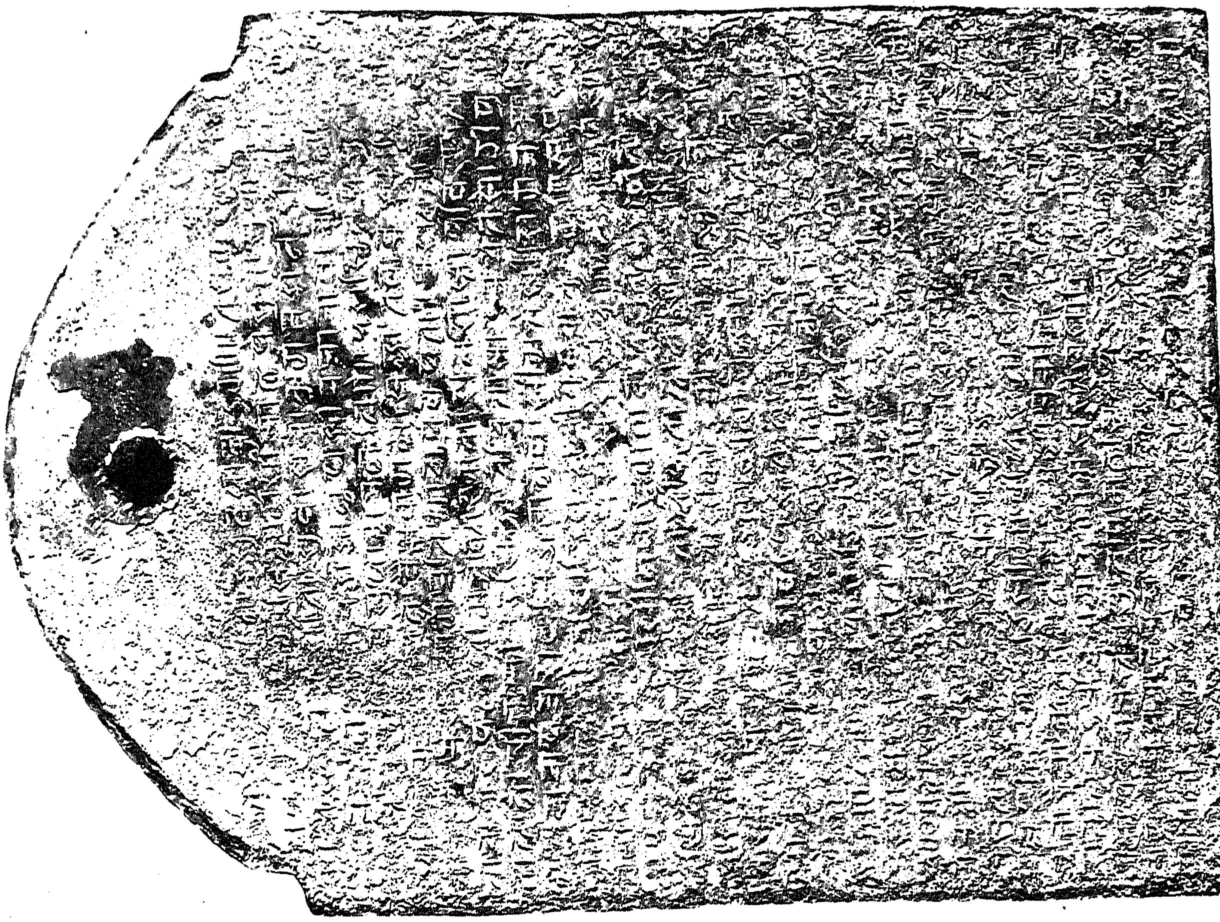

Before

TABLE II

| 1 Serial No. | 2 Date | 3 Voltage | 4 Amperage | 5 Metre Reading | | 6 No. of units | 7 REMARKS |
|---|---|---|---|---|---|---|---|
| | | | | Initial | Final | | |
| | | | | | | | |

In conclusion, the author desires to express his thanks to Prof. Erlam Smith who suggested the problem to him and to Dr. F. H. Gravely for giving him the necessary facilities for carrying out the work.

REFERENCES


1. R. J. McKay and R. Worthington, *Corrosion Resistance of Metals and Alloys*, American Chemical Society Monograph, 1936, Chapter II, 29–47.

2. Friedrich Rathgen, *The Preservation of Antiquities*, Cambridge University Press, 1905, 125–28.

3. "Natural Patina and Artificial Patina," *Revue de Chimie Industrielle*, 1904, **15**, 169–74.

4. "Bronze Patinas," *Ibid.*, 1911, **22**, 304–10 and 331–32.

5. "Contribution of the Experimental Sciences," *Rassegna d'Arte*, 1920, **7**, 258–64.

6. *The Restoration of Ancient Bronzes and Other Alloys*, The Metropolitan Museum of Art of New York, First Report, 1923.

7. *The Cleaning and Restoration of Museum Exhibits*, (Bulletin No. 5) Department of Scientific and Industrial Research, 1921.

*Ibid.*, Second Report.

8. *Restoration of Ancient Bronzes and Cure of Malignant Patina*, Field Museum of Natural History, Museum Technique Series No. 3, 1930.

9. *Journal of the University of Pennsylvania*, 1929, 246.

10. *Loc. cit.*, pp. 15–49.

11. H. W. Nichols, *loc. cit.*, 45–46.

12. H. W. Nichols, *loc. cit.*, 45–47.

13. McKay and Worthington, *loc. cit.*, 29–49.

R. J. Gettens, *Mineralisation, Electrolytic Treatment and Radiographic Examination of Copper and Bronze Objects from Nuzi*, Technical Studies, 1933, **1**, 119–33.

G. D. Bengough, R. M. Jones and R. Pirret, "Fifth Report of the Corrosion Committee," *Journ. Inst. Met.*, 1920, **23**, 65–158.

U. R. Evans, *Corrosion of Metals*, Edward Arnold and Co., London, 1926.

W. F. Collins, "The Corrosion of Early Chinese Bronzes," *Journ. Inst. Met.*, 1931, **45**, 23–55.

14. "Corrosion and Rusting," *Ency. Brit.*, 1936, **6**, 469–70.