Gold Foil, Strip, and Wire in the Iron Age of Southern Africa

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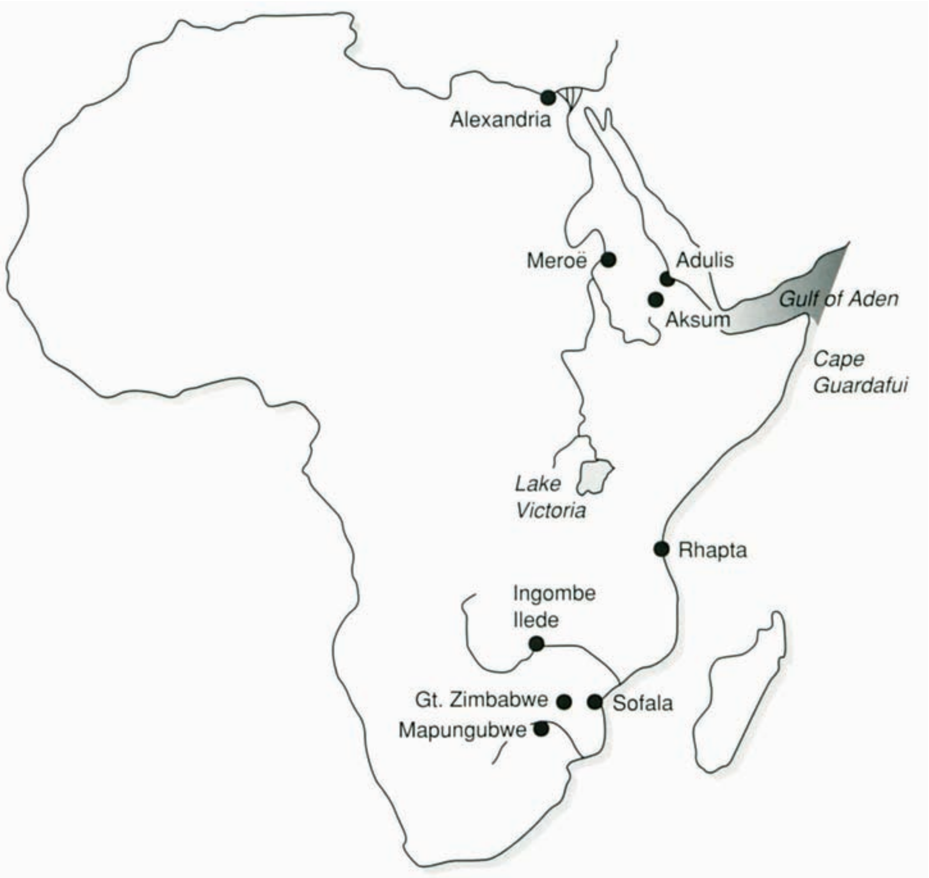
Gold has been an important metal in the southeastern part of Africa for at least the last millennium, and possibly longer, and many sites show signs of primitive (although usually undated) mining activity (Summers 1969). There are three main sites in Southeast Africa where gold artifacts from the later Iron Age have been found: Mapungubwe in the northern Transvaal, which flourished in the eleventh and twelfth centuries; Great Zimbabwe, which flourished in the thirteenth and fourteenth centuries; and some rich burials at Ingombe Ilede in Zambia, which date from the late fourteenth and/or fifteenth centuries.

Gold was one of the commodities that brought early explorers and traders south on the Red Sea. Although in the time of Solomon the ships had probably reached only as far south as the Gulf of Aden, by the first century C.E. at the latest, Greeks from Egypt had rounded Cape Guardafui and sailed down the East African coast, probably as far as Rhapta opposite the island of Zanzibar (Casson 1989). The map (Fig. 1) shows this ancient route. It is likely, however, that Arabs had penetrated into the Indian Ocean well before this time; Arab traders subsequently reached as far south as Sofala, establishing trading posts along the coast, at least from the ninth century C.E. These posts were outlets for the products of the interior, of which gold was probably one of the most important.[1]

As a result of the settlements by Arabs and their intermarriages with the indigenous peoples, the Swahili culture developed along the coast, and this culture had maritime trading connections with the Red Sea, the coast of Arabia, and ultimately with India. Even shards of Chinese ceramics dating from the Sung Dynasty (C.E. 960–1279) onward have been found at Great Zimbabwe (Summers 1963:46, fig. 14).

The tenuous contacts with the cultures of Arabia and India, which are proven by imports from these regions, raise the question of when external influences first penetrated the African interior. The cultural origins of the great stone ruins in modern Zimbabwe, the best example of which is Great Zimbabwe, were much debated in the earlier part of this century. It has long been recognized, however, that the ruins were

FIGURE 1. *Map of Africa showing principal sites mentioned in the text.*



built by a wholly indigenous (Bantu) civilization. This recognition stands, despite ongoing arguments for the penetration of the gold-producing areas by Indians and even Indonesians at least two thousand years ago (Hromník 1981).

In fact, the history of gold use is intimately bound up with that of other metals. It is also well known that the exploitation and use of metals by the peoples of the African continent varies greatly from region to region. The great natural barriers created by geography and climate meant that the use of metal did not show the same pattern of development in West and East Africa, nor in the Mediterranean coastal regions north of the Sahara. During the early first millennium C.E., iron use occurred at sites in eastern sub-Saharan Africa as far south as the Transvaal, but its method of introduction has been much debated and is still unclear. The beginnings of food production and the first working of iron appear to be roughly contemporary, however. At about the same time, a movement of peoples took place, accompanied by the spread of the Bantu family of languages. Whether these concurrent cultural changes all resulted from the same event or were purely coincidental is still being argued. In the past it has even been suggested that iron smelting was an independent discovery in sub-Saharan Africa, but the increasing availability of radiocarbon dates for Iron Age sites now supports the view that knowledge of iron was introduced from the north and spread southward (Phillipson 1985:149).

One of the links in the chain was, presumably, the kingdom of Meroë, which was established in the sixth century B.C.E. in what is now Sudan, where vast deposits of slag from iron smelting have been found. Meroë is separated from Egypt by desert. For this and for political reasons, communications were established in other directions, particularly eastward toward the Red Sea and southeastward toward the emerging Aksumite civilization in the highlands of Ethiopia. The heyday of iron production at Meroë was apparently during the last centuries B.C.E. when iron was exported in return for luxuries from the north and east, which were imported via the Red Sea route. Iron use appears to have been established in the area around Lake Victoria during the last few centuries B.C.E., and reached as far south as Natal by about C.E. 300. It is noteworthy that over an enormous area of eastern and southern Africa, the earliest iron-using communities show a remarkable degree of cultural homogeneity (Phillipson 1985:171ff).

This all began to change in about the tenth century C.E. when the Iron Age population began to expand. Domestic animals became more common, and actual mining for metal ore supplanted—or at least augmented—collection from the surface. At the same time, regional differences in the material culture became marked in the archaeological record. Powerful kingdoms began to emerge in which trade and the resultant wealth were controlled by an elite stratum of society. In the area of present-day Zimbabwe, many sites preserve remains of stone-built monuments dating back to the early centuries of the present millennium (MacIver 1906). Few of these sites have been excavated systematically, and many were deliberately ransacked in the nineteenth century by treasure hunters searching for gold; but some archaeological investigations have been carried out that have preserved evidence for the use of gold by the indigenous Africans. Gold artifacts are known to have been found—either by excavation, treasure hunting, or accident—on about twenty sites altogether, all of which are within or close to the main gold fields in present-day Zimbabwe.

The earliest site to have produced gold in any quantity is the acropolis at Mapungubwe, a site in the northern Transvaal, about two kilometers south of the Limpopo River. The acropolis consists of a long, narrow, steep-sided sandstone hill, which has only two paths to the top and was, therefore, very easy to defend. At the top are traces of stone walls and rock-cut cisterns. It is thought that the thin covering of soil must have been transported to the top in baskets and that the hilltop was the living area as well as the burial place of the nobility.

Serious excavations at Mapungubwe began in 1933. Several of the site's rich graves, thought to date from the twelfth century, were found to contain iron-wire bangles, ivory bangles, bone tools, pottery, and gold. Excavations on the site have continued intermittently since then (Fouché 1937; Gardner 1963). Four different types of gold objects have been identified: coiled-strip anklets, wire circlets, objects made of gold foil, and beads.[2]

GOLD SHEET (FOIL)

The best known of the finds from Mapungubwe is a small rhinoceros (Fig. 2) made of gold sheet. Although rather crude in appearance, the body and legs are all made from one piece by hammering, indicating a passing familiarity with the principles of *repoussé* work. The front hips are nicely delineated, but on the whole, the execution of the rhinoceros does not exhibit much skill, as the shaping has been partly achieved by folding and creasing the gold.

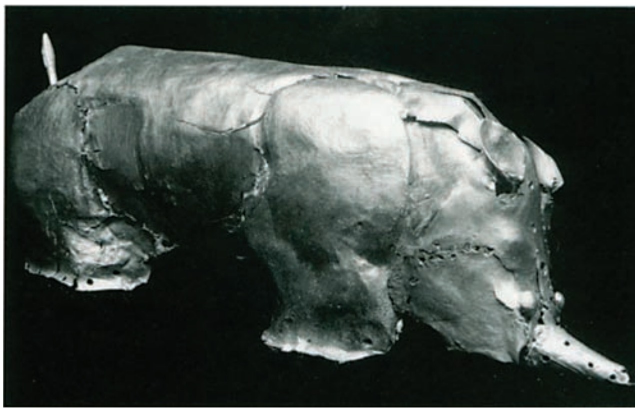


FIGURE 2. *Gold-foil rhinoceros from Mapungubwe. Pretoria University. Inv. no. DAPU 33.170.*

One feature of the rhinoceros that has raised questions about the manufacture of the goldwork is the animal's single horn. It thus appears to be an Indian rhinoceros rather than the African species, which has two horns. This discrepancy clearly presents a problem of interpretation, since the figurine could also represent a young animal that has not yet started to develop a second horn. However, the more likely explanation may simply be that the artisan lacked the skill necessary to fit the head with more than one horn. The head is, in fact, made from a separate piece of gold to which the ears and horn have been added. The tail is also separate. No archaeological evidence is available to indicate the methods of manufacture of the gold sheet from which the rhinoceros was made, but since the technology was already available for smelting iron, it was certainly available for melting gold. One might postulate, then, that gold was collected from rivers and streams and possibly obtained by mining, then melted and cast into flat sheets that were subsequently hammered on an anvil to form the thin foil out of which the sheet-gold objects were formed.

The inside of the rhinoceros is not visible, but when the other sheet-gold finds are examined, a clear difference may be seen between the surface textures on the two sides of the foil. The surviving finds from Mapungubwe include gold-sheet fragments of several other incomplete animal figurines. Microscopic examination shows that the outer surfaces were polished with a coarse abrasive, which left deep scratches on the surface (Fig. 3). The inner surfaces, however, have a rough, granular-looking finish which shows no sign of polishing (Fig. 4). The most plausible explanation is that the inner surfaces represent the underside of the gold sheet as it was hammered out, and the granular texture reflects the texture of the surface of the anvil, which was most likely made of stone. To ascertain whether a stone anvil was used, it is necessary to carry out some replication experiments; in this case, by beating out thin gold sheet using a large boulder from Mapungubwe to support the gold.

A stone anvil was in fact excavated "behind Mapungubwe Hill" in 1937 in an area that was interpreted as an iron-smelting site (Gardner 1963:12–13). Even though gold beads were found there "under a small red rubble floor," the site was postulated to be Venda. This presumably means that the excavator thought that the anvil should be dated considerably later than the rich burials containing most of the gold objects. This conclusion may well need to be revised.

The hammers used for beating out the gold sheet were most likely made of metal, probably iron, although no hammers have been identified among the exten-

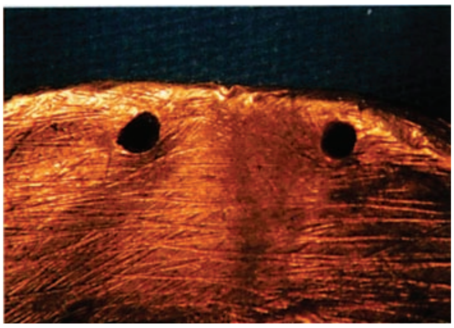


FIGURE 3. *Outer surface of a piece of gold foil, near right, showing deep polishing scratches.*

FIGURE 4. *Inner surface of gold foil, far right, showing granular texture. Note the presence of small gold nails originally used to attach the gold to a wood former.*

sive range of metal tools, weapons, and articles of personal adornment excavated at Mapungubwe. Iron chisels, awls, spikes, and lumps of iron have been found, however (Gardner 1963:93–168), so it is reasonable to assume that iron hammers were also known. Hammer stones from the site have been identified (Gardner 1963:93–168).

Once the gold sheet was made and formed into the required shapes, the artisan needed to join the various components of the object. How this was accomplished is uncertain. No evidence exists for the use of soldered or fused joins on any of the gold objects from Mapungubwe or its related sites. The gold sheet was supported by being attached to an organic former with small gold nails. Since gold nails are soft, the former must have been made of wood, which was certainly worked at this period (Voigt 1983:77–79, 111–19). Nail holes can be seen on many of the gold-sheet fragments, in some cases with the nails still in situ (Fig. 4). This proves that the nail holes were made by the process of hammering the nail through the gold sheet into the wood. Although it is clear that the nail holes were not preformed, the gold sheet may have been pricked with an awl to facilitate the first penetration of the point. Nails have been found in considerable numbers, and an examination of empty holes and of loose nails sometimes shows that the nail head has been deformed by the hammering process. Nails were tapered and either round or rectangular in cross section. Typical dimensions (in millimeters) are as follows:

length	*diameter just below head*	*diameter near tip*
4.9	1.1	0.6
4.6	1.0	0.5
3.8	0.9	0.7
4.9	1.2	0.9
3.5	0.9	0.6
3.7	1.1	0.5
4.5	1.3	0.8
4.9	1.0	0.6

A few tapering nails similar to those described above have also been found at the later (seventeenth- to eighteenth-century) site of Dhlo Dhlo and are now preserved in the Queen Victoria Museum in Harare. They are among a find of metalworking debris consisting of globules of gold, nuggets, and fragments of wire and foil, much of which is made of debased gold that clearly contains a considerable proportion of copper. The British Museum contains similar metalworking waste from an unknown site in Zimbabwe, which includes about forty similar nails (Fig. 5); some of these have round shanks and some have square ones.[3]

When two pieces of an object needed to be joined, the gold was overlapped and the pieces were nailed together. Patterns of nail holes in the center of sheet fragments attest to this practice. Evidence for an overlapping join is visible on the scepter (Fig. 6), one of the other more complete gold-sheet objects. The scepter is mounted on a modern wooden former, which is not quite the right size, resulting in the failure of the corresponding nail holes along the overlapping edges to align correctly (Fig. 7). The edges of the gold sheet are very rough and do not show evidence of having been cut with a metal (iron) blade. The original staff of the scepter was carved with a barley-sugar twist, to which the gold was fitted with some difficulty, resulting in creasing to improve the fit (Fig. 8). Despite the lack of skill shown in the three-dimensional shaping of the gold, the scepter is decorated with lines of indented "dots" (Fig. 9), made by pressing a blunt-pointed tool, perhaps made of bone, into the surface. Pointed-bone tools have been preserved from the site (Voigt 1983:77; 101ff). The head and shaft of the scepter are covered with separate pieces of gold sheet.

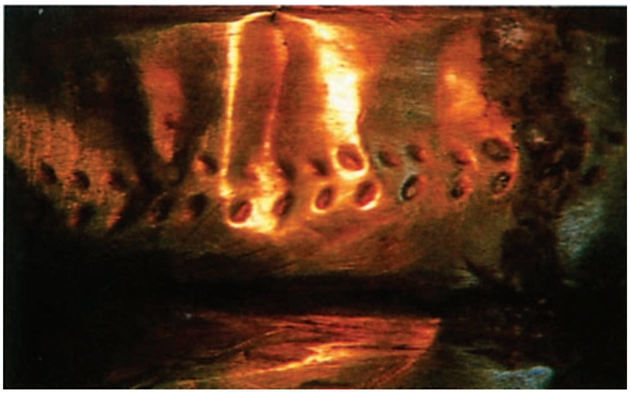
FIGURE 5. *Small gold nails from an unidentified site in Zimbabwe. British Museum, Ethno 1923:12-11(9).*

FIGURE 6. *Gold foil-covered scepter from Mapungubwe, below left. Inv. no. DAPU 33.174A.*

FIGURE 7. *Detail of Figure 6, below right, showing overlapping join of the gold foil.*

FIGURE 8. *Detail of Figure 6, showing creasing of the gold foil.*

FIGURE 9. *Detail of Figure 6, showing indented dot decoration of the gold foil.*



One other essentially complete object has survived: a gold bowl which is now, and presumably was originally, mounted on a wooden former. It was partly shaped by *repoussé* work, but it is also pleated near the rim.

Other fragments of gold sheet are sometimes recognizable as parts of animals, but some appear merely to be decorative plaques, perhaps originally attached to wooden household objects or used as jewelry. The most intriguing are three parts of what seem to be the same animal, from which one pair of legs has been recovered (Fig. 10), together with a head (Fig. 11). This animal is interesting for three reasons: It has been much more skillfully shaped by the *repoussé* technique than was the rhinoceros; its patterns of indented decoration are more advanced in design, and its species is uncertain. The animal has sometimes been interpreted as a horse (Voigt 1983:130), indicating either contact with horse-riding traders from the coast as early as the twelfth century, or a later period for these particular fragments. This interpretation relies on the presence of ears and the decoration along the head, which is assumed to represent a harness. But the elongated snout is also characteristic of a crocodile, in which case the decoration along the snout could represent teeth. Yet the ears are difficult to reconcile with those of a crocodile, and, furthermore, the teethlike decoration on the snout reoccurs on the torso. Perhaps the animal is supposed to be a hippopotamus after all, a creature with short legs, ears, and plenty of teeth!

Microscopic examination of the chevron pattern on the torso and legs reveals markings made by scribing the outside of the sheet with a blunt-pointed tool while the gold was resting on a pliable surface. The same conclusion is reached by

FIGURE 10. *Gold-foil legs of an unidentified animal from Mapungubwe. Inv. no. DAPU 33.173D.*

FIGURE 11. *Gold-foil head of the unidentified animal in Figure 10. Inv. no. DAPU 33.173E.*

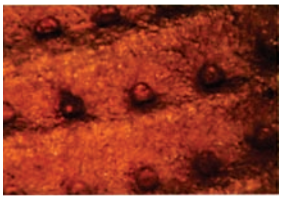


FIGURE 12. *Detail of Figure 11, showing indented chevron pattern on the animal's head.*

FIGURE 13. *Half-moon pieces of gold foil from Mapungubwe, second from left. One piece appears to be included in inv. no. DAPU 33.170. The other is part of inv. no. DAPU 33.173.*

FIGURE 14. *Decorated half-moon pieces of gold foil from Mapungubwe, third from left. Inv. no. DAPU 33.173.*

FIGURE 15. *Detail of the back of a decorated half-moon piece of gold foil, top right, showing the sharpness of the circular punch marks made from the same side of the sheet and the diffuseness of the lines made from the other side.*

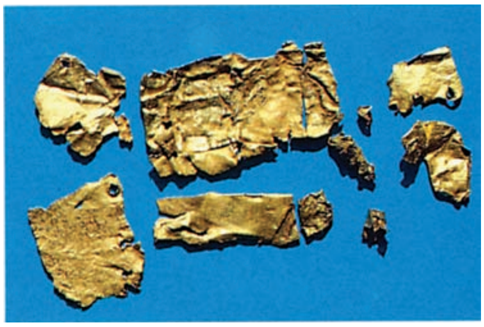
examining the pattern on the head (Fig. 12). However, at a high magnification, the pattern is seen to include scratches that suggest the tool used to indent the gold was metal rather than bone. In fact, some bone tools fitted with iron points have survived at Mapungubwe (Voigt 1983:104–5).

The gold-sheet fragments from Mapungubwe also include two half-moon-shaped pieces, pierced with five holes (Fig. 13), and some similarly shaped pieces which are also decorated with impressed dots and lines (Fig. 14). The dots were impressed from the back of the gold sheet using a blunt punch with a diameter of 0.3 mm (Fig. 15). The lines have been rubbed onto the front surface with a pointed tool. Again, the presence of scratches suggests the use of a metal tool.

Gold foil is rarely seen among the finds from the other sites, although the material from Great Zimbabwe in the Queen Victoria Museum in Harare includes a group of crumpled fragments (Fig. 16) that are also pierced with holes and have one rough and one smooth side. Also found at this site were a fragment from the Ridge ruins at Great Zimbabwe[4] and pieces from at least three other unspecified locations at this site.[5] One of these pieces is folded; another has a polished front, but its back is covered in slight, longitudinal ridges, suggesting that it might have been originally burnished on a piece of wood.

One very small tubular gold foil bead (approximately 9 mm long and about 2 mm in diameter) was excavated from the Chiwona ruins by Caton-Thompson in 1929 and is thought to be contemporary with Great Zimbabwe (Caton-Thompson 1931:127). A similar but much larger tubular bead is made of rolled-up gold sheet (Fig. 17). This bead (7.3 mm long and 4.25 mm in outside diameter) was found in one of the rich graves at Ingombe Ilede in Zambia (Fagan 1969:64–78), which are now dated as late-fourteenth and fifteenth centuries (Phillipson and Fagan 1969). These graves are most important for their gold beads (Oddy, in preparation).

FIGURE 16. *Fragments of gold foil, near right, from Great Zimbabwe. Inv. no. QVMH 7297(6)(a)(2).*



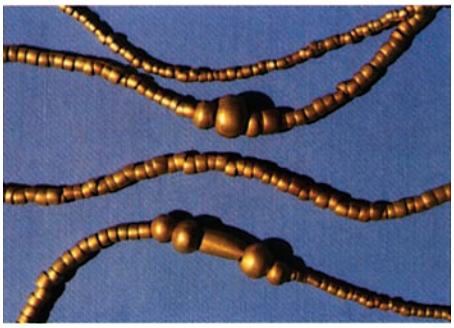


FIGURE 17. *Detail of beads excavated from burials at Ingombe Ilede in Zambia. The tubular bead is made of rolled-up gold foil. LMZ, in a glass bottle labeled II/1.*

FIGURE 18. *Goldsmiths' waste from an unknown site in Zimbabwe. Note the presence of a very small, tubular, gold-foil bead. British Museum, Ethno 1929:12-1(11).*

Both the Queen Victoria Museum in Harare and the British Museum contain quantities of gold-casting waste, half-made beads, and small cast spheres. The British Museum material[6] is known to originate from somewhere in modern Zimbabwe, while the Harare material[7] is known to have been found at Dhlo Dhlo, a site that flourished in the seventeenth and eighteenth centuries. Both lots contain fragments of foil, and there is yet another tubular foil bead (5 mm long and 1.5 mm in outside diameter) at the British Museum (Fig. 18).

In addition, two gold-wire anklets from the Belingwe Hills (southeast of Bulawayo) have added rectangles of gold sheet wrapped around the twisted and coiled wire (Figs. 19, 20). Finally, a string of gold beads from an unspecified site in Zimbabwe includes one large iron bead covered with gold foil (Fig. 21).

FIGURE 19. *A pair of gold-wire anklets, near right, from the Belingwe Hills in Zimbabwe. The anklets have pieces of gold foil wrapped around them. British Museum, Ethno 1929:11-14(1+2).*

FIGURE 20. *Detail of gold-wire anklets, far right, shown in Figure 19.*

FIGURE 21. *Strings of beads from an unknown site in Zimbabwe. One of the beads is made of iron and covered with gold foil. British Museum, Ethno 1929:12-11(1).*

GOLD STRIP AND WIRE

Apart from the gold sheet, the finds from Mapungubwe also contain long lengths of spirally wound gold strip (Figs. 22, 23), the spirals having an outside diameter of 12–15 mm. The spirals are very neatly made (Fig. 24), but where they have been deformed it is possible to see how the strip was cut and how it was made into spirals. Examination of the backs of the strips (inside the spirals) shows that they were cut from a sheet of gold foil by repeatedly scoring or cutting with a metal blade (Fig. 25). In some cases this process was not carried out to completion, and the final separation of the strip appears to have been achieved by tearing along the partially scored line. Definite evidence for the scoring, presumably using a straightedge and a metal blade, can be seen in some places where repeated cuts have not followed exactly the same line. The cutting was always carried out from the rough side of the gold sheet, as the smooth side of each strip is always wider than the rough side. The strips were wound into a spiral around a core made of some sort of fibrous material, traces of which survive. Lengths of strip were not joined together physically, but simply intercoiled for a few turns when a new length was needed.

FIGURE 22. *Spirally wound gold strip from Mapungubwe. Inv. no. DAPU 33.168.*

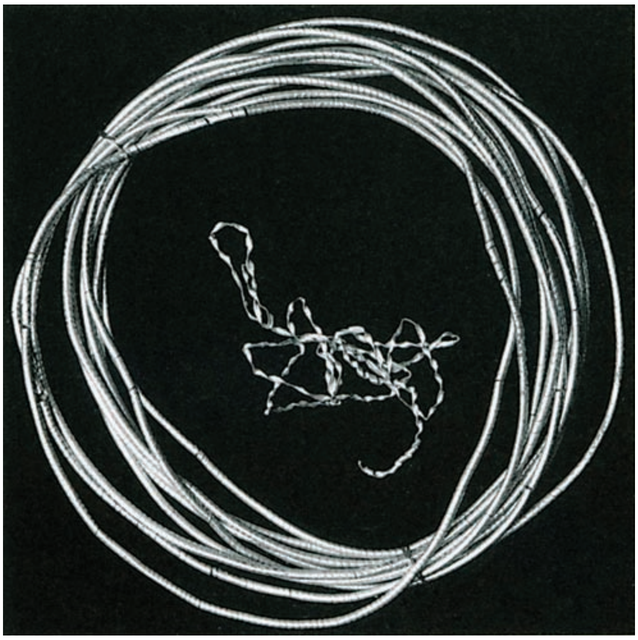


FIGURE 23. *Detail of spirally wound gold strip shown in Figure 21.*

FIGURE 24. *Magnified detail of spirally wound gold strip shown in Figure 21, near right.*

FIGURE 25. *Detail of the back of the gold strip from Figure 21 showing scored lines made when the strip was cut from the edge of a sheet of gold foil, far right.*

Apart from the long lengths of coiled spiral strip from Mapungubwe, one similar fragment from Zimbabwe, now in Harare, is stored in a modern glass vial with numerous pieces of wire.[8] Fragments of spiral made of copper strip that were cut from sheet in exactly the same way as the gold spiral was made have also been found at Mapungubwe.[9]

Finally, there are the artifacts that are made out of wire. In Europe, the modern method of making wire by drawing is thought to have been invented in the early Middle Ages (Oddy 1983). Before this date, wire was made by hand using one of several different techniques (Oddy 1977, 1987); therefore, it is of interest to identify the techniques used in the African Iron Age and, in particular, to note when wiredrawing was introduced.

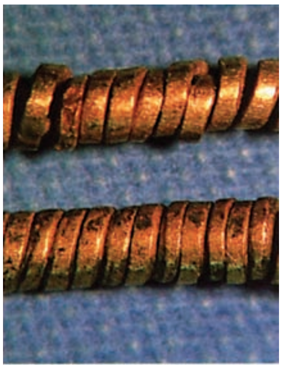


FIGURE 26. *Detail of coiled gold-wire bracelets from Mapungubwe. Inv. no. DAPU 33.169 and part of the contents of a cigar box labeled "B Mapungubwe sites S_1, P.S_2."*

Four bracelets from Mapungubwe are made of gold wire that has been coiled into a spiral and then bent into a loop (Fig. 26). The outer surface is flat, but whether this is the result of manufacture or of wear over a long period has not been determined. The surface within the spiral is rough, with longitudinal striations. This cannot be taken to indicate wiredrawing, as the wire varies in diameter on the four bracelets as follows: 0.40–0.55 mm, 0.60–0.65 mm, 0.63–0.70 mm, and 0.50–0.60 mm.

Two short lengths of gold wire were found to have a D-shaped cross section (measurements across the flat part of the circumference are 0.45–0.55 mm). It is most likely that this wire was made by hammering, and that the striations are the result of a smoothing process. The D-shaped wire may have been swaged (hammered into a semicircular groove cut into the surface of an anvil).

Finds of gold wire are more common from Great Zimbabwe.[10] Some of these are obviously hammered, with facets in some cases, and are uneven in diameter. Typical diameters of twenty-three different pieces of wire are (in millimeters):

0.40	0.55	0.40	0.40	0.40
0.35	0.40	0.25	0.40	0.45
0.40	0.20	0.30	0.30	0.45
0.40	1.40	0.40	0.40	
0.55	1.40	0.70	0.30	

Some of the wires have been twisted together as pairs, and some have been coiled into a spiral. However, the most interesting aspect of the gold wire from Great Zimbabwe is that some of it appears to be drawn.[11] The diameters of two of these drawn pieces are 0.55 mm each and a third is 0.50 mm. Some of the wire has a

D-shaped cross section and appears to have been made by drawing and swaging.[12] Four of the seven pieces are 0.30 mm in diameter, two are 0.35 mm, and one is 0.20 mm.

Of the other sites in Zimbabwe, the gold-manufacturing debris from Dhlo Dhlo (seventeenth to eighteenth centuries) included small pieces of wire. Some were hammered and some drawn. The objects, presumed to be anklets, and found in the Belingwe Hills southeast of Bulawayo, are made of hammered wire (Fig. 20).

One other important site for gold is a series of burials dating from the late fourteenth and/or fifteenth centuries that was found at Ingombe Ilede in Zambia. Most of the gold consisted of beads, but wire was found in one burial and consisted of several lengths of paired wires that were apparently twisted together and then wound into spirals (Fig. 27). Found at the left elbow of the skeleton, these appear to be parts of armlets. The outer surfaces show evidence of wear but the inner surfaces, where visible, are rough and uneven with facets and other marks typical of hammering. The wire is nevertheless remarkably even in diameter, varying between 0.33 mm and 0.45 mm. As with all the wire objects, there is no soldering, and lengths are mechanically joined by interlocking separate pieces together for a few turns of the spiral.

FIGURE 27. *Detail of wire spirals from Ingombe Ilede. These consist of pairs of wires twisted together and then wound into a spiral.*

In addition, the Ingombe Ilede burials contain spools of drawn copper wire and wiredrawing dies made of iron (Fagan 1969). These tools are of a type that has been recorded as having been used by the Bantu in relatively recent times. It must be assumed that wiredrawing had reached the interior by about the fourteenth or fifteenth centuries at the latest. Unfortunately, it is impossible to date the drawn-wire fragments from Great Zimbabwe, which could well be earlier than this.

CONCLUSION

In its earliest phase, as represented at Mapungubwe, gold working by the indigenous Bantu was at a rather primitive stage. Gold wire and thin sheet, or foil, were made by simple smithing techniques, and the latter was cut with a metal knife to form gold strip. The wire and strip were wound into spirals, and pairs of wires were often twisted together. Some knowledge of *repoussé* techniques and impressed decoration are evident on the gold sheet, but neither process shows any degree of sophistication.

Even after wiredrawing was introduced, no knowledge of soldering is evident. Wiredrawing may, therefore, have been an independent invention in this part of Africa, but since it occurred at a period that has yielded plenty of evidence of trading contacts with the coast, this innovation more likely reflects those increasing influences.

ACKNOWLEDGMENTS

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University; N. M. Katanekwa of the National Monuments Commission, Livingstone; M. Mukela at the Livingstone Museum in Zambia; and Carolyn Thorp at the Queen Victoria Museum in Harare. To all these colleagues he is very grateful. Copies of the detailed report, and of the 126 color slides which illustrate it, have been deposited at all three museums and at the Department of Ethnography in the British Museum, London, whose successive keepers, Malcolm McLeod and Dr. John Mack, kindly made their relevant material available for examination.

NOTES

1. Evidence for the chronology of the gold trade along the coast of East Africa has recently been summarized by Horton (1986).
2. All the Mapungubwe gold that was examined is in the collection of the Department of Archaeology, Pretoria University (DAPU). The gold from Ingombe Ilede is in the Livingstone Museum, Zambia (LMZ); and that from sites in Zimbabwe is in the Queen Victoria Museum, Harare (QVMH). An outline of the gold technology has recently been published (Oddy 1984), and a fuller description of the beads is in preparation (Oddy in preparation). It is the purpose of this chapter to describe the gold sheet (foil), strip, and wire from these and other sites in greater detail.
3. The British Museum's register records that this material was presented by Franklin White, Esq., and that it is "from ancient ruins, Rhodesia, Zimbabwe."
4. Inv. no. QVMH 7297 (6)(c).
5. Inv. nos. QVMH 7297 (6)(K); 7297 (1); 7297 (6)(M).
6. British Museum, Ethno 1923:12-11(10-11).
7. QVMH, not numbered.
8. Inv. no. QVMH 7297 (6)(a)(4).
9. In a cigar box labeled "B Mapungubwe sites S_1, P.S_2."
10. Inv. nos. QVMH 7297 (6)(a)(1); 7297 (6)(a)(4); 7297 (6)(c) "Ridge ruins"; 7297 (6)(M).
11. Inv. nos. QVMH 7297 (1); 7297 (6)(M).
12. Inv. no. QVMH 7297 (6)(a)(4).

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BIOGRAPHY

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Conservation of Architectural Metalwork: Historical Approaches to the Surface Treatment of Iron

FRANK G. MATERO

The history of the development and use of structural and ornamental metalwork in the building arts represents a long and complex interrelationship between function, aesthetics, and design played against the backdrop of architectural theory and scientific invention. In this regard, the great technological developments and economic growth experienced during the latter half of the nineteenth century, especially in North America, brought about an unprecedented increase in the use of metals—particularly iron and steel—for all aspects of building. An article titled "Art Iron at the Fair" in the July 1893 issue of *Ornamental Iron* describes this trend (1893:65):

> Iron in its various uses, constructional and ornamental, occupies a greater prominence in architecture than in Europe. Iron skeleton construction for high buildings is essentially an American conception. Also iron stairways, store fronts and elevator inclosures are here used to an extent without a parallel anywhere else in the world. This has chiefly resulted from the necessities of modern American office building.

To meet the demand for new construction, architects and engineers sought immediate, inexpensive building methods that would at the same time satisfy current design trends. Cast and rolled iron and sheet metal satisfied these requirements because they could be quickly and inexpensively fabricated and assembled into almost any architectural form desired. Historians of architecture and building technology have long been fascinated by these materials—structural iron and steel, in particular—for their contribution to the development of prefabrication and the evolution of the modern steel-frame skyscraper.[1]

While the promise of iron and steel as new structural materials for building became a major issue both in North America and in Europe during the nineteenth century, of equal interest was the subject of their surface treatment and finishing for protection against corrosion and for decoration. In a relatively short period of time, the technological developments reported in the numerous scientific and metal trade journals became commercially available and were embraced by the building profession, as the following excerpt indicates (Swank 1892):

> Mention has been made of the artistic finish of some of our iron and steel work, but the subject seems worthy of further notice. It is not only in stove-founding, in the graceful designs of bridges and elevated railways, and in the delicate combination of iron and steel with other materials in the construction and ornamentation of buildings that American ironworkers have displayed both taste and skill. . . . Some of the castings have been colored to represent bronze and others to represent steel, while others again preserve the natural color of iron.

The surface treatment of architectural metals has been largely neglected, especially in the preservation of many significant nineteenth- and twentieth-century structures, resulting in a poor understanding of the original appearance and function of these metallic surface finishes. The current restoration of Burnham and Root's Rookery in Chicago, Illinois, has allowed an in-depth study of the finishing techniques of what was considered in its day to be the largest, most exuberant display of ornamental ironwork set within a building (Fig. 1), according to a period account in *Ornamental Iron* (1893:[1]94–98).

Although iron founding and casting are known to have been practiced in the ancient world, cast iron arrived on the modern scene in the early eighteenth century as one of the outcomes of the Industrial Revolution (Smith 1981:127–73). Previously limited in production due to the requirement for sufficient quantities of iron ore and charcoal in close proximity, cast iron became more readily available after 1709 with Alexander Darby's use of coke, a distillate of pit coal, as a suitable and available charcoal substitute in the smelting of iron. Within a short period of time, domestic arti-

FIGURE 1. *The Rookery, light court, view looking northwest, 1888.*

cles and industrial components such as steam engine cylinders, rails, and tram rail plates became common manufactured items. In 1755 Sir John Smeaton employed the first large pieces of cast iron for mill and engine work (Lee 1983:100–1). However, it was not until 1779, when the first major cast-iron structure, the Iron Bridge at Coalbrookdale, was constructed across the Severn River in Shropshire, England, that the tremendous potential for the new material was demonstrated for the first time (Condit 1964:5).

The exploitation of cast iron as a structural and decorative building material during the first half of the nineteenth century was largely based on the knowledge gained through its early experimental manufacture and use in production (casting and cooling), component design (shape), and assembly (joining techniques).[2] Unlike traditional wood and masonry construction, cast and rolled iron possessed a combination of advantages, including excellent compressive and tensile strengths, respectively; limited fire resistance; the ability to be molded or rolled in a wide variety of shapes and designs; and reproducibility. These qualities made it an attractive building-material alternative, especially for utilitarian structures such as bridges, fire towers, markets, and mills (Condit 1964:6). But perhaps one of the most lavish applications of its architectural potential was demonstrated to the public with the 1851 erection of Joseph Paxton's Crystal Palace in Hyde Park, London, and Carstensen and Gildemeister's 1853 Crystal Palace in New York City (Condit 1964:6–7).

In the early decades of the nineteenth century, American iron foundries produced only a limited amount of cast wares and building elements, despite the availability of iron ore. The rapid rise of the industry began with the development of the hot-blast furnace in 1829, coupled with the discovery that the abundant supplies of anthracite coal in Pennsylvania and New Jersey could be utilized for the production of pig iron (Porter 1915:78–79). These technological developments were largely responsible for the significant increase in the tonnage of pig iron produced in America after 1850[3]; however, other factors contributed to the rapid and widespread use of the material after 1840.

Improvements in furnaces, foundry machinery, and workshop appliances allowed for larger production of molten metal. In addition, increased knowledge of iron metallurgy and fuel, together with advances in pattern making and molding produced finer and larger castings (Spretson 1878:v). A growing national transportation network of railroads not only provided a more efficient means of transport for the raw materials of iron ore, flux, and fuel required for production, but it also allowed manufactured goods to reach even the most remote cities and towns. Manufacturers were quick to recognize the potential of iron's availability and quickly developed the trade catalogue as a persuasive marketing device for promoting and selling building elements and even entire architectural assemblies.[4] These factors, in conjunction with relevant building issues such as the growing concern for fireproof construction and the enactment of building codes for the country's overcrowded and expanding cities, encouraged the use of both rolled and cast iron; this use reached immense proportions by the end of the century. Foundries specializing in the production of architectural ironwork rapidly developed to satisfy the nation's building needs. As one architectural foundryman remarked (Fryer 1876:1):

> This branch of iron manufacture has increased enormously within the past fifteen years, and the possibilities are that the future will develop a still greater proportional growth. It is a commonplace saying that as a nation we have but just begun to use iron.

Architectural Use

The second half of the nineteenth century witnessed rapid technological developments in the manufacture and assembly of architectural iron and steel. The early experimental structural systems of cast-iron lintels on piers and columns were soon replaced by midcentury with larger rolled-iron beams, which in turn were replaced at the close of the century by steel frames of immense dimension, span, and strength. According to one period source, improved manufacturing techniques were also responsible for creating large architectural castings of great artistic finesse which would not have been possible earlier (*The Inland Architect and News Record* 1889:18):

> The demand for [ornamental ironwork] has improved the processes of manufacture, until we have . . . castings which a few years ago would have been impossible. Large castings for centuries have been made, but the castings of pieces large in area and so thin that they become only a veneer, at the same time keeping them from warping, and so free from blow holes that the lines of a delicate tracery ornament are not broken, is another matter, and requires the highest skill and the greatest facilities for handling.

In addition, foundry mechanization through the invention of the first hand-operated molding machine in 1879 by Frank Reinholds of New Haven, Connecticut, allowed for increased production of castings and eventually led to fully mechanized molding around 1900 (Worrilow 1949:478).

As a result of these material improvements and innovative production methods, cast iron became an accepted and even preferred material not only for structural systems but for interior and exterior cladding, stairways, railings, balustrades, and ornamental details of all types. In 1884 James Swank, in his *History of the Manufacture of Iron in All Ages* (1892:527), commented:

> We [Americans] make liberal use of both cast and wrought iron and steel in the construction of public and private buildings. Our use of iron and steel for these purposes has rapidly increased in late years, and in much of our work of this character we have given truly artistic effects to these metals. We probably excel all nations in the use of iron and steel for ornamental purposes in connection with masonry, brick-work, and wood-work. Fine illustrations of the artistic combination of iron with other materials ten years ago may be seen in the interior of the new State Depart-

> ment building [Old Executive Office Building, 1879] at Washington and in the interior of the passenger station of the Pennsylvania Railroad at Philadelphia, while upon every hand are seen later illustrations of our artistic uses of iron and steel.

As noted earlier, a lavish use of structural and ornamental ironwork was especially evident in the interiors of large public and commercial buildings under construction in industrial cities such as New York, Washington, and Chicago during the last quarter of the nineteenth century. Because of their multistory height and volume and the inadequate illumination levels delivered by gas and electric lighting, many such buildings required open courts with stairs and galleries designed to bring the natural light into the core of the building. In these situations, cast iron had immediate applicability as a low-fire-resistant material easily cast into the requisite repetitive designs, and possessing the necessary strength for use on interior stairs, railings, and skylights. In addition, the incorporation of the newly invented elevator in high-rise structures required the installation of elaborately ornamented metal enclosures and grilles.[5]

Traditional Protective and Decorative Surface Treatments

Despite the technological advances in smelting and founding of iron and steel, and improved casting techniques and increased production, the corrosion of ferrous metals remained a major problem and concern for their use as both structural and decorative architectural elements.

The noble metals most commonly employed in architecture—copper, bronze, and brass—generally did not require any additional surface protection or enhancement since their natural or artificially induced patina was considered an aesthetically acceptable and even desirable finish. Where unique conditions such as highly polished or colored surfaces were desired, clear or tinted coatings were sometimes applied for protection, enhancement, and ease in maintenance of the finish.[6]

The less noble metals—tin, zinc, and iron—were almost always protected against atmospheric corrosion, usually by painting. However, painting was only one of three possible systems available at this time for surface protection and decoration of iron and steel. The other two systems—protection by metallic deposition such as hot dipping (tinning) or electroplating, and protection by oxide surface conversion such as Barffing (discussed later)—were direct results of the application of scientific discoveries and did not come into widespread commercial use until the latter part of the nineteenth century.

Except for strictly utilitarian situations, most architectural surface treatments were selected in accordance with current aesthetic trends. During the second half of the nineteenth century, architectural critics formed strong opinions concerning what they believed to be the proper finish treatments for architectural cast iron and sheet metal. These authors identified with one of three groups of opinion: those encouraging the use of imitative finishes such as stone and bronze, the imitation restricted only by good taste; those who rejected imitative finishes as being deceptive but did not denounce metal finishes that referred to another material obliquely in order to achieve an intended effect; and those who sought a treatment for metals that would be expressive of the material in its own right, as well as of the architecture that it served.[7]

Paints and Coatings

Protective coatings of linseed-oil-based paints pigmented with red lead and iron oxide were the most commonly recommended primers for iron and steel during the nineteenth century. Of the two pigments, red lead was considered by most technical writers to be superior to iron oxide.[8] Although less effective, iron oxides were used more extensively as primers due to their low cost and light stability. Other pigments such as zinc oxide were not seriously considered or available until their production in America around 1850; carbon graphite, introduced later in the century, was received with cautious optimism.[9]

Other brush-applied surface coatings such as black or colored asphalt, linseed oil, vulcanized rubber, hot coal tar, fossil-resin (coachmaker's) varnish, spirit varnish, white wax or paraffin, and lime water were also recommended.[10] With the exception of lime water, all these treatments relied on the hydrophobic nature of the film to isolate the reactive surface of the metal from moisture. Depending on the pigments employed, many treatments were also believed to reduce or prevent corrosion by galvanic action of the metallic oxides and carbonates.

A more utilitarian treatment for ferrous metalwork was the black japanned finish commonly used for wrought-iron and hardware grilles and fences. Lacquer for wrought iron could consist of either shellac or an oil varnish, while japan was commonly made with lamp-black pigment in a copal or similar oil varnish.[11] The glossy nature of the japan tended to highlight the metal's tool marks or imperfections, whereas a flat-black finish, achieved by thinning with turpentine, could be used to obscure these markings.

Surface protection and decoration could also be achieved by gilding and bronzing. These applied surface treatments were frequently employed on interior architectural ironwork, although generally only as accents or highlighting. Gilding could be performed at the foundry as mercury or fire gilding.[12] It could also be applied after installation in situ as oil gilding with an oil or oleoresinous size and a wide variety of metal leafs, including gold and gold-and-copper alloys, as well as silver, aluminum, and nickel.

Bronzing involved the use of brass powders of various composition and color, brushed or pressed onto drying oil or oleoresinous mordants applied to the iron surface and then varnished for luster and protection.[13] By varying the color of the mordants, the powders, and the varnishes or glazes, diverse variations in the imitation of bronze, copper, and other metals could be achieved.[14] Bronzing powders could be applied over the entire element or, more typically, used as highlights on painted surfaces.[15] Despite criticisms of their instability, bronzing powders were widely advocated in the literature and used (Gardner 1888:114).

ELECTROPLATING

Of all the surface finishing techniques utilized for architectural ironwork, perhaps none was more versatile in its applications than electroplating. Developed in the late 1830s and 1840s,[16] the process, along with electrotyping, or so-called galvanoplastic work, was in commercial use for architectural ironwork by the late 1870s in America.[17] Promoted for its decorative as well as protective benefits, electroplating enjoyed increased use in finishing an infinite variety of small and medium-sized elements, the latter easily assembled into large architectural features such as staircases and enframements.

In the commercial advertisements and descriptions of projects published in the trade journals and catalogues of the day, manufacturers listed a wide variety of plated and oxide-surface finishes for ironwork.[18] Of the electroplated finishes in vogue at the end of the nineteenth century, copper and the cuprous alloys—brass and bronze—were generally considered the most versatile for their ability to be patinated in any number of imitations of cast bronze.[19]

Where cost allowed, bronze was often the preferred metal for ornamental use on interiors and exteriors, however less expensive imitations abounded, including plated and painted ironwork and even glazed terra-cotta.[20] The process of electroplating was expensive relative to other surface treatments and required a high degree of skill; to be effective under adverse conditions, a heavy deposit of the finishing material was required. "Duplex and triplex electro-bronzed" ironwork, as it was termed by its manufacturers, was widely promoted and employed in numerous commercial buildings after its introduction sometime around 1890 (Wilson 1915:68–69).[21]

Ornamental Iron was a trade periodical published by Winslow Brothers Company to promote the use of architectural metalwork in general and the company's own production in particular. The magazine published a series of articles discussing the development and introduction of electroplated ironwork for exterior use, describing the technical evolution as follows (*A Front of Bronze* 1893:22)[22]:

> Electroplating on cast iron has been attempted heretofore, both in this country and in Europe, but never with success, as the wrecks of a number of otherwise fine structural objects in this city [Chicago] and abroad attest . . . where the plating has so entirely failed of its ornamental purpose as to require painting in order to hide its ugliness and retain its preservative qualities. As a result of a long series of experiments these obstacles have been overcome and a method of treatment has been perfected whereby the surface of the iron receives the deposit directly, and an adhesion secured which is impervious to all attacks and gives an enduring quality to the work never before secured. We speak advisedly in asserting that this process is peculiar to the duplex bronze on iron products by the Winslow Brothers Company, and that, by no other process yet devised or at present in use can or has a satisfactory result been secured. The metal itself is a form of bronze, practically indestructible . . . except that a slow oxidation gradually brings about a change in the surface color,

> which enhances rather than diminishes its beauty of tone, giving to it an added artistic charm.

Although bronze was listed as the most desirable of the electroplated finishes, true bronze-plating, the deposition of bronze—an alloy of copper and tin—was not largely practiced due to difficulties in achieving even plating. According to one period source, "What is erroneously misnamed 'bronze-plating' is really a light-colored brass deposit formed by taking a good copper-cyanide solution and adding to it just sufficient zinc solution to give the required shade" (Field and Weill 1951:471).

Copper alone was also used as the electrodeposited base for chemical patinations simulating a wide variety of so-called bronze finishes "from red to bright yellow and dark to light green."[23] However, copperplating on iron by means of direct, acidic copper-sulfate baths was limited due to the spongy nature and poor adhesion of the copper deposited. Therefore most copperplating on iron and steel required an initial thin plating, or "strike," of copper deposited in an alkaline copper-cyanide bath prior to continued plating in the acid-sulfate bath (Burns and Bradley 1967:258).

In addition to chemical patination, other modulations of color and luster could be easily achieved by light abrasion and polishing of the patinated surfaces. A variety of surface qualities could also be achieved by the application of bronzing powders, glazes, and gilding. These effects may be observed in buildings with preserved metalwork such as the Rookery, which was described in the original manufacturers' literature (Poulsen and Eger n.d. [ca. 1890]):

> On our stair work, and other work of a similar nature, we electroplate in Bronze, Brass and Antique Brass, the railings, newels and ornamental parts, and as much as possible design our work so that all high relief lines and mouldings are polished to afford artistic contrast. The electro-plate is thoroughly substantial and durable.

Oxide Conversion Coatings and the Bower-Barff Rustless Process

In addition to the techniques already described for the coloring and protection of iron and steel, thermal oxidation of ferrous metals received much attention during the late nineteenth century for its value in producing corrosion-resistant or so-called rustless coatings. These stable oxidation films, formed directly on the surface as integral components of the parent metal, could range in color from brown to black to blue-black. Depending on their formation process, these films produced a hard, wear-resistant skin of varying thickness (Burns and Bradley 1967:577). Several distinct methods of forming oxide films on ferrous metals by heating were in use during the late nineteenth century, each producing finishes of varying color and thickness. For general coloring, low-temperature heating (200–500 °C), which produced interference tints in combination with oil or other organic preservatives, could produce thin colored surface films of limited protective value. Surface conversion could also be induced by chemical means in conjunction with heat.[24]

However, by far the most significant protective oxidation coating to be developed and employed on architectural iron and steel was the so-called Bower-Barff Rustless Process invented by Professor Frederick S. Barff of Kilburn, England, who published his method in 1877.[25] The process was later modified by George Bower. Despite variations in the processes later developed by Bower, Wells, Gesner, and others, the treatment essentially consisted of heating the cleaned iron or steel to dull or bright red in contact with air in special ovens or furnaces, and then admitting superheated steam to the furnace. This process produced an oxide layer of magnetite (Fe_3O_4) or magnetite and wustite (FeO). Later improvements in the process allowed complete conversion to magnetite by reduction through continued heating in a producer-gas atmosphere of hydrogen and carbon monoxide until the desired thickness of magnetic oxide coating was obtained.[26]

Barff was not the first to observe the formation and stability of magnetite on ferrous surfaces.[27] Antoine Lavoisier (1743–94) first noted the formation of magnetitic mill scale and commented on its stability and impervious character. Later Michael Faraday (1791–1867), the British chemist and physicist, similarly described the protective action of the oxide formed in the tubes of a steam superheater (Wilson 1915:47). According to Barff, his interest in magnetite as a protective measure for iron and steel began around 1875 during his observations of a pipe carrying superheated steam (Barff 1877:255). His process, which was first made known in 1876, consisted of heating the ironwork to 1000 °C and passing steam superheated to 538 °C over it.

The process developed by Barff and later perfected by Bower was immediately publicized by the architectural, engineering, and metal trade journals as a solution to the problem of iron corrosion.[28] Barff clearly recognized the value of the process to architects and engineers, stating in his first lecture to the Society of the Arts (Barff 1877:256):

> I cannot over-estimate the advantages which the employment of this process must confer on architects, who will be by it enabled to employ iron, whether wrought, or cast, much more largely, not only in the decoration, but in the construction of their buildings.

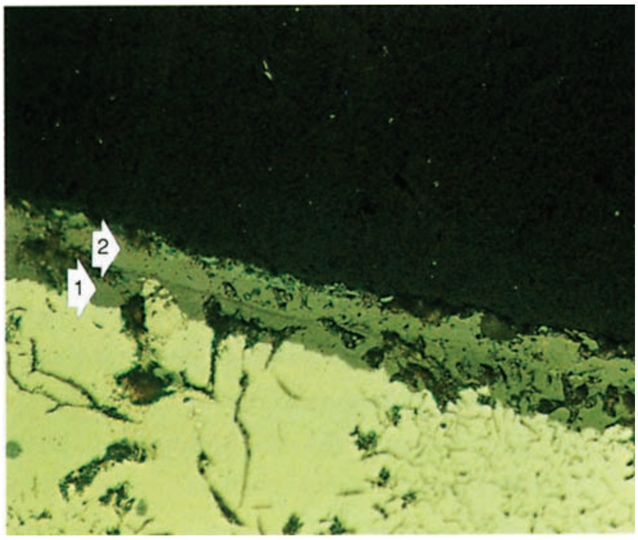
The following year, on Wednesday June 5, 1878, Barff presented his discovery, as well as treated samples, at the General Conference of the Royal Institute of British Architects. The process was received with great enthusiasm and considered “of incalculable value . . . elevating the metal [iron] almost to the level of bronze and the costlier metals,” according to the conference proceedings (1878).[29]

Early reports on Barff’s process described problems with film adhesion and a lack of film uniformity; however, with improvements in the furnace, large-scale commercial application was reported in London by 1880.[30] George and Anthony Bower, of St. Neats, England, attempted to improve Barff’s process by using air instead of steam, but they were unable to obtain the desired results until they employed producer gas of hydrogen and carbon monoxide to reduce the red oxide formed by heating the parts in air. The air treatment lasted 40 minutes and the gas treatment 20 minutes, these being repeated alternately four to eight times. Finally they purchased the Barff patent, and the Bower-Barff process was patented in 1881. That same year, George Bower delivered a paper before the Iron and Steel Institute of the United Kingdom describing his process and the large-scale works already in operation in France, Germany, and the United States.[31] The right to use the process in the United States was acquired by George W. Maynard of New York, and the first furnace was erected at the Hecla Architectural Iron Works in Brooklyn, New York (Wilson 1915:47–48), the same company that provided all the ornamental ironwork for the Rookery in Chicago. The process was described several years later after its acceptance and widespread use, as follows (Brannt 1896:297–98):

> Barffing is so called from the name of its discoverer; and its purpose is to render the surface of metallic articles treated, resistant to acids and impervious to humid oxidation. Iron and steel that have been properly Barffed will not rust. The process belongs in no sense to the chemical laboratory, and requires no particular scientific knowledge or technical skill for its success. Highly polished work retains its finish after the process, although the treatment changes the shining polish to a dark slate color. But working parts, such as sliding and rubbing surfaces, retain their smoothness, and work as freely after as before the process; plugs, valves, and stems for cocks, gates, and faucets, for instance, working just as smoothly as though they had not been Barffed.

Although the Bower-Barff process was considered expensive and its use restricted to elements that did not require precision fitting due to the slight volumetric increase (machinery parts), the process offered excellent corrosion resistance for architectural ironwork, which could be painted or coated with paraffin or oil for additional protection. Where necessary, the magnetite coating could be built up for maximum protection by repeated treatments[32] (Fig. 2).

FIGURE 2. *Photomicrograph of cross section of a Bower-Barff finished window handle (Appendix: Sample 1) under visible light taken at ×400 (Zeiss metallographic microscope). Note the 25–30 micron double layer of the artificially formed oxide film (1, 2).*



Subsequent modifications in the basic process resulted in a number of patented treatments, including the Wells Process, the Gesner Process, the Bradley Process, the Bontempi Process, and Coslettizing. These commercial processes produced magnetite coatings of better color, uniformity, and thickness for less cost (Wilson 1915:48–49).

The Bower-Barff Rustless Process afforded a durable, efficient finish for protection against corrosion and for the decoration of wrought and cast iron and steel. Used alone or in combination with other finishes such as electroplating and bronzing or gilding, the deep black finish quickly became a popular treatment for interior ironwork and, in particular, hardware and ornamental wrought iron. By avoiding the disadvantages of paint-film obfuscation and repeated maintenance, and providing a nonimitative black appearance, the Bower-Barff process was considered "the best and only proper finish for art ironwork."[33]

By the last decade of the nineteenth century, a full array of protective and decorative finishes for architectural ironwork was available and in widespread use. Although painting continued as the most common means of protection and decoration, especially for exterior work, electroplating and the Bower-Barff process rapidly became the most popular finishing techniques for common and ornamental interior and exterior ironwork as indicated by the many significant commercial buildings employing these finishes.[34] The situation was well summarized in the introduction to the *Illustrated Catalogue [of the] Hecla Iron Works* of about 1890 (Poulsen and Eger):

> We desire to call attention to our several methods and styles of finish of our Ornamental and Architectural Cast and Wrought-Iron Work as illustrated herewith, where such finishes are desired beyond mere painting.
>
> Our processes are comparatively new in their application to this class of work and go far toward enhancing its artistic value; and at the same time compare favorably in expense with the usual methods of bronze-painting and decorating. In the past few years we have been successful in introducing these finishes in combination with stair and ornamental ironwork furnished by us in most of the prominent buildings recently erected in New York, Chicago, and most of the principal cities in the West.
>
> Our standard of work is high and by intelligent application of these various finishes, combined with good workmanship, it is possible to most nearly approach the artistic in architectural and ornamental ironwork.
>
> Electroplating—On our stair work and other work of a similar nature, we electroplate in Bronze, Brass and Antique Brass, the railings, newels and ornamental parts, and as much as possible design our work so that all high relief lines and mouldings are polished to afford artistic contrast. The electro-plate is thoroughly substantial and durable.
>
> Bower-Barff Rustless Process—This process imparts to the surface of the iron a blue-black color on rougher castings, while on polished work the iron retains its lustrous appearance with a beautiful steel-blue shade that harmonizes well with electroplated work where used in combination. . . .

> It not only prevents rust but ornaments the surface of the iron as well, and has a wide application for interior and exterior ornamental cast and wrought iron work.

Case Study: The Rookery

The investigation and analysis of the architectural finishes of the principal interior spaces—light court, lobbies, and library—of Burnham and Root's Rookery (1885–88) were undertaken from 1989 to 1990 in preparation for the long-awaited restoration of the building. It was the focus of these investigations to examine and analyze the exterior and interior architectural materials to ascertain the type and extent of surviving original finishes, significant alterations made over time, and their existing conditions. Assessment was based on in-situ investigation and laboratory analysis supplemented by written and photographic documentary sources.

Based on the scope of the project and the time allotted for site work, paint sampling and surface-finish investigation were confined primarily to selected areas within the locations noted above. Wherever possible, known elements dating to the building campaigns of Burnham and Root (1885–88), Frank Lloyd Wright (1905–7), and William Drummond (1927–32) were examined and sampled for comparison. More than 150 samples of existing paints and coatings and representative metalwork were removed for laboratory examination and analysis.

Once these materials were characterized, identified, and documented, a program of field testing was conducted to determine the feasibility of retaining those original or subsequent finishes identified for conservation. Overpainted or lost finishes were studied to replicate their established historical appearance. The original surface finishes of the metalwork—the electroplated and Bower-Barff finishes on the ornamental ironwork—were studied further, and methods of overpaint removal, cleaning, and presentation were tested and assessed. In each test situation, a broad range of materials and conditions was considered, and treatments were selected which were found to be simple but effective in their application, involved minimum health risks, and conserved as much of the original surface as possible.

Burnham and Root's Rookery of 1885–88 (Figs. 1, 3–9) is widely considered to be one of the major masterpieces of commercial architecture built in America during the last decades of the nineteenth century. From the beginning, it was considered "a design of great fertility: bold, original, and inspiring with its glass-covered light court" and flying staircase (Condit 1964:64). In context, the design and materials of the Rookery relate to the progression of commercial buildings built by Burnham and Root during the 1880s and 1890s. Their preference was for intensely colored red brick, terra-cotta, and natural building stone for the exterior, and a contrasting use of light-colored marble and ornamental metalwork for the large open vestibules and light courts of the interior. These contrasting elements became hallmarks of their commercial architecture and were quickly emulated elsewhere.

As dark, warm, and massive as the Rookery's exterior was, its internal light court was the complete antithesis—light, cool, and reflective (Fig. 5). In addition to providing much-needed light to the inner tiers of offices, Root's light-court designs, first

FIGURE 3. *The Rookery, light court, view looking southwest, 1888.*

seen in the Burlington and Quincy General Office Building of 1882–83 (destroyed) and later developed in the Insurance Exchange Building of 1884–85 (destroyed), the Phenix Building of 1885–87 (destroyed), and the Rookery, "made light thematic . . . and an arena in which to explore the aesthetics of motion through light and space" (Hoffman 1973:32).

In the case of the Rookery, this effect was largely achieved through the construction of an independent skeleton wall of cast-iron columns joined by wrought-iron spandrel beams, thus maximizing the amount of light entering the inner offices. The architects also made use of light-colored reflective materials—white-glazed bricks and gold-glazed terra-cotta lintels, sills, and copings; gilded cast-iron mullions; and a glossy white-painted skylight and exterior oriel stair. This orchestration of light with highly reflective white, black, and "gold and dark bronze" metallic-colored surfaces must have created a dazzling effect and one which contrasted greatly with the exterior.

FIGURE 4. *The Rookery, light court, below left, view looking southwest, 1985, before restoration.*

FIGURE 5. *The Rookery, light court, below right, view looking southwest, 1991, during restoration. Note exposure of the copper electroplated and Bower-Barffed finishes.*

Root's achievement of dynamic balance between the exterior and interior of the building is dramatized at each entryway. Entrance from either Adams or LaSalle streets opened onto large, bright, double-height vestibules with elaborate marble stairways leading to sweeping balconies and the elevators beyond. Below these stairways, the vestibules became compressed past the elevators, suddenly opening up to the light and space of the light court beyond. The light court was a masterpiece of circulation planning. A grand staircase, centered on the east side, allowed access to the glazed office suites lining the mezzanine balconies of the light court's perimeter. On the west wall a double flight of stairs was flamboyantly cantilevered into the court, connecting the mezzanine via a single-run return staircase to the third floor (Fig. 5). This rose up through the building as a unique hemihelix oriel staircase, heavily ornamented with cast ironwork and glass (Fig. 8). The entire light court was enclosed with a complex skylight composed of ornamental cast-iron trusses and braces and ribbed glazing to provide directed diffuse light.

As in Burnham and Root's other commercial projects, the finest materials were used in the decoration and finishing of the Rookery's interior public spaces, including polished Italian marble walls, polychromatic floor mosaics, and elaborate cast- and wrought-iron metalwork. However, by far the most lavish ornamental work in the interior was the decorative ironwork—including the light court's main and double stairways, skylight framing, elevator cars and grilles, newel posts, electroliers, and oriel staircase—all furnished by the Hecla Iron Works Company of New York.[35]

It is difficult to comprehend the novelty and impact this exalted use of ironwork must have had at the time, given the almost immediate popularity and widespread use it enjoyed in other commercial buildings in the ensuing decades. The significance of the design, quantity, and finish of the Rookery's ironwork can be best understood through a feature article on the building's ironwork published in *Ornamental Iron* in November 1893, five years after the building opened[36]:

> The ornamental iron in the Rookery was furnished by the Hecla Ironworks of New York, Poulsen and Eger, proprietors, who were the pioneers in this branch of industrial art work in this country, being the first to practically electro-plate and Bower-Barff ornamental iron work for buildings. The work in the building was largely the result of their intelligent cooperation with the architects. With the exception of two other buildings in Chicago which had shortly before this been furnished with a high grade of ironwork by the same firm, ironwork in this city had been of the commonest description—so much so that it would have been a misnomer to call it "ornamental." Owing to the immense quality of ornamental iron in the Rookery it was let by the architects as a separate contract and this was really the beginning of this practice, which had since become general. It was the largest contract for ornamental iron ever let up to that time, and one of the largest on record up to the present time. The oriel stairs extending to the top of the building were the first ever built in this form of iron. Oriels of a similar nature have since been built by the Winslow Brothers Company in the Mills building, San Francisco; Hotel Midland, Kansas City; and Northern Hotel, Chicago [all by Burnham and Root].

> The immense skylight in the court over the first floor was also a novel feature being of ornamental cast-iron construction. The lights are in small sizes and set in elaborate cast iron frames. A very striking feature is the grand staircase in the court to second floor balcony, with imposing cast iron newels and electroliers at the start. If these electroliers were to be made at the present time the treatment of the iron would be different in some respects but at that time they represented a great stride in the art of ironwork in this country. Hammered leafwork, which is so beautiful and appropriate for purposes of this kind had its inception in this country at a later date. The round pipe uprights in the elevator enclosures were a new feature, and proved to be of such excellence both as to appearance and practicality that their use has continued to this day. More expensive constructions for elevator enclosures are coming into use now for the lower stories especially broad lightly ornamental cast pilasters, but the round upright has had a long and honored service. Although it was not customary to give ironwork more than a six hour electroplating, instead of twenty-two hours as at present, the electroplating in the Rookery has successfully withstood eight years handling by the public, and the rubbing and scouring of the janitor. What impresses one very forcibly in looking at the Rookery work, is that although other buildings erected at the same time or shortly before are now old fashioned, the Rookery is still one of the most modern of modern office buildings.

According to *Ornamental Iron*, the Rookery's ironwork represented the largest contract for ornamental architectural ironwork for its time. In addition, the application of the Bower-Barff finish would have been among the earliest (only five years after its patent) and certainly the largest application of the technique for architectural work. Used in conjunction with patinated and polished copperplated cast-iron elements, the effect was both durable and elegant. This complex treatment of the Rookery's ornamental ironwork was described almost exactly by Poulsen and Eger in their *Illustrated Catalogue [of the] Hecla Iron Works* (1890):

> We electro-plate in bronze, brass and antique brass the railings, newels, and ornamental parts, and as much as possible design our work so that all high relief lines and mouldings are polished to afford artistic contrast. The electro-plate is thoroughly substantial and durable. The Bower-Barff Rustless Process imparts to the surface of the iron a blue-black color on rougher castings, while on polished work the iron retains its lustrous appearance with a beautiful steel-blue shade that harmonizes with electro-plated work, where used in combination.

Although concealed by layers of subsequent overpaint (Figs. 4, 6), nearly all of the Rookery's interior ornamental ironwork, with the exception of the painted and gilded skylight, was originally finished by patinated electroplating and in the Bower-Barff manner with surfaces ranging in color and luster from matte black to dark reddish-brown bronze to light gold-colored highlights (Figs. 6, 7). This was confirmed through examination and analysis of representative samples of metalwork, as detailed in the Appendix (Lins and Meighan 1991), as well as the discovery of Root's

FIGURE 6. *The Rookery, oriel stair newel posts, above, overpainted condition before restoration.*

FIGURE 7. *The Rookery, oriel stair, near right, eleventh-floor newel post and stair risers cleaned and lacquered to reveal original patinated copperplate on the newel post black and Bower-Barff finish on the stair risers.*

FIGURE 8. *The Rookery, oriel stair wall ironwork, above far right. Cleaning tests to reveal original surface finishes.*

notations on his drawings of the stair metalwork. Root describes "the finish of the stairs to be of dark and gold bronze" and "the leaves to be touched with gold bronze not too freely used and rest of dark bronze."[39]

In general, textured flatwork with little or no relief such as the pierced stair risers and window muntins of the oriel stairs were Bower-Barff finished to a matte black or a lustrous blue-black as seen on the smooth surfaces of the window and door hardware (Fig. 9). Metallographic examination and analysis (Lins and Meighan 1991)[40] of an original window handle (Appendix: Sample 1) identified the hardware as grey cast iron with rosettes of flake graphite and a surface patina approximately 25–30 µm thick, consisting of two clear zones of equal thickness of dark grey to black material (Fig. 2). The inner zone clearly displays metallurgical features, such as the remnants of the cast-iron microstructure and voids, which are continuous with the bulk metal. This zone appears to be the cast-iron substrate, which was oxidized by the superheated steam of the Bower-Barff process. This zone may also be described as a depletion zone from which iron ions moved to the outer zone, an oxidation layer grown on the original finished surface of the cast iron during the process. On the uppermost surface of the outer zone there is generally a very thin (1–2 µm) grey-black layer, often separated from the underlying zone by voids. This may represent the alteration of the finish over time or from an initial quenching. No intentional organic coating or residue from an oil quenching was detected using high-power UV microscopy (×1000). Identification of the patina as magnetite using X-ray diffraction was conclusive, although both the sample and the standard appear to be either cryptocrystalline or poorly crystallized (Appendix: Table 1).

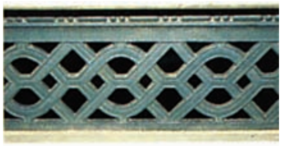


FIGURE 9. *The Rookery, oriel stair riser. Cleaned original Bower-Barff finish.*

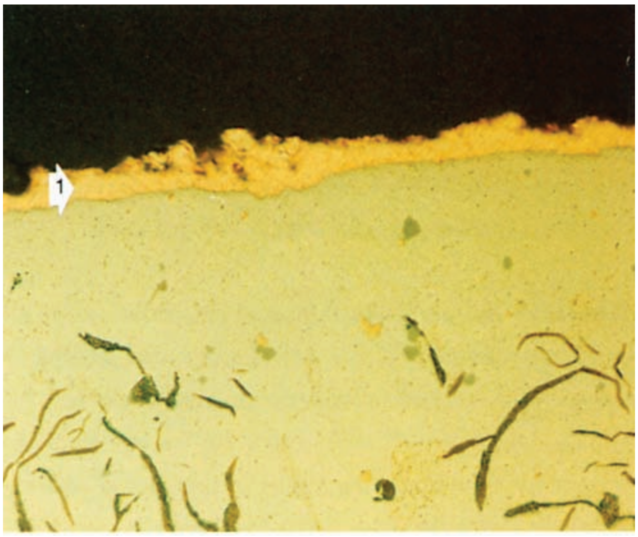
High-relief work such as the oriel stair wall panels and stair railing appears to have been copperplated and chemically patinated to a rich dark-brown finish. This may have been somewhat highlighted by the selective removal of the patina; however, the evidence of the degree of removal is unclear. Areas that clearly show intentional mechanical abrading and polishing of the plated surface for highlighting can still be observed on the flat fillet borders and foliate borders of the oriel stairs, wall panels, and stair newel posts as well as on the curvilinear details of the stair-railing balusters and stringers (Fig. 8).

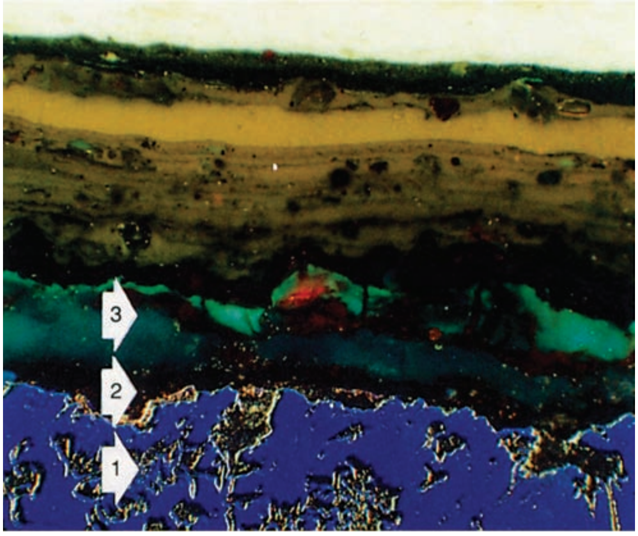
A cross section of a typical oriel stair baluster (Appendix: Sample 3) shows the microstructure to be grey cast iron, with coarse-flake graphite in rosette patterns (Fig. 10). A distinct layer of copper is evident on the surface, varying in thickness from 10 to 20 µm. Analysis of the copper by emission spectroscopy revealed copper with no tin and only a trace of zinc (less than 10 ppm). The plating is therefore copper and not brass or bronze. No evidence of original organic coatings was found using ultraviolet microscopy, suggesting that chemical patination, not resolvable by the analytical means available, probably provided the original final finish.

Root's drawings of the ironwork, as well as period photographs of the original interior, indicate that a combination of finishes was designed and executed as planned. Examination and analysis of a detail of the foliate design of the pierced grille of the light court's main stairs (Appendix: Sample 2), annotated as "gold bronze" on Root's original drawings, suggest a surface treatment different from the "dark bronze" and polished highlighting observed on the elements described above. Here, the surface treatment of the grey cast iron is relatively complex in cross section (Fig. 11). A thin, highly discontinuous layer containing copper was observed on the surface of the iron, which is relatively rough for plating. This copper is most probably a very thin electroplate layer or "strike" coat. Directly above this is what appears to be the original surface-finish coating of a colorless layer approximately 50–75 µm thick, with golden reddish-brown particles in its uppermost levels, suggesting that the method of application may have been by dusting dry colorants onto a warmed or fresh varnish. Fourier transform infrared (FTIR) spectroscopy analysis of a microtomed cross section of the layers above the metal indicates that both the clear and golden reddish-brown layers are natural (tree) resins. Areas of green staining observed within this layer are probably attributable to corrosion of the copper.

FIGURE 10. *Photomicrograph of cross section, below left, of an oriel stairs baluster (Appendix: Sample 3) taken under visible light at ×400. Note the distinct layer of copperplating (1).*

FIGURE 11. *Photomicrograph of cross section, below right, of the ornamental grillework of the main stairs carriage (Appendix: Sample 2) taken under mixed ultraviolet and visible light at ×200 (Leitz Laborlux S ultraviolet microscope with filter block D, BP 355–425). Note the thick resinous layer (3) above the copper film (2) and cast-iron substrate (1), believed to be an original varnish highlighting.*





Although it is possible that the thin cuprous layer found above the iron and below the resinous layer is fallout from cuprous "bronzing" powders used in the overlying varnish, it is more likely that the highlighting designated as "gold bronze not too freely used" on the drawings was additional enhancement with tinted varnish of the overall patinated copper electroplate. Such practices employing varnishes, cuprous bronzing powders, or both on both plated and painted iron surfaces were frequently practiced as described in the trade manuals.[41]

This range of integral black and metallic bronze finishes with polished and applied highlights provided a subtle yet dramatic contrast against the white marble walls and white painted and gilded skylight of the Rookery's principal public spaces. Although it appears that this combination of finishes was employed by Root in earlier commissions, the Rookery was by far the most successful and dramatic of his interior designs and his most ambitious use of ornamental iron at that time. This exuberant use of darkly finished Bower-Barffed and richly patinated copperplated ironwork became a requisite feature for succeeding generations of high-rise commercial office buildings throughout the country. It was documented in countless examples in the pages of *Ornamental Iron* and architectural periodicals, such as the following from the January 1885 issue of *Carpentry and Building*:

> It is mainly in city buildings of a business character . . . that the resources for architectural purposes are best illustrated. While iron enters largely into the purely constructive features of these loftier and more substantial erections, it is also made contributory to decorative treatment. . . . Iron balustrades for stairways date far back, but . . . now made in arabesque and other open patterns, they add greatly to interior structural beauty. Architects have turned handsome balustrade designs to good account in bordering successive landings in the spacing and deep wells that furnish interior light to some of our city buildings. Coated with color and picked out with gilt, the designs are sometimes rich and intricate, like interlaced ornamentation; in others, they may be likened to a succession of central bosses, from which radiate curved and spiral forms; occasionally they are a certain arabesque style, with graceful curvilinear lines set between slender shafts.

In addition to their great beauty and richness, these finishes provided extremely durable and maintenance-free surfaces predicted by Barff ten years earlier. As noted in *Ornamental Iron* (1893:[1]97–98), "the electro-plating in the Rookery has successfully withstood eight years handling by the public, and the rubbing and scouring of the janitor." Certainly the predictions of durability have proven true for the surface finishes as well as for the electroplated finishes revealed after the recent paint removal and cleaning.

The application of new technology, fine craftsmanship, and innovative design all contributed to the realization and appreciation of Root's new architectural sensibility. The completed building was widely published in its day and continues to be revered as a work of great creativity, "an improvisation in tones and harmonies both delicate and strong, spontaneity of expression with profundity of thought, all fashioned with the inspiration of genius" (Tallmadge 1941:151). The Rookery's structural and ornamental ironwork played a critical role in the building's acclaim and contributed toward the establishment of architectural ironwork as principal structural and decorative components of the modern commercial high rise.

Appendix

EXAMINATION REPORT: THREE EXAMPLES OF METALWORK FROM THE ROOKERY

209 South LaSalle Street, Chicago, Illinois
Original architects Burnham and Root (1885–88)
Alterations by Wright (1905–07) and Drummond (1931)
P. Andrew Lins and Melissa S. Meighan

Three samples from different areas of original metalwork in the Rookery were submitted for metallographic evaluation, with particular emphasis on surface finishes. The three samples are the following:

1. Window hardware, consisting of the handle proper, a long, biconical "bead," the rod which passes through the bead and which has threaded, decorative spiral knobs at either end, and the two mounting brackets which screw to the window frame and which have projecting arms which are pierced to accommodate the rod. Overall dimensions assembled are $6\frac{5}{8}$ inches wide, $1\frac{7}{8}$ inches deep, and 2 inches high. The finish, a dense, smooth, lustrous black, is assumed to be the original surface and to have been produced by the Bower-Barff process.
2. A section of the ornamental screen or grate, which partially encloses the space under the main staircase in the light court, basically a one-sided, stylized stem with curling leaves and some cast in decorative patterns. Dimensions are $19\frac{1}{2}$ inches long, $4\frac{3}{4}$ inches wide, and $\frac{11}{16}$ inches thick at the maximum. The sample has several layers of overpaint, the last being a cream-white color.
3. A relatively simple baluster from the stair railing, consisting of square upper and lower portions, $5\frac{1}{2}$ and $7\frac{1}{4}$ inches long, with two of four surfaces having vermiculated decoration, and a plain, central shaft of alternating balls and lengths of rod with flaring ends. Overall dimensions are $26\frac{1}{4}$ inches long, $1\frac{3}{8}$ inches square at top and bottom. The baluster has been overpainted black.

Each sample was cross-sectioned using a Leco diamond saw (Vari/cut VC-50) and mounted in Leco epoxy. Each sample was polished to 600 grit with SiC using water or Shelsol, followed by 6 µm and 1 µm diamond using oil as lubricant. The sections were examined at magnifications up to ×500 on a Zeiss metallographic microscope and to ×1000 on a Leitz Laborlux S microscope with a LEP 50W Hg vapor as well. Due to the range of surface treatments employed on the samples, a variety of other analytical techniques were utilized in our analyses, as described below.

SAMPLE 1. WINDOW HANDLE WITH BOWER-BARFF SURFACE TREATMENT

The cross section of this sample (Fig. 2), taken from the bracket, showed typical grey cast-iron structure, with rosettes of flake graphite (maximum flake length approximately 65 µm, with many flakes 10 µm or less). The castings, probably sand casts, are of good quality, with relatively few flaws, and well finished. The surface patina, approximately 25–30 µm thick, consists of two clear zones of approximately equal thickness, of dark-grey or black material. The inner zone has metallurgical features, such as remnants of the cast-iron microstructure and voids, which are continuous with the bulk metal. This zone appears to be the cast-iron substrate that reacted with (was oxidized by) the superheated steam of the Bower-Barff process. This zone also may be described as a depletion zone, from which iron ions moved to the outer zone, an oxidation layer grown on the original finished surface of the cast iron during the Bower-Barff process. On the uppermost surface of the outer zone there is commonly a very thin, approximately 1–2 µm thick maximum, grey-black layer, often separated from the underlying zone by voids, which may represent the alteration of the finish over time or from an initial quenching. Examination under the UV microscope up to ×1000 indicated that there was no intentional organic coating, or residue from an oil quenching, on the finished Bower-Barff surface.

The patina is relatively hard (Mohs 6–6½). It was sampled by scraping with either a glass rod in areas where there was cleavage between the two main layers noted above or with a quartz crystal. Samples were analyzed by X-ray diffraction (Phillips PW 1729 and 1840) in a Gondolfi camera, by emission spectroscopy (Baird Assoc. emission spectrograph, and Fourier transform infrared spectroscopy (FTIR—Nicolet 510P FT-IR Spectrometer, with a Nic-Plan IR microscope). High-purity iron (Puratronic, iron powder, grade 1), Fe_3O_4 (Johnson Matthey, Puratronic, iron [II,III] oxide, 99.999% metals basis), Fe_2O_3 (Johnson Matthey, iron [III] oxide, grade 2), and FeO (Johnson Matthey, iron [II] oxide, 99.9% metals basis) were purchased and used as standards for comparison.

The patina sample and the standard were not readily analyzed and they appear to be either cryptocrystalline or poorly crystallized. The Fe_3O_4 standard produced eight relatively weak lines, seven of which matched d-spacings for JCPDS pattern 19–629, or magnetite. The sample produced nine weak lines, seven of which matched the most significant lines for magnetite, JCPDS 19-629. The patina is definitely magnetite, with minor impurities (Table 1).

The sample and several standards were tested with a magnet. The Fe_2O_3 (red) was only very slightly magnetic. The FeO (wustite, black) was magnetic. The Fe_3O_4 (black) standard and the sample, both identified by X-ray diffraction as magnetite, were—not surprisingly—highly magnetic.

Emission spectroscopy was run on approximately 2 or 2.5 mg of sample; each of the standards noted above mixed with equal amounts of graphite in order to burn more thoroughly. This analysis indicated the presence of small amounts of silicon in the patina (analysis for sulfur or phosphorus was not undertaken). A cross section was analyzed by Nick Spencer of the Research Laboratory of W. R. Grace, Baltimore,

TABLE 1. *Data from X-ray diffraction analysis of Bower-Barff patina on a window handle from the Rookery.*

d-spacings (I/II$_1$) sample from handle	*d-spacings standard Fe (II,III) oxide Fe$_3$O$_4$ 99.999% metal basis*	*d-spacings JCPDS 19-629 (Fe$_3$O$_4$)56F Magnetite*
	4.90 (VW)	4.85 (8)
3.50 (VW)		
2.98 (W)	2.96 (M)	2.97 (30)
2.55 (S)	2.52 (S)	2.53 (100)
	2.43 (VW)	2.42 (8)
2.10 (VW)	2.10 (M-W)	2.10 (20)
1.71 (VW)	1.71 (VW)	1.71 (10)
1.62 (M)	1.62 (M)	1.62 (30)
1.53 (VW)		
1.49 (M)		1.48 (40)
	1.38 (M)	(6 lines I=10 or below)
1.09 (VW)		1.09 (12) (11 lines I=8 or below)

by means of a scanning electron microscope and energy dispersive analysis. Sulfur and silicon were identified both in the bulk of the sample and in the Bower-Barff layers. The data on his analyses will be forthcoming. These elements may be responsible for the unidentified lines in the X-ray diffraction pattern.

The IR analysis in the 200–600 cm^{-1} region, coordinated by Beth Price and carried out on a Nicolet 800 series FTIR instrument at the Chemistry Department of Princeton University by John Eng, gave information in the negative sense, since the sample showed an absence of strong absorption bands in the far IR, comparable to the spectra exhibited by the Fe_2O_3 and Fe_3O_4 standards.

SAMPLE 2. UNDERSTAIR ORNAMENT

The metallographic section of this piece of ornamental metalwork revealed a typical grey cast-iron structure, with the graphite flakes (maximum length approximately 150 µm, most 50 µm) in random and rosette configurations (Fig. 10). The surface treatment of the metal was relatively complex. A thin, highly discontinuous layer containing copper (average thickness 2–5 µm, with maximum thickness 10–15 µm) can be seen on the surface of the iron, which is relatively rough for a plated surface. The copper (not analyzed due to difficulty in sampling) is probably a very thin electroplate layer or "strike" coat, but could be copper or brass particles that have settled out of the overlying varnish layer. Above the copper is what appears to be the original surface-finish coating, a colorless layer approximately 50–75 µm thick, with golden red-brown particles in its uppermost and lowermost levels, suggesting that the method of application may have been dry pigments brushed onto a warmed (stoved) lacquer. Areas of green staining can be seen within this layer and are probably attributable to the presence of copper. It is impossible to state if this green component is the result of corrosion of the copper discussed above or from degraded copper particles or copper-based pigments intentionally added to the colored coating. Finally, it must be pointed out that if a chemical treatment or patina had been applied to the copper to alter its appearance before the application of the colored coating, such a layer would only be nanometers thick and, even if unaltered, would not be resolvable with the instrumentation employed.

FTIR analysis on a microtomed cross section of the layers above the metal indicates that both the clear and golden red-brown layers are natural (tree) resins, not cellulose nitrate, shellac, or wax. Examination of the clear layer under the UV microscope indicates by the strong autofluorescence that the material is a resin.

Above this original coating are numerous other layers. Most interesting is the zone directly above, approximately 60–150 µm thick, presently a very dark brown in visible light and fluorescing ochre in ultraviolet, which is built up of 8 to 15 applications of what appears to be a pigmented, resinous material. This layer was not analyzed, but it can be suggested that this labor-intensive coating might be associated with the Wright renovation.

SAMPLE 3. BALUSTER

The cross section of the baluster shows the microstructure to be grey cast iron, with coarse-flake graphite (100 µm long, on average, with the longest flakes approximately 250 µm) in rosette patterns. In this example there is a very distinct layer of copper on the surface, varying in thickness from 10 to 20 µm (Fig. 11). The copper layer was sampled and analyzed by emission spectroscopy to evaluate its purity; that is, to determine whether it might be brass or bronze plating. Approximately 2.5 mg of the sample and of several standards were mixed with equal amounts of graphite to promote more thorough burning. The comparison standards were: Aesar zinc powder, −100 mesh, 99.9999%; Morton Thiokol copper (I) oxide, 99.95% metal basis; Morton Thiokol tin powder, −20 mesh, 99.9%. No tin was detected, and only a trace of zinc (less than 10 ppm) was found. The plating was found to be copper, not brass or bronze. Such low amounts of zinc could be a contaminant from a variety of sources, such as overpaint. The match with copper was excellent, with some traces of silver.

The examination of the cross section on both the metallographic and ultraviolet microscopes showed no organic coatings that could be associated with the original surface. This suggests that chemical patination, not resolvable by the analytical means available as mentioned above, originally provided the final finish.

ACKNOWLEDGMENTS

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Nick Spencer of W. R. Grace for their generous assistance in the metallographic examination and analysis of the Rookery ironwork. Their work was crucial to the understanding and interpretation of the materials and techniques under consideration.

NOTES

1. For example, see Condit 1964.
2. Structural economy lent impetus to studies of the strength of materials—the most notable being that of the English engineer T. Tredgold and his publication of 1822, *Practical Essay on the Strength of Cast Iron*—and the mathematical theory of design. This, together with early scientific speculations on crystallization and solidification and an understanding of the relationship between microstructure and performance, resulted in improvements in production (see Smith 1981:153–61).
3. "After 1840, blast-furnace practice gradually improved, [but] it was not until about 1850 that 150 tons of pig iron could be produced in a week. In 1875 several furnaces existed which could produce 700 tons of pig iron in a week, in 1880 several producing 1,000 tons per week, in 1890 one furnace could make 502 gross tons/day. By 1886, the United States was the largest steel-making nation in the world" (Swank 1892:535).
4. Among the earliest printed trade catalogues were those for metalwork and hardware published in England during the late eighteenth century. By the mid-nineteenth century, all types of metalwares and building components, especially in cast iron and zinc, were available.
5. Many of the ironwork catalogues of the period contain a great many elaborate designs for elevator grilles and enclosures in a wide variety of styles and finishes. For example, see *Illustrated Catalogue [of the] Hecla Iron Works* (Poulsen and Eger n.d.[ca. 1890]).
6. These coatings were usually shellac or copal varnish and, if tinted with colorants, were referred to as "changing varnishes" (Gardner 1888:64).
7. For a complete discussion, see Hawkes 1980.
8. Because it forms a lead linoleate soap with linseed oil, red lead was preferred because it provided the more protective, tough, durable, and elastic coating, and its ability to enhance "drying" favored its use as a shop- and site-applied coating. Its major drawbacks were expense, poor hiding power, light instability, and toxicity. In addition, its adulteration with brick dust was cited as one reason for its decline in reputation (Condit 1882:145).
9. See *739 Paint Questions Answered* 1904:227.
10. See Experiments on the preservation of sheet-iron from rust in India. *Journal of the Franklin Institute* 20 (October 1835):280–82.
11. See *739 Paint Questions Answered* 1904:188.
12. "The gilding of bronze and brass castings is performed, in the dry way, by making the surface perfectly smooth, then brushing it over with an amalgam of gold, and dissipating the mercury by heat, which leaves a durable film of gold over the surface. This surface may be burnished or deadened. The amalgam is made by heating one part of gold, in thin laminae, in a crucible, and when it becomes faintly red, pour over it eight parts of mercury, pour the combined gold and mercury into cold water, and squeeze the surplus

mercury out. The amalgam is then enclosed in canvas or chamois leather, and some more mercury pressed out; the remainder will contain one part of gold to four parts of mercury. This amalgam is rubbed over the objects to be gilded: it may be had in its true composition from the gold mines of Virginia, and of the best quality from North Carolina. It is advisable to brush the brass over with a thin solution of nitrate of mercury and some free nitric acid, as this facilitates the adherence of the amalgam. The gilt and burnished articles may be coloured by a simple process to any shade from a bright and crimson red to a violet and deep blue, by being submerged in a bath of caustic potash in which some metallic oxide is dissolved" (Field and Weill 1951:243–44).

13. "Metals are bronzed either by chemical agents or by the application of bronze powders. The latter are brass powders of varying shades applied to coats of drying varnish, pigmented or unpigmented by means of badger brushes and then coated with a transparent varnish" (Brannt 1896:148). "Bronze powders are alloys of varying composition of copper and zinc, with small amounts of iron, silver, [and] tin producing colors yellow, pale green, lemon, copper-red, orange, pale yellow, and crimson" (Brannt 1896:154).
14. "Copper Bronze, Red Bronze, [and] Green Bronze [are] produced by varying the color of the base lacquer followed by dusting of the powder" (Brannt 1896:149).
15. These techniques are described in various sources, as follows:

> "Iron railings should first be painted a deep bronze green. The green is made by mixing chrome yellow with lampblack to the desired color, with carriage-rubbing varnish and turpentine. Then, before the paint is dry, take the velvet dauber, and dipping it into the bronze rub it gently over the most prominent parts, or those which project from the surface of the tips of the rods or spearheads, etc." (Gardner 1888:83).
>
> "In bronzing iron it is very advantageous to first coat it, without regard to the succeeding colors, with red oxide of iron, rubbed up in varnish, and then apply the actual colors. A very neat bronzing is produced with a paint of graphite and varnish, the last coat of which is dusted over before becoming entirely dry with aluminum powder, the whole acquiring thereby the appearance of polished iron" (Brannt 1896:149).
>
> "Cast iron may be bronzed by dipping it in a thin solution of sulphate of copper, or muriate of copper, and when sufficiently covered with copper, it is washed and painted with oil varnish. All objects to be bronzed may, however, be painted of any colour, either a shade of green, from the faintest to an almost black green, or of a blue or bluish green. The paint cover should be coated with pure varnish, and when that is nearly dry, a metallic powder is dusted over it by a dusting-bag, or rubbed on by the fingers, a linen pad, or a paint-brush. The metallic powder is generally mosaic gold, which is made of almost every shade, and is of great beauty; or it may be copper in powder, gold leaf, silver lead, and similar articles; dry paint of a convenient shade may also be used. The highest parts of the articles are generally bronzed so as to appear as if rubbed and worn by use. Over the whole of these, a last coating of spirit varnish is laid on" (Overman 1872:242–43).

16. During this period simultaneous experiments in electrochemistry revealed the potential for commercial application. In 1839 T. Spencer of the Liverpool Polytechnic School

described the electrotype process, and in 1840 de Roulz patented a process for electrogilding and silvering and electrodeposition of copper, lead, tin, cobalt, nickel, and zinc. By 1847 George Elkington established at Birmingham, England, the first plant for practical electroplating. For a chronicle of the specific discoveries and events (see Goodale and Speer 1920).

17. Construction of the first dynamo for electroplating in 1875 by Edward Weston led to the firm establishment of the plating industry in America (Burns and Bradley 1967:56).
18. "We are thoroughly equipped for the special finishes of Electro-plating in Bronze, Brass, Copper, and Silver, The Bower-Barff Process, and Electro-graphic or Galvano-plastic work. Duplex electro-bronze work, for outdoor purposes—Store Fronts, Front railings, Grilles, Etc." (Poulsen and Eger n.d. [ca. 1890]).
19. "Electro-bronzing is a process of preserving and beautifying iron heretofore much neglected. Its possibilities in a decorative way are without limit, since it may be applied wherever desired, and in a number of shades. In combination with other metals, the variety of colors is limitless" (*The Inland Architect and News Record* 32 [September]1889:19).
20. In his initial design for the Schlesinger and Mayer Store (now Carson Pirie Scott) in Chicago (1899–1904), Louis Sullivan originally intended the elaborate ground- and second-story metalwork to be cast "statuary bronzework"; however, this was later changed in the specifications of 1898 to be of electroplated cast iron. Ironically, even this was not done for lack of money, and instead the ironwork was painted with a primer of asphaltum and alternating layers of red and green to simulate the appearance of patinated bronze (see Siry 1988:178).
21. The ornamental ironwork of Sullivan's Schlesinger and Mayor Store (now Carson Pirie Scott) was specified to be cast iron "Duplex electroplated in copper bronze" by immersing the metal in an acid bath for 36 hours longer than the standard 22 hours used for electroplating interior metalwork (*Specifications* Section F [December 10] 1898:4).
22. In recounting the commercial introduction of exterior electroplating in America in 1889–90 for use on the ironwork of the rehabilitated Chamber of Commerce Building in Chicago, *Ornamental Iron* states: "The Duplex-Bronze process, original in its application to artistic metal work, with this company [Winslow Brothers], was here applied practically for the first time after repeated and costly experiments. It has fully met the requirements in affording an imperishable envelope to the metallic base, and a surface finish, equal in appearance to solid bronze, fully as durable, and at a greatly reduced cost . . . as perfect now as when was first put in place" (*Ornamental Iron* 2 [March]1895:79).
23. For patination recipes, see Overman 1872:241–42.
24. Brannt describes these methods in various passages from chapter 6 of his "Bronzing and Coloring" as follows ([1890] 1896):

> From page 154:
> Bronzing of Cast-iron.—To give cast-iron the appearance of bronze coat the polished iron with a thin layer of linseed oil or linseed oil varnish and thoroughly heat it in the air to bring about the oxidation of the metal. The temperature must be higher or lower according to whether a pale yellow or dark brown coloration is to be produced. The so-called Tucker bronze is obtained by greasing the polished iron and exposing it for 2 to 5 minutes to the action of vapors produced by a bath composed of equal parts

concentrated nitric and hydrochloric acids, then coating the iron with vaseline and heating until the latter commences to decompose.

To Bronze Cast-iron.—First clean and smooth the surface and then coat it uniformly with a layer of vegetable oil, for instance a poor quality of olive oil. Then heat, without, however, raising the temperature to the burning point of the oil. In this manner the cast-iron at the moment the decomposition of the oil takes place absorbs oxygen and a brown surface of oxide is formed on the surface which adheres very firmly and acquires a good polish, so that the surface of the cast-iron assumes a bronze-like appearance.

Bronze-like Surface on Iron or Steel.—A very fine bronze-like surface, and one that will prevent rusting, may be produced on iron or steel as follows: The object to be acted upon must be cleansed, so as to take off all oxidation or other impurity. It is then exposed for two or three minutes to the action of the vapors of a heated mixture of hydrochloric acid and nitric acid in equal proportions, at a temperature ranging from 550 to 650 degrees F. After the objects have cooled, they are to [be] rubbed over with vaseline, and again heated until the vaseline begins to decompose. This treatment with the vaseline has to be repeated once. Should a lighter coloring than bronze be desired, it can be produced by mixing acetic acid with the other acids. In using the above-named chemicals great care should be observed in handling and preserving.

From page 166:
A very beautiful and durable black color is produced upon articles by dipping or sponging them with platinum chloride solution . . . [described as] “dead black.” Lustrous black color is obtained by polishing with a soft piece of leather moistened with oil, and a lustrous grey-black color by polishing with the burnisher or burnishing stone. The color, especially when polished, is very durable, since platinum is not changed by the action of the air.

Steel and iron articles could be given a fine blue color with a coating of a thin film of a lead sulphide.

To Blacken Small Iron Articles in bulk.—A deep black upon small iron articles is produced by heating them in bulk in connection with oiled saw-dust. . . . The coloring agent consists of an intimate mixture of 10 parts of dry saw-dust and 1 part of linseed oil. The saw-dust thus oiled is shaken in the drum together with the articles to be blackened and exposed to the heat while revolving the drum. The saw-dust undergoing combustion evolves a thick smoke which cannot immediately escape from the drum, it passing out slowly through the aperture in the funnel. This smoke coats the articles with a firmly adhering black color.

From page 18:
Lustrous Black on Iron is obtained by the application of a solution of sulphur in spirits of turpentine prepared by boiling upon the water bath. After the evaporation of the spirits of turpentine a thin layer of sulphur remains upon the iron, which, on heating the article, intimately combines with the metal.

> By another method the cleansed and pickled iron articles are coated when dry with linseed oil and heated to a dark red. If pickling is omitted the coating with linseed oil and heating have to be repeated twice or three times. . . . According to Meriten a lustrous black on iron is obtained by placing the articles as anode in distilled water heated to 158 degrees F and using an iron plate as cathode. A layer of ferroso-ferric oxide is formed which, however, can only be obtained in a firmly adhering state upon wrought-iron. The lustre appears by brushing with a soft waxed brush. The current conducted into the bath must only be strong enough to decompose the water without perceptible development of gas.
>
> Brown-black Coating with Bronze Lustre on Iron.—Heat the bright iron objects and brush them over with a concentrated solution of potassium bichromate. When dry heat them over a charcoal fire and wash until the water running off shows no longer a yellow color. Repeat the operations twice or three times. A similar coating is obtained by heating the iron objects with a solution of 10 parts of sulphate of iron (green vitriol) and 1 part of sal-ammoniac in water.

In his chapter 10, "Decorating, Enamelling, Engraving, Etching," in the same work, Brannt provides the following information:

> From page 196:
> Iron and steel tools protected by an acid-resistant lustrous black coating which resists acids by placing cleaned tools in a box by burning crushed blacksmith's coal and coating tools.
>
> Ward's Inoxidizing Process.—Cast or wrought iron articles are coated by means of a brush or by immersion with a silicate, heating, and after cooling forming a dense uniform coating of a dead-black color, which does not change by the action of the atmosphere nor crack off from the article. Could be colored as well.
>
> From pages 296–97:
> Inoxidizing Process for Cast-iron.—The cast-iron articles, entire gas-chandeliers, water pipes, ornamental pieces, railings, kitchen-pots, etc., are placed upon an iron-carriage and first exposed in a reverberatory furnace of special construction at a temperature of from 112–1292 degrees F for 15 minutes to the oxidizing, and then for 20 minutes to the reducing action of gas generators. After removal from the furnace and cooling, the inoxidized articles acquire a uniform slate color; they may, however, be enamelled and decorated in any manner desired. . . . Various articles exposed in the open air for two years to all kinds of atmospheric influences showed no trace of deterioration. Numerous experiments have demonstrated that the tensile strength of the iron is but little decreased by inoxidation, in fact, no more than by annealing. As regards the durability of the surface layer with a high load, it has been determined that from wrought-iron bars it cracked off in the form of small lamina with an average tension of 4,025 lbs., but from cast-iron it did not crack off even with a breaking load.

25. Professor Barff's process was reported in the *London Times* of March 6, 1877. He delivered a paper describing it in detail before the Society of Arts, London. The paper, titled "Zinc

white as paint, and the treatment of iron for the prevention of corrosion," was delivered on Wednesday, February 14, 1877 and appeared in *The Journal of the Society of Arts* on February 16, 1877, The lecture was reprinted in its entirety for the American audience in *The Iron Age* on April 26, 1877:5–7, and notices of the discovery were published in *The Journal of the Institute of Iron and Steel* in 1877.

26. Current practice indicates that exposure to superheated steam at 500 °C and upward produces an adherent black coating that varies in composition, thickness, and corrosion resistance with the steam temperature. Resultant films can be 2–3 µm at 500 °C to over 10 µm at 600 °C. Cast iron subjected at 700 °C produces a film of 37 µm in 60 minutes. A magnetite film of 25–30 µm was observed on the Bower-Barffed hardware at the Rookery. See Fishlock 1962:229.
27. At least one member of the Institute of Iron and Steel took exception to the unique credit given to Barff for the alleged "discovery" of the magnetite formation on ferrous metals (see Percy 1877).
28. Barff published articles on the process in *Van Nostrand's Eclectic Engineering Magazine* 16(April 1878):300–2; and 18(April 1879):350–54.
29. The paper was subsequently published as "The corrosion of iron." In *Royal Institute of British Architects Sessional Papers* 1878:265–76. London: RIBA.
30. Published as "The Barff process for the protection of iron," *The Iron Age* (January 22) 1880:7.
31. These proceedings were published in *The Journal of the Institute of Iron and Steel* 2, 1881:167–70.
32. "In this process the parts to be treated are heated to nearly 900 degrees C in a closed retort; superheated steam is then led in for twenty minutes and a coating consisting of a mixture of the black and red oxides of iron is formed. Producer gas is now substituted for the steam and passed in for about the same length of time. If the coating thus formed is not sufficiently thick, these operations are repeated as often as necessary. Paraffin or some other oil is afterward applied to the parts, whereby a fine black color is obtained and additional protection afforded. As regards cost, this process is expensive, the price ranging from $5 to $20 per ton, but it can be applied to almost anything which will not be injured by the heat and is small enough to be placed in the furnace, and it affords very efficient protection, especially against sea-water, acid fumes, and like influences. Paints and enamels can be applied and adhere strongly. Parts given this treatment will stand almost any degree of heat without injury, but they may not be bent or machined. Of course, the process is not applicable to tools or tempered pieces. Also, the parts are enlarged slightly so that those which must maintain close limits on dimensions should not be given this treatment" (Wilson 1915:48–49).
33. This was presented in response to an article published in *Iron Age* and reprinted with commentary in *Ornamental Iron* (Art iron at the fair 1893:19–20).
34. "The durability of these finishes has been well established, and they have had such substantial recognition by our leading Architects that we need not enlarge upon them." "Announcement" for the Winslow Brothers Company Artistic Metal Work in *Illustrated Catalogue [of the] Hecla Iron Works,* ca. 1890.
35. Hecla Architectural Bronze and Iron Works, owned by Poulsen and Eger, was located between North 10th and 11th and Berry streets in Brooklyn, New York, and employed the

first furnace for the application of the Bower-Barff process in the United States (*Ornamental Iron* 1[November]1893:94–98).

36. Winslow Brothers Company of Chicago, Illinois, had their city office and exhibit rooms as well as their publication office for *Ornamental Iron* in the Rookery beginning in 1893 (*Ornamental Iron* 1[November]1893:94–98). According to *The Architect and Contractor*, the firm had the largest plant for the manufacture of ornamental ironwork in the country and was the recipient of eight medals awarded at the Columbia Exposition, including "most successful application of the Bower-Barff Rustless Process" and the most "successful electroplating of bronze on iron . . . and on wood" (*Ornamental Iron* 1[April–May]1894:165).
37. Design no. 2044—railing panels of the light court mezzanine and grand stairs; no. 2048 (Design A)—railing panels and turned balusters of the light-court double-cantilevered stairs and oriel staircase, and (Design B)—skylight muntin pattern; no. 2049—stairs and mezzanine newels and stringers; and no. 3563—electrolier and column bases of the light court, in Poulsen and Eger, *Illustrated Catalogue [of the] Hecla Iron Works*, n.d. [ca. 1890].
38. Root's geometric designs for the ornamental incising of the marble, the floor mosaics, exterior terra-cotta and stone, and the metalwork can all be traced to plates of designs of "Arabian," "Turkish," and "Moresque Ornament" in Owen Jones's *The Grammar of Ornament*, published in London in 1856 and later in America in 1880. Of the metalwork, the oriel stair railings are very similar to the square diaper pattern of "Moresque no. 4" (Plate 42, no. 6) and the risers and stringers to the interlaced patterns of "Arabian no. 5" (Plate 35) and "Moresque no. 1."
39. Burnham and Root, Drawing no. 73, "Grand Staircase, Rookery Building," revised October 1887 (Burnham Library, Art Institute of Chicago).
40. All technical descriptions and observations are verbatim from Lins and Meighan 1991 (see Appendix).
41. "Cast iron may be bronzed by dipping it in a thin solution of sulphate of copper, or muriate of copper, and when sufficiently covered with copper, it is washed and painted with oil varnish" (Overman 1872:242).

> Gold Bronze of Great Lustre on Iron.—Dissolve 3 oz. of finely powdered shellac in 1¾ pints of spirit of wine. Filter the varnish through linen and triturate a sufficient quantity of Dutch gold with the filtrate to give to it a lustrous appearance. The iron, previously polished and heated, is brushed over with vinegar and the color applied with a brush. When dry the article may be coated with copal lacquer to which some amber lacquer has been added (Brannt 1896:154).

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Techniques of Mercury Gilding in the Eighteenth Century

MARTIN CHAPMAN

The art of gilding flourished to an unparalleled degree during the Age of Enlightenment. As Diderot's *Encyclopédie ou Dictionnaire Raisonné des Sciences, des Arts et des Métiers* claimed in its section on gilding,

> *"Cet art n'etoit point inconnu aux anciens, mais ils ne l'ont jamais poussé à la même perfection que les modernes"* [This art was not unknown to the ancient world, but it never reached the same level of perfection as that of today](Diderot and d'Alembert 1751–57, vol. 5:57).

In other words, though gilding was performed by techniques that had been practiced for centuries, the richness and refinement in the finish of eighteenth-century gilding raised it far above that of its predecessors.

From the seventeenth century, gilding had been in great demand for the decoration of interiors. In their treatise on japanning, Stalker and Parker declared in 1688, "We are all great admirers of Gold and by consequence must be enamoured with Guilding, which is so nearly related to it." Gilding was highly desirable in adding that necessary touch of richness to the Parisian luxury interior. The trades of Paris practiced the many traditional techniques of gilding on wood, plaster, and metal to respond to this demand.

Of all methods of gilding practiced in the eighteenth century, that done by the mercury process was the most remarkable. This technique, known as early as the ancient world, was developed to its highest degree during the eighteenth century in the hands of skilled Parisian craftsmen. Mercurial gilt bronze became an essential and conspicuous part of Parisian interior decoration from the early eighteenth century, partly because of its rich, metallic glow, and also because of its durability, especially when compared to gilding on wood or plaster. Gilt bronze was applied in the form of mounts to furniture and to any furnishings that formed the focal point in a room. Elaborate mounts were applied to the most expensive pieces of furniture and decorative objects. They virtually overwhelmed the primary material—whether it was wood, stone, or porcelain—with their brilliance and often assumed the leading theme of ornament. Gilt bronze was favored for any purpose associated with artificial light—such as the chandelier, candlestick, or fire dog—where the flames would be attractively reflected in the rich, gilded surfaces. Gilding was also used for clock cases hung on the wall, on a piece of furniture, or on a chimneypiece.

This predilection for gilt bronze led to manufacturing methods that became more sophisticated as the century progressed and richer, more refined finishes were sought. At the beginning of the century, the gilding trade was geared to a perfunctory execution of the process more or less as it had been practiced for centuries. By the 1780s, however, the final stages of mercury gilding were refined to a degree that ensured the surface color and richness of fine gold and the most subtle contrasts of light and texture. These later developments were closely guarded trade secrets, but some of them were derived from a variety of contemporary accounts, both French and English.

THE GILDING PROCESS

The process of mercury gilding in the eighteenth century was, in essence, the same as that described by Theophilus in the twelfth century in his *Treatise on Divers Arts*. Briefly, the method consisted of forming an amalgam of gold and mercury and depositing it in prescribed amounts on the metal to be gilded, then volatilizing the mercury by heat application to leave the gold alloyed to the surface of the metal. This could be done with silver as well as bronze.

The best-known contemporaneous source for discussing the mercury gilding process is Diderot's *Encyclopédie* (1751–57). This is an important compendium for details of techniques used in the eighteenth century, but it is by no means the first or indeed the fullest account of mercury gilding. The version quoted by Diderot under "Dorure," the section of the *Encyclopédie* devoted to gilding, is lifted straight out of Chamber's *Cyclopaedia*, published in London in 1728, and to a lesser extent Stalker and Parker's *A Treatise of Japanning and Varnishing* of 1688. Diderot's description of the process outlines the general principles rather than providing an eyewitness account of the contemporary practice used in Parisian workshops of the mid-century.

If Diderot's text is somewhat perfunctory, his illustrations are not. They are, in fact, the first visual accounts of Parisian trades in operation. In the section "Doreur, sur Metaux," he shows the interior of a gilding workshop where workers are performing different techniques. His illustration (Fig. 1) shows the two processes of gilding on metal—mercury gilding and leaf gilding—which were used extensively in the eighteenth century, sometimes in combination (Verlet 1987:174).

Leaf gilding was simpler (and probably cheaper) to perform but was less durable than mercurial gilding. Also, the leaf process was inappropriate for chased work, so it tended to be used only when brilliantly polished effects were required. The workman in the back center of the scene is gilding a crucifix using the leaf process. The gilder is shown lifting the gold leaf with a gilding knife and applying it to the cross.

FIGURE 1. *The metal gilder's workshop, detail of plate I from Diderot's* Encyclopédie *(Diderot and d'Alembert 1751–57).*

Kneeling in the foreground, a worker in a tricorn hat is blueing a piece of bronze by heating it over a brazier, which was the necessary preliminary step in leaf gilding. The person at right, near the window, is burnishing part of a candlestick, which was also gilded by the leaf process.

The remaining workmen in the scene are performing various steps of the mercury-gilding process. (The earlier stages, which involved the preparation of the gold, are not illustrated.) First the gold would have been obtained from the gold beater. According to Diderot, ready-ground *or moulu* (powdered gold) cost 104 livres an ounce in the 1750s compared with leaf gold, which cost 90 livres (Diderot 1751–57:737). The term *or moulu* meant more than just ground gold; by association it came to describe the finest type of gilding. It was assimilated into the English language as the term *ormolu* about 1760.

Next, the amalgam was formed by putting the gold into a crucible onto a charcoal fire. Then mercury was added in proportions of about one part gold to eight parts mercury.[1] When heated together the two metals readily combined to form a silvery amalgam the consistency of putty. The amalgam was poured into a vessel of water and then squeezed through chamois leather or muslin to remove the excess mercury. This excess was often kept for further use as it inevitably contained some residual gold.

Preparation of the Casting

The casting arrived in the gilding workshop already chased in the finest details. Though the term *gilt bronze* is generally used, the casting was actually made of brass; that is, a copper-zinc alloy rather than the copper-tin alloy usually associated with bronze. The terms *bronze* and *brass* were somewhat vague in both England and France at this time, as was the composition of the metals; the proportions of copper and zinc used for casting varied from foundry to foundry. Matthew Boulton, the Birmingham ormolu manufacturer who turned his hand to producing gilt bronzes in the 1760s and 1770s, recognized that a high-copper content was necessary to provide the best foundation for gilding (Goodison 1974:70, 73). Indeed, what is described as gilding metal today is what Boulton advocated: about 95% copper, 5% zinc. However, as late as 1818 the chemist Jean Pierre Joseph d'Arcet, after much research into the question, recommended a rather different alloy comprising 82 parts copper, 18 zinc, 3 tin, and 1½ lead (1818:vii). Investigations of the collection of gilt bronzes in the Victoria and Albert Museum show a wide fluctuation in the composition of the alloy.[2] This is undoubtedly due to the haphazard foundry practice of throwing old bronzes into the melting pot. By tradition and superstition it was thought that old bronzes improved the consistency of the alloy, with the result that the material contained a curious mixture of different metals that were recycled from one generation to the next (Hachet n.d.:36).

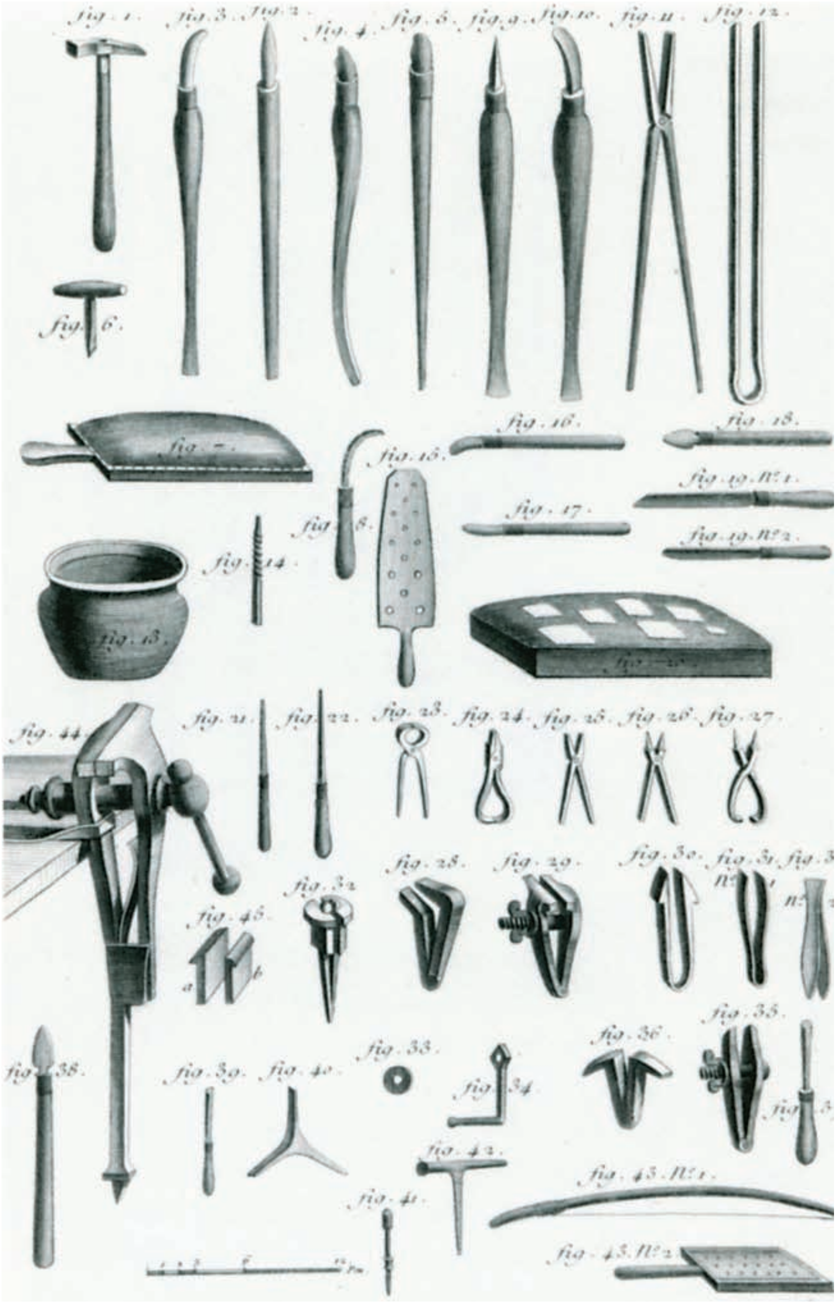
In preparation for receiving the gilding, the casting was cleaned with nitric acid. This process was known as *dérochage*. The workman at the low bench in the foreground of Diderot's workshop (Fig. 1) is working the surface of what appears to be a large furniture mount with a scratch brush made of metal wire dipped in nitric acid. If the piece were especially dirty, it would be left to soak for half a day in *eau seconde*, a weaker solution of old nitric acid that was kept in the tubs shown at the extreme right in the illustration. Apparently this solution had the added advantage of lending the brass a reddish color, which was an appropriate foundation for gilding. The purpose of this treatment was not only to clean the surface of the brass, but also to open up the metal's pores to receive the gilding. As the *Dictionary of Arts and Sciences* suggests:

> The use of aquafortis or nitric acid . . . is not, as is generally supposed, confined to merely cleansing the surface of the metal to be gilt . . . ; but it also greatly facilitates the application of the amalgam to the surface of the metal, probably in the following manner: it first dissolves part of the mercury of the amalgam; and when the solution is applied to the copper, this latter metal, having a stronger disposition to unite with the nitrous acid than the mercury has, precipitates the mercury upon the surface . . . When the metal to be gilt is thus covered with a thin coat of the precipitated mercury, it readily receives the amalgam (Gregory 1806–7:843–49).

Whether this interpretation is correct I leave to the chemists to determine.

The amalgam, kept in a pot like the one shown in Diderot's second plate (Fig. 2), was then applied to the casting with a stiff brush made of brass wire, such as the one shown in Figure 3 (fig. 10 in illustration). Sometimes a layer of pure mercury was applied first to facilitate adherence of the amalgam. The gilder first dipped the wire brush into water, then into the amalgam, which he deposited across the surface of the casting, working in small areas to ensure that the entire exposed surface was covered. Invisible areas on the back of a furniture mount, for example, were left

FIGURE 2. *Tools and instruments, such as those used by workers in Figure 1. Detail of plate I from Diderot's* Encyclopédie *(Diderot and d'Alembert 1751–57).*



untouched by gilding. It is frequently a sign of later electrogilding if the back or underside of an object, which was not intended to be seen, is covered with gilding.

The amalgam-coated casting was then put onto a hot charcoal fire, the heat of which, Diderot says, can only be judged by experience (1751–57, vol. 5:59). This temperature was crucial, as the amalgam would run if it were too hot (Goodison 1974:69). When the casting reached a certain temperature, which was usually judged by the workman spitting on the piece, the mercury was volatilized in clouds of vapor, leaving the gold alloyed with the metal. The workman standing at the far right in Diderot's illustration (Fig. 1) is performing this part of the process. This was the most dangerous part of the operation, as the fumes were excessively toxic. Gilders had a short life expectancy, suffering most commonly from nervous system disorders such as the shakes, paranoia, and eventually madness. The expression "mad as a hatter" derives from the unfortunate effects of mercury on workers who came into

FIGURE 3. *Tools and instruments, detail of plate II from Diderot's* Encyclopédie *(Diderot and d'Alembert 1751–57).*

contact with it in England's hat trade during the nineteeth century. Ravrio, a successful manufacturer of gilt-bronze, left a legacy of 3,000 francs in his will to be awarded by the Academie des Sciences to anyone who found a method of gilding that avoided the hazards of mercury. It was awarded to the chemist d'Arcet in 1818 for his adaptation of the muffle kiln to improve chimney drafts and conduct fumes away from the workers. However, the only precautions visible in Diderot's workshop are the hood above the fireplace to collect rising fumes and the door at the back which is left ajar for ventilation (Fig. 1). D'Arcet remarks that more workers were poisoned in winter than in summer, as the doors and windows which created drafts and allowed fumes to escape were often closed in cold weather (d'Arcet 1818:ch. 13).

FINISHING THE OBJECT

After the mercury had evaporated, the casting acquired a yellow (straw) color with a dull finish. In order to achieve the appearance of fine gold, further processes were used to modify and improve the appearance of the surface. The Parisian gilders refined these methods to an art, drawing on the experience of the past and employing the traditional methods used by goldsmiths in the gilding of silver.

With a huge tool, the worker at the far left in Diderot's illustration (Fig. 1) is burnishing a mount held in a vise. Burnishing was the process of polishing a surface by rubbing it with a hard material until it became mirrorlike. In some cases the burnishing would be enough to finish the piece, especially if there were no modeled or chased areas. The curved tools in the center row of Diderot's plate II (Fig. 3) are burnishers. Several are tipped with *pierre sanguine*, a red hematite stone imported from Germany. Diderot mentions the *ferrette d'Espagne*, a similar stone brought back from Spain by pilgrims, presumably from their journey to Santiago de Compostella. Agates and hounds' teeth are often erroneously mentioned as burnishers in accounts of mercury gilding, but these materials were better suited for softer leaf gilding and gilding on wood.

The process that gave gilding its richness of color was known as *mise en couleur de l'or*. According to Diderot, this was the gilders' secret. Diderot provides no detailed account of its composition under his section on gilding. He only mentions the process used in minting coins, which involved common salt and *tartre de Montpellier*, the latter derived from the crust formed inside wine casks during fermentation. In other sections of the *Encyclopédie* Diderot describes a concoction of tartar, sulfur, and salt mixed with water, in which the object is left to soak until the desired color is achieved (1751–57, vol. 5:59). Diderot lifted this recipe straight from the pages of Stalker and Parker's account of 1688, and therefore it was hardly a secret in the 1750s. Some recipes for coloring the gold simply called for the addition of a yellow coloring agent, such as crushed licorice, turmeric, or saffron. The workman second from left in Diderot's workshop (Fig. 1) is painting the stem of an altar candlestick, probably with this type of varnish in the small pot beside him.

Stalker and Parker discuss another way to heighten the color of the gilding. The recipe involves sal ammoniack (ammonium chloride), saltpeter (potassium nitrate), sandiver (glass gall, "a liquid saline matter found floating over glass after vitrification," as defined by the *Oxford English Dictionary*), verdigris (cupric acetate), white vitriol (zinc sulphate), and green vitriol (either cupric or ferrous sulphate). The process is described as follows: "Grind them together with white wine vinegar, which lay all over your work, then lay it on a fire, and give it a small heat that it may make it smoak, then take it off and quench it in urine" (Stalker and Parker [1688] 1971:66).

A similar recipe is quoted by Goodison in his book on Boulton, the English ormolu manufacturer. Boulton was particularly anxious to learn "the secret whereby the French give that fine colour to their sconces," and he asked his agent, Solomon Hyman in Paris, to investigate it for him there (Goodison 1974:73). Some of the recipes that have come down to us in Boulton's notebooks may therefore have been obtained from Parisian workshops. For coloring the gilding a "pale, middle or clearing colour," a recipe such as this would be tried, as quoted by Goodison (1974):

	oz	*dwt (pennyweights)*
Sal ammoniack	1	10
Green copperas	1	10
Salt	1	—
Verdegrees	0	15
Salt petre	0	15

Goodison analyzes the process as follows: "Copper was introduced into the solution in the form of cupric acetate ('verdigris') . . . and was induced to precipitate with the gold by the use of iron or zinc in the form of ferrous sulphate or zinc sulphate ('copperas')" (1974:71–72).

More than twenty-five recipes for coloring the gilding are quoted by Godfrey Smith in his book, *The Laboratory*, first published in 1755. Many of these formulas are variations on the concoctions already mentioned. One, called "Nuremberg gilding wax" (Smith [1755] 1770:21), seems to follow the same principles but uses beeswax as the medium. This method was undoubtedly derived from the German silversmithing trade, which had a high reputation for gilding, even in France.[3] Diderot gives recipes for two of these Nuremberg waxes under his section on *or moulu*. Both recipes seem to employ the formula of verdigris, white vitriol, borax, and *sanguine* (red chalk) mixed with yellow wax (Diderot 1751–57, vol. 11:529).

Stalker and Parker ([1688] 1971) provide the ultimate solution to coloring the gilding by resorting to the hopelessly expensive expedient of layering it over and over with gold amalgam. They suggest, "You may again, quicken it with quicksilver [mercury] and aqua fortis [nitric acid] and guild over and over again after the former method [i.e., the application of the amalgam already described] and repeat it so often as you please, till your gold lies thick as your nail upon the metal." This of course is cheating. By gilding the bronze over and over again the right effect of fine gold would be achieved, but at what cost? This last process was possibly used in the eighteenth century, but probably not by economically minded gilders who wanted to survive in a fiercely competitive business.

Matt Gilding

The last refinement in the gilding process is that of matt gilding.[4] Diderot does not discuss this process, probably because the technique was not introduced to the Parisian gilt-bronze trade until the last quarter of the eighteenth century. Matt gilding is actually another form of coloring; it imparts a dull sheen by breaking up the surface texture, providing a pleasant contrast with the high polish of the burnishing. Matt gilding produces a more delicate surface than can be achieved mechanically by chasing, which breaks up the surface by the application of patterned punches.

The detail of the foot and handle of a vase in the Victoria and Albert Museum, dating from the 1780s, demonstrates the subtlety of this finish (Figs. 4, 5). The modeled areas of the handle are matt gilded, enhancing the naturalistic qualities of the sinewy ivy branch and the arrangement of the leaves (Fig. 4). The lions' heads on the foot of the vase (Fig. 5) are matt gilded to enhance the sculptural quality of the lions' angry, growling expressions. Contrast is achieved through mirrorlike burnishing of the plinth. On a tiny scale, these mounts show the use of the most delicate, satiny matt gilding as well as the most brilliant burnishing, which together enliven the vase's sculptural detail.

According to Goodison, matt gilding is achieved by the action of chlorine etching the surface of the gold. One of the recipes in Boulton's notes for achieving what he called the "dead colour" contains "2 oz sal petre, 1 oz allum, and 5 pennyweights salt." Goodison interprets this as the salt (sodium chloride) and the "sal petre" (potassium nitrate) dissolving the gold and then redepositing it by "allum" (potassium aluminum sulfate; 1974:71), the essential role being played by the chloride.

FIGURE 4. *Handle of a vase, detail, above left. Black marble and gilt bronze, France, ca. 1780. This magnified detail shows the use of matt gilding to enhance the naturalistic qualities in the modeling of the ivy branch and leaves. Jones Collection, Victoria and Albert Museum, London, inv. no. 1144-1882.*

FIGURE 5. *Foot of the vase shown in Figure 4, detail, above right. Note both matt and burnished gilding; matt gilding is applied to the highly modeled faces of the lions, while mirrorlike burnished gilding is employed on the plinth.*

D'Arcet learned in 1818 that a similar substance known as *mat* was sold ready-mixed to Parisian gilders. He found it to contain 40% saltpeter (potassium nitrate), 25% alum (potassium aluminum sulfate), and 35% sea salt (sodium chloride; d'Arcet 1818:65[i]). In the early nineteenth century matt gilding was widely used by the large bronze-making firms, and it is present on many so-called Empire bronzes. However, the finish on these objects lacks the vitality observed in the finest pieces dating from the late eighteenth century. The tendency toward a more mechanical finish was augmented by the invention of electrogilding in the 1840s, which produced a perfectly even and therefore rather bland surface.

CONCLUSION

We look back to the work of the Parisian gilders of the late eighteenth century for the most beautiful gilding effects. As Diderot said, most of these were achieved by drawing on traditional techniques. It was perhaps less the invention of these diverse methods and more the strenuous application of them that produced the most beautiful objects of the period. Most of the chemistry, whether it was understood or not, had been already devised by previous generations dating as far back as the ancient world. But the Parisian gilders were inquisitive and resourceful enough to gather up all these processes and use them to their greatest advantage in producing the most delicate and sophisticated gilt bronzes.

NOTES

1. Proportions vary from account to account, but this seems to be the most frequently cited figure. See d'Arcet 1818:viii.
2. By X ray performed by Graham Martin, all pieces tested were copper-zinc alloys.
3. While German gilding was acknowledged as being more brilliant, the silver was considered inferior, as it was alloyed with more copper than French silver. See Diderot 1751–57:vol. 9:529.

4. Until quite recently it was often claimed that matt gilding was the invention of the great *bronzier* Pierre Gouthiere (1743–1813), who was at the zenith of his career during the 1770s and early 1780s (Verlet 1987:174). Though he frequently exploited the beautiful effect of matt gilding, the technique seems to have existed earlier in the repertoire of the medalist and goldsmith.

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BIOGRAPHY

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Production and Restoration of Nineteenth-century Zinc Sculpture in Denmark

KNUD HOLM

Danish productivity of cast statuary between approximately 1840 and 1940 is rather remarkable, at least from the standpoint of Denmark's cultural history. During the seventeenth and eighteenth centuries, Denmark, like several other small European countries, had to turn to France whenever a major sculptural project was under consideration and a suitable sculptor and skilled founder needed to be found.

The fact that the work was done by French artists or artisans, however, does not necessarily mean that it was fabricated in France. One of the foremost examples of French sculpture in Denmark is the eighteenth-century equestrian statue of King Frederik V at the Amalienborg Castle by the sculptor Jacques-François-Joseph Saly, cast by Pierre Gor in Copenhagen (Holm 1981). This statue took seventeen years to complete. During that time, Saly became director of the Royal Danish Academy of Fine Arts. Both Saly and Gor subsequently left Denmark. Another well-known French statue is that of King Christian V on Kongens Nytorv in Copenhagen, sculpted by Abraham César L'amoureux (d. 1692), assisted by his brother, Claude. This statue was cast in lead in Copenhagen and gilded.

Early Discoveries in Sculpture Casting

In Denmark today, sculpture casting is performed by only a few small workshops; most sculptures are sent to foundries in Italy for casting. During the period from about 1840 to 1940, however, a number of enterprises accomplished this work in Denmark. Yet only one, the firm owned by Lauritz Rasmussen, extended its activities beyond the death of its founder. This establishment operated for three generations and closed finally in 1967. The first sculpture-casting workshop in Denmark, founded by Jørgen Balthasar Dalhoff (1800–90), is also perhaps the most interesting.

Dalhoff was a goldsmith who took up sculpture casting in bronze, zinc, and terra-cotta. He was very quick to employ new techniques and new materials. During

Dalhoff's time, zinc was considered a rather new material, at least as far as sculpture casting was concerned. Dalhoff's first zinc statues were made in 1841–42.

Zinc played another important role related to the manufacture of statuary: It was an essential element in the discovery of electrical current (c. 1800). The Italian physicist Alessandro Volta demonstrated that piling up multiple, small, galvanic elements based on copper and zinc results in a lasting source of electricity. Since then, zinc has been used as a common component of electrical elements.

One of the earliest technical applications of this discovery led to another discovery: the electrolytic deposition of copper or other metals on a surface through the action of an electric current (1837). The reduction of metals from a solution was known early in the century, but the production of a coherent layer of copper was quite new. This led to the development of electrotyping by M. H. Jacobi, who published his work in St. Petersburg under the German title *Die Galvanoplastik* in 1840. The same year, Dalhoff exhibited some small works made by electrotyping. He did not continue to pursue the process, however. Other workshops took it up, but as far as can be determined, the production of large-scale objects never became their principal business.

A number of statues made in copper by electrotyping can be found in Copenhagen. Many are copies of figures from classical antiquity, such as those situated in Copenhagen's Botanical Garden. These statues were produced in Germany and presented to the city of Copenhagen by the brewer Carl Jacobsen, either as a private donator or through his foundations—the Albertina Foundation (named after Bertel "Alberto" Thorvaldsen) and the New Carlsberg Foundation.

Another new material was found at the beginning of the century: aluminum. In 1825 the Danish chemist and physicist Hans Christian Ørsted (Oersted) was the first to produce a sample of the metal in the laboratory. He was followed by Friedrich Wöhler in 1827. A purer aluminum was obtained by another reducing method devised by Henri Sainte-Claire Deville in 1854 (Rancke-Madsen 1984).[1] This innovation made it possible to produce aluminum utensils and other objects. Aluminum was extremely expensive at first, even more costly than platinum. Nonetheless, Dalhoff made an aluminum helmet for King Frederik VII, which is now in the Chronological Collection of the Danish Kings at Rosenborg Castle in Copenhagen.

The St. Ansgar Statues

The zinc statues cast by Dalhoff in 1841–42 were made by sculptor Gotthilf Borup (ca. 1800–79) to decorate the facade of the new Catholic Church of St. Ansgar in Copenhagen. Five biblical figures—Isaiah, Moses, David, Aaron, and Elijah—stand in individual niches on the upper front of the church, and two kneeling angels are positioned at the base of the roof. These pieces are among the few of Borup's works that still exist. Borup's most important work is said to have been a large pedimental group on the front of the second Christiansborg Castle in Copenhagen, cast in terracotta by Dalhoff. The original sketch for the piece was made by Thorvaldsen. Borup received the commission after the death of another sculptor, Hermann E. Freund,

FIGURE 1. *David by G. Borup, cast in zinc by the lost-wax method by J. B. Dalhoff. St. Ansgar Kirke, Bredgade, Copenhagen. Before restoration.*

who was also Thorvaldsen's pupil. Christiansborg Castle burned down in 1884, and only fragmentary remnants of this sculpture remain today. In 1852 Borup left Denmark for the United States and settled in New Haven, Connecticut, where he remained until his death. His work in America, if any, is unknown.

The St. Ansgar figures were cast in zinc by the lost-wax method (Fig. 1), which had been known since prehistoric times. It was developed and perfected during the Bronze Age, as exemplified by Greek sculpture, Nordic lures, and other artifacts. In later years the lost-wax method became the principal technique for casting large sculptures in one piece, such as the many equestrian statues erected in Italy and France during the seventeenth and eighteenth centuries.

Before producing the St. Ansgar statues, Dalhoff traveled to Berlin as well as to Nuremberg, Munich, and Vienna to study casting techniques. He also scheduled a visit to a large foundry in Lauchhammer, Silesia, in east-central Europe. Dalhoff must have known, however, that it would be very difficult to obtain all the technical information he needed, since most foundries jealously guarded their secrets. He evidently did not find out until later that the lost-wax method is not very suitable for zinc casting. Zinc easily develops a number of cracks when it cools and solidifies, since the inner core of the hollow cast prevents the metal from shrinking (Fig. 2). In addition, Borup's models were delivered to Dalhoff in clay, not plaster, so they were only meant to be used once (Dalhoff 1915–16:258). Models are not necessarily

FIGURE 2. *Detail of the inside surface of one of the statues from the church of St. Ansgar.*

FIGURE 3. *Detail of the head of Elijah showing cracks and holes, church of St. Ansgar.*

destroyed immediately during the process of making molds, but when the lost-wax method is used for large castings, the foundry worker almost always tries to salvage the results of the first casting. Even an extensive repair effort is often easier than starting all over again.

Each figure was cast in two major pieces, an upper half and a lower half. The heads were cast separately, as were the hands and the figures' various symbolic attributes. For these reasons, the casting of the five St. Ansgar figures was far from perfect (Fig. 3). However, because the statues were designed to be painted, nothing prevented Dalhoff from using lead for the bigger repairs and linseed-oil putty for the smaller. Even concrete was used to keep the hand of one figure in place.

Installation of the statues was similarly problematic, since the niches in the church facade were not deep enough to accommodate the cast figures. It was not feasible to make the niches deeper, so the backs of all the figures were cut away along with a portion of their square bases. This operation seriously impaired the stability of the work.

After the St. Ansgar figures, Dalhoff went on to cast a number of bronze statues in Copenhagen, including four colossal statues at Christiansborg Castle (originally placed in niches on the facade of the former castle) and the quadriga on top of the Thorvaldsen Museum.

The Restoration

When restoration was initiated, the St. Ansgar statues were found to be very dirty. Their interiors were partly filled with pigeon dung and nest material. Some parts of the figures were missing. When the statues were removed from the building, special precautions had to be taken to prevent them from falling apart. The statues did not suffer extensive surface corrosion, although they were exposed to exhaust fumes from the city's rather heavy traffic. Their recessed niches sheltered them from wind and heavy (acid) rain.

The statues were cleaned with water using a high-pressure water jet and careful sandblasting. Loose parts were soldered on with lead-tin solder.[2] An inner armature of stainless steel was also tailored to fit each figure. For reinforcement, ribs of zinc were cut to shape from a 7-mm-thick plate and soldered to the inner surface of the zinc at appropriate points. One of the heads was cast so thinly and had so many cracks and holes, that it was necessary to reinforce it by adding a layer of zinc to the inside. This was done using the slush-casting method.

In slush casting, molten metal is poured into a hollow form and then poured out again afterwards, leaving only a thin layer of solidified metal along the walls of the form. To restore the shape of a head that has a number of gaps, it is necessary to cover the head with a shell, which could consist of aluminum foil, clay, and gypsum. The head must be cleaned inside by sandblasting. Before receiving the molten metal, the shell must be dry and the whole head heated to some degree. The old and new metals will not necessarily combine very well, and it is often wise, therefore, to solder the joints from the outside. In cases such as this, a tin solder with a resinous core is advisable. Larger gaps should be modeled before making the shell.

The greatest challenge to the restoration of the St. Ansgar figures lay in reconstructing the proper shapes of two of the figures' attributes: David's harp, which was incomplete, and Aaron's censer, which was missing. The missing parts of the harp had been replaced earlier with a very poor imitation of the instrument; and the censer, which had originally been in Aaron's hands, required an appropriate prototype from which to create a new model. Old photographs did not provide much detail for these objects, so new ones were created and cast in zinc. Since the original statue was made of zinc, there was no reason to introduce other materials for the missing parts. Some existing parts, however, were originally made of other materials. For example, the harp strings were presumably made of steel wire that rusted away long ago; these were replaced with stainless-steel wire. The molds were made with gypsum (Fig. 4).

A few small remnants of paint and a couple of old pictures of the statues indicated that the figures were originally painted green to resemble the natural patina of bronze. To restore their original green color, the statues were painted using a modern acrylic PVC paint called ICOSIT-Dickschicht 5530 (Lechler Chemie GmbH, Stuttgart, Germany). The paint was sprayed on with airless spraying equipment. No primer was used.

The two angels by Borup have not yet been restored. Dalhoff used a different casting technique for these figures, which are made from a number of pieces that were soldered together. Therefore, it appears that Dalhoff adopted the sand-casting method, which became the standard and most readily available technique for producing zinc sculpture, at least when only a few items were needed. Sand casting originated and became widespread primarily for the casting of iron. Eventually sand casting supplanted the need for lost-wax casting of bronze as well, especially in Germany and Denmark. However, lost-wax casting never died out completely, and currently seems to be regaining some degree of popularity. Dalhoff's first zinc castings remain an exception for being cast using the lost-wax method during the 1840s in Denmark.

FIGURE 4. *The five statues by G. Borup. From the left: Isaiah, Moses, David, Aaron, Elijah. After restoration.*

OTHER ZINC CASTING IN DENMARK

Once Dalhoff had introduced the casting trade to Denmark, other foundries began to appear, with sand casting as the principal method. They included those of Thomas Christian Thomsen, Carl Frederik Holm, Lauritz Rasmussen, Vilhelm Bissen, and Oluf Schieltved. Christian Lundqvist is known to have cast at least one statue.[3] All of these foundries cast other objects as well.

The largest example of zinc casting in Denmark was a group of figures created for the new Royal Theater (Fig. 5) by the sculptor Ferdinand Edvard Ring (1829–86). The theater opened in 1874, but the building itself was not completed until 1883. In 1878 Ring's sculpture was placed on top of the facade. The original group of figures was 6.5 m high and about the same width. It depicts Apollo and Pegasus at the Hippocrene spring along with Thalia and Melpomene, the muses of comedy and tragedy. Holm was at first commissioned to have cast this group, but it seems that Rasmussen may have cast it (Clemmensen 1929).[4]

In 1959 the Ring sculpture was dismantled and taken down, since the iron armature inside the casting had become severely rusted. The work was stored in various places and was eventually considered beyond repair. A replica was made, this time in bronze, by the Italian founder Fonderia Artistica Battaglia in Milan. In 1987 the replicated group was returned to its location at the Royal Theater. Fragments of the original statue were sold to finance the replication. Unfortunately, possibilities for restoration of the original were never explored and cannot now be determined.

Another building of interest in regard to nineteenth-century zinc casting is the so-called Marble church, or Frederiks Church, in Copenhagen (Nationalmuseet 1933). This church was planned as a landmark in Frederiksstaden, the new part of Copenhagen named after King Frederik V. The king laid down the foundation stone in 1749, and building was started later the same year. In the following years, plans often changed, including the choice of materials and the architect. In 1770 funds ran

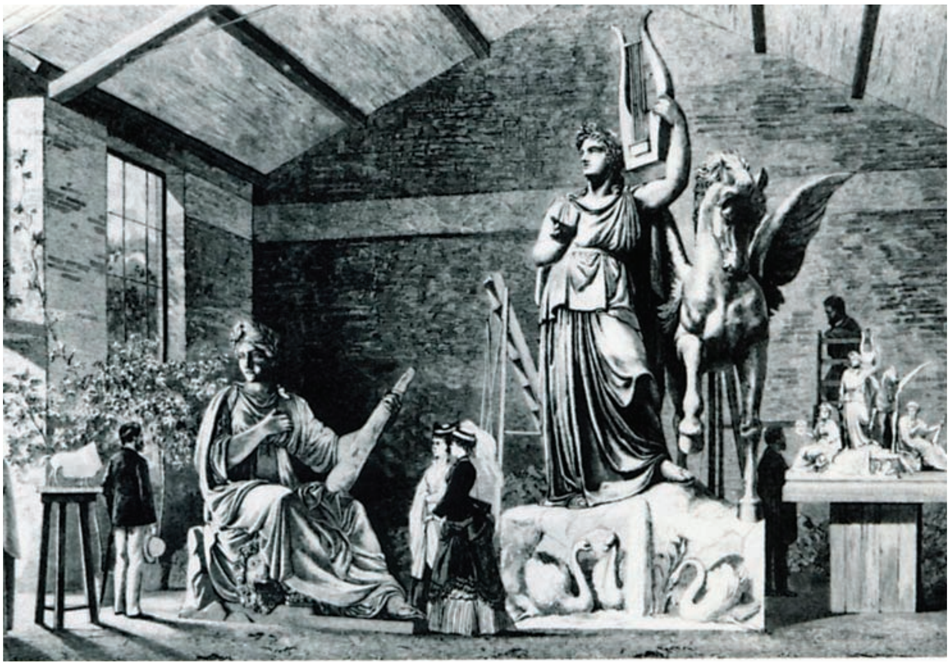

FIGURE 5. *Illustration from the periodical* Illustreret Tidende *(1874) showing the group of figures for the Royal Theater in Copenhagen in the studio of Ferdinand Edvard Ring.*

out and the project was canceled. For more than a century the unfinished building stood as a picturesque ruin in the middle of the otherwise fashionable town quarter. Many proposals for renovation were introduced. Finally in 1874 the ruin was bought by Carl Frederik Tietgen, a finance magnate and bank director who hired the architecture professor Ferdinand Meldahl to build a church on the existing foundations.

A number of statues stand at ground level around the church. However, eighteen large statues made of zinc, which are placed halfway up the building are of prime importance here. Tietgen was very interested in the design and in the choice of figures for the church. He commissioned all the figures and had them produced between 1883 and 1885 by ten different sculptors (Nationalmuseet 1933) and four different founders. The sculptors were Otto Evens (1826–1895), Georg Christian Freund (1821–1904), Johannes Gelert (1852–1914), Aksel Hansen (1853–1933), Johannes Hoffmann (1844–1920), Carl Christian Peters (1822–1899), Ferdinand Edvard Ring (1829–1886), Carl Rohl Smith (1848–1900), August Saabye (1823–1916), Theobald Stein (1829–1901), and Bodelsen and Engelstoft (1947–52).

Gelert went to Chicago in 1887 and to New York in 1898. Rohl Smith emigrated to the United States in 1886 and soon established himself as a sculptor of public monuments. He created a bronze statue of Benjamin Franklin in Philadelphia and another of General William T. Sherman on horseback, which stands in Washington D.C. The Iowa State Soldiers and Sailors Monument in Des Moines and a statue on a street corner in Chicago that commemorates the massacre of American Indians in 1872 are also by Rohl Smith.

The four founders who cast the figures for the Marble church were Holm, Lundqvist, Rasmussen, and Schieltved. The eighteen statues they produced are currently in poor condition and require restoration. Their marked surface corrosion is clear in comparison to the almost uncorroded surfaces of all the solder seams (Figs. 6–9). It is interesting to note that in a written report in 1968 an engineering firm that inspected the statues stated that the figures showed no sign of crumbling, loosening,

FIGURE 6. *Figure of Luther by Theobald Stein, below left, cast in zinc by C. F. Holm. Frederiks Kirke, Frederiksstaden, Copenhagen.*

FIGURE 7. *Back of figure of Athanasius by Carl Rohl Smith, below center, cast in zinc by O. Schieltved. Frederiks Kirke.*

FIGURE 8. *Detail, far right, of one of the figures from Frederiks Church showing tin-solder seams standing out against the corroded zinc surface.*

FIGURE 9. *Detail of one of the figures from Frederiks Church showing places where water could be trapped by the shape of the figure. These areas have been filled with mortar to prevent damage from freezing water or to prevent water from seeping in through cracks and holes.*

or development of cracks. The statues still carry traces of paint, indicating that they were finished to resemble sandstone. The most common colors used for this purpose were brown-bronze or yellow or whitish sandstone imitation. Analysis of the patinas has not yet begun, and research is still underway concerning their treatment histories. It is uncertain, therefore, whether these statues have been painted since 1884, but they may have been refinished during an earlier restoration in 1938–39.

The eighteen statues commissioned by Tietgen for the Marble church are unique. In addition to their inherent aesthetic qualities, they stand out in respect to the vast majority of zinc castings that were made in quantity during the same period and could be selected from catalogues.

Conclusion

The many zinc statues cast in Denmark between about 1840 and 1940 now require restoration and repair, work at which the National Museum of Denmark has acquired some experience. The restoration and conservation of outdoor zinc sculpture is in some ways not so problematic as that of bronzes, simply because most of the zinc statues were meant to be painted, and proper maintenance of them has taken that fact into account. However, some zinc statues have been left to form a natural mineral crust, or patina. Generally speaking, zinc does not corrode as much as might be expected from its electrode potential. This is due to the formation of a thin layer of hydroxides and carbonates or, when heated, oxides. Today the increased acidity of the precipitation is an additional threat to those zinc statues that are not protected by a surface coat.

Most of the restoration work that has been carried out has had to deal with structural problems, such as disintegrating inner armatures and the renewal of long-absent surface coatings. Traditional oil paints do not last on zinc. Modern surface-coating materials with better bonding properties on zinc are commercially available, however. The technical and historical study of the Danish sculptures of different periods will continue to contribute to the conservation of each statue.

Notes

1. The English translation of Rancke-Madsen's book (1984) is "The History of the Discovery of the Elements." References to Sainte-Claire Deville and his work can also be found elsewhere in the chemical literature. J. R. Partington mentions it briefly in his *A Short History of Chemistry*, although he fails to mention Oersted in connection with aluminum. Rancke-Madsen describes the method used by Oersted to produce aluminum. This paper was originally published in "Oversigt over det kongelige Danske Videnskabernes Selskabs Forhandlinger, 1824–25," in the proceedings of the Royal Danish Academy of Science and Letters 1824–25. Oersted was the secretary of the academy at this time. A sample of the metal was presented before the academy on April 8, 1825, and is also described in "H. C. Oersted's Scientific Papers I–III" (1920) collected edition, including two essays on his work by Kirstine Meyer, vol. 2:463–66, Copenhagen.

2. One important technique in soldering zinc is the use of a hydrochloric-acid solution (15% in water) instead of an ordinary commercial flux, whether water, resinous, or other type. The solder was lead-tin solder of different composition. The sand used in sandblasting was an ordinary quartz sand. In some other cases, glass beads were used.
3. Thomsen was an apprentice of Dalhoff, Rasmussen of Holm. It is not known where Holm learned to cast statues. He was an apprentice of a brazier by the name of Løchte, but as far as we know, Løchte never made statuary. Bissen was primarily a sculptor. He established a foundry in order to cast his own statues but employed French foundry workers.
4. The group was originally planned to be cast by Holm, according to a contemporaneous press source in Copenhagen (*Illustreret Tidende* 1874: vol. 15, no. 783), but archive documentation fails to confirm this or to provide the name of anyone else who cast this group. A 1929 book (Clemmensen) celebrating the seventy-fifth anniversary of the Lauritz Rasmussen firm, however, mentions that the group was cast by Rasmussen. Although this source is not infallible, it is probably safe to surmise that it is correct in this case.

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BIOGRAPHY

Knud Holm is chief conservator and former keeper of the Department of Conservation 2 at the National Museum of Denmark, where he has worked since 1951. Holm studied chemistry, physics, and radiography at the University of Copenhagen; metallography at the Technical University of Denmark; and conservation of antiquities at the National Museum. His specialty is metals conservation. He has served as a member of International Institute for Conservation, the ICOM Committee for Conservation, and the Ministry of Cultural Affairs committee reporting on the organization of conservation in Denmark and the establishment of a school for conservation. He has written numerous articles on cultural history, conservation, and the history of technology.

Real-time Survival Rates for Treatments of Archaeological Iron

SUZANNE KEENE

> I there behelde the bones of a man . . . and round about him . . . such nailes were found, wherefore I coniectured them to be the nailes of his coffin. . . . I caused some of the nayles to bee reached vp to mee, and found under the broad heades of them, the olde wood, skant turned into earth. . . . I reserued one . . . but the nayle lying drie, is by scaling greatly wasted.
>
> —John Stowe, *Survey of London,* 1603

Since the 1970s, a series of excavations in London has uncovered a mass of archaeological evidence for life in the capital from pre-Roman times onward. During the short-lived property boom of the mid-1980s, there was an exponential increase in new building and redevelopment in the city of London. The museum was fortunate in persuading many developers to fund excavation on these developments. It was found that progressive land reclamation and revetment along the north bank of the Thames, the main trade route, had resulted in large, stratified dumps of rubbish from the Roman and medieval city. The waterlogged and anaerobic conditions in these sites ensured the survival of the objects contained there, including an unparalleled number and range of objects made of iron.

The Nature of the Problem

The stabilization of archaeological iron presents difficult problems. Iron is a relatively reactive metal, and in the presence of an electrolyte such as ground water, it mineralizes to a greater or lesser extent. The minerals formed will vary depending on burial conditions (Turgoose 1982b). In aerobic conditions, objects often corrode out entirely, although their form can remain embodied within the corrosion products (and can sometimes be recovered by skilled conservators). In anaerobic conditions, corrosion may proceed to a much lesser extent. Such objects often appear extremely well preserved and are sometimes assumed to be stable. Experience has shown, however, that such is not the case.

Whatever the apparent condition of the objects when excavated, they actually consist of a highly complex metal-and-mineral system. Many of the minerals are only stable within the particular burial environment—with its specific redox potential, pH, and so on. When brought above ground, these conditions no longer exist, and different minerals begin to form, due either to changes in the original minerals, or to fresh corrosion at the metal-corrosion interface (Turgoose 1982b).

Because they are so well preserved, these objects are an excellent source of evidence for their manufacture and use. London iron is often decorated by tooling or shaping; it can be tinned or inlaid; tool marks from manufacture or sharpening are preserved in surfaces. But unfortunately for the conservator, most of this detail is contained in the mineral layers, as John Stowe observed nearly 400 years ago. If objects recorrode, fresh mineralization at the metal surface pushes off these delicate surfaces, leaving only the familiar powdery red rust.

Existing Knowledge

The work of Turgoose (1982a, 1982b, 1985) and others (Gilberg and Seeley 1982) has done much to explain the corrosion mechanisms sustained by archaeological iron after excavation. However, developments in treatments to stabilize this material have lagged behind theoretical understanding to some extent.

The "Holy Grail" of iron conservators has been removal of every trace of chloride from the corrosion and metal. Until the 1970s, there was a meager choice of treatments for iron: boiling in purified water, reduction using electrolysis, or soaking in sodium carbonate. These methods were widely found to be unsuccessful; objects treated in this way frequently recorroded within a few years. Other methods have been more recently introduced: hydrogen reduction, chemical reduction, and gas plasma reduction. These are very aggressive treatments, however, and all of them place at risk the delicate corrosion surface of the objects or the metallurgical evidence that they embody, both of which are prime reasons for preserving the objects. Some of them rely on heat, which compromises the metallurgical evidence (Tylecote and Black 1980).

Other measures that do not depend on chloride removal are desiccated storage, storage in an atmosphere of vapor-phase inhibitor (VPI), and storage in atmospheres of nitrogen or with an oxygen scavenger. However, treatments not involving chloride removal, such as corrosion inhibitors, have scarcely been seriously explored.

In the United Kingdom at least, there is a strong body of opinion that treatments for iron are no more effective than simply storing objects at a low relative humidity. Turgoose (1982b) identified 15% RH as the level at which all water will be removed from iron minerals, thus preventing alteration. Therefore, many conservators in the United Kingdom have adopted storage at, or as close as possible to, 15% RH as their preferred procedure for stabilizing this material.

The Reason for This Study

Conservators at the Museum of London were faced with an influx of beautifully preserved but unstable objects, as shown in Figure 1, but no clear professional con-

FIGURE 1. *Well-preserved iron objects from Swan Lane, treated using various methods.*

sensus on the most effective treatment for them. Excavation funding included an element for conservation, but this was project-based and only available for a fixed time; decisions could not be deferred.

In 1983–84, in order to gather some objective evidence, a study of iron previously treated by the author was undertaken and published (Keene and Orton 1985). The results of this study suggested that all the treatments that were assessed improved the stability of the objects. Since then, the policy of the Museum of London has been to actively treat iron destined for its collections. The museum also considered it desirable to keep this policy under review. Therefore, in 1983, anticipating an eventual formal assessment, finds from a particular site (Swan Lane, SWA 81) were divided into four batches, and each batch was treated using a different procedure. The objects have since been stored and handled in exactly the same way as are other objects in the museum's collections.

Assessment Design and Procedures

The present study is based on empirical observations of the stability of excavated iron treated in various ways and untreated. The aim was to establish whether any of the treatments that are used confer greater stability than no treatment or storage at RH lower than 15% (desiccated storage).

The sample in the assessment summarized in Table 1 may be described as follows: (a) four batches of iron from the Swan Lane site, treated at one time; (b) iron from the same excavation, not treated and stored in desiccated and ambient conditions; (c) iron from other Museum of London sites, some batches stored in desiccated conditions, some in ambient environments; and (d) iron from completely different areas and types of sites (excavated by the Passmore Edwards Museum), stored using the best practicable means to maintain a low RH.

TABLE 1. *Summary of the data from the assessments of the batches of objects.*

Excavation code and date	Treatment or storage type	Year treated or stored	Number in batch	Years since treatment or start of storage																							
				2			3			5			6			7			8			9			13		
				Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Uns	Mis	Sta	Unc
a. Museum of London, Swan Lane site: treated batches																											
SWA 81	NaOH	1983	24	0	24	0				0	24	0							1	22	1						
SWA 81	Alk. sulf.	1983	19	0	19	0				0	19	0							5	13	1						
SWA 81	Water/VPI	1983	31	7	27	2				4	18	7							3	16	3						
SWA 81	Electrol.	1983	17	6	10	1				3	6	6							2	6	4						
b. Museum of London, Swan Lane site: batches stored without treatment																											
SWA 81	Ambient	1983	31																			0	10	21			
SWA 81	Dessicated	1983	10																			0	3	7			
c. Museum of London, other sites: batches stored without treatment																											
OPT 81	Dessicated	1982	32																			0	23	9			
OPT 81	Ambient	1982	33																			0	13	20			
BWB 83	Dessicated	1984	17													0	9	8									
MOG 86	Dessicated	1986	15							0	2	13															
MOG 86	Ambient	1986	15							0	2	13															
BOY 86	Dessicated	1986	15							0	6	9															
BOY 86	Ambient	1986	20							0	3	17															
d. Passmore Edwards Museum: batches stored without treatment																											
WA/AM 78	Dessicated	1978	164																						0	8	156
BA 85	Dessicated	1985	47										0	10	37												
TF 88	Dessicated	1988	72					0			22		50														
TF 89	Dessicated	1989	26		0			20			6																

Notes: 1. An object is only counted unstable once, and is thereafter omitted from the table.
2. If an object was missing from an assessment but is found at a later one to be stable, it is counted as stable in the earlier assessments.
3. In this table, an object may be considered missing at one assessment but observed as unstable at a subsequent one.
See Table 2 for further details of these points.

The treatment procedures, detailed in Appendix 1, may be summarized as follows:

Water/VPI: Soaking in deionized water with dissolved vapor phase inhibitor (Dichan, dicyclohexyl ammonium carbate, marketed as Shell VPI 260)
Alkaline sulfite: Soaking in changes of alkaline sulfite, followed by changes of deionized water
Sodium hydroxide: Soaking in a dilute solution of sodium hydroxide
Electrolysis and soaking: A short period of electrolytic reduction followed by soaking in water/VPI as above

Objects were allocated to the four treatments in rotation by their accession number; those that were heavily corroded, very delicate, or had tinned or decorated surfaces were not treated with alkaline sulfite nor with sodium hydroxide. Electrolytic reduction was not used as it usually is—to strip away all corrosion to the metal—but rather to loosen corrosion layers in order to make it easier to expose fine detail. In this, it was very successful. The selection for treatment was similar therefore to any typical selection process and was not completely random. A higher proportion of delicate and heavily corroded objects are typically allocated to treatments either by electrolysis or by using water with VPI, although there is no reason to assume that such objects are inherently more or less prone to corrosion. These treatments are summarized in Table 2.

After treatment, the objects were stored at 15% RH in sealed boxes containing silica gel, according to normal practice. Their condition was reviewed in 1985, 1988, and 1991: two, five, and eight years after treatment. The most recent review included untreated objects from the same site stored in the ambient environment but not treated, and a similar sample that had been stored at 15% RH.

To provide further data, objects both from other Museum of London sites and from a completely different context were also examined. A neighboring museum, the Passmore Edwards, has a climate-controlled chamber operated at 18–20% RH. Hygrothermograph records confirm that these conditions were maintained throughout the period of study. Excavated iron has been stored within this chamber in sealed boxes containing completely desiccated silica gel monitored with indicator strips since 1982. The objects have thus been doubly protected. Prior to that time, silica gel in sealed boxes alone was used to create desiccated conditions. The museum is therefore an excellent exponent of the technique of desiccated storage.

In assessing instability, as in the earlier study, an object was graded "unstable" if there was the slightest sign of fresh corrosion or lifting of mineral layers. In the current review of Museum of London iron, microscopic examination was used to settle doubtful cases, and this resulted in regrading a few objects from "unstable" to "stable."

In most cases of treated iron, instability consists of one or two very small flakes or cracks, as shown in Figure 2. Often, however, untreated iron has almost disintegrated, as shown in Figure 3.

FIGURE 2. *A treated iron object, above, slightly unstable.*

FIGURE 3. *An untreated iron object, right, almost disintegrated.*

DATA AND ANALYSIS

A total of 588 objects were examined. The data from these assessments are summarized in Table 1. Table 2 shows an example of the data for one batch, which was treated using water and VPI. For each object, the following data were available: year

TABLE 2. *Observations for the batch treated using water/VPI.*

Date of assessment (treated in 1983)	*April 1985*	*October 1988*	*July 1991*
Registration number: SWA 81			
462	m	x	out of trial
463	[o]	[o]	o
468	[o]	[o]	o
470	m	m	x
472	o	[o]	o
474	o	o	o
506	[o]	[o]	o
656	o	m	x
657	o	[o]	o
695	[o]	[o]	o
780	m	x	out of trial
926	o	[o]	o
946	o	m	m
1045	m	x	out of trial
1362	x	out of trial	
1530	x	out of trial	
1591	o	o	o
1739	[o]	[o]	o
1762	[o]	o	m
2230	[o]	o	x
2239	[o]	[o]	o
2240	m	x	out of trial
2313	o	o	o
3068	o	x	out of trial
3079	o	m	x
3091	o	o	o
3273	[o]	o	o
3382	[o]	[o]	o
3388	m	x	out of trial
3863	[o]	[o]	o
3951	m	x	out of trial
Totals:			
Number entering interval (= number from last interval minus number then unstable)	31	29	22
Missing	7	4	3
Newly unstable	2	7	3

Key: m = missing; o = observed stable; [o] = inferred stable from later re-appearance; x = newly unstable of excavation; year treated or storage begun; stable, unstable, or not present on one or more occasions after treatment; years elapsed from start date to examination.

In the precursor to this study (Keene and Orton 1985), the probability of recorrosion and the related parameter of half-life were also calculated. It was not necessary to use this sophisticated technique again, since the new data were considerably simpler. However, complications did arise. On first sight, in fact, it was difficult to determine how to extract all the information these data obviously contained. Batches of objects had been examined at different points in time; some objects were not present for assessment but were found on subsequent occasions when others were missing.

A very similar research situation exists in medicine when clinical trials are undertaken to compare survival rates for different treatments. Patients may survive, or they may die of the disease being treated or from another cause. They may miss checkups, then subsequently return. It was found that the techniques used to assess test results with these kinds of variables could also be applied to the "survival" of archaeological iron. The techniques are described fully in Mould (1981:65–69). Data similar to those available for the iron objects are used to construct "Life Tables." A Life Table for the batch treated using water with VPI is shown in Table 3; the headings summarize the method.

What is calculated is the probability that an object will "survive" (be stable) at any given year after it was treated or stored. The probabilities for different batches of objects can then be compared (Fig. 4, Table 4). These survival probabilities are, in fact, familiar figures, often quoted in press reports for treatments. A probability of 0.33 can be expressed as "one in three will survive beyond x years," or as "a 30% chance of survival" (Fig. 5).

RESULTS

The question being examined is: Does treatment confer greater stability than no treatment or than desiccated storage? This can be expressed as a null hypothesis: At a given year T, there is no difference between the probability of survival for an iron

TABLE 3. *Life table for the batch treated using water/VPI.*

Year	*Interval number*	*Years since treated*	*Observed unstable*	*Missing*	*Number entering interval*	*Number at risk* (li − $^1/_2$ wi)	*Prob. of instability at interval* i	*Prob. of surviving*	*Prob. of surviving to Year T*
	i	T	di	wi	li	ni	$qi=di/ni$	$(1-qi)$	$PT=(1-qi)$ $(1-qi)$ (percent)
1983	0	0	0	0	31	31.00	0.00	1.00	100
1984	1	1	0	0	31	31.00	0.00	1.00	100
1985	2	2	2	7	31	27.50	0.07	0.93	93
1986	3	3	0	0	25	25.00	0.00	1.00	93
1987	4	4	0	0	25	25.00	0.00	1.00	93
1988	5	5	7	4	25	23.00	0.30	0.70	65
1989	6	6	0	0	19	19.00	0.00	1.00	65
1990	7	7	0	0	19	19.00	0.00	1.00	65
1991	8	8	3	3	19	17.50	0.17	0.83	53

FIGURE 4. *Survival probabilities compared for batches of objects treated in different ways, and batches stored untreated. Lines for the stored batches are straight because they are calculated from one assessment in year 9, while those for treatments are the result of three sequential assessments (see Table 4).*

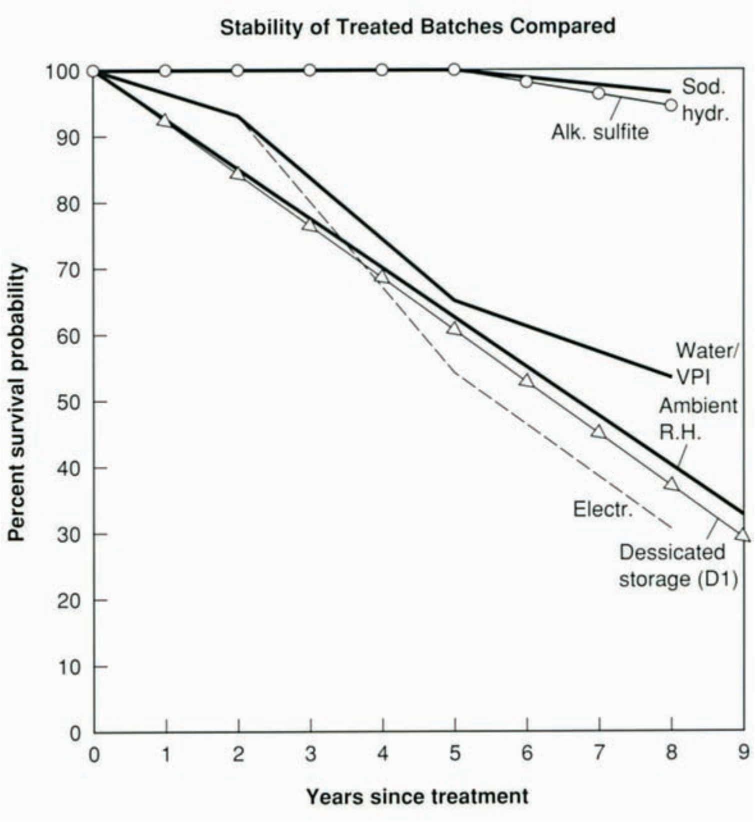

TABLE 4. *Percent survival probabilities at Year* T *for all the assessed batches.*

Year since treatment/ storage	*Treated iron: Swan Lane, SWA 81*				*Stored at ambient RH*				*Stored at l5% RH*								
					Site codes:				*Site codes:*								
	Sodium hydroxide	*Alkaline sulfite*	*Water/ VPI*	*Electrol./ soak*	*MOG 86*	*BOY 86*	*SWA 81*	*OPT 81*	*TF 89*	*TF 88*	*MOG 86*	*BOY 86*	*BA 85*	*BWB 83*	*SWA 81*	*OPT 81*	*WA/AM*
(Year *T*)																	
0	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
1	100	100	100	100	—	—	—	—	—	—	—	—	—	—	—	—	—
2	100	100	83	94	—	—	—	—	77	—	—	—	—	—	—	—	—
3	100	100	83	94	—	—	—	—	—	31	—	—	—	—	—	—	—
4	100	100	83	94	—	—	—	—			—	—	—	—	—	—	—
5	100	100	65	52	13	15	—	—			13	40	—	—	—	—	—
6	100	100	65	52			—	—					21	—	—	—	—
7	100	100	65	52			—	—						53	—	—	—
8	96	94	61	26			—	—							—	—	—
9							32	72							30	39	—
10																	—
11																	—
12																	—
13																	5

object, whether it is treated, stored in desiccated conditions, or simply stored in the ambient environment.

The comparative survival probabilities at the different assessments of the Swan Lane batches are compared in Figure 4. Survival probabilities at the end date (year 8) are compared in Figure 6, showing a very considerable difference between the best treatments (soaking in sodium hydroxide and alkaline sulfite), which more than doubled the probability of survival over storage at ambient RH and over electrolysis

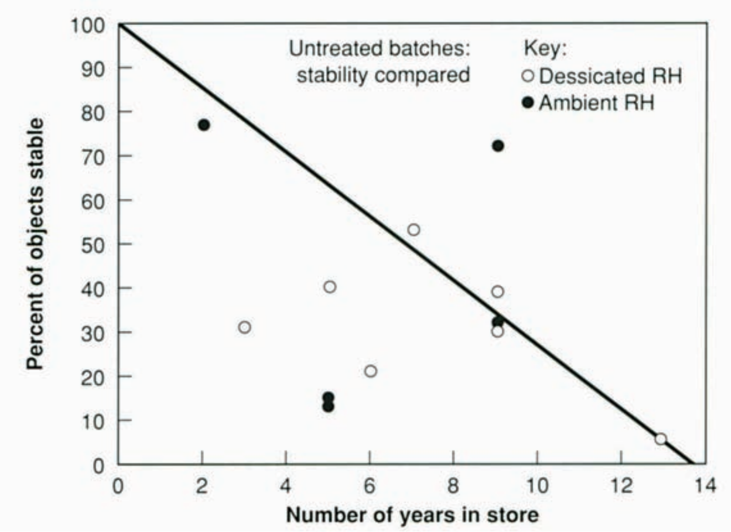

FIGURE 5. *The percentage of stable objects compared for batches of untreated stored objects.*

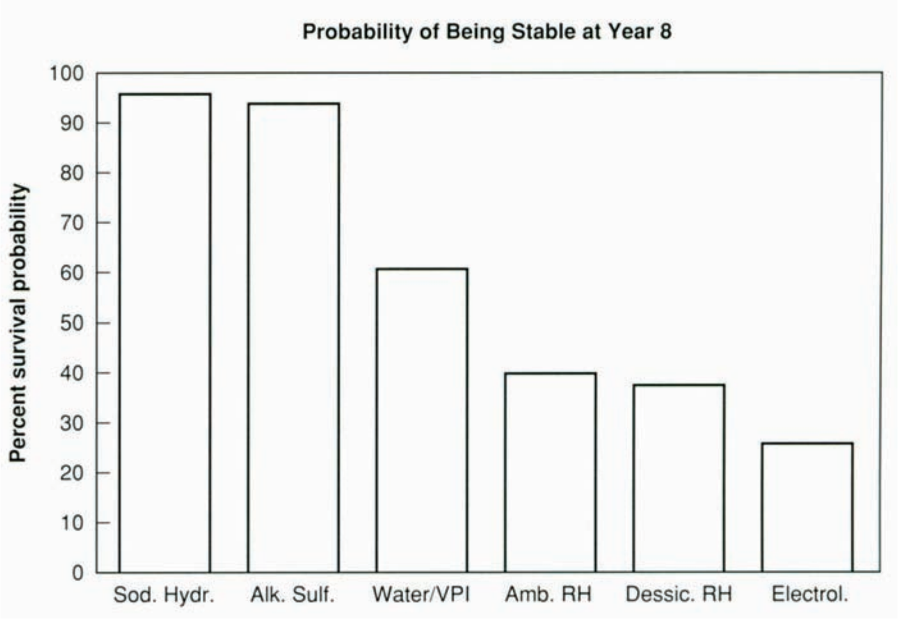

FIGURE 6. *The probability of being stable at year 8: outcome of treatments and storage compared.*

followed by soaking, which in this study gave the worst survival rate of all. Soaking in deionized water with VPI doubled the survival chance over that of untreated iron. The interpretation of these results is discussed later.

But are these differences only apparent? The chi-squared test of significance was applied to a table of numbers of objects, stable and unstable, for the treatment batches compared to the untreated iron (all for the Swan Lane site, to reduce variables). The results were significant at the 0.5% level, and so the null hypothesis can be rejected; there is a real difference between active treatment and storage alone. Further tests of significance (binomial tests) show that electrolysis is significantly worse than the average of the other three treatments, and that water with VPI is probably worse than sodium hydroxide and alkaline sulfate.

The results for the batches that were not treated but stored in different ways are equally interesting. In order to compare results with those for the treated batches, the simple percentages of objects stable at the year of inspection were calculated (Fig. 6). The result for the batch longest in storage (also the largest batch by far), from which the percentage of objects surviving is very small, has been used to plot the line in Figure 6, which gives a notional average. If objects in desiccated storage survived longer than objects stored at ambient RH, then the markers for these batches would be located in the upper right-hand part of Figure 6. But they are, in fact, randomly distributed, as are the markers for batches stored at ambient RH.

Because the batches were assessed at different numbers of years after storage, it was not possible to carry out a chi-squared test of significance for the untreated objects. Other possible tests do exist, but they are complex, and it is likely that the differences would not be statistically significant.

INTERPRETATION

Instability in iron has a number of contributing factors, as Turgoose and others have shown (Turgoose 1982a, 1982b, 1985). Given these factors—the chemical nature of the iron's corrosion, particularly perhaps the chloride content; the physical nature (thickness and impermeability) of the mineral layers; and the relative humidity and oxygen content of the storage environment—it is difficult to evaluate the success of treatments as well as explain the causes of failure.

The nature of the object is one consideration. Watkinson (1983) has shown that if an object is completely mineralized, then it is not likely to recorrode. The Museum of London anaerobic iron does not fall into this category; the objects each have a relatively thin corrosion layer and a metal core. It seems that little of the dry-site iron from the Passmore Edwards Museum is protected by this factor either, but time will show whether, for example, the few remaining objects from the batch longest in storage (thirteen years) will eventually break down.

Iron from the Museum of London was from wet, anaerobic sites. Results for these batches are no different from those for the Passmore Edwards dry-site iron (Tables 1, 4), although the mineral layers on the objects look very different. In this case, the burial context of the objects has not had a strong influence on their survival.

The concentration of chloride ions is another factor. There is a correlation between the amount of chloride ion removed during treatment and the probability of stability, as illustrated in Figure 7. The comparative chloride-extraction rates for the different treatments have been confirmed in measurements made by other conservators at the Museum of London in the course of treating other batches of objects, as well as by Rinuy and Schweizer (1981), and North and Pearson (1975, 1978). In iron conservation, one questions the basis for any assumption, but it is widely assumed that if sufficient chloride can be removed from an archaeological object, then the object will be stable. An empirical test by Rinuy and Schweizer (1981) did indicate that iron does not corrode in the complete absence of chloride, even at elevated relative humidities.

It is quite surprising that sodium hydroxide alone produced such a good result. The treatment was tried as a result of North and Pearson's article discussing its use on marine iron (1978). The ill effects subsequently predicted by Turgoose seem not to have occurred (1985a:14). It was tried because it prevented obvious corrosion and was less disruptive than alkaline sulfite to mineral layers.

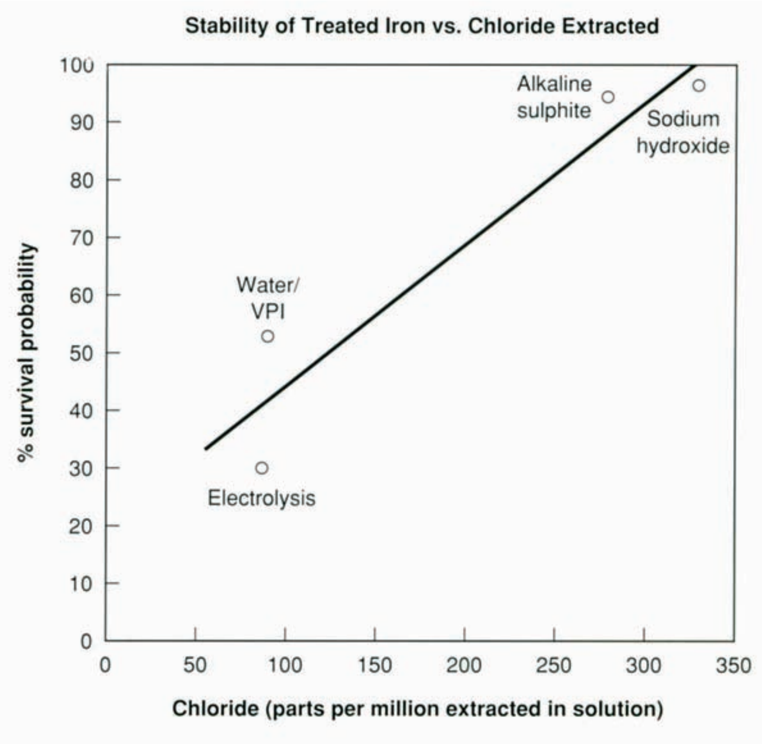

FIGURE 7. *The probability of being stable at year 8 plotted against the amount of chloride extracted during treatment.*

Pretreatment using electrolysis had a markedly adverse effect on the stability of the objects. This procedure was used to make the corrosion layers separate more easily for cleaning delicate, decorated surfaces; and it accomplished this purpose very effectively. It was postulated that electrolysis would make the mineral layers more porous and allow soluble chloride to escape more easily during subsequent soaking. Perhaps this pretreatment also allows oxygen and humidity to penetrate more easily during subsequent storage. If this is the course of its lack of success, then it may be possible to prevent this effect by consolidating the corrosion layers.

The results from this study seem to indicate that the storage environment has much less influence on the stability of iron than had been supposed—a great deal less than do most treatments. There may be an explanation for this. Even if a desiccated environment is maintained, as it was for the Passmore Edwards material, the phenomenon of interstitial condensation may mean that pockets of high humidity are formed in the plentiful pores and cracks in the mineral coatings of the objects (Schreir 1976). Any free water will leach out soluble salts, such as chlorides, and concentrate them in these small areas.

Should it be confirmed that desiccated storage has no real advantage over storage in ambient conditions, this information will have far-reaching consequences for the techniques used to store archaeological iron. Many more samples need to be assessed, however.

CONCLUSIONS

These results reinforce the tentative conclusions from the first study that, in real-time assessments after long periods in storage, active treatment improves the survival chances of iron. Treatment appears to have a much greater effect than does controlled storage at low relative humidity. The most effective treatments are those that remove the greatest quantity of chloride, but this study cannot demonstrate cause and effect here.

Following the first study and the encouraging early results of the second, the Museum of London has continued to treat its archaeological iron, using the procedures outlined in Appendix 2. These include soaking in the corrosion inhibitor triethanolamine, as suggested by Argo (1985:31). This method has not yet been formally assessed, although it has been observed that quite a large amount of chloride is extracted in this way. The museum will revise its standard treatments again to take account of present findings, and and will also consider whether to use sodium hydroxide rather than alkaline sulfite, should it be less disruptive to the mineral layers.

The effects of treatment on the objects' surfaces are also being studied by Dana Goodburn Brown, using the scanning electron microscope to record surface detail before and after treatment. At present, selected objects are being carefully cleaned, and silicone-rubber molds (Dow Corning 9161) are being taken of the surfaces before and after treatment. The four different treatments described in Appendix 2 are being assessed; and, in addition, a treatment is being developed at the Institute of Archaeology at University College, London. The same area of each object will be examined in order to evaluate the effect each treatment has on the surface.

Further work is suggested. Turgoose is currently engaged in a collaborative research project under the European STEP initiative at the University of Manchester Institute of Science and Technology, assessing the corrosion potential of archaeological iron. In parallel with this work, studies based on the real-life assessment of actual objects are clearly useful. Accelerated aging tests in high relative humidity for mineralized iron are likely to introduce other complications arising from the nature of the mineral layers and will not give convincing results. Some of the protocols set out for clinical trials in medicine, described by Mould (1981), might be adopted.

The development of more effective treatments—including less aggressive ones, perhaps not involving chloride removal—should also be encouraged. It is tantalizing to read abstracts of published work on the effects of silicates and corrosion inhibitors (Art and Archaeology Technical Abstracts 27-815, 27-907), and discussions of the use of corrosion inhibitors (Turgoose 1985b). It is encouraging to report that Ahmed al Zaid, at the Institute of Archaeology at University College, London, is researching the use of silane products on iron.

APPENDIX 1. TREATMENT PROCEDURES USED IN THE TRIAL

MECHANICAL REMOVAL

Mineral layers overlying the original surface were first removed using mechanical means: a scalpel or power pen. For ease of comparison of treatments, each batch consisted of iron objects totaling approximately the same weight, and all soak baths contained 1 L of solution. The temperature of all the treatment baths was maintained at 50 °C in a laboratory oven. Sealed polythene boxes, completely filled with liquid, were used to keep oxygenation to a minimum.

ALKALINE SULFITE

For general discussion of this method, see North and Pearson (1975). Only relatively robust objects with no tinning were selected for this treatment, since tin will dissolve in alkaline solutions. The procedure was as follows:

1. Chloride removal: Objects were immersed in four successive baths of 0.5 M alkaline sulfite (Na_2SO_3 + NaOH). The duration of each bath was one week.
2. Removal of alkaline solution: Objects were immersed in changes of deionized water and Dichan VPI until no more chloride could be detected. There were fifteen solution changes. The total time of treatment was twenty weeks.[1]

SODIUM HYDROXIDE

For a discussion of the benefits of using washing solutions at raised pH, and especially sodium hydroxide, see North and Pearson (1978). Only relatively robust objects with no tinning were selected for this treatment, since tin will dissolve in alkaline solutions. The procedure was as follows:

1. Chloride removal: Objects were immersed in five successive baths of 0.5 M sodium hydroxide (NaOH).
2. Removal of alkaline solution: Objects were immersed in changes of deionized water with 0.5% w/v Dichan VPI until no further chloride could be detected. There were thirteen solution changes. The total time of treatment was nineteen weeks.

ELECTROLYSIS FOLLOWED BY DEIONIZED WATER

The procedure was as follows:

1. Corrosion softening: The electrolyte was sodium carbonate. A low density current was passed until the corrosion layers had softened and separated sufficiently for easy removal.
2. Chloride removal: Objects were soaked as a batch in changes of deionized water with 0.5% w/v Dichan VPI until no more chloride could be detected. There were fifteen changes of solution. The total time of treatment was twenty weeks.

DEIONIZED WATER AND VPI SOAKING

The procedure was as follows:

Chloride removal: Objects were soaked in changes of deionized water with 0.5% w/v Dichan VPI until no more chloride could be detected. There were fifteen changes of solution. The total time of treatment was twenty weeks.

DRYING AND PROTECTION

After treatment, objects were dewatered through two changes of industrial methylated spirits and coated with two coats of Incralac lacquer.

APPENDIX 2. DESALINATION TREATMENTS IN CURRENT USE

Desalination treatments for iron currently used as standard at the Museum of London involve a choice of method as follows:

ALKALINE SULFITE

This method of chemical reduction makes corrosion more porous and allows Cl− to diffuse out. It also extracts the most chloride and appears not to damage silver or copper (black deposit on the latter can be scraped off).

Contraindications: Alkaline sulfite dissolves tin, weakens adhesives, and can disintegrate fragile, heavily mineralized objects. It may also damage original surfaces.

SOAKING IN TRIETHANOLAMINE (TEA) SOLUTION

TEA is thought to react with iron oxychlorides, freeing chloride ions. It has the next best chloride extraction rate after alkaline sulfite. TEA is a corrosion inhibitor, so it inhibits flash rusting. It seems not to damage silver or copper (copper may stain) and does not damage fragile objects. It is possibly suitable for organics such as bone.

Contraindications: TEA damages tin. It is less damaging to adhesives than is alkaline sulfite.

SOAKING IN DEIONIZED WATER WITH CORROSION INHIBITOR (DICHAN VPI)

The corrosion inhibitor prevents rusting during the soak; this may enhance chloride removal. It is possible that traces remaining in the object will confer some corrosion protection. Deionized water with VPI does not damage nonferrous metals, adhesives, or leather.

Contraindications: Do not use this method with wood or iron composites, as the VPI soaks into the wood and produces quantities of crystals as it dries.

TANNIC ACID

This is used as a surface coating for "maintenance" of unstable objects.

ACKNOWLEDGMENTS

The author thanks Ruth Waller, the research assistant for this project. Reg Davis, of the Royal Marsden Hospital, kindly drew the author's attention to the use of medical statistics for monitoring survival rates. Clive Orton, the coauthor of the earlier study, has again provided invaluable advice and support with the statistical assessment. The conservators at the Museum of London have encouraged this renewed assessment of treatments, and particular thanks are extended to Rose Johnson and Jill Barnard, who organized a stimulating colloquium on the subject in early 1992.

NOTE

1. North and Pearson recommend neutralizing the sodium sulfite using barium hydroxide. Simply soaking to remove it was judged preferable, since barium hydroxide can leave unsightly white deposits.

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BIOGRAPHY

Suzanne Keene qualified in conservation at the Institute of Archaeology in London. She worked in the Winchester Research Unit on the material from the well-known excavations there. After a period in private practice, she became head of Archaeological Conservation at the Museum of London, then head of the Department of Conservation there. She now works as head of Collections Management at the Science Museum of the National Museum of Science and Industry in London. Her research interests include conservation information and the stabilization of archaeological iron.

Conservation of Corroded Metals: A Study of Ships' Fastenings from the Wreck of HMS *Sirius* (1790)

IAN DONALD MACLEOD

The study of corroded metal objects recovered from historic shipwrecks provides conservators with a unique opportunity to examine the effects of salts, water movement, depth of burial, and the level of dissolved oxygen on the degradation of a wide range of artifacts. Normally, the chronology of shipwrecks is well defined, and this helps quantify the rates of deterioration that occur. Previous work in the Materials Conservation Laboratory of the Western Australian Maritime Museum at Fremantle has concentrated on the identification of corrosion processes and how, by studying the deterioration of these objects, conservators can improve their techniques for stabilizing such artifacts (North 1976:253–58; MacLeod 1987a:25–40).

In the field seasons of 1985, 1987, and 1988, a team of maritime archaeologists led by Graeme Henderson of the Western Australian Museum's Department of Maritime Archaeology recovered a variety of metal artifacts from the wreck of HMS *Sirius*. The wreck is located on a coralline reef off Norfolk Island, which lies at 29.48° south latitude and 167.59° east longitude, about 1,500 km from Sydney and 1,000 km from Auckland, in the south Pacific Ocean. The copper, brass, and bronze objects recovered—including nails, bolts, sheathing, and other fittings (Figs. 1–3)—were all worn and had apparently been used in the construction of the *Sirius*.

FIGURE 1. *Clinch rings from the HMS* Sirius.

FIGURE 2. *Bronze sheathing tacks from the HMS* Sirius.

FIGURE 3. *Brass belt buckles from the HMS* Sirius.

HISTORICAL BACKGROUND

HMS *Sirius* was originally named the *Berwick*. It was built in 1780–81 as a Baltic trading vessel, but in 1781, while the ship was still in dry dock at Christopher Watson's shipyard at Rotherhithe on the Thames in England, it was purchased by the British Admiralty. The Admiralty intended to make the *Berwick* the flagship of the First Fleet, to serve in establishing settlement in the newly founded colony of Australia. Initially, however, the *Berwick* was fitted out as an armed storeship for service to North America and the West Indies. After being coppered in early 1782, it sailed for Nova Scotia and New York. In 1783 the *Berwick* returned to England, where it was docked for repairs before sailing to the West Indies. Finally, in 1786, after undergoing a comprehensive refit, the ship was renamed HMS *Sirius* and set sail on its First Fleet voyage to Australia.

The *Sirius* was wrecked at Kingston on Norfolk Island at noon on March 19, 1790 (Fig. 4). Due to a change in wind direction, the ship was driven against a reef while unloading cargo and passengers. Other ships that went down in the rough surf off Norfolk Island include the *Mary Hamilton*, sunk to the west of the *Sirius's* principal stranding site in 1873; and the *Renaki,* a three-masted auxiliary schooner thrown up on the reef in 1943. The site of the *Rapid*, which sank in 1811 near the Northwest Cape, western Australia, is more sheltered than that of the *Sirius*, and objects recovered from the former were used for corrosion comparisons. The *Mary Hamilton* went down west of the principal stranding site of the *Sirius*, causing some contamination of a portion of the site, although testing results reveal differences between the artifacts of the two vessels. The *Renaki* was wrecked in an area so distinct from that of the *Sirius* that site contamination did not pose a problem; the few remains of the schooner that were not salvaged are clearly identifiable.

Because of where the *Sirius* was stranded, most of the ship's supplies were salvaged in 1790, and the bulk of the shipwreck remained intact for almost two years thereafter. This fact clearly attests to the skill and strength of the ship's construction, considering the area's rough-breaking seas. To this day, large ships cannot tie up at wharf on the island because of the treacherous waters, and all cargo must be unloaded in deeper water and brought ashore with small boats.

The artifacts from HMS *Sirius* are scattered around the main site, which is located some 70 m offshore. The undersea terrain in this area is a very gently sloping plane of hard calcareous rock in water varying in depth from 1.5 to 4.5 m. The wreck site itself consists of flat beds of overlying coralline reef materials with a series of gullies and depressions in the seafloor. The configuration of the island and the particular location of the wreck site means that submerged objects are subjected to the effects of continuously breaking surf. During a storm, the wave action is sufficient to shift a 1.5 ton concrete plinth 30 m across the seabed. The ship's submerged remains primarily consist of about two hundred concreted cast-iron ballast blocks, a few

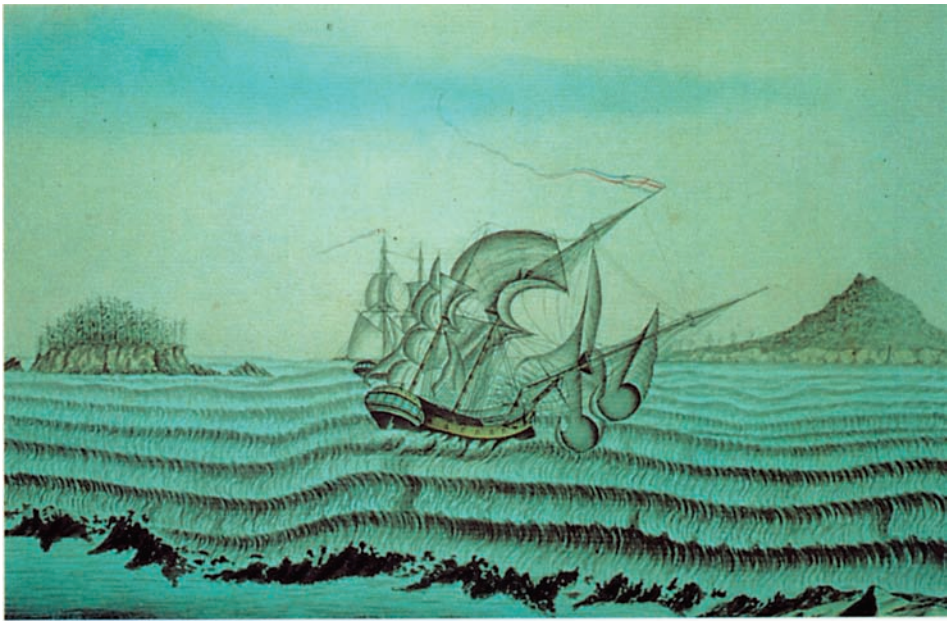

FIGURE 4. *"The Melancholy Loss of His Majesty's Ship Sirius, wrecked on Norfolk Island, on Friday Noon March 19th 1789 taken from the Flag Staff on the Beach." Watercolor by George Raper, 1790.*

anchors, and one remaining carronade. Smaller artifacts are either trapped within the coralline corrosion matrices or under the ballast. The warm seawater (20.80 ± 1.96 °C), a mean annual salinity of 35.77 ± 0.04 ppt, and dissolved-oxygen levels of 7.7 ± 0.3 ppm constitute a highly corrosive environment for these objects.

Analysis of the corrosion properties and materials performance of the various alloys of the recovered artifacts was undertaken for two purposes, one of history and one of materials science. The primary historical purpose was to establish the quality of the materials used in the construction of the *Sirius;* several accounts indicate that it was poorly built, whereas the archaeological evidence supports the contrary. The second purpose of this research was to learn how a very aggressive shipwreck site degrades different materials, and what conservation problems this presents to the conservator (MacLeod 1989b:227–29).

Experimental Method

Eight samples of copper sheathing, a brass bolt, and bronze sheathing nails were examined metallographically and electrochemically after they had been sectioned and embedded in Araldite D (Ciba-Geigy's two-part epoxy resin, which is cured with an amine catalyst). Surfaces were prepared by grinding with wet and dry carborundum paper to 1,200 grit and polishing with diamond paste to 0.25 µm; the etchant was 2 wt % ferric chloride in ethanol. Some objects were sectioned in several places with a number of longitudinal sections (LS) and transverse sections (TS) representing the tail (shank), body, and head regions of the fittings.

Drilled core samples (360 ± 100 mg) were analyzed at a commercial laboratory (ANALABS) using atomic absorption techniques. Core samples were taken in an attempt to overcome the problems associated with analysis of archaeological metals (Caley 1964:1–15). Results are listed in Table 1.

TABLE 1. *Composition of ships' fastenings and sheathing from HMS* Sirius *(1790).*

Type	*Copper sheathing*	*Copper sheathing*	*Copper sheathing*	*Brass bolt*	*Sheathing tack*	*Clinch ring*	*Eroded tack*	*Sheathing nail*
Sample	*SI 357*	*SI 465A*	*SI 491*	*SI 15*	*SI 465*	*SI 254*	*SI 228A*	*SI 228B*
Cu	99.4%	99.4%	98.9%	67.7%	91.1%	99.1%	91.4%	90.0%
Sn	25.6	15.3	75.9	402	7.69%	1010	8.16%	8.00%
Pb	1750	1710	99	6670	520	1000	2720	4680
Zn	48	16	28	31.5%	108	120	257	7680
As	2410	2550	8260	460	6390	4380	<200	<200
Sb	300	302	185	92.7	216	183	52.9	49.3
Bi	500	525	1130	173	2240	935	265	1020
Ag	177	665	49	161	680	394	400	530
Ni	190	185	350	275	850	300	180	185
Fe	44	76	104	370	170	220	460	5130

Copper values are calculated by difference. Results are in ppm unless otherwise stated. Due to the small size of some samples it was not possible to accurately determine the amount of arsenic. The symbol < denotes values less than the detection limit.

Vickers microhardness measurements on the polished sections were made using a Tukon model 300 operating on a 600 g load with a x20 objective. All the sections were examined under the scanning electron microscope (SEM) at the Commonwealth Scientific and Industrial Research Organisation's Division of Mineralogy, using the back-scattered electron/low-vacuum mode before and after the corrosion experiments. Semiquantitative elemental analyses were made using energy dispersive analysis by X rays (EDAX) attached to the JEOL scanning electron microscope (JSM2) after calibrating the instrument with standard bronze, brass, and copper alloys (Robinson and Nickel 1979:1322–28).

Electrical connections were soldered to the metal sections prior to encapsulation in resin. The corrosion potentials were measured using a Titron silver-silver chloride reference electrode (saturated with KCl), which was calibrated against a platinum electrode in a quinhydrone solution at pH 4.0. (Voltages are all relative to the Ag/AgCl unless otherwise stated.) The seawater temperature in the laboratory studies was 24 ± 1 °C. Dissolved-oxygen measurements were taken using an Imperial Chemical Industries (ICI) oxygen meter (411) after correction for the salinity of the seawater (35.67 ppt). The seawater was filtered after collection from the ocean, but no preservatives were added. The current voltage curves for polarization-resistance measurements were recorded using a Princeton Applied Research (PAR) potentiostat with a platinum auxiliary electrode and an XY recorder; the data were collected over a range of ± 25 mV around the corrosion potential (E_{corr}) with the voltage scanned at ± 1 mV per second. The effects of dissolved oxygen and stirring on E_{corr} were determined using a combination of E_{corr} and polarization measurements. Tafel slopes were determined on the same samples used in the polarization studies. The measurements were made in a specially designed polarographic cell that allowed side mounting of the metal sections.

Corrosion Potentials and Polarization Resistance

When copper and its alloys are immersed in oxygenated seawater, they will corrode at a rate that is dependent on their chemical composition and microstructure and on the amount of dissolved oxygen in the water (Gilbert 1982:47–53; Bjorndahl and Nobe 1984:82–87). In aerated solutions, the E_{corr} is the voltage of a corrosion cell consisting of the anodic (oxidation of metal) and cathodic (oxygen reduction) half-cells. The way in which the corrosion rate changes with the voltage of a corrosion cell is very complex, but it can be simplified in two extreme sets of conditions. At voltages close to the corrosion potential, the metal obeys Ohm's law, since there is a direct relationship between the voltage and the current, according to the formula $E = iR$, where E is the voltage, i is the current, and R is the resistance. In other words, there is a linear relationship between ohmic resistance and the voltage. At applied voltages several hundred millivolts removed from the E_{corr}, the increase in corrosion rate with applied voltage has a logarithmic rather than a linear response. The characteristic slope is called the Tafel slope. Corrosion in the Tafel region is often characterized by the presence of a passivating film on the surface of the metal.

The corrosion rate (current) at the E_{corr} can be calculated from the rate at which the current varies with small variations in the potential. For voltages within 30 mV of the E_{corr}, the polarization resistance (R_p) is calculated from the slope of the current voltage plot via the expression:

$$\left(\frac{\delta E}{\delta i}\right)_{\delta E \to O} = R_p$$

The corrosion rate (current) is inversely related to the polarization resistance by the expression:

$$R_p = B/i_{corr}$$

The constant B can be calculated via Faraday's laws relating to weight-loss data, or it can be determined from analysis of electrochemical polarization data. In physical terms, the value of B can be obtained from the Stern-Geary (1957) relationship,

$$B = \frac{b_a \cdot b_c}{2.303\,(b_a + b_c)}$$

where b_a and b_c are the anodic and cathodic decadic Tafel slopes, as described above. The values of B depend on the composition of the objects and the types of corrosion products on the surfaces.

The Tafel slopes of the various fittings tested fell into two groups, one of which had characteristic b*c* values of 52 ± 5 mV, while the other had values of 39 ± 2 mV. The former is typical of cathodic Tafel slope values for concreted bronzes, and the latter is characteristic of machined samples. The individually calculated values of B were used to determine the corrosion currents, shown in Table 2, using the above relationships. The anodic Tafel slope (b_a) of the samples varied from 42 to 85 mV. These calculated corrosion currents are based on measurements of R_p after twenty-one days of exposure of the samples to seawater. As such, they are approximately one order of magnitude too high for the bronzes and should be regarded as initial

TABLE 2. *Corrosion rates of copper alloys from the wreck of HMS* Sirius.

Registration	*Type*	*Corrosion current* *μA cm^{-2}*	*n*[*]
SI 465	Bronze tack	3.3 ± 0.3	1.04
SI 228A–1	Bronze tack	3.6 ± 0.6	1.05
SI 228A–2	Bronze tack	8.7 ± 1.1	1.05
SI 357	Copper sheathing	2.0 ± 0.4	1.00
SI 254	Copper ring	4.3 ± 0.1	1.00
SI 15	Brass bolt	19.2 ± 4.1	1.31
SI 228B–3	Bronze tack	9.2 ± 0.2	1.05
SI 228B–1	Bronze tack	10.8 ± 0.6	1.07
SI 228B–4	Bronze tack	13.0 ± 0.6	1.08
SI 228B–2	Bronze tack	16.6 ± 1.4	1.10

[*] *n* is the number of electrons in the rate-determining step.

corrosion rates rather than average long-term values (Taylor and MacLeod 1985:100–4). In contrast, the copper corrosion currents fall within the normal range of long-term corrosion rates (Lush and Carr 1979:1079–88).

Results and Discussion: Corrosion Potentials

The sectioned copper alloys were immersed in fresh seawater (pH 8.18), and the corrosion potential was monitored for a period of three weeks. All the samples showed significant changes in the corrosion potential as the polished surfaces reacted with the seawater during the first ten days. The bronze sheathing tack (228B) shifted by more than 200 mV, whereas the copper sheathing samples and the clinch ring showed anodic shifts of only 20 mV over the same period. During the monitoring of E_{corr}, the level of dissolved-oxygen seawater was varied to see how sensitive the metals were, since the microenvironment at the site may be significantly different from the macroenvironment, which is fully oxygenated. The solutions were saturated with pure oxygen (14 ppm) or with air (8.2 ppm) or degassed with instrument-grade nitrogen to give a reading of 0 ppm. Three distinct types of response were observed. The E_{corr} of the sections of the bronze sheathing tack moved anodically by 9.0 ± 0.4 mV/ppm, and the brass bolt moved by 4.8 mV/ppm O_2, while all the copper fittings and the copper sheathing tacks (465 and 228A) moved by 2.4 ± 0.5 mV/ppm O_2. The latter samples also showed no increase in corrosion potential above the air-saturated, dissolved-oxygen level. These results indicate that, above this concentration of oxygen, the rate of corrosion is controlled by the anodic oxidation of copper metal. For the copper samples, the anodic shift of 24 mV per tenfold increase in oxygen concentration corresponds closely to the theoretical response of the oxygen half-cell of 29 mV. The corresponding values for the brass and bronze fittings are much higher than the theory would suggest, but they are consistent with the observations of others who saw shifts as great as 160 mV per decade for pure tin (Butler et al. 1969: 715–38). The ratios of the E_{corr} sensitivity of the alloys to oxygen are 4:2:1 for the bronze, brass, and copper fittings, respectively. These ratios are the same as the number of electrons commonly involved in the oxidation of tin, zinc, and copper.

Although the wet-chemical analyses listed in Table 1 show the overall composition of the alloys, it is readily apparent from the SEM EDAX analysis of the corroded surfaces that wide variations exist between the composition of the surface layers and the inner sections of some of the cast-bronze sheathing tacks. Apart from the brass bolt (SI 15), all the other materials from the *Sirius* site showed a similar dependence of E_{corr} and the size of the voltage shift when the seawater was deoxygenated. The response of the fittings to the change in levels of dissolved oxygen is given by the relationship:

$$\overset{O_2}{E_{corr}} = 0.236 \cdot \overset{N_2}{E_{corr}} - 99\ \text{mV}$$

The apparently anomalous behavior of the brass bolt is not really surprising, since it came from a part of the wreck site that had been contaminated with material from another ship. Inspection of the analysis in Table 1 shows that this anomalous bolt has a composition essentially identical to a modern, yellow, low-leaded brass (Miner and Seastone 1955:2–325). When compared with artifacts recovered from vessels of similar age to the *Sirius*, the low level of impurities in this fitting adds further weight to the conclusion that the bolt did not originate from the flagship of the First Fleet (MacLeod 1987b:280–91). The bolt most probably comes from the wreck of the *Mary Hamilton* (1873).

Composition and Corrosion Rates

Bronzes

Several fittings were sectioned in sequentially to gain an understanding of how differences in microstructure and composition affect the rate at which different parts of the same object corrode. It has always been a major problem in stabilizing corroded artifacts to reliably determine what sort of variation is possible within one object. Results from the corrosion of the square-headed bronze sheathing nail (228B) illustrate the point. The corrosion current increases linearly with increases in the surface concentration of tin (Fig. 5), according to the equation:

$$i_{\text{corr}} = 0.886x + 1.44$$

where x is the wt % tin in the sample and the corrosion current is expressed in $\mu\text{A/cm}^2$. The effect of the increased tin concentration is also seen in the corrosion potentials of the fastenings in oxygenated seawater: the lower the tin content, the more negative the E_{corr}, and the lower the corrosion rate.

It should be noted that the corrosion data above relate to the fully oxygenated site of HMS *Sirius*. The sensitivity of the bronzes to dissolved oxygen has previously been noted (MacLeod 1985:10–13). A difference appears to exist between these studies of the *Sirius* fittings and the data from studies of long-term corrosion of artifacts

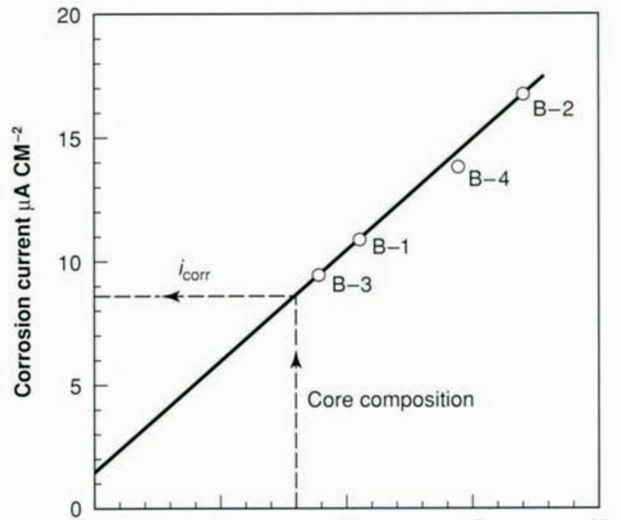

FIGURE 5. *Diagram showing the effect of tin on the corrosion rate of a bronze sheathing tack (SI 228B).*

recovered from other less aggressive sites. Interestingly, the corrosion of archaeological bronzes on land sites is similar to that of bronze objects found in marine sites with a low level of oxygenation.

From the SEM EDAX analysis of the surfaces of the corroded sections of the 228B bronze sheathing tack, it is clear that significant amounts of antimony are present in the tin-rich phases despite the total content amounting to only 0.00493 wt %. Tin and antimony readily form intermetallic compounds that are less reactive than the parent, tin-rich areas (North and MacLeod 1987:90–91). Increased amounts of antimony in the ($\alpha + \delta$) phase of the bronze effectively promote interdendritic corrosion of the sections that have higher tin concentrations, as seen in Figure 6. In addition, increased amounts of antimony in the bronze fittings decrease the sensitivity of the corrosion potentials to changes in the value of E_{corr} when the seawater is deoxygenated. These observations confirm the theory that very small amounts of impurities, such as antimony, can have a major effect on corrosion performance.

The sensitivity of bronzes to impurities such as iron can be seen by comparing the corrosion currents, shown in Table 2, for the SI 228A and SI 228B sheathing tacks. Inspection of the analytical data in Table 1 shows that 228B has eleven times as much iron as 228A. The effect of this greater concentration of iron is seen in a doubling of the mean corrosion rate of SI 228B compared with SI 228A, which otherwise has a very similar composition. For the sections of SI 228B that corroded the fastest, SEM analysis showed that significant amounts of iron were found in the corroded, tin-rich surfaces.

The variability of the corrosion rates in the bronze fittings is also seen in the microhardness measurements, which show a direct dependence on the composition of the alloys. The bronze sheathing tack (SI 465) showed a linear dependence of microhardness on the amount of tin over the range of 4–10 wt % according to the following relationship:

$$\mathrm{HV}_{465} = 41.3 + 10.2x$$

where x is the amount of tin at the point of measurement. The maximum value of 145 is essentially the same as that measured by Samuels (1983) on an identical bronze tack from the *Sirius*. Apart from localized hardness, possibly due to so-called tin sweat and coring segregation, the other cause of the decrease in microhardness from the heads of the nails to the tips is that the nails had all been hammered in use; in other words, the fittings had not been cargo but part of the vessel, and thus they had been work-hardened.

Copper

Corrosion performance of the copper hull fastenings and the copper sheathing was an essential factor in ensuring that the *Sirius* remained a seaworthy vessel. Physical examination of two samples of copper sheathing, SI 357 and SI 491, indicates that they are similar, whereas another sample, SI 465A, is much thicker and appears to be tougher. Analysis of the samples shows that the chemical composition of SI 357 and

SI 465A is identical and that the apparently similar material clearly has a different composition from that of the other samples, the latter sheathing being typical of most of the recovered materials.

The main impurities in the copper sheathing are arsenic and lead. One major effect of arsenic in copper is that it causes an increase in the microhardness of the metal during cold-working. Using the average values for each of the sheathing samples and the clinch ring, the following relationship between microhardness and the amount of arsenic was established:

$$HV_{Cu} = 26y + 74$$

where y is the wt % of arsenic in the material. It should be noted that the maximum amount of arsenic in these alloys is 0.826%, which is at the lower end of the range for ancient alloys (Scott, personal communication, 1991).

Since the maximum amount of arsenic occurs in the bulk-sheathing material, it is reasonable to assume that the vessel was covered with good-quality copper sheathing. The thicker sheathing (465A) showed negligible signs of intergranular corrosion and had been extensively worked, as indicated by the presence of annealing twins and the oblate Cu_2O inclusions (approximately 30 µm across). The grain size ranged from 50 to 60 µm. Erosion appears to have been the main corrosion mechanism for this material, which was subjected to the most turbulent waters of the wreck site. Localized current flow during the descent of a typical 4 m wave breaking on the site at a water depth of 3 m produces a velocity of 12 ms^{-1} at an angle somewhat steeper than 45° (Cresswell 1989:46–70). Such flow rates are typical when erosion is an important factor in the rate of copper degradation (Lush and Carr 1979:1079–88).

The copper clinch ring (SI 254) shows twice the corrosion rate of the copper sheathing (SI 357), as listed in Table 2. The reason for this is readily apparent from the differences in their microstructures. The sheathing has a very fine recrystallized structure as a result of extensive working, with typical grain sizes of 35–45 µm. Apparently, the large amount of nonmetallic inclusions does not have a deleterious affect on corrosion performance. In contrast, the clinch ring displays severe intergranular corrosion. The small amounts of tin and lead, approximately 0.1 wt %, were apparently concentrated at the grain boundaries and promoted intergranular corrosion (Fig. 7). The iron impurities were also concentrated at the grain boundaries and also appear to be involved in the increased corrosion rate. The normally beneficial effect of arsenic as an inhibitor of intergranular corrosion may have been lost by the even distribution of the arsenic in solid solution.

The surface hardness of the clinch ring was 107 HV, but this rapidly falls to a typical annealed value of 56 ± 12 HV within 1.3 mm of the surface. The mechanical stress of the working of the surface probably increases the corrosion rate (MacLeod and Pennec 1990:732–38). The composition of the clinch ring is the same as the large copper bolt examined by Samuels (1983) and was probably made from the same batch of metal produced by the Swansea copper refinery. The properties of the different alloys provide evidence for the two periods of construction of the vessel, which confirms other archaeological evidence. The two distinct batches of copper sheathing reported in Table 1 probably relate to the ship's initial fitting out (SI 491)

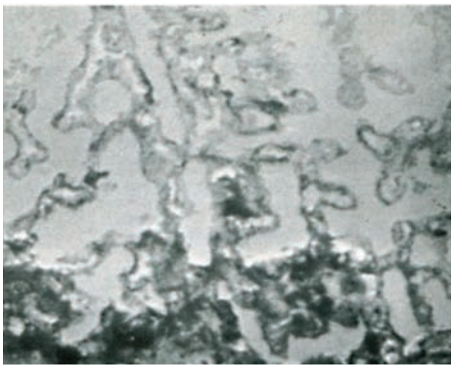

FIGURE 6. *A scanning electron micrograph of the interdendritic corrosion at the seaward edge of an eroded bronze sheathing tack (SI 228A). Full width of the image is 306 µm.*

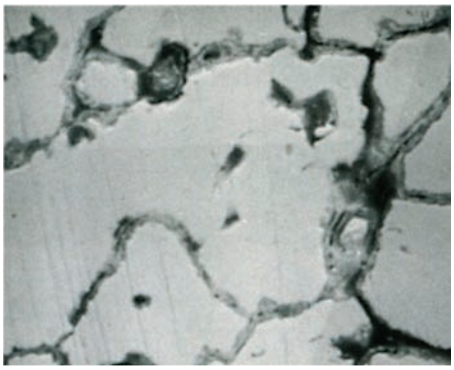

FIGURE 7. *A scanning electron micrograph of the intergranular corrosion on a copper clinch ring (SI 254). Full width of the image is 306 µm.*

in 1781 and to its subsequent refurbishing (SI 357 and SI 465A) in 1786 (Henderson and Stanbury 1988:36–53).

Brass

Although the brass bolt (SI 15) comes from a different shipwreck, some of the corrosion properties of this important class of copper alloy are worth noting. The microstructure of the bolt indicates that it was either hot-worked or cold-worked and then annealed. Extensive intergranular corrosion is present, with preferential corrosion of the zinc-rich beta phase at the grain boundaries. Microhardness measurements of the head of the bolt show work-hardening of the outer surface to yield maximum values of 149 HV, which fall to 105 ± 13 HV within 2 mm of the surface. The shank is fairly uniform in section with an average value of 80 ± 12 HV. SEM micrographs of the surfaces reveal an uneven distribution of lead in the structure of the alloy. The high corrosion current of 19.2 ± 4.1 µA in the fully oxygenated environment reflects a maximum corrosion rate; if the material had continued to corrode at that rate, it would have ceased to exist in the form in which it was recovered. The extent of corrosion is consistent with a longer-term passivation of the corrosion process.

Conservation of the Metals

Having established the corrosion mechanisms for the various fittings from the shipwreck of HMS *Sirius,* one must look at the practical consequences of these observations. The largest difference in corrosion is found in iron artifacts, since they are inherently more reactive than copper and its alloys. A cast-iron carronade from the *Sirius* site, for example, released a total of 26.09 kg (5.36 wt %) of chloride ions during conservation treatment. In comparison, a cannon of similar weight from the more sheltered site of the *Rapid* (1811) released a total of only 4 kg (1.12 wt %) of chloride ions during the same period (MacLeod 1989a:7–16). When the amount of corrosion on the more sheltered site is normalized to account for the shorter period of immersion, the chloride content only increases to 4.6 kg (1.29 wt %). Even after this correction, results show the cannon from the *Sirius* to be four times more corroded than the similar object from the *Rapid* site.

Likewise, the copper, brass, and bronze alloys recovered from the *Sirius* wreck site show higher chloride contents than similar materials from a number of wreck sites off the Western Australian coast. Conservation treatment of the bulk of the copper sheathing on Norfolk Island involved the extended washing for two years in a series of 2.5 wt % sodium sesquicarbonate solutions. During this time, the wash solutions were analyzed for chloride ions; the total amount released was 0.07 wt % chloride, which is almost three times the average amount extracted from other wreck sites. The effect on brass and bronze artifacts was even more marked; the average amount of chloride removed under similar conditions was 0.52 wt %, a factor of more than eight times that of average sites (MacLeod 1987c:1079–85).

Measurements of the corrosion potential of artifacts on the site prior to recovery can now be used as a guide to the level of conservation that is probably needed. The in situ E_{corr} value of a copper bolt from the gun carriage of the remaining carronade was −121 mV. This voltage (an inherent indicator of the corrosion rate) is the same as the laboratory measurement of the clinch ring in oxygen-saturated seawater. The consistency of these results may indicate that similar corrosion problems will be found among other artifacts from the *Sirius*. Further studies are needed to confirm the reliability of such indicators.

CONCLUSION

A study of the corrosion characteristics of a series of copper, brass, and bronze fittings from the wreck of HMS *Sirius* shows that bronzes are very sensitive to the amount of dissolved oxygen in seawater. The electrochemical data reveal how differences in the distribution of alloy elements in the same object can lead to major variations in the materials performance of that artifact. The sensitivity of bronzes to the amount of dissolved oxygen indicates that artifacts recovered from low-oxygen microenvironments, such as those found under the concretions associated with iron objects, should be very well preserved without the need of direct galvanic protection. There is, however, a limited range of conditions that provide low-oxygen microenvironments without stimulating the activity of anaerobic bacteria. In addition, copper alloys recovered from sites with a high level of microbiological activity can be extensively corroded as a result of the high concentration of sulfides.

Minor amounts of impurities, such as antimony and iron, have a major influence on the corrosion mechanism of archaeological bronzes. Differences in performance of copper fastenings and sheathing can be rationalized in terms of the influence of arsenic and the metallurgical microstructure. The turbulent and highly oxygenated nature of the HMS *Sirius* wreck site has a direct influence on the extent of corrosion of the artifacts found there. In light of these findings, the conservator should be alert to the special care that is needed to treat such materials.

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BIOGRAPHY

Ian Donald MacLeod received his doctorate from the University of Melbourne, where he studied the electrochemistry of metal fluorides dissolved in anhydrous hydrogen fluoride. During a two-year fellowship at the University of Glasgow, he studied organometallic chemistry. He spent three years at Murdoch University in Perth, where he concentrated on copper chemistry in association with mineral processing. For the past thirteen years, Dr. MacLeod has worked in the Materials Conservation Laboratory of the Western Australian Maritime Museum at Fremantle and is currently head of the Department of Materials Conservation. His research has focused on the problems of conservation and corrosion of metals recovered from historic shipwrecks. He has learned to scuba dive and perform in situ conservation experiments on iron artifacts on the seabed. In addition to his work with shipwrecks, he has an active research interest in the conservation of aboriginal rock art.

The Conservation of Outdoor Zinc Sculpture

CAROL A. GRISSOM

Zinc sculpture of the nineteenth century was principally an imitative art form and, probably for this reason, little has been written about its history. In Europe a few monumental zinc sculptures were widely discussed; these include the *Amazon on Horseback Attacked by a Tiger* by August Kiss and a statue of Queen Victoria cast by Paillard, which were prominently displayed in 1851 at the Crystal Palace Exhibition in London (*The Crystal Palace Exhibition Illustrated Catalogue* [1851]1970:xvii, 37; Tomlinson 1852:vol. 1, xcvi; vol. 2, 1047). In America, a few monumental pieces were made by known sculptors. For example, the Bohemian-born Caspar Buberl, best known for the terra-cotta frieze on the Pension Building in Washington, D.C., was commissioned to make the grouping *Columbia Protecting Science and Industry* (1880), which decorates the north entrance to the Arts and Industries Building of the Smithsonian Institution. Commissioned sculptures were the exception, however, and by far the majority of zinc sculptures were modeled by anonymous artists.

While the influential architect Karl Friedrich Schinkel did promote zinc for architectural use, citing its use for a cornice during restoration at “our university” in Berlin (*The Builder* 1849; Snodin 1991); this occurred relatively early, when the use of zinc for artistic purposes was still a novelty. Most sculptors seem to have held zinc in low esteem, including the prominent American sculptors John Quincy Adams Ward and Daniel Chester French, who rejected the use of zinc for sculpture (Shapiro 1985:79–80). Although in his youth Lorado Taft made models for a zinc company,[1] he does not mention zinc sculpture even once in his chronicle of American sculpture first published in 1903 (Taft [1903, 1924] 1969), nor is zinc sculpture mentioned in the most comprehensive present-day book on American sculpture (Craven 1968).

Written information is limited principally to accounts of nineteenth-century industrial expositions and ephemera such as advertising pamphlets and the trade catalogues through which most sculptures were sold. One exceptional book, bearing the unlikely title of *Artists in Wood*, discusses early American zinc foundries and models (Fried 1970). Jacques de Caso's discussion of nineteenth-century serial sculpture in France also has much pertinence to zinc sculpture in America (1975).

In the summer of 1978, when Phoebe Dent Weil and the author saw the parts of a disassembled monument that had been identified as being made of White Bronze, it was not known for certain that the material was zinc because the use of zinc for sculpture was unfamiliar at the time. However, the Fourth Ohio Infantry Monument at Gettysburg National Military Park, Pennsylvania, had been leaning dangerously prior to disassembly, and the Center for Archaeometry received a small contract to examine the monument and recommend treatment. Preliminary research quickly revealed that the conservation literature contained no information on the subject. A National Museum Act Grant was obtained which allowed in-depth study of written information, and coincident requests for the treatment of a range of zinc sculptures provided experience in treatment (Grissom 1982). Since then, a number of conservators have studied and treated zinc sculptures, and now a small body of literature on the subject can be found (Gayle et al. 1980; Keck et al. 1983; Nosek 1987; Scott 1987; Weil 1987; Klingelhofer 1990; Wypiski 1990).

Several reasons may be proposed for this recent interest in zinc sculpture. In the past, zinc sculptures were likely to have been repaired by local metalworkers or concerned citizens; many are located in small towns where knowledge about conservation would have been minimal (Knapp 1980). Awareness of the deterioration of outdoor sculpture of all kinds has increased dramatically during the last twenty years, however, and now a number of outdoor-sculpture conservators work throughout the country. Perhaps because taste has changed or because zinc sculptures now qualify as antiques, these sculptures have increased in value, warranting the expense of professional care. Recently a pair of zinc Newfoundland dogs was sold for $18,500 at the Winter Antiques Show in New York (Reif 1987). Finally, the likelihood of damage has increased because zinc artwork has been weakened by a century outdoors. A sculpture such as the larger-than-twice-life-sized *Goddess of Liberty* (1888), which crowned the Texas State Capitol until 1985, cannot be ignored when its security becomes questionable (Weil 1987:168).

While the following discussion is intended to summarize all aspects of the conservation of zinc sculpture, an effort has been made to present material that has not been previously published. In particular, the emphasis is on American material.

HISTORY

Zinc sculpture was popular from about 1850 to the beginning of the twentieth century, although a reference to a zinc sculpture made as early as 1826 has been found (Servant 1880:7). The use of zinc for sculpture began after large-scale refinement of zinc in the West made the metal available at relatively low prices.[2] The invention of electroplating (1838) and the introduction of slush casting (1845) contributed to the use of zinc, particularly in France, because it allowed inexpensive reproductions to be made that looked like bronze but cost about one-sixth to one-eighth the amount (Tomlinson 1852, vol.1:xcvi). Later, the introduction of stamping allowed for even less expensive items to be made. A stamped zinc soldier cost $300 in 1891, while the same-sized sand-cast statue cost $450 (Mullins 1891; Monumental Bronze Company 1882).[3]

Zinc was used to depict a variety of sculptural subjects, and the sculptures themselves were displayed in a range of situations. Zinc copies of antique sculptures and works by contemporary masters such as Canova, Carrier-Belleuse, and Carpeaux were available on both sides of the Atlantic (Mott 1875; Poiré 1880:624). However, while small-scale copies of such sculptures were made in large quantities in Paris for domestic display, they do not seem to have been much produced in the United States.

Many zinc sculptures were publicly displayed. In Europe they were used to decorate the Cathedral in Helsinki, Finland; the Royal Opera House in Berlin; and a post office in Hanover, Germany (Deveranne 1845, 1847; *Scientific American* 1882). During this period in the United States, the rapid growth of cities created a demand for sculpture, and zinc sculptures were purchased throughout the country to decorate new county courthouses, parks, and cemeteries. Statues of Justice, fountains, and Civil War memorials were typical. The Civil War memorials, together with tombstones produced by the same companies, are probably the most numerous zinc items in the United States, and they are largely an American phenomenon.

Another type of zinc sculpture that seems peculiar to the United States is the show figure. Often used for advertising, show figures were frequently humorous. For example, a sculpture of a baby elephant that had been born to the Barnum, Bailey and Hutchinson Circus was available holding either a clock or cigars in its trunk. It was to be used as a sign for a watchmaker or tobacco shop, or as a fountain with water spewing from its trunk (Monumental Bronze Company 1882). A rotund King Gambrinus, now exhibited at the Arts and Industries Building of the Smithsonian Institution, was once mounted on the American Brewery in Baltimore, Maryland, as its symbol. A Rampant Colt decorated the dome of the Colt gun factory in Hartford, Connecticut, and two statues of Puck, the symbol of *Puck Magazine*, still decorate the Puck Building in New York City. Sculptures of stereotypical American Indians, originally introduced as substitutes for wooden cigar-store Indians, were popular items for parks and municipalities (Fried 1970; Knapp 1980).

In addition, a variety of utilitarian materials and objects, including architectural decoration, roofing, weather vanes, toys, coins, and household items such as buckets, were made with zinc.

Surface Treatment

The surfaces of zinc sculpture were invariably treated to imitate other materials, including bronze, gold, marble, brownstone, granite, polychromed wood, and plaster. Surface appearance was of primary importance to the original owners of these sculptures; hence, it remains a principal concern today. The introduction to an American zinc catalogue of the period contains a description of surface treatment that is worth quoting at length because it is both explicit and rare (Mott 1875).

> All the Statuary represented in this Catalogue is cast in Zinc, which is superior to Iron for this purpose from the fact that it can be cast in pieces, and when carefully fitted by skilled workmen, retains nearly all the delicate finish and beauty of line to be found in the original. It is also more enduring, as it cannot be affected by the weather like stone or marble; and again, should any part of the figure by accident be broken, it can easily, and at a mere nominal expense, be repaired; whereas, with Iron or Marble such damage is irreparable.
>
> Although the figures can be painted or bronzed in any style to suit the taste of the purchaser, we however, take this opportunity of giving our opinion as to the style and manner of painting or bronzing, which we think most suitable for the various figures.
>
> Animals, such as Game Dogs, Deer, &c. may be painted to imitate their natural color with very good effect. Mythological subjects, such as the Sphinx, Griffins, Dragons, large Dogs such as the Antique and St. Bernard, also Lions and Horses, should either be painted a stone color, or bronzed; large emblematic figures such as Industry, Justice, Commerce, and other figures used chiefly for buildings, look well bronzed, but can be painted white, or sanded in imitation of brown stone, whichever is more suitable for the building on which they may be placed.
>
> Our Figures, representing the best works of art, ancient and modern, can either be bronzed or painted white to suit the taste of the purchaser. Such figures as Kiss' *Amazon*, for instance, should always be bronzed, in fact nearly all the Statuary herein represented look well bronzed, although we should prefer such Figures as are used for Cemetery purposes painted white as being more appropriate, also Figures which show but little drapery can be painted white with good effect.

In practice, identification of the original paint on zinc sculptures can be difficult. Paint adheres poorly when exposed outdoors for as long as one hundred years, and original paint is either substantially lost or overpainted. Moreover, because the choice of a particular painted coating was often left to the purchaser, the type of paint chosen is not always predictable. Analyses of cross sections along with historical research can prove successful in determining the original coating, however. Although many sculptures were probably sold unpainted, some American trade catalogues do specify the availability of sculptures with different paint coatings at different prices. These include "painted one coat," "bronzed," "gilded," "painted natural," and "paint in colors" (Mott 1890). A listing of such catalogues and their library locations is found in Grissom (1982), and a fuller version that includes itemization of sculptures in trade catalogues is planned for future publication.

A discussion of what was meant by *bronzed* in American sculpture catalogues merits further discussion because it is not clear if the term denotes copperplating or a metal-flake paint (usually copper, but it could be brass or another alloy). Copperplating of zinc is almost unfailingly specified in European discussions of zinc sculpture, and many copperplated examples of European origin are known, including the famous statues of Amazon, Queen Victoria, and Liberty Enlightening the World. However, one may speculate that when American sculptures were bronzed, this generally meant that a copper-flake paint was applied. Although a translation of an influential French book on electroplating and electrotyping was published in Philadelphia (Roseleur 1872), these methods seem to have been less well known in the United States (Shapiro 1985:98–100). No specification of the use of electroplating of zinc sculptures is found in American literature until well into the twentieth century (Stone 1914; Rigg and Morse 1915, 1916). Indeed, it seems implausible that catalogues such as Mott's would not mention copperplating if it had been used, since these catalogues describe materials with some degree of specificity, and the use of plating would have been a feature to boast about.

Only one very late American sculpture is known which was originally copperplated.[4] However, evidence of the application of copper-flake paint has been found on a number of zinc sculptures. Bronzing is specified in a 1893 letter from the J. W. Fiske Iron Works regarding the purchase of a fountain at Sailors' Snug Harbor: "I will forward to you my #209 Neptune fountain in one coat of paint and when delivered at the grounds and set in position I will send one of my best men to bronze it in a first class manner giving it a final coat of spar varnish" (Fiske 1893). Analyses of cross sections of paint from the fountain show that a white-lead paint was applied first, apparently as the delivery paint; that thereafter a reddish-brown paint was applied, presumably as a background layer for the copper-flake paint; and, finally, that the copper-flake paint and two coats of varnish were applied (Fig. 1).[5] A bronze paint might be confused with plating on cursory examination, but when exposed to moisture during outdoor display, the surfaces of copperplated statues acquire an unmistakably pimpled appearance caused by pinhole corrosion (Fig. 2). Paint can also be readily distinguished from plating when examined in cross section with a microscope, although it would not be distinguished by elemental analysis.

Traces of gilding have been found on a number of zinc sculptures, including five larger-than-life-sized sheet-metal sculptures made by the Bakewell and Mullins Company for the San Diego County Courthouse, now in the collection of the San Diego Historical Society; and a statue of Puck on the Puck Building in New York City. On the courthouse sculptures, an oil size appears to have been applied to the sheet metal and then to the metal leaf, which proved to be nearly pure gold when

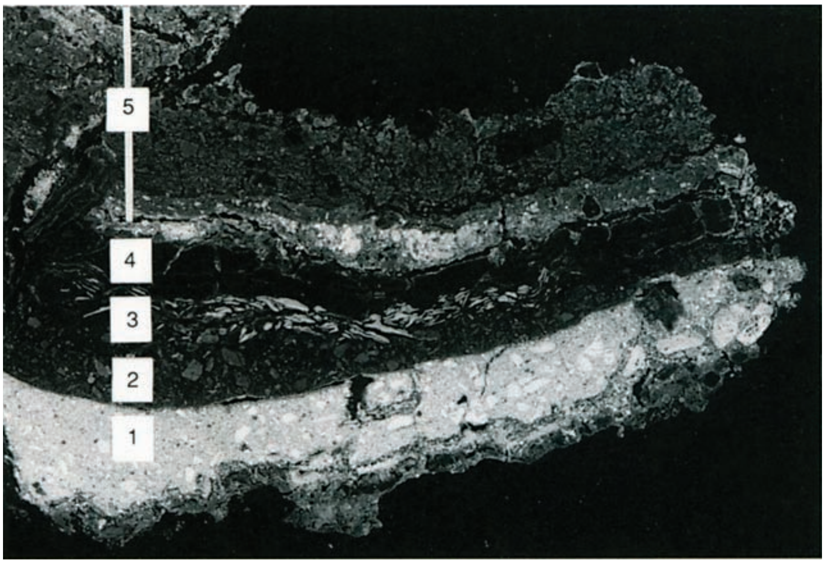

FIGURE 1. *Scanning electron photomicrograph (backscatter mode) of a cross section of paint from the Neptune Fountain, Snug Harbor, N.Y., sand-cast by the J. W. Fiske Iron Works, 1893. Numbered layers are as follows: (1) white-lead paint, (2) reddish-brown paint, (3) copper-flake paint, (4) varnish, and (5) overpaint. Magnification 56×.*

FIGURE 2. *Detail of pinhole corrosion on the left hand, Candelabrum, from the Old Merchant's Exchange Building, St. Louis, made of copperplated zinc.*

analyzed. On the sculpture of Puck, the leaf gold was applied over a white lead paint (Keck et al. 1983).

On some European sculptures, the zinc was patinated directly, usually black. Many patination recipes appear in the European literature, and examples of patinated European sculptures are known (Neumann 1869; Richter 1883:34; Hiorns 1892; *La coloration des métaux* n.d.; Jett 1982). However, there are no indications that this treatment was used in the United States.

The original surface treatment is fairly obvious to the informed observer when one technique was used. White Bronze was the trade name for a material produced by the Monumental Bronze Company and its affiliates.[6] The process was unusual: After models were sculpted to imitate stonework and cast in large sections in sand molds, they were sandblasted at the foundry to produce a uniform stonelike appearance (Fig. 3). White Bronze was used mainly for Civil War memorials and cemetery monuments, many of which bear the marks of one of the foundries.

METAL FABRICATION

The fabrication methods used for zinc sculptures were sand casting, slush casting, and stamping.[7] Sand casting was the primary method for both iron and bronze casting in the nineteenth century, and it was the first method widely used for the fabrication of zinc sculptures. Sand casting was almost certainly used for unique sculptures and monuments, because there would have been less labor in making sand molds than in making metal molds for slush casting. It was also invariably the method used to make White Bronze monuments. Because the White Bronze monuments were sandblasted rather than coated, a minimum number of seams was desirable; this could be achieved by casting very large sections in sand. Sandcast sculptures, stiff and with relatively thick walls, were generally made without armatures unless they were very large; large White Bronze monuments, for example, have rudimentary supports in the lower sections. A sand cast can be identified by the remnants of sprues on the inside, and interior surfaces often have sandy textures.

Slush casting is said to have been first used to cast zinc in 1845. For a time thereafter in Paris it seems to have been used almost exclusively for the serial pro-

FIGURE 3. *Sandblasting white bronze (Western White Bronze 1893).*

duction of large quantities of zinc sculptures (Servant 1880:7). The molten zinc was poured into open bronze molds and the excess immediately poured back out, leaving a layer of zinc. This process was quick, and many copies could be made that retained fine details from the bronze molds, precluding the need for expensive chasing. However, the process permitted no undercutting within individual castings, and only relatively small sections were produced because the mold size was limited to that which a man could hold and pour. An 1871 advertisement for American show figures notes "a heavy outlay for Design, Moulds &c." This suggests that metal molds might have been purchased. By contrast, sand molds would have been remade for each casting (Fried 1970:34).

There is reason to question the extent to which slush casting was used in America, however. Bronze molds could have been readily supplied in Paris because of the active bronze industry there, but in the United States it would have been difficult to obtain good molds until very late in the century, given the state of sculpture founding (Shapiro 1985). An 1871 advertisement for American show figures notes "a heavy outlay for Design, Moulds & C." This suggests that metal molds might have been purchased; by contrast, sand molds would have been remade for each casting, and they could not have been purchased (Fried 1970:34). However, no American sculptures have shown evidence of slush casting, and no mention has been found of zinc slush casting in America until well into the twentieth century, and then the method was used mainly for light fixtures and small ornaments (Stone 1914; Rigg and Morse 1915, 1916).

Slush casting was generally not used for large sculptures, and sculptures cast in this way do not have armatures. Slush casts have smooth rather than sandy interior surfaces. Sometimes an artifact of pouring the molten zinc out of a mold can be found, visible as a lip marking the edge of the pour. Sprues, impressions of mold-parting lines, and undercuts within individual cast sections—all characteristics of sand casting—are not present on slush-cast sculptures.

Stamping of ornaments from sheet zinc is reported to have been discovered in France in 1849 and was in full force by 1865 (Turgan 1865:236). In America, the use of stamping is said to have begun in 1871 with importation of samples, machinery, and labor from France and Germany by a major zinc producer, the Matthiessen Zinc Company in La Salle, Illinois (*Sheet Metal Builder* 1874–75:120). The industry evidently grew rapidly, and after about 1880 most of the American trade catalogues selling zinc artwork are those of sheet-metal manufacturers. Rarely were stamped and cast items sold by the same companies. Stamped items were made primarily for architectural use, with the same designs made from rolled sheets of copper, brass, bronze, or zinc as the purchaser desired. One account describes the process in some detail: Dies were made from plaster models, the lower die of cast zinc and the upper die of lead. The metal was heated, then placed between the dies and smashed into shape with a drop hammer (Lemonte 1947:28). Sheet-metal sculptures are readily distinguished by their thinness, light weight, and smooth surfaces. They always have armatures because of their flexibility, although the armatures are often relatively flimsy.

Most zinc sculptures were made in small sections and subsequently joined with lead-tin solder. This was apparently because of the ease of joining zinc with solder, the fact that small sections were easier and cheaper to cast or stamp, and the fact that a surface coating would invariably hide the solder seams. Solder can be readily identified by its smooth, shiny surface, which often appears dark against the white corrosion products of weathered zinc. According to several catalogues, riveting was sometimes used for assembling stamped zinc sculptures.

The method for joining White Bronze monuments was altogether different. Lead-tin solder was not used except to spot-join sections prior to fusing, a process in which a large quantity of molten zinc was poured into the joint area from the back. The identification of the fusing material as zinc has been corroborated by analysis (Table 1).

Identification of the Metal

A zinc sculpture can be readily identified by simple examination techniques. Zinc has a characteristic luster, light bluish-gray color, and white corrosion products. The hardness of the metal is about the same as a fingernail (2.5 on the Mohs' hardness scale), and it is harder than lead. It does not rust like iron, nor is it magnetic. The metal to which zinc is most similar in appearance is aluminum, but zinc was used for artwork when aluminum was still relatively expensive. When broken, cast zinc reveals a highly characteristic large-grained fracture to the naked eye.

Other properties that are pertinent to conservation include the following: Zinc has a low melting point (419.58 °C), is brittle at ordinary temperatures, becomes malleable from 100 to 150 °C, and is brittle again at 200 °C. The thermal expansion of polycrystalline pure zinc is 39.7×10^{-6} cm/cm per °C, which is the highest of all common metals (Lyman 1948:1086). It recrystallizes at room temperature or below; as a result, it does not strain harden (nor can it be annealed) like copper alloys, contributing to its inability to resist continuous deformation.

Compositional analyses of zinc artwork are compiled in Tables 1 and 2. While performed by several analysts using a range of methods, the results nevertheless are remarkably consistent and show that the zinc used for statuary was relatively pure. The highest total for nonzinc elements is about 5%, but 1–2% is more typical.[8] Chiefly, lead, iron, and cadmium—which occur naturally in zinc ore—are found in zinc sculptures. However, lead may also have been added to improve fluidity, and iron may have been picked up from the crucible or ladle. The addition of 3–5% tin is reported to have been desirable in nineteenth-century German-language literature, and tin does appear in some analyses of American sculptures (Richter 1883:26; Hartmann 1863:288). Copper is present in these analyses only in low amounts. Aluminum was found in a measurable quantity in only one sculpture, in contrast to modern zinc alloys, which often contain 4% aluminum for use in die casting.

Although the number of comparisons is limited, higher-quality workmanship seems to correlate with higher percentages of zinc. Monuments produced by the Monumental Bronze Company are well made and carefully finished; several analyses show high purity, equivalent to the refined Missouri zinc from which they would have likely been made. This also confirms a contemporary statement that the company used "refined zinc of almost absolute purity" (Saw 1910:191).

TABLE 1a. *Elemental compositions of Civil War monuments made by the Monumental Bronze Company, Bridgeport, Connecticut.*

	Percentages											
	Zn	*Cd*	*Fe*	*Pb*	*Al*	*Cu*	*Ni*	*Sn*	*Mg*	*Ti*	*Mn*	*Total Non-Zn Measured*
Academy Hill Monument[a] (1889)												
	99.78	.091	.085	.039	.002	.001	<.002					.218
Appomattox Monument[b] (1886)												
Soldier	96.9	.084	.12	.58	.0062	.011		.69	.0063	.0013	.0003	1.499
Shaft	99.59	.054	.076	.27	.001	.0008		.0066	.0005	.0021	.0001	.411
Fourth Ohio Infantry Monument (1887)												
Shaft[c]	95.7		.29	.27	(<.03)	.002		(<.01)			(<.01)	.562
Fusing metal[d]	97.8		.19	.85	.9*	(<.01)		.12			(<.01)	2.07*

TABLE 1b. *Elemental compositions of sculptures made by other American foundries.*

	Percentages											
	Zn	*Cd*	*Fe*	*Pb*	*Al*	*Cu*	*Ni*	*Sn*	*Mg*	*Ti*	*Mn*	*Total Non-Zn Measured*
Concordia[c]												
	90.8		.38	2.41	.32	.017		1.71			(<.01)	4.837
Columbia Protecting Science and Industry[d] (1879)												
	95.0		.58	.91	(<.03)	.13		(<.01)			(<.01)	1.62
Captain Jack[d]												
	98.0		.25	1.35	.2	.09		.1			(<.01)	1.99
Flora[d]												
	96.0		.10	1.12	(<.03)	.09		.1			(<.01)	1.41

TABLE 1c. *Elemental compositions of a sculpture and fountain made by European foundries.*

	Percentages											
	Zn	*Cd*	*Fe*	*Pb*	*Al*	*Cu*	*Ni*	*Sn*	*Mg*	*Ti*	*Mn*	*Total Non-Zn Measured*
Liberty Enlightening the World[d] (1875)												
	98.5		.09	.07	(<.01)	.5*		(<.05)			(<.01)	.66*
Szymanow Fountain[e]												
Small bowl 1	97.3	.02	.21	1.2		.1		1.15			.01	2.69
2	93.3	.04	.20	1.1		.8		2.55			.01	4.7
3	84.8*	.02	.26	6.5*		.2		8.2*			.01	15.19*
Nodus	99.2	.01	.15	.25		.07		.08			.01	.57
Conch shell	99.3	.11	.1	.2		.06		.09			.01	.57
Base	99.4	.01	.15	.25		.05		.12			.01	.59

* Possible error in sampling or analysis.
(<) Indicates the detection limit.

TABLE 1d. *Elemental compositions of contemporary refined zinc from Missouri ores (1896).*[f]

	Percentages										
	Zn	*Cd*	*Fe*	*Pb*	*Al*	*Cu*	*Ni*	*Sn*	*Mg*	*Ti*	*Mn*	*Total Non-Zn Measured*
1	99.30	.006	.010	.653			trace					.704
2	99.34	trace	.032	.630			none					.661
3	99.27	.001	.055	.673			none					.727
4	99.54	trace	.052	.411			none					.463
5	99.04	trace	.023	.872			none					.956
6	99.65	trace	.028	.306			none					.346
7	99.38	trace	.036	.586			none					.623
8	99.58	trace	.039	.377			none					.416
9	99.68	.019	.048	.251			none					.318

Notes to Table 1

[a] Analyses (method not identified) by the AMAX Zinc Company at Sauget, Illinois (Michel, pers. comm. to Donegan, 1987). Percent zinc was determined by difference. The Academy Hill Monument is located in Stratford, Connecticut.

[b] Analyses by F. R. Sauerwine, Palmerton, Pennsylvania (Technical Services Report, The New Jersey Zinc Company, Sept. 7, 1983). The percentages of zinc, lead, and tin in the soldier were determined by atomic-absorption analysis, while the remainder of the analyses were made with an inductively coupled plasma spectrometer except for the percent zinc in the shaft, which was determined by difference. The Appomattox Monument is located at Jim Thorpe, Pennsylvania.

[c] Atomic-absorption analyses by Randy Korotov of the Earth Sciences department at Washington University in St. Louis, Missouri (Grissom 1979:11). The Fourth Ohio Infantry Monument is located at Gettysburg, Pennsylvania. The statue of Concordia is inscribed with the name Henry Dibblee of Chicago and is located on the Cairo Public Library Building in Cairo, Illinois.

[d] Atomic-absorption analyses by Harold Westley made at the Conservation Analytical Laboratory, Smithsonian Institution, in 1986. The statue of *Columbia Protecting Science and Industry* was sculpted by Caspar Buberl and is located over the north entrance to the Arts and Industries Building of the Smithsonian Institution. The statue of Captain Jack appears to be identical to a sculpture sold by Charles M. Demuth of New York and is located at Bear Brook State Park in Allentown, New Hampshire (Fried 1970:50, 61). These two sculptures may have been cast by M. J. Seelig, who made the monumental sculpture of Fulton for Buberl and who is said to have made the show figures for Demuth (Fried 1970:62–64). The statue of Flora, shown in a J. W. Fiske Iron Works catalogue, was located on the Waterworks of Louisville, Kentucky, from about 1895 until it was broken during a storm around 1977 (Starr, personal communication, 1991). The statue of *Liberty Enlightening the World* is inscribed with “Avoiron, Paris”; its present location is unknown. Copper found in the analysis of the Liberty statue may be contamination from copperplating on the sculpture.

[e] Atomic-absorption analyses (Nosek 1987:255–256). The small bowl is made of cast zinc. Variation in its tin and lead content is said to reflect variations in the melt, but it seems more likely that the third sample was contaminated by solder. The nodus, conch shell, and base are made of sheet zinc. The fountain is identified as eighteenth century, although this seems improbable because of the lack of availability of sheet zinc until rolling was perfected at the beginning of the nineteenth century.

[f] Analyses (method not identified) were done under the supervision of W. H. Seamon on ores from Missouri obtained from “nearly every smelter working” (Seamon 1896:462). Analyses were also done for arsenic, sulfur, bismuth, and antimony. With the exception of one sample that showed the presence of 0.06% sulfur and another that showed 0.035% arsenic, these elements were identified as either “trace” or “none.” Percent zinc was determined by difference. As early as 1875 and until at least 1908, the Joplin, Missouri, district furnished ore from which 75% of the U.S. spelter output was derived (Ingalls 1908:289).

The finely finished Parisian sculpture of Liberty also shows a high degree of purity, particularly if the copper present is due to contamination from plating. The sculpture was most likely made of zinc from the Vieille-Montagne Company, not

TABLE 2a. *Percentages of six metals measured in samples from zinc sculptures made by the Monumental Bronze Company.*

	Total	*Pb*	*Fe*	*Cd*	*Sn*	*Cu*	*Al*
Academy Hill Monument (1889)	.22	.04	.09	.09	—	.001	.002
Appomattox Monument (1886)							
Soldier	1.49	.58	.12	.08	.69	.011	.006
Shaft	.41	.27	.08	.05	.01	.001	.001
Fourth Ohio Infantry Monument (1887)	.56	.27	.29	—	<.01	.002	<.03

TABLE 2b. *Percentages of six metals measured in samples from zinc sculptures made by other American foundries.*

	Total	*Pb*	*Fe*	*Cd*	*Sn*	*Cu*	*Al*
Flora	1.41	1.12	.10	—	.10	.09	<.03
Columbia Protecting Science and Industry (1879)	1.62	.91	.58	—	<.01	.13	<.03
Captain Jack	1.99	1.35	.25	—	.10	.09	.20
Concordia	4.84	2.41	.38	—	1.71	.02	.32

TABLE 2c. *Percentages of six metals measured in samples from zinc sculptures made in France.*

	Total	*Pb*	*Fe*	*Cd*	*Sn*	*Cu*	*Al*
Liberty Enlightening the World (1875)	.66	.07	.09	—	<.05	.50	<.01

(<) indicates the detection limit for atomic-absorption analysis.

only because this was the main source for the Paris trade but also because the company's product was reported to be very pure (Tomlinson 1852, vol.1:xcvii; Lami 1888:1136; Société 1900:31). At the other end of the spectrum is the statue of Concordia, a sculpture that was made casually enough to incorporate a large piece of iron into its fabric and shows the highest percentage of nonzinc elements. The sheet metal used for the Szymanow Fountain is notable for its purity and consistency, which one would expect for sheet metal.

For metallographic examination, zinc samples are most commonly etched with aqueous chromium trioxide (CrO_3) activated with sodium sulfate (Na_2SO_4; Anderson 1959:400–8). Definition of grain structure can best be obtained by using polarized light. The columnar structure of cast zinc, which crystallizes by the hexagonal close-packed system from the mold wall inward, is readily distinguished (Figs. 4, 5). Grains vary in size, but in sand-cast zinc they are often very large, as long as 3.5 mm. Mechanical twins are usually visible as light-colored bands. Iron-zinc intermetallic crystals ($FeZn_{13}$) are usually present and are very distinctive. Their size and number give an approximation of the amount of iron; a sample from the sculpture of Columbia shows many particles (Fig. 6), in keeping with its high-iron content. Lead, which is insoluble in zinc, is often visible as dark globules segregated at grain boundaries. Copper (in amounts up to about 1%) and cadmium (in the usual low amounts) form solid solutions with zinc, and they produce no change in microstructure except for coring. Tin or aluminum in a binary system with zinc results in eutectic structures at grain boundaries, even at low concentrations.

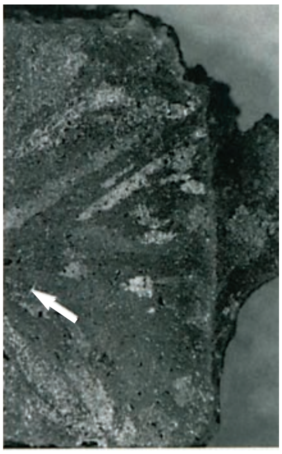

FIGURE 4. *Macrophotograph of a cross section of zinc from Columbia, sculpted by Caspar Buberl, 1890, Smithsonian Institution, Washington, D.C. Note columnar grains in the sand-cast zinc; an iron-zinc intermetallic particle is indicated with an arrow. The sample was taken from the edge of a casting; solder is visible at the right. Magnification ×15.*

DETERIORATION

Inherent vice is one of the principal reasons for the deterioration of zinc sculpture. The brittleness of cast zinc allows it to be easily broken, and its tendency to creep results in distortions, particularly on large monuments. Environmental factors also play a role. Painted coatings do not endure outdoors for as long as a century and leave exposed surfaces disfigured by crisscrossing lead-tin solder seams. Airborne sulfur dioxide causes serious corrosion of uncoated zinc. The presence of water as an electrolyte results in galvanic corrosion of copperplated zinc. Conservation treatments also have considerable potential for damage when inappropriate materials are used.

Breakage is probably the single most common reason why treatment for zinc sculptures is sought. Unlike bronze sculptures, from which a sword is occasionally stolen or an arm broken off, zinc sculptures tend to fragment into a large number of pieces when broken. Breakage seems to occur most frequently because of vandalism. Many zinc sculptures are situated in isolated locations in parks or cemeteries, which makes them easy targets; many are poorly maintained, which tends to attract further damage; and, above all, they are simply easy to break. Natural events sometimes cause damage, such as the tornado that resulted in the loss of zinc sculptures from the porch of the Louisville Waterworks of Louisville, Kentucky, in 1890. These were replaced with a second set of sculptures, one of which was smashed in a thunderstorm in about 1979. Damage from handling, transport, and removal from buildings is common, although usually less dramatic; solder seams open up, or protruding appendages such as arms are cracked or broken off. Breakage of stamped sculpture is much less common than for cast sculptures. Stamped sculptures are more often bent from trauma or separated at the solder seams.

Sagging and bulging as a result of the tendency of zinc to creep most often affect large zinc monuments, notably the soldiers' memorials made by the Monumental Bronze Company and its affiliates. Measuring 9 m or more in height, many of these monuments display nearly identical deterioration. The figure of the soldier shown in Figure 6, originally made with the rifle positioned vertically at the center of the body, now sinks into the base at the right heel and leans noticeably as a result, while lower sections of the monument sag and bulge on the same side.[9] In one case the soldier holds a large flag at his side and leans in that direction.[10] Although historic photographs and past treatments indicate that the sagging of these monuments has been occurring for a long time, recent concern about sagging has led to the installation of internal support systems[11] or disassembly in anticipation of treatment. In fact, so many of these monuments have either been treated or are presently disassembled that it is difficult to obtain a good photograph showing the extent of lean. Slight sagging has also been noted around points of reinforcement. Load has resulted in cracking at points of stress, as in areas adjacent to reinforced corners (Fig. 7) or where bulging has occurred. Sheet-metal sculptures are less affected by creep, but they are often distorted by physical actions. Their armatures usually require replacement because they have become bent or corroded.

Corrosion is negligible on sculptures that have been continuously coated, but many have weathered to a significant extent after coatings have been lost. In the case of White Bronze monuments, many have weathered significantly because such monuments were never coated at all. The extent of corrosion can sometimes be estimated by examining surface relief at solder seams. Assuming that the zinc and solder were originally level, loss of zinc can be measured against the solder, because the solder corrodes very slowly. Corrosion has a particularly large impact on the strength of sheet-metal sculptures because of their intrinsic thinness, made even thinner at the extremities from being stretched during stamping. Perforations are not uncommon on stamped sculpture.

Because the corrosion of outdoor bronze sculptures is familiar, it is useful to compare damage from atmospheric corrosion of zinc with the corrosion of copper and copper alloys. In cemeteries where both bronze and White Bronze sculptures of the same age are found, the zinc sculptures often appear to be in better condition. This is probably because the surfaces are of a relatively uniform white hue, while bronze sculptures are typically streaked and irregularly pitted. It is unfortunate that no data are available for cast bronze or cast zinc. Studies of long-term corrosion rates are limited to those for sheet zinc and sheet copper. Annual losses tend to be about twice as high for sheet zinc as for sheet copper, depending on the environment. It should be noted that the corrosion rates for zinc are far lower than those for steel, which is one of the reasons that zinc is used so extensively for galvanizing iron (Anderson 1956).

Relatively insoluble zinc-carbonate films form on zinc in clean air. While these films are believed to be stable and somewhat protective, data for rural State College, Pennsylvania, show a 1.12 µm per year loss of zinc sheet compared to a 0.75 µm per year loss of copper sheet over a seven-year period.[12] Never-coated White Bronze

FIGURE 5. *Photomicrograph of a cross section of zinc from the Neptune Fountain. Corrosion of the surface is visible at the edge as well as between columnar grains; white bands are mechanical twins. Magnification ×12.*

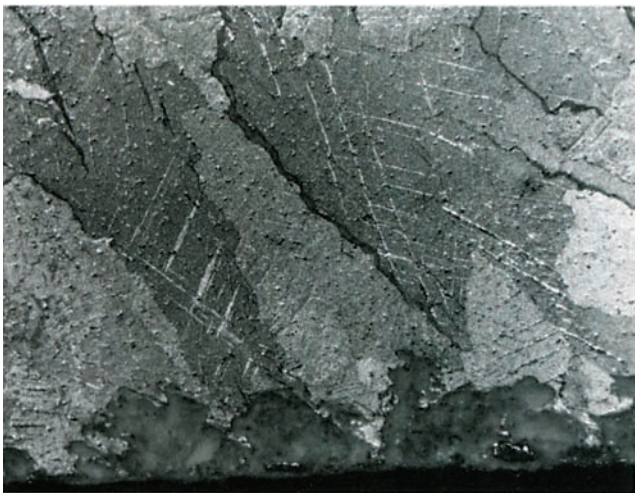

FIGURE 6. *Photomicrograph of a cross section of zinc from Columbia. The dark-colored geometric structures are iron-zinc intermetallic particles. Magnification ×35.*

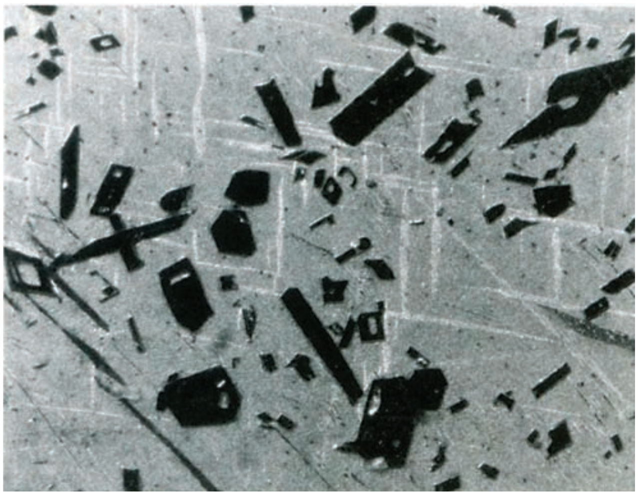

FIGURE 7. *Soldiers' Monument, Winneshiek County Courthouse, Decorah, Iowa, sand-cast and sandblasted by the Western White Bronze Company, 1886.*

monuments located in rural environments display little apparent surface loss or pitting. However, metallographic examination of sections taken from sculptures such as the Fourth Ohio Infantry Monument at Gettysburg shows some attack at the grain boundaries.

By contrast, high levels of sulfur dioxide in the air result in dissolution of the zinc-carbonate film on the surface of zinc, and soluble zinc sulfates are formed. Data for an industrial site at Newark, New Jersey, show a 4.1 µm per year loss for zinc sheet compared to a 1.45 µm per year loss for copper sheet. The Neptune Fountain, which is located on Staten Island, New York, directly across from a large industrial area, exhibits severe corrosion (Fig. 9). Sulfur has been detected in its corrosion products, in addition to an unusual vanadium compound that might also derive from industrial pollution (Wypiski 1990). A metallographic section made from this sculpture shows fairly uniform surface dissolution on both the exterior and interior of the sample, unrelated to grain boundaries, in addition to intergranular corrosion (Fig. 5).

FIGURE 8. *Detail of stress cracks, Fourth Ohio Infantry Monument, Gettysburg National Military Park, Gettysburg, Pennsylvania, sand-cast and sandblasted by the Monumental Bronze Company, 1887.*

Chlorides are thought to play a smaller role in zinc corrosion than they do in bronze corrosion, unless sculptures are directly sprayed with seawater. While experimental samples exposed 80 feet from the sea at Kure Beach, North Carolina, showed high levels of damage similar to those for industrial areas (4.1 µm per year for zinc sheet and 1.66 µm per year for copper sheet), at 800 feet from the sea the rates of corrosion were similar to those for rural exposure. White corrosion products on a black-patinated French sculpture that was exposed outdoors have been identified by X-ray diffraction analysis as zinc hydroxychloride; however, the source of the chlorides in this case is probably the coloring solution used to patinate the sculpture (Jett 1982).

Trapped water can cause catastrophic perforation of zinc, a phenomenon known as white rust or wet-storage stain. This is believed to occur because the dense, somewhat protective zinc-carbonate film does not form when the surface has remained wet, restricting access of carbon dioxide. Many instances of the perforation of zinc roofs from water trapped on the underside are reported in the literature, especially

FIGURE 9. *Detail of the severely corroded right wrist, Neptune Fountain. Dark material is lead-tin solder.*

when hygroscopic roofing papers or other materials were used (Pourbaix 1948). Perforation attributable to white rust has not been observed on any zinc sculptures, probably because the sculptures are hollow and generally drain well. However, sealing between the sections of a large zinc monument, as is sometimes proposed by analogy to masonry monuments, is not desirable because moisture might be trapped inside. Furthermore, use of interior support materials—such as concrete, glass-reinforced polyester, or epoxy resins—might trap water between the zinc and the filling material if contact is imperfect or if voids occur upon weathering or aging.

Zinc is less noble than gold, silver, copper, lead, tin, or iron; in theory it should corrode in the presence of these metals. In practice the corrosion of zinc depends on the particular alloy and the atmosphere in which the two metals are found.[13] The most common alloy found in contact with zinc is the lead-tin alloy used for soldering. Solder joins often stand in relief above cast zinc, yet for the most part corrosion on these sculptures has been observed to be no more severe at the interface of solder and zinc than it is in other areas. Similar observations have been made in regard to zinc roofing (Schikorr 1965:6.1). Lead strips are sometimes used to support areas that are sagging, and no corrosion problems have been noted, although the softness and pliability of lead tend to make statues repaired in this way more vulnerable to vandalism.

Copperplating on zinc sculptures produces severe pitting when a sculpture is exposed outdoors (Fig. 2). Of two copperplated zinc exemplars of the Statue of Liberty that have been examined, only the sculpture stored outdoors shows pitting attack. Stainless steel, carbon steel, and aluminum are used as metals for auxiliary supports, and brass, carbon steel, stainless steel, galvanized iron, and aluminum bolts and washers are often used to replace the original zinc hardware used to secure sections of White Bronze monuments. Although there is considerable potential for damage from many of these metals, particularly the steel and copper alloys, in practice little damage has been observed on zinc monuments or sculptures. This is probably because the metals are usually isolated by air gaps, paint, or other materials.

Data are conflicting about the attack of zinc building materials in contact with Portland cement mortar or concrete (Jones 1957). Theoretically, concrete should attack zinc because concrete is alkaline, and damage could also be caused by calcium-sulfate salts, which are contained in Portland cement, and result in the formation of zinc sulfate.[14] Probably more serious, however, are problems that might arise because of the lower thermal coefficient of expansion for concrete, which ranges from 5 to 14 times 10^{-6} cm/cm per °C (Lea 1971:412). Stress would be created by expansion differences as the temperature rises and falls: cracking might appear in the zinc at points of weakness, or gaps might occur that could result in damage from trapped water, either from the formation of white rust or from water expansion upon freezing. Concrete is difficult to remove, and its presence inhibits repair. Finally, concrete is stronger than zinc and, should any force be applied, the latter would be damaged first. Unfortunately, concrete is a popular repair material.[15]

Zinc is attacked by strong acids and alkalis. Hence, alkaline paint strippers that contain sodium and/or potassium hydroxide (lye) should not be used to remove paint from zinc. Care should also be taken after soldering to rinse the surface of zinc immediately and thoroughly to remove all traces of flux (usually hydrochloric acid).

TREATMENT

Treatment of zinc sculptures that are located indoors is rarely a problem. Damage is typically minor, and these sculptures can be repaired by conventional conservation methods. Treatment of outdoor zinc sculptures is more problematic. Damage tends to be more severe, the sculptures are in worse condition, and there are few precedents for treatment. In some cases, one reluctantly comes to the conclusion that a zinc sculpture should not be placed outdoors after treatment. The Goddess of Liberty on the Texas State Capitol was replaced with an aluminum copy (Weil 1987:168).

Repair of broken zinc is probably the principal and most difficult treatment problem. Soldering is the traditional method of repair, and its past performance as the original method of joining provides evidence that it generally holds up well outdoors. It has two other desirable attributes: it tends to break instead of the zinc, and it can be removed by careful heating because of its lower melting point. Pieces can generally be soldered if the zinc is in good condition. Some conservators report difficulties with the adhesion of solder to aged zinc, however, and in some cases, the number of cracks and breaks renders soldering unfeasible. There are two other drawbacks: soldering requires aggressive surface cleaning, and heating the metal permanently alters its structure, weakening it further where it has already been weakened by breakage. While soldering may prove to be appropriate for the treatment of other broken zinc sculptures which are to be painted, it is never a suitable treatment for a damaged White Bronze monument because the solder will disfigure the uncoated monument.

Use of welding has been reported in a few instances, most particularly where it was believed that structural strength was required or where a sculpture had previously been repaired by welding. However, this method is irreversible, and when further breakage occurs, the zinc rather than the weld tends to break.

One alternative to these methods of repair is the use of glass-reinforced resins. Glass-reinforced polyester resins have been used successfully for many years for making boats, vehicle bodies, and water tanks. Glass-reinforced epoxy resins, which are more expensive but are usually considered more weather resistant, have been used for high-load-bearing and engineering applications. Moisture is considered the most serious environmental hazard for these composites, as it causes swelling of the resins. Nevertheless, survival in excess of twenty years is hypothesized (Davis and Sims 1983:266–87). While conservators may be familiar with the use of these composite resins for the treatment of museum objects, they generally have very little experience in using them for outdoor treatments. Problems could be caused by differences in thermal expansion rates between zinc and the resins, although the expansion rates of the resins can be modified by judicious use of fillers. Furthermore, removal of these resins would most likely be an unpleasant task.

In some cases, broken areas can be effectively repaired with metal armatures, straps, or plates. A metal support might be bent or cast to conform to the shape of the broken area and attached mechanically or with solder or resin.

Large losses have most often been filled with cast-zinc sections. If the new section is to be soldered in place, zinc alloys containing aluminum should be avoided.

New sheet-zinc sections can be readily shaped to fill missing areas on stamped zinc sculptures. Small losses in zinc were traditionally filled with lead-tin solder, and this method is still used (Nosek 1987). Use of epoxy and polyester putties, some metal-filled, are probably more common.

On the one hand, distortions in cast metal, whether from breakage or sagging, should be regarded as permanent, and no attempt should be made to force them back into position. On the other hand, sheet metal can tolerate some hammering. Warming to 40–50 °C ("just too hot to touch") is recommended (*Data Sheet* 1983).

Installation of an internal metal structure is generally the best solution for the large zinc monuments that are sagging and leaning. The support should be carefully designed so the zinc does not sag around points of contact and the statue at the top is supported independently of the remainder of the monument. The design should also permit adjustments of level to be made during erection, because distortions of some sections may require visual compromises to be made on site. Stainless steel is generally the material of choice, although it is expensive. A carbon-steel support could be used, but it would be difficult to maintain and would probably be more expensive over the long term. Recently a carbon-steel tower was replaced inside the Academy Hill Monument because it had been allowed to deteriorate. Points of contact between the structure and the zinc should be isolated. These monuments will likely still appear to be leaning even after great sums have been expended for support structures, because the damage is permanent; this should be emphasized to clients in advance.

A range of cleaning methods has been reported for removal of extraneous material prior to repainting or coating, but further work seems warranted on the relative effectiveness and safety of these methods. The author's microscopic examination of a corroded sculpture fragment which was abrasive-blasted with walnut shells showed that loose corrosion products were removed but more adherent corrosion products remained. The zinc did not appear to be damaged by the blasting, although at high pressures the lead-tin solder joins were slightly dimpled.[16] No studies are known on damage to zinc from blasting with glass microspheres, but their use has been reported both with an air-abrasive unit to remove thick accumulations of paint and repair putties and with standard blasting equipment to remove paint (Klingelhofer 1990; Weil 1987). Corrosion removal seemed to be controllable and safe on a copper-plated zinc sculpture that was cleaned by the author with an air-abrasive unit using glass beads; pustules of zinc corrosion products were removed without turning the surface bright copper. Sandblasting should be avoided because it damages the zinc. Successful use of high pressure washing with water has been reported for removing the localized zinc corrosion on copperplated zinc sculptures at Osborne House on the Isle of Wight.[17] High-pressure water spraying was used to remove paint from a sheet-metal cornice on the Verona apartment building in New York City, although care was required not to dimple sheet-zinc portions (Pieper 1990). Use of methylene-chloride-based paint stripper or neat organic solvents may be sufficient if removal of paint alone is required. As mentioned previously, the use of alkaline paint strippers should be avoided.

With the exception of White Bronze monuments, outdoor zinc sculpture should be coated for both durability and aesthetic reasons. An attempt should be made to ascertain the nature of the original coating, and if that cannot be determined, a suitable choice should be made based on similar sculptures. Assuming that there would be far too little of any original coating to permit simply retouching areas of loss, the appearance of the original coating should be replicated with high-quality paints. Use of a good-quality primer and compatible vinyl-acrylic copolymer paint would be suitable. If applied by a professional paint shop, use of a more durable system might be attempted, as with an inorganic zinc primer and aliphatic polyester polyurethane paint. In any case, the ephemeral nature of paint should be emphasized to clients, and a schedule for repainting put into writing.

Recopperplating a zinc sculpture that is to be displayed outdoors is not recommended. Replating requires very aggressive cleaning of a sculpture, and the weathering prospects for a copperplated sculpture are poor. A metal-flake paint of similar coloration would be the best alternative.

Regilding a sculpture requires careful selection of the metal leaf, and consideration might be given to the application of a protective coating. Ten years after regilding with 22-carat gold on a potassium chromate primer, the statue of Puck showed signs of gilding wear, as well as lifting of the paint primer in areas that tended to remain wet. Application of a transparent protective coating had originally been planned, but by the time the oil size had dried, the scaffolding had been removed (Silver, personal communication, 1991).

Application of benzotriazole to the surface of a White Bronze monument has been proposed, apparently based on the beneficial effects it can have on the corrosion resistance of copper and other metals. However, a laboratory study has shown that stimulated corrosion occurs when zinc sheets are dipped in solutions of water, sulfur dioxide, and benzotriazole, particularly when the sheets are first dipped in a benzotriazole solution and then soaked in solutions of water and sulfur dioxide. A sulfuric acid and benzotriazole solution also increased the dissolution of the zinc (Walker 1974).

Conclusion

A considerable body of knowledge is now available concerning the history and conservation of outdoor zinc sculpture. The repair of broken zinc fragments remains a major problem, and care should be given to the replication or preservation of original surface appearance. However, as always in the case of outdoor sculpture, regular maintenance is the most difficult issue.

Notes

1. Taft made models for the Western White Bronze Company from about 1886 to 1892. His letters indicate that this was primarily to pay his bills: “Papa needn’t worry *yet* over my finances for I drew on the White Bronze Co., only for $50.00 to pay my rent so there is still the same am’t coming from them when ever I get the critter cast” (May 13, 1886), and “I have been having so much small work in the studio of late, little medallions, advertising novelties, etc. . . . There is a prospect of making considerable money in that way even if high art seems to prove something of a failure and fame a ‘goak’” (March 10, 1889).

2. European production increased from less than 5,000 English tons (2240) per annum in 1830 to 17,000 in 1840 and 70,000 in 1855. The price of zinc fell steadily from 1808 to 1820, rose somewhat from then until 1825 with the extension of sheet rolling, and then fell back to low levels. In the United States sheet zinc was imported from as early as the 1820s, but regular production of zinc did not occur until 1859. By 1870, 4,500 English tons were produced per annum and 21,000 by 1880 (Smith 1918:14–17,151–152). The price of zinc remains among the lowest of all metals.
3. These sculptures were listed as measuring 6 feet high, and they were probably copied after J. Q. A. Ward's bronze *Seventh Regiment Soldier* for Central Park in New York City. The contract for that 10-foot-high statue specified payment of $23,000, including $3,000 for installation (Seventh Regiment Memorial Association 1868). A sheet-zinc soldier of similar height (9 ft) sold for $450, which is less than one-twentieth the price of its bronze prototype (Mullins 1891).
4. The author has examined a copperplated zinc tag inscribed CHICAGO NEW YORK/ORBRONZE/TRADE MARK/DAPRATO STATUARY CO. which was formerly attached to a lamentation group (dated to the 1920s) in the Catholic Cemetery in Fort Wayne, Indiana. The plating on the figures was described as badly abraded and erupting with "small barnacle like flowers," which led to sandblasting and painting as part of treatment in 1978 (Doyle, pers. comm. 1982). John G. Waite reports that the sculpture of an American Indian in Schenectady, New York, was originally copperplated, with copper found by instrumental analysis. The sculpture was replated after glass-bead blasting, so the original coating is no longer present. However, an identical statue located at Forest Glen in Washington, D.C., retains copper-flake paint under several coats of repaint. A second copperplated sculpture of a soldier in Berlin, New York, is reported by Waite (1991). However, no convincing evidence of plating could be found when that sculpture was examined.
5. Elemental analyses of the Neptune Fountain and the San Diego Courthouse sculptures were performed at the Conservation Analytical Laboratory of the Smithsonian Institution using a JEOL JXA-840A scanning electron microscope with energy-dispersive X-ray analyzer, with the assistance of Melanie Feather. Contradictory results for paint from the Neptune have been reported, but the sample used for those analyses has been subsequently found to consist only of overpaint (Wypiski 1990).
6. These included the Western White Bronze Company of Des Moines, Iowa, the American Bronze Company of Chicago, the Detroit Bronze Company, and the St. Thomas White Bronze Company of St. Thomas, Ontario, Canada. Further historical information on the companies is provided by Rotundo (1989).
7. Use of several other methods are mentioned in the literature, but they appear to have been rare. Gelatin mold casting is reported for small sculptures in one publication (Hartmann 1863:289–90). In the French literature, good results with lost-wax casting by the French founder Blot are noted late in the century, but the impliction is that this was unusual (Susse 1894:32–33). Examples of Danish sculptures cast by the lost-wax method have been examined by Holm (herein).
8. By contrast, considerably higher amounts are found in Indian bidri ware. Copper (2–10.1%), lead (0.5–19.9%), tin (0.1–11.4%), and iron (0.1–1.2%) were found in twenty-six atomic-absorption analyses of bidri objects (La Niece and Martin 1987).

9. The soldier on the Fourth Ohio Infantry Monument at Gettysburg National Military Park leaned backward and slightly to his proper left before being dismantled. The soldier at the top of the Appomattox Monument at Jim Thorpe, Pennsylvania, leaned backward 21 cm off-center and slightly to one side when bidding specifications were written in 1984 prior to repair. The soldier on the Western White Bronze Company's Soldiers' Monument at Decorah, Iowa, leaned backward 37 cm off-center and somewhat to its proper left prior to recent dismantling. A Western White Bronze Company monument in the Union Cemetery in Humboldt, Iowa, is an exception: it tilts forward. Two other soldiers' monuments are found in Iowa, a Western White Bronze Company monument in Eldora and a Detroit Bronze Company monument in Mason City, and they are also said to be deformed (Brown 1986).
10. The soldier at the top of the Academy Hill Monument in Stratford, Connecticut, holds a flag to his proper left. Although his right heel also sinks downward, producing a slight backward lean, most of the lean has been toward the flag at his left, measured as 20 cm off-center prior to installation of a new support structure in 1987. After reassembly, measurements show that the soldier still leans 7 cm off-center, because distortions did not permit complete correction.
11. The installation of a steel tower was proposed for the Appomattox Monument at Jim Thorpe, Pennsylvania, in 1984, and a stainless-steel tower has been installed inside the Academy Hill Monument at Stratford, Connecticut, after the failure of an earlier carbon-steel tower. Around 1986 the Hardin County Civil War Monument at Eldora, Iowa, was filled with reinforced concrete.
12. Two twenty-year exposure studies were carried out by the American Society for Testing and Materials (ASTM) at a range of sites throughout the United States, beginning in 1931 and again in 1957. While all of the more recent data for zinc has been published, only data measured at the seven-year mark have been published for copper. As a result, comparisons are made here for the seven-year data from the 1957 study, between high-grade zinc and tough-pitch copper (Dunbar and Showak 1982:534; Thompson 1968:133). Rates for tin bronze (8% Sn/92% Cu) were also determined in the 1931 study, and they are substantially higher than rates for tough-pitch copper at the most polluted and salt-ridden sites but lower than those for zinc (Copson 1956). However, in the 1931 study samples were displayed vertically, which introduces some error, contrasting with the now-standard disposition at 30° from the horizon. A recent runoff study carried out for the National Acid Precipitation Assessment Program shows lower damage rates than both ASTM studies, although neither the method of measurement nor the sites are strictly comparable (Cramer and McDonald 1990).
13. Testing has shown that in outdoor atmospheres strong effects occur when zinc is placed in contact with stainless steel, carbon steel, copper, silver, gold, and platinum. On the other hand, only small effects, except in very aggressive atmospheres, were found when zinc was placed in contact with nickel and its alloys, chromium, aluminum and its alloys, cadmium, magnesium and its alloys, lead, tin, and lead-tin alloys (Barton 1976:164).
14. On Edwardian and Victorian roofs in England, sheet-zinc soakers were widely used at the abutments between parapet walls and chimney stacks, with cement fillets in place of flashings. The destruction of the soakers has been reported at this juncture, attributed to the soluble salts in the cement (Melville and Gordon 1973:492, 524).

15. The Academy Hill Monument in Stratford, Connecticut, has been filled to a height of 28 cm, and cracking seems to be associated with the presence of the concrete. The sculpture *Columbia Protecting Science and Industry* at the Smithsonian Institution has been filled to a height of 66 cm, but lack of documentation makes it more difficult to attribute the considerable damage found on the sculpture to the concrete. The entire Hardin County Civil War Monument in Eldora, Iowa, was filled with reinforced concrete around 1986 after the interior was coated with epoxy to prevent reaction with the zinc; this monument has not been examined.
16. Blasting with English walnut shells was performed by Nicholas Veloz of the National Capitol Parks using standard equipment at the same time that a bronze sculpture was being cleaned. The walnut shells, Agroshell AD 10.5B, were purchased from MDC Industries in Philadephia, Pennsylvania. In an attempt to induce damage, a maximum pressure of 80 lbs. per square inch was tested, using a $^5/_{32}$ inch nozzle held approximately 4 cm from the sample, and this pressure produced dimpling of the solder. Less pressure (35 lbs. per square inch) seemed to produce similar cleaning of the zinc without dimpling the solder and is thought to be more suitable for actual use. A fountain which was reported by a symposium participant to have been damaged by walnut-shell blasting has been subsequently identified as being made of lead.
17. The sculptures, some of which were made by the Geiss foundry in Berlin and some of which were made by French foundries, were purchased for the garden of Queen Victoria's estate (Harris, pers. comm. 1991).

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