

# HISTORIC MONEL—PART II: TESTING AND ANALYSIS OF ATMOSPHERIC CORROSION PRODUCTS

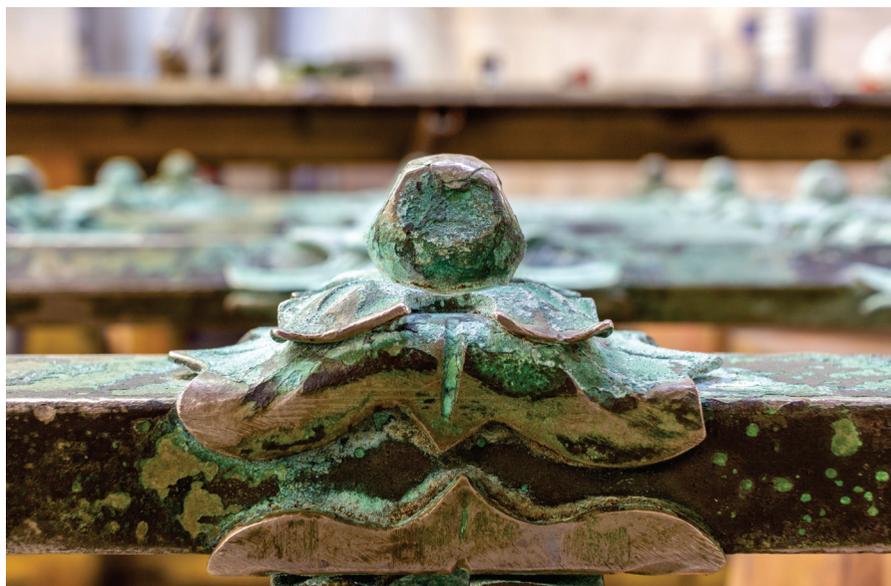
A look at Monel after decades of exposure to the environment shows more work is needed to address the lack of scientific research and conservation literature.

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Monel 400, a decorative metal with a five-decade-long span of architectural use in the first half of the 20th century, suffers from a two-fold predicament<sup>[1]</sup>. A victim of its own success, Monel's anti-corrosive properties see the metal given short shrift by conservators, relegated to the back burner as more delicate materials demand immediate treatment, while the untold loss of proprietary research from the disbandment of the International Nickel Company has left a wide chasm in the body of knowledge.

## TESTING

With an aim to begin the investigation and establish potential cleaning avenues for architectural conservators in the field, a range of testing was carried out on historic and modern samples of Monel towards the end of 2019. A quantitative and qualitative two-stage process was formulated based on standard methods. The first stage utilized a portable Bruker x-ray fluorescence (XRF) device and initially tested material inside the historic preservation laboratory at Columbia University. Testing then migrated to three case studies, with the addition of x-ray diffraction (XRD), Raman spectroscopy, and gas chromatography-mass spectrometry (GC-MS) to help qualify corrosion compounds



and identify, where possible, organic coatings.

Samples in this testing session included two historic Monel sheets from the Metropolitan Museum and Battery Maritime Building's roofs in New York City, one historic Monel rod from the Bryn Athyn Historic District, Pa., (see Fig. 1) and two modern Monel sheets, both provided courtesy of Special Metals Corporation. The historic items had been fully exposed to the atmosphere and dated to the mid-1930s. They exhibited different surface coatings that included corrosion product and apparent paint. Using the Alloy 2 setting provided

by Bruker, calibration was verified with an iterative and comparative test using a laboratory ingot report. Percentage deviation was less than 0.1% for nickel, 0.5% for copper, and between 1-2% for low compositional elements such as manganese and iron.

Tests were then carried out pre-clean, post-acetone, post paint stripper (where required), and post-sanding back to bare metal. Silicon carbide paper was used for sanding. Surface was then cleaned with acetone to remove potential contaminants. In comparison to contemporary Monel, historic Monel averaged 1-1.5% more nickel and over

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Metropolitan Museum Monel Side A



Metropolitan Museum Monel Side B



Battery Maritime Building Monel Side A



Battery Maritime Building Monel Side B



Bryn Athyn Historic District Monel rod



**Fig. 1** — The three historic samples of Monel chosen for laboratory sampling using portable XRF.

2% less copper. Silicon, cobalt, and sulfur averaged 0.75%, 0.51%, and 0.17%, respectively, in historic Monel versus nil or trace amounts in contemporary Monel. The silicon reading was skewed by the historic rod at 1.57%, likely a casting grade of Monel, sold from the 1910s. The author has uncovered at least 17 types of Monel that were utilized before their eventual phasing out from the 1980s. See Table 1 for further details and compositional content. Most interestingly, contemporary Monel registered 0.48% chromium versus trace amounts in historic. Claimed as residual due to production bleed, the proprietary nature of the alloy and modern tolerances leave question marks. Chromium was verified as effective in maintaining sheen in nickel as early as the 1920s. In W.H.J. Vernon's seminal work

"The 'Fogging' of Nickel," W.R. Barclay notes experiments under Mond circa 1927 found just 2.5% chromium had a marked effect on nickel, while another article by W.A. Wesley noted chromium plating of as little as ten millionths of an inch stopped the fogging effect<sup>[2,3]</sup>.

## CASE STUDIES

Three case studies were chosen based on weathering, location, and historic significance. Two of the sites at Woodlawn cemetery in New York are 700-feet apart, built in the same workshop within three months of one another, yet are remarkably different in weathering and coloring. The third, the Bryn Athyn historic district, northeast of Philadelphia, had notably variegated corrosion throughout. All sites were chosen as a conscious attempt to

emulate previous studies in urban and rural environments.

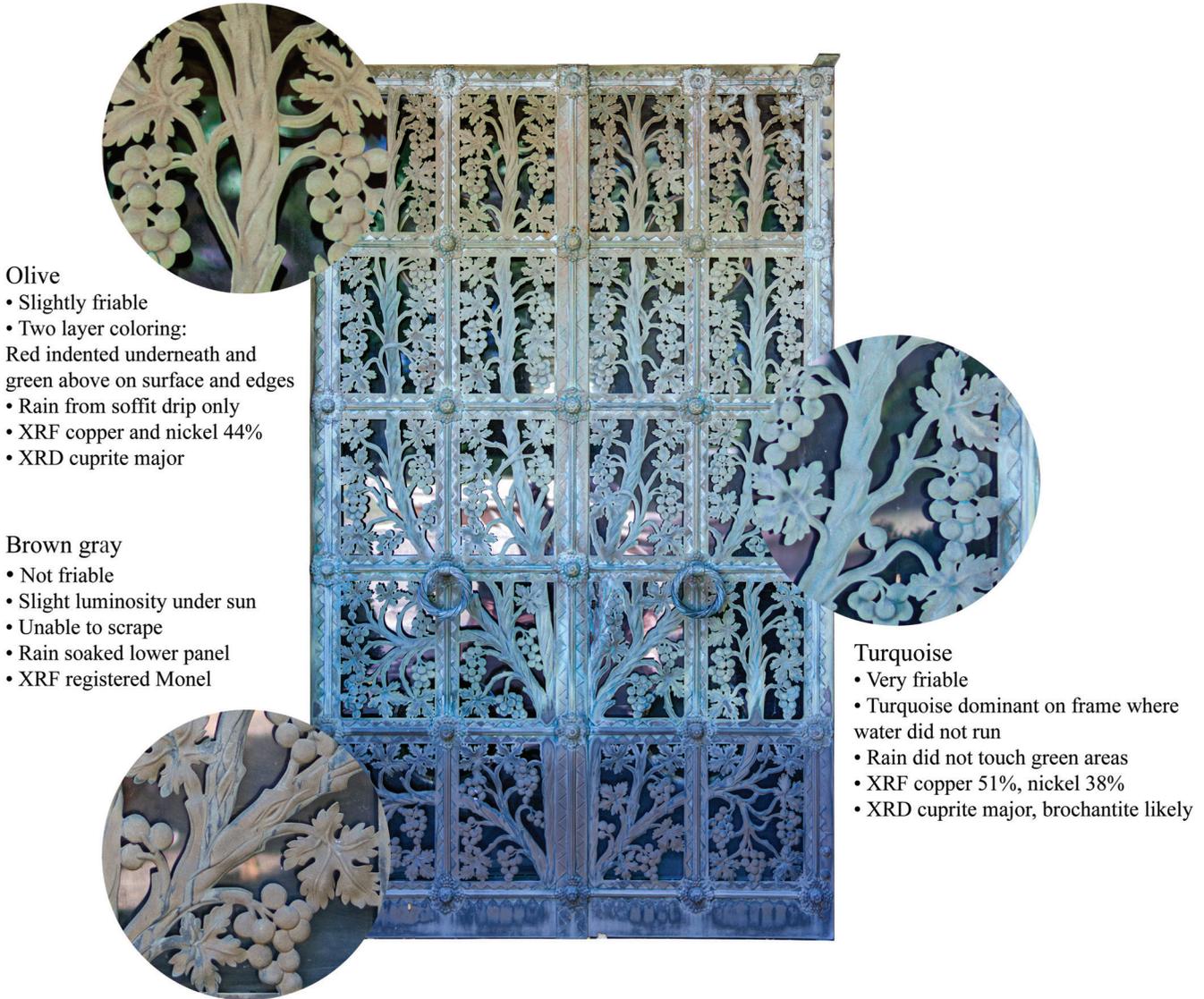
**Jesse I. Straus Gate:** Handcrafted by the Samuel Yellin workshop in 1929, the Straus gate, one of three for each heir to the Macy's fortune, depicts a grape and leaf design. A glass filled metal frame with ventilation was likely installed later. Visual examination revealed a relief flattened by friable turquoise corrosion, olive coloring along the upper row from a green top and red lower layer, and brownish gray on the base plate. XRF showed vastly different elemental readings. Turquoise areas registered copper up to 51%, nickel 37%, and sulfur 3%, versus the typical Monel readings at the base. A thinner turquoise layer on the interior saw copper dropping below 40%, showing the importance of exposure. XRD revealed major phases of cuprite and brochantite around the turquoise areas and possible chalcantite, but the brown layer was non-scrapable and could not be identified. Samples were analyzed using copper radiation tubes with scans run over the range of 5 to 80°, a step size of 0.0131° and an accumulated counting time of 500 s/step. Such thin layers could likely only be studied through x-ray photoelectron spectroscopy, XANES or XAFS but were beyond the scope of this study. A lack of identification of the base metal, hydrates and hydroxides by the databases used showed the limitations of testing an under-researched alloy.

**James Norman Hill Gate:** Worked in the same shop, the Hill gate, built for an heir of the Northern Pacific railroad fortune, depicts seed motifs topped by fleur-de-lis, ensconced in leaves. While also housing a glass filled metal frame, a lack of ventilation netting, in comparison to Straus, has impacted corrosion significantly on the rear side. Examination revealed a waxy black coating over the majority of the exterior, spotty turquoise corrosion at the top, a yellow area around the high-traffic hand area, and gray at the base. Turquoise was difficult to measure with the XRF due to a lack of flat surface, but the elements of the handle presented copper of 47% and nickel of 41%, while the black and

**TABLE 1 – MONEL ALLOYS, NOT INCLUDING WIRE PRODUCTS**

Original Name	Modern Name	Found*	Producer	Composition and Changes	Notes
Monel	Monel Alloy 400 aka M-35 Monel	1905	Special Metals	Ni 66%, Cu 31.5%, Fe 1.35%, Mn 0.9%, Si 0.15%, C 0.12%, S 0.005%	All types of applications where rust-less and corrosion-proof material is necessary with excellent mechanical properties.
Cast Monel	Monel Alloy 410	1910s	Produced in market	Ni 66%, Cu 30.5%, Si 1.6%, Fe 1%, Mn 0.8%, C 0.2%, S 0.008%	Silicon added to improve ductility. Later noted that cannot go above 1.5% and sulfur preferred.
“K” Monel	Monel Alloy K-500	1923	Special Metals	C 0.18%, Ti 0.5%, and Al 2.8%	Age-hardened overnight at a lower 1000°F, doubling hardness to 275 Brinell. Non-magnetic.
“R” Monel	Monel Alloy R-405	1931	Special Metals	C 0.18%, S 0.05%	Free-machining grade with higher sulfur content acting as chip breakers.
“G” Monel		1935	Discontinued	Unknown	A wrought alloy used as in-between regular Monel and “K” Monel in doctor blades and beater bars.
“H” Monel	Monel Alloy 506	1935	Discontinued	Fe 1.5%, Si 3.2%, Cu 30%	Cast alloy harder and stronger than Monel with as-cast strength of 110 ksi. Loss of ductility as a result.
“S” Monel	Monel Alloy 505	1935	Produced in market	Similar to “H,” Fe 2%, Si 4%, Cu 29%	Cast alloy harder than “H” for non-galling with as-cast strength of 130 ksi. Can be age-hardened up to 350 Brinell.
“KR” Monel	Monel Alloy 501	1940	Discontinued	Similar to “K” Monel but C 0.23%	Age-hardened like “K” but machinability similar to “R” due to precipitated graphite. Non-magnetic.
“326” Monel	Monel Alloy 402	1949	Discontinued	Ni 58%, Mn 0.9%, Fe 1.2%, Cu 39.8%	For cable shielding, pickling and lower susceptibility to hydrogen embrittlement when galvanically coupled to steel.
NA	Monel Alloy 403	1950s	Discontinued	Similar to 402, Mn 1.8%, Fe 0.5%	Composition changes to remain non-magnetic at the freezing point of seawater for minesweepers. Used also for electronics.
“RH” Monel	Monel Alloy 507	1950s	Discontinued	C 0.55%, Fe 1.5%, Si 2.7%, Cu 30.5%	Cast alloy with similar properties to “H” but adapted for machining.
“LC” Monel	Monel Alloy 406	1950s	Discontinued	Ni 84%, Cu just 13%	“Low Copper” for water piping and tanks, used for corrosion resistance to mineral waters
“E” Monel	Monel Alloy 411	1950s	Discontinued	Similar to Cast Ni 62%, Cu 32.5%, Fe 1.5% but Nb 1.3%	Niobium used to stiffen without an age-hardening treatment. Used in food-handling equipment, tanks, and boilers.
NA	Monel Alloy 401	1950s	Produced in market	Ni 44.5%, Mn 1.7%, Fe 0.2%, Cu 53%, Co 0.5%	Low temperature coefficient of electrical resistivity, used for wire-wound resistors.
NA	Monel Alloy 404	1950s	Produced in market	Ni 55%, 0.01% Mn, 0.05% Fe, 44% Cu, 0.02% Al	Low magnetism and excellent brazing characteristics, suitable for wet hydrogen in electronics.
NA	Monel Alloy 474	1965	Discontinued		Similar to 404 but higher purity and free from non-metallic inclusions. Non-magnetic.
NA	Monel Alloy 450	1980s	Produced in market		70-30 cupro-nickel resisting corrosion and aiding against bio-fouling. Used in seawater applications.

\* Likely dates, not definitive



**Fig. 2** — Visual and technical identification of the Jesse I. Straus gate at Woodlawn cemetery.

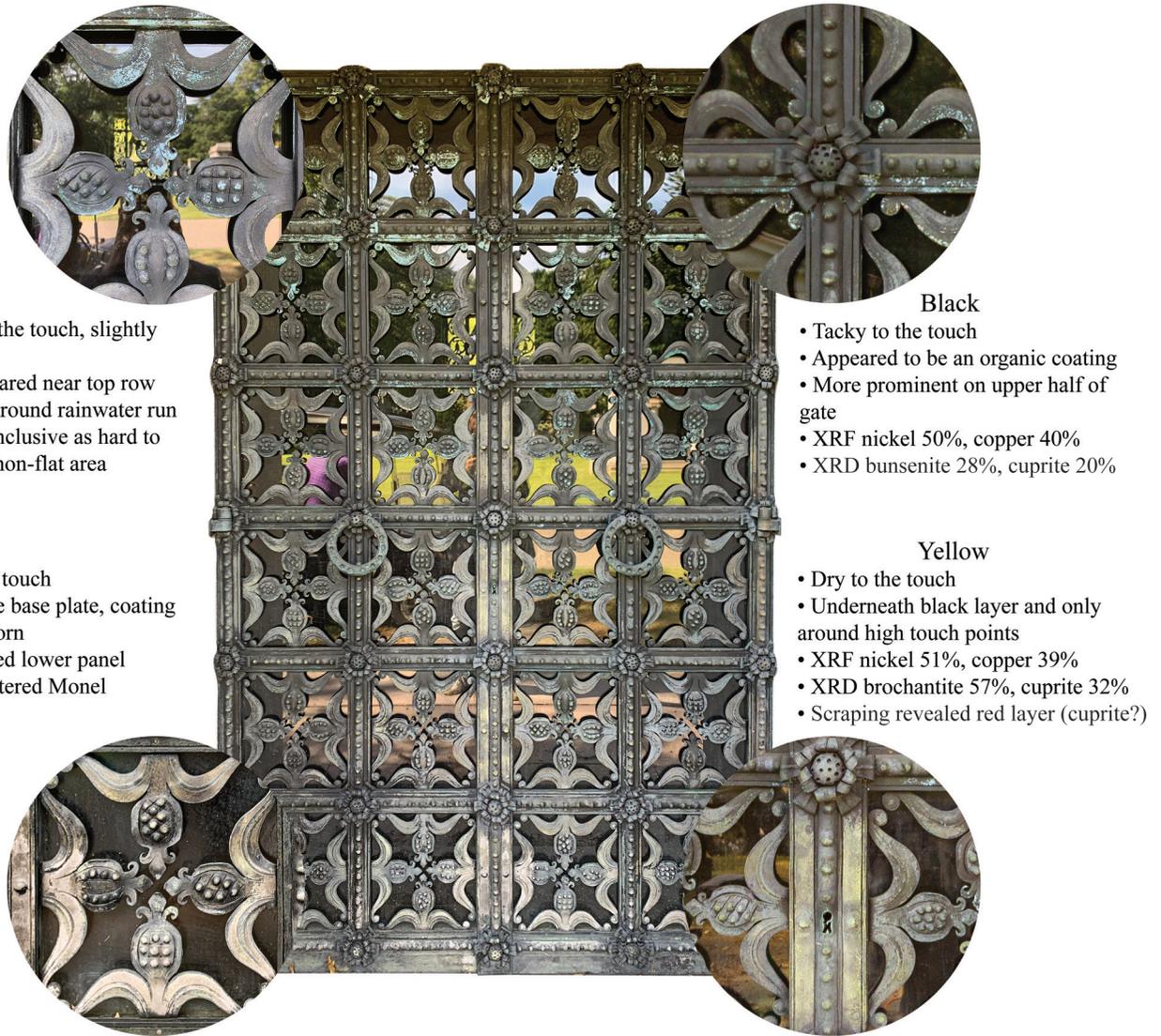
yellow areas 40% and 51%. In all three, sulfur was elevated 2-3%. The gray base area registered Monel. XRD, only successful for the black and yellow areas, confirmed roughly equal amounts of cuprite, bunsenite, clinoatacamite, and a hydrated nickel compound for the former, but nearly 60% bunsenite and 30% cuprite for the latter, with minor tenorite.

While the Straus gate revealed little in organic analysis, the Hill gate was positive for a beeswax application. Such treatment may have impacted the weathering of the Monel and should be further investigated<sup>[4]</sup>. Visual analysis of both gates after rain revealed turquoise areas were dry, the top panels received water drip from soffits and the bases were all but saturated. Given some green run-off seemed to stain

the mausoleum stone and the alloy was marketed as non-staining to masonry, this, and the solubility of all the corrosion layers need to receive attention. The presence of bunsenite, an under-researched and undiscussed corrosion product for conservators, at Hill is interesting. A mineralized form of nickel(II) oxide, it is pistachio in color, with recent studies on nickel atmospheric corrosion finding it as an inner layer enclosed by theophorite or nickel hydroxide<sup>[5]</sup>. Finally, Clinoatacamite was not picked up by the XRF due to calibration—Bruker's alloy setting does not test for chlorides, a key corrosion element for metals, unless customized to do so. Oversight of this omission could create assumptions on the part of conservators and should be noted for future users.

**Bryn Athyn:** The final case study looked at interior and exterior samples at Glencairn, the historic home of Raymond Pitcairn in the Bryn Athyn Historic District, Pennsylvania. Monel, used in construction throughout every residence and the cathedral in Bryn Athyn from the late 1910s through to the late 1930s, showed unusual coloring, with chemical patination posited by the resident blacksmith, Warren Holzman. While archives revealed orders of sal ammoniac and other chemicals and old photographs held clues, no definitive documentary proof was found.

For the interior investigation, a beam and grille were subsequently tested from the Upper Hall. The beam was teal throughout with a paste-like film, while the grille, similar to the Hill



#### Turquoise

- Grainy to the touch, slightly friable
- Only appeared near top row
- Grouped around rainwater run
- XRF inconclusive as hard to process on non-flat area

#### Gray

- Dry to the touch
- Only at the base plate, coating appeared worn
- Rain soaked lower panel
- XRF registered Monel

#### Black

- Tacky to the touch
- Appeared to be an organic coating
- More prominent on upper half of gate
- XRF nickel 50%, copper 40%
- XRD bunsenite 28%, cuprite 20%

#### Yellow

- Dry to the touch
- Underneath black layer and only around high touch points
- XRF nickel 51%, copper 39%
- XRD brochantite 57%, cuprite 32%
- Scraping revealed red layer (cuprite?)

Fig. 3 — Visual and technical identification of the James N. Hill gate at Woodlawn cemetery.

gate, saw turquoise corrosion at the top and a black waxy film towards the bottom. XRF registered levels close to Monel, but with a few strange anomalies. Iron was elevated at 4.2% on the turquoise part of the grille, while sulfur also was 2.7-3.7%. Both acetone and naphtha raised iron further, suggesting a potential ferric patination compound, but the presence of aluminum may indicate aberrations with the device or environmental contamination. Ferric chloride is known to be part of a green patination recipe for cast bronze, with a mixture of either copper nitrate, zinc nitrate, and hydrogen peroxide, or copper sulfate and water, both for gray brown or black brown bronze<sup>[6]</sup>. Initial XRD investigation was inconclusive, but Raman spectroscopy revealed

antlerite, which was then discovered as a minor phase in XRD alongside a major retgersite phase with minor bunsenite. Retgersite, a hydrated nickel sulfate, is emerald green in color and was first discussed by Vernon in the 1920s. Vernon described the formation in nickel of nickel sulfate  $\text{NiSO}_4 \cdot 0.26\text{H}_2\text{SO}_4$  that subsequently turns into a basic nickel sulfate  $\text{NiSO}_4 \cdot 0.33\text{Ni}(\text{OH})_2$  that cannot be removed without abrasion<sup>[3]</sup>. The notable absence of cuprite and rare natural antlerite formation in temperate climates reinforced the patination theory<sup>[7,8]</sup>.

Investigation of the exterior surfaces included the railing in the tower of Glencairn on the ninth floor, which had entirely different coloring. While largely brown, the decorative scrolls, joints, and weldings showed a clear outbreak

of black and yellow green mottled corrosion product. Firmly encrusted, the black was raised from the now yellowed surface and was most noticeable next to hammered tenon joints through the balustrade, which was entirely matte gray with no corrosion whatsoever. The majority of brown areas, along with the tenon joint, registered Monel. The yellow and black area, however, registered 49% nickel and 41% copper, with solvents raising the copper reading as high as 54% and sulfur from 2.3% to 3.8%. XRD for these areas revealed over 30% brochantite, 15% bunsenite, and slightly less cuprite.

Organic analysis revealed beeswax on the interior grille. As with Hill, it may have kept the formation of the turquoise corrosion product at bay. XRD's



#### Joints

- Notable source of corrosion
- Focused around welding points
- Appears flaky, but product encrusted with black raised areas, not pitting.
- XRF nickel 47%, copper 42%
- XRD brochantite 31%, bunsenite 16%, cuprite 12%

#### Cracking

- Evidence of surface cracking may indicate over-welding

#### Gray tenon

- Balustrade work hardened on site likely according to archival footage
- No corrosion present
- XRF registered Monel with 2% silicon and 1% aluminum

#### Brown

- Similar color to Straus
- Minor scratch yielded silver substrate
- XRF registered Monel

**Fig. 4** — Visual and technical identification of the tower railing at Glencairn, Bryn Athyn.

discovery of bunsenite and retgersite confirmed green and yellow coloration of the alloy is not solely due to the presence of copper. The discovery of retgersite, the rare but natural mineral form of nickel sulfate was again novel for conservator literature. Its phase in Monel would be revealed more clearly by pH diagrams. The noticeable difference in corrosion at the tenon joint also exposed the importance of work hardening and annealing on corrosion of historic metals with potential impurity issues. At the Statue of Liberty, for example, differences in weathering along edges of copper panels found softer annealed sheets corroded, whereas non-annealed sheets did not, due to smaller grain size, greater hardness, and reduced electric potential<sup>[9]</sup>.

## CONCLUSIONS

Current literature for Monel generally relies on dated information gleaned from original International Nickel Company marketing materials and claims, among other things, Monel cannot be extruded, has green corrosion product due solely to copper content, and is still produced with a matte process that was halted from 1947. All of these statements have now been proven to be incorrect, yet remain widely disseminated<sup>[10-11,4]</sup>. Surviving independent empirical data from the British Non-ferrous Metals Research Association (BNFMRA) and ASTM International is dated. The Atmospheric Corrosion Research Committee largely operated in the 1920s for the BNFMRA and was dominated at the

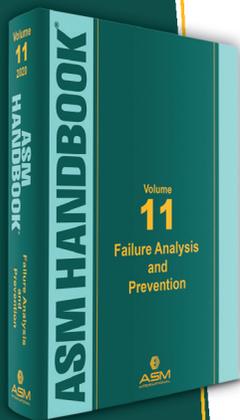
time by the work of W.H.J. Vernon and J.C. Hudson. ASTM performed multi-decade studies that took place between 1925-1964, 1957-1977, and 1976-1996. A modern quantitative analysis for Monel on the oxides and sulfates, as well as thermodynamic, kinetic, and equilibrium parameters on their formation is desirable. Potential pH and schematic diagrams that were started in the 1990s on nickel and similar work would help unravel the Monel corrosion matrix<sup>[12,13]</sup>. It is hoped this new research will just be the beginning of work to rediscover this most modern of American alloys.  
~AM&P

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