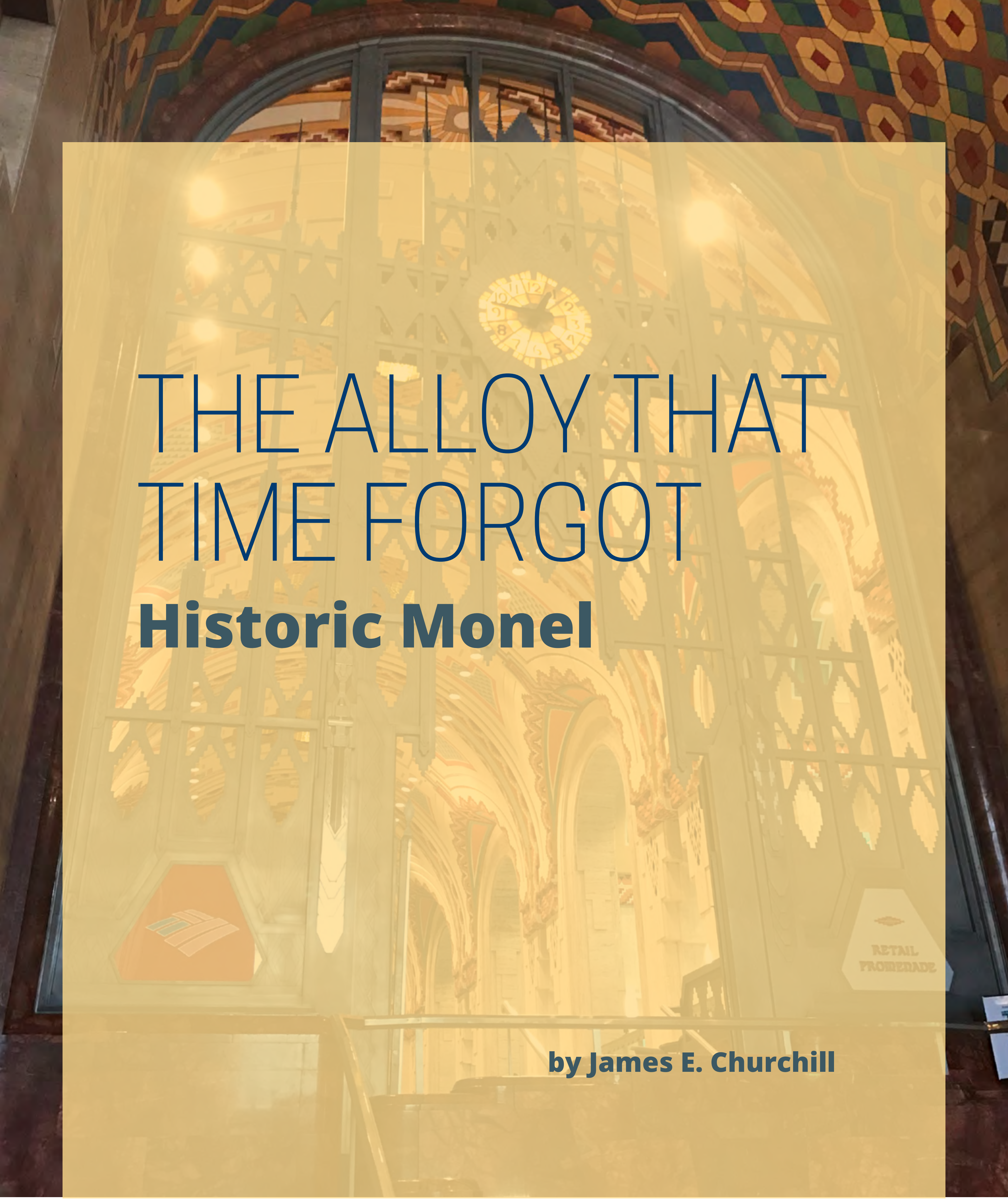


THE ALLOY THAT TIME FORGOT

Historic Monel

by James E. Churchill

This text is a summary of a two-part article found in the *Advanced Materials & Processes* magazine of ASM International:

- Historic Monel - Part I: The Production and Processes of the International Nickel Company into World War II, September 2020 issue of AM&P Vol. 178 No. 6
- Historic Monel - Part 2: Testing and Analysis of Atmospheric Corrosion Products, November/December 2020 issue of AM&P Vol. 178 No. 8

Historic Monel

Production and testing of a forgotten alloy

Monel® alloy 400* has been with us in the industrial and built environment since 1905. A short-lived architectural metal, it was replaced by its cheaper cousin, stainless steel, from the mid-1930s. Suffering from limited support, focus shifted towards newer alloys as extensive competition and nickel procurement issues harmed growth in the 1940s. Today it remains a specialty alloy used mostly in the marine field.

The early years

Monel was born out of joint research into a more affordable route to nickel silver by three metallurgists, David H. Browne, Victor Hybinette and Robert C. Stanley. Stanley ultimately solved the process and refined the first proto super-alloy ingot; fortuitous given his presidency of the future International Nickel Company fifteen years later.

The International Nickel Company

At the dawn of the twentieth-century, American business interests seized control of the world's nickel market. Despite ore sitting in British-held Canada, a lack of technology and financing saw the Canadian Copper Company tie-up with the Orford Copper Company of New-Jersey, patent-holder to the "tops and bottoms" refining method.

In 1902, Orford teamed up with United States Steel and J. P. Morgan to corner the market. The International Nickel Company was born. All tools of the corporation were manipulated – supremacy through power. Competition was squeezed with scale and aggressive trade, including dumping, ensured a 60% global supply monopoly by the mid-1920s.

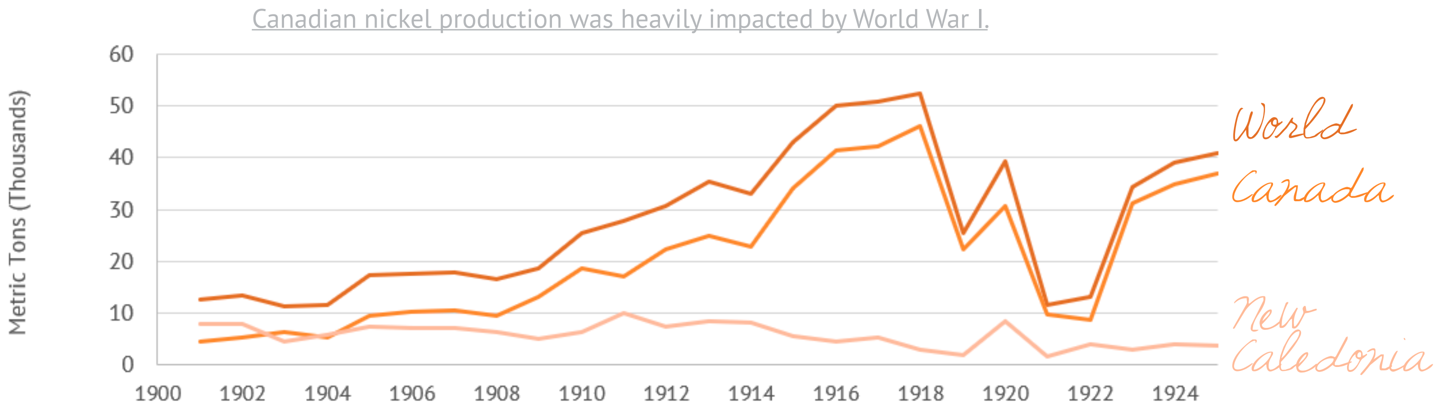


Fig 1. Nickel production by country, data from the United States Bureau of Mines, Materials survey, nickel, 1950. Graph by James E. Churchill.

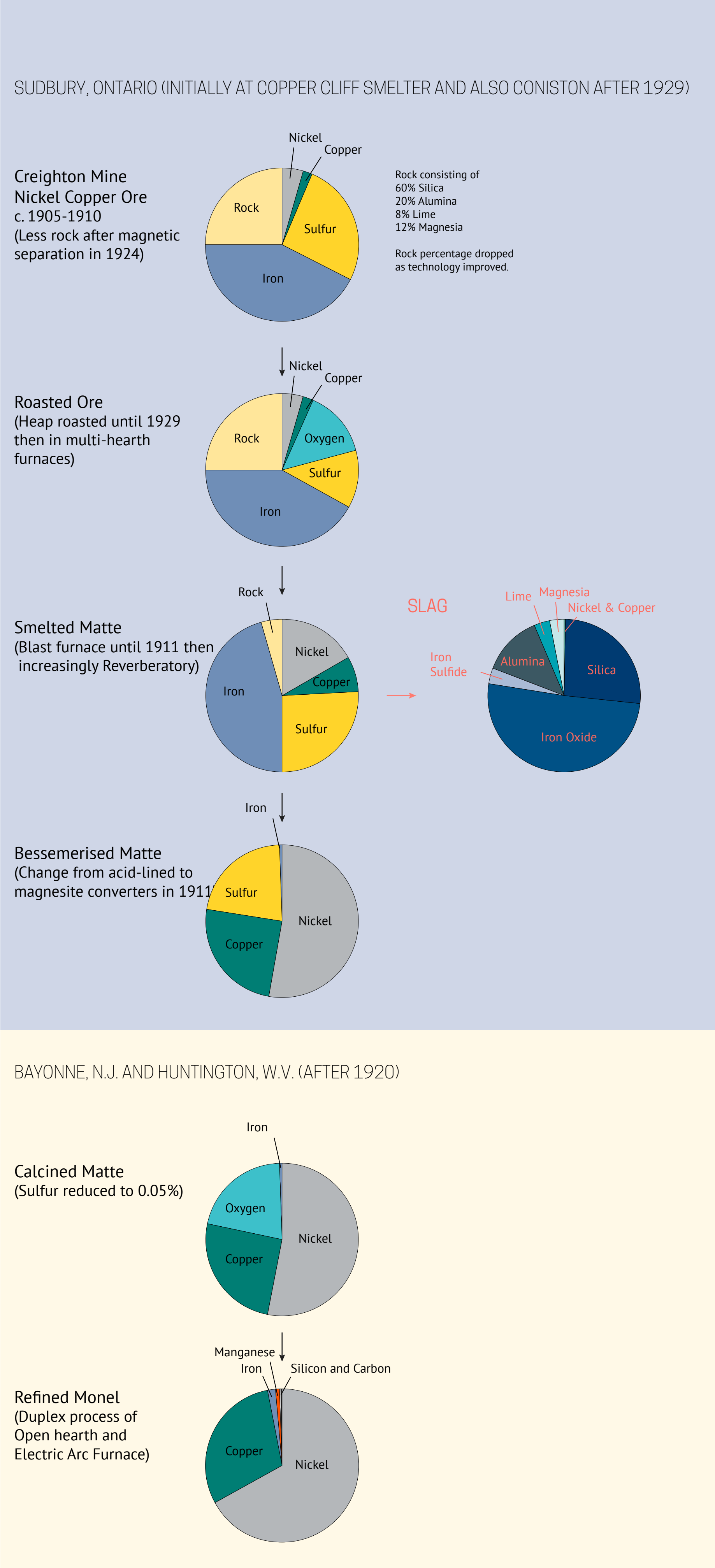


Fig 2. The ore to refined process of Monel production. Data extrapolated partially from Ontario Bureau of Mines, Ninth report of the Bureau of Mines, 1900 and Alex Gray, The Nickel-Copper Industry of Ontario-III, The Mining World XXXII, no. 22, 1910 and other research. Piechart by James E. Churchill.

West Virginia

Both the lead-up and aftermath of World War I had profound effects on nickel demand. Used extensively for vessels and munitions, it caused a twenty-five-year uninterrupted demand that vanished in the aftermath of disarmament treaties in 1918. Monel was for the cut.

Yet Stanley, now First Vice-President of the International Nickel Company, went all in at the height of the crisis. Seeing the need to diversify from mining, he lobbied for a Monel refining plant and research division that paid off as demand recovered in the mid-1920s.

Mining and smelting

Early on, ore was separated into "a mixed copper-nickel ore, copper pyrites, pyrrhotite and diorite rock," with nickel content 1.28-8.12% and copper 0.49%-15.71% between 1892-99[1].

It was at Creighton, mined from 1901, that pyrrhotite with a 2.3:1 nickel copper ratio was discovered and became synonymous with Monel's natural composition. Sorted into "coarse," "ragging" and "fines," product was roasted in yards to lower sulfur from 30% to ~7%[2]. Sintering and reverberatory techniques gained from 1911 with outside roasting banned in 1929. Bessemerized in a converter, 40% iron content was removed through slag (not collected until the 1970s) that was shipped to New Jersey for refinement.

* Monel is a registered trade name of Special Metals Corporation. The alloy referenced is produced today by several companies worldwide as UNS N04400. Monel® alloy 400 is also known as Historic Monel® and alloy 400

[1] David H. Browne, "The Composition of Nickeliferous Pyrrhotite," *The Engineering and Mining Journal* LVI (1893): 566.

[2] United States Department of the Interior and David T. Day, Chief of Division of Mining Statistics and Technology, "Mineral Resources of the United States, Calendar Year 1888," ed. Bureau of Mines (Washington, D.C.: United States Government Publishing Office, 1890),114.

Refining

Honed over years, the original patent calcined matte to remove sulfur, reduced with carbon, and then added copper or iron to alter composition appropriately. In 1909, lime separated sulfur through a slag. Huntington mechanized processing with crushers, a 4-hour automated calcining furnace, "open hearth" furnaces and an electric furnace to produce two-ton ingots[3]. Imperfections were "milled" and "chipped."

By 1928, superheated steam stopped lining damage to the converter. Matte production ended in 1947 when the company shifted to a nickel sinter and copper ingot charge. Today the process uses air induction.

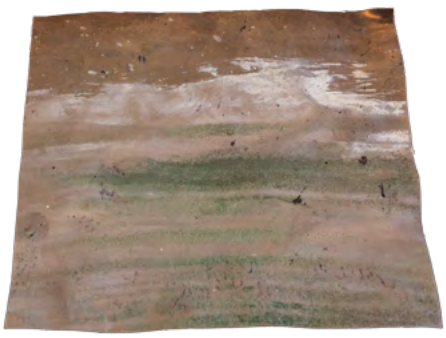
The problem

Despite marketing to the contrary, Monel did not stay "silvery" and saw discoloration from the 1920s. One report noted Monel turned white within a year of instalment, a "fogging" problem discussed by the foremost corrosion scientist W. H. J. Vernon[4]. While weight loss was minimal, variegated corrosion showed high deviation from a "pewter-like" color anticipated[5].

Today, atmospheric corrosion research of nickel alloys is lacking. Monel's anti-corrosive properties see it set aside by conservators as other materials demand immediate treatment, while the loss of the International Nickel Company left a knowledge chasm[6].

Metropolitan Museum Monel Side A

Metropolitan Museum Monel Side B



Battery maritime building Monel Side A

Battery maritime building Monel Side B

Fig. 3-5. The three historic samples of Monel chosen for laboratory sampling using portable XRF

Photographs by James E. Churchill.

Bryn Athyn Historic District Monel rod

Testing

With an aim to help architectural conservators, testing was carried out at the end of 2019. A quantitative and qualitative process using X-ray fluorescence and X-ray diffraction was formulated with additional tests where necessary. Historic sheets from the Metropolitan Museum and Battery Maritime Building's roofs of New York City, a historic rod from the Bryn Athyn Historic District (see Fig. 3-5) and two modern sheets were compared. Calibration was confirmed by a laboratory ingot report. In-situ architectural elements were studied at Woodlawn cemetery, NY and Bryn Athyn historic district, PA.

Laboratory findings

In comparison to contemporary Monel, historic Monel averaged 1-1.5% more nickel, 2% less copper and 0.75%, 0.51% and 0.17% silicon, cobalt and sulfur versus nil or trace amounts. Silicon was skewed by the rod at 1.57%, likely a casting grade sold from the 1910s. Most interestingly, contemporary Monel registered 0.48% chromium versus trace in historic. Claimed as residual from production, the proprietary nature and modern tolerances leave question marks. Chromium was verified in maintaining sheen as early as the 1920s.

Woodlawn findings

Visual examinations revealed notable differences in Monel, made in the same workshop within three months of one another, and just 700 feet apart. The James N. Hill mausoleum, coated in a partially identified beeswax, displayed black, turquoise, yellow and gray. XRF of turquoise areas identified the highest levels of copper at 47% and nickel 41% while gray areas at the base of the gate registered Monel. XRD revealed 60% bunsenite and 30% cuprite, with minor tenorite.

At the Jesse I Straus mausoleum, with no apparent applied compound, turquoise, olive and brown were found. Similar findings saw 51% copper and 37% nickel at turquoise areas and brown registering Monel. XRD, however found no bunsenite, but brochantite and cuprite. Rain revealed exposure and water solubility was a likely factor.

[3] "The International Nickel Company's Rolling Mills," *The Metal Industry* 20, no. 11 (1922): 421.

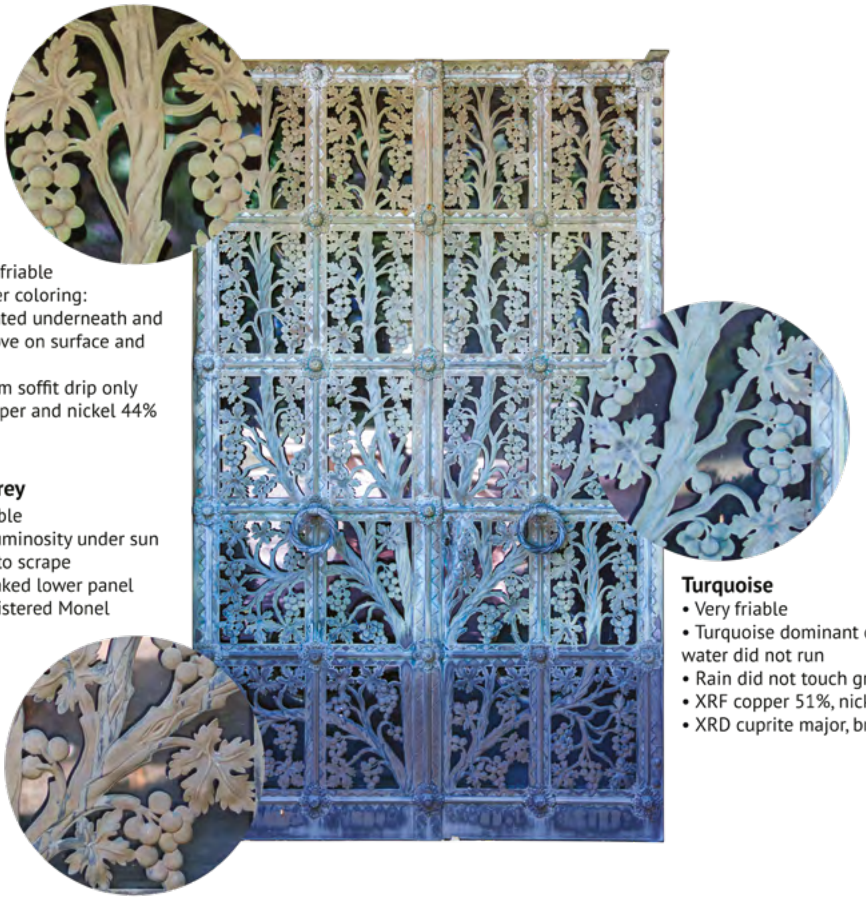
[4] W. H. J. Vernon, "The "Fogging" of Nickel," *Journal of the Institute of Metals* 48 (1932).

[5] ASTM carried out

[6] AATA Getty and also Nickel Institute.

[7] 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.

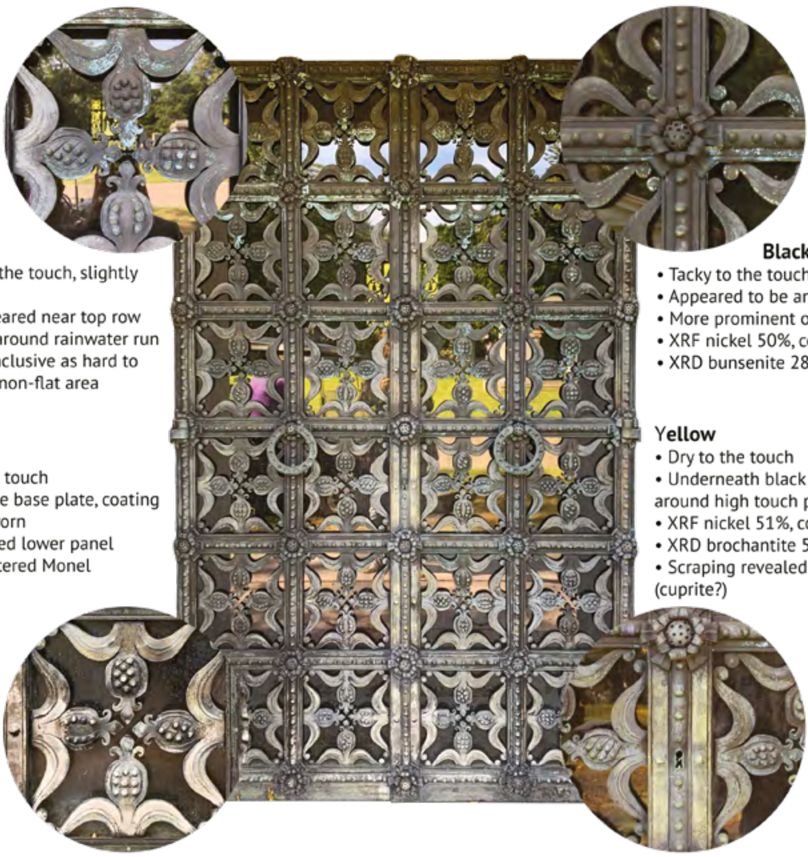
[8] In W. H. J. Vernon's seminal work "The 'Fogging of Nickel," Mr. W. R. Barclay notes experiments under Mond in c. 1927 found just 2.5% chromium had a marked effect on nickel, while another article by W. A. Wesley noted chromium plating of as little as ten millionths of an inch stopped the fogging effect. Vernon, "The "Fogging" of Nickel."; W. A. Wesley, *The Behavior of Nickel and Monel in Outdoor Atmospheres Symposium on Atmospheric Exposure Tests on Non-Ferrous Metals* (West Conshohocken, PA: ASTM International, 1946).



Olive
- Slightly friable
- Two layer coloring:
Red indented underneath and green above on surface and edges
- Rain from soffit drip only
- XRF copper and nickel 44%

Brown grey
- Not friable
- Slight luminosity under sun
- Unable to scrape
- Rain soaked lower panel
- XRF registered Monel

Turquoise
- Very friable
- Turquoise dominant on frame where water did not run
- Rain did not touch green areas
- XRF copper 51%, nickel 38%
- XRD cuprite major, brochantite likely



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. 6 and 7. Monel gates and railing. Visual identification of the Jessie I Straus and James N Hill gates at Woodlawn cemetery Photographs by James E. Churchil

Fig. 8. Visual and technical identification of the tower railing at Glencairn, Bryn Athyn. Photograph by James E. Churchil

Bryn Athyn findings

The final case study tested interior and exterior Monel. A black and turquoise beam and grille had a waxy film, similar to Hill. Chemical patination was posited. XRF registered levels close to Monel, but iron at 4.2% indicated a ferrous compound may have been applied[9]. Raman spectroscopy revealed antlerite, later confirmed by XRD alongside retgersite with minor bunsenite. The notable absence of cuprite and temperate climes reinforced a patination theory[10]. An exterior railing in comparison had black, yellow, brown and grey coloring. Around weldings, black and yellow corrosion registered 49% nickel and 41% copper with XRF, but hammered gray tenon joints along with non-decorative brown areas registered Monel. XRD revealed 30% brochantite, 15% bunsenite and slightly less cuprite.

[9] 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 sulphate and water, both for grey brown or black brown bronze. See recipes 1.127 and 1.151 in Richard Hughes and Michael Rowe, *The colouring, bronzing, and patination of metals* (New York: Watson-Guptill Publications : Whitney Library of Design, 1991), 97 and 102.

[10] Helena Strandberg, "Reactions of copper patina compounds - I. Influence of some air pollutants," Atmospheric Environment 32, no. 20 (1998): 3512; AM Pollard, RG Thomas, and PA Williams, "The stabilities of antlerite and Cu3SO4(OH)4.2H2O: their formation and relationships to other copper (II) sulfate minerals," *Mineralogical Magazine* 56, no. 384 (1992).

Summary

The discovery of bunsenite and retgersite confirmed green and yellow coloration of Monel is not solely due to the presence of copper. The difference in corrosion at the Bryn Athyn tenon joint also exposed the importance of work hardening and annealing on historic metals. At the Statue of Liberty, 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.

What's next?

Current literature for Monel relies on dated information gleaned from original International Nickel Company marketing materials and dated empirical data from the British Non-ferrous Metals Research Association and ASTM International. Monel requires a modern analysis of its oxides, sulphates and formation metrics. It is hoped this new research will just be the beginning of work to rediscover this most modern of American alloys.

[11] Richard A Livingston, "Influence of the environment on the patina of the Statue of Liberty," *Environmental science & technology* 25, no. 8 (1991): 1407.

[12] 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. The ASTM multi-decade studies took place between 1925-1964, 1957-77 and 1976-1996.

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