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Corrosion Mineralogy of Pennies, Nickels, and Dimes in Different Environments

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Abstract

Coin currency will degrade when left to the natural environment, forming mineral products as corrosion rinds. The purpose of this study was to determine what mineral products form from the corrosion of certain coins, and their relative extent under different environmental conditions. Two types of pennies (new and old), dimes, and nickels were placed in three different aquatic environments, allowed to corrode, and periodically analyzed. Methods for analysis included scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) and powder X-ray diffractometry (XRD). Coins exposed to salt water, at Emerald Isle Marsh and Anderson Dock, had more severe corrosion than coins in freshwater, at Bent Creek. A total of eight minerals were identified as copper corrosion products. No nickel corrosion minerals developed on any of the samples.

1. Introduction

Coin currency has been used for monetary exchange since the production of the first circulating coins, copper cents, in March of 1793¹. Although taken for granted in a physical and pecuniary sense, coin currency will degrade when left to the natural environment, forming mineral products through corrosion². The objective of this study was to document the corrosion mineral products of certain coins in three different aquatic environments. The results of this study may expand on the limited information available on corrosion mineralogy from previous research studies, and may be useful to forensic scientists from an evidentiary standpoint.

2. Methodology

2.1 Sampling and Field Characteristics

Nickels, dimes and pennies were used for this study. Nickels are composed of cupronickel, 75% Cu and 25% Ni, and dimes are made of cupronickel-clad copper. Pennies were made from mostly copper prior to 1984 which we labeled as old pennies and copper-clad zinc since then, which we labeled as new pennies³.

The three environments chosen included Emerald Isle Marsh, a salt water tidal flat; Bent Creek, a highly oxygenated, fresh water stream; and Anderson Dock, a brackish water coastal inlet (Figure 1). Environmental conditions influencing the rate and degree of corrosion included: reactivity of the material, levels of dissolved oxygen, carbon dioxide, and microbial activity within the environment, as well as the temperature, pH, and salinity of the surrounding conditions⁴. Differences in salinity of the three environments was the primary focus for comparison of corrosion products as a result of surrounding conditions. Plastic vials (35-mm film canisters) containing coins were placed in each environment for approximately four years. Exposure to environmental conditions at each sampling site was made possible with small holes drilled in the plastic vials. Old pennies, new

pennies, and dimes or nickels were buried beneath the sediment surface at Bent Creek, submerged in the water column at Anderson Dock, and buried in tidal flat mud at Emerald Isle Marsh. Several coins of each type were placed in each environment and retrieved annually for observation and analysis.

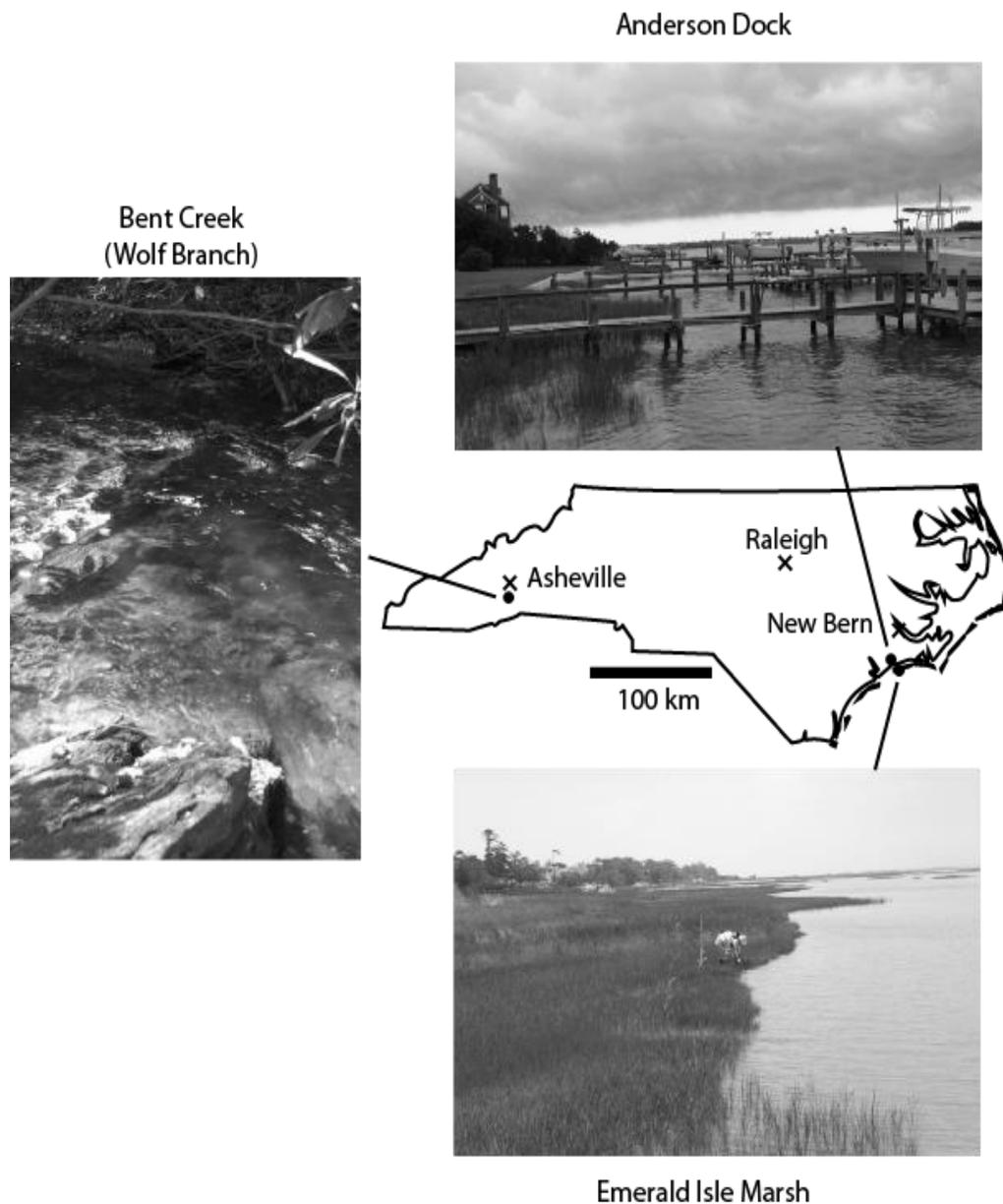


Figure 1. Sample site locations. Bent Creek Experimental Forest is located within the Pisgah National Forest near Asheville, North Carolina and is part of the USDA Forest Service Southern Research Station. Anderson Dock and Emerald Isle Marsh are located near the coast of North Carolina. Anderson Dock is a seawater site near Swansboro, and Emerald Isle Marsh is a coastal salt marsh on the sound side of Emerald Isle.

2.2 Sample Preparation

On an annual basis, one of each coin type from the three environments was cast in epoxy, ground, and polished for corrosion analysis. Coins cast in epoxy were coated with a thin layer of carbon prior to SEM analysis. The duplicate coins from each environment were scraped at the surface for powder X-ray diffraction mineral analysis.

2.3 Analytical Methods

Methods for analysis included scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) and powder X-ray diffractometry (XRD), using an FEI Quanta 400 scanning electron microscope equipped with an Oxford Inca 450 energy dispersive spectrometer, and a Philips PW 4030 powder X-ray diffractometer. The SEM provided visual and textural analyses, EDS provided mineral identifications based on chemical analyses of samples as small as 1×10^{-6} meter diameter, and XRD provided mineral identification based on crystal structure.

3. Results

The environmental conditions at Anderson Dock were saline, and resulted in corrosion products that were comparable to those found on coins at the brackish Emerald Isle Marsh. The environmental pH at Anderson Dock was 7.9 and the coins were visibly corroded. Anderson dock coins showed development of hydroxide, oxide, and sulfide minerals including cuprite (Cu_2O), chalcocite (Cu_2S), and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \times \text{H}_2\text{O}$) on young pennies (Figure 2), and atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) on old pennies. Nickel samples from both Emerald Isle Marsh and Anderson Dock had cuprite and atacamite (Figures 3, 4). Nickel coins from Emerald Isle Marsh also exhibited chalcocite.

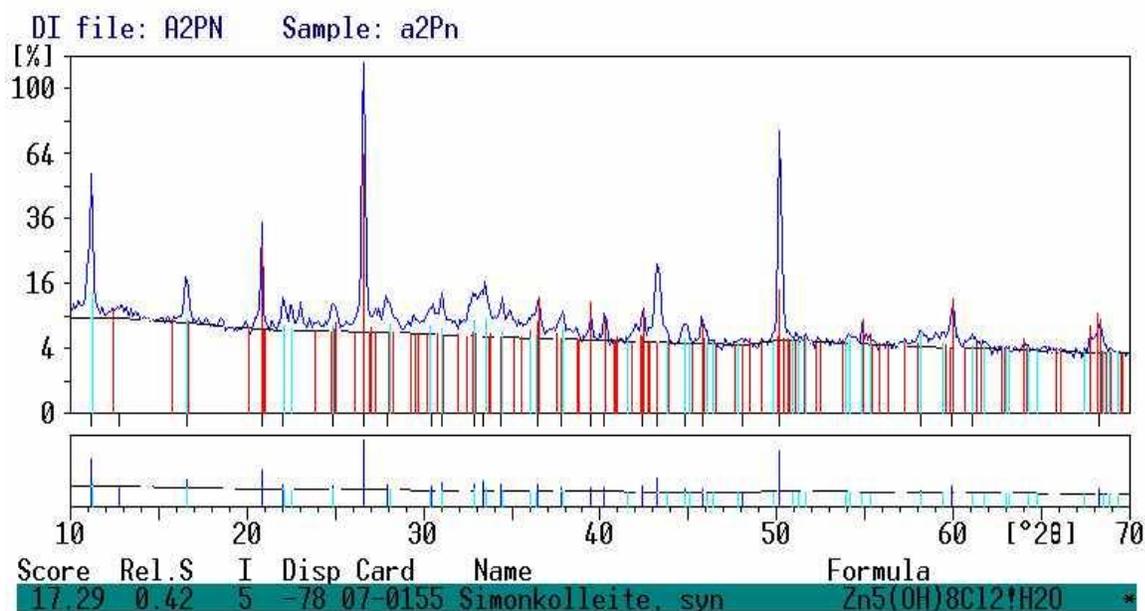


Figure 2. XRD spectrum for Anderson Dock young penny shows a strong match for the presence of simonkolleite minerals in the sample. Aqua blue markers show peaks for simonkolleite, and other colors represent other phases, such as cuprite and zinc.

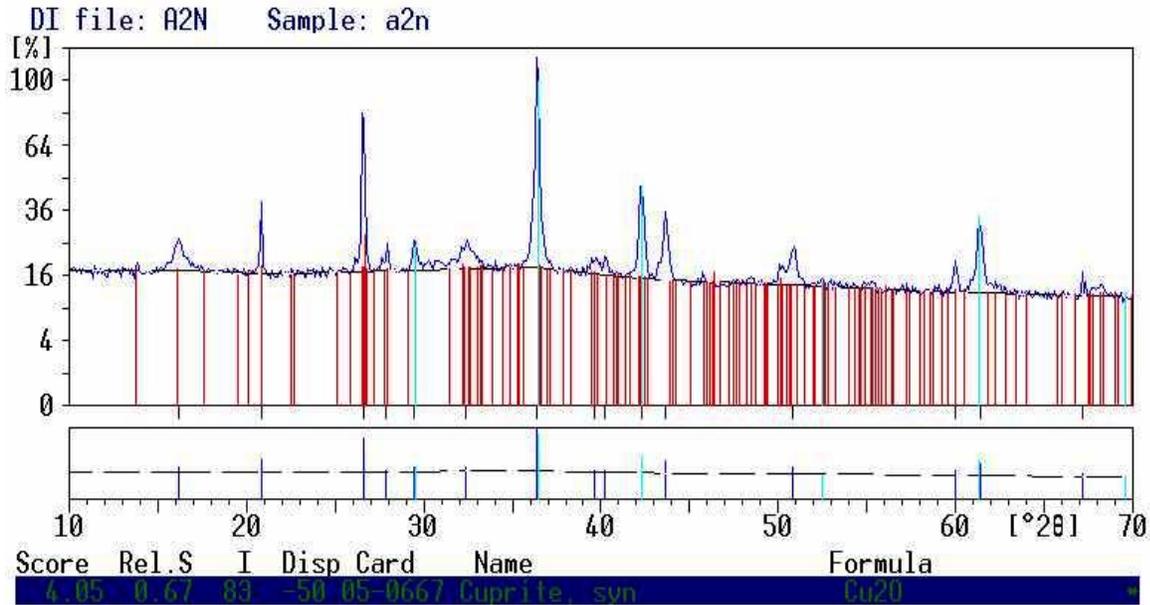


Figure 3. XRD spectrum for Anderson Dock nickel showing strong peak matches for the presence of cuprite (aqua blue markers) in the sample.

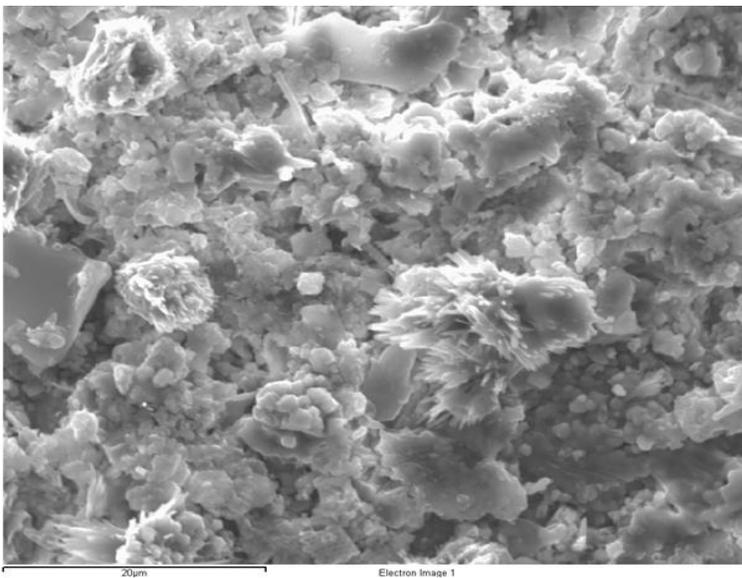


Figure 4. Anderson Dock nickel SEM image of the formation of cuprite and atacamite crystals as corrosion products. Atacamite mineral formation is shown by the platy crystals and cuprite formation is shown in the granular crystals⁵. Scale bar represents 20 μm.

Mineral identification was done through comparison of elemental weight percents, determined by EDS spectrum chemical analysis, with the results from powder XRD spectrum analysis (Figure 5). At Emerald Isle Marsh, bornite (Cu_5FeS_4) developed on old pennies, whereas weathering products on new pennies included atacamite, connellite ($\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32}\times 3\text{H}_2\text{O}$), and smithsonite (ZnCO_3). The reducing and oxidizing conditions of the Emerald Isle Marsh had an environmental pH of 6.1, which in conjunction with the high organic matter content of the enclosing mud, at least subjectively appeared to facilitate coin corrosion as compared to conditions at Bent Creek and Anderson Dock⁶.

The interior of young pennies is made of zinc. The Emerald Isle Marsh young penny (Figure 6), illustrates the phase development of various zinc and copper minerals due to corrosion. The copper originally present in the young penny was oxidized, forming cuprite as a corrosion product. Corrosion products progressing from the zinc interior toward the exterior of the young penny consisted of simonkolleite, phasing to cuprite, and then smithsonite and cuprite on the surface edge of the penny⁷.

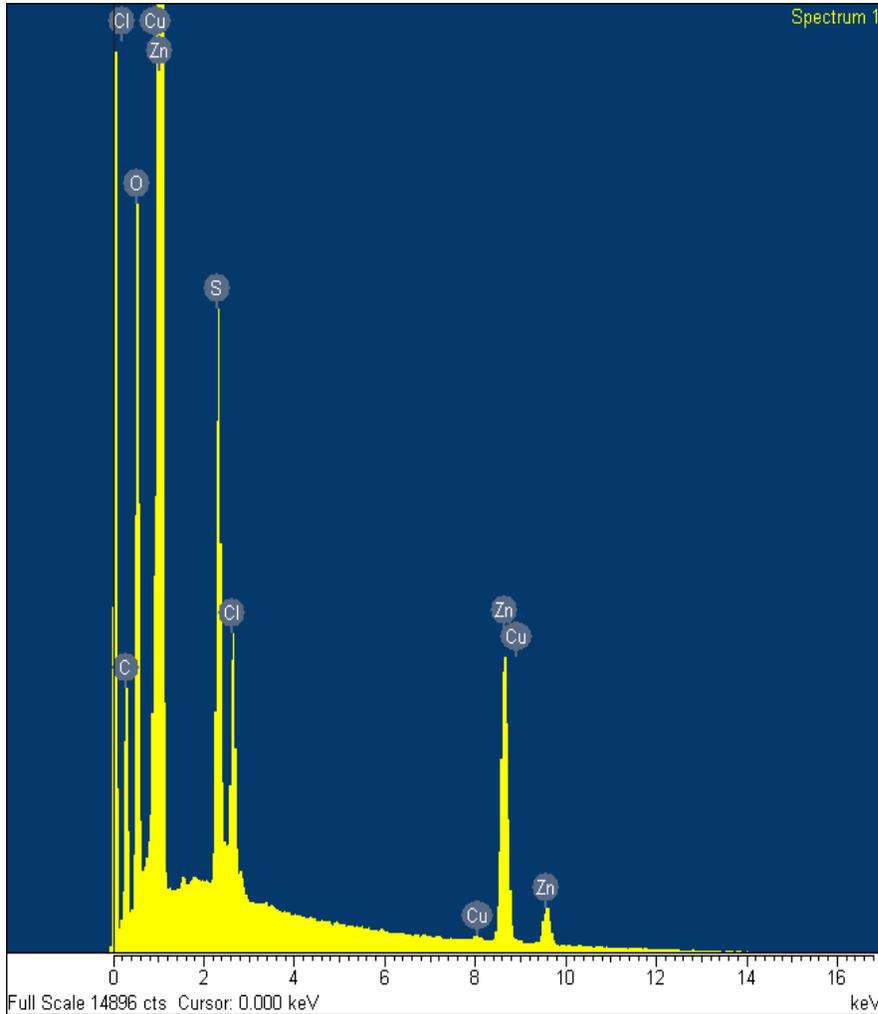


Figure 5. EDS spectrum showing the chemical composition of the Emerald Isle Marsh young penny. ESD spectrums provided elemental atomic and weight percentages at specific points (1 μ m) on the coin samples.

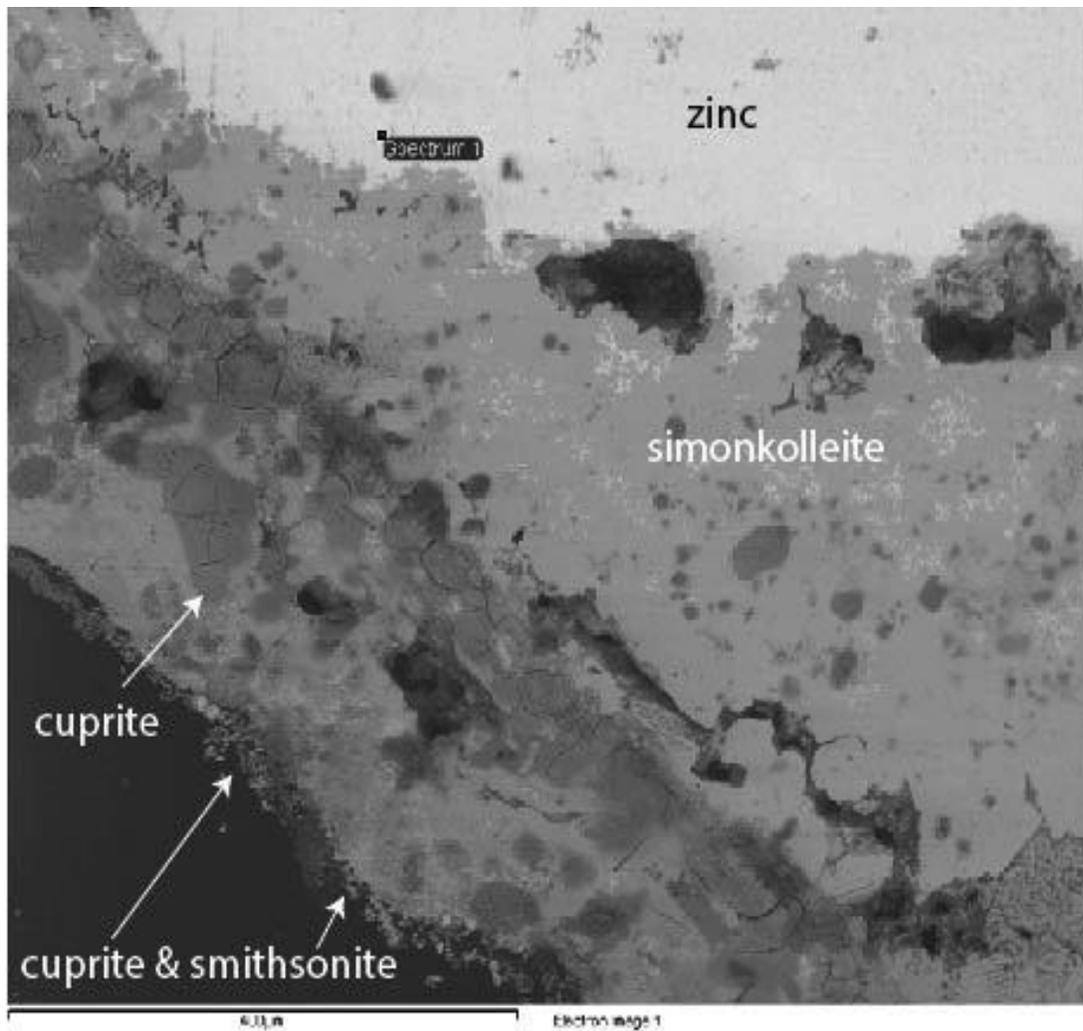


Figure 6. SEM image of the Emerald Isle Marsh young penny showing the phase development of copper and zinc minerals: zinc core, phasing to simonkolleite, cuprite, and a thin outer layer of cuprite and smithsonite. Scale bar represents 400 μm .

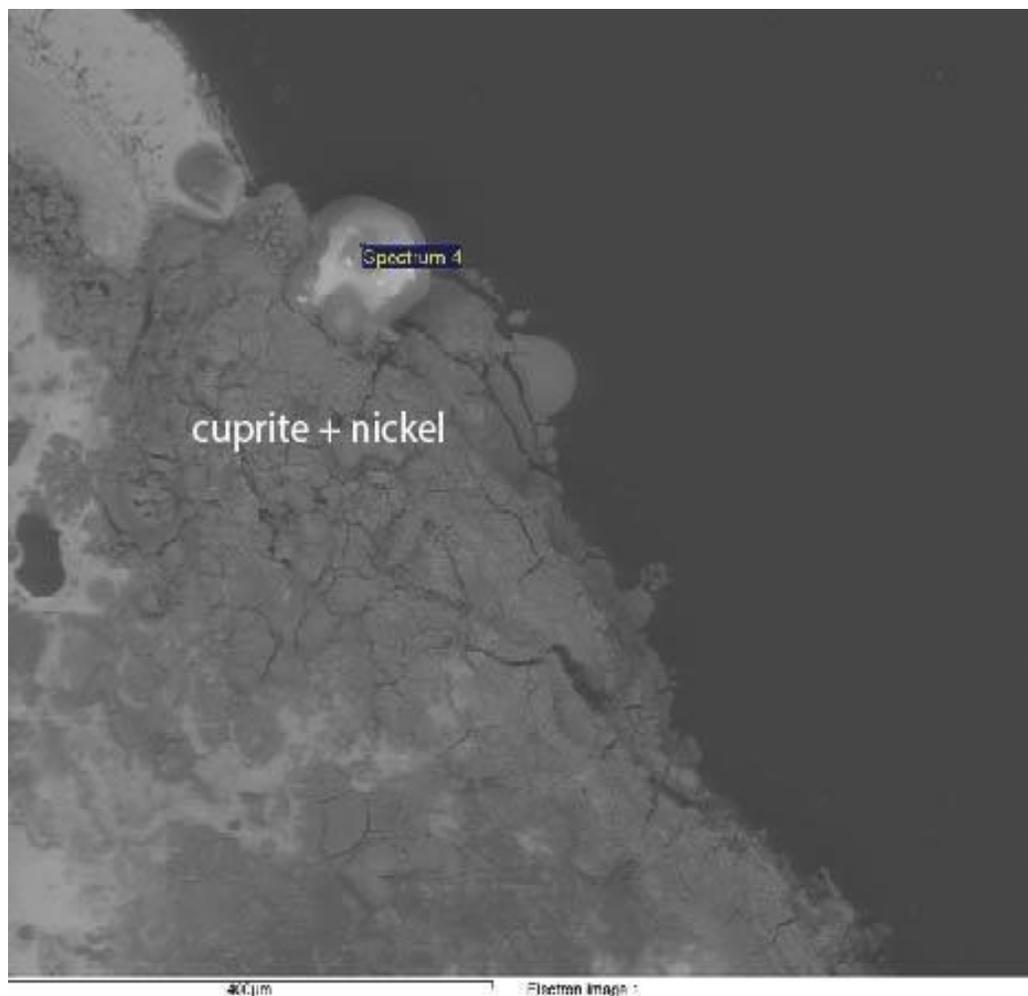


Figure 7. SEM image of the Bent Creek dime shows the development of cuprite minerals near the surface, with intermittent nickel remaining present; however, no nickel corrosion minerals were found to have developed. Scale bar represents 400 µm.

Bent Creek had the least corrosion activity of the three environments tested. The running freshwater environment at Bent Creek had a pH of 5.3. Green minerals visible under the light microscope suggest that small amounts of atacamite or malachite formed on coins buried at Bent Creek. Malachite was identified on young and old pennies, based on matching XRD patterns. Weak XRD matches existed for both atacamite and malachite, but the matches are stronger for malachite. Additionally, chloride minerals, such as atacamite, are unlikely to form in freshwater environments, so we conclude that the green mineral is malachite⁸.

Other than development of some dark green and light blue coating on portions of exposed copper rim, dimes at Bent Creek had hardly any evidence of corrosion. The copper coating on young pennies dissolved away, exposing portions of interior zinc through holes on the surface. Old pennies had small amounts of dark green and light blue mineral coatings. The blue mineral found on coins at Bent Creek may have been azurite or some other copper mineral, but occurred in amounts too small for positive identification.

No nickel corrosion minerals developed on any samples from the three environments. This is most likely due to dissolution of the nickel, leaving behind no nickel corrosion products. Dimes, made of copper with a cupro-nickel clad, formed cuprite minerals as a copper corrosion product, with intermittent nickel remaining present but lacking any evidence of corrosion (Figure 7). We know the Cu is corroding due to the existence of Cu corrosion minerals. If the Cu corroded but Ni did not, we would expect to see a net-like or mosaic texture where the copper had corroded, leaving behind nickel. Another possibility could be that the alloy cupro-nickel itself is resistant to corrosion, but if that were the case, nickel coins would not show evidence of corrosion.

The metallurgy study done in 2002, “High Nickel Release from 1- and 2-Euro Coins”, provides evidence on the solubility and release of nickel into the environment; specifically concerning the disappearance of nickel as a result of exposure to salinity in the environment. It was determined that significantly higher amounts of nickel are released into the environment from coins made from cupro-nickel and/or nickel-brass alloys than from coins made from purely nickel. Data gathered from this study offers quantitative evidence on the release of nickel into the environment. Nickel alloys, more specifically cupro-nickel metal alloy made of 75% copper and 25% nickel by weight, release notably higher amount of nickel into the environment⁹.

Research based evidence, resulting from this prior investigation into the solubility of nickel, supports our hypothesis that the cupro-nickel metal alloy, present in both dimes and nickels, released into the surrounding environment prior to the formation of any nickel corrosion minerals. The little time required for dissolution of nickel in metal alloys, particularly of cupro-nickel, is likely the cause for our results showing no nickel minerals products forming from corrosion.

Table 1. Minerals identified and the environments in which they formed

Mineral Name	Chemical Composition	Environments Found
Atacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	Anderson Dock (Po, N); Emerald Isle Marsh (Py, N)
Bornite	Cu_5FeS_4	Emerald Isle Marsh (Po)
Chalcocite	Cu_2S	Anderson Dock (Py); Emerald Isle Marsh (N)
Connellite	$\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32}\times 3\text{H}_2\text{O}$	Emerald Isle Marsh (Py)
Cuprite	Cu_2O	Anderson Dock (Py, N); Emerald Isle Marsh (N)
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$	Bent Creek (Py,Po)
Simonkolleite	$\text{Zn}_5(\text{OH})_8\text{Cl}_2\times\text{H}_2\text{O}$	Anderson Dock (Py); Emerald Isle Marsh (Py)
Smithsonite	ZnCO_3	Emerald Isle Marsh (Py)

Po=Penny, old; Py=Penny, young; N=Nickel

4. Conclusions

A total of eight minerals were identified to form as corrosion products (Table 1). Coins exposed to salt water at Emerald Isle Marsh and Anderson Dock had more severe corrosion than coins in freshwater at Bent Creek. The conductive nature of salt water due to electrolysis increases the rate of corrosion in saline environments. Emerald Isle had the most corrosion minerals, including copper minerals atacamite, bornite, chalcocite, connellite, and cuprite; and zinc minerals simonkolleite and smithsonite. Anderson Dock contained the same minerals, excluding bornite, connellite, and smithsonite. Conversely, malachite was the only corrosion mineral identified on Bent Creek samples, but no zinc minerals.

No nickel corrosion minerals were identified on any coins in any environment. Further research regarding the release of nickel from metal alloys, influential factors promoting the release of nickel, and mobility of nickel within the environment, may help explain why no nickel corrosion mineral formed.

The results of this study will benefit forensic science by illustrating how coins weather with time under certain aqueous conditions. Furthermore, the United States Treasury and other metal users could use the findings of this study for developing improved protection against the corrosion of coin currency and metals it contains.

5. Acknowledgments

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