Comments and Communications

The Electrochemical Restoration of Badly Corroded Silver-Copper Alloy Objects

The ancient Egyptians and the peoples that followed were well acquainted with the hardening effect of copper upon silver (sterling silver contains from 7.5% to 10% copper). Accordingly, it is not uncommon to come upon so-called "silver articles" during explorations and excavations of historical sites in Egypt or other countries bordering on the Mediterranean Sea.

The objects we investigated were found in graves or buried in the soils of Egypt, Greece, and elsewhere. The objects when found presented the appearance of badly corroded bronze objects with no indication that they were silver alloys. Accordingly, the objects were classified as copper-tin "bronze." They had the usual green-gray crust of corrosion products comprising the basic carbonates of copper, malachite, and azurite, together with a substructure of red cuprite. Intimately mixed with these copper compounds was a porous mass of clay or sand.

Accordingly, we treated the objects by our standard method for bronzes, making the objects cathode in a 2% solution of sodium hydroxide. It was not until the copper compounds had been reduced to metal that we met with the first indication that silver was present in this or that object. This silver was in the metallic state and located underneath the reduced copper. On the basis of the restoration results of a number of copper-silver objects we have enough evidence to indicate that the silver copper alloys were selectively corroded, copper going into solution in the acid or salt solutions found in soils. As long as any metallic copper was present this would protect the silver by causing it to become cathodic. Accordingly, we find the silver metal imbedded in a mass of copper compounds.

The corrosion of silver does not take place until all of the accessible neighboring copper has been oxidized. Corrosion proceeds radially from the original surface, and at a certain distance away from the original phantom surface the silver is precipitated, forming a structure that is frail but that reveals, somewhat magnified, the details of design of the original object. After the copper metal has been eliminated the silver is attacked by soil acids or soil salts in solution in the moisture in the soil: the reduction of the several silver compounds, notably the chloride and the black oxide, proceeds without much difficulty.

In a number of cases we have observed that the silver coin was larger in total volume than the original coin. The same observation applies to other silver objects. It would seem, therefore, that in the corrosion of a silver-copper coin there are a number of more or less distinct steps or stages:

1. The attack of the copper constituent by the corroding liquid in the soil.
2. The migration of the copper compounds, such as chlorides and sulfates into the porous or veined loamy soil. Eventually these copper compounds migrate until they reach the air and are then converted into basic salts such as malachite.
3. The dissolution of the copper constituent of the coin or other "hard silver" object continues through many years until only the silver remains.
4. During this process of copper dissolution, the silver constituent is electrochemically protected as long as metallic copper is present.
5. As soon as the copper is all corroded its protective action on silver stops, and the corroding agents attack the silver.
6. Silver salts migrate through the soil and pass copper salts until they encounter organic plant and animal matter. This matter has a strong reducing action on the silver salts and after considerable time has elapsed, a somewhat enlarged pure silver replica of the original "hard silver" object is formed.
7. These replicas are isolated during the process of restoration. The reduction of silver compounds to silver metal may not take place in the soil but it will take place during the electrolytic process of restoration.

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A Third Record of the Whale Shark, *Rhineodon Typus,* in the Caribbean Sea

In 1935, I published an article on the geographical distribution of the whale shark in which all known specimens were located. Because of its occurrence in the Gulf of Mexico, off Havana, Cuba, in the Florida Keys, and off the East Coast of Florida, I had long felt sure that Rhineodon must be found in the Caribbean Sea. In 1926 and in 1934, second- and third-hand reports came in that a great shark (thought to be Rhineodon) had been seen off Trinidad in the Gulf of Paria, and that another had been repeatedly observed off San Juan Harbor, Puerto Rico. Every effort was made to get definite data for each shark, but in the end these fish had to be put down as unverified possibilities of whale sharks.

First Record. Better fortune came later. On April 26, 1934, the *New York Herald-Tribune* recorded a great shark rammed and killed by the Grace liner *Santa Lucia,* on the run from Cristobal (Colon, Canal Zone) to Cartagena, Colombia. Correspondence with the Grace Line officials resulted in a visit to my office by Chief Officer A. E. Richards, who gave an exact description of the great fish. Here, then, was the first definite record of the occurrence of the whale shark in the Caribbean. This observation I published in 1937.

Second Record. Further definite evidence that Rhineodon occurs in the Caribbean came in 1937. The curious behavior of a great shark in the harbor of St. Marc, Haiti, around the steamer *Colombia* of the Colombian Steamship Company, was noted in a newspaper clipping sent me. A letter to the office of the company brought an answer from Pres. C. H. C. Pearsall, who at the time was on the steamer in the harbor of St. Marc. His description of this great fish positively identified it as Rhineodon, and this was verified by his inspection of a photograph in my office.

Mr. Pearsall carefully described the unusual behavior of this greatest of the sharks. It "hung around" the steamer while she was loading bananas under a strong electric light. A number of shots were fired at the unwelcome visitor, but they glanced harmlessly from his body armor of denticle-covered 4-inch skin. Once Rhineodon came up under the companionway, raised its head and dislodged the platform at the bottom of the ladder. The shark was about 25 feet long and when it bumped into the side of the ship, the impact was noticeable. An account of this fish and its behavior appeared in 1939.

Third Record. And now comes another authentic account of a whale shark in the Caribbean. Mr. Arlo Kalsheim, second officer of the tanker *Marathon* of Oslo, Norway, has kindly sent me a letter, via the U. S. Hydrographic Office, Washington, D. C., giving the following data. The *Marathon*, on a passage from Lisbon, Portugal, to Puerto La Cruz, Venezuela, had arrived on January 14, 1949, and anchored in that harbor in the afternoon. The officers were on the bridge awaiting orders from shore, when the captain called attention to a huge shark swimming near the vessel. Mr. Kalsheim writes that it was about 30 feet long and was swimming toward the ship. He had seen my article and figure published in the Hydrographic Bulletin in 1934 and at once recognized the visitor as a whale shark. He wrote that it was covered with spots over its whole body, as the published figure showed, and he estimated the width of the huge mouth at 4 feet. The great shark swam about the ship until dark, feeding on swarms of small fish and on other organisms at the surface. None of the ship's company had ever seen a shark of this size, shape, and color. It stayed on the shady side of the ship and hence it was impossible to take a photograph.

This behavior of the third Caribbean whale shark parallels that of the second specimen noted in these waters and of the two others which were reported by hearsay that could not be verified. This third Rhineodon had no fear of the ship or the crew, who, to a man, were hanging over the rail keenly interested. This behavior is typical of the whale shark. Secure in its armor of 4-inch-thick hide of tough fibers, the adult can be harmed by nothing that swims the seas. It has no enemies but man, and his harpoons and bullets will not penetrate its skin save when this is relaxed and shots are on the perpendicular—at an angle they glance off harmlessly. Man's surest way of killing this sluggish monster is by ramming it with a steamship—and a considerable number of such cases have been reported by the present writer (1940).

Those interested in the habits and behavior of *Rhineodon typus* will find all available material presented in my article, "The Whale Shark Unafraid," published in 1941.

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Some Current Misconceptions of N. L. Sadi Carnot's Memoir and Cycle

Recent authoritative texts state erroneously that Carnot (1824): (a) employed the discredited substantive or so-called caloric theory of heat, (b) discovered the second law without appreciating the first law, and (c) incorrectly pictured the descent of heat (*chute de calorique*) through an engine as analogous to the flow of water through a mill.

These misconceptions have arisen from improper interpretations of Carnot's terms *feu* (flame), *chaleur* (heat), and *calorique* (translated as "caloric" but should be interpreted today as entropy following Brønsted).

Clapeyron (1834) misunderstood Carnot and introduced unnecessary mistakes which Carnot had been careful to avoid. (Callendar, H. L. "Heat" in *Encycl. Brit.*, 1911, *et seq.*). Clapeyron's mistake still dominates the literature a century later.

Kelvin (1849–51) interpreted the three terms indiscriminately as heat and unjustly criticized Carnot's proof. Clausius (1850) was acquainted with the memoir only through the work of Clapeyron and Kelvin. Ostwald (1892, *Klassiker* No. 37) remarked that Carnot used *chute de calorique* consistently when emphasizing the motive power of heat, but *chaleur* for general consideration, never *chute de chaleur*.

Brønsted (1937–47, *Phil. Mag.*, 1940, **7**, 29: 699), has developed a new self-consistent and symmetrical system of energetics in which the reversible transport of any extensive quantity (entropy, mass, electric charge, etc.) through a corresponding conjugate difference in potential (temperature, gravitational or electric, etc.) is necessary for the production of work. (La Mer, Foss and Reiss, *Conference on molecular interaction*, New York Academy of Sciences, Am. N. Y. Acad. Sci., 1949, **51**, Art. 4).

Carnot's cycle thus represents the conversion of thermal energy (TS) into mechanical work A by the fall of entropy through a potential difference $(T_2 - T_1)$

$$\delta A_{\text{thermal}} = \delta S(T_2 - T_1)$$

Brønsted's interpretation simplifies the presentation and renders unnecessary the accepted compensation theory of Clausius developed to harmonize Carnot's ideas (as Clausius understood them) with the first law.

This communication is based on a paper presented at the January 29 meeting of the American Physical Society. A fuller account documenting the assertions will be submitted to the *American Journal of Physics*.

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