



## C21 *In-Situ* Hardening of a Steel Tank: Carbon Diffusion Over 35 Years at Ambient Temperatures

Anastasia Micheals, MS\*, Forensic Materials Consulting, 1784 Sanchez Street, San Francisco, CA 94131-2741

After attending this presentation, attendees will understand the importance of diffusion in materials, particularly in surface hardening of steel.

This presentation will impact the forensic science community by presenting a case study where low temperature diffusion has a large impact on the properties of steel.

Municipal water storage tanks are reservoirs that ensure both adequate supply and pressure to customers during low and high usage periods. Typical materials used in ground-located water tank are environmentally robust materials such as fiberglass, plastic, or stainless steel. Corrosion-sensitive carbon steel is also used. Modern methods to protect tanks from corrosion include silica glass coatings, applied to panels, processed at high temperature and then assembled. Historically, the choice for protecting carbon steel tanks from the combination of water and air that cause corrosion was a coating of coal tar pitch epoxy. Coal tar pitch is the semi-solid that remains after distillation of the coal tar by-product of coal gasification. Fairly inexpensive, it is water-resistant and long lasting. However, being a fossil fuel derivative, it is composed of a number of long chain hydrocarbons, phenols, and polycyclic aromatic hydrocarbons (PAH). Exact composition depends on the coal source material. Various PAHs are known carcinogens, mutagens and teratogens, so protective equipment must be used when applying or removing coal tar pitch.

During recoating of the interior of a 35-year old, 1.2 MG municipal water tank, the interior coal tar pitch epoxy coating was being removed by sandblasting; the goal was a white metal, or SSPC-SP 5, finish, so that a new coating could be applied to clean metal. Initial sandblasting was performed with silica, which resulted in unexpectedly low removal rates. Time was of the essence, as the tank needed to be on-line within a specified timeline, so the abrasive was switched to steel abrasive, a more expensive material. The blasting still took much longer than scheduled and anticipated.

A three inch diameter,  $\frac{7}{32}$  inches thick disk was cut from the roof of the tank. This disk was cut in half; *Piece A* was not cleaned in any way, and *Piece B* was sweep blasted with the steel abrasive. Optical microscopy, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) was performed on both *A* and *B*.

Under the optical microscope, a cracked, black coal tar pitch epoxy coating was observed on un-cleaned *A* (Figure 1). In some areas, the coating had spalled away, and, in the presence of both air and water, red iron oxide scale formed. *A* was then examined by scanning electron microscopy, in a region containing both coating and corrosion (Figure 2). The corrosion has an appearance typical of iron oxide (Figure 3). The coal tar coating (Figure 4) shows some surface deposits. It also shows a typical surface crack in the coating.

Elemental analysis of *A* by EDS was unremarkable. Carbon, iron, and oxygen were the major elements present. Minor elements were silicon, aluminum, potassium, magnesium, calcium, sulfur and chlorine. The major elements are from the coal tar coating and steel tank material; the minor elements are likely deposits from the well water held in the tank.

Optical microscopy of *B* showed that the sweep blasting, while incomplete, had removed most of the coal tar coating (Figure 4). Residual red iron oxide was observed, as well as some black regions that were consistent in shape and density with the coal tar coating seen on the un-cleaned piece. *B* was examined in the SEM. The surface was somewhat rough, indicating incomplete sweep blasting. EDS of the area again revealed no unexpected elements.

Spot elemental analysis was performed on an area of sweep blasted *B*, where a cross-section from the pitch coating to the bare steel was visible (Figure 6). Elemental measurements were made at three locations; pitch coating, mid coating, and bare steel. The analysis results are summarized in Table 1. The additional elements detected, likely deposits from groundwater, are silicon, calcium, aluminum, magnesium, potassium, sulfur, and chlorine.

Element	Atomic %		
	Spot 1	Spot 2	Spot 3
Carbon	50.1	33.2	1.7
Oxygen	34.9	31.8	22.6
Iron	0.4	30.1	65.3
Additional elements	14.6	4.9	10.4

Table 1. Concentration of elements found at three different spots on a cross-section of *Piece B*.

At Spot 1, the top of the coating, carbon from the coal tar pitch epoxy was detected. Hydrogen is also likely present, although the EDS technique cannot detect it. At Spot 2, a significant amount of iron was detected, in addition to carbon and oxygen. The ratio of iron to oxygen is approximately 1:1, which suggests iron oxide of the form FeO, a black oxide. The presence of carbon suggests carbon diffusion into the iron oxide. At Spot 3, the primary element present is iron. The oxygen present may be due to debris from the sweep blasting process. A very small amount of carbon is present as well.

*Piece A* is representative of the present condition of this 35-year-old tank and coal tar coating. Its condition is reasonable considering the age and environmental history of the system. With time and temperature fluctuations, volatile organic compounds evaporated from the pitch, causing it to lose elasticity. Cracks in the coating were then initiated and grew in the stiffened coating, as the pitch shrunk due to the loss of the volatile material, and as the steel substrate expanded



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or contracted with changing ambient temperature. Water then penetrated through the cracks to the steel, and formed ferrous oxide (FeO), the iron corrosion that forms in limited-oxygen environments. The corrosion propagated underneath the coating (Figure 7); the corrosion continued underneath the coating, allowing pieces to spall off. The iron, then exposed to oxygen from the air, converted from black FeO to red Fe<sub>2</sub>O<sub>3</sub>.

**Piece B** reveals a second process occurring, that of carbon diffusion. Carbon will readily diffuse into iron, at a rate dependent on temperature. The carbon gradient discovered in Piece B indicates that the carbon diffusion process has been taking place over the 35-year lifetime of the tank. Although the maximum ambient temperature was relatively low (~100° F), the long time allowed significant carbon diffusion to occur, causing surface hardening of the low carbon steel. This diffusion rate was verified by Fick's Second Law.

The goal of sandblasting was to remove the pitch layer, and the top surface of the steel, leaving a clean steel surface for recoating. The increase in hardness, from that of the expected low carbon steel material, to a high carbon steel of around 2.5%, resulted in exceptionally low material removal rates by sand blasting.

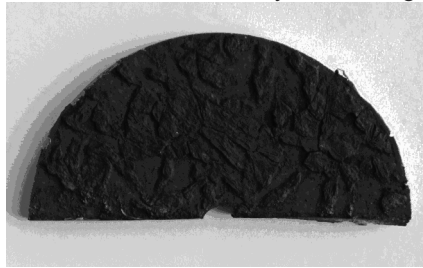


Figure 1. Water tank specimen, **Piece A**, no cleaning.

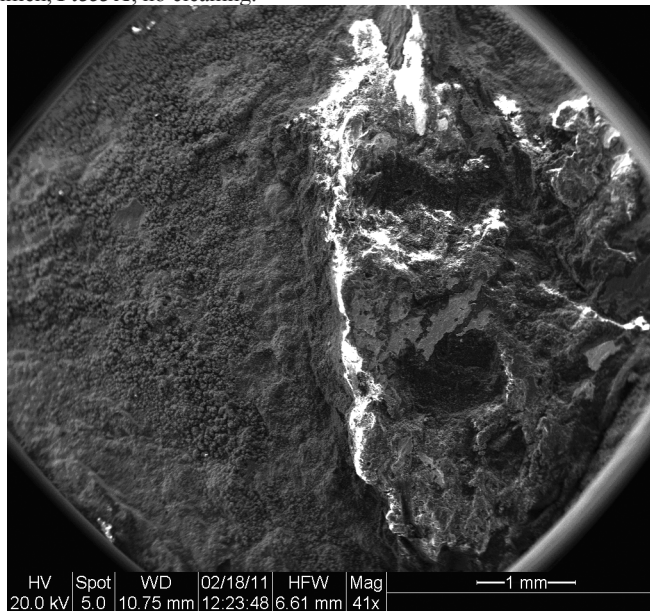


Figure 2. Electron micrograph of **A**, in a region with both red iron oxide corrosion and pitch epoxy coating.

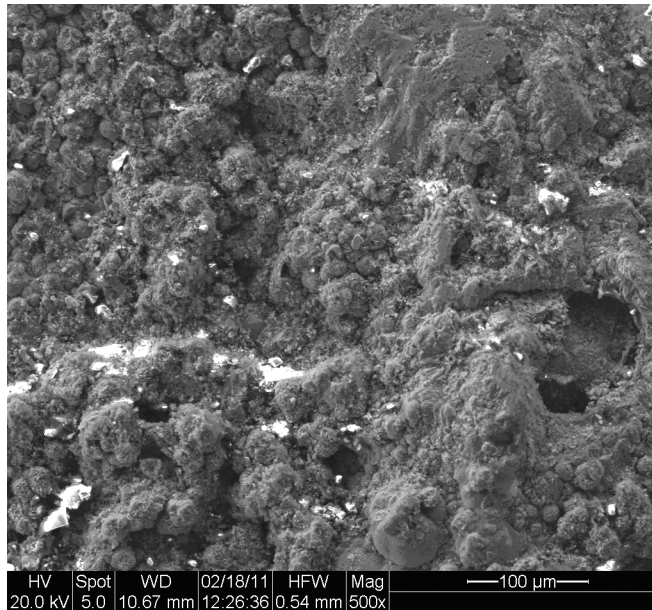


Figure 3. Electron micrograph of corrosion from *A*. The bubbles are typical of rust; EDS analysis confirmed the composition of the rust to be  $Fe_2O_3$ .

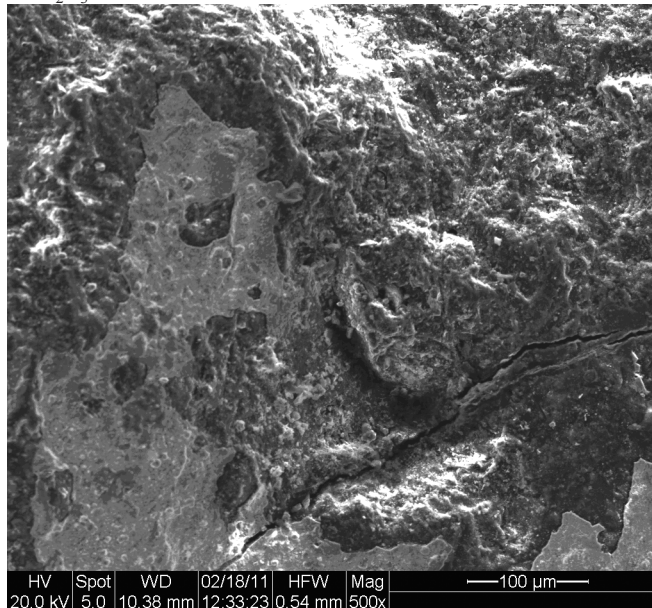


Figure 4. Electron micrograph of the pitch epoxy coating from *A*. The light areas are surface deposits. The crack is typical of those found in the coating.

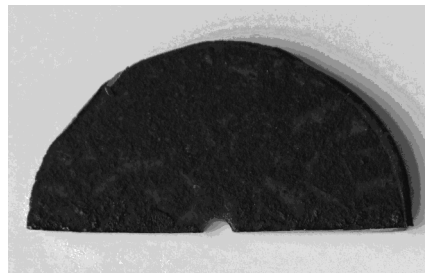


Figure 4. Water tank specimen, *Piece B*, sweep blasted.



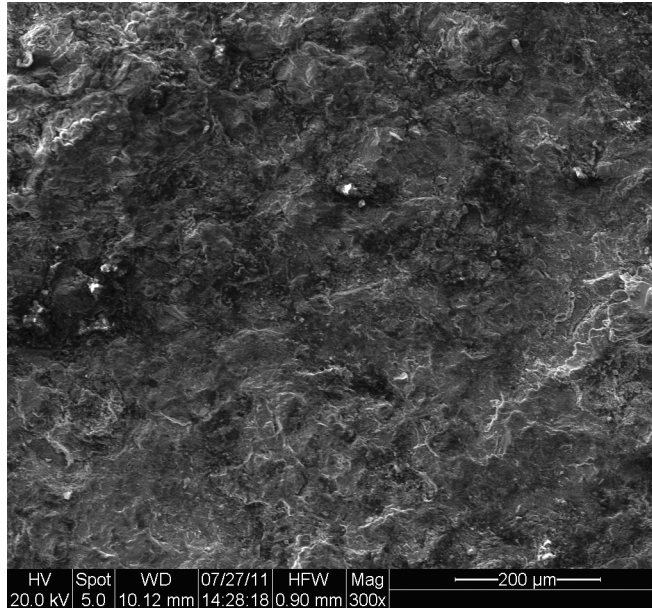


Figure 5. Electron micrograph of **B**. The rough surface is a result of sweep blasting with steel abrasive, which did not penetrate to the steel substrate.

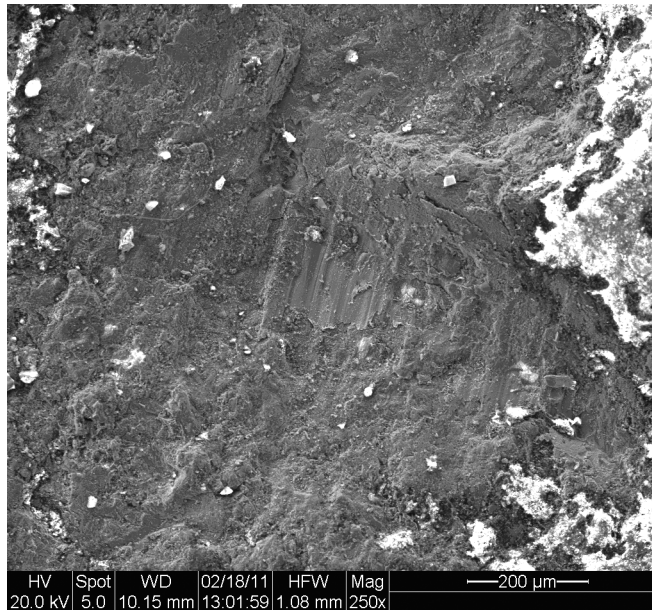


Figure 6. Area of EDS analysis.

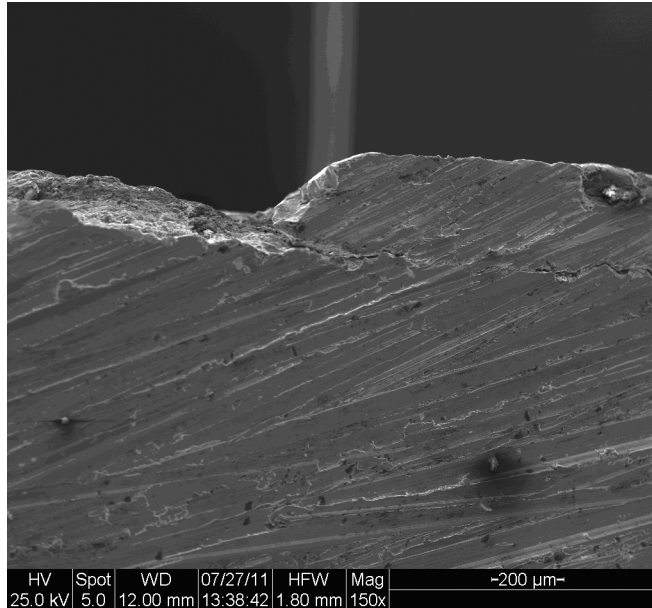


Figure 7. This cross section shows the propagation of corrosion beneath the coating.  
**Diffusion of Carbon in Steel, Oxidation, Corrosion**