

Copper Tube Pitting Corrosion: An Integral Approach*

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The Variables. Corrosion specialists and recent metatechnological research agree, pitting corrosion chemistry, causation and mitigation is complex and multifactorial involving the following interdependent electrochemical and physical variables.

- A. **Oxidation:** dissolved gasses *i.e.* oxygen, carbon dioxide, hydrogen sulfide and the sulfur reducing bacteria that produce it. Aggressive waters typically contain over 3 mg/L O₂, 25 mg/L CO₂, 15 mg/L chloride, 17 mg/L sulfate.¹
- B. **Acidity:** pH, alkalinity, dissolved carbon dioxide as carbonic acid (H₂CO₃).
- C. **Electrical (Galvanic) Action:** TDS (total dissolved solids). The metal ions in high TDS conduct electrical current. Low TDS (low alkalinity) cannot buffer or neutralize the acidity present. Thus both high and low TDS waters are aggressive. Other cathodic anomalies include electrical currents from dissimilar metal pipe fittings and other sources, and protective sacrificial anodes in hot water heating equipment which in the presence of high TDS and iron or manganese may produce hydrogen sulfide H₂S and black or red particulate corrosion byproducts.
- D. **Physical Factors:** Water temperature, velocity or flow rate, pressure, system design (hydraulics, electrically incompatible materials, flow rates), copper tube annealing impurities and other manufacturing defects. An integral approach to corrosion requires an ongoing awareness of the relationships among the variables of these four categories. The common view of corrosion as simply a function of pH and calcium carbonate saturation as expressed by the Langlier Index is simplistic, failing to integrate other key variables, particularly dissolved CO₂ and O₂, as we shall see.

Causation. Therefore, metal corrosion is electrochemical, deriving from the flow of current between electrodes—the anodes (negative) and cathodes (positive) between metals or on the interior or exterior surface of a single metal tube. Corrosion occurs at the anode. CO₂ is a cathodic depolarizer moving electrolysis toward the threshold for pitting attack.

I have come to believe that the inherent resistance to corrosion of copper tubing is the result of an initial oxidation attack on new copper that forms a passivating semisoluble cuprous oxide film (Cu₂O) on the interior of the tube that inhibits further attack. Industry experience demonstrates that a water with pH between 7 and 7.7 may be corrosive. Why? In addition to hot water dissolved oxygen (DO) we must also look to cold water dissolved CO₂—carbonic acid—which at levels above 25 mg/L, even in the above neutral pH range, is aggressive. Carbonic acid H₂CO₃ dissolves the critical protective copper oxide film exposing the base metal interior surface to further attack.¹ Flow rates greater than 4 fps and water hammer effect may prevent or remove this passivating layer.

When CO₂ dissolves in water, hydrogen ion concentration is increased, pH is depressed and corrosive carbonic acid H₂CO₃ is produced. By this reckoning then, the relative rate of copper tube pitting corrosion is proportional to pH where solubility and subsequent loss of the initial Cu₂O protective film increases with pH values below 8 (but also above 9).

The Langlier Saturation Index. Langlier measures the pH change required to bring calcium carbonate CaCO₃ to saturation equilibrium where it is neither dissolved nor deposited (LSI=pH-pH_s). This state is expressed as an LSI value of zero or neutral as to scale deposition/dissolution chemistry. LSI is an index of CaCO₃ solubility or tendency to scale, not of corrosivity. Why then is LSI a reliable, if imperfect measure of a water's corrosive potential? It is perhaps not generally appreciated that negative LSI values increase solubility of the passivating cuprous oxide layer, dissolving it along with CaCO₃ scale and exposing the copper base metal to further oxidation attack. Positive LSI values tend to precipitate CaCO₃ creating non-corrosive but problematic hard water scale.²

Contrary to some industry opinion, hard water scale is not effective in preventing pitting corrosion in copper tubing. At the varying temperatures and flow rates of residential, commercial and industrial water environments deposition and maintenance of a uniform passivating scale is stochastically, if not absolutely precluded. Scale serves only to obstruct line surfaces with calcium deposits. Softening then removes such deposits without contributing other corrosion factors, such as low TDS. Unlike corrosive naturally soft low TDS waters which lack the TDS to buffer acidity, water softened by cation exchange does not demineralize the water and alters none of the electrochemical variables that cause (or abate) corrosion, *i.e.* TDS, O₂, CO₂ acidity, alkalinity, temperature, conductivity.¹

Mitigation. EPA OCCT and WQA control methods include calcite/magnesium oxide acid neutralization wherein insoluble carbonates in the sacrificial limestone media combine with the carbonic acid H₂CO₃ to form benign soluble bicarbonates.³ Note hardness, alkalinity and pH are all increased. The offending H₂CO₃ cannot exist in waters with a pH above 8.3. Other treatment methods include degasification with oxygen scavengers (non-potable water), soda ash feed to neutralize acidity, and polyphosphate or sodium silicate feed (hot water) to coat and passivate the exposed interior surface of the copper tube and to sequester dissolved metal ions (*e.g.* iron, manganese, calcium). Maintain pH at less than 8.4, total alkalinity between 60-140 mg/L, DO below 0.5 mg/L and, if possible, water temperature below 125°F. In high TDS replace magnesium anodes.

¹ Similarly, the corrosion byproduct zinc carbonate protects galvanized pipe from further corrosion attack. www.corrosion-doctors.org; www.nace.org; www.wqa.org; www.hydratechnm.org; www.watertechonline.com.

² For the limits and paradoxes of LSI, and suggestions for an incipient corrosion index that includes the variables of dissolved CO₂ and O₂, see the unedited article below.

³ H₂CO₃+CaCO₃→ Ca (HCO₃)₂