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OCCURRENCE AND CONTROL OF CORROSION IN COPPER WATER TUBE SYSTEMS

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ABSTRACT

Copper water tube systems have had a long and successful application history. On rare occasions, however, corrosion-related failures have occurred due to aggressive water, defective workmanship, inappropriate materials selection or improper system design or operation.

This paper describes the various North American and some of the European standards to which plumbing system components are manufactured. These include the standards covering: tubes, fittings, solders, fluxes and the general guidelines for the assembly by soldering of copper tube systems.

Also discussed is the responsibility of water purveyors and their consultants to provide non-corrosive waters to their customers.

INTRODUCTION

Copper and its alloys continue to be the dominant plumbing materials for domestic and industrial water systems. This is understandable because these materials develop a protective cuprous oxide layer which effectively passivates the metal and isolates it from the water conveyed. Although copper and its alloys are essentially immune to corrosion, incidents of corrosion do occur.

The forms of corrosion which can occur include: general corrosion[1,2] (cuprosolvency), cold water pitting[1-4], hot water pitting[5], erosion-corrosion[6] and oxygen differential-type concentration cell corrosion.[7]

Depending on the form of corrosion involved, the following simple techniques can effectively prevent its occurrence: appropriate materials selection, proper system design, adherence to industry standard workmanship installation procedures and workmanship practices and effective water treatment.

It is well established that proper water treatment can mitigate cuprosolvency as well as cold and hot water pitting. Erosion-corrosion can be best controlled by proper system design and installation workmanship.

Oxygen differential-type concentration cell corrosion which most often is related to deposits (suspended solids) in the water, can be prevented by filtration of the suspended solids from the water. Alternatively, the suspended solids can be eliminated by mitigating the corrosion of ferrous-base materials upstream of the copper tube system.

NORTH AMERICAN PRACTICE

Copper used in the manufacture of seamless copper plumbing tube may originate in the ore body of open pit or underground mines or from rigidly controlled recycled high grade copper scrap. According to the Institute for Scrap Recycling Industries (ISRI), high grade copper scrap consists of copper wire or other unalloyed miscellaneous material such as busbars, commutator segments or tubing generally having a nominal copper content of 96% or greater.

The ore is crushed, milled, concentrated by flotation, smelted to form a matte, converted to blister copper and finally refined by either the electrolytic refining or electrowinning processes to produce copper cathode. This electrochemical final refining step results in the deposition of virtually pure copper with the major impurity being oxygen.

Electrolytic cathode copper produced to ASTM B115 or high grade copper scrap or a combination of them is then remelted and cast as logs (up to 30-foot long, with diameters up to 12-inches and subsequently sawed into 15-30 inch length billets. These billets are then reheated to about 1500°F and extruded on extrusion presses (whose capacities may customarily range up to 6300 tons) to produce tube shells.

Water Tube

The next operations are tube diameter/wall thickness reductions to achieve the final product sizes desired according to the requirements of Standard Specification ASTM B88 (Alloy C12200). Since this specification was first adopted in 1932, it has undergone numerous but trivial changes. During the extrusion operations on the bull or spinner blocs, the only die lubricants permitted are those which will not leave a greasy residue on the tube surface.

Copper No. C12200 (Phosphorus Deoxidized, High Residual Phosphorus) contains a minimum of 99.9% copper (incl. silver) and a phosphorus range of 0.015-0.040%. While other coppers were permitted in the past, only C12200 is presently recognized. The primary difference among these various coppers rests with their electrical and thermal conductivities, properties which are unimportant for plumbing systems.

Should a soft tube be specified, the next manufacturing operation is an annealing cycle. This enables the tube to be coiled and packaged for eventual uncoiling and installation as service lines in the trench between the underground water main and the and the water meter at either the curb stop or in the home's basement.

The non-destructive eddy current test (ASTM E243) comes next to ensure that there are no outside tube surface defects more severe than those permitted by the specification. The final operation is the permanent (incise) marking and color coding for product identification: Type K - Heavy Wall (green), Type L - Standard Wall (blue) and Type M - Light Wall (red).

Valves, Fittings and Meters

Companion wrought fittings (normally made from Alloy C12200) are produced to ASME B16.22 - Wrought Copper and Copper Alloy Solder Joint Pressure Fittings.

Valves and water meters are typically produced to either ASTM B62 (Alloy C83600) - Composition Bronze or Ounce Metal Castings, ASTM B584 (Alloy C84400) - Copper Alloy Sand Castings for General Applications, ASTM B763 (Alloy C84400) - Copper Alloy Sand Castings for Valve Application or AWWA C700 - Cold Water Meters - Displacement Type, Bronze Main Case and AWWA C800 - Underground Service Line Valves and Fittings.

Solders

A 1986 Amendment[8] to the **1974 Safe Drinking Water Act,**[9] prohibited the use of lead-containing solders for joining copper water tube systems. Acceptable solders presently include 95:5 tin-antimony, several tin-silvers and some proprietary alloys. These permissible solders are identified in ASTM B32 - Solder Metal.

Fluxes

Until recently, nearly all copper plumbing system components were covered by at least one specification. The exception was soldering flux, a product produced by numerous manufacturers to varying degrees of aggressiveness.[10] Not unexpectedly, this culminated in many occurrences of flux-induced pitting corrosion. Pitting attack associated with excessive flux application and/or the use of unusually aggressive fluxes during plumbing system assembly is well established.

Pitting attack is not restricted to the near-vicinity of joints but can occur over extended distances from the joints. Generally, a pitting attack occurs at the periphery of sticky, petrolatum-base soldering flux runs or along relatively narrow bands which are essentially parallel to the longitudinal axes of the tubes/fittings.

Soldering flux-induced pitting attack can be prevented by using industry standard materials when installing copper water tube systems. Fluxes used to assemble copper water tube systems should satisfy the requirements of Standard Specification ASTM B813 - Liquid and Paste Fluxes for Soldering Applications of Copper and Copper Alloy Tube.

Workmanship

Adhering to the general guidelines presented in ASTM Standard Practice B828 - Making Capillary Joints by Soldering of Copper and Copper Alloy Tube and Fittings should prevent many copper tube corrosion problems including flux- induced pitting attack.

In addition to the flux-induced pitting concern, poor workmanship can result in erosion-corrosion. This form of attack is readily recognized by the absence of residual corrosion products on the locally deteriorated surface and the presence of horse-shoe shaped pits. It typically occurs immediately downstream of unreamed cut tube ends, or where there are globules of solder on the inside surfaces, sharp reductions in tube diameter, dents or dings in the tube and other locations where laminar flow has been disrupted and localized turbulence exists.

Often, erosion-corrosion occurs when the water flow makes numerous changes in direction over relatively short distances. As with the approach to overcoming flux-induced pitting attack, workmanship-related erosion-corrosion can be prevented by following the procedures outlined in ASTM B828.

UNITED KINGDOM PRACTICE

During Britain's massive reconstruction of war-damaged housing in the late 1940's, a serious epidemic of pitting corrosion in England was circumstantially associated with the presence of heavy films of carbon inside copper water tube. As a result of Campbell's original and subsequent investigations and reports[11], tube production practices were introduced in British brass mills intended to produce tube that were free from the so-called "deleterious" films in the bore.

Based on the belief by the British tube mills that pitting corrosion was associated with carbon films, tube manufacturers began to introduce cleaning operations designed to remove these allegedly-deleterious films from the bores of copper tubes. Abrasive-cleaning using water-borne alumina or a variety of air-borne abrasives were processes that were widely introduced[12] that were claimed to be effective in removing surface residues.

While it may be scientifically sound to associate the presence of carbon films in the bores of copper water tube with the occurrence of cold water (Type 1) nodular pitting corrosion, the dispute remains among corrosion investigators. Many have maintained that an aggressive water can cause the pitting of copper even in the absence of "deleterious" films and that pitting cannot occur without exposing the tube to an aggressive water.

EUROPEAN PRACTICE

European copper water tube producers employ two manufacturing methods. The first is essentially the same process as used in North America. The second uses a proprietary process for producing a carbon-free tube bore and whose product is marketed under the registered trademark SANCO[R].

Baukloh[13] reported that of all corrosion failures experienced in continental Europe, 80% were associated with the annealed temper product because the annealing operation is where the residual die lubricant can be cracked to carbon.

From the pilger mill, tube is passed onto spinner blocs, where after a number of drawing passes, it reaches its final dimensions by close control of the lubricant and by use of drawing dies optimally designed to avoid the formation of insoluble carbonaceous films on the inner surface.

At its final size, the tube bore is internally cleaned with a suitable solvent to achieve a maximum residual surface carbon content of 0.20 $mg/dm.^2$ Exactly what this solvent is has not been disclosed. Following this solvent washing, the tube is passed through a continuous annealing line whose speed as well as ambient internal oxygen content have been optimized for each dimension.

In the annealed temper, the tube is characterized as having an oxidized internal surface free of any "deleterious" films. Despite the claims that use of SANCO(R) tube has resulted in the almost total elimination of copper water tube corrosion, it is known that both annealed and half hard (drawn) temper copper water tube are still subject to occasional cold and hot water pitting corrosion and blue water (cuprosolvency) concerns.

Recent investigations published by the Urban Water Research Association of Australia have shown that cuprous oxide films having p-type semiconducting properties are more corrosion resistant than such films having n-type semiconducting properties. Those investigators found that the cuprous oxide which forms in the bore of the tube during certain annealing procedures is a p-type semiconductor film[14]. With respect to pitting, it has been found that p-type cuprous oxide films are beneficial while n-type cuprous oxide films are detrimental. Reportedly, the desirable p-type cuprous oxide film can also be formed by exposing copper to dilute hydrogen peroxide solutions.

THE WATER PURVEYOR'S RESPONSIBILITIES

Water utilities and their consultants have no responsibility to ensure that either residential or commercial copper water tube installations (residential or commercial) comply with local community building codes. However, they are responsible for ensuring that the water distributed to these installations is not unacceptably corrosive to the materials conveying it.

Prudent plant operations ensure that the water distributed will provide a product at the faucet which complies with all the requirements of the **1974 Safe Drinking Water Act**[9] and its subsequent amendments.[8,15]

Numerous U.S. water utilities have acknowledged that the solution to overcoming pitting corrosion has been to treat the aggressive water with additions of lime, caustic soda, soda ash, sodium silicates or certain phosphates.

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