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Understanding EPA/NMED Secondary Water Contaminants

pH: pH denotes “potential of hydrogen” and is a measure of hydrogen ion activity or concentration—expressed in gram atoms per liter—of the intensity of acidity or alkalinity of a solution. The pH scale ranges from 0 to 14 with a neutral value of 7. pH values greater than 7 indicate alkaline solutions where intensity of alkalinity increases exponentially as pH values become greater. pH values less than 7 indicate acid solutions where intensity of acidity increases exponentially as pH values become lesser. It is important to remember that pH is an exponential function. A pH value of 5 is 10 times more acidic than a pH of 6, 100 times more acidic than pH 7 and 1000 times more acidic than pH 8. High or low pH values are problematic for the following reasons:

- * High pH may cause a bitter taste to drinking water.
- * High or low pH may cause TCLP leaching toxicity from pipe scale and from copper and galvanized (lead) plumbing.
- * High pH causes alkaline hard water scale in plumbing and appliances, increasing replacement and repair. High pH reduces the efficacy of disinfection strategies resulting in increased chlorination and longer contact times which raise disinfection costs.
- * Low pH causes pitting corrosion in copper plumbing.

The EPA and NMED Secondary Maximum Contaminant Level (SMCL) for pH is 6.5 to 8.5. Low pH may be neutralized by calcite magnesium oxide feed. High pH may be adjusted by citric acid feed.

Conductivity: Conductivity or specific conductance is a measure of electrical conductance in a solution at 25°C and increases with total dissolved solids (TDS), electrolytes, ions or salts. High TDS makes water an efficient electrical conductor that promotes corrosion. High TDS may impart problematic taste and odor to a water, and causes mineral scale deposits in plumbing and appliances. In New Mexico, where calcium is the primary cation in natural waters, water hardness is directly proportional to TDS. Multiply specific conductance by 0.7 to estimate TDS. EPA and New Mexico Environment Department (NMED) recommend a conductivity limit of 1000 microSiemens per centimeter (uS/cm) in order to avoid economic and aesthetic problems. Conductivity is reduced by lowering TDS.

Total Dissolved Solids (TDS): The EPA SMCL or action level for TDS is 500 mg/L (ppm). TDS is the total dissolved inorganic water contaminants/impurities (minerals) in solution as ions—cations (+ charge) and anions (- charge). These electrically charged dissolved ions, when concentrations are high (water with high mineral content) make water an effective electrical conductor thereby causing galvanic corrosion in copper or galvanized plumbing. Low TDS or deionized water (no TDS) has a high electrical resistance and is a measure of a water’s purity. This water is also corrosive due to the lack of alkalinity (carbonates, bicarbonates, hydroxides or bases). It is this alkalinity that buffers or neutralizes the aggressive (corrosive) acid (dissolved carbon dioxide) present in such high mineral content waters. Dissolved cationic solids include calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), iron (Fe^{++}) and manganese (Mn^{++}) and cause hard water scale damage and expense. They are removed by cation exchange water softening. Dissolved anionic solids include bicarbonate (HCO_3^{-}), Chloride (Cl^{-}), Sulfate (SO_4^{--}), nitrate (NO_3^{-}) and Carbonate (CO_3^{-}) and may cause taste and odor problems. They are removed by anion exchange or by reverse osmosis.

Alkalinity: The EPA regulates alkalinity through its SMCL for TDS (500/mg), and for pH (6.5 to 8.5). Water alkalinity is defined by its capacity to neutralize acid and is caused by carbonates, bicarbonates and hydroxides (bases). Bicarbonates are the predominant cause of alkalinity in water, but phosphates and silicates also contribute. Alkaline water has an acrid taste. Alkalinity is adjusted through control of TDS and pH through reverse osmosis, anion exchange and lime soda ash.

Sulfate and Chloride: The EPA SMCL for each of these anionic dissolved solids is 250 mg/L. High sulfate (SO₄) imparts a fizzy, soda taste and/or a medicinal taste and has a laxative effect. However, low concentrations of both sulfate and chloride add palatability to drinking water. Calcium sulfate (gypsum) ionic concentrations impart an astringent/bitter taste. High chlorides (Cl) impart a salty or briny/brackish taste. Both sulfates and chlorides are dissolved mineral ions and thus contribute to total dissolved solids (TDS) which increases electrical conductivity and thereby corrosivity. These anionic compounds may be removed by reverse osmosis, anion exchange, deionization (demineralization) or distillation.

Fluoride: The EPA Primary Contaminant (health related) MCL for fluoride is 4 mg/L. The SMCL is 2 mg/L. High fluoride in drinking water is a precursor to dental fluorosis and skeletal fluorosis in humans and animals. Horses are especially susceptible (equine bone disease). Dental research indicates that a fluoride concentration of 1 mg/L is optimal. Fluoride exceedences are mitigated by reverse osmosis, anion exchange and activated alumina.

Nitrate: (nitrate nitrogen NO₃⁻): The EPA MCL for nitrate is 10 mg/L. Nitrate is an anionic primary (health related) contaminant resulting from water seepage through nitrate bearing soil, fertilizers, decomposition of animal and human wastes (septic systems, refuse dumps, livestock lots) and natural geologic deposits. Nitrates in ground or surface water may indicate septic or sewage contamination of the water supply. Nitrate nitrogen in concentrations as low as 10 mg/L may cause methemoglobinemia (Blue Baby Syndrome). Infants and small animals are especially at risk. EPA “Best Available Technologies” (BATs) include reverse osmosis, anion exchange and distillation.

Turbidity: The EPA SMCL or action level for turbidity (sediment) is <1 nephelometric turbidity unit (NTU). Turbid, cloudy water is aesthetically objectionable and may prevent disinfectants from removing microbial contaminants. Turbidity is *suspended* organic and inorganic particulate matter. TDS is *dissolved* (ionic) inorganic solids. EPA BATs for turbidity include multimedia filtration (depth filters), coagulation/filtration, ultrafiltration, reverse osmosis and cartridge filtration. Zeolite (Chemsorb®) is an effective filtration media.

Anoxic Contaminants: Iron, Manganese, Hydrogen Sulfide, Iron Bacteria, Methane. The EPA SMCL for iron is 0.3, for manganese 0.05 and 3 TON for odors. Anoxic contaminants are economically and aesthetically objectionable because they cause taste and odor problems, staining and reduced life of industrial, commercial and residential plumbing, equipment and appliances. Hot water heating equipment is especially susceptible.

1. Iron: iron exists in three states: elemental iron, ferrous (clear water) iron (Fe⁺⁺) and ferric (red water) iron (Fe⁺⁺⁺). Ferrous iron is found in well water as a result of carbon dioxide action on elemental iron. Iron remains in its ferrous state in an anoxic (low oxygen) environment underground. Upon natural aeration at the surface ferrous iron oxidizes to ferric ions to create insoluble ferric hydroxide with its characteristic rust color which then precipitates out as rust particles which damage plumbing and equipment. Other forms of these three states of iron include organic or colloidal iron which is quite problematic for treatment strategies.

2. Manganese: Manganese (Mn⁺⁺, Mn⁺⁺⁺) is found less frequently than iron in iron bearing waters and is chemically very close to iron because it occurs in nearly the same states and forms. Oxidized manganese appears as brown or brown-black stains and is more difficult to remove than iron by

oxidation/filtration due to its slower rate of oxidation. Manganese also appears in the problematic organic or colloidal (chelated) form. The colloidal forms of iron and manganese resist oxidation/filtration treatment because they are virus size (0.01 to 0.1 microns), yet insoluble and remain suspended as a very stable colloid without precipitating out of solution in order to be filtered. Manganese greensand or submicron filtration are the BATs here.

3. Iron Bacteria (Sulfur Reducing Bacteria) Iron bacteria are also found in iron bearing waters. They develop as long red-brown or pinkish filaments. As these masses decay and break away as odorous slime slugs they may obstruct plumbing and reduce flow rates. They cause unsightly water discoloration and taste and odor challenges. Iron bacteria exist as numerous species which include *Crenothrix*, *Leptothrix* and *Gallionella* and thrive in hot water systems where iron or manganese and oxygen are present.

4. Hydrogen Sulfide (H₂S) is a gas—the “rotten egg” gas—which occurs in natural and treated waters in concentrations usually less than 10 mg/L (ppm) and is more prevalent in well water. It is obnoxious in taste and odor and is organoleptically detectable in concentrations as low as 0.5 mg/L. Hydrogen sulfide is a weak acid and thus facilitates corrosion. In higher concentrations it is flammable and highly toxic. At concentrations as low as 0.5 mg/L it can foul cation exchange softener resins. H₂S generation is inversely related to flow rate so waste streams with slow rates possess higher levels of H₂S. The most common cause of H₂S is *Desulfovibrio desulfuricans* which is present in human and animal excreta and waste water.

5. Mitigation of Anoxic Contaminants: There are four classes of treatment strategies dependent upon the specific contaminant levels, state, solution pH and possible competing ions. 1. Cation exchange water softening 2. Oxidation/filtration: Oxidation (O₂, chlorine, ozone, potassium permanganate) of manganese dioxide media (Filox®), Greensand, Birm. 3. Submicron filtration, reverse osmosis. 4. Sequestration (polyphosphate, orthophosphate, sodium silica feed). Cation exchange softening with shallow shell technology resins (SST) abate iron up to about 15 mg/L and manganese up to about 5 mg/L. Higher concentrations require oxidation/filtration. Colloidal iron requires greensand or submicron filtration.

Corrosion Control: Pitting corrosion chemistry, causation and mitigation is complex and multifactorial involving the following interdependent electrochemical and physical variables.

- A. **Oxidation:** dissolved gasses, *ie.* oxygen, carbon dioxide, hydrogen sulfide and iron bacteria.
- B. **Acidity:** pH, dissolved carbon dioxide as carbonic acid (H₂CO₃).
- C. **Electrical (Galvanic) Action:** The metal ions in high TDS conduct electrical current. Low TDS (low alkalinity) waters cannot buffer or neutralize acidity. Thus both high and low TDS waters are aggressive. Other cathode anomalies include stray electrical currents from dissimilar metal pipe fittings, and sacrificial anodes in hot water heating equipment.
- D. **Physical Factors:** water temperature, velocity or flow rate, pressure, system design (hydraulics, electrically incompatible materials), copper tube annealing impurities and defects.

An integral approach to corrosion control requires an ongoing awareness of the interplay of these four variables. The common view of corrosion as simply a function of TDS, pH and calcium carbonate saturation as expressed by the Langelier Index is useful, but fails to integrate other key variables, *ie.* dissolved CO₂ and O₂. Dissolved CO₂—carbonic acid—at concentrations greater than 25 mg/L, even in pH between 7 and 7.7 may result in an aggressive water. Moreover, a natural water with dissolved O₂ above 0.05 mg/L is also aggressive. Why? Carbonic acid and dissolved oxygen dissolve the protective copper oxide film (Cu₂O) on the interior of copper plumbing exposing the base metal of the tube interior to corrosion attack.

Corrosion Mitigation: EPA OCCT and Water Quality Association (WQA) control methods include calcite/magnesium oxide neutralization, sequestration (polyphosphate and sodium silicate feed) and reverse osmosis to reduce TDS. Maintain pH between 7.3 and 8.4, LSI between -0.5 and +0/5, alkalinity between 100 and 200 mg/L and TDS less than 500 mg/L. Other treatment methods include oxygen scavengers and soda ash feed to neutralize acidity. Replace copper unions with non-conductive unions, copper tube with CPCV. Use the Langelier Index. PH, TDS and calcium hardness are not sufficient to diagnose aggressive water.

(Visit www.hydratechnm.org for my unedited article on corrosion mitigation and for the limits and paradoxes of the Langelier Saturation Index in predicting corrosion in natural waters.)