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Is the Fluoride in Municipal Water Problematic for you Titanium Equipment?

Author
Marc Cook – Technical consultant / Materials Specialist

Tricor Metals – Wooster OH

Titanium does not have good resistance to fluorides. It is frequently recommended to avoid any fluorides for equipment constructed with reactive metals like titanium, zirconium and tantalum. As a practical screening guideline, 5 mg/L (ppm) is often offered as a practical limit, but I have not been able to find the primary source of this number or technical basis. So the question has been asked, "Should we be worried about lower levels of fluoride, like the levels found in many city water supplies in the United States?".

A little background on fluoride levels in municipal water sources is appropriate first. Around 70% of Americans had fluoridated water as their water source as of 2020. The CDC recommends water fluoridation at a level of 0.7 -1.2 mg/L (ppm), depending upon climate. Around 3.5% of the US population is on water supplies that have naturally occurring fluoride at or above these recommended levels. The current maximum level mandated by the EPA's Safe Drinking Water Act is 4.0 ppm. States are able to set more stringent standards. For example, the upper limit in New York is 2.2 ppm.

Fluoride acts to increase the dissolution of the titanium oxide surface layer and even small concentrations can be sufficient to remove or disrupt the surface layer. Titanium normally depends on a stable TiO_2 passive film. Fluoride, especially as HF or in hot/concentrated/stagnant environments, can dissolve or destabilize that film. Once the film is being chemically attacked, the presence of oxygen or other oxidizing species may not be sufficient to maintain passivity.

The degradation mechanisms that can occur in titanium due to fluoride can vary. However, the most likely types of degradation are:

- Localized corrosion / crevice corrosion — practical concern, especially stagnant hot water and gasketed/flanged geometry.
- General/accelerated corrosion — possible in sufficiently aggressive fluoride/HF environments.
- Hydrogen absorption/hydriding — secondary concern if actual corrosion is occurring, especially with low pH, cathodic conditions, galvanic effects, or elevated temperature.

The amount of corrosion that can occur is dependent upon several factors. Risk factors that increase the risk that corrosion occurs and the rate, include:

- Increasing fluoride concentration
- Decreasing pH (pH of 3.2 is a significant threshold)
- Increasing temperature
- Increasing presence of stagnant water
- Equipment with an increased presence of crevices

At pH values above approximately 3.2, most fluoride is present as F^- rather than undissociated HF, and the aggressiveness increases markedly once hydrofluoric acid forms. However, free fluoride concentration at higher pH's can still destabilize the protective oxide film at reasonably low levels (10's of ppm). The presence of multivalent cations like Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+}, and others can reduce the activity of free fluoride through precipitation or complexation. This can make a given total fluoride concentration less aggressive than the same total fluoride concentration in a low-hardness, low-ionic-strength water. However, the protective effect depends on pH, temperature, cation concentration, competing ions, and whether stagnant crevices allow local chemistry to change.

Many plants choose to do their own pre-treatment of municipal water for use in process equipment. Many treatments, like reverse osmosis and ion exchange resins, reduce fluoride concentration substantially from the water. If a plant intends to utilize water from a municipal water supply as a raw material for a chemical process, a water treatment process to remove fluorides as well as other contaminants is recommended.

The risk of titanium damage due to fluoridated water varies depending upon the circumstances of how it is used:

- Untreated municipal water with fluoride levels below the EPA Safe Drinking Water Act limit of 4 ppm, used at ambient temperature and not mixed with other chemicals is considered to be negligible risk of equipment damage.
- Using untreated municipal water with fluoride levels below the EPA Safe Drinking Water Act limit of 4 ppm for hot applications like equipment boil-outs may cause equipment damage, especially if crevices are present in the equipment or if the water is left in for an extended period and allowed to get stagnant. Coupon testing could be done to determine the extent of the risk if this type of application is planned.
- Using untreated municipal water with fluoride levels below the EPA Safe Drinking Water Act limit of 4 ppm and mixing it with aggressive process chemicals like strong acids increases the chance of equipment damage and is not recommended. Each of the risk factors mentioned above play a role so each individual situation needs to be evaluated, but removal of most of the fluoride with pre-treatment is recommended.

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