Effect of Chlorine on Common Materials in Fresh Water

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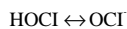
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Long-term corrosion data for common materials of construction from test spool exposures in chlorinated fresh water are reported. Data from the published literature on the effect of chlorine in fresh water on materials are reviewed. Experience with high initial dosages used to sterilize potable water systems is discussed. Case histories of chlorine as an oxidant and biocide on corrosion behavior are given. Guidelines are developed for alloy use in fresh waters.
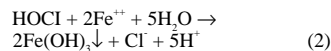
Chlorine is the primary oxidant, other than oxygen (aeration), used in treating cooling water, potable and waste water, and water used in swimming pools. Chlorine is added to potable water as:
- Chlorine gas dissolved in "chlorine water."
- Liquid sodium hypochlorite (NaOCl), the common household bleaching agent.
- Calcium hypochlorite (Ca[OCl]$_2$ 4H$_2$0) granules.

In whatever form added, chlorine comes to equilibrium at pH 7.5 as hypochlorous acid (HOCl) and hypochlorite (OCl$^-$):

$$HOCl \leftrightarrow OCl^-$$

Below pH 7.5, HOCl predominates; above pH 7.5, OCl$^-$ predominates. Chlorine is a very strong oxidizing agent for all metallic and organic species present. The reaction with iron is:

$$HOCl + 2Fe^{++} + 5H_2O \rightarrow$$
$$2Fe(OH)_3\downarrow + Cl^- + 5H^+ \qquad (2)$$

Ferric hydroxide (Fe[OH]3) precipitates out and normally is deposited on the walls of the piping material. The pH is depressed and the chloride ion concentration is increased by the addition of chlorine.

Chlorine also reacts with manganese and other metallic ions present, although to a lesser degree than with iron. Excess chlorine from these reactions with metal ions reacts with ammonia and organic matter, forming chloramine, chloro-organics, and other organic compounds. Chlorine, in excess of the demand from metallic and organic compounds present, is reported as free available chlorine (FAC), or often less precisely as "chlorine residual."[1] Of the common oxidizers, chlorine is the only one that has a residency time long enough to keep potable water disinfected from the treatment plant to point of use. However, chlorine reacts so readily with metallic and organic materials that the residual is consumed within a few days in most waters.

Test Rack Program

Corrosion behavior was studied by the International Nickel Co. (INCO) during the post World War II era until 1982 by placing test racks with 2-in. (5-cm) diameter specimens of different materials in field environments and reporting weight loss, corrosion rate, and localized corrosion

(Figure 1). Details of the data collected in this program, including information concerning the exposure locations and testing methodology; were reported.[2] Figure 2 summarizes the corrosion behavior of various alloys in raw and chlorine-treated fresh water. The important findings and conclusions are given below.

General Corrosion

The corrosion rate of cast iron (UNS F10001) was slightly greater than that for carbon steel (CS) (G10100), but followed the same pattern. Both cast iron and CS exhibited increasing corrosion rates as chlorine increased. The maximum rates were above 5 mpy (0.13 mm/y) even at low concentrations. Materials that corrode at rates >5 mpy generally require good protective coatings or inhibitors and substantial maintenance compared to materials that corrode at 1 mpy to 2 mpy (0.025 mm/y to 0.051 mm/y), which are generally used bare without coatings.

The corrosion rate for aluminum 6061(A96061) and 1100 (A91100) and copper-based alloys, such as 90/10 Cu-Ni (C70600), 70/30 Cu-Ni (C71500), and 8-5-5-5 red brass (C83600), was slightly depressed up to ~2 mg/L chlorine. The rate increased substantially for aluminum 3003 (A93003) at chlorine concentrations of 3 mg/L to 5 mg/L. Copperbased alloy specimens were not exposed at concentrations that were higher than 2 mg/L.

Austenitic nickel cast iron (F41002) and aluminum and copper-based alloys all had low general corrosion rates, allowing them to be used uncoated in most chlorinated waters.

Localized Corrosion

Stainless steel (SS) and nickelbased alloys had insignificant general corrosion rates of <0.1 mpy (<0.0025 mm/y) in all chlorinated fresh waters in these exposures. Corrosion of these materials, when it occurred, was localized.

Aluminum 3003 suffered base plate pitting of just under 10-mil (0.25mm) depth in unchlorinated water and up to 26-mil (0.67-mm) depth in
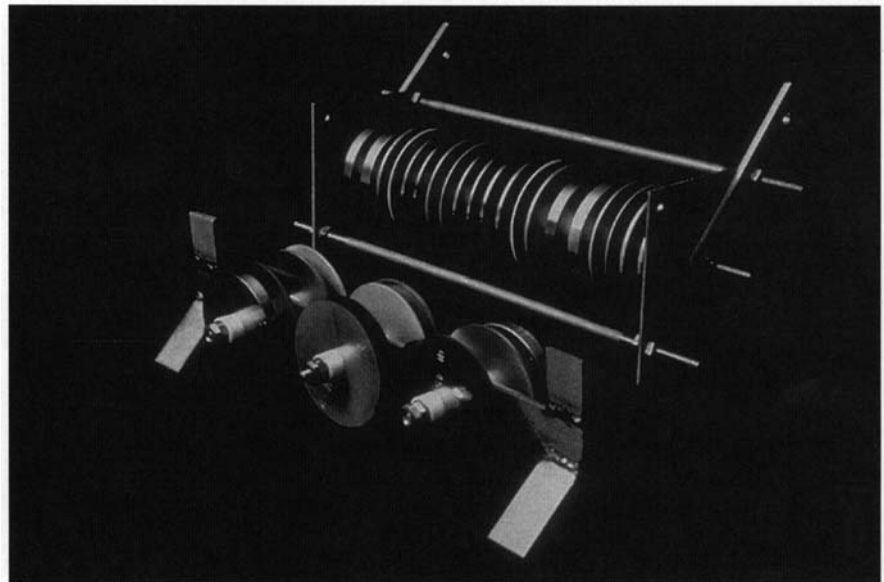

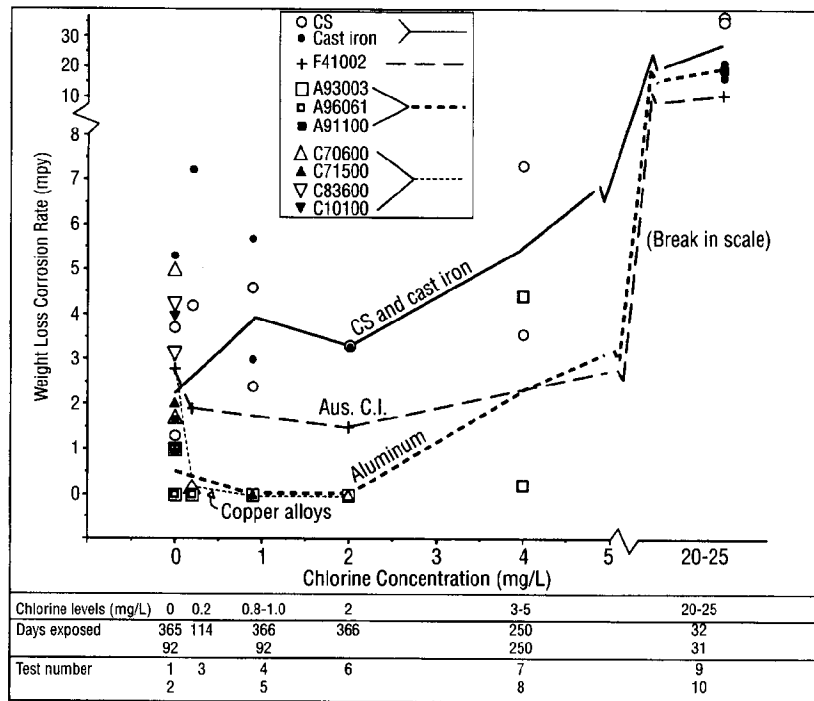**FIGURE 1**
INCO Test Spool Piece.

FIGURE 2
Corrosion Behavior of Various Alloys in Raw and Chlorine-Treated Fresh Water. The four 0 ppm to 2 ppm residual chlorine tests were made at Rochester, New York, but the chlorine content was not reported in the original work. The plant is reporting 23 ppm chlorides currently. The fifth test was made at a Midwest treatment plant at which site the original data included 790 ppm chlorides.

chlorinated waters. Aluminum 6061 was resistant in unchlorinated water but suffered up to 18-mil (0.46-mm) depth of base pitting in chlorinated waters. Both aluminum alloys exhibited 5-mil to 7-mil (0.13-mm to 0.18-mm) depth of crevice corrosion in unchlorinated water and up to 15-mil (0.38-mm) depth in chlorinated water. The low general corrosion rate and the moderate depth of localized corrosion were within ranges that permit use of
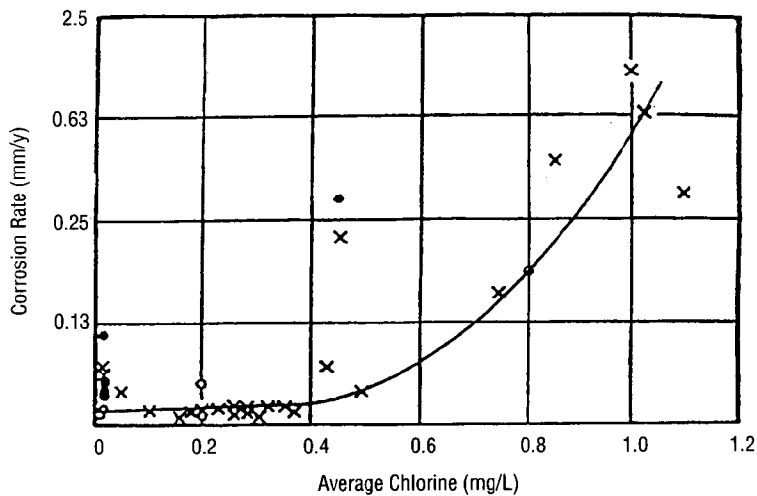
FIGURE 3
Effect of Free Chlorine on Corrosion of Mild Steel.[3]

these aluminum alloys in applications where some surface corrosion and maintenance can be tolerated, such as slide gates.

Types 304 SS (S30400) and 316 SS (S31600) were resistant to localized corrosion in unchlorinated and chlorinated fresh waters up to 2 ppm chlorine. At 3 mg/L to 5 mg/L chlorine, there was incipient pitting of type 304 base plate and 16-mil (0.41-mm) depth of attack in creviced areas. There was no general or localized corrosion of types 304 and 316 specimens in 31- to 32-day exposure at 20 mg/L to 25 mg/L chlorine.

These data indicated types 304 and 316 and the low-carbon grades, types 304L SS (S30403) and 316L SS (S31603) that are used for welded fabrication, should resist long-term exposure in most chlorinated fresh waters. This is in agreement with general experience.

These data also indicated that for long-term, continuous exposure toward the high end of the 3 mg/L to 5 mg/L range of chlorine, type 316L would be a somewhat more conservative choice than type 304L.

Types 317 (S31700); 17-4PH (S17480); alloys 700 (N08700), 20Cb-3* (N08020), and 825 (N08825); and Ni-Cr-Mo alloys C (N10002), B (N10001), G (N06007), and 625

(N06625), were resistant to chlorinated waters with up to 2 mg/L chlorine. Alloys 700, C, and 625 were resistant in waters with 3 mg/L to 5 mg/L chlorine. (Alloys C, B, and G now have been replaced by improved alloys B-2 [N10665], C-276 [N10276], and G-3 [N06985].) Ni-Cu alloy 400 (N04400) suffered severe crevice corrosion in chlorinated fresh waters with 2 mg/L or less chlorine. Alloy 20Cb-3 suffered 5-mil depth of local corrosion in the 3 mpy to 5 mpy exposure.

Literature Data

Many papers have been published on the effect of chlorine on materials in saline waters, but few on the effect of chlorine on materials of construction in fresh water. Boffardi found that chlorine additions of up to 0.5 mg/L had little significant effect on the normal corrosion rate of CS in potable water in 3- to 4-day tests.[3] Above 0.5 mg/L chlorine, the corrosion rate increased rapidly, reaching 0.63 mm/y (25 mpy) at 1.0 mg/L chlorine (Figure 3).[3]

The much lower corrosion rates from the INCO test rack program, compared to Boffardi's data, are believed due to the *reduction* in corrosion rate that occurs in longer exposures with scale formation. Boffardi's data were for 3- to 4-day exposures of bare steel before any significant

film or scale could form. The INCO test rack data were for 30- to 365-day exposures, time enough for films/ scale to form and reduce the initial unfilmed corrosion rates that Boffardi measured.

Disinfection

Common practice is to disinfect potable water systems with 25 mg/L minimum chlorine for 24 h before placing the system in service, after major overhauls, or long outages. AWWA Standard C653, "Disinfection of Water Treatment Plants,"[4] requires injection of sufficient chlorine to produce 25 mg/L minimum chlorine and testing at the end of 12 h to ensure that the concentration has not dropped below 15 mg/L. If below 15 mg/L, the disinfection must be repeated.

Contrary to what might be expected from the long-term data above, short-term exposure to 25 mg/L to 50 mg/L chlorine dosages appeared to be beneficial, not detrimental, to SS performance. Lewus, et a1.,[5] in studies of metal pickup in potable water, reported: "A significant feature of the static exposure tests (at 50 ppm Cl_2 for 24 h) was that the release into water was reduced for the second exposure of the sample in the solution." An important finding was that for continuous exposure at 1.5 ppm to 3.0 PPM Cl_2, metal release rates decreased markedly with exposure time.

In other work, the beneficial effects of short-term exposures to 25 ppm chlorine in reducing metal pickup in ultra high-purity water systems were observed.[6]

An explanation is that these short-term exposures allow chlorine to oxidize some of the unoxidized material in the film, enhancing its corrosion resistance. On the other hand, long-term exposures to more modest levels of chlorine are likely to be detrimental, shown by data from the test rack program.

Other Chlorine Effects

The principal reason chlorine is added to potable water is for disinfection (i.e., control of bacteria harmful to humans). Chlorine also is used in fresh waters for other effects.

*Trade name.

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Precipitation of Iron and Manganese

Chlorine is added in potable water treatment to precipitate iron and, to a lesser extent, manganese so these elements can be filtered out.

Potassium permanganate ($KMnO_4$) often is added, in addition to chlorine, to precipitate manganese more effectively. $Fe(OH)_3$ and manganic hydroxide $Mn[OH]_3$ precipitates form a black deposit on pipe walls. The deposit is not harmful to SS base metal nor to SS welds themselves. However, it has led to corrosion in the heat-affected zone (HAZ) of welds covered by heat-tint scale in fresh waters of low chloride ion content, a location where under-deposit corrosion (UDC) would otherwise be unlikely to occur.[2,7] HAZ of welds that had the heat tint removed with rotating fiber brushes were found to be as resistant as the base metal, although covered with the black deposit.[2] This indicated that types 304/304L and 316/316L in the absence of the heattint scale are resistant to UDC-as would be expected in low-chloride fresh waters.

Control of Microbiologically Influenced Corrosion (MIC)

The addition of chlorine to water systems will control bacteria that are harmful to metals, and in this respect is quite beneficial to the performance of SS and other materials used for handling fresh water. When bacteria harmful to metals are not controlled, or in special situations where chlorine is not fully effective, MIC of steel, cast iron, SS, and other materials may occur.[8] Chlorine can enhance performance by controlling bacteria, or alter environments by precipitating deposits that may degrade performance, or even enter into synergistic effects when Gallionellia bacteria are present.

An interesting study was reported concerning severe localized corrosion of SS in a chlorinated, high manganese, fresh water in which Gallionella bacteria were present in substantial quantities.[9]

Continuous vs intermediate Injection in Cooling Water

Chlorine also is used to treat cooling water for process units and air conditioning, although this use is being increasingly curtailed–sometimes with adverse effects as the following case shows.

Short-term exposure to 25 mg/L to 50 mg/I, chlorine dosages appeared to be beneficial, not detrimental, to SS performance.

Chlorine had been injected into a cooling water system using type 304 heat exchanger tubing for ~8 years with excellent tubing performance. Dosage was continuous but low, 0.5 mg/L to 1.0 mg/L chlorine. Restrictions on chlorine discharge forced a change to intermittent injection: 12 mg/L for 6 min, declining to 0.5 mg/ L to 1.0 mg/L at the end of an hour. Eight years later, the type 304 tubing was uniformly pitted, in some cases to perforation, because of exposure to the higher chlorine residual for extended times.

Chlorine Introduction and Control

Chlorine is available as liquid chlorine in steel containers,[10] as NaOCI solution, as calcium hypochlorite granules, and sometimes as chlorine dioxide (ClO_2). Liquid chlorine is drawn from the bottle through gas flow meters and is normally introduced as "chlorine water," that is, water in which 50 ppm to 100 ppm of gaseous chlorine is dissolved. Liquid NaOCI also may be metered through small metering pumps into water to be treated.

Chlorine water or NaOCI also should be introduced into the center of the pipe to mix thoroughly with the full volume of the water. It should not be introduced at the pipe wall where high concentrations can run down the side of the pipe and cause localized corrosion. It also is important to carefully monitor and control the addition and avoid overdosing. Severe corro-

sion of SS water piping in several Mideast desalination plants resulted from chlorine overdosing.

When calcium hypochlorite granules are used, they should not be broadcast in a manner that permits settling on SS piping. The micro-environment around these granules resting on wet SS piping can lead to serious pitting.

Venting of Chlorine Vapors

Chlorine vapors above chlorinated water have caused general pitting of half-full SS piping of SS ladders just above the water line in clear wells, and on the outside of SS piping in poorly ventilated chambers. Adequate venting is essential to prevent corrosion of SS in the gaseous phase above chlorinated water.

Summary and Conclusions

- The corrosion rate of CS and cast iron increases significantly with as little as 0.5 mg/L chlorine and continues to increase as the residual increases. The rates are sufficiently high to indicate that coatings or inhibitors and maintenance are needed for these materials in chlorinated fresh waters.

- The corrosion behavior of austenitic nickel cast iron is not significantly affected up to 2 mg/L chlorine in fresh water.

- For copper-based alloys, corrosion behavior is not significantly affected up to 2 mg/L in fresh water.

- Aluminum alloys suffer measurable general corrosion and localized corrosion in raw and chlorinated raw water, but not enough to preclude their use for applications where corrosion and maintenance can be tolerated.

- Chlorine has beneficial effects on the corrosion behavior types 304/ 304L and 316/316L:
    - Additions can limit bacterial activity that, in the absence of chlorine or other biocides, might lead to MIC.
    - Initial short-term 25 mg/L to 50 mg/L dosages for 24 h for disinfection appear to enhance the resistance of the normal protective

- Long-term corrosion test spool data in chlorinated fresh waters with up to 5 mg/L chlorine support the widespread use of SS in municipal waste water and potable water treatment plants, fresh watercooled condensers and heat exchangers, swimming pools, and other similar fresh-water applications.
- For applications in which chlorine concentrations are expected to be in the 4 mg/L to 5 mg/L range for much of the time, type 316L would be a more conservative choice compared to type 304L.
- More highly alloyed SS and chromium-containing nickel-based alloys are not corroded in waters with up to 5 mg/L chlorine. However, Ni-Cu alloy 400 can suffer severe crevice corrosion in mildly chlorinated fresh water.
- Heat-tint scale from welding SS should be prevented or removed. Chlorine injection into raw water results in precipitation of insoluble $Fe(OH)_3$ and manganic and other metallic hydroxides. Crevice UDC or MIC can occur in HAZ of welds that are covered by heat-tint scale in low chloride waters in which iron manganese deposits cover the weld area.
- Other precautionary measures associated with chlorine additions include injecting in the center of the pipe, avoiding overdosing, and venting moist chlorine vapors from confined areas.

Acknowledgment

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