August / août
17 - 20, 1986
Toronto, Ont.

25th ANNUAL CONFERENCE OF METALLURGISTS - 1986
25è CONFÉRENCE ANNUELLE DES MÉTALLURGISTES - 1986

H_2O: Nickel's Contribution to Distilled Water, Dams, and Condensers

Arthur H. Tuthill, P.E.
Consultant to the Nickel Development Institute
Tuthill Associates Inc.
Riverside, CT, U.S.A.

ABSTRACT

Nickel alloys are used extensively in the production, handling and treatment of high-purity, natural and waste waters. The corrosion resistance of these alloys in various waters is examined. Examples of nickel's contribution in applications ranging from hospitals through large scale dams, municipal treatment plants and power plants are provided.

HIGH-PURITY WATER APPLICATIONS AND CORROSION

When it was decided to embark upon large nuclear plant construction, a new engineering requirement arose. It was necessary to limit the total dissolved solids (TDS) to an order of magnitude less than in the most pristine fresh waters.

The limit of lppm TDS decided upon was so far below the solubility of most common materials in water that a new phrase, *hungry water,* was coined to describe the corrosiveness of lppm TDS high-purity water.

Water is such a good solvent for nearly all materials that at this artificially depleted level it will leach silica out of glass, leaving a frosty or etched appearance.

Few materials, other than stainless steel, can contain lppm TDS water without losing some species to the water and increasing TDS. Clean stainless steel can hold lppm water without a measurable increase in TDS over long periods of time. This ability to keep high-purity water just that – high purity – is a major reason that stainless steel has become the standard material of construction for nuclear power plants.

The ability of stainless steel to hold high-purity water is due to the highly protective, tenacious and self-replenish-ing nature of the chromium oxide film that forms on stainless steel. The film is so thin as to be transparent, so readily formed that when scratched it reforms instantly in air or water, as long as there is any oxygen present.

Figure 1 is a picture of a nuclear power plant with the containment dome in the background. *Figure 2* is a schematic diagram of a nuclear power plant. The high-purity water is required in the primary reactor-to-steam generator circuit in order to minimize the buildup of radioactivity in this circuit. Inconel 600, which also keeps high-purity water's high purity, is used in the steam generator.

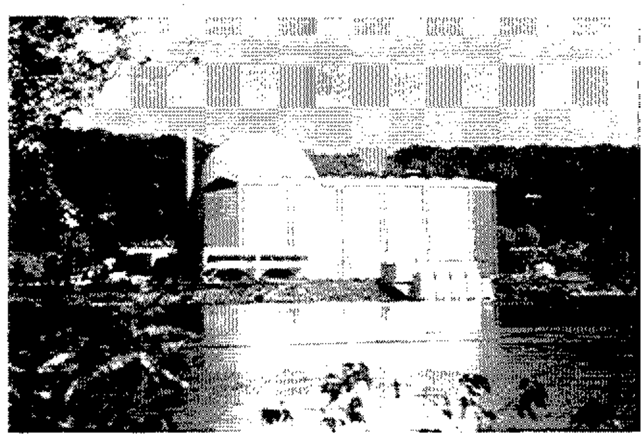


Figure 1: Nuclear power plant

The condenser, which is outside the nuclear circuit, is tubed with high-molybdenum stainless steels such as ALEX, with copper alloys C70600 and C71500, or with titanium – depending upon local conditions and preferences.

Figure 3 shows a 120-ton AISI Type 304L stainless steel, heavy-wall pressure vessel for a nuclear plant under construction. Note the man on the far wall inspecting the vessel. *Figure 4* shows some large CF8M centrifugal-cast flowmeter bodies for a nuclear plant.

Nuclear plants are not the only users of high-purity water. Pharmaceutical plants, biological laboratories, and hospitals also require dependable supplies of high-purity water.

Figure 5 shows an all-Type 304L vapor compression distillation unit produced by Mechanical Equipment Company for hospitals and laboratories. This unit, which is fabricated to the same exacting cleanliness requirements as nuclear power plants, provides hospitals, pharmaceutical plants and biological laboratories with the lppm TDS they require.

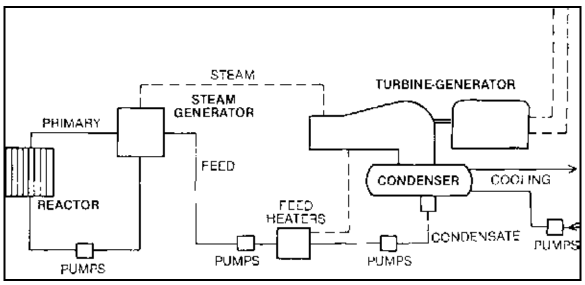


Figure 2: Flow diagram - nuclear plant

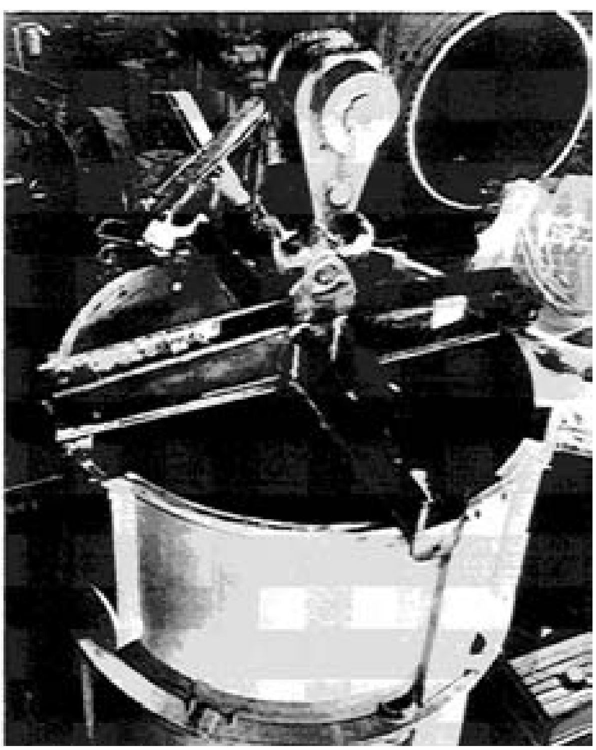


Figure 3: 120-ton Type 304L nuclear pressure vessel

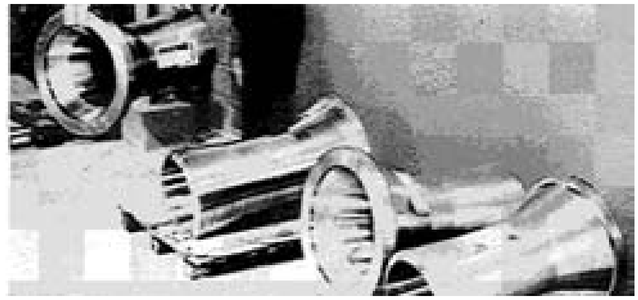


Photo courtesy Wisconsin Centrifugal, Inc.

Figure 4: Four CF8M centrifugal-cast flowmeter bodies – nuclear plant

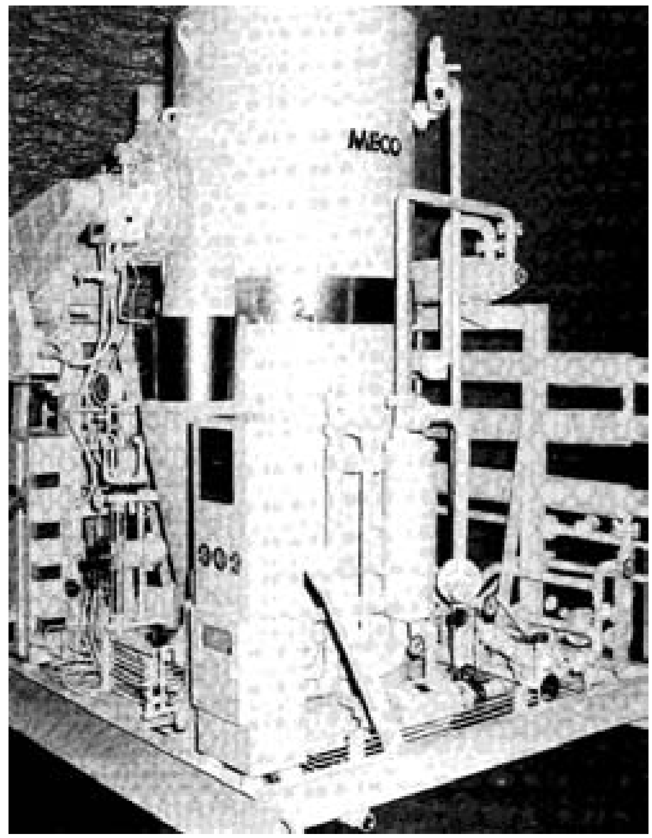


Photo courtesy Mechanical Equipment Company

Figure 5: Vapor compression high-purity water distillation plant.

HIGH-PURITY WATER PROBLEMS

Both nuclear plants and high-purity water distillation units must be fabricated to strict cleanliness standards. It is necessary that all surfaces in contact with high-purity water be entirely stainless steel, free of embedded iron, oil, grease, dirt and other imperfections.

ASTM A380 identifies practical ways in which iron contamination can be minimized in fabrication, removed in post-fabrication clean-up, and tested for in a simple ferroxyl test.

Nitric-HF pickling by immersion, or locally along welds, is the most common and effective method of removing embedded iron, heat tint and other metallic con-tamination of the surface. Organic material must be removed by degreasing in a *non-chlorinated* solvent. Chlorinated solvent degreasing of fabricated stainless steel has led to a number of failures of stainless steel by stress corrosion cracking (SCC) in later service, due to residual chlorides in creviced areas.

At the high temperature, welded Type 304 is subject to chloride SCC especially in the heat-affected zone of welds. The subject has been extensively studied and reported on in the nuclear industry. Welded Type 304L is more resistant and is standard for construction of high-purity water distillation units. The one case of SCC in these Type 304L units the author is aware of turned out to be SCC from the outside, beneath wet insulation.

FRESHWATER CORROSION

The principal nickel-containing alloys used in freshwater are Types 304/304L, 316/316L, precipitation hardening (PH) stainless steels, C70600, and an austenitic nickel cast iron, Ni-Resist. Corrosion rates are shown in *Table 1*.

TABLE 1

Material	Corrosion rate	Chloride limit for crevice corrosion
PH stainless steel	Nil	150 ppm, estimated
Type 304	Nil	150-200 ppm
Type 316	Nil	1 000 ppm, approximately
C70600	0.1-1 mpy	resistant
Ni-Resist	1-3 mpy	resistant

While water does not corrode stainless steel, as it does carbon steel, and to a lesser extent copper alloys . . . when chloride ion concentrations reach 150-200 ppm, Types 304/304L and related non-molybdenum grades are subject to crevice attack under certain conditions.

Table 2 plots the maximum depth of crevice corrosion and shows the percentage of total creviced sites at which crevice attack occurred for Type 304 at chloride ion concentrations from 100 to 1 000 mg / l. Temperatures ranged from 30°-70°F, and exposure periods from 30 to 120 days.[1]

These data indicate that when crevice and water conditions are such that crevice attack of Type 304 may occur in such waters, it is likely to occur only at a small percentage of apparently identical crevice sites. Neither temperature nor length of exposure up to 120 days appear to have a significant effect on the incidence or depth of crevice attack. Removing the mill finish by grinding to standardize the surface finish is shown to be detrimental.

Type 316 specimens exposed in a parallel program were resistant to crevice attack at all but one site in these waters. These data indicate that although Type 304 may be subject to some crevice attack in waters when chlorides are greater than about 150-200 ppm, it has useful resistance up to about 1 000 ppm in services where some maintenance and repair can be tolerated. Above 150-200 ppm chlorides, Type 316 has substantial advantages over Type 304 when better resistance is needed.

FRESHWATER APPLICATIONS

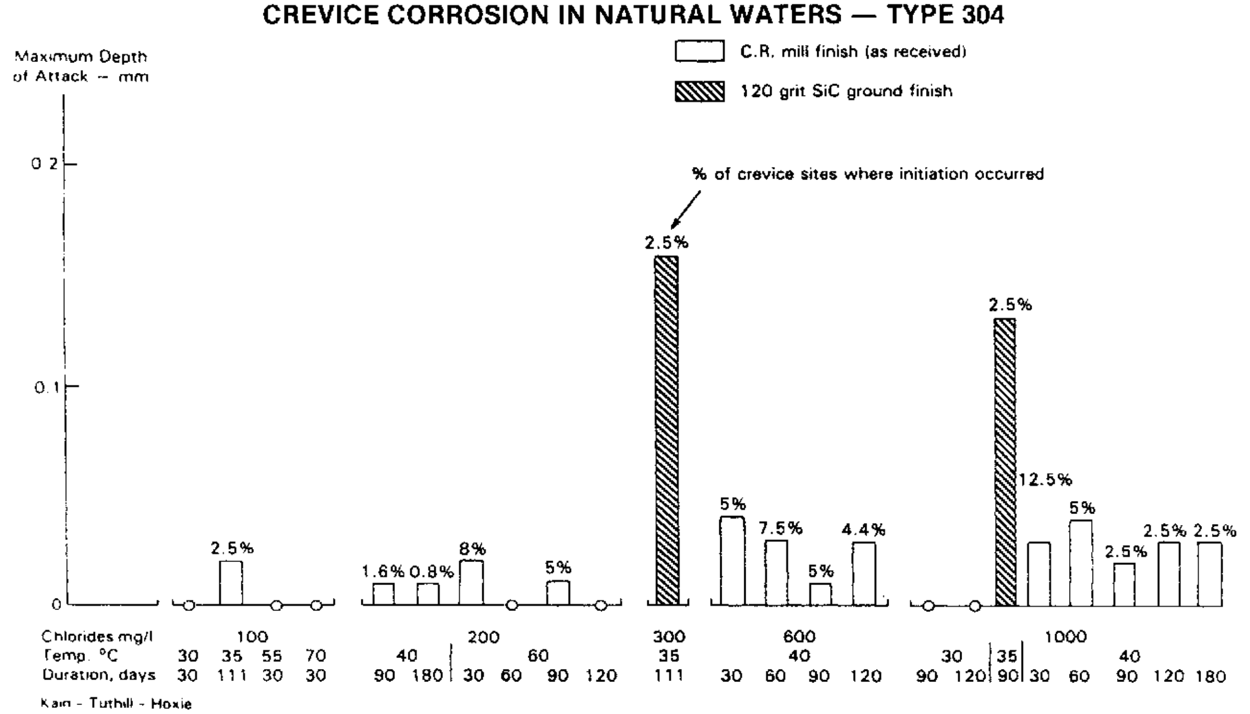
Total dissolved solids are generally in the 20 to 100 range for most natural freshwaters in the United States, although they do range up to about 600 in the lower Colorado River and even higher in many well waters. Chlorides are generally <100 ppm.

Type 304 and 304L are used for freshwater piping and welded fabrication. Both are tolerant of weld defects, surface condition and crevice forming deposits in low chloride content freshwaters. Embedded iron leads to rusty-looking surfaces or rust streaking and is generally removed, more for appearance's sake than for corrosion resistance.

Figure 6 is an aerial view of a modern municipal waste treatment plant. About 1970, waste treatment plants upgraded from galvanized and coated carbon steel to stainless steel, especially in the extensive aeration piping systems these plants use.

TABLE 2

CREVICE CORROSION IN NATURAL WATERS — TYPE 304



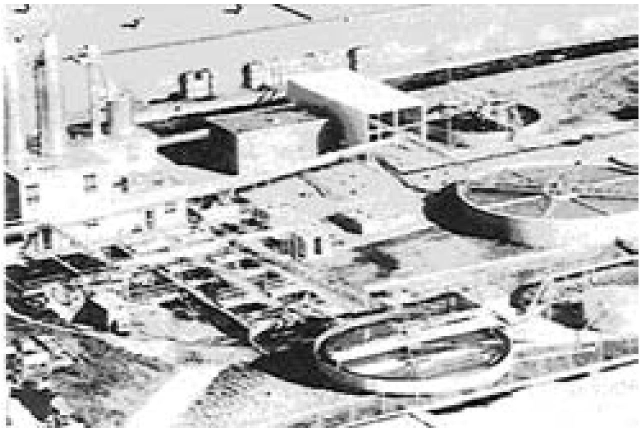


Figure 6: Municipal waste treatment plant

Figure 8: Type 304 aeration piping

Figure 7 shows a Type 304 12-inch aeration pipe conducting air to the Type 304 distribution piping and nozzles shown in *Figure 8*.

Figure 9 shows a Type 304 microstrainer built and installed in a Chicago area treatment plant.

Figure 10 is a Type 304 floating aeration pump for open basin aeration.

Figure 11 is a large water manifold for a plant being fabricated in Brismet's Bristol, TN, shop. Since 1970, both Type 304 and Type 304L, as welded piping and tankage, have proved to be quite successful in the wide variety of waters in this kind of plant in the United States.

Types 304 / 304L and 316 / 316L have also been used in process plant cooling water systems. The regular grades

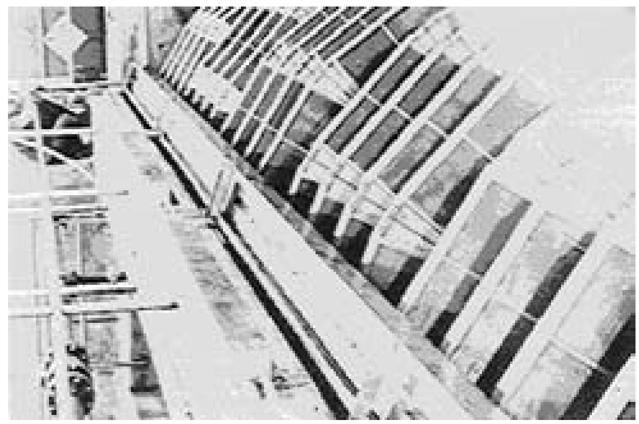


Figure 9: Microstrainer 12 ft. x 30 ft., Type 304 with 0.002-inch Type 316 woven wire cloth

Figure 7: Type 304 aeration header

Figure 10: Type 304 floating aeration pump

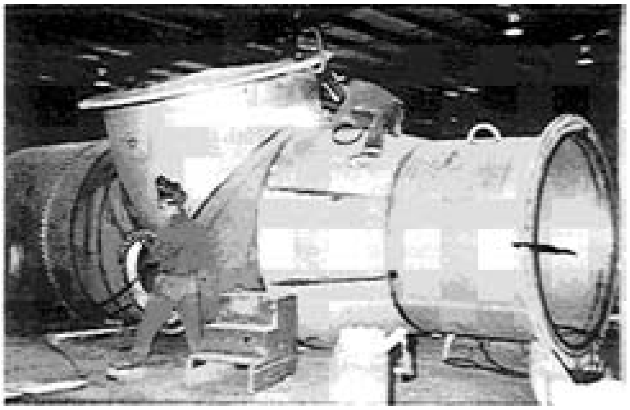


Photo courtesy Bristol Metals Inc.

Figure 11: Type 304 water manifold waste water treatment plant.

are used for tubing and the L grades for welded fabrication. *Figure 12* shows two Type 304L water boxes; *Figure* 13, Type 304 tubing in a power plant condenser; and *Figure 14,* Type 304 tubes in a Type 304 tubesheet. Type 316L is preferred for the higher chloride-content freshwaters.

Inland power plants use Type 304 and C70600 tubing as an alternative to Admiralty. Overall experience with C70600 has been excellent in freshwater, except in some auxiliary coolers with design flow so low that under-sediment corrosion occurred. The experience with stainless steel tubing has been generally good, although there are several situations where problems arise.

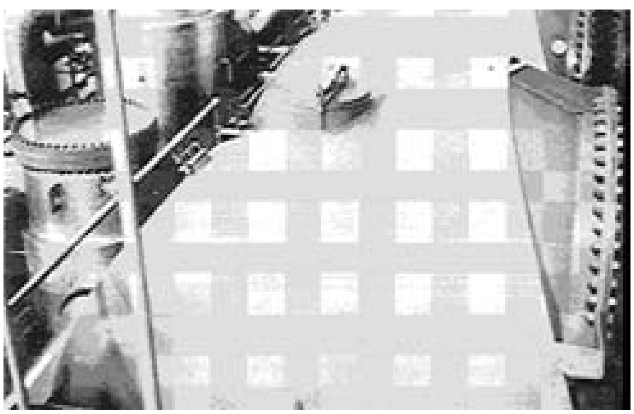


Figure 12: Type 304L waterboxes – power plant

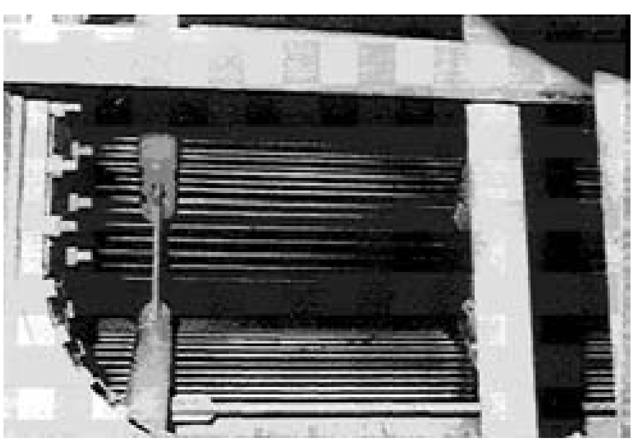


Figure 13: Type 304 tubing - power plant condenser

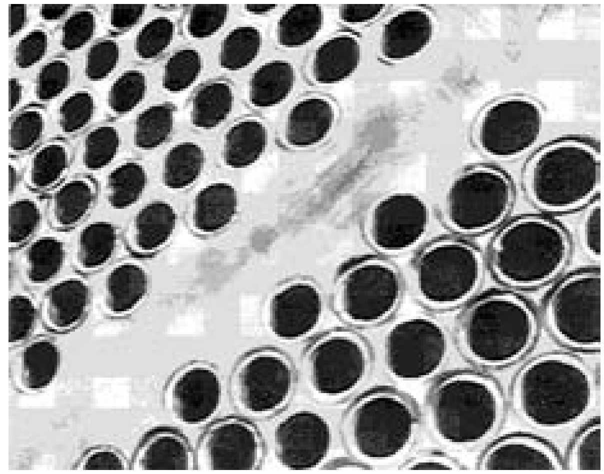


Figure 14: Type 304 tubing and tubesheet - process plant

OTHER USES OF STAINLESS STEELS IN FRESHWATER

Figure 15 shows the common stainless steel drinking fountain where sanitary considerations have made stainless steel the principal material of construction. *Figure 16* is an underwater view of a bather climbing a Type 304 stainless steel ladder in a swimming pool. Stainless steel has been the overwhelming choice for swimming pool hardware. The stainless steel cap screw shown in *Figure 17* is one of the many varieties of fasteners, nails, screws, bolts, and

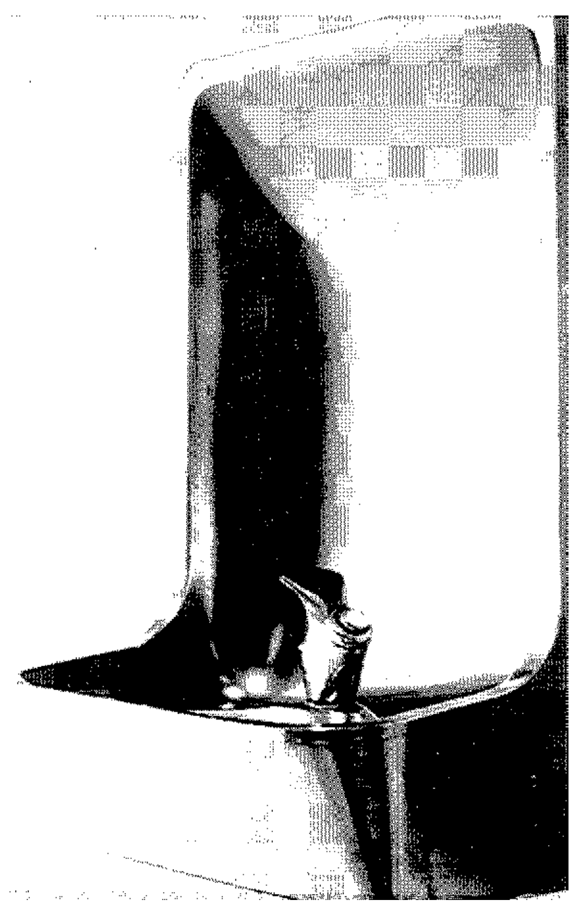


Figure 15: Type 304/CF8 drinking fountain

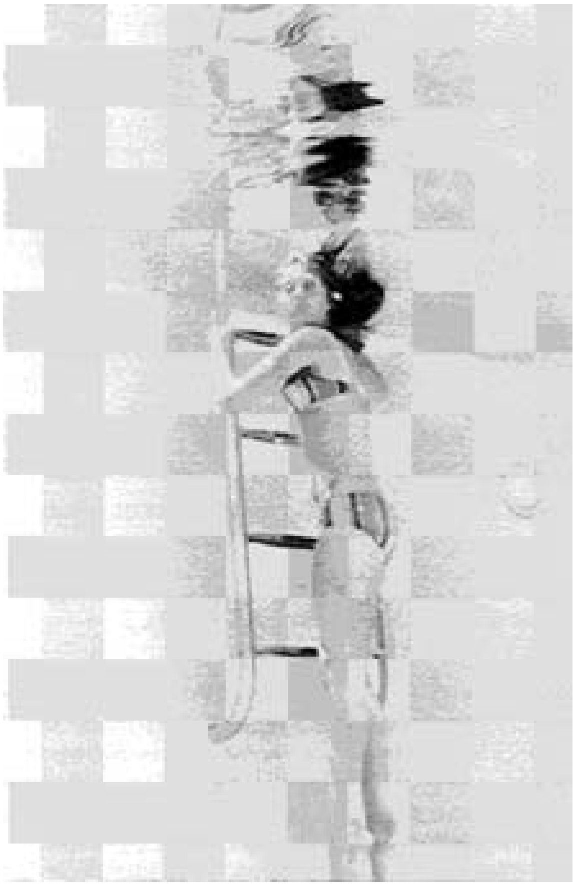


Figure 16: Type 304 swimming pool ladder

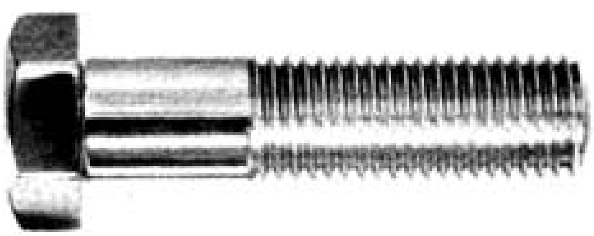


Figure 17: Type 304 cap screw

staples that are used to join carbon steel, aluminum, and nonmetallic as well as stainless steel components used in water-related applications.

FRESHWATER PROBLEMS

Vertical condensers

The chemical industry uses a number of vertical condensers with the hot gas stream to be condensed entering at the top and condensing inside the tubing. The cooling water is on the outside (shell side) of the unit. The water enters at the bottom and leaves at the top.

Noncondensable gases collect under the tubesheet and form a pocket where tube wall temperatures can reach 180° to> 200° F. The water evaporates from the hot outside surface of the tubing in this area leaving behind whatever salts happen to be present in the cooling water. This arrangement is ideal for concentrating chlorides at temperatures where stress corrosion cracking can occur.

Both Types 304 and 316 suffer stress corrosion cracking beneath the top tubesheet in these vertical condensers within several months to a year or so. There is no known threshold limit for chlorides in the cooling water below which SCC of Types 304 and 316 will not occur in such units. The author has experienced SCC of Type 316 tub-ing in vertically tubed units when chlorides in the water were as low as 14 ppm.

A variety of measures are used to cope with this problem.

Condensers and coolers are placed in the horizontal position whenever possible with the hot gases to be condensed on the shell side and the cooling water on the tube side. SCC is not a problem in horizontal units.

Some plants drill through the top tubesheet and install a vent to eliminate the pocket of noncondensables under the top tubesheet. Others use C70600, C71500 or other cop-per alloy, copper alloy/stainless steel bimetallic, higher nickel content austenitic, duplex or ferritic alloy tubing. All of these measures have been successfully applied.

Stagnant and low flow conditions – sediment

When the flow rate drops below about 3 fps in pipe or tubing, entrained sediment drops out and collects in the bottom of heat exchanger tubing, piping, on the lower tubesheet of vertically tubed condensers, on the bottom of tanks and other vessels. If left unremoved for long periods of time, under-sediment corrosion of copper alloys and stainless steels may occur.

Stagnant and low flow conditions – microbiological-influenced corrosion (MIC)

Stainless steel heat exchanger tubing and piping has suffered multiple pitting-type corrosion when water is left standing for long periods or is incompletely drained from the units. Type 304 condenser tubing has failed in freshwater service where chlorides were 50 ppm. and where there were unusually high concentrations of manganese.

Stainless steel tanks and piping have suffered severe pitting-type corrosion, especially near welds, when very low-chloride water used for hydrotesting was not drained and removed from this equipment promptly after testing. Initially it was felt that chlorides were responsible, but attacks persisted even when chlorides were strictly controlled at minimal levels.

It now appears that the role of microbiological organisms may have been underestimated. Several aerobic and anaerobic microbiological species have been found to colonize and proliferate rapidly in some stagnant and slow-moving waters. Nutrients are known to play a major role in colonization and growth of these organisms. Several bacteria, Desulfovibrio (SRB), Siderocapsa (Fe/Mn) and Gallionella (Fe) have been shown to be responsible for unexpected corrosion of stainless steels in freshwaters. Given the difficulty of identifying the role micro-organisms play in corrosion failures of stainless steels, it is little wonder that their role has been somewhat overlooked. Korbin gives an excellent case history-summary of the present state of our knowledge of microbiological-influenced corrosion (MIC) of stainless steel.[2]

Korbin outlines a scenario for MIC in four stages:

1. Attraction and colonization of Fe and Fe/Mn bacteria
2. Concentration of Fe and Mn compounds, particularly chlorides
3. Oxidation (microbiological) to ferric and manganic chlorides (known to be severe pitting corrodents of stainless steels)
4. Local breakdown of the protective film under deposits where the film has already been weakened by oxygen depletion

If these recent findings are correct, then nutrients, temperature and other factors favoring microbiological growth and colonization may be more important in determining the incidence of pitting of stainless steels in stagnant and slow-flowing waters than the other extensively documented and studied aspects of water chemistry. In any event, microbiological organisms appear to play a larger role in corrosion than many have yet appreciated.

DAMS

There is a large variety of functional components in the water control components of dams that depend upon nickel alloys for their proper operation. Ni-Resist, the precipitation hardening (PH) stainless steels and Type 304 are the principal nickel-containing alloys used. The structurals are either cast iron, higher strength (> 40 000 psi) nickel cast iron, fabricated carbon steel, or high-strength, low-alloy steel.

Figure 18 shows some large slide gates in the final stages of fabrication. *Figure 19* shows a portion of the down-stream face of Grand Coulee dam with the gates in place and a stainless steel fish ladder to the left.

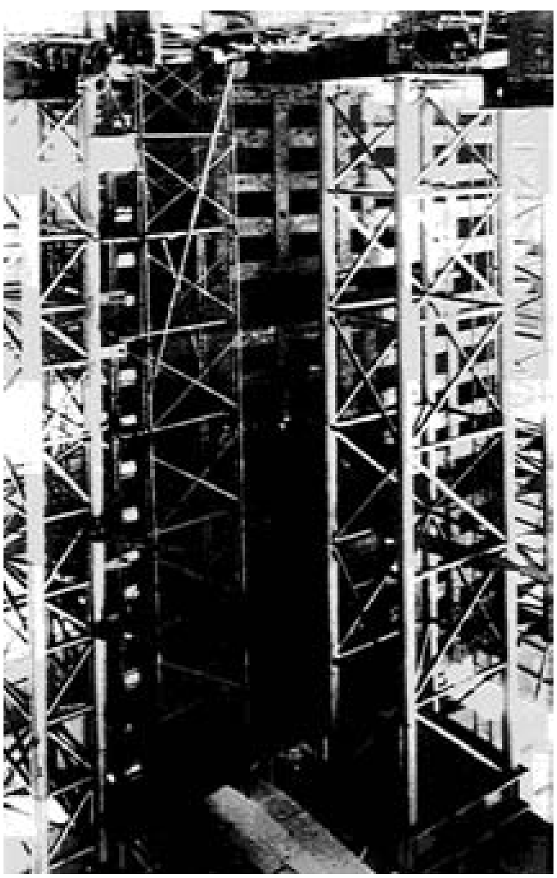


Figure 18: Dam slide gates

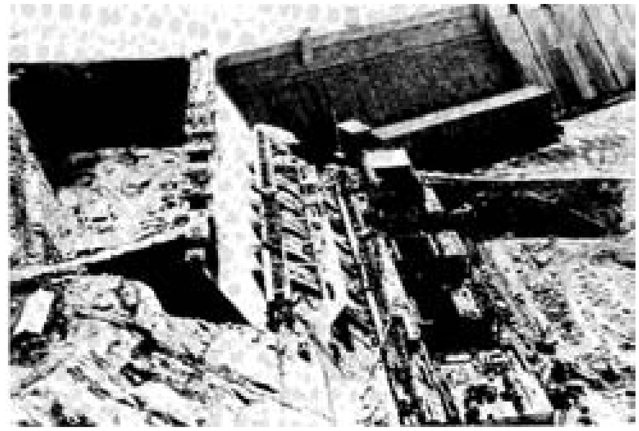


Figure 19: Downstream face, Grand Coulee dam

Sealing surfaces

The sealing surfaces of all water control gates are designed to prevent leakage of water when closed. The sealing surfaces are subject to corrosion and to galling, arid roughening when opened or closed. Type 304 is usually used for one face because its surface will remain clean and free of corrosion for the 50-100 years of design life. The mating surface in large units is usually either Ni-Resist or bronze which will allow the necessary movement during operation without galling the Type 304 face. On smaller units, neoprene is often used against the Type 304 face.

Tracks, rollers and wheels

On large gates, the great forces from water pressure require the gate to be rolled into position. PH stainless steels are used for the heavily loaded components such as wheel rims, rollers and downstream track. Type 304 is used for the upstream track which is not so heavily loaded - track ends and guides, sill and foot plates. Ni-Resist is also used for track.

Guide bars and brackets

These are used to accurately control final positioning of the gates. Clearances are small. Type 304 is used for the guide bars and guide tubes, Ni-Resist for the brackets.

Taintor gates

These large spillway crest gates frequently use clad Type 304 for the gate skin, side seal plates and retainers.

Smaller slide and flap gates

Ni-Resist is used for the frame and leaf. The seal face is Type 304 or Monel 400 if coastal or saline waters are being handled.

Fasteners

Types 303 and 304 are the principal fasteners used.

Valve stems and nuts

Sizes vary considerably. Stems are Type 304 or PH stainless steel. Nuts are Ni-Resist or bronze.

Pumps

CF8, the cast counterpart to Type 304, is used for impellers and Type 304 or PH stainless steel for shafts.

BRACKISH WATERS

Condensers

Brackish waters are usually tidal or high TDS well waters. There are a number of power plants on tidal estuaries. These tidal waters are often fresh (< 100 ppm) most of the year and become brackish or saline only in the late summer or fall when runoff is low. Chlorides may reach 10 000 ppm but 2-4 000 ppm is a more common maximum at most locations.

C70600 is a principal tubing material used in brackish waters. There is limited use of Type 316, substantial use of ALEX, a high Mo austenitic, some use of Sea-Cure, a ferritic; and more recently another high Mo austenitic, 254 SMO, as well as titanium.

While the overall performance of C70600 has been sat-isfactory, problems related to extended startup periods and low velocity continue to be reported from a few locations. Frequent start and stop operations are characteristic of the long extended startup periods of current power plants. Provided the cooling water is kept circulating and a regular cleaning schedule to remove sediment is maintained, few problems with copper-nickel tubing are encountered.

In poorly maintained condensers, decay of organic matter in sediment that remains unremoved for months or even years leads to anaerobic conditions, sulphate-reducing bacteria (SRB) and generation of hydrogen sulphide at the sediment to copper alloy interface. The normal oxide film is converted to a black sulphide film. Although the sulphide film is protective, it is easily disturbed. Multiple pitting-type corrosion can follow. Sediment must be re-moved on a regular schedule based on the amount of sedi-ment deposited in order to prevent under-sediment corro-sion of copper alloys.

In the case of stainless steels, sticky deposits of sediments, grease, crayon marking and adhesive tape on Type 316 tubesheets are all sites where crevice attack has occurred in brackish waters.

BRACKISH WATER
CREVICE CORROSION OF STAINLESS STEELS

Crevice corrosion develops in four stages.

Deoxygenation: The dissolved oxygen in the water is very quickly consumed in a tight stable crevice.

Hydrolysis and chloride buildup: Hydrolysis of the metal ions, particularly chromium, decreases the pH. Chloride ions migrate into the creviced area to balance the charge.

Breakdown of the alloy's protective film within the creviced area: If the pH drops low enough, and the chloride ion concentration within the crevice becomes high enough to reach levels at which the protective film breaks down, then crevice attack begins. If critical values are not reached there is no initiation at that crevice site.

Propagation: Once initiation occurs, propagation can follow. Many factors influence propagation. Two of the more influential factors are the cathodic area outside the crevice and the availability of oxygen to the cathodic areas outside the crevice.

It turns out that crevice geometry is also critical, the smaller and tighter the crevice, the greater is the probability of reaching critical pH and chloride levels. *Figure 20*, from Todd and Oldfield, plots the average crevice gap in microns at which initiation will occur in seawater for a number of common austenitic alloys.[3]

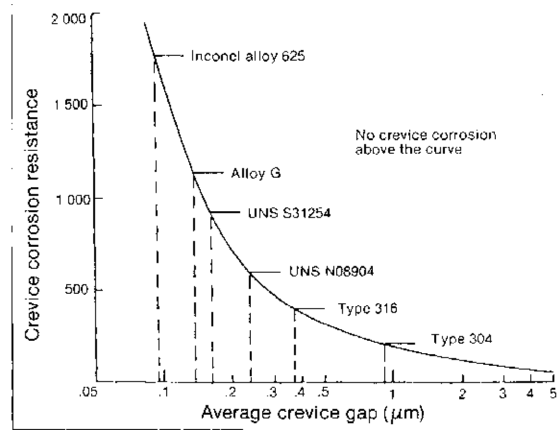


Figure 20: Prediction of crevice corrosion in seawater-Todd and Oldfield

The very tight gap dimension is at the limit of experimental determination. Minor, almost undetectable, changes in the gap dimension have a major influence on whether initiation will or will not occur at any given crevice site. The criticalness of 0.1 micron changes in the gap dimension is undoubtedly responsible for the many variations in crevice attack as reported in the literature.

Crevice attack of stainless steel condenser tubes is rare if the tubes are properly cleaned. Crevice corrosion of the flange faces of stainless steel piping, crevice corrosion of stainless steel tubesheets in rolled joints and under adhesive tape, crayon markings, as well as biological fouling, however, is reported with depressing regularity in brackish waters.

BRACKISH WATERS
REVERSE OSMOSIS

Reverse osmosis (RO) desalination units: Type 316 piping has become the standard material of construction on these units which are most frequently used domestically to purify high TDS well waters. The arrangement is such that the Type 316 piping is joined in a socket or sleeve-type nonmetallic fitting fractionally smaller in diameter. This forms an ultratight crevice.

Although there have been crevice corrosion failures of Type 316 RO piping in domestic well waters, the incidence is not yet to a point where upgrading to a more resistant material has been undertaken by the manufacturers of these units. The frequency with which critical levels of pH and chlorides are reached in the crevices of RO units seems to be low enough to be acceptable to users.

This is a rather good example of the statistical nature of crevice corrosion and the practical aspects of dealing with crevice attack in the marketplace. Immunity is not often required; however, the level of maintenance and replacement must be acceptable to the user.

CORROSIVITY OF WATER

Water itself, even seawater, is not aggressive enough to break down or penetrate the highly protective chromium oxide film on stainless steel.

Kain's polarization curves for Type 304 in seawater at 12°, 28°, and 50° C, *Figure 21*, show the corrosion potential to be well below the pitting potential at normal temperatures.[4] A major shift in potential would be necessary for breakdown and pitting of stainless steels to occur in water. Strong oxidizers and low pH, if present, could lead to breakdown and pitting of the general surface of stainless steels but neither are present in most high-purity, fresh or brackish waters.

Corrosion problems with stainless steel in water services can be traced to tight crevices, sticky deposits, stagnant and low-flow conditions favorable to MIC, vertical condensers, certain galvanic couples, and, most commonly, to embedded iron and other surface imperfections.

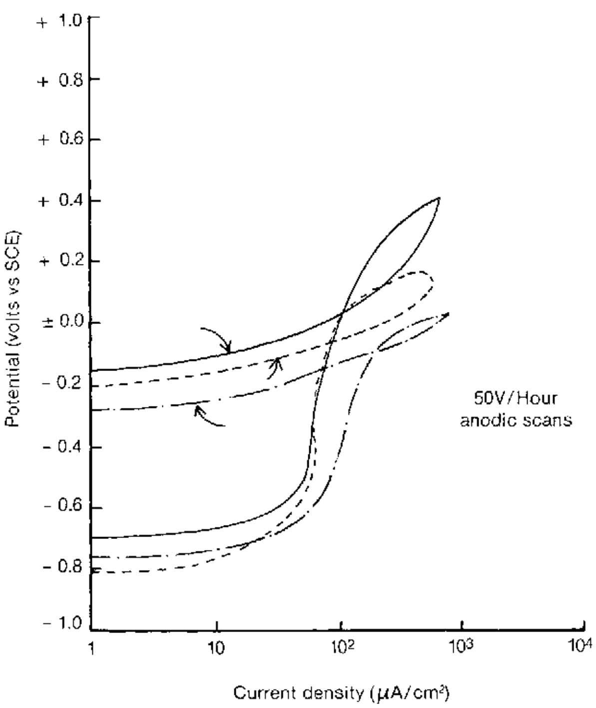


Figure 21: Effect of temperature on cyclic polarization behavior for Type 304 stainless steel in sea-water

SUMMARY

The highly protective nature of the chromium oxide film has made stainless steel a most useful and widely used material for handling high-purity fresh, and brackish waters. Under most conditions corrosion problems arise, not from the water itself, but from surface contamination, tight crevices, stagnant and low-flow conditions favoring MIC, improper fabrication, and certain galvanic couples.

The normal oxide-type film on C70600 has allowed this copper-nickel alloy to give satisfactory service in clean, fresh, and brackish waters. As is the case with stainless steels corrosion problems arise, not from the water itself, but from sediment, stagnant, and low-flow conditions.

The PH stainless steels have given good service in water control equipment where high strength as well as corrosion resistance is required.

Ni-Resist has given good service in water control equipment, especially as a mating surface against stainless steel where wear and galling resistance was required.

ACKNOWLEDGEMENT

The assistance of Inco United States Inc., especially Martin Tennant, in locating and making available the illustrations of the many applications of stainless steels in water services, is gratefully acknowledged.

REFERENCES

1 Kain, R. M., Tuthill, A. H., Hoxie, E. C., *The Resistance of Types 304 and 316 Stainless Steels to Crevice Corrosion in Natural Waters; Journal, Materials for Energy Systems; V.* 5 No. 4, March, 1984.

2 Korbin, G., *Reflections on Microbiologically Induced Corrosion of Stainless Steels;* presented at the International Conference on Biologically Induced Corrosion, Gaithersburg, MD; June 10-12, 1985.

3 Todd, B., and Oldfield, J., *The Use of Stainless Steels and Related Alloys in Reverse Osmosis Desalination Plants;* paper presented at the International Maritime Engineering Conference, Bahrain, Oct., 1984.

4 Kain, R. M., *Localized Corrosion Behavior in Natural Seawater: A Comparison of Electrochemical and Crevice Testing of Stainless Alloys;* No 74, Corrosion/80, Chicago, IL, March 1980.

Trademark	Product of
AL-6X	Allegheny Ludlum Steel Corp.
Inconel 600	Inco Family of Companies
Mone1400	Inco Family of Companies
Ni-Resist	Inco Family of Companies
Sea-Cure	Crucible Steel Company
254SMO	Avesta Jernverks AB