Selecting Tubing Materials for Power Generation Heat Exchangers

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Abstract

A power plant engineer has many choices when selecting tubing materials for his condenser, feedwater heater or balance-of-plant application. The wide variety of stainless steel choices available (ASTM lists over 75 alloys) gives the engineer greater flexibility to choose the best candidate to meet budgetary constraints and still provide the performance needed for the lifetime of the plant. Unfortunately, upset conditions are common in power generation, and these can result in premature unexpected failure of tubing and piping materials. These may include differences in operation modes from design, changes in water chemistry due to leaks in other parts of the system, corrosion from unexpected sources, impact of improper lay-up practices, and the effect of corrosion product transport to other parts of the system. The motivation to build modern combined-cycle and coal power plants for the lowest cost per kilowatt has stretched the envelope for materials performance resulting in many tube failures.

This paper provides an overview on a number of factors known to cause failure of a tube material. Knowing the limitations of material is crucial when making a selection for a specific application. This paper helps to identify the factors that need to be considered when selecting a material. Properties compared in this paper include corrosion resistance, stress corrosion cracking potential, thermal and mechanical properties, erosion resistance, vibration potential, and temperature limitations. The property comparison guides are intended to be quick tools to assist the user in selecting a cost-effective material for a specific application.

Corrosion

Corrosion may be grouped into two broad categories, general corrosion and localized corrosion accelerated by an electrochemical mechanism. The latter group can be divided into several well-known specific mechanisms.

General Corrosion

General corrosion is the regular dissolution of surface metal. The two most common encountered are the rusting of carbon steel and the wall thinning of copper alloys. As long as a major change in the water chemistry does not occur, general corrosion is not catastrophic. With proper planning, a heat exchanger can be designed to accommodate general corrosion. In many instances, an alloy susceptible to this type of corrosion may be a cost-effective design option. Heat exchanger designers commonly add a "corrosion allowance" to a high-pressure carbon steel feedwater heater to allow for a 10 to 25 year lifetime.

Copper alloys are often chosen for condensing and BOP heat exchangers, and 25-year lifetimes are not uncommon. In some applications, copper alloys are expected to slowly dissolve to maintain some resistance to biofouling, as the copper ion can be toxic to the microorganisms that may attach to the tube wall. Unfortunately, on the steam side of the tubing, copper transport to other locations due to this slow dissolution may cause other problems. The copper can deposit on the HP turbine blades or boiler tubes. When it deposits in the turbine (Figure 1), it can cause as much as 5% decrease in MW generation resulting in income losses of several million dollars per year (ref 1,2), or on

boiler tubes, resulting in premature failures due to liquid metal embrittlement. Although the discharge values on the cooling water side may be less than one ppm, total copper metal discharge for a medium-sized condenser over the tubes' lifetime can exceed several hundred thousand pounds per unit. Regulators are recognizing this and new discharge permits are now as low as 12 ppb preventing the reuse of copper alloys in power plant heat exchangers.



Figure 1 Copper deposits on HP turbine at Pacificorp Huntington Unit 2 (ref. 2)

Electrochemically Driven Mechanisms

The electrochemically driven mechanisms are the dangerous ones as the leaks can be very unpredictable. Therefore, they cannot be accommodated by design. These failure mechanisms usually have two stages: an incubation or initiation period, and a propagation mode. The time of initiation is rarely determinable. It could be as short as in a few weeks or take years. Once initiated, the second mode can occur rather quickly, driven by the electropotential between the two regions. Conductivity of the water may be a dominant factor. Higher conductivities allow higher current densities. Higher current densities are proportionately related to metal removal rates.

Pitting

Pitting corrosion is a highly localized attack that can result in through-wall penetration in very short periods of time. Failures may occur in less than four weeks. Once a pit is initiated, the environment in the pit is usually more aggressive than the bulk solution because of the pit's stagnant nature. Even if the bulk solution has a neutral or basic pH, the pH in a pit can drop below two. When this occurs, the surface inside the pit becomes active. The potential difference between the pit and the more noble surrounding area is the driver for the galvanic attack. As the surface area of the anode (pit) is small and the cathode (the passive surface surrounding the pit) is large, a very high current density in the pit is possible. For TP 316 in seawater, the voltage difference between the active site (a pit) and the passive region surrounding it can be 0.4 volts. This, combined with high current densities in the pit region, will result in very high

localized corrosion rates. Through-wall pitting in condenser tubes has occurred in less than 3 weeks.

The most common initiator of stainless steel pitting is chlorides. Several alloying elements, such as chromium, molybdenum, and nitrogen, promote chloride resistance in this group of alloys. Not all have the same effect. By investigating the impact of each element, Rockel developed a formula to determine the total stainless steel resistance to chloride pitting (ref. 3):

$$PREn = \% Cr + 3.3 (\% Mo) + 16 (N)$$

PREn represents the "Pitting Resistance Equivalent" number. This formula can be used as a quick reference on chloride resistance based upon the chemistry. In this formula, nitrogen is 16 times more effective and molybdenum is 3.3 times more effective than chromium for chloride pitting resistance. The higher the PREn, the more chloride resistance an alloy will have. It is interesting to note that nickel, a very common stainless steel alloying element, has little or no effect on chloride pitting resistance. However, it does have a profound impact in stress corrosion cracking which will be discussed later.

Crevice Corrosion

Crevice corrosion has similar driving forces to pitting corrosion. However, since the tighter crevice allows higher concentrations of corrosion products (less opportunity to flush with fresh water), it is more insidious than pitting. This drives the pH lower resulting in attack that can happen at temperatures 30°-50° Centigrade lower than pitting in the same environment. This is the reason why tubing can perform flawlessly for years while clean, and then suddenly start to have problems once a deposit forms. The critical pitting temperature (CPT, above which pitting starts to occur) may be above the operating temperature while the critical crevice temperature (CCT), could be below and attack initiates.

The potential for crevice corrosion in chlorides is commonly measured by the ASTM G 48 Method B test. Kovach and Redmond evaluated a large database of existing crevice corrosion data and compared it to the PREn number described earlier (ref. 4). They developed relationships between the PREn and the G 48 critical crevice temperature (CCT) and plotted the relationships. Figure 2 is the result of that work with the additional modification on the right axis that allows it to be used as a tool for determining maximum chloride levels for an alloy of a particular chemistry, particularly at lower PREn.

Ferritic stainless steels were found to have the highest CCT for a particular PREn, above the duplex grade of the same PREn, followed by the austenitics. Each specific stainless structure provides a separate parallel linear correlation. After a typical or minimum chemistry is determined, the PREn can be calculated. To compare the corrosion resistance of two or more alloys, a line is drawn vertically from the calculated PREn for each alloy to the appropriate sloped line for the structure. The vertical line should stop at the bottom line for austenitics, such as TP 304, TP 316, TP 317, 904L,

S31254, and N08367. Duplex grades, such as S32304, S32003, S33205, and S32750, fall on the center line. The G48 crevice corrosion results of the ferritics, such as S44660 and S44735, follow the top sloped line. From this intersection, a horizontal line should be drawn to the left axis to determine an estimated CCT. A higher CCT indicates more corrosion resistance.

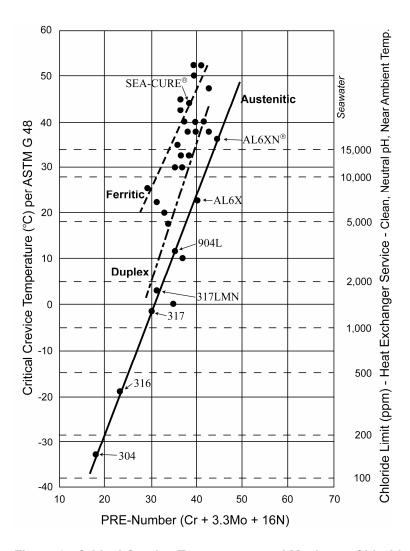


Figure 2 Critical Crevice Temperature and Maximum Chloride Levels versus PREn of Various Stainless Steels

What are Maximum Chloride Levels can we use?

One of the most common questions asked is "What is the maximum chloride level that can be tolerated for a particular grade of stainless steel?" The answer varies considerably. Factors include pH, temperature, presence and type of crevices, and potential for active biological species. A tool is added on the right axis of Figure 2 to help in this decision. It is based upon having a neutral pH, 35° Centigrade flowing water (to prevent deposits from building and forming crevices) common in many BOP and

condensing applications. Once an alloy with a particular chemistry is selected, the PREn can be determined and then intersected with the appropriate sloped line. The suggested maximum chloride level can then be determined by drawing a horizontal line to the right axis. In general, if an alloy is being considered for brackish or seawater applications, it needs to have a CCT above 25° Centigrade measured by the G 48 test.

When using this guide, additional caveats need to be considered:

- 1. If the temperature is higher than 35° Centigrade, the maximum chloride level should be lowered.
- 2. If the pH is lower than 7, the maximum chloride level should be lowered.
- 3. This guide is based upon having a clean surface. If deposits are allowed to form, the pH can be significantly lower under the deposits, and the chloride levels may be much higher than the bulk water.

The 300 series maximum chloride levels shown in this guide are approximately 50% of what was considered acceptable 15-20 years ago (ref. 5). For example, TP 304 was commonly considered to be acceptable to 200 ppm chloride, and TP 316 was acceptable up to 1000 ppm. The difference is not related to a change in the data, but rather to a change in the steel making process. Because of improvements in stainless steel melting practices and the current competitive nature of the business, typical 300 series stainless steels are now being made with chromium, nickel, and molybdenum content very near the bottom of the ASTM requirement. See Table 1 for a listing of ASTM stainless steel composition limits. Twenty years ago, typical TP 304 had a chromium level of approximately 19%, and TP 316 had a molybdenum content of typically 2.6%. These earlier alloys had a higher PREn than today's versions, and thus, the higher chloride limits were justified. For today's 300 series grades, the minimum ASTM limits should be used to do the calculations. For grades other than the 300 series, contact the manufacturer of the alloy for typical minimum chromium, nickel, molybdenum, and nitrogen levels before calculating the PREn to rank the alloy.

Table 1 ASTM Composition Limits of Stainless Steels

Minimum Unless Otherwise Specified

Ferritic - ASTM S268

| UNS | Commonly Used Name | | Ni | Мо | Mn | Si | С | N | P | S | Other |
|--------|-----------------------|-------------|-------------|-------------|------|------|------|-------|-------|-------|--|
| S43035 | TP439 | 17.0 - 19.0 | 0.50 | | 1.00 | 1.00 | 0.07 | 0.040 | 0.040 | 0.030 | 0.15 Al, $Ti = 0.20 + 4 (C+N) min$. |
| S44660 | SEA-CURE® | 25.0 - 28.0 | 1.00 - 3.50 | 3.0 - 4.0 | 1.00 | 1.00 | 0.06 | 0.040 | 0.040 | 0.030 | 6(C+N) |
| S44735 | AL29-4C® | 28.0 - 30.0 | 1.00 | 3.60 - 4.20 | 1.00 | 1.00 | 0.03 | 0.045 | 0.040 | 0.030 | 6(C+N) |

Duplex - ASTM A789

| UNS | Commonly Used Name | | Ni | Мо | Mn | Si | С | N | P | S | Other |
|--------|-----------------------|-------------|-----------|-----------|------|------|------|-------------|-------|-------|-------|
| S32003 | AL2003® | 19.5 - 22.5 | 3.0 - 4.0 | 1.5 - 2.0 | 2.00 | 1.00 | 0.03 | 0.14 - 0.20 | 0.030 | 0.020 | |
| S32205 | 2205 | 21.0 - 23.0 | 4.5 - 6.5 | 3.0 - 3.5 | 2.00 | 1.00 | 0.03 | 0.14 - 0.20 | 0.030 | 0.020 | |
| S32750 | 2507 | 24.0 - 26.0 | 6.0 - 8.0 | 3.0 - 5.0 | 2.00 | 0.80 | 0.03 | 0.24 - 0.32 | 0.030 | 0.020 | |

Austenitic - ASTM A249

| UNS | Commonly Used Name | | Ni | Мо | Mn | Si | С | N | P | S | Other |
|--------|-----------------------|-------------|-------------|-------------|------|------|-------|--------------|-------|-------|-----------------|
| S30400 | TP304 | 18.0 - 20.0 | 8.0 - 11.0 | | 2.00 | 1.00 | 0.08 | | 0.045 | 0.030 | |
| S30451 | TP304N | 18.0 - 20.0 | 8.0 - 11.0 | | 2.00 | 1.00 | 0.08 | 0.110 - 0.16 | 0.045 | 0.030 | |
| S31600 | TP316 | 16.0 - 18.0 | 10.0 - 14.0 | 2.00 - 3.00 | 2.00 | 1.00 | 0.08 | | 0.045 | 0.030 | |
| S31700 | TP317 | 18.0 - 20.0 | 11.0 - 15.0 | 3.00 - 4.00 | 2.00 | 1.00 | 0.08 | | 0.045 | 0.030 | |
| S31725 | TP317LM | 18.0 - 20.0 | 13.5 - 17.5 | 4.00 - 5.00 | 2.00 | 1.00 | 0.030 | 0.020 | 0.045 | 0.030 | |
| S31254 | 254SMO [®] | 19.5 - 20.5 | 17.5 - 18.5 | 6.0 - 6.5 | 1.00 | 0.80 | 0.020 | 0.18 - 0.25 | 0.030 | 0.015 | 0.050 - 1.00 Cu |
| N08367 | AL6XN® | 20.0 - 22.0 | 23.5 - 25.5 | 6.0 - 7.0 | 2.00 | 1.00 | 0.030 | 0.18 - 0.25 | 0.040 | 0.030 | 0.75 Cu |

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MIC

Microbiological Influenced Corrosion (MIC) is often confused with pitting corrosion and generally occurs in water normally considered benign. The term "influenced" is used since the bacteria does not actively cause the corrosion. Commonly, the bacteria forms a film or slime that creates a crevice. This isolates the water chemistry on the metal surface from the bulk water chemistry. The bacteria may also metabolate a product that can be very aggressive (ref. 6). Table 2 lists common bacteria types known to influence corrosion.

Table 2 Bacteria Commonly Associated with MIC

| Organism | Action | Problem |
|---------------|-----------------|--|
| Thiobacillus | Sulfate Reducer | Produces H ₂ SO ₄ |
| Desulfovibrio | Sulfate Reducer | Produces H₂S |
| Gallionella | Mn/Fe Fixer | Precipitates MnO ₂ , Fe ₂ O ₃ |
| Crenothrix | Mn/Fe Fixer | Precipitates MnO ₂ , Fe ₂ O ₃ |
| Spaerotilus | Mn/Fe Fixer | Precipitates MnO ₂ , Fe ₂ O ₃ |
| Nitrobacter | Nitrate Reducer | Produces HNO ₃ |

The most common MIC attack in North America is a result of the influence of manganese reducing bacteria. Although the mechanism is complicated, following is the one most likely. The bacteria assist in the oxidation of the soluble Mn ion to form an insoluble MnO₂ layer on the metal surface. This creates a crevice. When the operator detects an increase in condenser back pressure, sliming is suspected and chlorination is initiated. The chlorination intended to kill the bacteria and assist in slime removal further oxidizes the manganese oxide layer to a permanganate. Under the layer, the combination of the generated hydrogen and chloride ions react to form hydrochloric acid. The acid attacks the stainless's passive layer which initiates the attack.

Recent studies have found that manganese concentrations as low as 20 ppb can initiate the problem (ref. 7). This mechanism most commonly attacks TP 304 and TP 316, but higher molybdenum containing grades and some duplexes have also been attacked. In general, an alloy needs a minimum CCT of 25° Centigrade in the G 48 crevice corrosion test to be considered resistant to MIC.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a rapid failure mechanism that can occur when a specific combination of conditions coexist. Figure 3 shows transgranular stress corrosion cracking in TP 304N feedwater heater tubing. This failure mechanism is identified from other brittle-type failures, such as fatigue, by the branching and secondary cracking. In 300 series stainless steels, it most usually occurs in the

desuperheating zone of a feedwater heater, where conditions can concentrate chlorides.

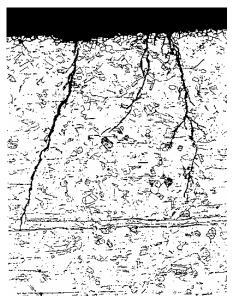


Figure 3 Transgranular Stress Corrosion Cracking in TP 304N Feedwater Heater Tubing

Figure 4 shows the three combined factors needed to cause stress corrosion cracking of an alloy system: tensile stress, a specific corrodent, and a minimum threshold temperature. The stress we need to be concerned is a combination of all sources including residual stress, thermal induced stress, load applied stress (such as hoop stresses from the pressure inside the tube), and stress from other sources. Common sources of corroding media in the power industry include ammonia for the copper alloys and chlorides for the stainless steel alloys. A minimum threshold temperature is needed, below which the cracking will not occur. For example, chloride SCC in stainless steel steam surface condenser tubing is not a problem because the metal temperature is below the threshold.

Corroding Media + Stress + Temperature

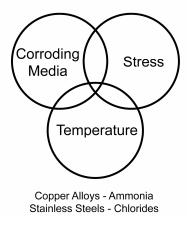


Figure 4 Three Factors Necessary for Stress Corrosion Cracking

Not all stainless steels are equally susceptible to SCC. Copson determined that a direct relationship exists between the time to failure and the nickel content (ref. 8). Using stressed chromium, nickel, and iron wires in a boiling magnesium chloride bath, he was able to determine the effect of varying nickel content and cracking resistance. This is evident in Figure 5. The time to failure varied dramatically vs. nickel content. The stainless steel nickel content with the quickest failure was 8%, which is the same content of the workhorse of the industry, TP 304. TP 316, that has approximately 11% nickel content, is still very susceptible, as can be seen by the slightly higher time to failure. Improvements in time to failure come from selecting an alloy with very low nickel, or very high nickel, such as the 6% molybdenum containing alloys or alloy 800. TP 439, with a specified maximum nickel content of 0.5% has not been shown to fail from chloride stress corrosion cracking. The high nickel alternative can be very expensive. Surprisingly, this curve shows that non-austenitic alloys can crack!

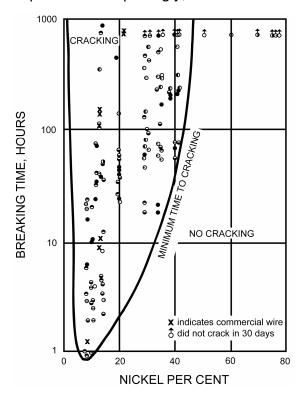


Figure 5 Fracture time of stressed chromium, nickel, iron wires in boiling magnesium chloride – known as the Copson Curve

Crucible Research tested a group of ferritic, duplex, austenitic, and high performance stainless steels in a series of autoclave tests duplicating faulted feedwater using u-bent strip samples (ref. 9). Table 3 shows the results. Mirroring the Copson curve, the alloys containing 8% nickel failed first. Interestingly, one of the most popular choices for high pressure feedwater heaters, TP 304N, failed more quickly than the non "N" version. Although this suggests that the chemical nature of the nitrogen addition makes the alloy more susceptible, the more likely reason is that the u-bend TP 304N specimen was stressed to a higher level than the non "N" version due to its higher yield strength and

the design of the test. One precaution is that the Section VIII of the Code allows higher stresses for the "N" derivative, driving its popularity. When using "N" grades, a user should specify that the tubing have a maximum residual stress and carefully control condensate chemistry. In the Crucible tests, only TP 439, the alloy containing no nickel, escaped cracking.

Table 3 28 Day Stress Corrosion Cracking Tests of Strip U-Bend Specimens in Aerated Neutral Chloride-Containing Waters*

| | | | Test Temperature (°F) | | | | | | | | | | |
|-----------|------|-----|-----------------------|-----------|--------|---------|-------|-------|--|--|--|--|--|
| | | | 250 | | 63 | 350 450 | | | | | | | |
| | | | | Chlori | | | | | | | | | |
| Grade | Ni % | 100 | 1,000 | 10,000 | 100 | 1,000 | 100 | 1,000 | | | | | |
| TP 439 | 0.4 | | | | | 0 | 0 | 0 | | | | | |
| SEA-CURE® | 2.0 | | | | | 0 | 0 | X | | | | | |
| 2205 | 5.0 | | | | | 0 | X | | | | | | |
| TP 304L | 8.0 | 0 | 0 | X** | X | X | X | X | | | | | |
| TP 304LN | 8.0 | 0 | X | X** | X | X | X | | | | | | |
| TP 316L | 11.0 | 0 | 0 | 0** | X | X | X | | | | | | |
| 254SMO® | 18.0 | | | | | 0 | X | X | | | | | |
| AL6XN® | 25.0 | | | | | 0 | X | X | | | | | |
| | | | | | | | | | | | | | |
| | | * | = Con | strained | U-Bei | nd Spec | imen | S | | | | | |
| | | ** | = Test | ing Term | ninate | d After | 15 Da | ays | | | | | |
| | | 0 | = No (| Cracks in | 28 Da | ays | | | | | | | |
| | | X | = Crac | ked Duri | ng Te | est | | | | | | | |
| | | | = Not | Tested | | | | | | | | | |
| | | | | | | | | | | | | | |

Effect of Other Material Properties

Table 4 is a listing of mechanical and physical properties for common copper base, titanium, and stainless steel tubing. These properties have a direct impact on many of the concerns considered in the selection process for an alloy in heat exchanger service.

Erosion-Related Problems

Erosion resistance is a function of the ability of the protective layer to remain attached to the substrate and the strength (hardness) of the substrate directly below the protective layer. Two types of erosion commonly cause problems in the power industry - flow assisted erosion/corrosion and water droplet/steam impingement erosion.

Flow Assisted Erosion/Corrosion

When the fluid velocity is so high that it will actually "scrub" the protective film from the metal surface, this is called "flow assisted erosion/corrosion". Table 5 summarizes flow rates that are commonly assumed or tested maximum safe velocities for an alloy. Higher velocities are desired as they result in higher heat transfer and they keep surfaces clean, reducing the surface interface resistance. In general, a minimum

Table 4 Mechanical & physical properties of various heat exchanger tube candidates, typical unless otherwise noted

| Property | Admiralty Brass C44300 | Aluminum Brass C68700 | 90/10 Cu/Ni C70600 | 70-30 Cu/Ni C71500 | TP 439 S43035 | TP 304/TP 316 S30400/S31600 | AL6XN [®] N08367 | SEA-CURE® S44660 | Ti Grade 2 |
|----------------|--|-----------------------------|-----------------------|-----------------------|------------------|--------------------------------|------------------------------|---------------------|------------|
| Ult. Strength | 53 ksi | 60 | 50 | 50 | 60* | 75* | 100* | 85* | 50* |
| Yield St. | 22 ksi | 27 | 15 | 25 | 30* | 30* | 45* | 65* | 40* |
| Elongation | 60% | 55% | 35% | 25% | 20%* | 35%* | 30%* | 20%* | 20%* |
| R. Hardness | RF 75 | RB 50 | RB 30 | RB 20 | RB 90** | RB 90** | RB 100** | RC 25** | RB 92** |
| Mod. Of Elast. | 16 x 10 ⁶ psi | 16.0 | 18.0 | 18.0 | 29.0 | 28.3 | 28.2 | 31.5 | 15.4 |
| Density | .308 lbs/in ³ | 0.301 | 0.323 | 0.320 | 0.280 | 0.29 | 0.29 | 0.278 | 0.16 |
| Thermal Expan. | 11.2 x 10 ⁻⁶ in/in/degree F | 10.3 | 9.5 | 9.5 | 5.6 | 9.5 | 8.7 | 5.38 | 5.2 |
| Thermal Cond. | 64 BTU/ft-hr-F | 58 | 23.0 | 17.0 | 12.3 | 8.6 | 7.9 | 9.9 | 12.5 |
| Fatigue Endur. | 20 ksi | 20 | 20 | 22 | 20 | 30 | 33 | 35 | 16 ksi |

^{*} Minimum ASTM Value

^{**} Maximum ASTM Value

Velocity of six feet per second is considered necessary to keep the tube surface relatively clean. Biofilms have been known to develop in lower flow rates.

Table 5 Commonly Accepted Maximum Water Flow Rates for Erosion/Corrosion

| Alloy | Maximum Velocity |
|--------------------------------|-------------------------|
| Admiralty | 6 FPS |
| 90/10 Cu/Ni | 8 FPS |
| 70/30 Cu/Ni | 10 FPS |
| 304/316 Stainless Steel | 30+ FPS |
| Ti Grade 2 | 100 FPS |
| Super-ferritic Stainless Steel | 100+ FPS |

Water Droplet/Steam Impingement Erosion

In some specialized conditions, it is possible to experience erosion of the tube OD surface due to localized impact of high velocity water droplets. This can occur near diverter plates that may focus steam velocity or during upset conditions. It often occurs in steam dump areas when the outlets are not properly designed. The resistance of this erosion is a direct function of the hardness of the metal substrate below the protective oxide. In general, higher hardness provides higher erosion resistance. Using a water droplet impingement device developed by Avesta Sheffield, alloys can be ranked by time to failure (ref. 10). By plotting hardness versus time to failure, a relationship can be determined. Other grades can then be added by comparing the hardness. Using titanium grade 2 as a reference of "1", the relative resistance of other grades can be ranked. The ranking is presented in Table 6.

Table 6 Relative Erosion Resistance Based Upon Water Droplet Impingement Tests

| Alloy | Hardness HV | Relative Erosion Resistance |
|----------------|-------------|-----------------------------|
| Admiralty | 60 HV | 0.4 |
| 70-30 Cu-Ni | 135 HV | 0.8 |
| Ti Grade 2 | 145HV | 1.0 |
| TP 304/TP 316 | 165 HV | 2.0 |
| Ti Grade 12 | 190 HV | 3.6 |
| 254 SMO/AL6XN® | 200 HV | 7.0 |
| Ti Grade 9 | 215 HV | 6.2 |
| SEA-CURE® | 240 HV | 7.2 |
| Alloy 2507 | 290 HV | 9.4 |

Values based upon water droplet impingement work presented in ACOM4-96 (ref. 10)

Sand Erosion

Another common form of erosion is due to suspended solids. The most common cause is sand or silt. Typically, those tubes that are softer or have a more friable patina are more susceptible.

Crucible Research (ref 11) developed a test using slurry of 50-70 AFS sized silica sand in synthetic seawater. Samples of the various metals tested were mounted on an impeller at a 30 pitch with respect to the direction of travel. The speed of the impeller was 250 RPM which calculated to 13.7 meters per second. The alloys tested were 90/10 Cu/Ni, S44660, N08367, and titanium grade 2. The results are reported in Table 7.

Table 7 Results of the silica sand/ synthetic seawater slurry test with velocity of 13.7 meters per second

| Alloy | Weight loss mg | Thickness loss cm x 10 ⁻⁶ per hr | | |
|-------------------------|-------------------|--|--|--|
| | | | | |
| 90/10 Cu/Ni | 18.1 | 1.40 | | |
| AL6XN® N08367 | 6.1 | 0.52 | | |
| SEA-CURE® | | | | |
| Superferritic Stainless | 4.3 | 0.39 | | |
| Steel | | | | |
| Ti grade 2 | 2.4 | 0.37 | | |

The 90-10 Cu-Ni had the greatest thickness loss followed by N08367. S44660 and titanium grade 2 were approximately equal in this test.

Vibration Resistance

Vibration is a major concern in condensers and other heat exchangers, especially during upset conditions or when inlet water temperature is very low. Many methods have been developed for calculation of spans considered to be safe from vibration damage. Each uses different assumptions but almost all rely upon tube material properties and sizes for the calculations. Although absolute value of the calculated span may vary considerably for each method, the relative relationship between the tube materials is similar for each method.

Coit, et al, developed a method to compare potential vibration in condensers as a function of material properties and steam velocity (ref. 12). Using this, maximum support plate spacing can be calculated in a specific condenser comparing OD, wall, and grade of various alloys. The following formulas are used:

L = 9.5 [(E I) /
$$\rho$$
 v² D)] ^{1/4}
I = Pi / 64 (D⁴ – ID⁴)

Where:

E = Modulus of Elasticity (psi)

I = Moment of Inertia (in⁴)

 $p = \text{Turbine Exhaust Density (lb/ft}^3)$

v = Average Exhaust Steam Velocity at Condenser Inlet

D = Tube Outside Diameter

ID = Tube Inside Diameter

It is clear from the formula, considering the same OD and wall tube, the property that has the largest impact on vibration is the modulus of elasticity. Higher modulus alloys are stiffer and have more vibration resistance. As seen in Table 4, titanium grade 2 has the lowest stiffness followed by the copper-based alloys and the austenitic stainless steels. Because of the very high modulus of the superferritic alloys, such as S44660 and S44735, these alloys have the highest resistance to vibration.

Using Coit's method, Table 8 displays a calculated condenser minimum wall using the same steam flow, tube OD, and support spacing for different alloys. For a given support spacing, alloys with low modulus may require twice the wall thickness as those with a higher modulus to prevent the risk of vibration damage. Alternatively, if a heat exchanger is newly constructed, the support plates need to be significantly closer on the lower modulus materials. Existing exchangers can be retubed with a lower modulus material if staking is used. However, this can add significant additional cost, and one should be very careful of stake selection as the reliability of stakes can vary significantly.

Table 8 Minimum Walls for Various Condenser Candidates for Similar Support Spacing Based upon a typical condenser with identical tube OD, support spacing, steam flow, and back pressure using Coit method for vibration

| <u>Alloy</u> | <u>Wall</u> |
|---------------|-------------|
| Admiralty | .049" |
| 90/10 Cu/Ni | .043" |
| 70/30 Cu/Ni | .034" |
| TP 439 | .025" |
| TP 304/TP 316 | .026" |
| N08367 | .027" |
| S44660 | .023" |
| Ti Grade 2 | .053" |

Thermal Conductivity

Although the pure material thermal conductivity of the various power-tubing candidates has a very wide range, as shown in Table 4, the actual variance of thermal performance is not as large. Several factors impact the total thermal efficiency of an alloy:

- 1. Actual wall thickness of the tube material selected. Because of the low modulus and mechanical properties and a need for corrosion allowance, copper alloy tubes are normally much thicker than stainless steel tubes.
- 2. Boundary layers on both the OD and ID surfaces can act as additional thermal resistances.
- 3. Deposits can form creating additional resistances.

Condensing studies done at Rochester Institute of Technology, used to develop heat transfer parameters for the HEI 9th Edition, show realistic differences between the alloys (ref. 13). The test results (Figure 6) are based upon new tubes, prior to the formation of oxides, scales, and slimes common after a few months of use. Once scales/patina deposits, the difference between the copper alloys and the stainless steels/titanium is less evident. In many cases, the stainless can be an advantageous selection. In condensing applications, copper alloys commonly develop steam side thermal barriers resulting from corrosion reactions with the chemicals normally added for oxygen control. This does not occur on stainless steels. Generally, the degradation of copper's overall conductivity gradually declines over the first year in fresh water service and even more quickly in sea and brackish water service (ref. 14). To account for this difference in condensing applications, the HEI method allows assignment of cleanliness factors for each application. The cleanliness factor chosen for unscaled copper alloys is typically 85%, while 90-95% is normally proven when stainless steels and titanium tubes are used.

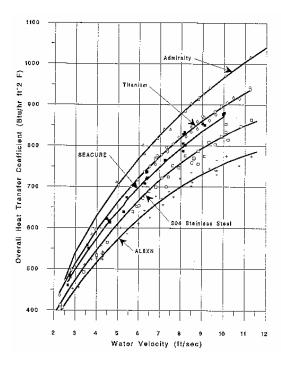


Figure 6 Heat Transfer coefficient for various alloys as tested by the Rochester Institute of Technology for HEI heat transfer coefficients.

Economic Considerations

A recent tube price comparison of various alloys is shown in Table 9. Prices can vary considerably depending upon quantity purchased, availability, and OD-to-wall ratio. The supply and demand in China has driven prices all over the map. Nickel prices have varied dramatically in the last few years, ranging from under \$2 per pound to over \$25 per pound. Copper has gone from \$.70/lb to \$4. Major swings have occurred in only a few months. Molybdenum has ranged from \$3.50 to \$40. Therefore, one should be very careful when assembling long-term budgets for alloys that have higher alloy contents such as TP 304, TP 316, cupro-nickels, and the 6% molybdenum containing alloys. Alloys with low nickel such as admiralty brass, TP 439, and the superferritics are more stable and predictable.

Table 9 Relative Prices of Heat Exchanger & Tubing Candidates

| Grade | Wall | Relative Price |
|-------------|--------|----------------|
| TP 304 | 22 BWG | 1.0 |
| TP 316 | 22 BWG | 1.3 |
| TP 439 | 22 BWG | 1.3 |
| TP 317 | 22 BWG | 1.6 |
| Al Brass | 18 BWG | 1.6 |
| 90/10 Cu/Ni | 20 BWG | 1.6 |
| SEA-CURE® | 25 BWG | 1.6 |
| 2205 | 22 BWG | 1.7 |
| Ti Grade 2 | 25 BWG | 2.2 |
| SEA-CURE® | 22 BWG | 1.9 |
| Ti Grade 2 | 22 BWG | 2.9 |
| AL6XN® | 22 BWG | 3.6 |
| 70/30 Cu/Ni | 20 BWG | 2.5 |

Approximate values as of 7/2007: Nickel at \$14.00/lb and copper at \$3.60/lb on LME, Ferromoly at \$35.00/lb

Precautions

Appendix 1 includes a ranking system for commonly chosen alloys in different environments. Each alloy has a 1 to 5 rating for the potential problem described earlier. A rating of 1 indicates that the alloy has high resistance to the environment. If an alloy has a rating of 5, it should not be considered.

Some additional precautions that should be considered are listed below:

885° F Embrittlement

Ferritic and duplex stainless steel alloys containing 12% chromium or greater are susceptible to 885° F embrittlement. This is caused by the formation of brittle

secondary phases during prolonged exposure to elevated temperature. ASME Section II cautions the use of these materials above 500° F (ref. 15). Although several thousand hours of exposure may be needed at the lower temperatures before the loss of ductility is noted, it can occur fairly rapidly at the peak temperature of 885° F. The exposure is cumulative. The time is additive for repeated excursions into the embrittlement range. The only way to eliminate this damage is to reanneal the material at the original solution annealing temperature. Once installed into a bundle, this is not normally an option.

Hydrogen Embrittlement

Titanium and superferritic stainless steels, such as S44660 and S44735, can embrittle with exposure to monotonic hydrogen. This commonly occurs in water systems that have poorly controlled cathodic protection. The problem is prevented when the system is controlled so that the voltage is maintained at a potential more positive than -750 millivolt. When the voltage is more negative, hydrogen bubbles develop on the surface. During the development stage, monotomic hydrogen develops which easily diffuses into the material.

Embrittlement of titanium occurs as an intermetallic phase develops on the surface in contact with hydrogen. This layer grows with exposure and eventually the progresses through the entire wall. These embrittled tubes have little mechanical strength. Tubes can be broken simply by leaning on them. This process is not reversible.

Fortunately, unlike titanium, the hydrogen in superferritic stainless steels resides in interstitial sites in the lattice structure, and does not form a compound. This allows the embrittlement in the stainless to be easily reversed. Once the source of the hydrogen is eliminated, the atoms in the stainless diffuse out of the structure, and the ductility returns. This normally occurs within 24 to 48 hours at 80° F, and the ductility can return in as soon as one hour at 200° F. One caution is that multiple hydrogen charging and discharging may create microcracking. Once this occurs, the tubing is no longer dependable.

Conclusion

Stainless steels can be the most cost-effective heat exchanger tubing choice. A number of factors need to be considered including potential for corrosion and erosion, maximum temperatures, vibration potential, and mechanical property requirements. When all factors are considered in the material decision, this group of alloys will provide service for the life of a plant.

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- 15. ASME Code, Section II, Part D, Appendix 6, paragraph 6-630, 2001 Edition, no addenda.

Appendix 1 Common Power Materials Performance Rankings

1 is Best, 5 is Worst

| | | Property/E | Environme | nt | | | | | | |
|---------------------|--------------------|---------------------|-----------------------------|-----------------------|------------------------------|-----------------|-------------------------|--------------------------|-------------------------|-----------------------|
| Alloy | UNS Designation | Chloride Pitting | Steam Droplet Erosion | Erosion/ Corrosion | Ammonia SCC & Grooving | Chloride SCC | Vibration Resistance | Sulfur/MIC Resistance | Fe/Mn MIC Resistance | Hydrogen Embrittle |
| Admiralty | C44400 | 4 | 5 | 5 | 5 | 1 | 5 | 5 | 3 | 1 |
| 90/10 Cu/Ni | C70600 | 3 | 4 | 4 | 4 | 1 | 4 | 5 | 3 | 1 |
| 70/30 Cu/Ni | C71500 | 2 | 3 | 3 | 3 | 1 | 4 | 4 | 2 | 1 |
| TP 304/L | S30403 | 5 | 2 | 2 | 1 | 5 | 2 | 3 | 5 | 1 |
| TP 304N | S30451 | 5 | 2 | 2 | 1 | 5 | 2 | 3 | 5 | 1 |
| TP 316/L | S31603 | 4 | 2 | 2 | 1 | 5 | 2 | 3 | 4 | 1 |
| TP 317/L | S31703 | 3 | 2 | 2 | 1 | 4 | 2 | 2 | 3 | 1 |
| TP 439 | S43035 | 5 | 2 | 2 | 1 | 1 | 2 | 4 | 5 | 1 |
| 2205 | S32205 | 2 | 1 | 1 | 1 | 3 | 2 | 2 | 3 | 1 |
| 904L | N08904 | 2 | 1 | 1 | 1 | 3 | 2 | 1 | 3 | 1 |
| 254SMO [®] | S31254 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 2 | 1 |
| AL6XN [®] | N08367 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 |
| SEA-CURE® | S44660 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 4 |
| Ti Grade 2 | R50400 | 1 | 3 | 2 | 1 | 1 | 5 | 1 | 1 | 5 |