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Corrosion Issues Associated with Austenitic Stainless Steel Components used in Nuclear Materials Extraction and Separation Processes

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Abstract

This paper illustrated the magnitude of the systems, structures and components used at the Savannah River Site for nuclear materials extraction and separation processes. Corrosion issues, including stress corrosion cracking, pitting, crevice corrosion and other corrosion induced degradation processes are discussed and corrosion mitigation strategies such as a chloride exclusion program and corrosion release testing are also discussed.

Introduction

The initial mission of Savannah River Plant (now called the Savannah River Site (SRS)) was the production of nuclear weapons materials. The mission began in 1950 when President Truman formally asked DuPont to design, construct and operate a nuclear facility. Construction began in 1951 and by 1956 construction of the basic plant was completed. In 1953 nuclear criticality was obtained in a nuclear materials production reactor. Radioactive operations in the chemical separation facility began in 1954 and the first high level wastes were transferred to waste storage tanks in the same time frame. SRS produced approximately 36 metric tons of ^{239}Pu between 1953 and 1988 when plutonium production operations ceased. The magnitude of this achievement is apparent in the 310-square mile footprint of the plant, in the number of major facilities constructed, including five reactors, two chemical separation plants, a nuclear fuel and target fabrication facility, a tritium extraction facility, as well as nuclear waste management facilities, and in the infrastructure necessary to move people and materials throughout the plant.

Nuclear materials production processes included the manufacture of fuel and target elements, irradiation of the manufactured elements in production reactors, storing the irradiated elements in water pools to obtain sufficient radioactive decay, transfer of the elements, dissolution of fuel and target assemblies, separation of the radioisotopes into production (^{239}Pu for example) and waste products, and storage and disposition of the nuclear wastes. The handling, storage and disposition of the legacy nuclear wastes by-products that resulted from the nuclear materials production operations continue to be major missions at SRS. Figure 1 illustrates some of the facilities and process flows associated with these waste handling missions.

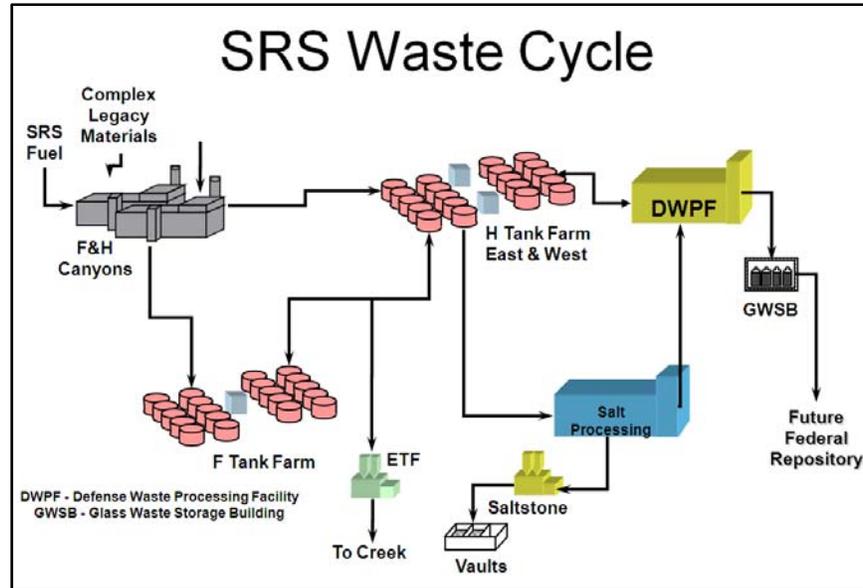


Figure 1 Schematic of SRS waste cycle from processing of nuclear materials.

The facilities and infrastructure that supported, and continue to support, the past, present and emergent SRS missions are both large and complex. As a rule, material issues generally accompany the construction, start-up, operation and closure of any new and complex facility. Although a National Science Foundation workshop on engineering system design stated that “our nation’s ability to develop large complex artifacts such as aircraft, space launch systems, submarines, and even automobiles is in disarray”¹, SRS has been proactive in developing safe and efficient operations through resolution of the material issues. The material issues frequently involve corrosion induced degradation processes as shown by the general observation that “the annual direct cost of metallic corrosion to the United States is approximately 3.1% of the gross domestic product and 25 to 30% of that cost could be eliminated if optimum corrosion management practices were employed.”² SRS has addressed corrosion throughout the Site and through corrosion engineering practices has successfully mitigated numerous material issues.

This paper provides an illustration of nuclear materials management through facility design and construction and discusses the mechanisms that have caused degradation of austenitic stainless steels used for selected systems, structures, and components (SSCs) of the nuclear materials separations and waste processing facilities at SRS. These facilities, referred to as canyons, contain processes for the dissolution of irradiated fuel and target elements, the separation of nuclear materials, the processing and storage of nuclear wastes and associated systems for the handling and transfer of nuclear materials and wastes. A wide variety of materials have been used throughout these material/waste processing areas. Some of these materials had corrosion issues which have been mitigated through corrosion engineering practices as illustrated in several other manuscripts in this issue of the *Journal of Nuclear Materials Management*³⁻⁶.

Scope

Degradation mechanisms were evaluated for their potential impact on austenitic stainless steels used in the construction of the SSCs for facilities involved with the separation of nuclear materials. The issues

discussed are primarily those affecting the SSCs that are safety class and safety significant systems which maintain both a confinement function and a safe, reliable processing capability. Confinement of the SSCs is demonstrated through evaluations, inspections where accessible and monitoring. The degradation evaluation consisted of compiling the service history of failures, reviewing inspection reports and literature data, and analyzing the material response of the fluid/gas retaining boundary to known environmental conditions. The evaluation also included a cursory assessment of confinement and process functions which these materials must provide to maintain safe operational facilities. The SSCs include the canyon building and process cells, process tanks, dissolvers, evaporators, cooling coils, and the ventilation system. An evaluation of aging of electrical and control systems is not included.

Confinement Function of Materials and Structures

Confinement is achieved through leak-tightness, structural stability, and administrative controls to mitigate identified leakage. This function of the SSCs maintains a boundary against radioactive process fluids and vapors releases to the environment and provides the building confinement function, e.g. HVAC, filters, fans, etc.

Degradation of the materials can lead to a loss in the confinement function and limit the useful service life of an SSC. Failures in confinement of process vessels and connecting piping would not necessarily violate the overall confinement of process solutions and waste streams provided by the canyon facilities. For example leakage from canyon processing equipment can be collected in the sumps (through the sloped grade construction of the cells). Understanding the degradation mechanisms along with monitoring of vessel conditions or operational parameters provide a means to manage the leaks effectively and plan for vessel replacement.

The SRS chemical separation building (only one remains in operation) contains processing systems to perform chemical separations of spent fuels and targets that had been irradiated in the SRS production reactors as well as legacy materials around the nuclear complex. The canyon buildings are Class 1 structures and required approximately 1,350 reinforced concrete slabs (individually weighing an average 18 tons). The buildings rest on a 5'6" thick concrete mat, 139' wide by 835' in length. Total quantity of materials of construction for the canyon buildings included 202,410 cu yd of concrete and 13,585 tons of reinforcing steel⁷. One building was started construction earlier so the second building was modified to incorporate design improvements and to reduce construction cost. The building structure serves to isolate the processing equipment from the public, environment, and operating personnel.

Process Function of Materials and Structures

The SRS separation buildings contain two parallel canyons separated from each other by a central operating and service section. One canyon is for radioactively hot processes and the other is for warm processes. Each canyon is divided into 18 sections, which are generally 43 feet long, and is designed for a single row of process vessels. Each section is subdivided into 4 process cells. The locations of tank trunnions and wall nozzles are the same in each of these sections as shown in Figure 2. The floors in each section are sloped 3/8 inch per foot so that spills, leaks, and overflows drain to a sump.

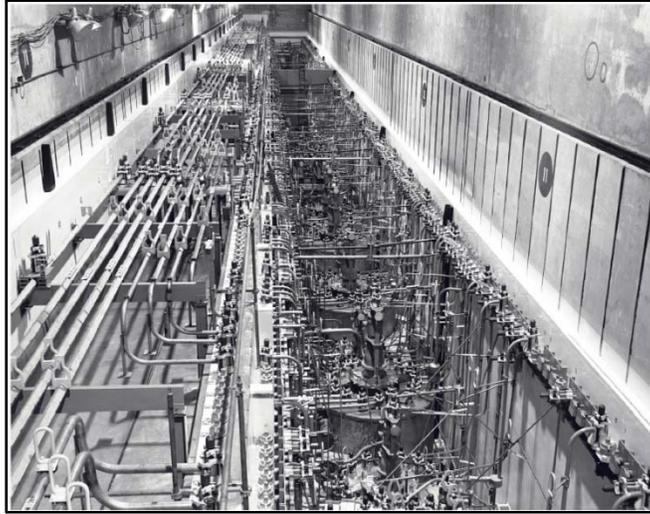


Figure 2 Interior of canyon building showing vessels and jumper piping

The hot canyon contains processing systems for highly radioactive materials and chemical solutions, such as nuclear material dissolution, high activity waste processing, and the first-cycle solvent extraction. The warm canyon contains lower activity chemical solutions including second-solvent extraction cycle and low activity waste processing. Remote operation of bridge cranes in both the hot and warm canyons provides servicing of the equipment including assembly and disassembly of process systems and equipment replacement. Due to the high radiation field and contamination potential, the reinforced concrete structures comprising the canyon cells of the H-canyon facilities are not readily repairable or replaceable. All other process equipment is replaceable. The magnitude of the resources required to provide a facility similar to the SRS separation capabilities of dissolving, separating and processing nuclear materials is almost overwhelming. Therefore, sustaining these capabilities is important to the USA's nuclear future.

Materials of Construction and Service Environments

A listing of the materials of construction and the service environment are shown in Table 1 for the SSCs that provide the containment and process function for the SRS separation facilities. The SSCs that were not fabricated from austenitic stainless steels are included since they demonstrate the complete containment function.

Table 1 Materials of Construction and Service Environments for the SSC for SRS Separation Facilities

SSC	Material of Construction	Service Environment
Canyon Building	Reinforced concrete slabs	Ambient air, temperature generally below 70 C, some leaking fluids
Process tanks	304L and 347 stainless steel (select vessels)	Nitric acid based solutions, temperatures generally below 100 C
Cooling coils	304L, 309Cb, 690	Internal - treated well water External - nitric acid solutions
Piping and valves	304L, 316, 416, 690, 309Cb, 347, 304 ELC,	Generally low temperature except for steam lines and dip tubes in heated vessels

	Hastelloy C	
Equipment ventilation system	Carbon steel, 304L	Ambient temperature, nitric acid fumes, temperatures generally below 70 C
Building ventilation	Reinforced concrete	Ambient temperature and humidity, nitric acid fumes
Sand filter	Reinforced concrete with multiple grades of filtering material	Ambient temperature and humidity

Summary of Service-Induced Degradation

After numerous years of service the SSCs continue to maintain confinement through the repair and replacement of degraded materials. AISI Type 304L stainless steel (304L) is the material of construction for many of the SSCs. Significant, wide-spread service-induced degradation of 304L process tanks has not been observed to date, although failures have occurred in heated vessels such as dissolvers and evaporators. Cooling coils made of 304L have failed as a result of corrosion mechanisms and act as an indicator for potential tank failure because they are thinner than the vessel wall. Replacement materials were investigated and coils made of Inconel 690 were used subsequently since this alloy was more resistant in these applications.

The concrete structures of the canyon facilities show some signs of aging. During periodic inspections, spalling of the concrete cells was observed. The spalling resulted from exposure to acidic process fluid which spilled, especially in the cells that have contained evaporators. Stainless steel plates have been used on the floor of the cells to maintain the vessels in a level position and continue process functionality.

Erosion of the concrete of the exhaust duct for the cells has also been observed. The exhaust stack brick liners are in good condition but show some minor cracking and or erosion/spalling. Debris from this concrete degradation has accumulated in the sumps.

Degradation Mechanisms

The primary degradation mechanisms of the SRS canyon facilities discussed in this paper are those that affect austenitic stainless steels even though carbon steels, and concrete materials are clearly affected by service conditions. The mechanisms discussed are those likely to be active under the conditions of service and could impact the integrity of the materials and structures within their desired service lives. The sources of information included failure analysis records and literature and scientific journals.

Austenitic stainless steels are widely used in the chemical processing industry due to their corrosion resistance and excellent fabrication characteristics. The corrosion resistance of austenitic stainless steel is attributable to the surface chromium-oxide film that forms in the presence of oxygen and is essentially insoluble, self-healing, and non-porous. A minimum of 12% chromium is required for film formation and the alloying of 18% Cr-8% Ni broadens the film forming range in non-oxidizing environments. The integrity of the oxide film must be maintained for corrosion resistance.

The corrosion of austenitic stainless steel is well documented and its behavior in many environments is readily predictable. The resistance of stainless steel to acids depends on the hydrogen ion (H⁺) concentration, the oxidizing capacity of the acid, the steel composition (chromium, nickel and carbon

content), and heat treatment⁸. Type 304L stainless steel is widely used throughout the canyon process equipment and is the material of choice for nitric acid service. Therefore, Type 304L stainless steel is the focus of much of this paper.

General Corrosion

General corrosion is the uniform attack over the entire exposed surface of a structure or component which results in gradual thinning of the material. General corrosion has not lead to any know failures for austenitic stainless steels in the canyon buildings. This type of degradation proceeds without any perceptible localized attack. Laboratory experiments have shown that at 16 °C the corrosion rate for Type 304 stainless steel (304) is 0.003 mm/yr (0.118 mpy) for all concentrations of nitric acid⁹. The corrosion rate increases to 0.2 mm/yr (7.9 mpy) in 65% boiling nitric acid¹⁰. Table 2 lists the corrosion rates for 304 and 304L to the different cold feed chemicals for canyon processes^{11,12}. If literature sources differed the higher or more conservative value was listed. These data are non-specific since actual conditions, i.e. material heat, surface morphology, aeration, flow rate, etc, are not well characterized and impact the actual corrosion rates.

Table 2 Corrosion Rates of 304/304L in H-Canyon Cold Feed Chemicals*

Cold Feed Chemical	Concentration (%)	Corrosion Rate (mpy)	Temperature Range (C)
34 % Aluminum Nitrate	Saturated	<20	<40
Boric Acid	16%	<2	22
Ferrous Sulfamate	40	ND	ND
Manganese Nitrate	ND	ND	ND
Mercuric Nitrate	10	<20	<100
Nitric Acid	0.75-50	20	<100
Potassium Permanganate	10-20	<20	<100
Sodium Carbonate	30	<20	<100
Sodium Hydroxide	50	<20	<100
Sodium Nitrite	40	<20	<100
TBP w/ Paraffin	7.5	ND	ND

* No data available

General corrosion of 304L exposed to nitric acid has not been a significant degradation mechanism at the processing conditions of the SRS separation processes. Ultrasonic thickness measurements of an canyon tank removed from service due to a coil failure revealed that after 25 years of service the observed wall thickness was approximately equivalent to the original nominal thickness¹³. There have been no failures that have been caused by general corrosion.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is an environmentally assisted, slow crack propagation process caused by the simultaneous combination of mechanical stress and corrosive chemical reactions with a susceptible material. For the stainless steel embedded piping, several environments are present in the canyon building which can lead to SCC. Table 3 lists the environments known to produce stress corrosion cracking for 304/304L¹⁴. The mechanical stress may be either applied or residual and usually are tensile

in nature. The residual stresses that are associated with fabrication, welding, and thermal cycling are generally responsible for the SCC catastrophic failure of pressurized equipment.

Table 3 Environments Known to Produce SCC in 304/304L

Environment	Temperature (C)
Hot acid chloride solutions such as MgCl ₂	>60
NaCl-H ₂ O solutions (and other halides)	>60
Seawater	>60
Concentrated caustic solutions	> 100
Condensing steam, Cl-bearing	> 100
Alkaline CaCl ₂	> 60

SCC may develop as intercrystalline or transcrystalline cracks typically with little or no evidence of general corrosion. For 304, cracking generally propagates along the intergranular pathways if the material is sensitized, but in non-sensitized material transgranular cracking is predominant. Intergranular SCC of austenitic stainless steels results from the precipitation of chromium, forming chromium--carbide particles (Cr₂₃C₆) along the grain boundary if heated and allowed to cool slowly (e.g., welding) over a temperature range of 500 to 850°C. This process is termed sensitization and depletes the chromium concentration in the surrounding matrix to below 12%, which is needed to preserve the protective nature of the surface oxide. The presence of manganese sulfides in the material, unlike the chromium carbides, has no effect on stress corrosion cracking in austenitic stainless steels.

Transgranular SCC is affected by numerous metallurgical factors, such as, crystal structure, yield strength, grain size and shape, composition, dislocation density and stacking fault energy. The key metallurgical factor is the alloying effects on slip planarity. The primary fracture facets for austenitic stainless steel tested in aqueous magnesium chloride at 155°C were on (100) planes¹⁵.

One additional metallurgical factor that affects stress corrosion cracking in austenitic stainless steels is the amount of cold work. The forming of a metal results in plastic deformation occurring to the metal which results in an increase in tensile and yield strength with a decrease in ductility. The cold work leads to a greater time to failure by SCC for a constant applied stress or a greater stress to obtain cracking in a similar time.

For chloride-bearing environments, defining a minimum chloride concentration below which SCC will not occur is difficult because of the effects of metallic cations, pH, oxygen concentration, and other reducible or adsorbed species. Some general minimum concentrations have been defined by API depending on the application. For example, API 650 which covers storage tanks specifies a maximum chloride concentration of 200 ppm for temperatures less than 40 °C and 100 ppm for temperatures between 40 and 65 °C, whereas API 651 specifies a maximum of 50 ppm for hydrotesting water. For SRS, an engineering standard specifies a maximum chloride level of 250 ppm at 740 °C¹⁶. As noted below, chloride levels as low as 5-10 ppm Cl can result in SCC.

The occurrence of SCC is a function of chloride concentration. As chloride concentration increases, the time to failure decreases. Figure 3 shows this effect for 304 stainless steels samples that were exposed at

100 °C under the concentration conditions of a Wick test. In this test the chloride solution is brought to the stainless steel surface through a porous medium. For the chloride concentrations shown, all the samples failed eventually.

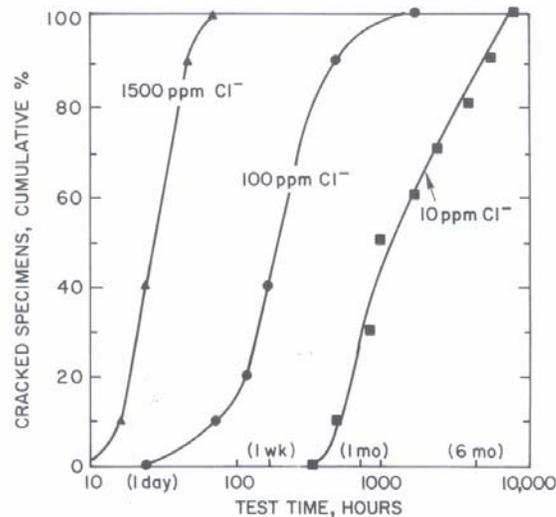


Figure 3 Effect of chloride concentration on the SCC susceptibility of 304 stainless steel exposed at 100 °C under the concentrating condition of the Wick tests¹⁷

The hydrogen concentration, i.e. pH, has a significant effect on cracking. As the pH is lowered time to failure via SCC decreases while at higher pH the failure time increases. In testing with 304 stainless steels, cracking was found at neutral pH (6-8) with temperatures at 185-200 °F (85-93 °C) and chloride levels as low as 5 ppm Cl. In a study by Rideout at SRS, sensitized 304 samples were found to crack in a 10 ppm Cl at 90 °C with pH in the range of approximately 2.5 to 7¹⁵. At lower pH values cracking was not observed since the solution pH was adjusted with nitric acid and the sample passivated.

Temperature also has a significant effect on SCC. A temperature of 60 °C was once thought to be a lower limit below which chloride stress corrosion cracking did not occur. Service failures over swimming pools and near marine environments have shown SCC can occur at room temperature¹⁷. Increasing temperature does lead to decreases in time to failure but also a transition from pitting to SCC. Figure 4 shows the results of a study with 304 in which the chloride concentration, pH and temperature were varied. These tests were performed in sodium chloride solutions with pH adjustments made with additions of either sodium hydroxide or hydrochloric acid.

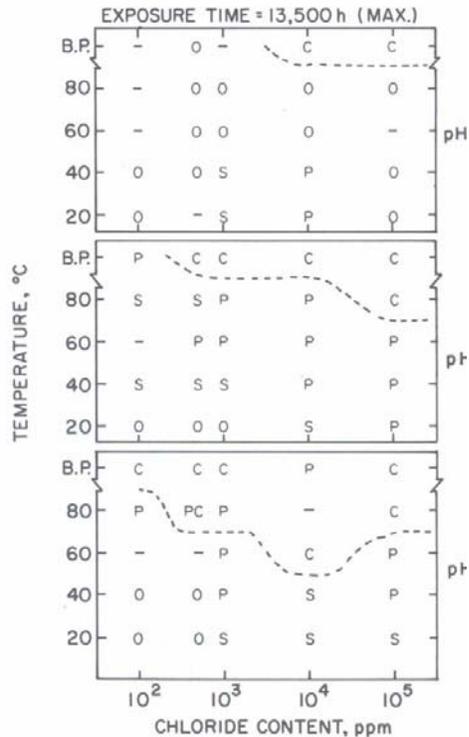


Figure 4 Effect of temperature, pH and chloride concentration on SCC susceptibility of 304 stainless steel in sodium chloride solutions (C=SCC, P=Pits, S=stains, O=no effect)¹⁸

Some additional factors that affect SCC are the presence of oxygen and metallic cations. Although not necessary for SCC depending on other conditions, the presence of oxygen can accelerate SCC. Metallic cations that are present can affect SCC occurrence. Mercury has been shown to aid in cracking and manganese does accelerate the attack intergranularly.

Embedded piping in the SRS canyon building has been subjected to a high chloride environment from the use of a PVC pipe wrap over cork insulation. This environment coupled with elevated temperature in steam piping led to SCC. Between 1956 and 1976 there were seventy-six embedded pipe failures with the chief cause of failure as chloride stress corrosion cracking. These cracks were tight since SCC was identified by macro-etching in hot 50% HCl but not by dye penetrant testing. The majority of these pipes/nozzles were used in steam or condensate service. These failures highlight the effect that chloride-bearing non-metallic parts, such as gaskets, can have on stainless steel components since degradation of these parts lead to SCC. Most of the other fluids that are fed through the embedded piping are free of chlorides or at ambient temperatures so are not expected to lead to SCC.

Nitric acid seepage past gasket material on HNO₃ absorber columns resulted in the stress corrosion cracking of 36% of the 240 (416 stainless steel) nuts and studs on one column. Only six of the nuts and studs were damaged in another column primarily because double gaskets were used as compared to single gaskets usage in the first column. Chemical analysis revealed that chlorides were present in undetermined quantities less than 200 PPM. These failures highlight that chlorides can concentrate during service and provide corrosion conditions.

The site has significantly reduced the instances of stress corrosion cracking in austenitic stainless steels through a chloride exclusion program that requires the leachable chloride content of any gasket, coating, tape, paint or ink contacting austenitic stainless steels be below 250 ppm.¹⁶

Pitting Corrosion

Pitting is an insidious localized form of corrosion which occurs on passivated metallic surfaces exposed to relatively specific aggressive environments. Small defects or discontinuities such as scratches, inclusions, or slight compositional variations in the passive film may selectively be attacked by the corrosive media and initiate a pit. Figure 5 shows the autocatalytic processes occurring in a corrosion pit. Pitting is influenced by temperature and is associated with velocity of the corrosive medium. Local aggressive chemistries develop in regions where stagnant conditions exist and mixing with the bulk solution is low. Once a pit has initiated an aggressive chemistry quite different from the bulk solution develops within the pit and may lead to rapid autocatalytic growth of the pit (in depth).

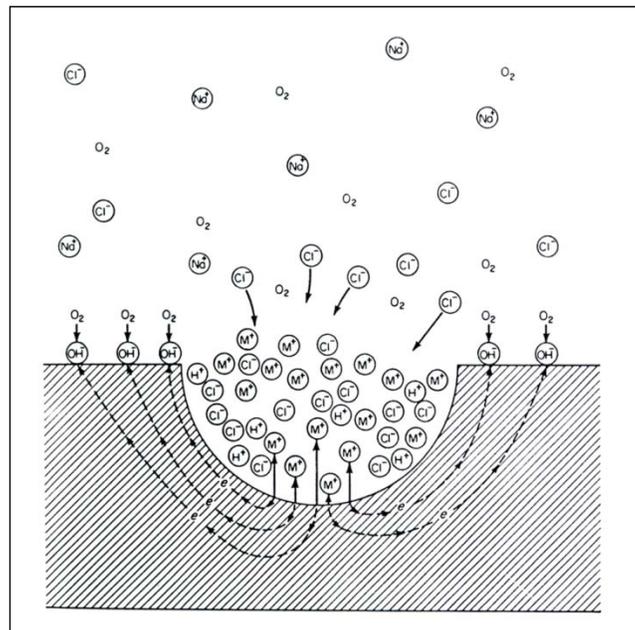


Figure 5 Autocatalytic growth of pit associated with metal dissolution, water hydrolysis and hydrogen or oxygen reduction leading to pit growth

Pitting is expected to occur most likely through the presence of chloride ions. These chlorides ions would be a contaminant in the piping. Material properties affect the pitting resistance in stainless steel. These properties include the presence of manganese sulfides, sensitization of the metal, surface condition and the effects of cold work. The effects of cold work have been found to either increase or decrease pitting resistance but this effect is small.

The presence of manganese sulfides is probably the most important factor contributing to the pitting resistance since the sulfides are sites of pit initiation¹⁸. The sulfides dissolve, especially in chloride bearing solutions, at the corrosion potential of stainless steel. A small pit without a protective oxide and containing an acidic environment is left for the dissolution of the base metal and propagation of the pit. The effectiveness of a sulfide inclusion as pit initiators is dependent on its shape, size and chemistry.

Welding of the piping can lead to sensitization of the base metal, which is the formation of chromium carbides that result from a thermal transient into a critical temperature range as discussed previously. These sites are more favored than the manganese sulfides. For 304, the manganese sulfides in the weld metal redistribute and provide a superior pitting resistance than the base metal.

The surface condition of stainless steel can alter the pitting resistance¹⁸. Heat treatments, grinding and abrasive blasting tend to decrease the pitting resistance. Pickling and passivation are beneficial due to the removal of manganese sulfides, embedded iron particles and the outer oxide layer which can be depleted in chromium.

The pitting process is also affected by the environment including the temperature, concentrations of aggressive species, oxygen and hydrogen ion (pH) concentrations. Aggressive species include chloride, thiosulfate (from manganese sulfides), mercury, and permanganate. For stainless steel the susceptibility to pitting increases with chloride concentration. A measure of this susceptibility is the pitting potential. The pitting potential is an electrochemical measure at which pitting is found to initiate and propagate in a given solution. As the concentration of chloride increases the pitting potential decreases logarithmically and pitting becomes more likely. The effect of chloride and temperature for 304 is shown in Figure 6¹⁹. At a given chloride concentration, the pitting potential decreases and pitting susceptibility increases with a rising temperature. These electrochemical changes are a manifestation of the change in the protective nature of the oxide film.

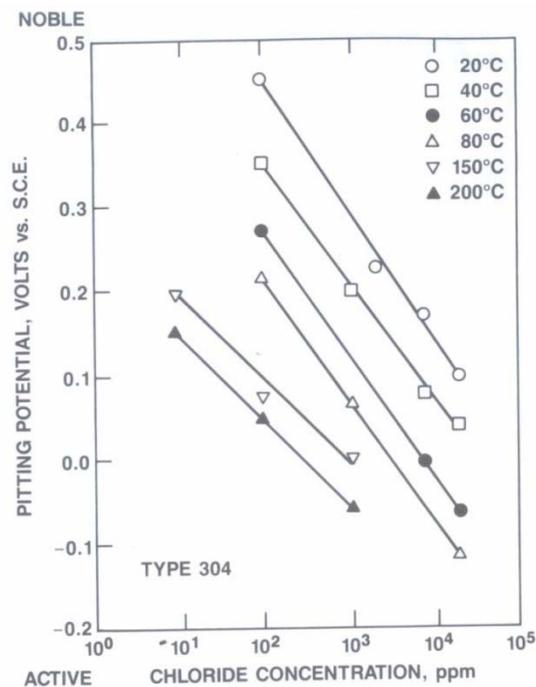


Figure 6 Effects of chloride concentration and temperature on the pitting potential of 304 stainless steel¹⁹

Even in the absence of chloride, pitting can occur due to the dissolution of manganese sulfides as discussed above. This dissolution leads to a local acidification and the formation of thiosulfate ions. For 304, pitting readily occurs in a solution (pH = 4.5) with 10 ppm thiosulfate at a temperature of 50 °C as

shown in Figure 7. 304 pitted at potentials even in the active range, i.e. less than 100 mV, which is well below the normal corrosion potential for stainless steel. .

The mercury and permanganate ions all act as cathodic depolarizers, i.e. they accelerate the cathodic reaction for the corrosion process¹⁸. This acceleration results from either increase efficiency of cathodic areas or as an additional cathodic reaction. The increased efficiency results from metal ions that deposit on the stainless steel surface which have a smaller overpotential for the cathodic reaction, which is oxygen reduction at neutral and alkaline pH water or hydrogen reduction in acidic water. For mercury, the concentration must be greater than 0.5 ppm to aggravate the corrosion due to the amalgamation of the stainless steel surface²⁰.

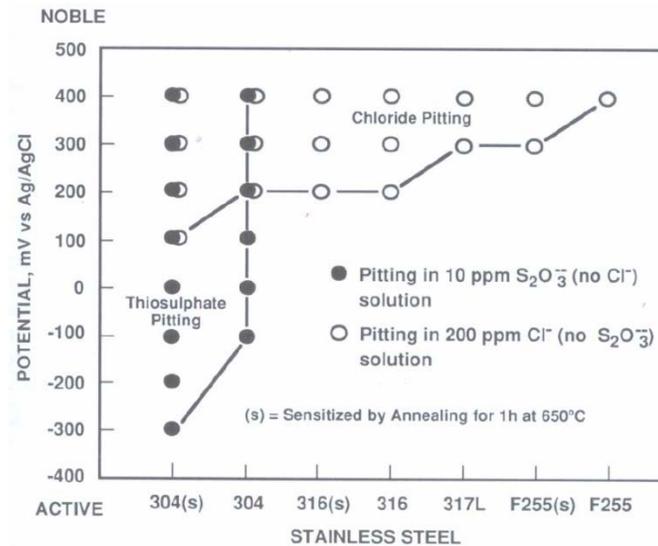


Figure 7 Pitting of stainless steels in chloride-containing and thiosulfate containing solutions at 24-hour potentiostatic tests¹⁸

Experimental evidence shows that although pit depths increase with time, pitting rates decrease. Because of the uncertainties in predicting the growth rate of the deepest pits, pitting control measures often depend upon the establishment of conditions under which pits do not initiate.

For H-canyon piping, mitigating actions for pitting include rinsing of the lines between changes in service, monitoring of chloride concentrations in feed water for steam system, and selection of low-chloride bearing non-metallic materials to be in contact with process equipment. Pitting attack of austenitic stainless steel is inhibited by the presence of nitric acid (i.e., nitric acid promotes the formation of a passive film layer on types 304 and 304L stainless steels), so using a low molar nitric acid rinse would be beneficial.

Crevice Corrosion

Crevice corrosion occurs at shielded locations with a stagnant solution such as under deposits (scale, corrosion products) or inside crevices (weld defects). These crevices can be at mating metal surfaces or where metal and non-metal surfaces are in contact. Concentration-cell attack is also used to describe this type of corrosion, although differences in metal ion or oxygen concentration are only part of the initiation

and growth process. Crevice corrosion can be an autocatalytic process, similar to pitting where metal dissolution is followed by water hydrolysis and the migration of chloride ions into the crevice. For the embedded piping, the source of chloride would be either non-metallic materials in contact with process equipment or introduced through chloride contaminated chemicals. Since the corrosion resistance depends upon the oxide film, which is destroyed by high concentrations of chloride and hydrogen ions, austenitic stainless steels are susceptible to crevice corrosion. This form of attack is shown schematically in Figure 8²¹.

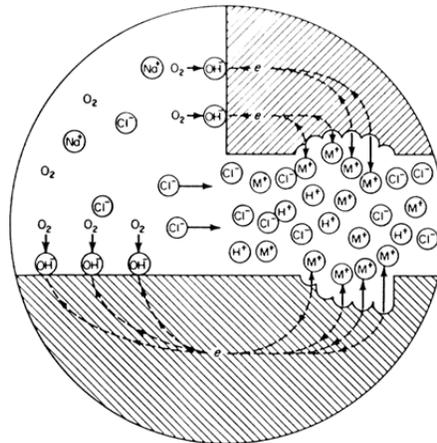


Figure 8 Schematic representation of crevice corrosion²¹

Crevice corrosion may initiate in stainless steel by several mechanisms¹⁸. For 304 in neutral low chloride solutions, the dissolution of manganese sulfide inclusions is the probable cause of crevice corrosion. As the manganese sulfide dissolves, the solution becomes acidic with the generation of hydrogen ions in addition to manganese and thiosulfate ions²². As the pH drops, the thiosulfate breaks down and anodic dissolution of the stainless surface commences. The corrosion products especially chromium cause water hydrolysis, which leads to further acidification of the water and migration of chloride ions into the crevice. This increased aggressiveness leads to general breakdown of the passive oxide.

In a higher chloride solution, the passive film could breakdown due to changes in the electrochemical nature of the passive film. This level will be influenced by temperature, the opening and depth of the crevice as well as other constituents in the solution. Mathematical modeling of the crevice corrosion process has been developed and with experimental inputs has been used to define predicted resistances to crevice corrosion of stainless steels in chloride-bearing waters²⁰. For 304, exceptional resistance is obtained at levels near 200 ppm. Others have reported a safe chloride limit of 100 ppm for 304²². Crevice corrosion and pitting are affected similarly by these variables because the mechanisms are similar. The effect of the solution constituents and temperature was discussed previously.

As referred to above, crevice size is a factor that contributes to the probability or likelihood of crevice corrosion occurring. Mathematical modeling has shown that the deeper the crevice and the narrower the opening or gap the more likely crevice corrosion will be to occur. The crevice size also affects the ratio of the cathode area to the anode area. Simplistically, the anode area is the active corroding portion of the crevice where the dissolution or anodic reaction is occurring. The cathode is generally the area surrounding the crevice on the exterior. As this ratio increases or the cathode size increases, the

probability of crevice corrosion increases as shown for stainless steels including 304 in Figure 9. The exposure was in flowing ambient temperature seawater for 30 days. The bold/crevice area ratio is the same as the cathode/anode surface area. However, the implication for embedded piping is still the same; crevice corrosion has a significant probability since the interior surface of the pipe can be the cathode.

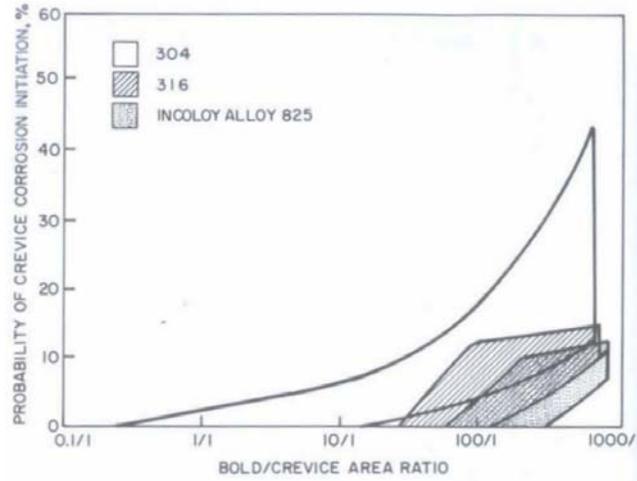


Figure 9 Probability of crevice corrosion initiation as a function bold/crevice area ratio¹⁸

Mitigation of crevice corrosion for the embedded piping would consist again of a thorough flush of chemicals that may increase cathodic depolarization such as manganous or permanganate ions and the minimization of chloride contamination. The low temperature of operation will aid in minimizing crevice corrosion. Back in the late 1960s and early 1970s, cooling water for process equipment and steam condensate was found to lead to crevice corrosion under deposits in the headers which were made of carbon steel^{23, 24}. This example demonstrates the importance of monitoring the chemistries of process fluids to control impurities.

Intergranular Corrosion

Intergranular corrosion (IGC) occurs when grain boundaries are attacked preferentially in a corrosive oxidizing solution. In IGC, the grain boundary is active whereas the grain is passive. Sensitization is the common cause of IGC especially in heat-treated or welded austenitic stainless steels. As discussed previously, sensitization of the metal structure occurs due to the formation of chromium carbides on the grain boundaries and depletion of chromium from the adjacent grain. This chromium depletion creates an oxide film on the surface next to the grain boundary susceptible to corrosion. Figure 10 depicts a schematic representation of carbide particle precipitation at the grain boundary during sensitization to IGC in stainless steel¹⁴. Low carbon (<0.3%) grades of stainless steel are made to minimize the occurrence of sensitization since an increasing amount of time is required for carbides to form as the carbon content is reduce.

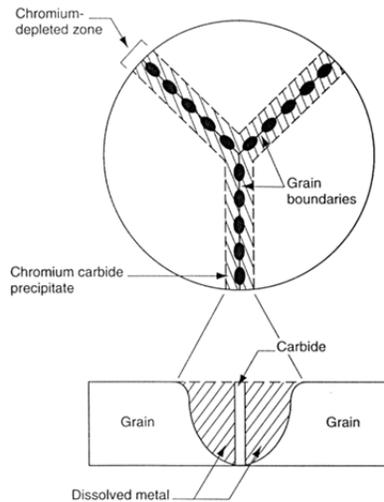


Figure 10 Schematic representation of carbide precipitation at a grain boundary during sensitization to intergranular corrosion in stainless steel¹⁴

Sensitization of austenitic stainless steels during welding is known as weld decay. Intergranular corrosion, the classic form of weld decay, is more evident at elevated temperatures as documented from the failure of several of the batch evaporators in the separation areas²⁵. The “weld decay” area in most cases is removed from the weld metal as shown in Figure 11. Because of microstructural inhomogeneities and temperature variations during the multi-pass weld, totally uniform through-wall attack is not anticipated. The degree of sensitization in a weld HAZ would determine the depth of attack.

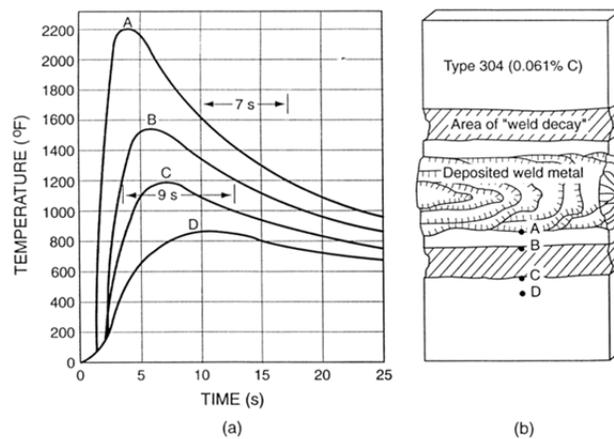


Figure 11 Thermal transients producing weld decay during welding of austenitic stainless steel: (a) temperature-time relationships; (b) location of thermocouples¹⁴

Other factors that affect IGC include the material composition, which is established for the embedded piping, microstructure, cold work, and exposure to radiation. Exposure to radiation would be the most of

these for the embedded piping since the other factors (besides composition) are unknown. Radiation increased chromium depletion at the grain boundaries without the precipitation of chromium carbides although a large neutron fluence is required.

Another form of IGC is end-grain attack where grain boundaries which are oriented parallel to the rolling direction of the material are preferentially attacked. Since there is an increased number of sites favorable for the initiation of corrosion in the longitudinal direction compared to that of other rolling orientations, this region is prone to increased corrosive attack. All components in repaired and new vessels are required to have any surface with exposed end grains weld overlaid. End grain attack has been observed in nozzles of several of the process vessels in canyon buildings, as well as one nozzle for piping.

There have also been other documented cases of IGC in the canyons although not with embedded piping. In a 1/2" 304 stainless steel tube was welded to the 13th tray draw-off line of the nitric acid absorber which was constructed of 304 ELC²⁶. It was found that part of the 1/2 " tubing which was inside the draw-off line showed intergranular attack at the weld. Another instance of intergranular corrosion of the HAZ involved a 2" Schedule 80, 304 stainless steel nozzle removed from the bottom of an HNO₃ tank²⁷. The thickness away from the HAZ ranged from 0.210" to 0.218" while the minimum thickness at the heat affected zone was 0.070".

IGC is not expected to lead to failure and is most likely to occur in embedded piping that carries the more concentrated nitric acids and only if other oxidizing species are present such as chromium or manganese ions. Again, rinsing piping prior to change in service will assist in minimizing this type of corrosion.

The incidences of intergranular corrosion have now been essentially mitigated by using a selection process for austenitic stainless steels and other austenitic alloys that required a corrosion release test, as summarized in Reference 6 which is included in this issue of the Journal of Nuclear Materials Management.

Corrosion Fatigue

Fatigue is the failure or fracture under repeated cyclic loads at stress levels below the yield point. Surface discontinuities such as notches, sharp corners or surface roughness act as stress raisers and serve as crack initiation points. Corrosion fatigue (CF), which is defined as the reduction in fatigue resistance due to exposure to a corrosive medium, results from the combined deleterious effects of cyclic stresses and a corrosive environment. Stainless steels possess a good corrosion fatigue resistance in water systems but may be susceptible to CF depending on oxygen content, temperature, pH, and composition of the exposure environment. The susceptibility is also markedly affected by stress-cycle frequency and is more pronounced at low frequencies.

Corrosive mediums that produce pitting are most prevalent to CF such as in chloride bearing environments. Pit sites are regions where aggressive environments may concentrate. The combined effect of a locally aggressive environment with cyclic stresses promotes the propagation of CF cracks. One of the embedded piping liner failures in a canyon building was associated with CF. The cycling was associated with the thermal cycling of the on/off use of the steam line²⁸.

A Type 309 stainless steel shaft exposed to an environment of acidified condensate containing 0.16% HNO₃ failed by corrosion fatigue. Fracture was noted to have begun at the edge of the keyway and crack growth was enhanced by the presence of the aggressive environment.

Erosion-Corrosion

Erosion corrosion results when abrasive particles or fluids flow flowing at a high rate impinge on the metal surface and remove the protective oxide layer. The nascent (bare) metal surface then reacts with the corrosive environment forming a new protective oxide layer. This cycle is repeated and rapid metal loss occurs.

An example of erosion corrosion in H-area is a return piping weld in a stainless steel evaporator column located in building 221-H²⁵. The return piping was contained within the vessel and was 50% to 75% eroded. The erosion-corrosion attack occurred from the inside out but, unfortunately, the contents of the tanks and the time in service could not be accurately established. The lack of all the information required to effectively address a corrosion problem is common in industrial/production situations and can inhibit mitigating the observed failure process. Fortunately, even though the exposure conditions were not conclusively established, a basic knowledge of the operating conditions (fluid flow, aggressive environment and turbulence) was sufficient to identify the erosion-corrosion process. Another important factor contributing to maintaining system integrity was that the eroded area was identified through routine examination of operating system.

Microbiologically Influenced Corrosion

Microbiologically Influenced Corrosion (MIC) may result when structural materials are exposed to stagnant or low flow aqueous environments (particularly untreated water) for long periods of time. This type of corrosion is observed in regions of a piping system, especially welds, where flow rates of less than 3 ft/sec exist. Stagnant systems promote the growth of various microbiological organisms which can form films and deposits on exposed metal that accelerate attack of the material. MIC would affect the inside of the pipes or vessels where flow may be reduced or in low points where water collects when the components are out of service for an extended period of time.

Microorganisms are present in virtually all natural aqueous environments; however the presence of bacteria does not necessitate their involvement in the corrosion process. Specific bacteria have been identified that lead to localized corrosion of stainless steel. Bacteria include iron and manganese oxidizing bacteria and sulfate reducing bacteria. Bacteria attach to surfaces and develop biological films or colonies, which contain both aerobic and anaerobic bacteria, where bacteria can have synergistic relationships. Bacteria affect the corrosion process by changing the local environment including pH, oxidizing power and concentration of aggressive species (Cl⁻, Fe⁺³). Along with these environmental changes, the presence of a non-continuous film leads to the development of oxygen and chemical concentration cells. The oxygen depleted regions are where the protective oxide breaks down and initiates the localized corrosion.

For stainless steels, welds and heat-affected zones are a frequent location for microbiological influenced corrosion (MIC), which is manifested as pitting¹⁸. The pits have a characteristic morphology with a minute pinhole penetration with large subsurface cavities. On the surface there are deposits which are

generally discrete mounds with colors distinctive to the type of bacteria, such as the red tubercles associated with iron-oxidizing bacteria (*Gallionella*). The pits are enriched with chromium and chloride. With chloride present, cracks can radiate from the pits depending on the surrounding stress field. The reasons that films or colonies develop are insufficient biocides and poor practices after hydrotesting including leaving standing impure water.

The bacteria growth and proliferation occurs over a broad range of conditions. Optimal conditions for bacteria associated with MIC are (parenthetic values show the range) for temperature, 15 – 45 °C (0 – 99 °C) and pH, 6 – 8 (0 – 10.5). The energy sources also cover a broad range including oxygen, nitrate, carbon dioxide and sulfate. The storage of heavy water in drums at warm temperatures (30-40 °C) without biocides and some amount of chloride makes it favorable for the development of biofilms if bacteria associated with MIC are present.

Microbiologically induced corrosion damage was discovered as a result of leaks which developed in two parallel 16-inch carbon steel piping systems between 1972 and 1976²⁹. This section of pipe was replaced with schedule 10S stainless steel pipe during a period when process operations were suspended. New leaks began to appear in this new section of pipe in 1991 due to low laminar flow (estimated at 2 gpm) conditions. A one-inch layer of mud which proved to contain anaerobic, sulfate reducing, and acid-producing types of bioorganisms covered the inside surface of the pipe.

Radiation Embrittlement

Type 304-L stainless steel is an extremely ductile and tough material even after irradiation. Experimental tests were performed to evaluate the fracture behavior of irradiated Type 304 and Type 304-L stainless steel at high radiation exposure levels for evaluating the structural integrity of the SRS reactor tanks^{30, 31}. Test results showed that some loss of fracture toughness occurs at exposures of 0.1 displacements per atom (dpa). The materials have high fracture toughness and the structures do not become embrittled threatening structural integrity even after exposures to 6.4 dpa. Canyon process vessels and piping would be exposed to high radiation fields (primarily gamma radiation) that would lead to displacement damage, but the lifetime exposure (100 years) would result in exposures roughly estimated to be much less than 0.1 dpa.

End Grain Attack

End grain attack is a type of corrosion that preferentially attacks defects (inclusions, stringers, etc.) and grain boundaries which are oriented parallel to the rolling direction of the material. Since there is an increased number of sites favorable for the initiation of corrosion in the longitudinal direction compared to that of other rolling orientations, this region is prone to increased corrosive attack. End grain attack was observed in thermowells for low activity waste evaporators due to an incorrect material chosen for the end tip. To combat this form of degradation, all components in repaired and new vessels are required to have any surface with exposed end grains weld overlaid. End grain attack in weld overlaid material has not been observed.

Knife Line Attack

Knife line attack occurs in “as welded” 347, 348, 321 309Cb and any other columbium or titanium stabilized grade stainless steel when sensitized in the temperature range of 1000 to 1500 °F. This is a special form of intergranular attack and occurs in sensitized regions near welds³². These regions are very thin (knife-line thin). Knife line attack is not a common degradation mechanism but has occurred at the Site. An Area Metallurgical Report filed in February 1956, describes the inspection of a 309Cb slag and crucible dissolver coil which showed 1/16” deep attack at the outer edge of the weld joining the coil of the riser³³. Knife line attack was shown to have occurred beside the weld. Another failure in November 1956 was reported as knife line attack of longitudinal welds of two 309Cb 3” O.D. Schedule 40 welded pipe risers of EP 311.12^{34,35}. Severe knife line attack was noted along the length of riser #2 on either side of the girth welds.

These examples of knife-line attack are given primarily to illustrate the potential for such degradation and to demonstrate that long term record keeping may add value to any process. The use of Cb stabilized steel was discouraged because of the potential for knife-line and new staff assigned to the areas can appreciate the reasoning when examples of failures are presented to support the avoidance of such materials.

Conclusions

The discussion of mechanisms that could cause degradation of the austenitic stainless steels used for 50 plus years in the SRS chemical separation facilities has illustrated:

- 1) Corrosion induced degradation of the austenitic stainless steels used in nuclear materials extraction and separation processes is not unique but is common to systems handling nitric acid solutions,
- 2) General corrosion of austenitic structures by nitric acid solutions can be avoided because its behavior in many environments is predictable from data available in the literature,
- 3) The potential for stress corrosion cracking can be reduced by a chloride exclusion program which required that materials with leachable chlorides be excluded from use in austenitic stainless systems,
- 4) The potential for intergranular corrosion can be significantly reduced by a materials selection program that requires a steel pass a corrosion release test before use in a wetted system,
- 5) End grain attack can be avoided by placing a weld overlay on surfaces which have exposed end grains, and
- 6) MIC can occur even when the exposure environment is radioactive so the attention to leaving water laid up in systems should be particularly avoided.

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