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Evaluation of Pad 18 Spent Mercury Gold Trap Stainless Steel Container Failure

T. E. Skidmore

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EXECUTIVE SUMMARY

Failure of the Pad 18 spent mercury gold trap stainless steel waste container is principally attributed to corrosion induced by degradation of plasticized polyvinyl chloride (pPVC) waste packaging material. Dehydrochlorination of pPVC polymer by thermal and/or radiolytic degradation is well-known to evolve HCl gas, which is highly corrosive to stainless steel and other metals in the presence of moisture. Degradation of the pPVC packaging material was likely caused by radiolysis in the presence of tritium gas within the waste container, though other degradation mechanisms (aging, thermo-oxidation, plasticizer migration) over 30 years storage may have contributed. Corrosion was also likely enhanced by the crevice in the container weld design and may have been enhanced by the presence of tritiated water. Similar non-failed spent mercury gold trap waste containers did not show radiographic evidence of plastic packaging or trapped free liquid within the container. Therefore, those containers are not expected to exhibit similar failures. Halogenated polymers such as pPVC subject to degradation can evolve halide gases such as HCl, which is corrosive in the presence of moisture and can generate pressure in sealed systems.

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LIST OF ABBREVIATIONS

ADS	Analytical Development Section
CCT	Critical Crevice Temperature
CPT	Critical Pitting Temperature
DOE	Department of Energy
FT-IR	Fourier Transform InfraRed
G Value	Molecules per 100 eV
GC-MS	Gas Chromatography-Mass Spectroscopy
Gray	International Unit of ionizing radiation absorbed, 1 Gy = 100 rad
HCL	Hydrochloric acid
HDPE	High density polyethylene
HE	Helium embrittlement
ICP-OES	Inductively-Coupled Plasma-Optical Emission Spectroscopy
IGC	Intergranular Corrosion
LDPE	Low density polyethylene
LME	Liquid metal embrittlement
MCWS	Melter Cooling Water System
MIC	Microbiologically-Induced Corrosion
NBR	Acrylonitrile-butadiene rubber (nitrile)
pH	Potential of hydrogen
PPE	Personal Protective Equipment
pPVC	Plasticized polyvinylchloride
PREN	Pitting Resistance Equivalent Number
PVC	Polyvinyl chloride
Rad	Unit of ionizing radiation energy absorbed (1 rad = 100 erg/g)
SCC	Stress-corrosion cracking
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SVOA	Semi-volatile Organic Analysis
SWMF	Solid Waste Management Facility
Tg	Glass transition temperature
Tm	Melting temperature
TRU	Transuranic
XRF	X-ray fluorescence

1.0 Introduction & Background

On May 23, 2016, during weekly Hazardous Waste inspection rounds on TRU (Transuranic) Pad 18 at the Solid Waste Management Facility (SWMF), a Production Operator discovered ~8-10 ounces of dark liquid inside a portable spill dike underneath four welded stainless steel cylinders containing spent mercury gold traps received from the Tritium facility. Some of the liquid was dried and some pooled. The First Line Manager (FLM) and the Shift Operations Manager (SOM) were notified and directed personnel to go 100 meters up wind. The Hazmat Team (Fire Department) entered Pad 18 and at approximately 2 feet from the liquid, the portable tritium (Scintrex) monitor began steadily increasing and read 38 to 41 x 10^{-5} µCi/cc. The team then backed off the Pad after opening the north and south doors. The team removed their personal protective equipment (PPE) and returned to the 100 meter zone. No contamination was found on Hazmat Team personnel. A 100 meter zone around Pad 18 was barricaded and access was restricted.

The leaking container (HMSF001220) was received from Tritium on 12/10/1985, initially placed into Culvert T3 in 643-29E, and was later removed from Culvert T3 and placed into Culvert T5. On 9/16/2009, the container was removed from Culvert T5 and stored on a pallet in 643-29E. The container/pallet was relocated from 643-29E to TRU Pad 16 on 4/14/2011. On 5/09/2014, the container/pallet was relocated to TRU Pad 18. The container is currently located inside a spill dike on Pad 18 with other similar containers (HMSF001221, HMSF001222 and HMSF001223), all containing spent mercury gold traps from the Tritium facility (Figure 1).

Inspection of the container (HMSF001220) revealed signs of corrosion on the suspected leaking end (opposite of lifting lugs), Figure 2. The container was rotated for examination and photographed. Significant staining was observed on the container consistent with the contact point with the storage pallet. Pitting was also observed on the container end weld (Figure 3). Minor corrosion is also evident on the ends of other containers, but is more consistent with iron contamination during container fabrication, welding and handling.

SWMF waste receipt records indicate the failed container (HMSF001220) contained 38,480 Ci of Tritium upon receipt in 1985. This initial tritium activity decayed to 2016 gives a current tritium value of 6,937 Ci. However, there are no records or indications that the tritium activity of this container at the time of waste generation was specifically measured. The tritium activity assigned to this container was taken as 50% of the total tritium activity of a shipment of two containers received from the Tritium facility on 12/10/85. Review of the 1985 Tritium Facility authorization/planning documents for removal of these spent mercury gold traps [STA 229] revealed a maximum expected tritium activity of 200 Ci in a spent mercury gold trap. The technical basis for the curie activity estimate in the SWMF waste receipts is not documented. Initial mercury content was reported at a concentration of 100 mg/kg, with a total mercury content estimated at 15 grams. The mercury is amalgamated with gold within the trap and is not in a liquid form.

The waste container is a stainless steel pipe cylinder, approximately 47.5" L x 18" D, SCH10 (wall thickness of 0.188", 35.76 lbs/ft, approximately 143 lbs empty weight) with a total loaded weight of approximately 367 lbs. The original weld design called for a fillet weld only, not a full penetration weld. This inherently leaves a crevice that can trap moisture and corrosive species, but the containers were not intended to contain liquid. The container was designed for a maximum pressure of 42 psig, presumably to account for tritium decay/helium formation and thermal cycling during storage.

The use of plastic packaging was primarily to reduce tritium exposure to workers during spent mercury gold trap removal and handling, and was not a shipping requirement. At the time of waste container closure (late 1985), there was not an active Waste Certification Program, there was no restriction against the use of plastic packaging (any type) or chloride-bearing materials, nor was there a requirement that the containers be free of liquid at the time of closure. Interviews of several Tritium Facility personnel, both current and retired employees, provided information and additional details of the practices used in the removing and packaging of these spent mercury gold traps. These interviews were conducted principally by Jack Alexander. A summary of these interviews is included in Appendix B in this report.

Figure 1. Spent Mercury Gold Trap Cylinders Stored on Pad 18
(current configuration after spill contained/observed)

Figure 2. Leakage initially found from gold trap container HMSF001220

Figure 3. Corrosion at the leaking end of cylinder HMSF001220 (rotated for examination)
(Pitting in weld area and staining consistent with pallet orientation, leak site not identified)

2.0 Liquid Analytical Results

The leaked liquid was sampled and submitted to SRNL/Analytical Development Section (ADS) for analysis. The following is a summary of analytical results provided by Charles Coleman in SRNL/ADS, with different analyses performed by several different researchers/analysts. The analyses were performed in a very timely manner. Details of the analyses performed are given in Appendix A.

The spill solution contained tritium at a concentration of 1.07×10^3 µCi/g as measured by liquid scintillation counting. The acid concentration was 3.8 N as measured by titration with base. Anion analysis by ion chromatography detected a chloride concentration of 1.48×10^5 mg/L (ppm) or about 4.2 M (comparable to the acid concentration). No other anions (fluoride, formate, nitrite, bromide, nitrate, sulfate, oxalate, or phosphate) were detected (above detection limits).

Considering the possible source of the chloride to be from degrading pPVC (plasticized PVC) packaging, the liquid was analyzed for evidence of species consistent with the presence and degradation of pPVC. Both semivolatile organic analysis (SVOA) by gas chromatography-mass spectroscopy (GC-MS) techniques and Fourier transform infrared (FT-IR) spectroscopy analysis detected significant quantities of the plasticizer bis(2-ethylhexyl)hexanedionic acid ester. The FT-IR analysis also detected the plasticizer dioctyl adipate (DOA). Both plasticizers are consistent with the presence and degradation of pPVC [1]. Since the organic compounds were not homogeneously distributed in the spill solution, these analyses should only be considered qualitative confirmation of PVC degradation products and not quantitative measurements.

X-ray fluorescence (XRF) analysis detected large peaks for elements consistent with stainless steel corrosion products (iron, chromium, and nickel). No mercury was detected in the solution by XRF analysis with a detection limit for mercury of about 1 mg/L. Stainless steel corrosion metals were also measured in the solution by inductively coupled plasma-optical emission spectroscopy (ICP-OES) as follows: iron: 4.72×10^4 mg/L; chromium: 1.71×10^4 mg/L; nickel: 1.52×10^4 mg/L. No other elements of consequence were detected in the solution by emission spectroscopy in the simultaneous analysis of 34 elements. Some of the other elements detected (Ca, Ba, P, Zn) may be attributed to stabilizers in plasticized PVC or other sources.

Analysis of the plastic itself would have to be performed to positively confirm pPVC presence, but the presence of acidic chlorides and plasticizers associated with pPVC, and absence of other corrosive species strongly supports the conclusion that the liquid is principally from the degradation of pPVC and generation of HCl. The source of the water is less conclusive.

Given the presence of tritium within the container, it is possible that some of the HCl gas generated by degradation of the pPVC packaging has converted to TCl via proton exchange. The extent to which this has occurred is unknown.

3.0 X-Ray Examination Results

X-ray examination of the failed waste container (HMFS001220) by AECOM personnel revealed the internal presence of a significant quantity of plastic packaging material as well as the presence of approximately 250 mL of remaining residual liquid. A total of approximately 500 mL of liquid is estimated to have been within the container prior to leakage, based on the leakage volume (~250 mL), the amount of sample obtained for analysis and volumetric estimation of remaining liquid from X-ray images. X-ray images of the failed container are shown in Figure 4a-b. Figure 4b shows the container elevated approximately 7° to confirm liquid shift. Note the distinction between plastic packaging external to the container and the packaging within the container and around the gold trap.
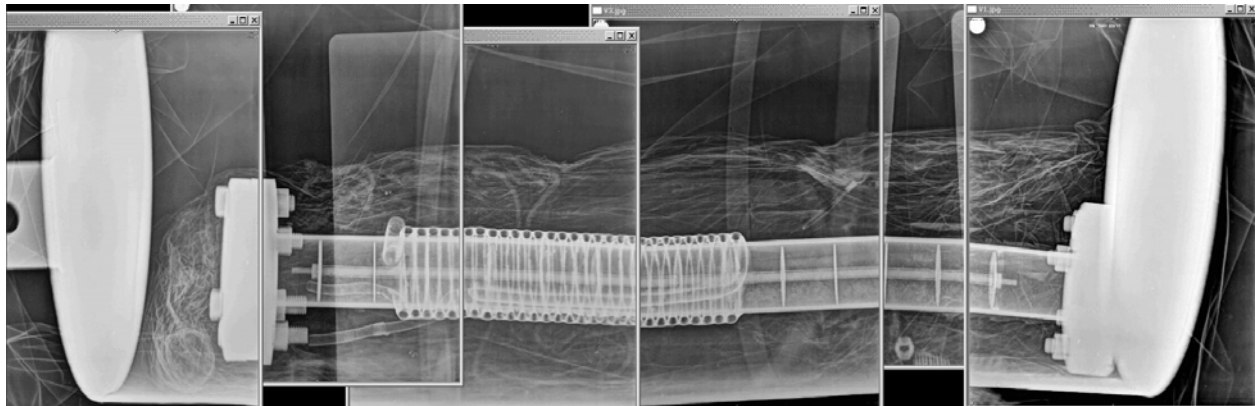
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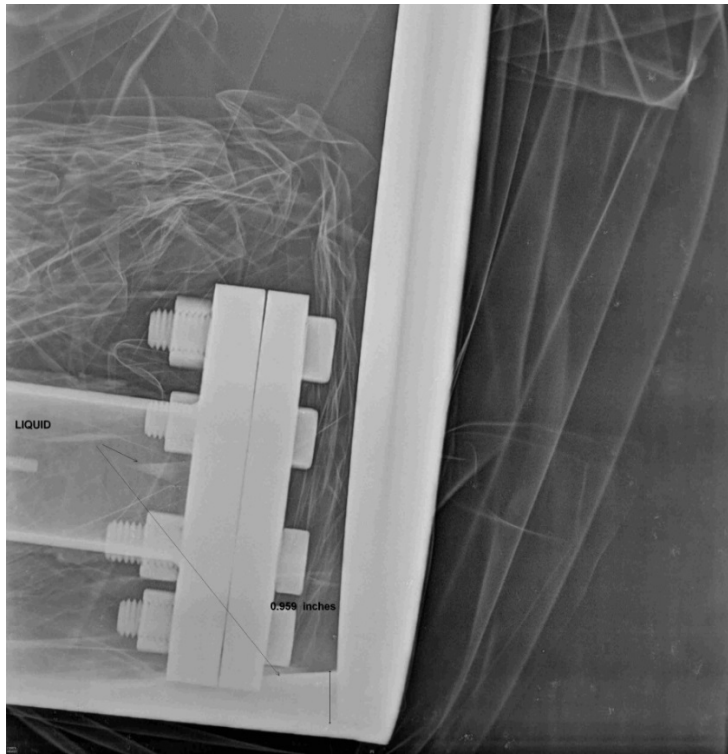
4b.

Figure 4a-b. X-ray images of container HMFS001220 with spent mercury gold trap
(liquid confirmed after a 7° elevation)

X-ray examination of the three other non-failed spent mercury gold trap waste containers showed no evidence of plastic packaging or trapped liquid within the containers. Therefore, those containers are not considered at risk for failure by the same mechanism. If there are any additional sealed waste containers that contain similar packaging subject to degradation and in the presence of water/moisture, they would be expected to exhibit similar behavior.

Based on physical examination, analytical and radiographic examination results, the main aspects of the failure are summarized below:

- Liquid has free acid normality of 3.8N
- Chlorides detected (148,000 mg/L), no other corrosive species were detected
- Pitting is observed on the exterior of the leaking container weld
- Plasticizers (esters, adipates) consistent with pPVC were detected
- X-ray examination confirmed plastic packaging and trapped liquid within the failed container. No liquid or packaging was observed within the non-failed containers.
- Tritium personnel confirm that pPVC was commonly used for tritium/contamination control at the time of interest (1985). There was no restriction on the use of plastic packaging (pPVC or other type) for the spent mercury gold trap shipments.
- Liquid appears external to the spent mercury gold trap, which appears to be sealed.
- There was no requirement to inspect for water within the container prior to closure.
- Tritium gas within the container is known to degrade organic materials, including pPVC, and contribute to corrosion in the form of tritiated water.
- PVC degrades via thermal and/or radiolytic dehydrochlorination, with HCl gas being the primary species evolved. HCl is very corrosive to many materials in presence of moisture.
- Dehydrochlorination is noted in literature to be autocatalytic.
- Plasticizer migration and aging over time can influence polymer stability and susceptibility to HCl evolution.

4.0 Degradation Mechanisms

Based on the analytical results, the liquid inside waste container HMFS001220 contains strong acid and high chlorides, essentially HCl, as well as plasticizers consistent with the presence and degradation of pPVC. Given these results, the absence of other corrosive species and the overall service conditions this container experienced during storage, the most likely failure mechanism is general and pitting/crevice corrosion due to aqueous HCl exposure. Hydrochloric acid is very aggressive to many materials, including austenitic stainless steel.

Per Tritium representatives, the use of pPVC packaging for contamination control was common practice in the time of shipment (1985). Therefore, it is reasonable to assume that the plastic packaging observed within the leaking waste container is pPVC. At the time of container closure and shipment, there was neither a restriction against the use of plastic packaging (of any type) nor any restriction or inspection steps to prevent and verify the absence of water/moisture within the container.

Assuming the packaging material to be pPVC, breakdown of pPVC packaging due to radiolytic decay in the presence of tritium gas as well as approximately 30 years of aging is considered the most likely source of the HCl within the stainless steel cylinder. The potential sources of the water are discussed in a later section. Additional discussion on HCl evolution from pPVC and corrosion of stainless steel is provided.

4.1   Degradation of Poly(vinyl chloride)/PVC

4.1.1 Thermal dehydrochlorination

Dehydrochlorination of poly(vinyl chloride) or PVC has been a known degradation mechanism since the early days of PVC production (1940s) [1]. HCl evolution caused early corrosion of PVC processing equipment in absence of heat stabilizers and other additives. Thermal dehydrochlorination of PVC has been studied by many investigators and is known to be is a very complex process. Thermal decomposition of PVC has been widely studied for many reasons such as toxicity and corrosive behavior during fire, pyrolysis products during incineration and potential degradation in service [2-15].

The basic mechanism of PVC dehydrochlorination is shown in Figure 5. Essentially, the carbon-chloride bond is broken, a double bond is formed, releasing HCl as a gas.
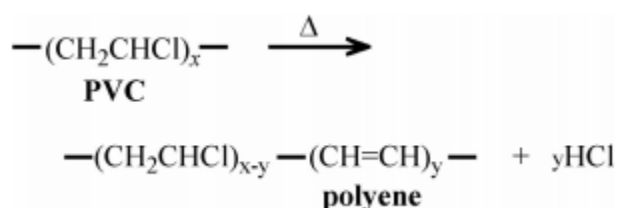
Figure 5. Dehydrochlorination of PVC to form HCl gas

Most literature references suggest that thermal dehydrochlorination of PVC does not significantly occur (or at all) below 100 °C, though some references indicate that HCl can be detected at temperatures as low as 70-80 °C, particularly for pure or non-stabilized polymer [5].

Being principally an amorphous (non-crystalline) polymer, rigid PVC exhibits a glass transition temperature (T_g) rather than a sharp melting temperature (T_m). The glass transition temperature of rigid PVC is typically reported in range of 70 to 105°C [1]. Unlike inherently flexible polymers, plasticizers must be added to PVC to impart flexibility. The addition of plasticizers is known to suppress HCl generation, but plasticizer migration over time can occur, possibly altering HCl generation behavior. Plasticized PVC (pPVC) compounds typically contain 25-35% plasticizer by weight, with some products containing 40 wt% or more [1].

Concerns regarding the thermal decomposition of pPVC contamination bags were identified in an Assessment of Plutonium Storage Safety conducted by the Department of Energy (DOE) in 1994 [16]. For nuclear material packaging applications, pPVC bags have been tested at various temperatures to investigate thermal degradation and pressure generation [17-19]. In Reference 17, testing of sealed outer rim food pack cans with PVC bags inside was performed at 85 °C, 110 °C, and 135 °C. Significant bulging of the outer sealed food pack cans was observed within weeks at 110 °C and 135 °C while no significant changes to the package were observed after 8 months at 85 °C.

This is consistent with other reports which suggest pPVC degrades in 1-2 months at 98 °C [18] and testing performed by SRNL/Separations Technology where decomposition begins at 194 °F (90 °C) [19]. Food pack can pressurization has occurred at Savannah River Site (SRS) where pPVC bags have been utilized, although can failure did not occur [20]. Corrosion has also been observed on the interior of such containers due to HCl generation.

In recent evaluations for Pu storage in K-Area, SRNL suggested 75 °C as a temperature threshold to preclude HCl generation within 9975 shipping containers due to thermal dehydrochlorination [21]. This temperature corresponds to a heat load of 7W. The impact of HCl evolution within containers that might see higher service temperatures due to higher heat loads was also evaluated [22]. At a maximum heat load of 19W, the average gas temperature in a 9975 shipping package PCV (primary containment vessel) during storage could reach 249.3 °F (120.7 °C) at a maximum recorded ambient of 104 °F. Reference 22 calculated the pressure contribution from 60 g of pPVC and other sources to be 172.4 psig within a sealed PCV containing $\leq$3000 g of plutonium oxide (with $\leq$6 g adsorbed moisture), a maximum heat load of 19W, and a free volume of 0.188 ft^3.

Since waste containers stored in the SWMF are not exposed to temperatures sufficient to cause thermal dehydrochlorination (>75 °C), thermal dehydrochlorination of the pPVC packaging material is not considered the primary cause of polymer degradation and generation of HCl gas within the spent mercury gold trap container. The combination of aging, thermo-oxidation, plasticizer migration and other mechanisms may have lowered the threshold temperature for thermal dehydrochlorination to occur, but temperatures in the SWMF are significantly lower than 75 °C.

4.1.2 Radiolytic Dehydrochlorination

Radiolytic degradation of organic materials has been studied for many years and reasons, principally to evaluate long-term performance of the materials in service, gas generation and pressurization within sealed systems, and for toxicity/corrosion concerns.

An abundance of data exists on the radiolytic degradation of organic materials during transportation and long-term storage in TRU waste environments [23-26]. CH-TRU and RH-TRU appendices provide significant data on the gas generation behavior of many polymers, including PVC, due to alpha/gamma radiolysis from TRU exposure. Several studies on the gas generation from polymers including PVC due to radiolysis have been performed [23-34]. Most studies have focused on either gamma or alpha radiolysis in air, though some have evaluated behavior in inert or low-oxygen environments or the effects of relative humidity (RH). Gas generation due to tritium exposure and beta decay has been less studied, though electron beam irradiation of polymers, including PVC, has been studied more extensively in recent years for sterilization and radiation processing.

A primary concern with storage of polymers in sealed containers is the formation of gases resulting from degradation, causing container pressurization and corrosion. Flammable gases such as hydrogen are of particular concern. Gas generation is typically expressed in G values (number of gas molecules formed or consumed per 100 electron volts (eV) of energy absorbed). Polyethylene is typically considered bounding for hydrogen gas generation from polymers, with $G(H_2)$ = 4.0. In contrast, PVC does not liberate significant hydrogen but G(total gas) and G(HCl) values for PVC can be much higher. G(total) values for PVC have been reported as high as 23, with the majority of liberated gas being HCl and other gases such as H_2, CO, and CO_2 evolved in lower amounts [23]. Such high values are usually associated with pure or non-stabilized PVC. Lower G(HCl) values are expected for most plasticized PVC formulations. However, if plasticizers and other stabilizers are lost over time, higher G values may apply.

Determining the amount of HCl liberated in a specific situation including the spent mercury gold trap container is difficult due to the many variables involved. The true tritium activity and the amount of polymer packaging within the container at the time of closure are unknown. This can be evaluated in more detail if needed, but is beyond the scope of this report. It is emphasized that whenever polymer materials are used within a sealed system, the potential for pressure generation and corrosion due to gas evolution should be considered.

A complicating aspect of radiolytic degradation of polymers is that many polymers have been found to be sensitive to the radiation dose rate. A notable industry failure of PVC-insulated cables occurred in the SRS K-reactor in the mid-1970s [35]. PVC-jacketed, LDPE-insulated cables that were qualified for 40-year service based on high dose rate qualification protocols failed in approximately 12 years at a dose rate of approximately 25 rad/hr. Post-failure investigation found that the cable insulation polymers were quite sensitive to the dose rate, Figure 6. Many studies have since been performed on cable insulation polymers to evaluate dose rate effects [36-37]. HCl generation from flexible PVC electrical cable insulations is one of the reasons for the development and use of halogen-free cable insulations in commercial nuclear facilities.
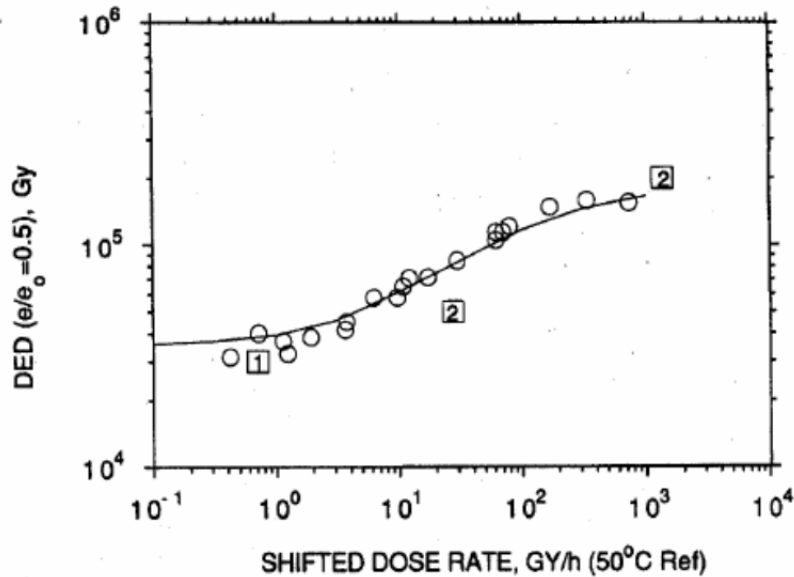
Figure 6. Dose Rate Effects in PVC-jacketed, LDPE-insulated cable (SRS K-Reactor) [35]

The threshold dose for HCl generation from PVC or pPVC is not well-established. Variation in factors such as formulation, total dose, dose rate, temperature, plasticizer type/loss rate, and sample environment make it difficult to establish a single threshold dose. Also, many studies are focused on specific doses associated with a particular service environment, rather than determining the minimum conditions at which HCl may be generated. Gamma doses of 1-3 Mrad have produced measureable quantities of HCl [23] and lower threshold doses may be possible. Several references note that dehydrochlorination is autocatalytic, so once the process starts, HCl production may continue without additional dose.

The time at which HCl gas began to evolve from the pPVC packaging material within the failed spent mercury gold trap waste container is unknown and likely depends on several variables. This aspect can be evaluated in more detail if needed, but is beyond the scope of this report.

4.1.3 Other PVC Degradation Mechanisms

Dehydrochlorination of PVC or pPVC is principally known to occur due to thermal and/or radiolytic mechanisms. PVC polymers are also susceptible to other degradation mechanisms, which may enhance the release of HCl to some extent in addition to mechanical property breakdown. These are briefly mentioned here for awareness but are not considered primary degradation mechanisms and causes of the gold trap waste container failure.

Many polymers including PVC will degrade over time due to thermo-oxidation, which is a diffusion-limited process. PVC polymers are also subject to degradation by ultraviolet light (photo-oxidation), ozone, certain chemical environments and even from biological attack [38-39]. While rigid, non-plasticized PVC is typically considered to be non-biodegradeable, plasticized PVC (pPVC) can be susceptible to microbiological attack in certain cases depending on the plasticizer(s) and biological species involved. The plasticizers detected in the gold trap waste container leakage sample (esters, adipates) are both possibly susceptible to degradation by bacteria and fungi [39].

In the gold trap waste container, photo-oxidation and chemical degradation of the pPVC packaging are not contributing degradation mechanisms (other than from autocatalytic HCl generation). Biological degradation may have contributed in some way to pPVC degradation within the container, but the biological activity of water/moisture present in the container has not been established.

Plasticizer migration is known to occur in plasticized PVC formulations and can potentially affect the threshold temperature and/or radiation dose at which HCl is evolved. The extent to which plasticizer migration may have initiated or occurred in the pPVC packaging formulation used in the gold trap waste container prior to dehydrochlorination and HCl evolution is unknown.

Another potential source of HCl may come from combustion or pyrolysis of pPVC, such as might occur during welding if the pPVC packaging were to be thermally degraded or catch fire (either by flash ignition or autoignition). HCl can be liberated above 100 °C and certainly above 220 °C, with flash and auto-ignition temperatures for plasticized PVC (varies with formulation) being in the range of 330-385 °C [1]. Being heavily chlorinated, pPVC packaging is relatively flame-retardant, but if ignited, significant smoke development and generation of HCl would likely occur.

Ignition of the pPVC packaging during welding of the failed waste container closure after loading the plastic-wrapped gold trap is unknown, but difficulty in either loading of the waste container or welding the lid due to the presence of pPVC packaging may explain the absence of packaging materials in the other containers examined.

4.2 Corrosion of Austenitic Stainless Steel

Analysis of the leaked liquid from waste container HMSF001220 characterized the liquid as a strong acidic aqueous solution with high chlorides (essentially HCl). This solution is considered the primary species involved in the failure of the spent mercury gold trap waste container. A brief description of corrosion of stainless steels by HCl and other possible degradation/corrosion mechanisms is provided.

4.2.1 General Corrosion

Austenitic stainless steels are very corrosion-resistant alloys. The formation of stable chromium oxide on the surface makes these alloys very resistant to many chemicals, including oxidizers such as nitric acid. However, reducing/halide acids such as HCl, HF, and HBr can rapidly corrode austenitic stainless steels at practically all relevant concentrations and temperatures. In HCl, general corrosion rates can be very high, ranging from a few mils per year to hundreds or thousands of mils per year (inches per year) depending on conditions [40].

The resistance of 300 series stainless steels (particularly garden-variety grades such as 304L and 316L) to hydrochloric acid is very low. These grades are not considered resistant to HCl at practically all concentrations and temperatures. Type 316L shows slightly improved resistance, presumably due the presence of Mo in the alloy, but the improvement over 304L is only marginal and not sufficient to warrant its selection for most applications involving HCl.

A general isocorrosion curve for 304SS in HCl is shown in Figure 7 [41]. The darkest region is for corrosion rates $\geq$ 30 mils/year. The lightest region is for corrosion rates < 5 mils/year. Note the very limited temperature/concentration range for which the lowest corrosion rate applies (< 5% HCl up to 40 °C). It is emphasized that isocorrosion curves do not account for all specific design and environment aspects (i.e. crevices, other corrosive species, concentration effects due to thermal cycling or evaporation, etc.). Such curves are for general design purposes only.
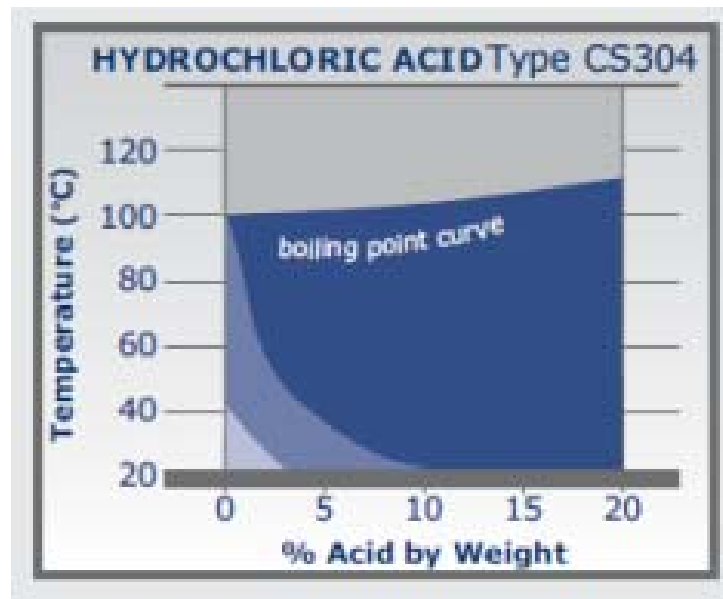

Figure 7. Isocorrosion curve for 304SS in HCl [41]

It is noted that carbon steel is sometimes used to handle non-aqueous or anhydrous gases of HCl, HF and HBR, since in the complete absence of moisture, such gases are non-corrosive. However, controlling moisture levels in industrial/plant operations or even small-scale experimental set-ups can be very challenging. Once moisture enters the system (e.g. in-leakage at a valve or gasket, maintenance shutdowns, etc.), severe corrosion can quickly lead to failure.

4.2.2 Localized Corrosion (Pitting/Crevice Corrosion)

For austenitic stainless steels, localized corrosion (pitting and crevice corrosion) is generally of more concern than general corrosion. Pitting corrosion is often discussed in conjunction with under-deposit corrosion, oxygen cell corrosion and other mechanisms. Pitting corrosion is most often associated with the presence of chloride ions, though it can also occur in the presence of other species including biological sources. MIC (Microbiologically-Induced Corrosion) is discussed in a separate section.

Pitting is a localized form of corrosion which occurs on passivated metallic materials exposed to aggressive environments. Small defects or discontinuities such as scratches, inclusions or slight compositional variations in the passive film may selectively be attacked by corrosive media and initiate a pit. Even heat tint, arc strikes/gouges and other surface defects related to fabrication and installation practices can affect the relative sensitivity of a given material to pitting and other mechanisms in certain environments.

Such areas may be depleted in chromium, which is essential for passivation and corrosion resistance. Pickling and passivation steps are sometimes needed to remove manganese sulfides, embedded iron particles and the outer oxide layer which can be depleted in chromium.

Figure 8 shows the basic pitting process [43]. Once a pit has initiated, the chemistry within the pit can change and become more aggressive, leading to an autocatalytic reaction and an increase in pit depth. Under the right conditions, pitting can rapidly lead to through-wall penetration, even when general corrosion rates are very low. This can occur in localized regions, even though nearby wall thickness measurement shows very little thickness loss.

The primary way to avoid pitting of stainless steel is to avoid the conditions that can initiate it. This requires sufficient cleaning of piping prior to lay-up or service, minimization of surface discontinuities to the extent practical, and avoidance of deleterious and aggressive species such as halides, deposits or microbial sources. However, complete avoidance of these factors is very difficult in practical operations.
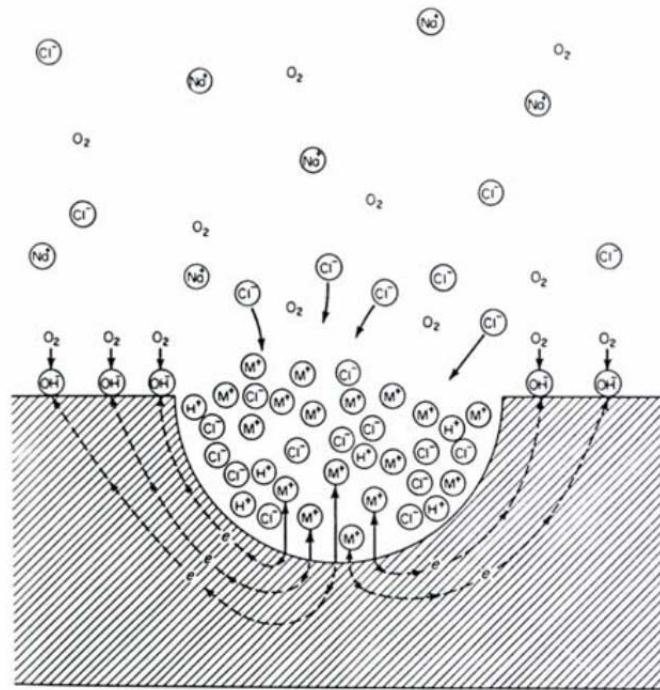
Figure 8. Basic Pitting Mechanism by Halides/Chlorides [43]

Another way to evaluate the pitting resistance of alloys is by use of the Pitting Resistance Equivalent Number (PREN), which usually follows the form(s) below depending on alloy composition and the reference. The higher the PREN value, the higher the pitting resistance. The PREN value for 304L stainless steel is typically 17.5-20.8, with PREN values for 316L ranging from 23.1 to 28.5. Higher PREN values are typically needed to truly preclude pitting.

$$PREN = Cr + 3.3Mo + 16N \text{ or } PREN = Cr + 3.3(Mo + 0.5W) + 16N$$

Similar to pitting corrosion, crevice corrosion is localized and can be very aggressive. In many cases, crevice corrosion is can occur at lower temperatures and/or concentration of corrosive species than pitting corrosion.

Alloys are often characterized by their Critical Pitting Temperature (CPT) and Crevice Corrosion Temperature (CCT) values, as determined by ASTM G48 and G150 standards. The CPT and CCT values for a given alloy can vary with test conditions, surface roughness and other factors. The CCT values for many alloys are often significantly lower than the CPT, indicating that crevice corrosion can occur at lower chloride levels and/or temperatures than pitting.

Figure 9 shows the CCT and CPT values for AISI 304 and 316 stainless steels as a function of chloride content in a solution saturated with oxygen [42]. Note the difference in chloride level required to initiate crevice corrosion vs. pitting corrosion in 304SS at various temperatures. These data show that the need to avoid crevices is very important, even in systems that are not inherently corrosive. As an example, industrial standards for stainless steels used in wastewater systems typically advise that 200-300 ppm chloride might be acceptable for 304L stainless steel in absence of crevices, but 50-100 ppm chloride (or lower) might pose issues if crevices are present [44-45].
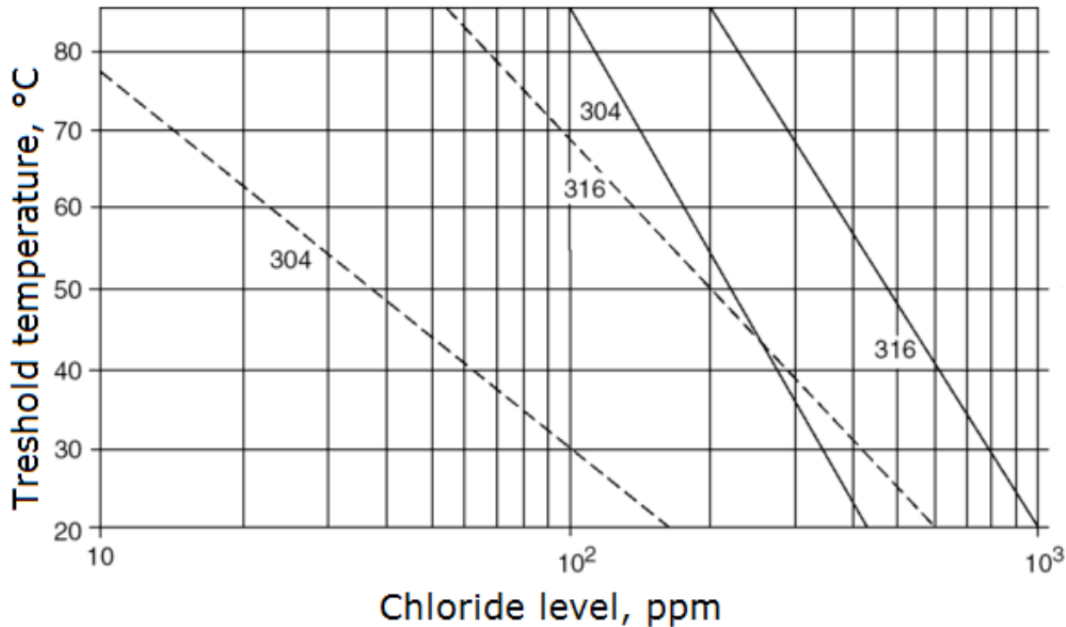
Figure 9. CPT (solid line) and CCT (dashed line) values for 304 and 316 stainless steel
vs. chloride content in an oxygen-saturated solution [41]

4.2.3 Intergranular Corrosion

Intergranular corrosion (IGC), or intergranular attack (IGA), is an aggressive form of corrosion that can occur in certain alloy/environment combinations. Typically, sensitization is the common cause of IGC in austenitic stainless steels, especially in heated or welded components. Sensitization in weld areas is often termed weld decay as during welding, carbides form at grain boundaries which leaves chromium-depleted regions that are more susceptible to attack in specific environments (notably nitric acid).

The longer the material is heated within the sensitization temperature range (425 – 815 °C), the greater the degree of sensitization, given sufficient carbon is present in the material. Figure 10 shows a schematic representation of carbide precipitation at the grain boundary during sensitization in stainless steel [43]. Time-temperature-sensitization curves are often used to show relative susceptibility of alloys to sensitization.

The use of low carbon (<0.3%) grades of stainless steel (L-grade) or dual grades (L-grade composition with standard grade mechanical properties) reduces the degree of sensitization and risk of intergranular corrosion, but does not absolutely prevent it. If sensitization occurs, intergranular corrosion still may not occur unless in a specific, aggressive oxidizing environment such as nitric acid.

The metallurgical condition and quality of the stainless steel used in the fabrication of the gold trap waste container is unknown. Not being for corrosive service, Corrosion Evaluation (CE) as SRNL performs for many SRS applications would not have been required [46]. In the presence of HCl and other reducing acids, general corrosion and localized corrosion (pitting, crevice) mechanisms tend to dominate the reaction. IGA/IGC is not considered a primary cause of the gold trap waste container failure.
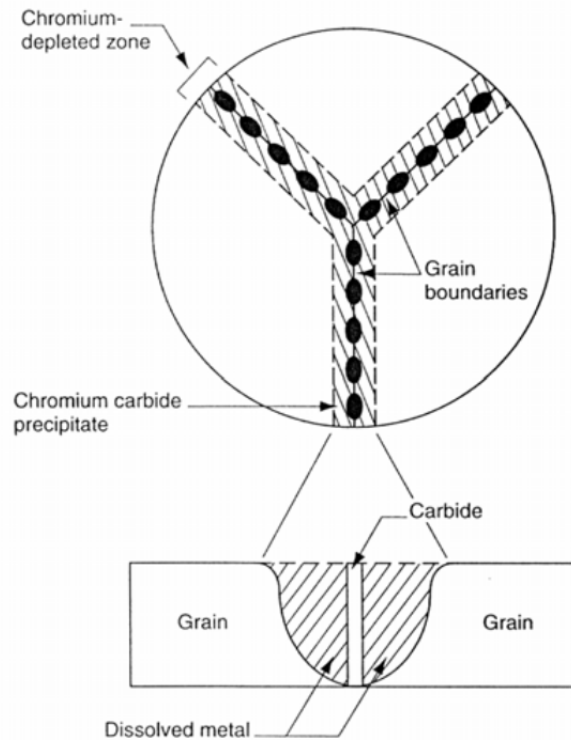
Figure 10. Schematic of grain boundary sensitization in stainless steel [43]

Another form of corrosion related to IGC is end-grain attack, which typically only occurs in specific environments such as hot nitric or nitric/HF solutions. End-grain attack occurs primarily when grain boundaries that are oriented parallel to the rolling direction of the material are preferentially attacked. In the gold trap waste container weld design (seal-welded, not full penetration), some end grain of the pipe is likely exposed in the crevice. End-grain attack, however, is not considered a likely or dominant mechanism in the presence of HCl. The presence of the crevice more likely promoted crevice corrosion, rather than end grain corrosion.

4.2.4 Stress-Corrosion Cracking

In austenitic stainless steels, stress-corrosion cracking (SCC) is principally caused by chlorides in conjunction with sufficient stress at relevant temperatures. Other species (e.g. NaOH) can cause stress-corrosion cracking (caustic cracking) but elevated temperatures are usually required. The mechanical stresses may be either applied or residual and usually are tensile in nature. The residual stresses that are associated with fabrication, welding, and thermal cycling often contribute to SCC failures of pressurized equipment. SCC may develop as intercrystalline or transcrystalline cracks typically with little or no evidence of general corrosion.

In 304L stainless steel, cracking generally propagates along intergranular pathways if the material is sensitized (as discussed in the Intergranular Corrosion section). In non-sensitized material, transgranular SCC is predominant.

An additional metallurgical factor that can affect SCC in austenitic stainless steels is cold work or strain-hardening. The forming of a metal results in plastic deformation occurring to the metal which increases tensile and yield strengths while decreasing ductility. Cold work can lead to a reduced time to failure by SCC for a constant applied stress or a reduced applied stress to obtain cracking in a similar time.

Defining a minimum chloride concentration below which SCC absolutely will not occur is complex. Many variables affect the susceptibility of an alloy to SCC, including the effects of stress, pH, oxygen concentration and the presence of other species. Some industry documents have specified minimum chloride concentrations for austenitic stainless steels to prevent SCC such as American Petroleum Institute (API) 650 which restricts chloride concentration at 200 ppm for temperatures < 40 ℃ and 100 ppm for temperatures between 40 and 65 ℃ [47].

Data commonly referenced (Truman) for when SCC can occur in 304 stainless steel as a function of chloride concentration, temperature and pH is shown in Figure 11 [48]. Chloride SCC has also been documented at temperatures below 40 °C, though less common and usually involving high stresses and/or high chloride concentrations.

Many industry references emphasize the need to remove surface iron contamination, heat tint and other fabrication artifacts to reduce corrosion failures in austenitic stainless steel. In one case, transgranular SCC was observed in 304L stainless steel dished ends even prior to fabrication of cylindrical vessels [49]. SCC was found to initiate during storage at rust spots from iron contamination on interior surfaces. All components with iron contamination developed cracks, while those without iron contamination did not. The authors of Reference 49 concluded that the rust particles preferentially absorbed moisture and halides from the environment during storage. This in combination with the high stress levels from dished head fabrication led to transgranular SCC prior to actual service.

At the SRS, chloride-induced SCC of 300 series stainless steels is addressed in SRS Engineering Standard, #05952 "Required Practices to Minimize Chloride Induced Stress Corrosion Cracking of Type 300 Series Austenitic Stainless Steel" [50]. This document specifies a maximum chloride content (total, not leachable) of 250 ppm at temperatures above 40 ℃ (104 °F) in applications that can get wet. This document primarily addresses the chloride content of materials in direct contact with stainless steel (gaskets, labels, adhesives, tapes, etc.), not aqueous solutions, process fluids or hydrotest waters. In such cases, even lower chloride values may be preferred to account for crevices and other design aspects.

This standard or a previous version was likely not imposed on the gold trap waste containers by either Tritium or Solid Waste facilities, either because the temperatures expected in storage were not excessive, no moisture was expected in the container, or that the waste container was not a process component. This standard is not always required and is sometimes imposed without regard to the actual service environment.
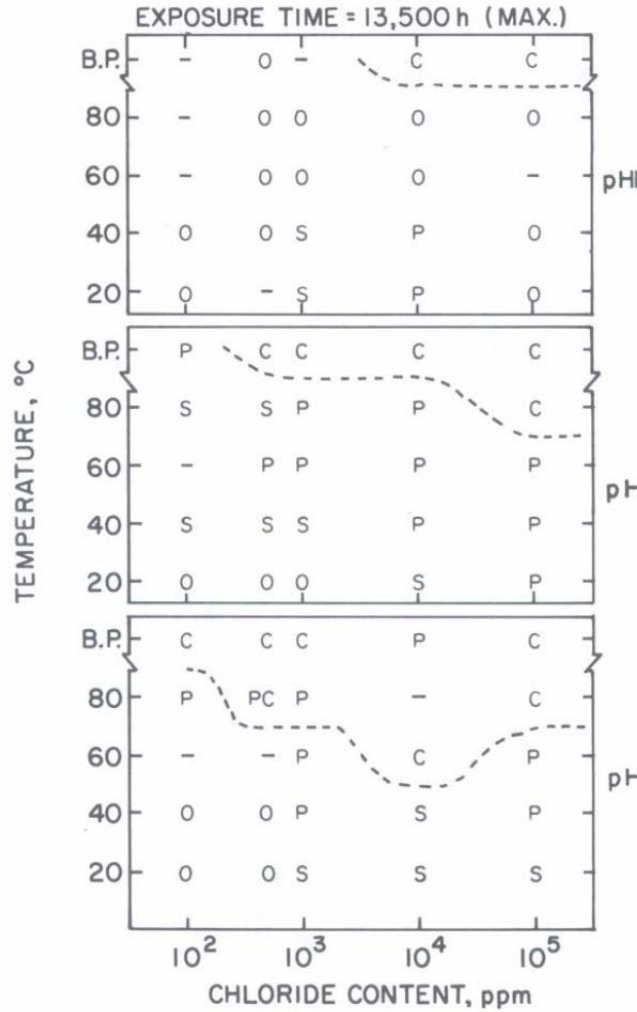
Figure 11. Effect of temperature, pH, and chloride concentration on SCC susceptibility of
304 stainless steel (C=SCC, P=Pits, S=stains,O=no effect) [48]

In HCl solutions, general corrosion, pitting corrosion and stress-corrosion cracking are all known to
occur. Which mechanism(s) dominates the situation depends on several factors. Tsujikawa et al. [49]
demonstrated that Cl-SCC only occurs when crack growth is more preferential than the rate of metal
removal by general corrosion or localized corrosion from the base of a crevice or pit. Other references
suggest that if general corrosion rates are > 10 mils/year, SCC is less likely to occur unless other aspects
important for SCC (high stress, higher temperatures) are also present [40, 51]. Residual stresses from
welding of the waste container may be present, but are not likely sufficient alone to induce SCC.

The specific possibility of Cl-SCC of stainless steel containers due to HCl gas generation as a result of
thermal or radiolytic degradation of PVC or pPVC materials is not well-documented. This is generally
because other corrosion mechanisms (general/pitting) have been observed primarily in cases where pPVC
materials have been used, or because container failure (e.g. food-pack cans) has mainly been due to
pressurization or deformation, not corrosion. In addition, the corrosive species are more often chlorides
from salts, rather than HCl directly.

The potential for chlorides and HCl gas generation to cause chloride SCC vs. other corrosion mechanisms has been studied for plutonium storage [52-59]. Though SCC has been observed in coupons at aggressive experimental conditions (high stress, boiling $MgCl_2$), the majority of corrosion observed in field surveillance of welded 3013 containers for Pu shipping and storage in K-Area has been limited to general corrosion/staining and pitting. In such environments, the chlorides present in the material are the dominant species causing corrosion, not HCl. However, gas analysis has shown that HCl can be generated in the alpha environment [58], but SCC was not observed.

Another possible contributor to SCC of the gold trap waste container could be the effect of tritiated water and the ionizing service environment, particularly in the crevice formed by the fabrication and weld design. Tritium/beta decay has been documented to cause or at least contribute to the stress-corrosion cracking of austenitic stainless steels [60]. Threshold tritium concentrations to cause SCC are not well-established and other metallurgical and design factors (stress, presence of corrosive species) also affect the probability of SCC in a particular component.

In the presence of HCl/chlorides, the contribution of tritium/beta decay to causing SCC is far less likely to be the primary cause of failure. Pitting is observed on the exterior of the container, likely due to post-leakage exposure on the pallet, which is consistent with chloride/HCl corrosion. Metallurgical examination would have to be performed to conclusively evaluate the possibility of SCC, but is not recommended at this time.

4.2.5 Microbiologically-Induced Corrosion (MIC)

Microorganisms present in aqueous solutions can form films and deposits on exposed metals and alloys. These films and deposits, along with the metabolic activity of the microorganisms, can influence corrosion of the exposed metal (Figure 12). This mechanism is broadly called microbiologically-induced corrosion (MIC). MIC is briefly discussed as it has occurred in SRS systems, but it is not considered a primary mechanism of failure of the spent mercury gold trap waste container.

Figure 12. Microbiologically-induced corrosion in a pipe (not SRS piping) [61]

Confirmed cases of MIC in industry have generally been associated with cooling water systems, construction lay-up, aqueous waste treatment systems and systems that contain natural water left from hydrotesting or other system evaluation procedures [61].

The environmental conditions most favorable to MIC include:

- Low flow (< 5 ft/s) or stagnant liquid
- Presence of organic matter
- Presence of inorganic material such as nitrite
- Interrupted operations or lay-up periods
- pH < 10.5
- Absence of a biocide chemical
- Temperature: 15 – 45 ºC (59 °F – 113 °F)

The time periods for the onset of MIC can range from a few days to several months or a few years, depending on service conditions. Austenitic stainless steels are particularly susceptible to MIC. The typical physical evidence for MIC is the formation of characteristic deposits (tubercles). These deposits are generally adherent and typically lead to localized corrosion such as pitting that is accompanied by sub-surface corrosion in the rolling or working direction of the material (Figure 13) [61]. Selective attack at welds and/or weld heat affected zones is frequently associated with MIC in austenitic stainless steels and other alloys.
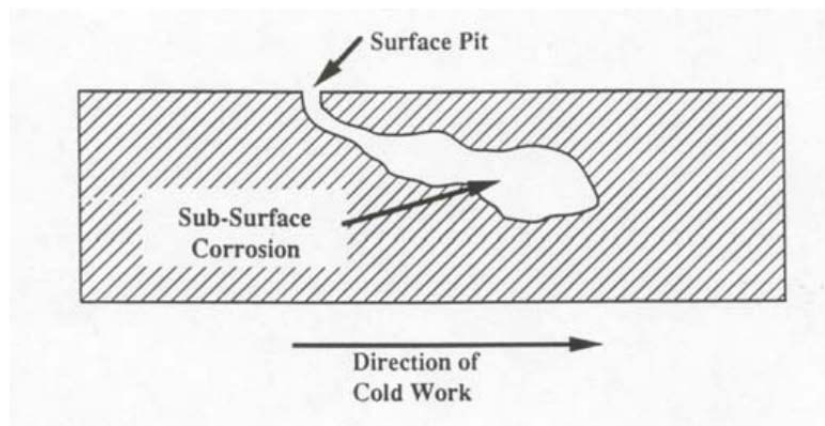
Figure 13. Schematic of sub-surface pit development in the material working direction [59]

Several cases of MIC in stainless steel and galvanized piping at SRS have been documented cases of MIC [62-63]. In 1991, during a routine walk-through inspection of the Melter Cooling Water System (MCWS) in the Defense Waste Processing Facility (DWPF), rust colored "bleed-through" was observed on the exterior of the piping near the welds (Figure 14). The MIC occurred due to initial system testing and flushing with neutral water without any biocide. When water quality problems were noted, the system was also drained and flushed with de-ionized water that was also not treated. The water was left stagnant in the line for several months. Even DI water has been shown to possibly promote MIC.
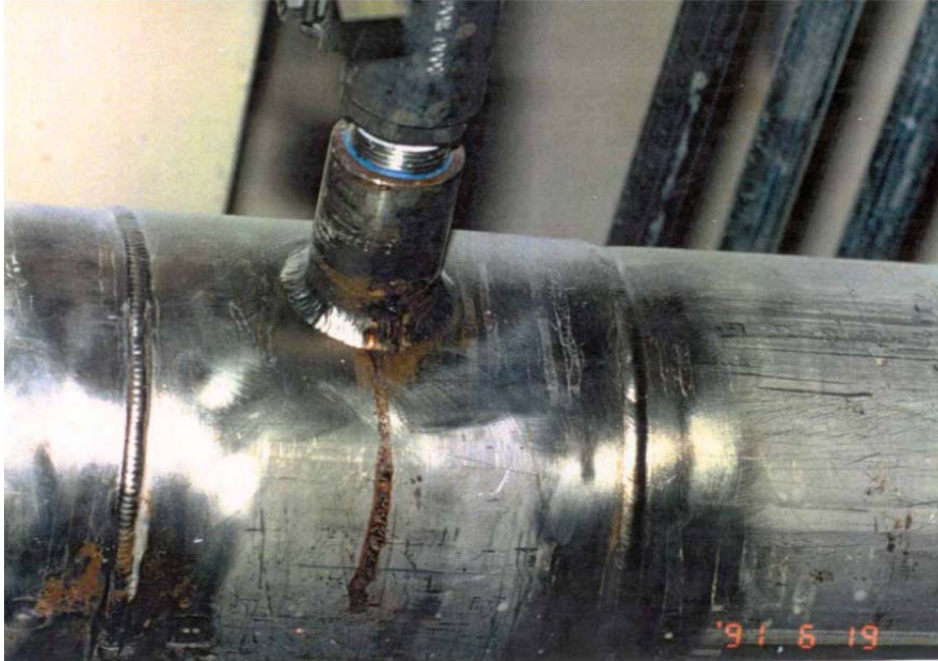
Figure 14. Evidence of MIC on the exterior of DWPF cooling water pipe [62].

Given the analytical results (chlorides/HCl, absence of other corrosive species), and absence of tubercules and subsurface defects on the X-ray images, corrosion of the gold trap waste container due to MIC is unlikely. MIC could possibly occur in the acidic/radiolytic environment but water with sufficient microbial activity and particular species would have to have entered the container prior to closure. MIC also tends to occur relatively quickly (days to months, not 30 years). External corrosion due to MIC from rainwater intrusion into the concrete culvert during storage or in other storage configurations is also unlikely. In the presence of concrete, the pH would likely be more alkaline which tends to mitigate MIC.

4.2.6 Other Forms of Environmentally-Assisted Degradation

Corrosion is a complex process. One mechanism is usually dominant, but it is not unusual to have more than one mechanism occurring that may initiate or contribute to final failure. The primary mechanisms for container failure have been previously discussed. However, a few additional environmentally-assisted degradation mechanisms are discussed here.

Austenitic stainless steels are known to be very resistant to hydrogen embrittlement (HE) and tritium beta decay/helium effects, hence their common use in tritium processes. Type 316L is often preferred over type 304L but both alloys are quite resistant. The austenitic structure is less permeable and/or more forgiving of such effects as compared to martensitic or ferritic stainless steels that also typically have higher hardness and strength. The austenitic alloys are not completely immune to such effects, as some failures have been observed. However, such failures usually involve high concentrations of hydrogen or tritium and/or very high stresses or pressures.

In the spent mercury gold trap waste container, none of these parameters are believed to be sufficiently present to significantly contribute to the failure. Tritium activity and concentration was not likely very high and pressures/stresses were also not likely significant.

Liquid metal embrittlement (LME) is known to cause failure of steels, stainless steels and even some corrosion-resistant nickel alloys. LME is usually associated with low melting elements such as zinc, copper, mercury and cadmium to a lesser extent, in contact with the steel during welding or if in the molten state. Some of these elements (Zn, Cu, Cd) were detected in the liquid analysis (< 100 ppm each) but were not likely in contact with the weld in the molten state or at concentrations significant enough to cause LME. Mercury is present, but is assumed to be amalgamated with gold within the trap, which appears sealed on X-ray images. In addition, no Hg was detected in the liquid sample above detection limits.

External sources of acidic chlorides exist, such as muriatic acid (typically 32% industrial strength HCl), which is often used for cleaning of concrete or in preparation for coatings application. However, the use of corrosive solutions around the failed spent mercury gold trap waste container or any of the non-failed containers in Solid Waste is not known to have occurred. The probability of the one failed container being exposed to such a solution and also being the only container with internal pPVC packaging and some tritium content is considered very low.

5.0 Sources of Moisture/Water

The presence of acidic chlorides in the liquid that leaked out of the container can be readily attributed to the degradation of pPVC packaging and HCl generation. The presence of pPVC packaging is reasonably assumed from Tritium personnel historical knowledge (see Appendix B) and X-ray examination results (Section 3.0).

However, HCl and/or chlorides are non-corrosive in the complete absence of moisture. Though atmospheric moisture will cause slight surface corrosion, free liquid is generally needed to cause significant corrosion. The amount of liquid estimated to have been within the waste container prior to leakage is ~500 mL, based on radiographic examination, analytical sample volume and container geometry.

The evaluation team considered several possible sources of this volume of liquid. The general sources were considered to fall into the following categories: 1) External water intrusion after closure (pinhole/corrosion); 2) Water introduced prior to closure; and 3) Water formed within the container during storage. Each of these sources was considered and is discussed below.

External Water Intrusion (pinhole/corrosion, atmospheric breathing)

External water intrusion via either corrosion or the presence of an existing flaw (pinhole) was considered. Intrusion of water due to external corrosion is unlikely, given the following aspects:

- overall corrosion resistance of austenitic stainless steel
- absence of severe corrosion on other cylinders
- unidentified source of corrosive species external to the container
- absence of corrosion/staining within the concrete culvert from which the containers were removed
- no indication the waste container contacted external water/liquid during storage in the SWMF

If a pinhole existed in a weld (and was not identified via dye penetrant), it might allow breathing of the container (and influx of water) during heating/cooling cycles, particularly if the container were stored with the pinhole submerged or in contact with water. However, this would only be expected to allow a few mL of water to be retained within the container. With internal pressure developed due to tritium/beta decay and pPVC packaging degradation, the extent to which atmospheric breathing would allow water retention is likely to be negligible. Also, there is no evidence that this container was stored (either in a closed concrete culvert in a covered building/storage pad or on a pallet on a covered storage pad) in a manner that allowed it to come in contact with liquid.

Another potential source of liquid trapped in the waste container is condensation of any humidity in the air at the time of closure. An estimation of water formed within the container due to condensation of humidity in the air at the time of closure is given below (per Bob Rabun):

Large container internal dimensions:
18"ID x 45"H
3.14 x 18^2/4 x 45 = 11445 cu. in. =6.6 cu. ft. = 0.187 m^3. = total free volume

At 25 °C and 1 atm, the moisture content of air at 100% RH is 22.9 g/m^3.

Max possible water from air condensation in the container:

0.187 m^3. x 22.9 g/m^3. = 4.3 g = 4.3 mL liquid

Thus only 4.3 mL of water could be attributed to condensation inside the closed waste container. The actual amount could be less because of the volume taken up by the gold trap and the removal of humid air due to argon purging during welding.

Water Introduced Prior to Closure

Per Tritium personnel, the containers were fabricated in a shop approximately 300 feet from the process room where the gold traps were staged after removal for packaging. The container bottom lids were pre-welded in the shop and dye penetrant tested. The containers were then moved to the process room.

At the time of initial gold trap removal (week of November 18, 1985), significant rainfall was recorded over a period of several days, with approximately 4" in H-Area during the week, 2.5" on 11/21/85 [64]. It is unclear where the empty waste containers were stored, how they were stored (covered, etc.) and for what period of time they may have been transported and/or staged outdoors prior to coming into the process room for gold trap loading. It is speculated that the failed container (no lid welded or sealed) was open to the environment for some period of time, possibly allowing rainwater to enter prior to weld closure.

An estimated water volume of 500 mL would be a depth of 0.120" (slightly over a 1/10") in the bottom of an 18" diameter container. Such a depth (presumed clear) would be difficult to detect at the bottom of a 4' tall container, unless the worker(s) involved with the task were specifically instructed to look for it or if became obvious in handling of the container prior to closure. No such inspection was required and workers were wearing PPE (plastic suits) and maneuvering a heavy, plastic-wrapped gold trap into a vertical 48" container. Such an activity would likely preclude the observation of this amount of liquid in the bottom of the container. Even if water was observed, water was not disallowed from the container prior to shipment.

Another possible source of water is if the plasticized PVC packaging were to ignite, such as might occur during welding of the container lid. Ignition could occur from either direct flame or autoignition if temperatures were high enough (330-385 °C). In the presence of oxygen, carbon dioxide (CO_2), carbon monoxide (CO) and water are formed from the dehydrochlorinated residue [3]. However, the amount of water possibly generated from ignition of the pPVC packaging would not account for 500 mL of water in the container. Other possible sources include wet rags or a water bottle that might be used if the plastic packaging caught fire during welding. However, no fire event was recorded.

Water Generated Internally

Another possible source of water within the closed waste container is internal formation of liquid water during storage. In the presence of air (~21% oxygen in dry air), hydrogen and/or tritium present could recombine with oxygen under certain conditions to produce water. Tritium, a hydrogen isotope, is known to recombine with oxygen at room temperature to produce T_2O or HTO (tritiated water) [65-66]. Hydrogen is also known to recombine with oxygen in Pu/alpha environments [67].

This behavior is a combination of many reactions, including production of ozone and peroxides, which can also enhance corrosion processes. However, given the amount of free volume/air within the cylinder and the amount of tritium estimated to have been in the cylinder at the time of closure, the amount of water possibly generated by oxidation of tritium would be far less than the 500 mL estimated to have been within the container prior to leakage.

An estimate of tritium oxide (T_2O) formed by reaction of tritium and oxygen within the container is given below (Bob Rabun input):

$T_2 + 1/2/ O_2 \;-->\; T_2O$ (6 grams of tritium forms 22 grams of tritiated water)
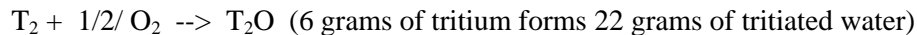
38,480 Ci / 9619 Ci/gT = 4.000 g tritium (T) (assumes all 38, 480 Ci of Tritium is converted to water)

4/6 * 22 grams = 14.7 grams tritiated water

Since T_2O is 20% more dense that light water this equates to approximately 12 ml.

Therefore, assuming all 38, 480 Ci of tritium is converted to water, only 12 mL of liquid water is formed. This cannot account for the quantity of water observed either in the waste container (~250 mL) or estimated to have leaked from the container (~250 mL).

In addition to the tritium in the waste container, hydrogen would also be generated by radiolytic degradation of the pPVC packaging material. Radiolysis of water might also be a competing mechanism. However, the amount of hydrogen liberated from PVC is normally far less than the amount of HCl generated. Some hydrogen would also be liberated due to corrosion processes, but such processes would not occur without some moisture already being present.

An estimate of the maximum amount of water that could be generated by reaction of all oxygen sealed within the container with any hydrogen present to form water is provided below (Bob Rabun input):

$0.187 \ m^3 = 187$ liters geometric free volume

Apply ideal gas law (PV = nRT):

n = PV/RT = 1 atm * 187 L / (.082 * 298K) = 7.65 moles air

7.65 * .21 mole fraction O_2 = 1.61 moles O_2

$2 \ H_2 + O_2 \ --> \ 2H_2O$ so consuming all of the O_2 to make water yields 3.22 moles H_2O.

3.22 moles H_2O * 18 grams/mole H_2O = 58 grams H_2O = 58 ml H_2O

Thus, assuming that all oxygen trapped in the waste container (and no additional oxygen is available from outside the container) reacted with hydrogen inside the container (from any source), this accounts for only a little more than 10% of the liquid estimated within the container prior to leakage.

In conclusion, the only mechanism identified that can account for the full amount of liquid discovered inside the failed waste container is introduction of water prior to closure of the container. Given the storage history of HMSF001220, there is no other mechanism that can account for ~500 mL of water inside the container. Also, there is no known mechanism of water formation inside the waste container after closure that can account for the estimated 500 mL of liquid.

The most likely source of the bulk of water within the waste container is speculated to be rainwater that may have been introduced prior to weld closure. Other contributions are possible but would not fully account for the amount estimated to have been within the container prior to leakage. Given that there was no restriction against water in the container, no required inspection step, meteorological conditions near the time of container closure and the nature of the task involved, the potential for water to have entered the container prior to closure is plausible. In absence of pPVC packaging and degradation, the presence of water alone would not likely have caused failure of the waste container.

6.0 CONCLUSIONS

Based on combined analytical results, visual observations, Tritium personnel historical knowledge and radiographic evidence, failure of the Pad 18 spent mercury gold trap stainless steel waste container is primarily attributed to corrosion induced by acidic chlorides (HCl), resulting from degradation of pPVC packaging. Dehydrochlorination of pPVC polymer via thermal and radiolytic mechanisms is well-known to evolve HCl gas, which is highly corrosive to stainless steel and other materials in the presence of water/moisture. Degradation of the pPVC material was likely caused by radiolysis due to tritium/beta decay within the container, though other mechanisms (aging, thermo-oxidation, plasticizer migration) may have contributed to material degradation over the 30 year storage period.

The definitive source of water within the container is unknown and more than one mechanism or source may have contributed to the total amount present. The most likely source is inadvertent water introduced prior to waste container closure. The amount of liquid estimated present (~500 mL) before leakage would have been difficult to notice during gold trap placement within the container. In 1985, there was not an active Waste Certification Program, there was no restriction against the use of plastic packaging (any type) or chloride-bearing materials, nor was there a requirement that the containers be free of liquid at the time of closure. Three additional spent mercury gold trap waste containers were examined and did not show evidence of plastic packaging or trapped liquid. Those containers are not expected to fail.

The use of halogenated polymers such as pPVC within sealed containers for extended storage periods should be avoided, particularly if the material can degrade. Halogenated gases evolved can cause pressure generation and corrosion, particularly if moisture or free liquid is present. Containment of corrosive liquids such as HCl typically requires resistant non-metallic materials such as fluoropolymers or HDPE (high-density polyethylene), certain composites or corrosion-resistant alloys such as Hastelloy B or C-276. The presence of tritium may preclude the use of polymeric materials for long-term containment.

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APPENDIX A – Analytical Reports

Radiochemistry-Liquid Scintillation Counting
Reporting Chemist: D.P. DiPrete, Analytical Development, SRNL

Tritium concentration was 1.07×10^3 µCi/g.
Acid Concentration by Titrimetric Analysis
Reporting Chemist: A.A. Ekechukwu, Analytical Development, SRNL

The sample was analyzed under Manual L16.1, Procedure ADS1207 "Titrimetric Analysis Using the Radiometer Analytical Tim870 Titration Manager with Autosampler". The system was calibrated using NIST traceable pH buffers (4,7, and 10). The check standard, 1.00 N hydrochloric acid, was run in triplicate before and after the sample analysis. The sample was run in duplicate and found to have 3.8 N acid. The sample was observed to be readily miscible with water. The titrated sample settled to the bottom of the titration vessel after analysis.

Anion Chromatography Analyses
Reporting Chemists: T.L. White, L.W. Brown, Analytical Development, SRNL

The sample was analyzed under Manual L16.1, Proceedure ADS-2310 "Analysis of Ions in Solutions" using a Dionex ICS3000 Ion Chromatography System" using NIST traceable standards. Using deionized (DI) water, the sample was diluted to within the calibration curve range of 1 to 50 mg/L. This method was set up to quantify fluoride, formate, chloride, nitrite, bromide, nitrate, sulfate, oxalate, and phosphate. The sample chromatogram was dominated by a large chloride peak (148,000 mg/L) with all other peaks below detection (<250 mg/L).

Organic Analyses by Fourier Transform Infrared (FTIR) Spectroscopy
Reporting Chemist: F. Fondeur, Environmental and Chemical Processing Technology, SRNL

The FTIR saw a lot of the three components below. One is a plasticizer (phthalates), the other possible degraded oil (or degraded adipate, which is also a plasticizer) and metal carboxylate (possibly iron). None of these show the typical C-Cl from 740 to 760 cm-1 (they are dechlorinated).

Semivolatile Organic Analysis by Gas Chromatography / Mass Spectrometry (GC/MS)
Reporting Chemist: S. L. Crump, Analytical Development, SRNL

One sample was submitted for semivolatile organic compound analysis. The only SVOA compound identified in the sample extract was Bis(2-ethylhexyl)hexanedioic acid ester at a concentration of 6.6 mg/L. This material is a commonly used industrial plasticizer. The reporting limit for this study is one mg/L for SVOA compounds, and the error associated with each value is +/-20%.

Experimental SVOC:

The sample was extracted with methylene chloride, and the extract was analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) to identify organic compounds in the samples. Analysis was carried out in building 773-A, laboratory B-123. It should be noted that ADS is not certified by DHEC for NPDES discharge compliance monitoring.

Analytical separations were carried out on an Agilent 7890 gas chromatograph, equipped with a 25 m DB-5 column, with 0.20 mm diameter and 0.33 um film thickness. Quantification was performed using an Agilent 5977 mass selective detector. The mass spectrometer tuning was confirmed using perfluorotributylamine.

Elemental Analysis by Contained X-ray Fluorescence Spectroscopy
Reporting Chemist: D.M. Missimer, Analytical Development, SRNL

Results
The contained X-ray fluorescence analysis of the Pad 18 spill solution showed only prominent peaks from the stainless steel corrosion products Fe, Ni, and Cr. No Hg was detected in the sample. The Hg levels are less than <1 ppm.

Principles of the analytical technique:

The Amptek system is a computer-controlled x-ray fluorescence spectrometer used for non-destructive elemental analyses of elements from Na (Z=11) to U (Z=92). A sample is irradiated with x-rays to cause the loss of inner shell electrons from the constituent atoms. These inner orbital vacancies can be filled by electrons in a higher energy shell. To maintain conservation of energy, an x-ray photon, whose energy is the difference between the two levels, is produced. The energy of each emitted x-ray photon is well-defined and characteristic of the element from which it originated. The rate at which x-ray photons are emitted by a particular element is related to the concentration of the element.

The Amptek system features an energy-dispersive lithium-drifted silicon detector and a silver transmission target miniature x-ray tube. The sample is fluoresced by the characteristic and brehmstrahlung x-rays emitted from the tube. An aluminum filter was inserted between the x-ray tube and the collimator to reduce background and improve detection limits for some elements (Hg). Five drops of the sample was mounted onto a 2" x 2" square plate (the plate has a circle cut out in the middle, Plexiglas sample holder was inserted into the SRNL designed vacuum sample chamber for radioactive samples, and positioned underneath the x-ray tube and spectrometer by a spring-loaded backing plate. A shield door, which covers the sample access area, must be slid into place and engage a microswitch before the x-ray tube can be energized.

Contained X-Ray Fluorescence Scan of Pad 18 Spill Material

Elemental Analysis by Inductively Coupled Plasma-Optical Emission Spectroscopy
Reporting Chemist: M.A. Jones, Analytical Development, SRNL

The E-area Pad 18 Spill sample (customer ID 16062-Spill) was analyzed on a Leeman Prodigy Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). This method provides multi-elemental analysis by measuring the light emitted from the nebulization and ionization of an aqueous sample in a high temperature argon plasma. The Leeman Prodigy ICP-OES is equipped with a high dispersion spectrometer and simultaneous detector that allow quantitative measurements of multiple wavelengths for over 30 elements in the sub- to mid- parts-per-billion (ppb) detection limit range.

The "ICP-OES Results, Pad 18 Spill" table below lists the results for various elements in the sample. Following calibration of vendor supplied standards and calibration checks with quality controls from different standards, 10000x and 100x instrument dilution factors were performed and measured. Visual solids were not noted in the dark sample; however, high concentrations of some elements prevented a lower dilution due to internal standard enhancement. The method detection limits reported for those elements on the table are derived from the instrument detection limit multiplied by the dilution factor. The uncertainties reported for those elements on the table are derived from the root sum of the squares of the method uncertainty (10%) and the sample uncertainty of three acquisitions. Following a cross-comparison between the X-ray and this ICP-OES data, the results are in agreement and are indicative of wear products from steel due to the high Cr, Fe, and Ni content measured.

ICP-OES Results

Description:	Pad 18 Spill
Travel Copy:	LW-AD-PROJ-160601-1
Instrument:	Leeman Prodigy ICP-ES
Reviewer:	Mark Jones
Comments:	
	N/A

Method Detection Limit (MDL) = Instrument Detection Limit (IDL) x Dilution Factor.
Uncertainty is the RMS of the method uncertainty and the sample uncertainty.

	USER_SAMPLEID:	16062_SPILL
	SAMPLE_ID:	LW1807
	UNITS:	mg/L
Element		
Ag	< 3.06	(N/A %RSD)
Al	233	(10 %RSD)
B	< 11.3	(N/A %RSD)
Ba	27.6	(10 %RSD)
Be	< 4.83	(N/A %RSD)
Ca	1750	(10 %RSD)
Cd	64.7	(10 %RSD)
Ce	< 11.4	(N/A %RSD)
Co	281	(10 %RSD)
Cr	17100	(10 %RSD)
Cu	48.8	(10 %RSD)
Fe	47200	(10 %RSD)
Gd	< 115	(N/A %RSD)
K	75.8	(11 %RSD)
La	< 2.46	(N/A %RSD)
Li	< 3.67	(N/A %RSD)
Mg	122	(10 %RSD)
Mn	2690	(10 %RSD)
Mo	< 4.66	(N/A %RSD)
Na	61.5	(10 %RSD)
Ni	15200	(10 %RSD)
P	128	(11 %RSD)
Pb	42.7	(10.6 %RSD)
S	< 1300	(N/A %RSD)
Sb	< 21.8	(N/A %RSD)
Si	< 17.2	(N/A %RSD)
Sn	< 13.1	(N/A %RSD)
Sr	4.62	(10.4 %RSD)
Th	< 19.9	(N/A %RSD)
Ti	< 4.65	(N/A %RSD)
U	< 21.4	(N/A %RSD)
V	< 1.4	(N/A %RSD)
Zn	63.7	(10 %RSD)
Zr	< 1.41	(N/A %RSD)

APPENDIX B – Tritium Personnel/Interview Results (Jack Alexander):

The following is a summary of Tritium employee interviews conducted and provided by Jack Alexander.

A number of Tritium Facility personnel, both present and retired employees, were consulted on their memory regarding spent mercury gold trap removal and disposition, specifically waste container HMFS001220. Mr. Alexander also consulted several documents from that time period about gold-trap disposition, including STA-229. Mr. Alexander was a Control Room Process Operator in 234-H from 1984 through 1987 and has been the Tritium Waste Program Representative (WPR) since 1996 and the SRTE Deactivation Manager, then SME, since 2001. In both of these capacities, Mr. Alexander has been involved in the disposition of gold-traps and other process equipment and waste packaged in stainless containers.

Summary from Interviews

A Cold Gold Trap (refrigerated) from EP 107C position in 234-H, room 69, process air-hood "M", was the first gold trap removed from the tritium process and placed into a welded stainless steel container. In service, this gold trap was cooled using cooling coils filled with FREON supplied from a compressor at all times while the trap was in the operating mode. The purpose of the vessel was to trap mercury vapor by amalgamating the mercury with gold in the trap. The mercury was fugitive mercury vapor from diffusion pumps used to move tritium gas in the process.

In December 1985, this trap (EP 107C) was prepared for removal through the standard procedure of preparing the line it was a part of for a line-break by flushing the gas lines, including the trap, several times with argon. The gas lines were then evacuated down to "micron" measurements, and a rate-of-rise was performed. The rate-of-rise would have been performed to ensure process operators that no water was in the line they were about to open. If the rate-of-rise failed, process personnel would sometimes use heat-trace to dry out the line while under vacuum. The presence of water would normally result in very high tritium oxide releases to the environment and high potential for personnel exposure during the line-break and removal of the trap, so every effort was made to ensure that no liquid water was present.

After line-break preparations, this trap would have been closed on each end with blind flanges as the trap was disconnected. The blind flanges would have been fitted with Buna-N (nitrile rubber, NBR or acrylonitrile butadiene rubber) gaskets. The trap was then removed from the walk-in process air hood. As it was removed, it would have been placed into a very large plastic bag to come out into the room. It may have been bagged multiple times to inhibit off-gassing into the room. The bags were sealed with black plastic tape before being placed into the stainless container pre-staged in the room. The container bottom was pre-welded on the container in the shop approximately 300 feet away.

The bags would have come off of a large roll stored in 234-H near the process. The welding equipment was already staged by running leads into the room and the lid was welded on by construction welders in the process room. The welds would have normally been dye penetrant tested. The memory of one maintenance mechanic who worked on this particular gold trap removal job was that there was no liquid water, and no special circumstances under which they were required to stop the job or move away from the hood. He also did not remember any higher than normal tritium releases. No one contacted who was affiliated with the 234-H process in 1985 remembers higher than normal releases from removal of gold-traps. High releases were often associated with liquid water.

Specific Interviews

Maintenance:
I was able to interview two mechanics who performed Mercury Gold-Trap work in 234-H in 1985. The first mechanic specifically remembered this job because it was the first time that a gold-trap had been removed and placed into a welded stainless container for disposal. Previously in the 1970's and 1980's spent gold had been removed and replaced, rather than removing the bed and replacing it. Without prompting he remembered the job, the room number (69) and the hood indicator (M-Hood). He also recalled that no liquid water was present during the job and that releases were relatively normal. He also recalled that the container was welded closed in the process room. The container would have been stored in ambient air in the construction welding shop and then brought into room 69 which was the coldest room in the process. The second mechanic did not recall this job; but he did recall that on other similar jobs that he worked on the tritium releases were generally lower when removing gold traps in this fashion, instead of removing and replacing gold. Neither mechanic was able to explain why this Gold Trap, EP 107C, was bagged and others were not. They surmised that since it was the first time they had done this, packaging was likely in the plan and they went with the plan. Subsequent similar jobs with gold traps may have not required plastic bags because the off-gassing was relatively low. It may also have been that welding near plastic bags did not work out well, and they avoided that problem on subsequent jobs since the bags were not absolutely necessary. They did not remember for sure about this.

Engineering/Operations Management:
I was not able to find anyone who was in management or engineering who could remember the actual work or actual work day that HMFS001220 (Gold Trap inside of Stainless "Pipe" style container) was loaded and welded. I did speak with one individual who was in engineering in 1985 and worked on the design of the container. He knew that the welds were supposed to be dye-checked after the container was welded closed and that the container was designed to 42 PSIG. He was also sure that the containers were not planned for staying in above ground storage indefinitely. There was no knowledge about water or other liquids. He recalled that liquid mercury would not be expected.

I talked with another individual who was not in the Tritium Facilities in 1985, but was before and after that year. He worked both in engineering and operations and was very knowledgeable about Gold Traps. He said he would be very surprised if liquid water would have been available to be introduced into these containers, other than moisture in the air condensing on the metal.

Bob Rabun and I talked a good bit about possible source of water and could not come up with likely sources of liquid water around the Gold Trap considering all the of work that went into line-break preparation to keep them dry.