

# **Assessment of the Corrosion, Stress Corrosion Cracking and Embrittlement Susceptibility of 30313 Storage Containers**

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## **Background**

The degradation of stainless steel container materials is a potential problem for long-term radioactive waste storage. Container materials will be exposed to significant ionizing radiation, elevated temperatures, embrittling and/or alloying agents (e.g., gallium), chloride-containing compounds, oxidizing compounds, and a limited quantity of moisture. Additionally, containers will incorporate welds that have heterogeneous compositions due to solute segregation and that may retain significant residual stress. All of the above-listed environmental and material conditions have been shown to be deleterious to material integrity under certain conditions. Research is ongoing into the corrosion, stress corrosion cracking (SCC), and embrittlement susceptibility of 3013 storage container materials. The goal of this document is to preliminarily assess the failure susceptibility of storage container materials by inference from the conditions which promote failure. Because laboratory research is incomplete, this assessment should be viewed as a working document. This document was written to support the update to a previous 3013 storage standard<sup>1</sup>.

## **Container Materials**

Different materials will be used for different portions of the 3013 container. Current plans are for the outer container (which is considered to be the "pressure vessel") to be composed of 316 L stainless steel (SS). The outer container will contain one or two welds (either laser or TIG welds). The inner container will be composed of 316 SS containing one weld. The convenience container composition will vary depending on its contents. Those that contain oxide will be composed of a 316 SS threaded body with a 416 SS lid. Those that contain metal

will be composed of a 304 L SS threaded body with a 416 SS lid. The heat treatment schedule / residual stress state of the container materials is not known at this time. The stress state is important because residual stress can play a strong role in SCC susceptibility.

The composition of the austenitic (300-series alloys) and martensitic alloys (416 SS) is shown in Table 1. In general, increasing Mo, Cr, and Ni is beneficial to the failure resistance of stainless steels. The primary difference between "L" grade materials and their corresponding base materials is the carbon content. Reduced carbon content is helpful to avoid sensitization during welding. Sensitization is the process whereby Cr is removed from solid solution through the formation of  $\text{Cr}_{23}\text{C}_6$ . This results in the depletion of Cr near grain boundaries. Since 12% Cr is required to make the material "stainless", material near the grain boundaries loses its stainless properties and rapidly corrodes or cracks. Careful welding practices are required to avoid this scenario. Reducing the carbon content allows a much wider error margin during welding. However, there is some tradeoff in mechanical properties (Table 2).

	Cr	Ni	C	Mn	Si	P	S	other
316	16-18	10-14	0.08	2.0	1.0	0.045	0.03	Mo 2-3
316L	16-18	10-14	0.03	2.0	1.0	0.045	0.03	Mo 2-3
304L	18-20	8-12	0.08	2.0	1.0	0.045	0.03	-
416	12-14	-	0.15	1.25	1.0	0.06	>0.15	Mo 0.6*

\* - optional

Table 1 - Chemical compositions of relevant stainless steels (wt %, remainder is Fe). All single values are maximum values.

	Tensile (MPa)	Yield (MPa)	Elong. (%)
316	579	290	50
316L	517	220	50
304L	558	269	55
416	517	276	30

Table 2 - Ultimate tensile strength, yield strength, and elongation-to-failure of relevant stainless steels in the annealed condition.

### Storage Environment

### *Temperature*

Initial estimates indicated that the container wall temperatures would not be expected to exceed 100°C.<sup>2</sup> Updated estimates indicate that the container wall temperatures will not exceed 150°C under "normal" conditions. However, for storage facility design purposes, it is desirable to allow for large temperature excursions in the event of cooling loss. Thus, the working number for the upper temperature limit of the containers during an off-normal condition is currently 250°C for 10 years.

#### *Radiation flux*

The radiation flux will vary between containers. It is expected that containers will contain between 30 wt% and 100 wt% Pu. However, the total stored mass and the presence of other compounds which produce and absorb ionizing radiation will vary between containers. Thus, the range of ionizing radiation flux is expected to be quite large.

#### *Water concentration*

It is expected that the stored materials may contain up to 0.5 wt% water. Assuming an upper storage limit of 5 kg, 25 g of water may be present. Relative humidities within the containers are expected to be low (less than 10% and possibly less than 1 %) due to the strong affinity of PuO<sub>2</sub> for water.<sup>3</sup>

#### *O<sub>2</sub> gas concentration*

Currently, the standard does not address the environment for packaging. Thus, the environment may be either air, argon, or some other cover gas. Rocky Flats is planning on using filling the containers with He gas.

#### *H<sub>2</sub> gas concentration*

The upper limit for H<sub>2</sub> pressure is 699 psig.<sup>4</sup> It is expected that this limit will never be approached in practice.

#### *Chloride concentration*

Chloride concentrations may be as large as tens of weight percent. Because stored materials will not necessarily be homogeneous, local concentrations may approach that of pure salts.

#### *Ga concentration*

Ga concentrations up to 1.2 wt% may be possible. The homogeneity of the Ga distribution within the stored materials is unclear at this time.

### **Literature Review**

Two previous reports detailed potential failure modes of 3013 containers at temperature below 100°C.<sup>5,6</sup> This information will not be reiterated here. Because the 1996 standard imposed a temperature limit of 100°C,<sup>1</sup> and because calculations suggested that container wall temperatures would be less than 100°C,<sup>2</sup> failure susceptibility above 100°C was not detailed. Since it is currently desirable to allow wall temperatures of 250°C, susceptibility at temperatures greater than 100°C must now be considered. This is discussed below. Additionally, gaseous hydrogen embrittlement of storage containers, which was not considered previously, is also discussed below.

#### Corrosion at Temperatures Exceeding 100°C

Localized corrosion at temperatures above 100°C is not expected to be a problem as long as the conditions within the container promote superheating of the steam. It has been stated that superheating of at least 20°C above the dew point avoids the formation of a significant aqueous layer on a SS surface.<sup>7</sup> In this condition where the moisture within the container remains essentially vapor, localized corrosion will not occur. Localized corrosion will not occur because localized corrosion requires a spatial separation of anode and cathode and an ionic pathway between them. In the absence of a thin condensate film, there is no ionic conducting pathway and thus no localized corrosion. For the situation where uniform corrosion occurs, the total amount of container dissolution can be calculated (see "Results-To-Date" below). Uniform dissolution is predicted to be inconsequential.

Increasing temperature has the effect of increasing the corrosion rate (both localized and general). However, the extent of corrosion, more so than the rate of corrosion, may dictate the life of the container, because the environment is a closed system (i.e., the oxygen and water are

mass limited). Thus, corrosion rate per se is not a significant issue in 3013 containers. Therefore, over a 50 year storage period, the primary effect of temperature is to alter the form of corrosion, rather than the extent.

### SCC at Temperatures Exceeding 100°C

There have been many studies on the SCC susceptibility of austenitic SS in steam environments. None of these studies is 100% applicable to the 3013 storage container situation because a) the containers will only contain a limited amount of water, b) the water vapor concentration will initially vary with time, c) the container temperature will vary with time, d) the oxygen gas concentration will initially vary with time, e) the container walls will be at a lower temperature than the stored material, f) ionizing radiation will be present to produce aggressive species such as  $H_2O_2$ . That said, the SCC susceptibility of austenitic SS in the presence of chloride deposits and steam has been characterized and is relevant to storage conditions. Some selected studies are summarized below.

A study by Shimose et al. examined the SCC susceptibility of "well-annealed" austenitic SS exposed to aqueous chloride solutions and their equilibrium vapors.<sup>8</sup> The materials examined were nominally 304 SS and 316 SS. Tests were performed in pressurized autoclaves and comprised solutions of 0 to 300,000 ppm chloride and temperatures of 130°C to 250°C. They found that below 150°C, no SCC of either material was observed during exposure to liquid, or the vapor above that liquid, regardless of chloride concentration. In temperature / chloride concentration / applied stress regimes where SCC was observed, the vapor phase was found to be more aggressive than the liquid phases (Figure 1). It was found that when the autoclave atmosphere was replaced with oxygen, the threshold stress required for SCC was significantly decreased. Conversely, when the atmosphere was comprised of argon, no SCC was observed in tests comprising

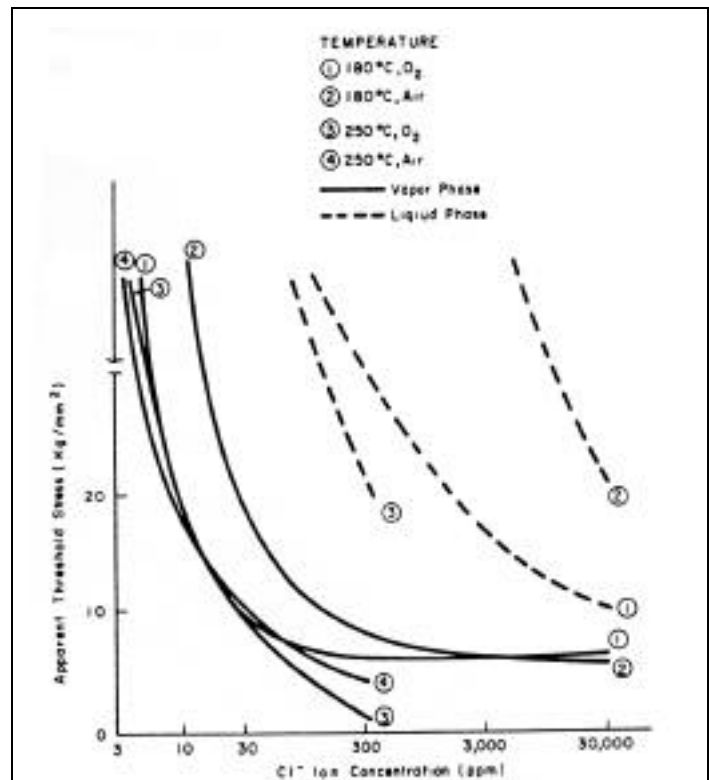


Figure 1 - Relationship between chloride ion

up to 30,000 ppm chloride at 180°C. It was hypothesized that oxygen was required to nucleate corrosion pits which in turn nucleated stress corrosion cracks.<sup>8</sup>

Much of the work by Williams et al.<sup>10</sup> is in agreement with that of Shimose et al.<sup>8</sup> Pressure vessel tests using 304 SS, 305 SS, 316 SS, and 347 SS indicated that a critical combination of oxygen and chloride is required for SCC at temperatures between 240°C and 260°C in stressed U-bend specimens. It was stated that "it does appear that the maintenance of oxygen at some value below 1 ppm (perhaps 0.5 ppm in critical areas) will provide reasonable assurance against stress corrosion failures at chloride levels likely to be encountered in steam generation equipment [ $<1000$  ppm]". It was also stated that residual stresses are sufficient to cause failure in environments highly conducive to stress corrosion. In contrast to Shimose et al., it was stated that stress corrosion can occur at temperatures as low as the boiling point of water.<sup>10</sup>

Edeleanu and Snowden also examined SCC of austenitic SS in steam systems.<sup>11</sup> Tests incorporated temperatures of 330°C to 508°C, steam pressures of 1500 - 1700 psi, and chloride contamination. It was found that cracking susceptibility increased with decreasing superheating. Thus, for identical steam pressures, higher temperature promoted less cracking because of increased superheating. Cracking was generally found to be fast within 20°C of the dewpoint. Otherwise, cracking was generally found to be slow or nonexistent. Results indicated that some contaminant (e.g., chloride) is required for SCC. As with the other studies above, it was found that oxygen was required for SCC. Indeed, tests incorporating 100 psi hydrogen at the dewpoint in 330°C revealed no SCC.<sup>11</sup> Thus, it appears that an atmosphere containing little moisture will not promote SCC.

Failure of one container via SCC would require the formation of crack initiation site such as a corrosion pit, an accumulation of moisture within that site, and a source of stress sufficient to initiate and propagate a crack. This scenario appears to be very unlikely. Further, the probability of penetration of a second container appears to be even more unlikely given that the conditions which would result in SCC of the first container would likely result in the consumption of the available water. In summary, it appears that the low humidity, low oxygen content, and generally reducing atmosphere of the containers<sup>4</sup> will be beneficial to the failure resistance of the 3013 containers.

#### Hydrogen Gas Embrittlement of Austenitic and Martensitic SS

There is scant information regarding pressure limits for the safe storage of hydrogen in stainless steel containers. A note in a diagram indicating the safe storage limits for carbon and low alloy steels states that "austenitic stainless steels are satisfactory at all temperatures and pressures".<sup>12</sup> As a reference, this diagram indicates that 1300 psi hydrogen can be safely stored in carbon steel at 250°C and that greater than 13000 psi can be safely stored in a 2% Cr, 0.5% Mo steel. Therefore, it may be inferred that austenitic stainless steels are safe for hydrogen storage to 250°C and 13000 psi. However, no particular pressure limits could be found in the literature. Note that safe storage limits do not account for any plastic deformation, pre-existing crack initiation sites, radiation damage, etc., which would reduce the limit for the safe storage of hydrogen gas.

There is some controversy in the literature regarding some aspects of hydrogen embrittlement (HE) of austenitic stainless steels. However, the basic facts of HE of stainless steel are not in dispute. Currently, it is widely recognized that austenitic stainless steels can be embrittled by gaseous hydrogen.<sup>13-27</sup> Austenitic stainless steel alloys that are metastable with respect to martensite formation (a phase that can be formed via a diffusionless transformation upon cooling or deformation) are more susceptible to HE than less metastable or stable alloys.<sup>13,14,15,17,18,19,22,24,25,27</sup> Austenite stability is imparted via alloying with many elements, most notably nickel. For 18 wt% Cr steels, additions of Ni beyond 10 wt% sharply decreases the volume percent martensite that is formed upon deformation.<sup>13,17,22</sup> Because martensitic stainless steels are more susceptible to HE than austenitic stainless steels, the formation of martensite is considered to be detrimental to the HE resistance of austenitic stainless steels. That said, martensite formation is not a requirement for HE, as HE has been noted in stable austenitic stainless steels such as 310 SS. Because the compositional changes required to increase the stability of austenitic stainless steels also increase the stacking fault energy of the material, it has been widely hypothesized that the stacking fault energy plays a strong role in HE susceptibility.<sup>13,15,17</sup> Reducing the yield strength of stainless steels is also thought to be beneficial.<sup>13,23,24</sup>

For austenitic stainless steels, the permeability and diffusivity of hydrogen is relatively low and the solubility is relatively high, as compared to other materials, particularly ferritic and martensitic stainless steels.<sup>13</sup> This renders even the most susceptible austenitic stainless steels relatively resistant to HE. It has been implied or stated that plastic deformation is required for HE.<sup>13,14,16,20,21,25</sup> This is attributed to the dislocation transport of hydrogen to trap sites<sup>14</sup> which nucleate cracks and to the relatively low permeability of and diffusivity in austenitic stainless steels. The quantity of hydrogen absorbed by a material is dependent upon many factors

including hydrogen partial pressure, oxygen partial pressure, surface film composition and microstructure, strain rate, presence of ionizing radiation, and temperature. It is conceivable that a long time, high pressure hydrogen exposure in an ionizing radiation environment would eliminate the requirement for dislocation transport, but no data is available to support or refute this hypothesis.

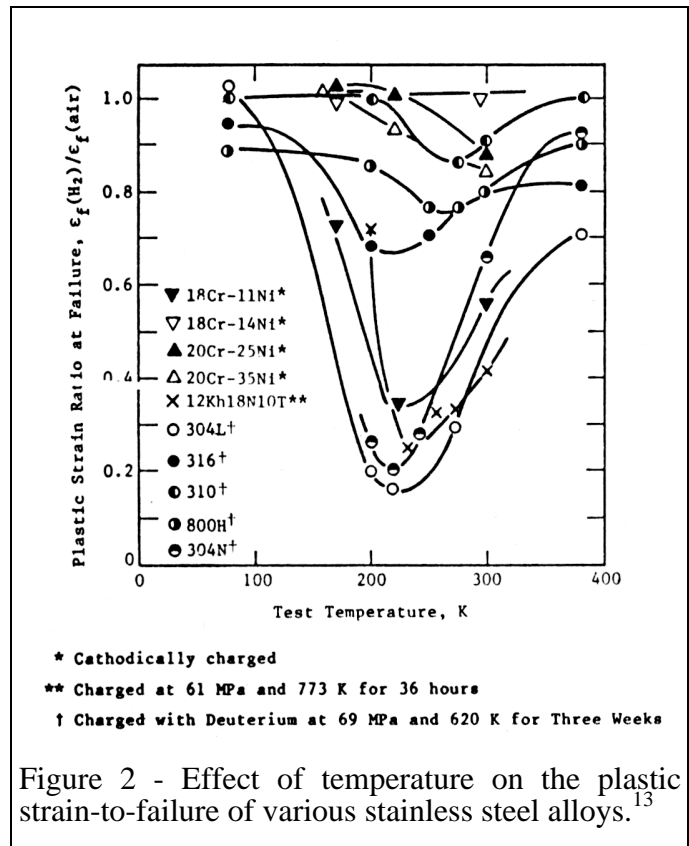
The quantity of hydrogen required to embrittle austenitic stainless steels is dependent on the alloy composition and microstructure, environment, the presence of a notch and the notch acuity, and test methodology. Therefore, no single value of internal hydrogen concentration can be said to be a threshold. Further, embrittlement is commonly measured by tensile tests which yield parameters such as yield strength, ultimate tensile strength, reduction of area, and elongation. These parameters describe the mechanical behavior of materials. However, they do not describe the resistance to fracture. The threshold stress intensity, a parameter which describes the resistance

to fracture, is less commonly measured. There is no quantitative way to relate the mechanical properties to the fracture properties. However, materials that display reduced ductility commonly display a lower threshold stress intensity.

Following is a summary of selected results from the literature which discuss the effects of various parameters on the behavior of austenitic stainless steels.

### *Temperature*

A minimum in resistance is observed at intermediate temperatures.<sup>13,14</sup> This minimum is typically found between  $-100^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ , although the position of the minimum is dependent on microstructure, composition, hydrogen content, strain rate, test parameters, etc. For 304L SS





and 316 SS charged with deuterium at 69 MPa for 3 weeks at 620°K, the resistance minimum (as measured by strain-to-failure) occurred at 225°K (Figure 2).

### *Hydrogen gas pressure*

Following are assorted results indicating the effects of hydrogen gas pressure or hydrogen concentration on HE susceptibility of austenitic stainless steels. Hydrogen uptake has been shown to be proportional to the square root of hydrogen gas pressure.<sup>13,14</sup> However, at hydrogen pressures above 150 atmospheres, there is little increase in embrittlement of 304 L SS.<sup>14</sup> Tests of 304 L SS in hydrogen gas of different

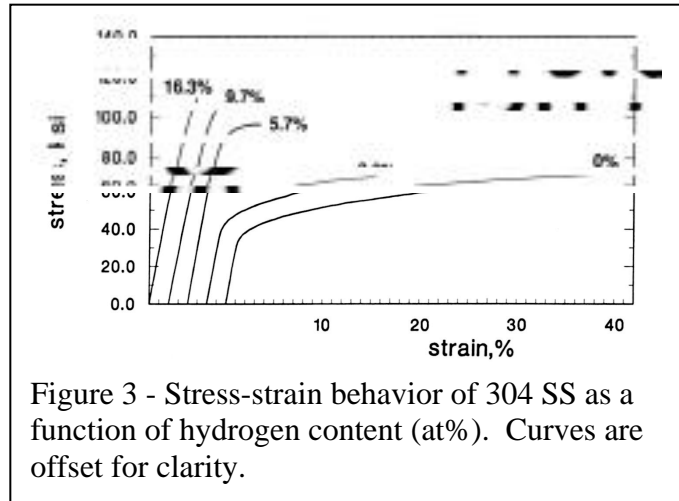


Figure 3 - Stress-strain behavior of 304 SS as a function of hydrogen content (at%). Curves are offset for clarity.

pressures revealed that increasing gas pressure increased the embrittlement as measured by decrease in ultimate tensile strength. Tests incorporating materials with a "sharp notch" showed 5.8%, 15.0%, 18.2%, 19.3% decrease in ultimate tensile strength during exposure to 2500, 5000, 7500, and 10000 psi hydrogen.<sup>21</sup> (These gas pressures are larger than the maximum expected in the containers (699 psig)). These materials were pre-exposed to the gas for 24 hours. Tests using a pre-exposure of only 3 minutes in 10000 psi hydrogen indicated a loss of 13.9%.<sup>21</sup> This demonstrates the importance of plastic deformation. Tests also showed that hydrogen embrittlement was reversible following hydrogen exposure and air testing.<sup>21</sup> Increasing hydrogen reduces ductility and increases the yield strength of 304 SS (Figure 3).<sup>15</sup> Tests using commercially pure iron - chromium - nickel ternary alloys indicated that 47 ppm hydrogen does not embrittle stable 18 Cr - 14 Ni steel and that 45 ppm hydrogen does embrittle metastable 18 Cr - 10 Ni steel.<sup>22</sup> Tests of notched 304 L SS bars indicated a 13% reduction in UTS and a 48% reduction in elongation during testing in 10000 psi hydrogen.<sup>27</sup> Unnotched bars were not as severely affected.<sup>27</sup> Tests in 69 MPa at room temperature resulted in a 48% reduction in elongation.<sup>13</sup> Additionally, slow crack growth was not observed in 304 L SS or 310 SS in 0.1 MPa hydrogen gas.<sup>13</sup> For 304 SS containing a hydrogen concentration of 200 mol/m<sup>3</sup>, the threshold stress intensity has been measured as 62 - 75 MPa m.<sup>23</sup>

### *Oxygen gas pressure*

Increasing oxygen content has been shown to decrease HE susceptibility.<sup>26,28</sup> It is unclear whether there is a critical concentration or a critical oxygen partial pressure required to inhibit HE due to contradictory results in the literature. However, as little as 0.1 ppm O<sub>2</sub> has been shown to have a beneficial effect on carbon steel.<sup>28</sup>

#### *Applied and residual stress*

Strain gauge measurements of a prototypic container indicated that the maximum plastic strain that a container would experience following an  $\alpha$  to  $\beta$  phase transformation of a Pu metal puck is 2%.<sup>29</sup> This value is well below the large strains applied in the laboratory testing discussed below so the tests discussed below may be considered to be far more aggressive than conditions experienced by the container. Furthermore, the strain gauge measurements used unrealistically conservative conditions (e.g. no container top and bottom) so the actual plastic strain that a container will experience will almost certainly be much smaller.

Significant applied loads are generally required to induce failure of austenitic stainless steels. A summary of tests including 304 SS, 304 L SS, and 310 SS indicated that crack propagation is only observed when the applied load is greater than 80% of the failure load.<sup>13</sup> Moreover, there is little evidence of hydrogen-induced slow crack growth, delayed failure, or sustained load cracking.<sup>14,19,23</sup> This implies that stable crack growth is not observed. Thus the materials will immediately crack to failure or will not crack at all. The minimum stress required to cause fracture decreases with increasing martensite start temperature.<sup>24</sup> This is not surprising given the relationship between martensite quantity and HE susceptibility.

It has been reported that prior cold work was found to increase the severity of hydrogen damage in some austenitic stainless steels as measured in tensile tests.<sup>13</sup> Electropolishing or annealing to eliminate the cold-worked surface layer produced by machining was shown to reduce the HE susceptibility.<sup>14</sup> (Note that the surface roughness per se has no effect on HE.<sup>14</sup>) Another set of experiments showed that sharply notched 304 L SS first loaded in air to approximately 85% of the UTS and then tested in 9600 psi hydrogen revealed a 15% loss in UTS.<sup>21</sup>

#### *Material composition and microstructure*

It is well established that 316 SS is more resistant to HE than 304 SS.<sup>13,18,19,24</sup> While sensitized 304 SS has been shown to be more susceptible to HE than nonsensitized 304 SS, the

same is not true for 316 SS.<sup>24</sup> Low-carbon grades of austenitic stainless steels (304 L, 316 L) are not necessarily preferable to the regular grades (304 SS, 316 SS). High carbon steels are the least susceptible to embrittlement in the absence of sensitization due to the austenite-stabilizing effect of carbon. However, in the presence of sensitization, high carbon steels are the most susceptible to HE because increasing carbon increases the sensitization.<sup>20</sup> Note that there have been some observations that indicate that sensitization of 316 SS does not increase the susceptibility to HE, even though it does increase the susceptibility of 304 SS.<sup>24</sup>

Welds in austenitic stainless steels may be more susceptible to HE than the base metal. Weldments commonly contain several percent delta ferrite which provides a preferred path for crack propagation in the presence of hydrogen.<sup>13</sup>

### *Ionizing radiation*

The effect of ionizing radiation on the HE of austenitic stainless steels is unknown. Because the effects of ionizing radiation on materials (defect formation, yield strength increase, etc.) are detrimental to the HE resistance of austenitic stainless steels, it is expected that ionizing radiation may enhance HE. The relationship between the radiation flux and the HE susceptibility is unknown but it is clear that radiation has the potential to significantly decrease the resistance to HE.

In summary, austenitic stainless steels are susceptible to HE under certain conditions. Fortunately, HE of austenitic material requires significant plastic deformation (ignoring the effects of radiation which are unknown). Additionally, even at 10000 psi hydrogen, mechanical properties are not severely degraded. Failure of containers would require extraordinary pressurization, plastic deformation, or radiation damage that is not anticipated. Thus, HE of container materials does not appear to be a concern.

### Los Alamos and Rocky Flats Container Corrosion Experience

Observations of unpackaged containers containing Pu materials (including salts) at Los Alamos do not suggest a significant corrosion problem. It has been stated that "We don't have any appreciable high-heat material at Los Alamos. Of what we do have, very little is associated with chloride salts. In any event, we have not noticed any corrosion (except a little discoloration) in containers of pyrochemical salts. This discoloration has been isolated only to

paint cans and [we have observed] nothing with SS cans...the plutonium has all been [weapons grade] material. None of this has been documented."<sup>30</sup>

The following information on Rocky Flats corrosion observations has been compiled:<sup>31</sup>

"Rocky Flats Environmental Technology Site (RFETS) has historically used pyrochemical processing to purify and or produce plutonium metal. These processes included Molten Salt Extraction (MSE) for the removal of americium, Electrowinning (ER) for the removal of impurities, and Direct Oxide Reduction (DOR) for the production of plutonium metal by calcium reduction of plutonium oxide. The principle reagents used in these processes were KCl, NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>. Completion of processing produced plutonium metal buttons along with a residue salt product containing varying amounts of plutonium. Equipment cleanup activities also produced some quantities of plutonium oxide with impurities consisting primarily of chloride salts. Residue salts were packaged in different types of containers including; Volrath (304 stainless steel) slip-lid cans, paint cans, produce cans, and vault (stacker-retriever) cans. With the exception of the vault cans, all cans were bagged from the glovebox using PVC bags and stored in drums. Materials evaluated in this study ranged in age from about 7 – 18 years."

"The salt characterization process required removal of a sample of the salt for various analytical procedures. A total of 113 stainless steel containers were sampled during this program. During sampling, the stainless steel containers were examined for corrosion. Evaluation of the condition of the container was subjective, but it did provide a qualitative assessment of any corrosion problems that might exist. The moisture content of the salt residue was determined by a Loss-on-Ignition (LOI) method at two successive temperatures, 110°C and 220°C. The results from these analyses ranged from 0.1% to 10.5% water. These two values are extreme and likely are the result of experimental errors. Average values on the order of 1-2% water are more reasonable."

"Seventy-nine of the cans examined had no evidence of corrosion. The 34 remaining cans showed evidence of corrosion, discoloration, or contamination from degraded plastic packaging materials. Actual corrosion is defined by evidence of rust formation. Four of the 113 containers had evidence of rust on the inside of the can. One can contained MSE salt, one contained ER salt, and two contained DOR salt. The moisture content of the salt in these four cans ranged from 0.5 to 1.8%. Some rust or non-specific corrosion was found on 10 additional cans, but it was not noted whether or not the rust was on the inside or outside of the can. The moisture content in these cans varied from 0.1 to 8%. In no case was the corrosion severe

enough to penetrate the can. The plastic packaging was expected to be thermally and radiolytically degraded. When this happens, some material can stick to or stain the outside of the cans. Eighteen of the cans had surface deposits or stains attributed to the plastic packaging. The following is a summary of the cans that exhibited rusting on the inside."

#### Summary of Chloride Salt Corrosion of Stainless Cans

Can No.	Packaging Date	Source of Salt	Moisture	Corrosion
D17290	4/17/80	MSE	1.5%	Rust
D77584	9/30/91	ER	1.6%	Rust
2904061	4/25/88	DOR	1.8%	Slight Rust
D37748	9/30/83	DOR	0.6%	Slight Rust

"Stainless steel cans containing chloride salts have been stored for periods up to about 18 years. The moisture content of the salts was greater than that permitted for plutonium oxide stored in 3013 type containers. Examination of 113 containers showed that corrosion was not a significant problem and 70% of the containers were neither corroded nor contaminated by degradation of the plastic packaging. Corrosion that did occur was minor and consisted of rust on inner or outer container surfaces. It appears safe to conclude that chloride corrosion will not be a problem in the storage of plutonium in 3013 type containers for long periods. Any corrosion is expected to concentrate on the convenience container and will not impact the overall integrity of the total package."

#### Nondestructive Inspection Techniques for Crack Detection

Nondestructive evaluation of containers for cracking can be an important means of surveillance. There are a variety of books that discuss the myriad of methods for nondestructive evaluation of materials. Methods all have benefits and drawbacks - no method is ideal. A few of the more common methods are discussed very briefly below.

Liquid penetrant inspection is a popular method for crack detection because of its economy, ease of use and interpretation, and ability to detect flaws as small as hundreds of nanometers. The primary drawbacks to this method are that it can only detect surface flaws (as opposed to subsurface cracks), that parts require handling / contact / cleaning, and that the method cannot be used on rough surfaces.

Eddy-current inspection is widely used in industry. The method uses electromagnetic induction to generate eddy currents in a part. Any crack in the part of interest will interrupt the

normal flow of eddy currents. Advantages of this method are that it is a noncontact method and that is relatively cheap to employ. One potential drawback is the sensitivity of the measurement which depends on the operating parameters and the part itself. A second drawback is the potential for difficulty in data interpretation.

Radiography is another potential method for crack detection. This method is noncontact and data is commonly easy to interpret. However, the ability of the method to detect cracks in cylindrical objects can be poor, but optimization of the setup can overcome this problem to some extent.

Ultrasound is a common method for nondestructive crack detection in parts. The method has excellent sensitivity and accuracy. Drawbacks include difficulty of operation and data interpretation, and the requirement for couplants.

## **Results-To-Date**

### How Much Uniform Corrosion Will Occur?

Assuming that only water is available for container oxidation, the cathodic charge corresponding to 25 g (0.5 wt% of 5 kg) of reduced water can be calculated:

$$25gH_2O \times \frac{1mol}{18g} = 1.4mols = 1.3 \times 10^5 C$$

The relationship between this charge and the mass of 316 stainless steel that is oxidized by this charge can be calculated, assuming that the oxidation states of Fe, Cr, Ni, and Mo are +2, +3, +2, and +3, respectively:

$$1.3 \times 10^5 C = 35g S.S$$

This corrosion penetration can be calculated from the mass, assuming a surface area (1100 cm<sup>2</sup>) and uniform corrosion:

$$35 g SS = 4.4 \text{ cm}^3 SS = 39 \mu\text{m penetration}$$

Because container walls will be much thicker than 39 μm, uniform corrosion by 25 g of H<sub>2</sub>O will not be a problem regardless of temperature. Again, this assumes that water is the only oxidizing specie and that only 25 g of water is available for oxidation of the container.

### Atmospheric Conditions Which Promote Localized Corrosion

Atmospheric corrosion below 100°C is defined by the presence of a very thin, sometimes discontinuous, aqueous electrolyte that forms on the surface of a material. This electrolyte often contains impurities from the environment in a concentrated form. This phenomenon has been characterized in the literature.<sup>32-39</sup> It is commonly accepted that relative humidities of less than 10% do not promote localized attack. However, testing is required under relevant conditions to ensure the absence of localized corrosion.

Atmospheric corrosion tests are ongoing. These tests attempt to define the conditions that promote localized corrosion of 304 SS and 316 SS as a function of temperature, humidity, weld, and deposit. Test durations are three weeks. Preliminary results suggest that 35°C and 60% relative humidity do not result in localized corrosion of 316 SS containing a NaCl deposit. Conversely, preliminary results suggest that 60°C and 90% relative humidity do result in localized corrosion. (Recall that the relative humidity within the container is expected to be less than 10%.) Due to equipment difficulties during testing, these results need to be replicated before they can be considered to be valid. Because the relationship between water concentration and relative humidity within the container is currently unknown, humidity measurements as a function of time would be required to relate our results to container environments. Moreover, because the container walls will be colder than the center line temperature, the container environment and atmospheric corrosion tests must be related by dew point not relative humidity.

#### Corrosion Susceptibility of TIG Welds

It is not anticipated that filler material will be used for container welds. Although containers can be safely welded using autogeneous welds (no filler material), the use of filler material can provide an extra margin of safety because the filler materials are typically composed of a more highly alloyed material. Thus, the use of filler is recommended where practical.

It is expected that both laser and TIG (tungsten inert gas) welds may be used to seal 3013 containers. 316 SS (16.15 Cr, 9.88 Ni, 0.23 C) was welded using a prototypic TIG weld (40 A constant current). Laser welds have not been evaluated.

Because atmospheric corrosion results from the presence of a thin adsorbed aqueous layer, the behavior of materials during atmospheric corrosion can be assessed by aqueous testing using electrolytes which approximate that thin layer. Specimens were tested using two methods and two different solutions which may approximate the composition of the atmospheric corrosion layer. The first method shorts a piece of welded material to a piece of base metal using

a potentiostat as a zero resistance ammeter. The galvanic corrosion current was positive which indicates that the welded material is more susceptible to corrosion than the nonwelded material. However, the galvanic current was approximately  $1 \mu\text{A}$  which corresponds to a corrosion rate that is less than  $25 \mu\text{m}$  per year less than the base material. Thus, the welded material will have a negligibly larger corrosion rate when shorted to the base material. Moreover, the corrosion on both materials was uniform. The second method used potentiodynamic polarization to assess the corrosion behavior of each material individually (Figure 4, left). Around open circuit (freely corroding condition), the two different materials reveal similar corrosion behavior in the more aggressive solution. At potentials more positive than open circuit ( $-0.3\text{V}_{\text{SCE}}$  to  $-0.1 \text{V}_{\text{SCE}}$ , which represents conditions that are more oxidizing), the welded material has a higher corrosion rate than the nonwelded material. However, both materials indicate active (uniform) corrosion behavior with no pitting. Comparison of welded and base materials in solutions which promote pitting (but are not necessarily prototypic of an adsorbed layer suggest that the welds are slightly more susceptible to pitting than the base material (Figure 4, right). Both the pitting potential and the repassivation potential (two separate measure of the pitting tendency of a material) were found to be more negative than for the welded sample than the nonwelded sample. This suggests that the welded sample is more susceptible to pitting although statistical analysis suggests that the difference is not large. In summary, even though TIG welds may be slightly more susceptible to corrosion than the base metal they do not appear to present a significant problem with respect to corrosion.

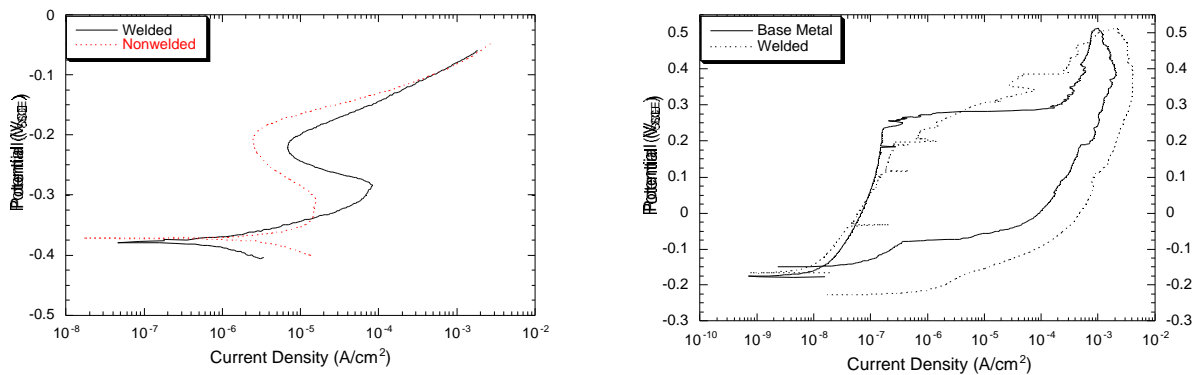


Figure 4 - Left: Comparison of welded and nonwelded material polarization behavior in 5 M NaCl (pH adjusted to 1.6 with HCl). Right: Comparison of welded and nonwelded material polarization behavior in borate buffered chloride solution ( $0.5 \text{ M H}_3\text{BO}_3 + 0.05 \text{ M Na}_2\text{B}_4\text{O}_7 + 0.2 \text{ M NaCl}$ ) (pH = 7.2).

#### SCC susceptibility of TIG welds



Boiling  $\text{MgCl}_2$  tests to assess the SCC susceptibility of TIG welds are ongoing. The boiling  $\text{MgCl}_2$  test is an ASTM standard test to assess the relative SCC susceptibility of stainless steels. The test is very aggressive and is not reflective of the absolute SCC susceptibility in the 3013 container environment.

Initial tests indicate that the TIG weld in a 304 SS minicontainer was not more susceptible to SCC than the base metal itself. These results are preliminary and additional tests are required to confirm this assertion. Tests to examine the effect of residual stress are planned.

Summary of the Effect of Increasing Property  
on the Failure Susceptibility of 3013 Containers

"- " is a detrimental effect, "+" is a beneficial effect

Property	Corrosion	Stress Corrosion Cracking	Hydrogen Embrittlement
Temperature	<b>- or +</b> Below 100°C, increasing T increases the localized corrosion susceptibility at a fixed relative humidity. Increasing T may reduce the relative humidity which reduces the corrosion susceptibility under some conditions. The transition from a water environment to a steam environment is beneficial. Increasing T increases the corrosion rate.	<b>- or +</b> SCC will tend to track with localized corrosion susceptibility. As with corrosion, the effect of T on SCC will depend on the environmental variables, particularly dew point.	<b>- or +</b> HE resistance is a minimum at intermediate temperatures (typically near room temperature).
[H <sub>2</sub> O]	<b>-</b> Because the extent of corrosion rather than the corrosion rate will determine container failure susceptibility, the total water content is important. Moreover, the relative humidity / dew point is critical to the localized corrosion susceptibility. In the absence of water or other oxidizers, corrosion will not occur.	<b>-</b> In the absence of water or other oxidizers, SCC will not occur. The relative humidity / dew point is critical to the SCC susceptibility.	<b>no effect</b> H <sub>2</sub> O could affect the passive film properties which in turn may affect the hydrogen permeability. If there is any effect, it is unknown and probably negligible.
[Cl]	<b>-</b> Chlorides promote localized corrosion.	<b>-</b> Chlorides or other contaminants are required for SCC.	<b>no effect</b> Cl could affect the passive film properties which in turn may affect the hydrogen permeability. If there is any effect it is probably negligible.
[Ga]	<b>no effect</b> Although there is no electrochemical attack, Ga can severely alloy stainless steel at elevated T (600°C). It is thought that stainless steel is immune to alloying by Ga at T < 200°C. The alloying behavior between 200°C and 600°C is unclear.	<b>no effect</b> Although there is no electrochemical attack, and thus no SCC per se, it is unclear whether Ga can liquid metal embrittle stainless steel.	<b>no effect</b> Ga could alloy with the material thereby altering the HE susceptibility. Any effect is likely negligible at storage temperatures.
[O <sub>2</sub> ]	<b>-</b> O <sub>2</sub> promotes localized corrosion.	<b>-</b> O <sub>2</sub> is required for SCC at temperatures above 100°C.	<b>+</b> Increasing O <sub>2</sub> inhibits HE susceptibility

[H <sub>2</sub> ]	+	+	-
	H <sub>2</sub> may inhibit localized corrosion under certain conditions.	H <sub>2</sub> may inhibit SCC by reacting with O <sub>2</sub> .	H <sub>2</sub> (or deuterium or tritium) is required for HE. HE increase with H <sub>2</sub> gas pressure.
Nonsensitized Welds	<b>no effect</b> TIG welds are not more susceptible to corrosion than the base metal in Cl solutions which mimic atmospheric thin layers.	<b>no effect</b> TIG welds are not more susceptible to SCC than the base metal in boiling MgCl <sub>2</sub> tests.	- Delta ferrite formation in the weld is detrimental to HE resistance.
Sensitized Welds	- Highly detrimental. Potential for severe intergranular corrosion.	- Highly detrimental. Potential for severe SCC.	- Detrimental to HE resistance if sensitization promote martensite formation.
Prior Cold Work	<b>no effect</b> Prior cold work can have a small effect under particular circumstances but that effect would be inconsequential for storage conditions.	- Can increase the SCC susceptibility.	- Prior work hardening promotes the formation of martensite and thus HE.
Active Plastic Deformation	- The effect is negligible unless persistent slip bands nucleate localized corrosion.	- A requirement for SCC under all but the most severe conditions.	- Typically required for HE. Deformation promotes martensite formation. and thus HE.
Ionizing Radiation	- The size of the effect is dependent upon container environment and on the extent of sensitization.	- The size of the effect is dependent upon container environment and on the extent of sensitization.	- Increases hydrogen trapping and diffusivity. Probably increases permeation.
%Cr in material	+	+	+
	Increases localized corrosion resistance.	Increases SCC resistance.	Increases HE resistance via austenite stabilization or increased stacking fault energy.
%Ni in material	+	+	+
	Increases localized corrosion resistance.	Increases SCC resistance.	Increases HE resistance via austenite stabilization or increased stacking fault energy.
%C in material	<b>no effect</b>	-	<b>- or +</b>
	No effect in the absence of sensitization.	Small adverse effect in the absence of sensitization.	Beneficial effect in the absence of sensitization. Detrimental if increased C promotes sensitization.

Recommendations for Storage of Radioactive Materials in 3013 Containers  
Considering Water, Oxygen, Hydrogen, Chlorides Only

*Temperature*

The effect of temperature on the corrosion, SCC, and HE behavior of 3013 containers is complex. For the cases of localized corrosion and SCC, there is a behavior discontinuity at the water / steam transition. Thus, increasing the temperature up to 100°C at a fixed relative humidity is detrimental to localized corrosion and SCC resistance. The effect of increasing the temperature at a fixed water concentration is unclear. Above 100°C, increasing the temperature appears to decrease the susceptibility to localized corrosion and SCC at a fixed water concentration (due to the increase in superheating). While increasing temperature increases the degradation rate of the containers, a fixed amount of reactant is present. Thus the extent of corrosion, cracking or embrittlement, rather than the rates will dictate the container lifetime. HE resistance is a minimum at intermediate temperatures. Although dependent upon many factors, this minimum is commonly observed at temperatures less than 100°C. It cannot be stated with certainty that this applies for 3013 containers.

Recommendation: There is no clear technical basis for the use of any particular temperature for storage between 25°C and 250°C. Temperature cycling is detrimental to the localized corrosion and SCC resistance of austenitic stainless steels and should be avoided.

*Water*

Water is the key ingredient for corrosion and SCC of 3013 containers in the absence of other oxidizers. Removal of all water (gaseous and liquid) will effectively eliminate corrosion and SCC susceptibility. Water has a negligible effect on HE. Because the rate of water liberation is unclear, the relative humidity inside of the container as a function of time is unknown. It is clear that if the water is liberated slowly enough such that the relative humidity inside of the container is low (< 10%),<sup>3</sup> only uniform corrosion will occur and the possibility of localized corrosion and SCC failure would be eliminated.

Recommendation: No water threshold can be recommended. Minimization of the water concentration is the highest priority of all recommendations.

*Chloride concentration*

Chlorides have no effect on the HE of austenitic stainless steels. However, chlorides play a key role in localized corrosion and SCC. In aqueous solutions, a particular chloride threshold for failure can be identified. However, stored materials will not be homogeneous. Thus, local salts activities will approach 1 regardless of the overall chloride concentration. Chloride is not the oxidizer (it can be thought of as a catalyst rather than a reactant) so failure can be controlled via control of the water and oxygen concentrations.

Recommendation: Because the local chloride concentration will not be controlled regardless of the overall concentration, there is no technical basis for setting a chloride threshold.

#### *Oxygen concentration*

Oxygen can strongly affect the corrosion, SCC, and HE susceptibility of austenitic stainless steels. Unfortunately, increasing the oxygen concentration has the opposite effect on HE than it does on the corrosion susceptibility. Only small amounts of oxygen are required to initiate pits and SCC cracks in steam environments. Conversely, small amounts of oxygen have been shown to inhibit HE. That said, the SCC susceptibility of austenitic stainless steels is more severe than the HE susceptibility so a reduced oxygen concentration is preferable. Hydrogen generated within the container will scavenge much of the available oxygen, producing a reducing atmosphere.<sup>4</sup> However, it is difficult to correlate the hydrogen generation kinetics with the pitting / SCC kinetics so it is conceivable that pitting could occur before a reducing atmosphere evolves. Like water, the amount of oxygen stored within the container is limited and may decrease with time as the container is oxidized. This provides some margin of error for storage.

Recommendation: Pack the containers in a dry, inert gas environment.

#### *Hydrogen concentration*

As discussed above, the presence of hydrogen is beneficial from a localized corrosion / SCC standpoint because the hydrogen will scavenge available oxygen.<sup>4</sup> Obviously, increasing the hydrogen partial pressure is detrimental to the HE resistance of the container. Since the hydrogen embrittlement susceptibility is proportional to the square root of hydrogen pressure (up to a certain point), there is no particular threshold for HE which can be identified.

Recommendation: Keep the total hydrogen concentration as low as possible while maintaining enough hydrogen to scavenge available oxygen.

#### *Welds (not sensitized)*

As shown above, testing indicates that nonsensitized, autogeneous welds are only slightly more susceptible to corrosion than the base material. Preliminary evidence suggests that the welds are not more susceptible to SCC than the base material. The presence of delta ferrite in austenite welds is potentially detrimental to the HE resistance. The use of filler material in the welds provides an extra margin of safety.

Recommendation: Use filler material where practical.

#### *Welds (sensitized)*

Sensitization greatly increases the likelihood of failure via corrosion, SCC, and HE.

Recommendation: Control welding procedures to prevent weld sensitization.

#### *Residual stress / annealing*

Annealing has very little effect on the localized corrosion behavior of austenitic stainless steels. High residual stress has been shown to be sufficient to cause failure in the absence of active loading. Residual stress contributes to the HE susceptibility of unstable austenitic stainless steels.

Recommendation: Use annealed material.

#### *Stainless steel composition*

Increasing the Cr and Ni content of austenitic stainless steels greatly reduces the failure probability under certain conditions. For instance, there is a critical Ni content (10-12%) above which stainless steels are much less susceptible to HE. Because the composition ranges of Cr and Ni are very wide for austenitic stainless steels, significant differences in susceptibility are possible between two batches of 316 SS. As for C content, the threat of sensitization outweighs any benefit in HE resistance in the absence of sensitization.

Recommendation: Purchase stainless steels that have the highest Cr and Ni contents. Low C grades are desirable.

#### *Convenience containers*

The use of convenience containers may greatly benefit the failure resistance of 3013 containers. Because the containers are in "series" with respect to contact with the stored material and because the package is a closed system, it is probable that the convenience container will act

as a sacrificial material. Also, because the convenience container materials are generally more susceptible to corrosion, SCC, and HE than 316 L SS or 316 SS it is possible that these materials would act as sacrificial anodes in the case of a convenience container breach, similar to the case of the plating on galvanized steel.

Recommendation: Always use convenience containers.

### **Summary**

The fixed amount of reactant (oxidizers, gas generators, etc.) within the containers affords a large margin measure of protection. Although one can conceive of failure means, they are considered to be very unlikely. This corresponds to the DOE site experience where no failures of stainless steel containers housing radioactive salts have been observed. While the interactions of all potential stored materials with the environment and container cannot be fully evaluated with the current technical data, the failure probability of a water, chloride, high temperature, hydrogen gas system can be assessed. The scenarios required to result in failure appear to be extremely unlikely.

Through-wall penetration of three containers by uniform corrosion is impossible assuming that the only oxidizing compound present is 25 g of water. Penetration by means of localized corrosion would require an extraordinary set of circumstances. Thus, container failure by corrosion will not be a problem in the absence of oxidizing compounds other than water.

SCC of containers has some probability for failure because the ingredients required for SCC (water and chloride) are present and catastrophic failure (i.e., critical crack propagation) can occur under certain conditions. However, given the expected low oxygen concentration and low relative humidity inside of the can, SCC of the convenience container is highly unlikely. SCC of all three containers (convenience, inner, and outer) appears to be extremely unlikely given the fixed quantity of reactant in the container.

HE also has some probability for failure given the presence of hydrogen gas. Small amounts of hydrogen have been shown to embrittle austenitic stainless steels. However, 316 SS is only slightly embrittled by hydrogen and embrittlement typically requires significant plastic deformation of the containers. In the absence of plastic deformation of the containers, hydrogen embrittlement is not expected to be a concern, even in the presence of ionizing radiation.

Preliminary testing of prototypic TIG welds reveals no additional concerns beyond those of the base metal. Prototypic laser welds have yet to be evaluated.

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