CHEMICAL COMPATIBILITY OF DWPF CANISTERED WASTE FORMS (U)

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CHEMICAL COMPATIBILITY OF DWPF
CANISTERED WASTE FORMS (U)

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CHEMICAL COMPATIBILITY OF THE DWPF CANISTERED WASTE FORMS

INTRODUCTION

The Waste Acceptance Preliminary Specifications (WAPS)¹ require that the contents of the canistered waste form are compatible with one another and the stainless steel canister. Item 3.9 of the WAPS follows:

3.9 CHEMICAL COMPATIBILITY SPECIFICATION

The contents of the canistered waste form shall not lead to internal corrosion of the canister such that there will be an adverse effect on normal handling during storage, and on an abnormal occurrence such as a canister drop accident. The producer shall describe the method of demonstrating compliance in the WCP. Corrosion, chemical interactions, and any reaction products generated within the canistered waste forms after exposure to temperatures up to the glass transition temperature shall be discussed in the WQR.

Rationale

The specification is required to assure that the canister can be safely handled during storage, transportation, and repository operations, and to provide needed data for assessment of long-term performance of the waste package components.

The regulatory requirements on the waste package as outlined in 10 CFR 60.135(b) (1) state that "The waste package shall not contain....chemically reactive materials in an amount that could compromise the ability of the underground facility to contribute to waste isolation or the ability of the geologic repository to satisfy the performance objectives."

This specification requires that the materials and fabrication methods used for production of the DWPF canisters provide vessels which are compatible with the radioactive waste glass and other canister contents such that no significant internal corrosion occurs. This will ensure confinement of the radioactive waste up to the time of packaging at the repository. Compatibility must also be maintained after a transient exposure of the glass to the glass transition temperature.

The canistered waste form is a closed system comprised of a stainless steel vessel containing waste glass, air, and condensate (volatile material condensed during glass pouring). This system will experience a radiation field and an elevated temperature due to radionuclide decay. This report discusses possible chemical reactions, radiation interactions, and corrosive reactions within this system both under normal storage conditions and after exposure to temperatures up to the glass transition temperature, T_g , which for DWPF waste glass will be between 440 to 460°C^{2,3}.

The earliest date for acceptance of waste at the federal repository is now set at 2015. This is approximately 20 years from radioactive start up of the DWPF. Since this is an optimistic schedule, this document is based on the assumption that the period of interim storage prior to packaging at the federal repository may be as long as 50 years.

SUMMARY

Overall, the DWPF canistered waste forms, produced under normal operating conditions and subjected to a radiation field and elevated temperatures, will not exhibit significant internal corrosion. Consequently, these canistered waste forms will ensure confinement of the radioactive waste during the estimated 50 year period of interim storage, handling, and transportation prior to packaging at the federal repository. Certain potential, atypical, conditions for the production of canistered waste forms were also considered. No significant corrosion is expected as a result of any of these conditions.

Specific conclusions are:

1. The gas occupying the free volume within the canister will undergo chemical changes as a result of the radiation field. Nitric acid will be generated using up all the water in the gas phase within three years (at anticipated dewpoints). Both nitrous oxide and nitrogen dioxide will also be formed. Eventually, the radiation field will bring about the destruction of the nitric acid yielding nitrogen dioxide and water. Up to 30% of the oxygen within the free volume gas will be consumed in the generation of the oxides of nitrogen (nitrogen fixation) during the first 50 years. No significant amounts of ammonia will be produced. None of these chemical changes will significantly affect internal corrosion of the canister over the 50 year period.

2. The waste glass does not chemically bond with the stainless steel during glass pouring. No chemical interaction between the glass and steel is expected due to a short excursion to T_g . Therefore, the passivating oxide layer of the stainless steel will remain intact after glass filling, and there will be no diffusion of glass components into the stainless steel or stainless steel components into the glass.

3. The waste glass does not chemically react with stainless steel and no internal corrosion of the stainless steel at the glass/stainless steel interface was detected over long storage periods at temperatures up to 300°C. Hence, the passivating oxide layer remains intact. These results indicate that the waste glass and the stainless steel will be compatible during the estimated 50 year period prior to packaging at the repository.

4. Oxidation of the internal surface of the stainless steel was not detected during any of the heat exposures anticipated for the canistered waste forms, including an excursion to T_g . Thus, no significant loss of stainless steel will occur in the DWPF canisters as a result of oxidation.

5. General atmospheric corrosion will not be significant for the inner surfaces of the canister during normal storage and anticipated heat exposures.

6 Microbiologically Influenced Corrosion is not of concern in the DWPF canistered waste forms.

7. Localized corrosion (pitting, crevice corrosion, intergranular corrosion, and stress corrosion cracking) from the inner surfaces of the DWPF canisters will not be significant over the estimated 50 year period.

BACKGROUND

This section describes the materials which comprise the canistered waste form (defined here as the canister filled with radioactive glass and sealed by upset resistance welding), the canister fabrication method, the radiation field present in the canister, the normal temperature profile for the canistered waste forms, and typical conditions of canistered waste form production within the DWPF.

Materials Contents of the DWPF Canistered Waste

Stainless steel The canister will be fabricated from stainless steel. The various types of stainless steel used for each of the components⁴ is given in Table 1⁵. These are low carbon stainless steels intended to reduce the formation of chromium carbides. This process of carbide formation is known as sensitization and can lead to accelerated corrosion over unsensitized stainless steel. In total, the canister will have a mass of ~1100 pounds (500 kg). Further discussion regarding these particular steels can be found in Volume 8 of the Wasteform Qualification Report⁵.

Table 1.

**ASTM Designations for the Canister Components.
From WQR (reference 5)**

<u>Component</u>	<u>ASTM Designation - Stainless Steel</u>
Cylinder	A240 Type 304L
Nozzle	A336 Type F304L
Taper Plug	A240 Type 304L
Repair Plug	A479 Type S21800 (Nitronic 60)
Neck Sleeve	A479 Type S21800 (Nitronic 60)
Heads	A240 Type 304L
Weld Plug	A240 Type 304L
Repair Cap	A479 Type S21800 (Nitronic 60)
Filler Material	ASME SFA5.9 ER308L or ANSI/AWS A5.9 ER308L

Ceramic ring The final weld plug is composed of three parts. Top and bottom stainless steel parts sandwich a ceramic ring. The pieces are held together through an interference fit by pressing the two stainless steel pieces together. The ceramic ring will be made from either alumina or steatite. The selection process to decide which of the two materials will be used is currently underway. The chemical composition of the two potential ceramics are given in Tables 2 and 3.

Table 2

Material Content for 665 Steatite for Ceramic Ring

<u>Component</u>	<u>Percentage</u>
SiO ₂	58.8
MgO	26.1
SrO	6.9
Al ₂ O ₃	6.1
Fe ₂ O ₃	0.4
CaO	1.3
K ₂ O	0.2
TiO ₂	0.04
Na ₂ O	0.2

Table 3.

Material Content for 614 Alumina for Ceramic Ring

<u>Component</u>	<u>Percentage</u>
Al ₂ O ₃	95.9
Na ₂ O	0.1
K ₂ O	0.03
SiO ₂	2.8
Fe ₂ O ₃	0.1
MgO	0.9
TiO ₂	0.03
CaO	0.14

Dow Corning 200 Fluid The current procurement specifications for the canister⁴ require the use of Dow Corning 200 Fluid to coat the outside surface of the sleeve which will be sealed to the inside surface of the nozzle by a heat shrinkage process. The specifications state that "The sleeve O.D. and the nozzle I.D. are to be wiped with Dow Corning 200 Fluid (viscosity 350 CS) and all excess material is to be removed by wiping". The Dow Corning 200 Fluid is a polymer, polydimethylsiloxane⁶. Its chloride content⁷ is less than the detection limit for neutron activation analysis (ADS ID No. 200067402). The total amount of fluid used per canister is estimated at 50 mg⁸.

Radioactive Waste Glass The radioactive waste glass will most likely be formed in the DWPF melter from 202 glass frit, sludge, and PHA. The chemical composition⁹ of the 202 glass frit is given in Table 4. The compositions of the sludge and PHA are given in a report by Baxter¹⁰. There could be times when sludge only glass is made. In this case a slightly different glass frit will be used. Final

fine tuning of the composition may be performed in the DWPF to remediate feed which would not otherwise satisfy the specifications, through use of trim chemicals. The radionuclides^{10,11,12} present in the design basis glass in terms of curies are given in Table 5¹¹.

Table 4.

**Chemical Composition Specification for Glass Frit 202
From Schumacher (reference 9)**

Component	Concentration (wt %)
SiO ₂	77.0 ± 1.0
Na ₂ O	6.0 ± 0.5
B ₂ O ₃	8.0 ± 0.5
Li ₂ O	7.0 ± 0.5
MgO	2.0 ± 0.25

Table 5.

**Radionuclide Inventory of the DWPF Design-Basis Glass
(5-year-old sludge, 15-year-old supernate)
From Plodinec (references 11 and 12)**

<u>Radionuclide</u>	<u>Inventory (Ci/canister)</u>
Ni-59	2.39E-02
Ni-63	2.97E+00
Se-79	1.70E-01
Sr-90	4.82E+04
Y-90	4.93E+04
Zr-93	1.12E+00
Nb-93m	1.12E+00
Tc-99	3.07E+00
Ru-106	2.28E+03
Rh-106	2.28E+03
Pd-107	1.47E-02
Sn-126	4.38E-01
Cs-135	9.92E-02
Cs-137	4.33E+04
Ba-137m	4.14E+04
Sm-151	2.39E+02
Th-230	2.00E-06
U-234	3.42E-02
U-238	1.05E-02
Np-237	8.86E-03
Pu-238	1.48E+03
Pu-239	1.29E+01
Pu-240	8.67E+00
Pu-241	1.66E+03
Pu-242	1.22E-02
Am-241	1.10E+01
Am-243	5.79E-03
Cm-244	1.07E+02

Condensate: Experience has shown that volatiles from the glass can condense onto the inner surface of the stainless steel above the glass line. The most likely source for these volatiles is from the pour stream. Jantzen¹³ has analyzed this condensate and found

mainly sulfate and chloride salts of potassium and sodium. The composition is given in Table 6. These materials were found on the interior canister walls, neck, and shoulder above the melt pour surface.

Table 6.
Chemical Composition of the Condensate
From Jantzen (reference 13)

Mixed (Na,K) Cl
Mixed (Na,K) SO₄
Mixed (Na,K) borates
Mixed (Na,K) fluoride phase (either NaF
or Na₂BF₄)

Free Volume Gas: The gas occupying the canister free volume has been analyzed for several canisters filled during the scale glass melter campaigns at TNX¹⁴. As expected, the gas is simply air with no other detectable components. The dew points ranged from -10.3 to +5.7°C. Further experiments are planned for the DWPF Startup Test Program which will analyze the gas in canisters filled in production equipment in the DWPF.

The internal gas pressure of prototypic DWPF simulated canister waste forms was determined to be less than atmospheric in the SGM campaigns (from 691 to 736 Torr). Langton¹⁵ obtained similar results using canisters filled in earlier large-scale melter tests (from 467 to 518 Torr). The lower than atmospheric pressure results from the fact that the canister nozzle must be at least 185°C before the tapered plug is inserted. If the temporary seal is inserted with the temperature of the canister nozzle at 185°C, then the internal pressure would be 495 Torr at 300°K. This assumes that the gas inside the free volume is also at 185°C at the time of sealing. Higher temperatures will lead to lower pressures. At 1 atm and 298.5°K, the amount of air inside the 110 liters of free volume (corresponding to 85% filling of the canister with glass) would be 4.49 moles or 129.5 grams. A reduction to 495 Torr internal pressure results in 84.1 grams of air in the free volume space. The actual amount will depend on the temperature of the gas when

sealed, the leaktightness of the seal, and the time between temporary seal formation and final upset resistance welding.

If sealed properly, the ICC leakrate will be less than 2×10^{-4} atm cc/sec for helium gas. This means that for air, at a 1 atmosphere differential pressure, 1×10^{-4} cc of air will leak in per second. The pressure differential is less than 1 atmosphere (0.35 atm at an internal pressure of 495 Torr) and hence the leak rate will be 0.35 times less than this. Therefore at a measured leakrate of 2×10^{-4} atm cc/sec for helium gas, 3 cc of air would leak in per day. It would therefore take 330 days for one liter of air to leak into the canister free volume space. This would increase the internal gas pressure from 495 Torr to 502 Torr and introduce 1.2 grams of air in this 330 day period.

Immediately prior to final welding, the sleeve and tapered plug are displaced by the ICC press 1.75 inches into the canister neck. This leaves about 0.25 inch engagement between the sleeve and the neck. The leakrate of this seal has been measured to be between 3.4×10^{-3} to 7.7×10^{-1} atm cc/sec helium.¹⁶ At the high end of the leakrate, approximately 1 liter of air per hour will enter the canister. Hence it is important that once the temporary seal has been displaced, the final upset resistance weld be made as quickly as possible to minimize inleakage of moist air.

The final weld has been shown to have leakrates less than 1×10^{-7} atm cc/sec for air¹⁷. Again, assuming an internal gas pressure of 495 torr, no more than 1.1 cc of air will inleak per year or, over a 50 year period, no more than 55 cc of air will be introduced in the canister for a final seal with this leakrate. In reality, the actual leak rates are orders of magnitude less than this and the seal is essentially leaktight. Therefore, effectively no inleakage of air will occur once the final weld is completed.

If 38°C is the maximum temperature within the Melt Cell, then the maximum amount of water which can be present in air at 1 atmosphere pressure is 46 mg water per liter¹⁸. If the pressure is 495 Torr, then each liter will contain $[495/760] \cdot 46$ mg/liter or 30 mg/liter. For the typical glass-filled canister, there are 110 liters of free volume. Hence the maximum amount of water which can be present inside the canister is 3.3 grams. However, measured values of the relative humidities and dew points give values of water content much less than this. This is partially due to the fact that

the relative humidities at such high ambient temperatures are much lower than 100% even on humid days. Another fact is that some of the water will be adsorbed onto the glass surface. A high dew point of the gas within the free volume is to be avoided since cooling of the canister during the winter months in the GWSB could lower the temperature below the dew point. In this case liquid water would form on the stainless steel surface. During the DWPF Startup Test Program, the temperature and relative humidity within the melt cell will be measured at the time of glass-filling for canisters that will be sampled for measurement of internal relative humidity. This will provide us with additional information on the maximum dew points which can be produced in the canistered waste forms.

There is one additional complicating factor in determining the concentration of gas within the canister. Prior to final welding the sleeve and tapered plug are pushed down into the canister by 1.75 inches. The final weld plug is then inserted on top of the canister nozzle. At this time the nozzle volume defined by this 1.75 inch length will be at ambient atmospheric pressure. At 1 atm pressure, this volume of 563 cc will contain 0.66 grams of air and a maximum of 22 mg of water. After final welding the pressure will actually increase inside the nozzle by 35% to a value of 1.35 atm. Since the temporary seal, after displacement, has a leakrate between 3.4×10^{-3} and 7.7×10^{-1} atm cc/sec helium, the pressures in the nozzle and free volume space will eventually equilibrate.

Glass Fracture and Voids, and Water Adsorption

The glass within the canister will most likely contain cracks and small voids. Use of computed tomography¹⁹ has corroborated the findings of cracks when a canistered waste form is sectioned. Computed tomography has also revealed small voids in canisters along the glass/stainless steel interface, and particularly in regions of interrupted pour¹⁹. The voids evidently have no impact on compatibility. The cracks, however, can play a role in interactions which affect the amount of water in the gas phase. The glass as poured is hygroscopic and will adsorb water from the air. Ebert et al²⁰ have shown that below 95% relative humidity, SRL 165 black frit adsorbs up to 18 statistical monolayers. At 80% relative humidity, the amount of monolayers adsorbed is 5. The surface area of the glass will determine how much water is actually depleted from the gas phase through adsorption. If all cracks are accessible through a network, then the available surface area for adsorption is

increased significantly. Langton¹⁵ demonstrated that the amount of water trapped in the canister free volume at the time of sealing actually decreases with time. In this experiment, she showed that the dew point fell from 2.5°C to -8°C before stabilizing after 10 days. This corresponds to a reduction in the amount of water in the air from 504 mg to 327 mg. This is roughly consistent with the TGA results of Harbour²¹ in which the amount of described water was measured from SRL165 white frit. An equilibrium will be reached in the canister between adsorbed and free water molecules which will depend on the relative humidity within the canister and the changes which occur as a result of irradiation and corrosion.

Canister Fabrication⁴

The canister nozzles, tapered plugs, and sleeves will be machined. The stainless steel portions of the final weld plug, the repair cap, and the repair plug will also be machined. The top and bottom heads are to be hot formed, solution annealed, and then reformed in the same die. The cylinder is to be rolled and welded. The heads are to be welded onto the cylinder and the nozzle onto the top head with SRS approved welding procedures. The welds are to be ground flush with the outside surface to within 1/32 inch. There is no requirement for grinding of the interior side of the welds. The sleeve is inserted following an approved procedure.

Two alphanumeric labels will be bead welded onto the outside of the canister. One will be on the shoulder and the other near the top of the cylinder part of the canister.

No annealing steps are done after any of the welding steps. The final canister will have two major circumferential (girth) welds, one major longitudinal weld, and a small circumferential weld to attach the nozzle to the top head. The labels will be bead welded, and the final seal will be formed by upset resistance welding¹⁶.

Glass Filling and Sealing^{5,8}

Canisters Filled on Pour Turntable⁵

The DWPF canisters will be received and stored in Building 210-S. As needed, the canisters will be transferred to the Melt Cell on a cart via a transfer tunnel. In the Melt Cell the canister can be placed on the pour turntable or placed in a storage rack using the in-

cell crane. Those canisters placed in the storage rack will have a cover placed over the nozzle to prevent foreign materials from entering the canisters.

After a canister is placed onto the pour turntable, the in-cell crane is used to insert a throat protector into the canister nozzle. The canister is then rotated on the turntable to a standby position. (The pour turntable holds four canisters). When this canister is needed, it is rotated to a position under the pour spout. A bellows is extended downward from the pour spout, and mates with the throat protector on the canister flange. Pouring is accomplished by maintaining a pressure in the canister plenum/bellows region about 1200 pascals less than that of the melter vapor space, thus drawing the glass up the melter riser, and into the pour spout, where glass falls into the canister. The molten radioactive waste glass will be captured by the DWPF canisters as it pours from the melter pour spout.

After filling, the canister is kept in contact with the bellows assembly for ~ 30 minutes to vent volatile materials. The bellows is then disengaged from the canister, and the pour turntable rotated such that the canister is removed from the pour spout. A Production Specialist uses the in-cell crane to remove the throat protector, and checks the temperature of the canister nozzle to ensure that it is hot enough to insert an Inner Canister Closure plug. The temperature of the nozzle must be above 185°C at time of insertion. The nozzle (with inserted sleeve) subsequently contracts during cooling to form a water-tight seal with the plug. The leak rate of the temporary seal of the canistered waste form is then measured in the Melt Cell. When the leak rate is acceptable, the canistered waste form is moved to the Canister Decontamination Cell where it is decontaminated using an aqueous slurry of glass frit. Smears are then taken to ensure that the amount of smearable radioactive materials present on the outside surface of the canistered waste form is within specification. After this is confirmed, the canistered waste form is transferred to the Weld Cell where the plug and sleeve are pushed down into the nozzle. A final weld plug is then inserted into the mouth of the nozzle, and a final weld is made by simultaneous application of high pressure and electric current for a short time duration. Smear tests are again taken at this time. The canistered waste form is then transferred to the Glass Waste Storage Building.

Canisters Filled on Drain Turntable⁵

Because the Drain Turntable is not normally accessible by the in-cell crane, the movement of these canisters is slightly different than that of canisters filled on the Pour Turntable. In order to remove these canisters, the Pour Turntable must be pulled away from the melter, and the Drain Turntable pulled to a position accessible to the overhead crane. Whenever a melter is drained, these movements of the turntables will be required.

The lack of ready access to the top of canisters filled on the Drain Turntable prevents formation of a shrink-fit seal in the same manner as for canisters on the Pour Turntable. Thus, after filling, these canisters are taken to the Inner Canister Closure Station, where an ICC plug is installed, and tested for leak tightness. The number of canisters filled from the Drain Turntable is expected to be much less than 1 % of the total number of canistered waste forms produced.

Radiation Field.

The radionuclides within the canister will produce a radiation field which will interact with the contents of the canister. There are basically four types of radiation present^{22,23}.

Alpha Radiation Dewberry²⁴ has calculated the amount of helium that will be generated from the radionuclide inventory of the DWPF design-basis glass as a function of time. The major sources of helium, and therefore alpha particles (there is a one-to-one correspondence here), are Pu-238, Pu-239, Pu-240, Pu-241, Np-237, and U-238. Over 300 years, a value six times longer than our 50 year estimate, and the shortest time reported by Dewberry, 0.34 moles of helium will be produced per canister. This implies that 2×10^{23} alpha particles will have been generated over this 300 year period. Plodinec¹² has also reported the radionuclide projection for the first four DWPF batches (~3650 canisters) and the projected radionuclide concentrations are less than the design-basis glass. Therefore, for at least the first four batches, use of the design basis glass inventory in the following calculations will overestimate the actual amount of alpha particles produced.

Alpha particles usually lose their energy through induced-ionization of the atoms/molecules of the medium in which they were

generated. In air, an average energy loss per ion pair formation is about 33.5 ev. For the 5 MeV alpha particles, this translates into 150,000 ion pairs produced per alpha particle in air. The charge on the alpha particle is constantly changing during these collisions and a single alpha particle will change charge ~1000 times during the time it loses its energy. As the velocity of this particle decreases the average charge continues to drop until it reaches zero after most of its energy has been dissipated. It is then a helium atom. Due to the short range of the alpha particles, none of the alpha particles will escape from the canistered waste forms.

Beta Radiation Beta rays are electrons which have been emitted from the nucleus during radioactive decay. The major sources of beta particles within the radioactive waste glass are cesium-137, strontium-90, and yttrium-90. The design-basis glass yields a value of 1.4×10^5 curies/canister or 5.2×10^{15} betas per second for these three radionuclides. The maximum energies for these three radionuclide beta particles are 0.52 MeV for cesium-137, 0.61 MeV for strontium-90, and 2.18 MeV for yttrium-90.

For yttrium-90, the maximum range is ~ 0.45 cm with an average range of 0.09 cm while for cesium-137 and strontium-90, the maximum range is 0.075 cm with an average range of 0.015 cm. Since the three radionuclides are present in approximately equal amounts, this implies that 2/3 of the beta rays will have ranges up to 0.075 cm and 1/3 will have a maximum range of 0.45 cm. Due to the short range of the beta particles, none of the beta particles will escape from the canistered waste form.

Gamma Radiation. The major contributing isotope to gamma dose rate in the DWPF waste glass is Cs-137. In this case Cs-137 decays by beta emission to Ba-137m, which further decays in 2.6 minutes by internal conversion, releasing a gamma ray with an energy of 0.662 MeV. The Ba-137m radionuclide accounts for 88% of the gamma dose for each canistered waste form. Other radionuclides contributing to gamma dose are: Eu-154 for 3.1%, Co-60 for 2.0%, Cs-134 for 1.9%, Ce/Pr-144 for 1.6%, Ru/Rh-106 for 1.4% and Sb-125 for 1.1%. These minor components emit gamma rays in a range of energies up to 2 MeV. Using the ANISN/QAD-CG code, a value of 5,570 R/hr (where R is Roentgen) for gamma flux at the surface of the canister was calculated using the isotope content specified in the design-basis glass.

Gamma rays interact with matter by several different processes. For low energy gamma rays, (less than 1 MeV), a major interactive process is the photoelectric effect. This interaction varies as Z^3 , where Z is the atomic number. This process will free electrons from an inner shell state of an atom. The second process is the Compton effect in which the photon interacts with a free or loosely bound electron. Part of the energy of the incident photon is transferred to the electron thereby reducing the frequency of the scattered photon. The amount of Compton interaction (incoherent scattering) depends on the energy of the incident photon and the atomic number of the substance being irradiated. For the relatively low Z stainless steel, and the low energy gamma radiation, the Compton process is significant. Thus, gamma interaction can lead to electrons and mimic beta radiation. Pair production can occur for gamma rays with energy greater than 1 MeV. In this instance, an electron and positron are created. Coherent scattering is also a possible interactive process between gamma rays and matter. It is generally so small that it can be ignored. Finally, photonuclear reactions can occur for photons of 10 to 20 MeV. In this case the photon is sufficiently energetic to eject a proton or neutron from the nucleus of an atom. This is not important for gamma rays emitted from the waste glass due to their lower energies.

Neutrons. Baxter¹⁰ lists the isotopes giving rise to neutrons within the glass matrix. Most of the neutrons come from the alpha emitting Pu-238, through the alpha, neutron reactions (7.5×10^7 neutrons/second/canister). However ~20% of the neutrons come from radionuclides which spontaneously fission. Cm-244 is the major isotope giving rise to neutrons through spontaneous fission (1.45×10^7 neutrons/second /canister). The total number of neutrons/second/canister from both the alpha, neutron reactions and spontaneous fission is $\sim 1 \times 10^8$. These neutrons are fast neutrons ($E > 0.1$ MeV). For a DWPF canister, this translates into an average flux of 2075 neutrons/sec/cm² at the glass surface provided all neutrons escape the glass matrix. This in turn leads to a value of 6.5×10^{10} neutrons/cm²/year initially. (For comparison, health tolerance levels for a 8 hour day correspond to 20 neutrons/cm²/sec for fast neutrons²⁵.)

Neutrons interact with matter at the nuclear level. There are essentially no interactions between the neutrons and electrons of the matrix (in this case the stainless steel and the glass). The neutrons lose energy by both elastic and inelastic collisions with

nuclei of atoms in the matrix. In elastic scattering, the atom accepts energy from the collision with the neutron. It can be displaced as in the formation of Frenkel pairs and/or the atom may cause ionization in the medium. Inelastic scattering usually occurs at higher energies with e.g., a neutron in, neutron out. A gamma ray can then be emitted by the excited state of the atom.

Temperature Exposures.

Filling the canister with molten glass will cause the metal to be heated to a maximum of $\sim 500^{\circ}\text{C}$. Subsequent to this, while the canistered waste form is stored within the GWSB, the temperature of the canister will be above ambient due to thermal heating from the radionuclides. In addition, the WAPS specification requires that a temporary excursion, due for example to a fire, to the glass transition temperature of the DWPF waste glass must also be considered.

Canister Temperatures During Glass Pouring. As the glass pour stream enters the canister, it cools by radiation and by conduction to the stainless steel and cooled glass. Within an hour of initiation of glass pouring, at the design basis filling rate of 240 pounds/hr, the canister walls have heated up to 200°C even at the 91 inch level²⁶. The temperature of the stainless steel at the level of the glass being poured is between 475 and 500°C . The canister nozzle and flange reach a temperature of between 200 to 220°C as the glass level reaches the upper parts of the canister. After filling, it takes up to 35 hours for the canister surface temperature to drop below 100°C .

Temperatures higher than this are anticipated for the canisters filled on the drain turntable. These values will be determined during the DWPF Startup Test Program.

Canister Temperature During Storage at GWSB. Plodinec¹¹ has published data which show that the heat generation by the design-basis glass is 710 watts at the time of glass filling. After 10 years, the heat generation has dropped to ~ 475 watts and after 95 years it has fallen to ~ 80 watts. Initial batches are projected to have heat generation rates which are less than the design basis glass. The actual surface temperatures and center-line glass temperatures for the canistered waste forms will be a function of

radionuclide content, time of emplacement in the GWSB, the number of canisters emplaced, and the temperature of the inlet air.

L. Lee²⁷ has developed a model for calculating the canister temperature as a function of decay heat for a fully-loaded GWSB. He has calculated the canister surface temperature for an inlet temperature of 0°F (-17.8 °C)²⁸. This corresponds to the coldest day during the winter in Aiken County. At 500 watts, the surface temperature will range from 150 °F (65.5°C) to 195 °F (90.6°C) depending on the location of the canister in the GWSB. However, as the heat generation rates drop to 200 watts, the surface temperature can reach 60°F (15.5°C). Calculations are currently being performed to determine these temperatures when the GWSB is not fully loaded.

The maximum temperature for the canister surface can be estimated from Lee's calculations. This will occur when the inlet temperature of the cooling air is 100°F. For a completely filled GWSB where all the canistered waste forms generate 700 watts, the canister surface temperature will be ~170°C and the glass center-line temperature, ~206°C. For canisters with thermal outputs less than 700 watts, the temperatures of the canister surface and glass center-line will be less than these values.

It appears, from the numbers presented by Plodinec¹¹, that each canistered waste form will be emitting ~ 150 watts heat after 50 years assuming that the canister was filled with the design-basis glass. This corresponds to a surface temperature of ~45°F (7.2°C) for a fully loaded GWSB from the calculations of Lee for intake air at 0°F (-17.8 °C). Hence the dew point of the free volume gas must be higher than this to prevent temporary condensation of water within the canister.

Temporary Increase in Temperature to T_g . The WAPS specification on compatibility requires that the effect of heating the canistered waste form to T_g be considered in light of compatibility. This is anticipated to be between 440 to 460°C². The amount of time that

the canistered waste form will be at this temperature was not specified. However, given a scenario of a fire, a maximum time of one hour at this temperature is assumed.

RADIATION INTERACTIONS.

The radiation field resulting from the radionuclides in the glass will interact with the stainless steel, the glass, the gas within the free volume, the condensate, the ceramic ring, and the Dow Corning 200 Fluid. The radiation-induced reactions which potentially affect corrosion of the canister are those which occur with the gas within the free volume and with the Dow Corning 200 Fluid. However, as will be discussed, the amount of Dow Corning 200 Fluid present in the canistered waste form is insignificant.

Free Volume Gas - Radiation Interactions.

The gas occupying the free volume of the canistered waste form will also be subjected to the radiation field produced by the radionuclides within the glass of each canister. The typical free volume for each canister will be ~110 liters (corresponding to an 85% fill factor) and will contain moist air at an internal pressure slightly less than atmospheric. The measured dew points of the free volume gas within the canistered waste forms are quite low (from -10 to +5°C). (Dew points will be measured again on selected canistered waste forms during the DWPF Startup Test Program). The free volume gas then, will be composed mainly of nitrogen (~80%), oxygen (~20%), and water (0.17% maximum). Carbon dioxide will also be present at a level equivalent to that of ambient air.

There have been a number of studies of the effect of radiation on both dry and moist air²⁹. The canistered waste forms are a complex, closed system, in which a variety of types of radiation will be incident on the free volume gas. No experiments have been conducted using radioactive DWPF glass in contact with air to determine the actual reactions. Nevertheless, from the reports in the literature, certain reactions are known to occur which, in turn, provide insight into what will occur when radiation interacts with the gas within the free volume space of DWPF canistered waste forms. This section identifies and roughly quantifies the products of these interactions.

All four types of radiation give similar products upon interaction with air. Gamma radiation interacts with the molecules in the air mainly by Compton scattering which releases high energy electrons. These electrons in turn interact with the gas molecules to produce ions and free radical species. Beta rays, which are free electrons, interact in the same manner as the Compton electrons. Alpha rays³⁰ also interact with gases by ionization of the molecules. Experiments with neutrons give results similar to those achieved with gamma rays³¹. As discussed by Spinks and Woods²², the products of irradiation in the gas phase are essentially independent of the type of radiation.

Dry Air/Radiation Interactions.

The major products of this interaction are the oxides of nitrogen. Lind and Bardwell³⁰ found, upon exposing dry air in a flow system to alpha rays, the generation of oxides of nitrogen and small amounts of ozone. For dry air, the long term products of gamma radiation were nitrous oxide (N_2O) and nitrogen dioxide (NO_2)^{22,29}. However, ozone and nitrogen pentoxide were also formed initially. The formation of ozone in stagnant systems (i.e., non-flow) was very low^{29,30} and was rapidly depleted. Nitrogen pentoxide is also short-lived in this system. This type of fixation of nitrogen (formation of oxides of nitrogen) is an oxidation process. Fixation of nitrogen to ammonia is a reduction process. Although ammonia has been identified in several cases (see discussion below), it is usually formed in reducing environments where the hydrogen/oxygen ratio is high. In the case of normal air, significant amounts of hydrogen are not present and consequently the hydrogen /oxygen ratio is low. This is also the case for the gas occupying the free volume space of the canistered waste forms, and consequently ammonia is not expected to form and be present in the DWPF canistered waste forms. Hence the main products of irradiation of dry air are the oxides of nitrogen.

Nitrous oxide (N_2O) is "very stable and rather inert chemically at room temperature."³². It is an anesthetic by inhalation and is known as laughing gas. Nitrogen dioxide (NO_2) on the other hand is "one of the most insidious gases." ³².

Moist Air/Radiation Interactions.

The irradiation of moist air leads to another product, nitric acid. Reed and Van Konynenburg²⁹ have provided a summary of data from three different studies on the effect of radiation on moist air. In all cases, the presence of water leads to the formation of nitric acid.

Primak and Fuchs³³ monitored the corrosion of a nickel wire exposed to air under a high gamma and neutron flux from the CP-3 heavy-water reactor at Argonne. From this study, it was demonstrated that both water and oxygen were necessary for the formation of nitric acid. Nitric acid formation was monitored by the corrosion of the nickel wire. Upon depletion of the water, corrosion of the nickel wire ceased. The initial partial pressure of water was 4 torr.

Jones³⁴ conducted a more quantitative study of products after irradiation of moist air using a 1 MeV beam of electrons. A dose rate of 370 Mrad/hr (370×10^6) was used in this experiment. Initially, the formation of nitric acid and ozone were observed. After the water was depleted (consumed during the formation of nitric acid), the electrons went on to decompose the nitric acid to nitrogen dioxide and water. The ozone was also destroyed. Nitrous oxide was formed continuously during irradiation. This study provided a quantitative determination of the efficiency of product formation in terms of G values (A G value is the number of molecules produced for every 100 eV of absorbed radiation energy). At 20% oxygen, G (HNO₃) was 2.0, G (N₂O) was 0.5, G (NO₂) initial was 8.0, and G(NO₂) asymptotic was 0.3. For destruction, G(HNO₃) was 8.0. The maximum G value for nitric acid production was 2.25.

Tokunaga and Suzuki³⁵ also observed nitric acid formation with 1.5 MeV electrons at high dose rates in moist air. These authors included either nitric oxide or nitrogen dioxide in the gas phase prior to irradiation. Nitric acid formation was a function of the amount of water in the gas phase. With dry air, no nitric acid was detected. Other oxides of nitrogen were also observed.

Other Relevant Radiation Studies.

Sato and Steinberg³⁶ found that gamma irradiation of an aqueous medium, constantly bubbled with air, produced ammonium ion in the liquid water. They also found nitrite but no nitrate. This work was

experimentally different than those studies discussed above in that liquid water was used rather than air resulting in a high hydrogen to oxygen ratio, which favors reductive fixation. Since there will be no liquid water in the canistered waste forms, neither ammonium ions nor ammonia is anticipated in DWPF canistered waste forms.

Recent results by Reed³⁷ in dry air gave a $G(N_2O)$ and a $G(NO_2)$ of ~ 0.5 molecules/100 eV with a production which was linear with absorbed dose. These results compare favorably with those of Jones. Reed's results in moist air depended upon the amount of water present in the system. Nitric acid was the primary product of gamma irradiation with a $G(HNO_3)$ value which ranged from 1 to 2 depending upon the relative humidity. Nitrous oxide was initially suppressed as was the nitrogen dioxide yield. It is argued that NO_2 is removed by the following reaction:

Reed also observed some ammonia at 1 to 10 ppm by volume but the concentration did not build up with time.

Carbon dioxide is practically unaffected by ionizing radiation³⁸. The amount of carbon dioxide in the canister is also very small and consequently no problems are anticipated for this species.

Wright et al³¹ used neutrons exclusively (4×10^{18} n/cm) to determine that irradiation of air/water mixtures produced nitrogen oxides.

Effects of gamma irradiation on corrosion have been carried out as well on aqueous solutions. Glass et al³⁹ have monitored the shifts in corrosion potential as a function of irradiation. They attribute certain of the changes to the production of hydrogen peroxide. The primary radical species are believed to be identical to that of moist air, but hydrogen peroxide has not been detected in the vapor state.

It is clear from the foregoing that the potential exists for chemical reactions to occur in the gas phase of the free volume as a result of the various types of radiation that are present in the glass. The major products of irradiation of the gas phase of the canistered waste forms will therefore be: N_2O , NO_2 and HNO_3 . However to determine whether the radiation field present in the canistered waste forms is sufficient to generate significant quantities of

nitrogen oxides and nitric acid, it is necessary to look at the magnitude of the radiation field from each of the types of radiation in the free volume. The following discussion presents rough estimates of the amount of products which will be formed due to the radiation fields of alpha, beta, gamma, and neutrons.

Gamma/Gas Interactions.

For gamma radiation, the dose rate just outside the stainless steel will be 5570 R/hour (where R represents Roentgen) for a canistered waste form containing the design basis radionuclide inventory. Consequently the dose at the surface of the glass will be slightly higher due to some attenuation of the gamma rays by the stainless steel. For this calculation, a value of 5570 R/hour is assumed at the glass surface. Since there are 0.870 rads/R in air, there will be 4845 rads/hour at the glass surface/free volume interface. The rad is defined as the absorption of 100 ergs/ gram of material and there are 6.24×10^{11} eV in 1 erg. Hence, the dose of gamma rays in the free volume space is equivalent to the absorption of 3×10^{17} eV/g/hour just above the glass surface. The free volume of 110 liters at 1 atmosphere pressure will contain ~142 grams of air. Assuming that the internal pressure will be ~0.8 atmospheres during the initial period of storage, the amount of air present in the free volume will be ~114 grams. Ignoring the fact that the dose rate will fall off with distance from the glass surface, the amount of energy absorbed by the air within the free volume space will be:

$$3.4 \times 10^{19} \text{ eV/hour}$$

The G value for nitric acid formation, $G(\text{HNO}_3)$ is ~2 / 100ev. This implies that

$$7 \times 10^{17} \text{ HNO}_3 \text{ molecules/hour or}$$

$$6 \times 10^{21} \text{ HNO}_3 \text{ molecules/year}$$

will be produced in the canister free volume. Nitric acid will only be produced for as long as there is water in the air. For a dew point of 0°C, it would take ~ 3 years to use up all the water within the free volume gas in the production of nitric acid. This would correspond to the creation of 0.6 g of HNO_3 . However, the G value for HNO_3 production will most likely decrease with decreases in both the water and oxygen concentrations. Furthermore, NO_2 will have an

affect on the production of HNO_3 . Initially, NO_2 enhances the production of HNO_3 , but as it builds up, it actually prevents further formation of HNO_3 . Simultaneously, the radiation from the gammas, betas, alphas, and neutrons will destroy nitric acid with the formation of water and NO_2 . At least initially then, HNO_3 will be formed with a consumption of water. Then, as equilibrium is approached, the nitric acid will be converted to water and the product, NO_2 .

Some nitrous oxide will also be formed. Using a G value for NO_2 and for N_2O production of 0.5, it is calculated that a total of 3×10^{21} molecules of NO_2 and N_2O will be produced per year. This implies that 2.25×10^{21} molecules of O_2 will be consumed per year. Initially there are 4.2×10^{23} molecules of oxygen present in the air occupying the free volume. Hence, 0.5% of the oxygen will be consumed each year due to nitrogen fixation by gamma irradiation.

Beta/Gas Interactions As discussed previously, the number of beta particles emitted per second within the waste glass is:

$$5.2 \times 10^{15} \text{ betas/second.}$$

For yttrium-90, the maximum range is ~ 0.45 cm with an average range of 0.09 cm while for cesium-137 and strontium-90, the maximum range is 0.075 cm with an average range of 0.015 cm. Since the three radionuclides are present in approximately equal amounts, this implies that 2/3 of the beta rays will have ranges up to 0.075 cm and 1/3 will have a maximum range of 0.45 cm. Hence for a cylinder of glass, only the beta emitting radionuclides present within the fraction of the cylinder defined by the height (range) x cross sectional area need be considered. Half of these radionuclides will emit beta particles whose direction will be below the plane defining the cross section. It turns out that approximately half of the beta particles whose initial direction is above this cross sectional plane, will actually escape into the free volume space. Finally, if the average range is also the mean, then only 1/2 of the beta particles will have a range sufficient for escape. For yttrium, this turns out to be

$$[0.09/231.14] \cdot [1/2] \cdot [1/2] \cdot [1/3] \cdot [5.2 \times 10^{15} \text{ betas/sec}] \text{ or}$$

$$1.7 \times 10^{11} \text{ betas/sec.}$$

For cesium or strontium, this turns out to be

$[0.015/231.14] \cdot [1/2] \cdot [1/2] \cdot [1/3] \cdot [5.2 \times 10^{15} \text{ betas/sec}]$ or

$2.8 \times 10^{10} \text{ betas/sec.}$

One-half of this total, or $1.13 \times 10^{11} \text{ betas/sec}$ will therefore escape from the glass into the canister free volume.

Next, it is assumed that the average energy of each beta particle escaping into the canister free volume is 0.05 MeV. This is a very rough estimate. The average energy of betas emitted from the the Sr-90/Y-90 pair is 1.13 MeV. The average range is 1/5 of the maximum range which is associated with an energy of 0.5 MeV. It is then assumed that 1/10 of this 0.5 MeV energy will remain with the beta particles which escape into the free volume. The assumption was then made that all of this energy is absorbed by the gas molecules occupying the free volume. (The linear energy transfer (LET) for beta particles in water is 0.2 KeV/micron in water.) Hence, the total energy per second incident upon the free volume gas from beta particles is

$5.7 \times 10^{15} \text{ eV/sec.}$

For a G value for HNO₃ production of 2, approximately 1.1×10^{14} molecules of HNO₃ will be formed each second. This corresponds to

$3.6 \times 10^{21} \text{ HNO}_3 \text{ molecules / year.}$

This is about a factor of two less than that calculated for gamma induced nitric acid formation. The production of oxides of nitrogen will also be less than gamma by a factor of two.

Alpha/Gas Interactions

The range of alpha particles is well defined for each radionuclide. As discussed above, the number of alpha particles emitted over a three hundred year period will be

$2 \times 10^{23} \text{ alphas/ 300 years}$

The range of alpha particles in aluminum is 23 microns and it is assumed that this range also applies for glass. The only alpha

particles which will escape into the free volume space will be those that are within this range. Roughly half of the alpha particles whose initial direction is above the plane defining the cross section, will escape the glass.

Therefore, the number of alpha particles escaping over 300 years is:

$$[0.0023/231.14] \cdot [1/2] \cdot [1/2] \cdot [2 \times 10^{23} \text{ alphas}/300 \text{ years}] \text{ or} \\ 5 \times 10^{17} \text{ alphas}/300 \text{ years}$$

The average energy of an escaping alpha particles is approximately 1/2 of its initial energy or ~ 2.5 MeV. This implies that there are:

$$1.25 \times 10^{24} \text{ eV}/300 \text{ years.}$$

For a G value for HNO_3 of 2, this implies that

$$2.5 \times 10^{22} \text{ molecules } \text{HNO}_3/300 \text{ years}$$

This value can be compared to the yearly value of gamma produced HNO_3 of 6×10^{21} . It is therefore concluded that alpha radiation will not significantly contribute to the chemistry changes in the free volume gas compared to gamma and beta-induced changes.

Neutron/Gas Interactions

The neutron flux for these canisters is quite low: 2075 neutrons/sec/cm² or 5.6×10^6 neutrons/sec at the top glass surface. For 1 meV neutrons, this corresponds to 5.6×10^{12} eV/sec. Assuming a G(HNO_3) of 2, and that all neutrons are absorbed, 1.1×10^{11} molecules of HNO_3 will be produced each second or

$$3.5 \times 10^{18} \text{ molecules of } \text{HNO}_3/\text{year.}$$

This production rate is insignificant when compared to the effects of both beta and gamma radiation. Hence, neutrons in DWPF canisters are not expected to play a significant role in the chemistry of the free volume gases.

From the above discussion, it is evident that both beta and gamma radiation, to first order, will produce roughly equivalent chemical

reactions in the gas phase. Alpha particles are next in producing changes in the gas phase, while neutrons are last.

The calculations indicate that all the water within the gas will be converted to HNO_3 within a few years. However, the continued exposure to all four radiation fields will bring about the destruction of HNO_3 fairly rapidly resulting in the reintroduction of water. Both NO_2 and N_2O will be formed continuously with time. Roughly, 3×10^{21} molecules of oxygen (0.15 grams) will be consumed per year. This corresponds to a depletion of 0.65 % of the oxygen in the canister per year. Hence, after 50 years, roughly 32 % of the oxygen will have been converted into oxides of nitrogen. As NO_2 builds up, it prevents the formation of additional HNO_3 . The oxides of nitrogen are fairly stable in the radiation field such that further reactions are not expected to be significant.

304L stainless steel is quite resistant to attack by liquid nitric acid and in fact is widely used in industry for all types of equipment handling nitric acid⁴⁰. The corrosion rate of 304L stainless steel in 20% nitric acid solution at a temperature of 130°C is only 4 mils per year⁴⁰. In fact nitric acid is used in pickling to passivate the surface through the formation of an oxide film. Hence the presence of nitric acid in the gas within the free volume of the canister is not expected to create any problems. Similarly, the oxides of nitrogen are not corrosive to the stainless steel. Therefore, in spite of the chemistry which is occurring in the gas phase as a result of radiation, no products are formed which will compromise the mechanical integrity of the stainless steel.

Dow Corning 200 Fluid/Radiation Interaction

The Dow Corning 200 Fluid is a polydimethylsiloxane polymer which will be confined mainly to the tapered surface of the temporary plug. Hence this polymer will be shielded from the alpha and beta radiation, but exposed to gamma and neutron radiation. Radiolysis of polymers generally results in bond cleavage. In this case cleavage of the silicon - carbon bond will generate the methyl radical which can combine with another methyl radical to produce ethane or be reduced to methane. The other product will be silicon dioxide. Some hydrogen could be generated. Again, the amount of Dow Corning 200 fluid used per canister has been estimated to be only 50 mg, which is insignificant. Hence the products of the interaction between the

radiation field and this polymer will not affect compatibility of the contents of the canistered waste form.

This polymer will decompose as the temperature reaches 500°C. Hence any temporary excursion to T_g may bring about the thermal oxidation of this polymer to silica and carbon dioxide.

EFFECT OF TEMPERATURE ON COMPATIBILITY

Canister Filling. The canister will be subjected to a heat treatment during glass filling. As discussed earlier, most of the canisters will be filled from the pour turntable under continuous flow conditions. The maximum temperature of the canister wall for a continuously filled canister was between 425 to 500°C. For a batch pour, the maximum temperature was 552°C. The maximum temperature of the canister is realized at the level of the glass pour. Generally, the steel, at a particular level, will be above 400°C for approximately two hours. The temperature of the canister cools to below 100°C within 33 to 36 hours after pouring is completed.

It is important to minimize sensitization and embrittlement in the welded regions of the canister during heat treatment. Sensitization (chromium carbide precipitation) may occur in the weld regions at the interface between the ferrite and the austenite. A lower limit of 1.40 for the chromium to nickel equivalent ratio was established to further reduce the potential for sensitization in the weld filler material. Hence the strategy here is to use low carbon base and weld filler materials and further limit the 308L to this lower limit in order to reduce potential for sensitization.

Embrittling phases such as sigma and alpha prime can potentially form during this heat treatment. To minimize the potential for these phases to form, the chromium/nickel equivalent ratio has been limited to <1.67 by the canister procurement specifications⁴. Since chromium and its equivalents stabilize ferrite in the weld regions, and since both of these embrittling phases form within the ferrite range, the imposition of an upper limit of 1.67 reduces the amount of ferrite and correspondingly the amount of embrittling phases, while still maintaining the beneficial effects of ferrite.

For canisters filled on the drain turntable, the temperature of the stainless steel is expected to be slightly higher due to more rapid

filling. This will be measured during the DWPF Startup Test Program.

Overall the time of exposure to this heat treatment is only a few hours and is at a temperature below that required to get significant sensitization. This relatively short heat treatment further reduces the potential formation of embrittling phases and chromium carbide precipitation. Therefore, this heat treatment due to glass-filling will not significantly enhance corrosion of the canistered waste form.

Compatibility Effects Due to Storage in GWSB.

The surface temperature of the canister will be a function of the inlet temperature of the forced air cooling, the wattage of the particular canister, and the number of canisters stored in the GWSB. For relatively high wattages (reference of 710 watts) and an intake temperature of 35°C, the temperature of the canister surface can reach 170°C. However, at least initially, the canister surface temperatures are expected to be closer to 100°C.

Experiments have been carried out with a canister emplaced in the WIPP for three years and heated to 100°C for two of those years. After removal from WIPP, this canister was sectioned and the inside surfaces of the stainless steel examined both below and above the glass line. No indications of interactions were observed in either location. This work is currently being completed and an internal report will be issued⁴¹.

As discussed in the section of glass/stainless steel interactions, work by Rankin and by McCoy revealed no detectable change of the inner surface of the stainless steel after several years of exposure to glass at 100°C.

Compatibility Effects Due to Transient Excursion to T_g .

The waste glass will not flow under conditions where the canistered waste form is heated up to T_g . Heating to this temperature may, however, reduce some of the radiation changes in the glass. Displaced atoms may return to a vacancy, and trapped electrons may be released to recombine with trapped holes. However no significant chemistry is expected at this temperature. The interaction of the

glass with the stainless steel at this temperature is discussed separately.

In a similar fashion, both the ceramic ring and the condensate may also reduce radiation effects frozen in at the lower temperatures. Again, no chemical reactions are expected for this brief exposure to T_g . The salts in the condensate such as sodium chloride have melting points in the range of 800°C. Therefore exposure to T_g will have no effect on the volatility of the condensate.

The gas within the free volume when heated in this closed environment will cause the internal gas pressure to rise to ~2.3 atmospheres. This pressure will return to its original pressure as the temperature returns to its value prior to the excursion. Research has shown that the volatility of the glass at T_g is not significant²¹. Therefore no release of gas will occur as a result of this temporary excursion to T_g . Corrosion rates in general will increase with temperature. However, for the short duration of this scenario, no significant corrosion is expected.

Glass has a thermal expansion linear coefficient of $1.2 \times 10^{-5}/^{\circ}\text{C}$. compared to 304 stainless steel with a value of $1.8 \times 10^{-5}/^{\circ}\text{C}$. Hence, when the canistered waste form is heated to T_g , the stainless steel will expand more than the glass. However, the glass will not be fluid at this temperature and consequently, upon cooling, the system should relax back to the original state.

GLASS/ STAINLESS STEEL INTERACTIONS

GENERAL

Many experiments have been performed by SRTC in which canistered waste forms have been sectioned. This was done, for example, to obtain glass and condensate samples, and to determine the degree of glass cracking and fines generation. Through this experience, it became evident that the glass does not adhere to the stainless steel. In fact, the glass pieces adjacent to the inner wall of the canister were easily removed, leaving a visually clean stainless steel surface. Schumacher⁴² confirmed this lack of interaction by exposing samples of stainless steel and glass to a variety of different heat treatments. The goal of his work was to provide samples containing bonded waste glass onto the stainless steel surface. (These samples were then subjected to treatment with a

needle gun to determine the efficacy of glass removal by this method.) In order to get the glass to adhere to the stainless steel, Schumacher had to heat the samples to at least 650°C for the onset of bonding and to 750°C to get good bonding. These heat treatments lasted one hour. Since the stainless steel of the canister reaches a maximum temperature of 450 to 550°C during glass pouring from the pour turntable, this observed lack of glass bonding to the canister is consistent with Schumacher's results.

The temperature profiles of three canisters will be determined during glass pouring in the DWPF Startup Test Program. One canister will be monitored during glass filling on the pour turntable. This will be typical of almost all canisters filled at the DWPF. As indicated above, canisters filled at TNX under prototypic fill rates, reached maximum temperatures between 450 to 500°C under continuous pour conditions. Another canister will be monitored during glass filling from the drain turntable. Since the rate of pouring will be higher, the maximum temperature of this canister should be higher. The final canister to be monitored will be one that is filled on the pour turntable and then transferred to the insulated canister storage compartment. This too, could reach a higher maximum temperature, although it is unlikely. The canisters will be sectioned or have part of the wall removed after cooling. A determination will be made at that time as to whether the glass has bonded to the stainless steel under these conditions.

A temporary heat treatment of the glass filled canisters to the glass transition temperature of the glass will not cause bonding of the glass to the stainless steel. This is because T_g is only between 440 to 460°C, well below the 650°C needed for bonding.

LONG TERM COMPATIBILITY

W. N. Rankin^{43,44,45} has done extensive work on the compatibility of waste glass with 304 L stainless steel. He prepared glass-stainless steel samples and subjected them to long term exposure at 100°C and 225°C. The samples were prepared by preheating the containers to 500°C, then filling them 3/4 full with molten glass at 1150°C, and finally furnace cooling them at 600°C. The intent of this procedure was to conservatively mimic glass filling conditions of canisters. After 20,000 hours (2.3 years), no measurable penetration of the glass into the stainless steel could be detected. For comparison, the loss of stainless steel through oxidation on the

outside of the specimen was detected but was less than 0.1 mil after 20,000 hours. Samples taken at intermediate times revealed no detectable interactions between glass and stainless steel.

Parallel measurements were also carried out using a low carbon steel with simulated waste glass. Again, no interactions between the low carbon steel and waste glass were observed, although the outside of the specimen exhibited a loss due to oxidation of 3.6 mils over the 20,000 hour period.

These experiments demonstrate that the glass is compatible with the stainless steel under temperatures even in excess of expected canister temperatures while in storage at the glass waste storage building. The fact that these experiments were carried out over a two year period provides confidence in the fact that no problems with compatibility between the glass and stainless steel will occur during storage at SRS.

Rankin's work is supported by the research of H. E. McCoy^{46,47} who carried out experiments to determine the extent of the interactions between various waste forms with selected canister materials. Part of this work focussed on 304L stainless steel and borosilicate glass. A capsule was fabricated containing thirty 12.7 mm diameter disks of 304L stainless steel sandwiched between thirty pieces of borosilicate glass. The glass pieces were fabricated:

"from powders that had been calcined and then melted at 1150°C in an Inconel 600 crucible in air. The molten glass was poured into preheated graphite molds to form square rods 1 cm on a side by 15 cm long. The rods were then annealed at 500°C for 1 hour. After cooling, the rods were cut into 3 mm thicknesses with a 0.25 mm thick diamond saw."

These glass pieces were pressed against the stainless steel discs using modest spring compression. One set of these capsules was then heat treated at 100°C for 6888 hours while another set was heated at 300°C for 6888 hours. The stainless steel discs were weighed and visually examined both before and after heating. The heat treatments were done in both helium and air atmospheres. No changes in weight or in visual appearance occurred in the stainless steel discs over this long period of exposure to elevated temperatures. These experimental results again demonstrate that

no significant interactions are occurring between the glass and the stainless steel.

Hence, both Rankin's and McCoy's work demonstrate that no significant interactions between the glass and stainless steel are expected at anticipated storage temperatures.

OXIDATION

Oxidation of the surface of stainless steels^{40,48} results in the formation of a protective oxide film, a process known as passivation. For 304L stainless steel, the film formed is mainly chromic oxide, Cr_2O_3 , with minor amount of iron and nickel oxides. A process known as "breakthrough" can occur under extreme oxidizing conditions leading to spinel oxide (FeCr_2O_4) and an outer layer of ferric oxide. Under these conditions, the oxide film can continue to grow resulting in scale which can subsequently crack and spall.

However, maximum service use temperatures in dry air for 304L stainless steel have been estimated⁴⁹ at 870°C for intermittent service and 925°C for continuous service. Morris⁴⁹ has indicated that these values should be reduced by 38 to 65°C if water is present in the air. These values are applicable for the interior of the DWPF canistered waste forms. Since the canisters will be exposed to a temperature of up to 550°C during pouring from the pour turntable, and to 450 to 500°C during a temporary excursion to T_g , no significant oxidation of the internal stainless steel surface is expected. Finally, exposure to the relatively low canister surface temperatures experienced in the GWSB should result in no significant oxidation of the internal surface of the stainless steel.

CORROSION

Perhaps the greatest concern for compatibility within the canistered waste form is internal corrosion of the stainless steel^{40,48}. If internal corrosion is significant, it could lead to a breaching of the canistered waste form directly. Corrosion-induced deterioration of the mechanical properties of the canister could also lead to breaching of the canistered waste form during normal handling or an accidental drop.

General atmospheric corrosion

The environment within the canister contains no liquid water and as a result, normal uniform aqueous corrosion of the 304L SST can not occur. Rather, the stainless steel is exposed to a gas phase containing some moisture. Hence, the stainless steel is susceptible to atmospheric corrosion. A number of studies have been conducted in which the uniform rate of atmospheric corrosion has been measured on samples left open to the atmosphere. A uniform corrosion rate of ~0.025 microns/year has been observed⁵⁰. This very low value translates to a total loss of only 1.25 microns (0.00125 mm) of material after 50 years. Corrosion rate data from LLNL⁵¹ on 304L demonstrate that the canister lifetime will not be limited by uniform oxidation in wet air and saturated steam at elevated temperatures. A corrosion rate of 0.10 microns per years was measured for saturated steam at 100°C. This translates to a 1% loss of a 1 cm thick 304L stainless steel canister after 1000 years. For reference, studies using 302 stainless steel (very similar to 304), immersed in seawater for one year, gave a uniform corrosion rate of 36.25 microns/year^{50,52}. Therefore even in the more corrosive aqueous salt solution, uniform corrosion would only be 1.8 mm after 50 years, a value still acceptable when compared to the overall thickness of ~ 10 mm of stainless steel.

Gdowski and Bullen⁵⁰ have summarized the potential of a variety of overpack candidates, including 304L, to general corrosion. They go into detail about a variety of other studies relating to atmospheric corrosion of austenitic alloys, all of which indicate that uniform corrosion will not be a problem.

Hence, general atmospheric corrosion of the inside surface of the stainless steel canister, although it will occur, will not be significant.

Microbiologically influenced corrosion (MIC)

Microbiologically influenced corrosion (MIC)⁵³ is a concern when stainless steels are exposed to stagnant or low flow aqueous media. Introduction of the microbe is of course essential, and this is usually accomplished by contact with untreated (raw) water. The fact that the DWPF canistered waste forms will have no liquid water within it, essentially precludes MIC. Closure of the canister while the nozzle is above 175°C and the intense radiation field present

provides an lethal environment to living things including airborne bacteria. Therefore, MIC is not considered to be a potential problem within the DWPF canistered waste forms.

Localized corrosion

As discussed above, general atmospheric corrosion is not expected to cause problems within the canistered waste form. A form of corrosion of greater concern for the DWPF canister is localized corrosion^{40,48}. Localized corrosion can occur autocatalytically and can in short periods of time, completely penetrate a stainless steel specimen. It is very important to exclude conditions that will lead to this form of corrosion. The following discussion considers various types of localized corrosion: pitting, crevice corrosion, intergranular corrosion, and stress corrosion cracking.

Pitting

As the name implies, pitting^{40,48} is a localized type of corrosion that generates pits within the metal, which once formed, may continue to grow in an autocatalytic or self-sustaining fashion. Once the surface oxide is destroyed and a pit is formed, the metal at the surface of the pit can continue to be oxidized and subsequently dissolved into the aqueous phase present in the pit. When present, chloride ions can migrate to the pit to maintain electroneutrality. This is followed by hydrolysis of the metal chloride to yield the metal hydroxide and hydrochloric acid. This acidic environment in the water within the pit encourages the process of dissolution. The corresponding reduction reaction is generally oxygen reduction on the surface of the bulk metal. Pits tend to form in the direction of gravity.

Pitting is a particularly insidious form of corrosion. There may be an extended initiation phase which lasts for months or years before pits can be actually observed. Once formed however, they may then penetrate the metal rapidly causing failures in short periods of time. This long initiation period requires that caution be used when applying laboratory tests as an indicator of potential pitting problems. 304L stainless steel is susceptible to pitting. On the other hand, minor pitting which does not lead to perforation is often tolerated for economic reasons.

A difficulty in discussing pitting (and the other forms of localized corrosion) is that almost all the discussion of the effects of variables on pitting, derive from exposure to aqueous solutions. For example, the pitting potential can be measured for a metal exposed to a particular solution. This may or may not be applicable for our case when liquid water is not present. In any event, the pitting potential can not be measured in the absence of water. Nevertheless, we have chosen to consider those factors which have been shown to enhance pitting in aqueous solution. The reasoning here is that, at high relative humidities, water may adsorb onto the steel and actually accumulate in certain regions thereby microscopically mimicing an aqueous environment. We will then present results by Langton⁷⁴ who exposed 304L stainless steel coupons to air at various levels of relative humidity and temperature to determine their potential for pitting.

Pitting is enhanced in the presence of chloride ions, oxygen, stagnant, non flowing water, a rough surface, a sensitized steel, delta ferrite, sigma, alpha prime, and sulfide or iron inclusions and higher temperatures.

The DWPF canistered waste forms contain chloride, oxygen, delta ferrite, and perhaps the possibility of some sigma and alpha prime in the welded regions. Sensitization in the heat affected zone of the welded regions may also be present and the expected temperature of the canister within the waste glass storage building is close to 100°C initially.

In order to control certain of these variables, the procurement specifications⁴ for the canisters require that any cleaning, cutting oils, lubricants, and marking materials used on the canisters must be certified to be less than 250 ppm halogen. This will reduce the introduction of additional chloride. Carbon steel contamination must also be avoided. This takes away potential initiation sites for pitting. Abrasive blasting is not permitted on the internal surfaces of the canisters. This avoids a very rough surface which could encourage pitting. Welding techniques shall be used to avoid weld splatter. Low carbon stainless steels are required which reduce the risk of sensitization. Inspections for foreign materials will be made at both the vendors' shops and prior to delivery to the Melter Cell in the DWPF.

The most significant factor in preventing pitting within the DWPF canistered waste forms is the exclusion of liquid water (see Volume 8, Waste Form Qualification Report). However, as already noted, the vapor phase will contain some water. It is therefore important to determine whether the DWPF canisters can exhibit pitting when exposed to moist air.

To address this issue, Langton⁵⁴ carried out experiments in which she coated actual coupons from a canister with chloride rich salts and exposed them to various levels of relative humidity and temperature for a six month period. These coupons were coated with salt condensate by suspending them inside of canisters being glass-filled during LSFM campaigns 5 and 6. The condensate contained submicron sized sodium chloride crystals. These canisters were filled prior to the modification of the offgas system, which significantly reduced salt condensation within the canister. In fact during these early campaigns, the amount of salt condensate was great enough to be clearly visible on the inner surfaces of the nozzle⁵⁵. The condensate was also visible on the coupons used in Langton's research. A matrix of experiments was performed in which the coupons were exposed to temperatures between 35 and 90°C and relative humidities between 10 and 90%. The only specimen to show pitting was a coupon cut from an actual canister exposed to 90°C and 90% relative humidity. After six months, pits were visible in the sensitized region of the weld made between the top head and the canister cylinder. The pitting was more extensive on the outside surface than the inside canister surface. Hence, under extreme conditions, pitting is evident on the chloride coated coupons of 304L stainless steel.

It is very important to recognize the differences between the water content measured in canistered waste forms and that used by Langton. At 90°C and 90% RH, there are 381 grams of water/m³ of air, whereas at the maximum measured dewpoint for canistered waste forms of 5°C, there are only 3.2 grams of water/m³ of air. The maximum concentration of water in the free volume is ~30 grams of water/m³ of air (for an internal pressure of 495 torr). Hence exposures of the stainless steel in these experiments by Langton are significantly higher than the values measured and expected for sealed canistered waste forms.

Langton's experiments provide direct evidence, that given high enough levels of humidity and temperature, pitting can be a problem

on the internal surfaces of the canisters. However, at 90°C and 90% RH, the amount of water in the vapor phase is over 100 times the maximum value measured for canistered waste forms. It is approximately 14 times greater than the calculated maximum amount. Therefore pitting is not expected to occur within the canistered waste forms.

Crevice Corrosion.

The mechanism for crevice corrosion is very similar to that of pitting^{40,48}. It is an autocatalytic process where the crevices must be of such a dimension, usually on the order of microns, as to allow influx of a corrodent solution, and simultaneously prevent escape of corrosion products. This defines a major requirement of crevice corrosion which is stagnation of the liquid within and around the crevice. Oxidation (dissolution of the metal) occurs in the crevice concurrent with reduction of oxygen. After the oxygen is depleted in the crevice, dissolution will still occur leading to the positively charged cation of the metal. Since oxygen is no longer being reduced to hydroxide, electrical neutrality is maintained by migration of chloride ions into the crevice. This species accelerates corrosion. The iron and chromium ions for example then react with water to generate the insoluble metal hydroxide and the hydronium ion. The hydronium ion also accelerates crevice corrosion. Certain experiments reveal that the metal ion that is hydrolyzed to lower the pH in the stagnant liquid phase may be the chromium ion. Stainless steels can exhibit crevice corrosion.

Like pitting, crevice corrosion may also have a long incubation period. Once started, the corrosion may continue at an ever increasing rate until failure, provided sufficient corrodents are available in the system. Crevices can be formed at metal/metal and metal/non-metal junctions. Typically crevice corrosion occurs with rivets, bolts, gaskets, valve seats, and solid deposits. The effect of temperature on crevice corrosion in salt solutions is not straightforward. In some instances, an increase in temperature increases the rate of crevice corrosion although, in other cases, it does not.

The DWPF canistered waste forms do not contain the typical type of crevices listed above. The only potential sites within a canistered waste form which may act as crevices are certain areas of the glass/stainless steel interface and at the ceramic ring/final weld plug interface.

However, crevice corrosion at the ceramic ring/final weld plug interface, even if it occurred, would not jeopardize confinement of the waste by the canister. A small gap may exist between the glass and stainless steel although very little condensate is expected below the final glass line.

Langton⁵⁴ performed crevice corrosion testing using a grooved delrin washer sandwiched between 304L stainless steel. This test provided 10 different sites on each side of the stainless steel and was done in triplicate. She used specimens which had been coated with the chloride rich condensate. Corrosion at multiple sites occurred in the crevice corrosion coupon after 6 months at 90°C and 90% relative humidity. Crevice corrosion was also observed after six months at 35°C and 90% relative humidity, and at 60°C and 60% relative humidity. No crevice corrosion was observed after six months on 304L samples at 35°C and 60% relative humidity, or at 60°C and 30% relative humidity. The crevice corrosion observed in these tests was superficial (i.e., could be easily removed by light brushing) with no loss of structural integrity or cracking observed over the 6 month period of the test.

At 60°C and 60% RH, there are 78 grams of water/m³ of air compared to the maximum measured amount of 3.2 grams of water/m³ of air in the canistered waste forms and the maximum calculated value of 30 grams of water/m³ of air. This fact, coupled with the lack of typical crevices and the superficial nature of the corrosion observed by Langton, indicates that crevice corrosion will not be a problem within the canistered waste forms over the estimated 50 year storage period.

Intergranular Corrosion

Intergranular corrosion is a localized form of corrosion that in austenitic stainless steels occurs as a result of preferential corrosion at the grain boundaries rather than on the grains themselves^{40,48}. Sensitization, which is formation of chromium carbides (Cr₂₃C₆) in the grain boundaries, is the process which makes stainless steels susceptible to intergranular corrosion. The chromium carbide formation results in depletion of chromium from the surrounding areas. When the chromium content falls below 12% by weight, the stainless steel is susceptible to corrosion.

Intergranular corrosion manifests itself as powder on the surface composed of the individual grains. Chloride ions and oxygen are particularly effective in causing intergranular corrosion. Sensitization by itself does not guarantee that intergranular corrosion will occur. A network must exist which allows for complete or nearly complete penetration before failure occurs.

In the DWPF canisters, sensitization may occur during welding in the weld decay zone adjacent to the weld. Sensitization can occur over the temperature range of 950 to 1450°F (510 to 787 °C). The weld decay zone is heated to 1200 to 1400°F (649 to 760 °C) during welding which is optimum for sensitization. Higher temperatures dissolve the precipitate and lower temperatures are not sufficient to generate carbide precipitates. Hence weld decay zones, which are in the base metal, are of specific concern for sensitization. The canisters are also subjected to a heat treatment during glass filling. However, in this case, the maximum temperature of the canister is ~550°C and therefore sensitization by this heat treatment is very unlikely. The excursion to T_g for an hour is also below the temperature required to produce sensitization.

Several steps have been taken in order to avoid intergranular corrosion in DWPF canistered waste forms. The biggest step for prevention is to use 304L, a low carbon (<0.03 wt%) stainless steel. The very limited amount of carbon present in 304L significantly reduces the amount of Cr₂₃C₆ which can form. The weld filler material used, as discussed above, is a 308L which has been further constrained in the chromium to nickel ratio to limit sensitization. Another step taken was to ensure that welding shall be in accordance with ASME B & PVC, Section VIII, Division I. All weld procedures and welders shall be qualified as required by ASME B & PVC, Section IX, Weld Procedures. These procedures are designed to limit the amount of sensitization due to improper heat treatments.

In addition, controls have been imposed in the canister procurement specifications which are intended to avoid carbon pick up. The vendor must degrease all components of the canister prior to welding, ensure that the stainless steel does not come in contact with oily rags, and in general makes sure that both the inside and outside surfaces of the stainless steel are free of oil. Carbonaceous material pickup by the 304L or 308L would increase carbon content in the steel thus making it susceptible to sensitization and intergranular corrosion.

The canister procurement specifications also require that the plate for the cylinder and the heads is to be hot rolled, annealed and pickled and that the heads shall be hot formed, then solution annealed, and then reformed in the same die. These annealing steps are included to remove any chromium carbides which may have formed. It should be noted that no solution annealing is carried out after any of the welds of the canister. Therefore sensitization, if it occurs as a result of welding will remain with the canister throughout its lifetime.

Langton carried out experiments to test for intergranular corrosion. A coupon containing part of the top head to cylinder weld was cut from the top of the canister, chloride coated, and tested in the environmental chamber under extreme conditions of 90% relative humidity and 90°C for six months. There was no evidence of intergranular corrosion.

Langton's results, combined with the use of low carbon materials, approved welders and weld procedures, controls to avoid contact with organics, and the avoidance of temperature exposure in the sensitization range after welding, indicate that intergranular corrosion will not be a problem in the canistered waste forms.

Stress Corrosion Cracking

Stress corrosion cracking occurs in austenitic stainless steels when there is a tensile stress, either applied and/or residual, coupled with the presence of a specific corrodent^{40,48}. Cracks actually propagate through the stainless steel generally at right angles to the applied stress. Those cracks that follow grain boundaries are referred to as intergranular cracks and those that cut across the grains as transgranular cracks. Both types of crack propagation can occur in austenitic stainless steels.

Chloride ion is the specific corrodent that causes most of the stress corrosion cracking observed in austenitic stainless steels. This type of stress corrosion cracking is called chloride cracking. Factors which control the rate of chloride cracking are: chloride ion concentration, temperature, the magnitude of the tensile stress (it has been argued that a threshold stress of approximately 10% of the yield stress is necessary before stress corrosion cracking will occur⁵⁶), and the presence of sensitization. Oxygen is another

corrodent, which can act independently from chloride to produce stress corrosion cracking. In DWPF canisters, residual stresses may be present in the welded regions, and the glass will exert a hoop stress to the canister. As in pitting, it is important to determine the conditions of relative humidity and temperature which will lead to stress corrosion cracking.

To determine those conditions required for stress corrosion cracking, Langton used 304L SST coupons (containing a weld made with 308L SST) which were highly stressed by bending them into a U shape. The coupons were then coated with condensate, and placed within controlled environments for up to six months. After two months, stress corrosion cracking of the coupon was observed in the region of sensitization in the heat affected zone of the weld, which was highly stressed by the bending. At 90°C and 60% relative humidity, and at 60°C and 90% or 60% relative humidity, only selected area attack of the surface was noted. However, this type of corrosion was superficial since light brushing removed any evidence of this type of corrosion. No stress corrosion cracking was observed on an actual canister coupon (without U bending) under these conditions.

Testing of U bent samples at either 60°C and 30% relative humidity or 35°C and 60% relative humidity, showed no evidence of any corrosion. In fact the chloride rich condensate film was still visible after six months of testing.

Actual stress corrosion cracking was only observed on a sample which had been significantly and artificially stressed in the sensitized region of the weld at 90°C and 90% relative humidity. Again this corresponds to 381 grams of water/m³ compared to the typically measured values of 3.2 grams of water/m³ of air.

Rankin⁵⁷ has also performed experiments in which he exposed 304L stainless steel capsules to Carlsbad salt for 5,000 and 10,000 hour periods (0.57 and 1.14 years respectively) at temperatures ranging from 80°C to 300°C. Some of the experiments were run in unsealed containers at 80 to 225°C. A sealed capsule was used for the 300°C experiments due to decrepitation of the salt. Decrepitation is an explosive event which occurs in the salt at ~250°C in which moisture is released. The 300°C runs were carried out for 5000 hours only. No changes in dimensions were observed for any of the

304L stainless steel capsules, indicating that no significant general corrosion or stress corrosion cracking had occurred.

Truman⁵⁸ has noted, from decades of experience, that chloride cracking is not a problem in austenitic stainless steels in contact with a chloride containing solution at ambient temperatures.

All of these results indicate that stress corrosion cracking will not occur in the canistered waste forms.

Low Temperature Sensitization

Fox and McCright⁵⁹ have considered the potential of low temperature sensitization (LTS) to lead to corrosion in canistered waste forms. The mechanism for LTS is one in which chromium carbides are nucleated due to a heat treatment such as welding and then develop over time during a long heat treatment at temperatures above ambient but less than what is normally required to produce sensitization. The relatively low temperatures of the canister during interim storage at the GWSB and the absence of extensive cold working, which increases LTS, make the probability of LTS very unlikely in the DWPF canisters.

Atypical Glass Filling and Canister Sealing

Listed below are some atypical conditions which may occur during DWPF operations. Their impact, if any, on compatibility is discussed.

Interrupted Pour Pouring may be interrupted before the canister is 85% full. If the bellows remains tightly in place, this will be no problem. After interruption, the pour is again initiated and the canister is filled to 85%. The interface between the two pours often contains small bubbles and voids¹⁹. This leads to the trapping of some additional air.

If the bellows is disconnected and the canister left unsealed for a period of time on the pour turntable, moist air will be in contact with the inside of the canister. This is, in fact, the condition of the canister prior to filling when it has been covered but not sealed. During glass filling the high temperature of the glass heats the canister walls to ~500°C and the upper head and nozzle region to

~200°C²⁶. These temperatures are high enough to drive off any water adsorbed onto the canister surfaces. A partial vacuum within the canister is required to initiate and maintain glass pouring. This vacuum will transfer the vaporized water out of the canister through the off-gas system.

Interruptions in the pour are therefore not expected to create any problems in terms of internal corrosion.

Unacceptable Temporary Seal.

If the measured leak rate is greater than 2×10^{-4} atm cc/sec, then some helium will leak into the canister. The severity of the leak will determine the amount of helium injected. The remedy for this failure is to rapidly heat the nozzle such that the sleeve and plug fall into the canister. A repair plug is then installed and sealed by heat shrinkage. A new helium leak test is carried out to determine whether this new seal is satisfactory. If not, the nozzle is again heated rapidly and this repair plug falls into the canister. The process is repeated until a "good" seal is made. In the very unlikely event that a "good" seal can not be formed, the canistered waste form will be treated as a nonconforming item and dealt with as a special case. In any event, it is possible that canisters may contain extra temporary plugs.

Heating the nozzle back up to 185°C for insertion of a repair plug may not heat the entire free volume gas to as high a temperature as present during normal operating conditions. In this case the internal gas pressure may not be as low as in the normal process, which in turn results in a slight increase in the amount of water per canister. (A test is planned to analyze one canister containing a repair plug for moisture content and pressure during the Startup Test Program.) This increase in water content, and the possibility of a small amount of helium within the canister, will not lead to a significant increase in internal corrosion.

Partial Fill During actual DWPF operation, a canister may be partially filled to a value less than 85%. In this case, the free volume will be greater and there will consequently be more air and moisture in the canister. Sealing of this canister with the temporary plug occurs when the gas in the free volume is not as hot as normal operating conditions. Therefore the gas pressure will also be higher than the pressure obtained under normal operating

conditions. However, no unusual gases will be introduced in this case. Although the total amount of water within the canister increases, the dew point will remain unchanged and therefore these canistered waste forms will perform equivalently to those filled under typical conditions.

Final Weld Failure. In the highly unlikely event that the canister's final weld is not acceptable, a repair cap will be welded onto the flange of the nozzle using the same DWPF welder. To make a repair weld, the welder system has to be changed and thus, there will be a time lag before the weld can be repaired. The inleakage of air in this case will be limited by the final failed weld (whatever its leakrate) and the displaced temporary seal with a leakrate¹⁵ between 3.4×10^{-3} to 7.7×10^{-1} atm cc/sec helium. If there is a gross leak in the final, failed weld, then the leakrate will be controlled by the leakrate of the displaced temporary seal. Hence the potential exists for the canister's internal pressure to reach atmospheric pressures in this scenario. There would be a corresponding increase in water content of the canister as a result. This does not change the limit of maximum water content in the canister of 28 grams of water/m³ of air and therefore internal corrosion will not be significant.

Overfilling. If the canister is inadvertently filled to a level greater than 85%, no problems should arise as long as the glass does not extend into the nozzle region. Filling to 90% will simply reduce the amount of air and water vapor trapped inside the canister. Again, no changes in the rates of internal corrosion are expected for this upset condition.

Other Problems. Unanticipated problems will be dealt with on an individual basis. If necessary, the canistered waste form will be classified as a nonconforming item and be dealt with according to Part 6, Item 300 of the WCP.

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