EXCLUSION OF FOREIGN MATERIALS FROM DWPF CANISTERED WASTE FORMS. COMPLIANCE ACTIVITIES FOR THE WAPS

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ABSTRACT

The Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS) will produce canisters of high- level radioactive waste glass, which must be acceptable for disposal in a Federal Repository. The repository acceptance requirements, in the Waste Acceptance Preliminary Specifications (WAPS), prohibit the presence of foreign materials which could compromise waste disposal. In this paper, the DWPF strategy for complying with the WAPS is presented along with results of experiments on prototypically filled, simulated canistered waste forms. In particular, the gas occupying the free volume region of the canisters was characterized by mass spectrometry. The internal gas pressure and dew point of the gas within the free volume were also determined. Thermogravimetric analyses of simulated waste glass samples removed from the canistered waste forms were carried out to determine if foreign materials are released when the temperature of the glass reaches the glass transition temperature. The results of calculations on the generation of radiogenic gases over time are presented. Finally, administrative controls and physical barriers used to exclude foreign materials from the canistered waste forms during production are discussed.

INTRODUCTION

The DWPF will incorporate high-level radioactive waste, currently stored in waste tanks at SRS, into a borosilicate glass which will then be poured into a stainless steel canister and sealed(1). The Department of Energy's Office of Civilian Radioactive Waste Management has issued the Waste Acceptance Preliminary Specifications(2) (WAPS) which detail requirements which SRS must meet for DWPF-produced canistered waste forms. These specifications require that certain foreign materials be excluded from the glass-filled canisters. These foreign materials include organics, explosives, pyrophorics, combustibles, free liquids (including water), and free gases. The free gas specification also requires an initial gas pressure of less than 7 psig at 25°C. In addition, no prohibited foreign materials are to be released upon heating the waste glass to the glass transition temperature, T_g (450 to 500°C).

The reasons for excluding foreign materials from the canistered waste form are to ensure product performance and to reduce dispersion of radionuclides in the event of an accidental breaching of the canister. An important foreign material is liquid water, which if present inside the canister, could result in corrosion of the stainless steel. Organics are to be avoided since they may complex with radionuclides thereby increasing the rate of release of the radionuclides. Organics may also break down under the radiation field to produce gases. A high internal gas pressure could lead to breaching of the canister and dispersion of radionuclides into the local environment. For this reason, the gas pressure must initially be below 7 psig at 25°C at the time of sealing. For the same reason, radiogenic gases, as they are produced during radioactive decay, must not increase the internal gas pressure of the canister over time to excessive levels. The avoidance of pyrophorics, combustibles, and explosives within the canistered waste would eliminate a fire or explosion within the canister and the possibility of canister breaching and subsequent dispersion of the radionuclide waste.

STRATEGY

The DWPF incorporates high-level nuclear waste into borosilicate glass which is subsequently poured into a stainless steel canister. The waste glass is the only substance purposely added to the canister and it does not contain foreign materials. The DWPF will prevent the inadvertent introduction of foreign materials into the canistered waste form through a combination of administrative controls and physical barriers. A series of experiments have been carried out on random canisters filled during large-scale pilot plant runs to confirm that foreign materials are in fact not present in the canistered waste forms. A similar set of experiments will be carried out on a series of canisters produced during the upcoming cold runs at DWPF. This latter set of experiments will confirm the absence of foreign materials during the prototypical operation of the DWPF. Calculations have been performed which predict the amount of radiogenic gas that will be generated as a result of radioactive decay. These calculations ensure that the internal gas pressure of the canisters will not be significantly increased as a result of radiogenic gas generation.

ADMINISTRATIVE CONTROLS AND PHYSICAL BARRIERS

The canisters will be inspected upon receipt from the vendors and prior to transfer of the canisters to the Melt Cell of the DWPF. Temporary caps will be placed in the nozzles to keep foreign materials out of the canisters prior to glass filling. After glass filling, an inner canister closure (ICC) seal is formed from shrinkage of the nozzle about an inserted plug as it cools. The leaktightness of this seal to helium gas is measured to ensure that a value below 2×10^{-4} atm·cc/sec is obtained. This value for the leaktightness has been shown to preclude the introduction of water into the canister(3). This is of particular importance due to the fact that an aqueous glass frit slurry is used to decontaminate the canister surface. The final weld plug is upset resistance welded to the nozzle to provide a seal which is leaktight to less than 2×10^{-7} atm·cc/sec of helium.

CHARACTERIZATION OF THE GAS WITHIN THE FREE VOLUME OF THE CANISTERED WASTE FORM

During production, glass will be poured into the canisters until ~85% of the canister volume is occupied by the waste glass. The remaining volume, approximately 105 liters, is referred to as the canister free volume. The composition of the gas occupying this free volume is basically the same as the ambient air in the Melt Cell. To confirm that no foreign materials are present in this free volume gas, experiments were performed to determine the gas composition. Four canistered waste forms, produced during large scale pilot plant operations, were utilized for this study. A system was designed (Fig. 1) which allowed for canister wall penetration by a punch assembly (Fig. 2) above the glass line without contamination of the internal gas by the outside air. The gas occupying the free volume was then transported to a mass spectrometer and analyzed. This system also allowed for the measurement of the dew point, relative humidity, and internal canister gas pressure.

The gas within the canistered waste form showed no additional components relative to air (this air was that present in the mass spectrometer laboratory). The only change noted was a reduction in the amount of carbon dioxide in the free volume gas relative to air. Therefore no foreign materials were present in the free volume gas.

Dew points for these four canistered waste forms ranged from -10.3°C to +5.7°C, while relative humidities ranged from 5.5% to 18.5%. These relatively low values for the dew point and relative humidity clearly indicate that no liquid water is present in the canister.

The internal gas pressure was less than atmospheric pressure for all four canisters and ranged from 691 to 735 Torr. Three of the four canisters were sealed with the ICC seal only, while one of the canisters had a final weld plug. All four canisters had been filled with glass and sealed at least two years prior to measurement of the gas pressure. This indicates that the seals were effective in maintaining a subatmospheric internal gas pressure. The reason for this low pressure is that the ICC is placed in the nozzle when the temperature of the gas within the free volume is still greater that 190°C. As the gas cools in this fixed volume, the pressure drops below atmospheric.

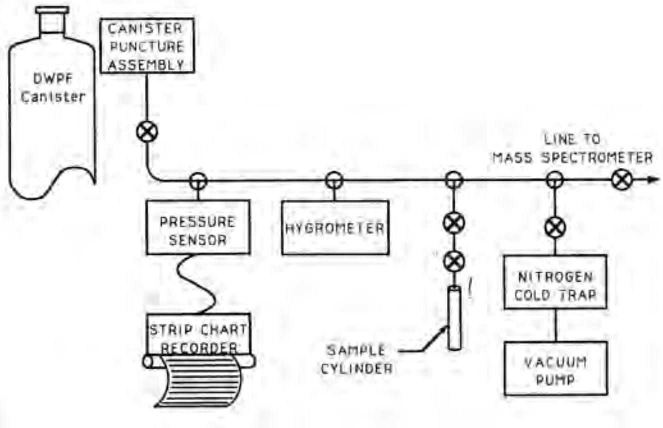

Fig. 1. Canister Sampling System.

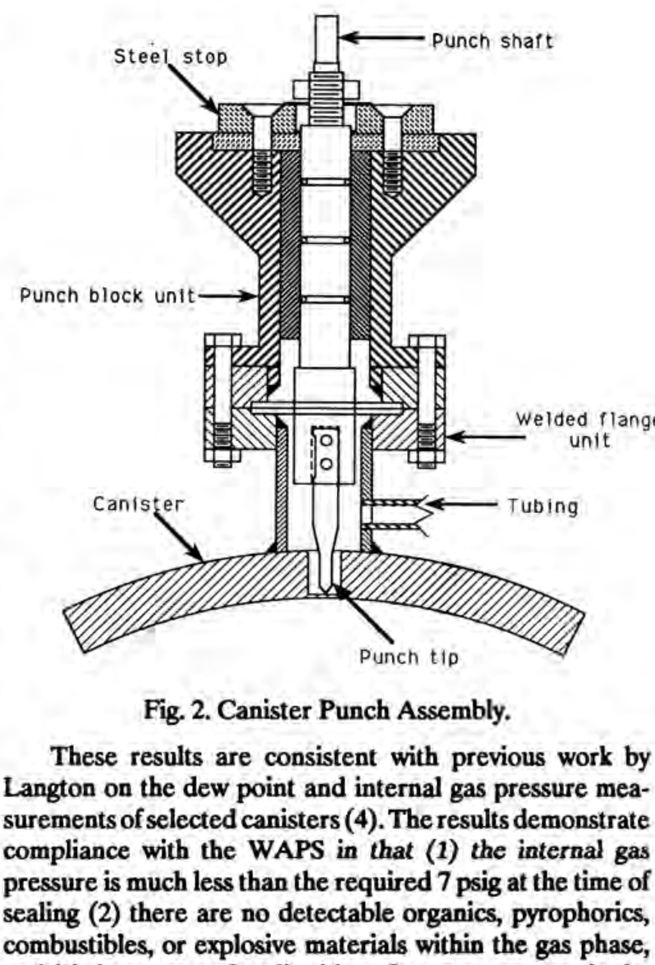

Fig. 2. Canister Punch Assembly.

These results are consistent with previous work by Langton on the dew point and internal gas pressure measurements of selected canisters (4). The results demonstrate compliance with the WAPS *in that (1) the internal* gas pressure is much less than the required 7 psig at the time of sealing (2) there are no detectable organics, pyrophorics, combustibles, or explosive materials within the gas phase, and (3) there are no free liquids or free gases present in the canister.

VOLATILITY OF WASTE GLASSES BY THERMOGRAVIMETRIC ANALYSIS (TGA)

As discussed, the WAPS require that no foreign materials be released or generated upon heating the canistered waste form to T_g. Gray(5) and Bonnell et al.(6) have shown that simulated nuclear borosilicate waste glasses have very low volatilities. In fact, both groups were required to heat their samples to ~900°C in order to even detect volatility. Other workers(7-11) have obtained similar results. To confirm these studies, it was decided to measure the volatility of glass samples taken from canisters that had been filled during large-scale, pilot plant operations at SRS and to carry out these experiments in the region of the glass transition temperature. TGA was selected as the method for measuring the glass volatility.

The results of these experiments revealed that the glass samples exhibited no weight loss upon heating to T_g, to the sensitivity limit of the TGA. In fact, the glass samples actually gained weight as they were heated. This small weight gain was due to oxygen uptake by the sample when FeO in the glass was converted to Fe_2O_3. This was confirmed by measuring the Fe^{+2}/Fe^{+3} ratio in the glass both prior to and after heating.

Volatility of the waste glass at T_g is expected to depend on the surface area of the glass. For the glass powders used in these TGA experiments, the surface area was $\sim 0.3\ m^2/g$ and the sensitivity of the measurement was 0.01 wt%. Since a canistered waste form has a glass surface area less than 125 m^2, these experiments demonstrate that the volatility per canister is less than 41 mg.

These results demonstrate compliance with the WAPS by revealing that no significant volatilization within the canistered wasteform will occur if the temperature is raised to T_g.

GENERATION OF RADIOGENIC GASES

The gas within DWPF canistered waste forms will also contain gas generated by decay of radioactive elements. The only two gaseous species generated from radioactive decay are radon and helium. R. A. Dewberry of SRS has calculated the amounts of these two species as a function of time for a canistered waste form containing an expected loading of radionuclides. The concentration of radon is extremely small at all times (maximum concentration of Rn-222 is 4.7 $\times 10^{15}$ atoms/canister at 10^5 years after production - assuming the canister still exists). The amount of He-4 generated after 10,000 years is calculated to be 0.621 moles per canister, which increases the pressure within the canister by 6730 Pa (or 0.98 psi) assuming a free volume of 140 litres at 25°C (again assuming the canister still exists).

The increased pressure due to radioactive decay in the canistered waste forms is therefore insignificant for the projected lifetime of the canisters.

CONCLUSIONS

The DWPF process incorporates high-level nuclear waste into borosilicate glass which is subsequently poured into a stainless steel canister. The waste glass is the only substance purposely added to the canister and it does not contain foreign materials. Administrative controls and physical barriers prevent the inadvertent introduction of foreign materials into the canistered waste forms. Experiments on glass volatility and characterization of the gas in the canister free volume confirm this lack of foreign materials in the canistered waste forms. The calculations on radiogenic gas generation reveal that the incremental change in gas pressure due to radioactive decay will be insignificant for these canisters. Thus these results demonstrate that the DWPF will be able to comply with the WAPS requirements on the exclusion of foreign materials from the canistered waste forms.

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