WSRC-MS-96-0244
CONF-960804--48

Dewpoint Internal Gas Pressure and Chemical Composition of the Gas Within the Free Volume of DWPF Canistered Waste Forms (U)

by

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A document prepared for SPECTRUM 1996 at Seattle from 08/18/96 - 08/23/96.

DOE Contract No. **DE-AC09-89SR18035**

DISCLAIMER

DEW POINT, INTERNAL GAS PRESSURE, AND CHEMICAL COMPOSITION OF THE GAS WITHIN THE FREE VOLUME OF DWPF CANISTERED WASTE FORMS

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ABSTRACT

The Defense Waste Processing Facility (DWPF) produced 55 canistered waste forms containing simulated waste glass during the four Waste Qualification campaigns of the DWPF Startup Test Program. Testing of the gas within the free volume of these canisters for dew point, internal gas pressure, and chemical composition was performed as part of a continuing effort to demonstrate compliance with the Waste Acceptance Product Specifications. Results are presented for six glass-filled canisters. The dew points within the canisters met the acceptance criterion of < 20°C for all six canisters. Factors influencing the magnitude of the dew point are presented. The chemical composition of the free volume gas was indistinguishable from air for all six canisters. Hence, no foreign materials were present in the gas phase of these canisters. The internal gas pressures within the sealed canisters were < 1 atm at 25°C for all six canisters which readily met the acceptance criterion of an internal gas pressure of less than 1.5 atm at 25°C. These results provided the evidence required to demonstrate compliance with the Waste Acceptance Product Specifications.

I. INTRODUCTION

The Waste Acceptance Product Specifications (WAPS)[1] for the DWPF canistered waste forms include specifications for the gas within the free volume of the canister. The canister free volume is that space within the canister not occupied by glass. Under normal operating conditions, the free volume will range from ~110 to 75 liters corresponding to a canister 85 to 90% filled with glass. The DWPF canisters, fabricated from 304-L stainless steel, become coated with a salt layer on the inside surface during glass filling. This salt layer results from volatilization of chloride and sulfate salts from the pour stream[2]. Due to the presence of the salt layer, the amount of water within the canister must be controlled to avoid localized corrosion. A dew point limit of 20°C for the free volume gas has been imposed to reduce the risk of localized corrosion.

Foreign materials are to be excluded from the DWPF canistered waste forms. A mass spectrometry method was implemented[3] to analyze the free volume gas to ensure that no foreign materials were present in the gas phase. In a closed system, any free liquids present in the canister would also partition between the gas and liquid states. Therefore, analysis of the gas phase can detect the presence of either foreign gases or free liquids.

To avoid excessive pressurization, the internal gas pressure is limited to 1.5 atm at 25°C immediately after glass filling and sealing. A system was developed[3] which allows for the measurement of the internal pressure as well as the dew point of the gas within the free volume of the canister.

In order to demonstrate compliance with the WAPS, data on the internal pressure, dew point, and chemical composition of the gas within the free volume of selected canisters filled during the DWPF Waste Qualification campaigns was required. Six canisters were modified prior to filling in order to obtain this data. This paper presents the results of the internal pressure, dew point, and chemical composition measurements on these six glass-filled canisters.

II. INTERNAL PRESSURE OF THE GAS WITHIN THE FREE VOLUME

The measured internal gas pressures of canisters S00162, S00007, S00210, S00208, S00405 and S00410 are shown in Table 1. Since the WAPS 3.2 criterion limits the internal gas pressure at a temperature of 25°C, the measured gas pressures were converted to a pressure at 25°C using the ideal gas law. The internal pressure of all six canisters readily meets the acceptance criterion of less the 1.5 atm (1140 Torr) at 25°C.

TABLE 1
MEASURED CANISTER INTERNAL PRESSURE

Canister	Pressure (Torr)	Temperature (°C)	Pressure @ 25°C (Torr)
S00162	689	24.0	691
S00007	717	22.0	724
S00210	249	27.2	247
S00208	254	28.3	251
S00405	657	28.3	650
S00410	692	28.4	684

The internal pressure depends mainly upon the glass fill height of the canister and on the elapsed time between filling and sealing of the canister. Canisters S00210 and S00208, which were filled to ~100 inches, were sealed on the pour turntable within minutes after filling. The pressures observed in these two cases were significantly below atmospheric pressure. In order to achieve these pressures, the average temperature within the canister free volume had to be ~630°C at the time of sealing. After the canister then cooled to room temperature, the internal pressure dropped to ~250 Torr. The remaining four canisters were not sealed on the pour turntable. These canisters were allowed to cool to room temperature and were then sealed at the next station in the process. The resultant internal gas pressures of ~675 Torr inside the canister implies an average free volume gas temperature of ~60°C at the time of sealing. This temperature results from heating the nozzle prior to tsealing

III. DEW POINTS OF THE GAS WITHIN THE FREE VOLUME

The dew points of the gas within the free volume space of canisters S00162, S00007, S00210, S00208, S00405 and S00410 were measured. Two hygrometers, calibrated to a tolerance of ± 2°C, were used to measure the dew points. The dew points measured for the six canisters are shown in Table 2. The acceptance criterion is a dew point less than 20°C. Therefore, the acceptance criterion was met for all six canisters.

TABLE 2
MEASURED CANISTER DEW POINTS (DP)

Canister	DP #1 (°C)	DP #2 (°C)	Melt Cell DP (°C)
S00162	-5.0	-5.0	-
S00007	+16.0	+13.5	11
S00210	+0.2	+0.1	12
S00208	-1.9	-1.9	17
S00405	+2.8	+2.8	15
S00410	+4.4	+5.0	16

The dew points within the canisters are a complex function of several variables: The dew point of the air in the Melt Cell, the time between filling and sealing, the glass fill height, and the presence of salts within the canisters. The dew point of the air in the Melt Cell at the time of temporary sealing is important since it is this air that ends up in the canister free volume space. The time between glass filling and sealing is a second significant variable in determining the canister dew point. This variable determines the temperature of the free volume air at the time of sealing. For example, both canisters S00210 and S00208, which were sealed within minutes of filling had relatively low dew points due to the high average gas temperature in the free volume space at the time of sealing. A third factor influencing dew points within a canister is the glass fill height. Higher fill heights increase the gas temperature in the free volume and can decrease the amount of water of absorption by the salt layer as discussed below.

The dew point result from canister S00007 implies that another factor also plays a significant role in determining the dew point within a canister. It has been observed that salt layers form on the inner canister surfaces during pouring. If the canister is not sealed immediately and remains open in the Melt Cell, then water can absorb onto the hygroscopic salt layer. When the canister is sealed, the water will equilibrate between the salt and the free volume gas. This can result in a higher dew point. It is therefore important to seal the canister on the pour turntable immediately after filling.

IV. COMPOSITION OF THE GAS WITHIN THE FREE VOLUME

Data obtained on the gas within the free volumes of canisters S00162, S00007, S00208, S00210, S00405, and S00410 did not reveal any compounds, other than air, to the sensitivity of the equipment. The acceptance criterion requires that there be no detectable foreign materials present in the free gas. Therefore, this acceptance criterion was met.

The gas within the free volumes of canisters S00162, S00007, S00208, S00210, S00405, and S00410 was analyzed using mass spectrometry. Scans from 1 to 200, 1 to 50, 40 to 95, and 90 to 200 mass units of the canister free volume gas were obtained. These data were compared to equivalent scans taken from room air. Air was defined as the standard since the gas within the free volume space of the canistered waste form should contain only air from the Melt Cell. No differences between the composition of the gas in the free volumes of the canisters and the room air were found.

Scans using a multiplier to increase the sensitivity of the technique were also performed from 45 to 90 and from 90 to 200 mass units. These scans cover the mass unit region where foreign materials would be expected. No differences were noted between these scans and the equivalent scans of air.

Two methods were used to estimate the sensitivity of the Extrel Questor II process mass spectrometer. The first method used isotopes of argon as a sensitivity indicator with the Ar-38 isomer present at ~ 6 ppm. The second method used benzene concentrations of 1, 10, and 100 ppm in air. Both techniques demonstrated sensitivities of less than 10 ppm, with an estimate of the actual sensitivity of ~5 ppm. The lack of detection of foreign materials in the free volume gas was therefore bounded by this sensitivity value.

CONCLUSIONS

Results on the internal gas pressure, dew point, and chemical composition were obtained from six canistered waste forms produced during the DWPF Waste Qualification campaigns. These results demonstrated that the Waste Acceptance Product Specifications were met for these properties. In all cases, the internal pressures of the sealed canisters were below atmospheric and readily met the acceptance criterion of 1.5 atm at 25°C. When the canisters were sealed within minutes of glass filling, the internal pressures were reduced to ~ 0.32 atm. The chemical composition of the gas within the six canisters tested was indistinguishable from air. This implies that there were no foreign materials within the gas phase and that there were no free liquids in equilibrium with the gas phase in the canisters. The sensitivity of the mass spectrometric measurements was ~ 5 ppm. Finally, the measured dew points of the six canistered waste forms were all less than the acceptance criterion limit of 20°C. Lower values of dew point were obtained when the canisters were sealed on the pour turntable within minutes of filling. If the filled canister is allowed to cool prior to sealing, additional water can be absorbed by the salt layer. This can result in a higher dew point after sealing. Clearly, the preferred option is to seal the canisters within minutes of glass filling since the lower dew points and internal pressures will further reduce the likelihood of localized corrosion of the stainless steel canisters.

ACKNOWLEDGEMENTS

This paper was prepared in connection with work performed under contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

REFERENCES

1. "Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms", Office of Environmental Management, USDOE Document 0093, Rev. 1 (1995).

2. M. K. Andrews, J. R. Harbour, C. A. Cicero, D. T. Herman, and N. E. Bibler, "Salts in the Interior of DWPF Canistered Waste Forms", WSRC-TR-95-0455, (1995).

3. J. R. Harbour, T. J. Miller, and M. J. Whitaker, "Exclusion of Foreign Materials from the SRS Canistered Waste Forms: Characterization of the Gas within the Free Volume", Proc. of the Second International Conference on HLRWM, April 28 -May 3, 1991, p. 728, American Nuclear Society, La Grange Park, Illinois (1991).