ENGINEERING CHANGE NOTICE

1. ECN **643390**Page 1 of 2Proj.
ECN

2. ECN Category (mark one) Supplemental ☐ Direct Revision ☒ Change ECN ☐ Temporary ☐ Standby ☐ Supersedeure ☐ Cancel/Void ☐	3. Originator's Name, Organization, MSIN, and Telephone No. Norman Scott Cannon, 8A200 L6-38, 376-0562	4. USQ Required? ☐ Yes ☒ No	5. Date 09/24/97
	6. Project Title/No./Work Order No. Retained Gas Sampler System/N2013	7. Bldg./Sys./Fac. No. FGWL Tanks	8. Approval Designator Q
	9. Document Numbers Changed by this ECN (includes sheet no. and rev.) HNF-SD-WM-CN-092, Rev. 0	10. Related ECN No(s). N/A	11. Related PO No. N/A
12a. Modification Work ☐ Yes (fill out Blk. 12b) ☒ No (NA Blks. 12b, 12c, 12d)	12b. Work Package No. N/A	12c. Modification Work Complete N/A Design Authority/Cog. Engineer Signature & Date	12d. Restored to Original Condi- tion (Temp. or Standby ECN only) N/A Design Authority/Cog. Engineer Signature & Date
13a. Description of Change The document HNF-SD-WM-CN-092, Rev. 0 was updated to produce HNF-SD-WM-CN-092, Rev. 1; these changes included additional field results allowing further evaluation of helium backfilled RGS samplers. Also included was a comparison of in-tank holding times with RGS oxygen levels to evaluate a possible oxygen/waste reaction, and a more detailed calculation of the sampler interface volume.			
13b. Design Baseline Document? ☐ Yes ☒ No			
14a. Justification (mark one) Criteria Change ☐ Design Improvement ☒ Environmental ☐ Facility Deactivation ☐ As-Found ☐ Facilitate Const ☐ Const. Error/Omission ☐ Design Error/Omission ☐			
14b. Justification Details Helium backfilling of RGS samplers was added to minimize sample contamination from air and purge gas trapped in the sampler interface volume. This revision includes additional field data to demonstrate the success of this design improvement.			
15. Distribution (include name, MSIN, and no. of copies) See attached distribution sheet.			
RELEASE STAMP SEP 29 1997 DATE: 97 STA: 97 HANFORD RELEASE ID: 22			

643390

18. Schedule Impact (days)

ENT

FNT

57

[1]

LI
FI

13
14

[1
[1

11

11
12

11
12

11

11

23
57

21
22

11
12

23
27

11
12

[]
[]

Document Number Revision

Date _____

Date _____

A-7900-013-3 (05/96) GEF096

Retained Gas Sampler Interface Volume

N. S. Cannon

SGN Eurisys Services Corporation, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: ECN 643390 UC: 510
Org Code: S1300 Charge Code: N2013
B&R Code: EW3120072 Total Pages: 34

Key Words: Retained Gas Sampler, RGS Contamination Volume, Interface Volume, Helium Backfill, RGS Air Contamination, RGS Purge Gas Contamination

Abstract: The maximum Retained Gas Sampler (RGS) interface volume was determined; this volume can trap contamination gases during the sampling process. A new technique (helium backfill) for eliminating contamination gases from the RGS sampler interface volume is described, and verification testing reported. Also demonstrated was that RGS data obtained prior to the introduction of the new helium backfill technique can be compensated for air contamination using the measured oxygen concentration and normal air composition.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

Christine Willingham 9-29-97
Release Approval Date

Approved for Public Release

RETAINED GAS SAMPLER INTERFACE VOLUME

N. S. Cannon

September 1997

CONTENTS

	Page
1.0 INTRODUCTION	4
1.1 Purpose	4
1.2 Retained Gas Sampler Interface Volume Description	4
2.0 INTERFACE VOLUME DETERMINED EXPERIMENTALLY	4
3.0 CALCULATED INTERFACE VOLUME	10
4.0 INTERFACE VOLUME HELIUM BACKFILL	11
4.1 Helium Backfill Technique	11
4.2 Helium Backfill Laboratory Verification Testing	12
4.3 Helium Backfill RGS Results	12
4.4 Oxygen Reaction with RGS Waste.	13
5.0 CONCLUSIONS	13
6.0 REFERENCES	16
7.0 ACKNOWLEDGEMENTS	16

Appendixes

A	INTERFACE VOLUME RAW DATA/ANALYSIS	A-1
B	INTERFACE VOLUME CALCULATION	B-1
C	INTERFACE VOLUME GAS TRANSFER DURING SAMPLING	C-1
D	IN-TANK HOLD TIME EFFECT ON RGS OXYGEN LEVEL - FIVE TANK DATA	D-1

Figures

1	Simplified Sketch of the RGS Geometries Producing the Interface Volume	5
2	Sketch of the RGS Sampler/Drill Bit Configuration Prior to Sampling.	6
3	Interface Volume Measurement Test Setup. Two configurations were used to determine the interface volume, as shown.	7
4	The Portion of Sampler Piston Protruding Beyond the Sampler Interface is Illustrated. The volume $V_p = \pi(0.99^2 + 0.93^2)/2 * (0.8 \text{ in}^3) = 9.48 \text{ cm}^3$. The rounded edges at the piston end have negligible effect on the volume.	9
5	Comparison Plot of Contamination Gas Volumes (at STP) for RGS "Five Tank" Data, Helium Backfill Lab Test Data and Helium Backfilled RGS "Three Tank" Data	14
6	RGS Oxygen Concentration Related to Lag Time. The time between sampler removal from the tank and the beginning of the extraction process is the lag time.	15
B-1	Detailed Sketch of Geometry Producing Interface Volume	B-2
B-2	Simplified Sketch of RGS Valve Housing Showing Ball Valve Mounting Flats.	B-3
C-1	Comparison of Sample Air (Determined from Oxygen Concentration) with Leakage Air (Calculated from Pretest "Leak-Rate") for Individual Three Tank RGS Samples	C-6
D-1	Five Tank Data Oxygen Levels (at STP) plotted versus In-Tank Hold Time	D-3

CONTENTS (Cont.)

Tables

A-1	Helium Backfill Verification Testing Raw Data: 7-3-96, Configuration 1	A-1
A-2	Helium Backfill Verification Testing Raw Data: 7-3-96, Configuration 2	A-1
A-3	Helium Backfill Verification Testing Raw Data: 7-15-96, Configuration 1	A-2
A-4	Helium Backfill Verification Testing Raw Data: 7-15-96, Configuration 2	A-2
B-1	Component Calculation Summary	B-4
C-1	Laboratory Simulation Tests - Helium Backfilled Samplers.	C-1
C-2	RGS Trapped Air Volume Determination.	C-3
C-3	Statistics for RGS "Contamination" Volumes at STP	C-4
C-4	Effectiveness of Helium Backfill Technique.	C-5
D-1	Five Tank In-Tank Hold Times	D-2

RETAINED GAS SAMPLER INTERFACE VOLUME

N. S. Cannon
(9-25-97)

1.0 INTRODUCTION

When a Retained Gas Sampler (RGS) is lowered down the drill string, there is an external "interface" volume in which air or purge gas can be trapped. During the actual segment sampling, some or all of this external gas may inadvertently be included as part of the RGS sample, adding to the sample gas composition and volume errors.

1.1 Purpose

The purpose of the work reported here was to determine the maximum value of the interface volume using an experimental method, and additionally by direct calculation. Also presented in this report is a new technique to minimize sample contamination from external gases trapped in the RGS interface volume by using a sampler helium backfill method. Validation testing results for this technique are included. In addition, it is shown that previous RGS tests (Shekarritz, 1996) performed before the helium backfill technique was developed can be compensated for air contamination by using the measured sample oxygen concentration results and normal air composition.

1.2 Retained Gas Sampler Interface Volume Description

A sketch of the valve end of the RGS (a simplification of details provided in drawing H-2-821608) is given in Figure 1. The RGS piston starts in an extended position (0.8 inches, 2 cm) beyond the sampler "interface" insert before the actual sample is taken. This extension lines up the end of the piston with the end of the drill bit, as illustrated in Figure 2. Having the piston flush with the end of the drill bit minimizes the amount of waste dragged along with the bit as the drill string is lowered into the tank. This positioning assures a more representative sample at individual tank locations.

As a sampler is lowered into the tank waste, the waste will trap air/purge gas in any volumes that exist between the sampler interface and the piston o-rings (see Figure 1). The total volume available to trap gas in this way is defined as the interface volume (V_i).

2.0 INTERFACE VOLUME DETERMINED EXPERIMENTALLY

A test was devised to measure this interface volume using pressurization of the sampler interface with helium or argon (starting with a known charge volume, pressure and temperature) and the ideal gas law. Two test configurations were used and are sketched in Figure 3.

RETAINED GAS SAMPLER INTERFACE VOLUME

Figure 1. Simplified Sketch of the RGS Geometries Producing the Interface Volume.

RGS SAMPLER/DRILL BIT CONFIGURATION

Figure 2. Sketch of the RGS Sampler/Drill Bit Configuration Prior to Sampling.

Figure 3. Interface Volume Measurement Test Setup. Two configurations were used to determine the interface volume, as shown.

In test Configuration 1, a polished surface "blank-off" disk was pressed against the attachment chamber's sealing o-ring, creating a basic system volume of V_b . The volume defined as V_b includes the attachment chamber volume, line volumes and the main vacuum chamber volume that are shown in Figure 3. The main chamber volume also includes two pressure transducers, PXD1 and PXD2, which are not shown in Figure 3.

The value of V_b was determined by charging the system, including the reference canister (of known volume V_c) with gas through Valve A (Valve B closed and Valve C open) to a starting pressure (P_1) at ambient temperature (T_a). Then, with Valves A and C closed, the remaining volume was evacuated through Valve B, leaving only V_c charged at P_1 . After evacuation, Valve B was closed and Valve C was opened allowing V_c gas to produce a new pressure (P_2) in V_b , eventually at the same temperature T_a . The volume V_b was then calculated from the ideal gas law as

$$V_b = \left(\frac{P_1 - P_2}{P_2} \right) V_c \quad (1)$$

The reference canister volume had previously been measured by weighing it dry, and then filling it with water (essentially bubble free) and reweighing it. Using the water density, the canister volume was determined as $V_c = 40.09$ mL.

In test Configuration 2, Sampler PR2 was mounted to the attachment chamber as also shown in Figure 3. The sampler piston was extended beyond the sampler o-ring insert assembly (sealing surface) 0.8 inches (2 cm), as is required when the sampler is placed in the drill string for tank sampling. The volume of the portion of the piston extending beyond the sampler sealing surface (defined as V_p) is easily calculated from the simple geometry sketched in Figure 4 as 9.48 mL. The new system volume (V_n) was then determined by charging the reference volume with gas and discharging it into the system volume as previously described, where

$$V_n = \left(\frac{P_1 - P_2}{P_2} \right) V_c \quad (2)$$

The sampler interface volume (V_I) can then be determined from

$$V_I = [V_n + V_p] - V_b \quad (3)$$

Data was obtained on July 3, 1996 using helium gas, and another set of data was taken July 15, 1996 using argon gas; raw data and analysis of this data are given in Appendix A. The helium gas tests resulted in a value of 6.08 mL for the interface volume while the argon test data produced a value of 6.10 mL.

Figure 4. The Portion of Sampler Piston Protruding Beyond the Sampler Interface is Illustrated. The volume $V_p = \pi(0.99^2 + 0.93^2)/4 * 0.8 \text{ in}^3 = 9.48 \text{ cm}^3$. The rounded edges at the piston end have negligible effect on the volume.

These are remarkably consistent values for V_i , considering that two different transducers (with different pressure ranges) were used for the volume determination. Also the test system volume was changed by about 0.9 mL between the two testing days while the system was used for other purposes.

3.0 CALCULATED INTERFACE VOLUME

Early in the RGS program, the interface volume had been estimated as about 1.1 mL, based on determining the "gap volume" between the sampler piston and the sampler tube. As a result of the experimentally determined interface volume of 6.1 mL, a re-evaluation of the valve assembly construction was performed. Details of the resulting calculation of the interface volume are given in Appendix B. A brief summary of these results follows directly.

Re-examining the schematic of the sampler valve assembly shown in Figure 1, it can be noted that there is a substantial annulus volume within the Valve Housing component that is occupied by a total of three sampler parts:

- Valve Stop - Stationary component behind the valve.
- Viton Seal - Stationary component in front of the valve.
- Rotary Ball Valve - Rotates 90 degrees during valve closure.

Using engineering drawing nominal dimensions, the empty volume of this annulus was calculated (see Appendix B) to be 30.2 mL. Note that this volume may vary somewhat from sampler-to-sampler due to the exact final position of the threaded Insert. However, inspection of several completed samplers indicated that this variation would affect the volume by less than ± 0.5 mL.

The next step was to determine the volume of the three individual components that occupy this annulus. This was done using weight and density data for each component. The results were as follows:

Valve Stop	= 9.9 mL
Viton Seal	= 5.6 mL
Rotary Ball Valve	= 9.2 mL
Total	= 24.7 mL

Therefore, the void volume for this section of the RGS valve assembly, which may be expected to be filled with air or other external gases when the sampler is inserted into the waste, is calculated to be:

$$30.2 \text{ mL} - 24.7 \text{ mL} = 5.5 \text{ mL}$$

This volume, coupled with a re-evaluated gap volume of 0.7 mL, results in a total void volume of approximately 6.2 mL, in close agreement with the volume determined using the ideal gas law.

Another test series should be mentioned which was performed by M. White to measure the interface volume using a water fill method (White, 1997). A syringe was used to force water into void spaces and displace air, with weight measurements resulting in an interface volume determination of 5.72 mL. This value is slightly smaller than those previously determined, which is not surprising considering that water's surface tension would reduce its ability to penetrate through small openings. However, it is clear that these three different methods for determining the interface volume are in relatively good agreement with a value of 6 mL.

4.0 INTERFACE VOLUME HELIUM BACKFILL

In most cases, oxygen was found in the RGS gas samples from the first five tanks tested (Shekarritz, 1996). This oxygen has been attributed to air trapped in the interface volume of the sampler as it was lowered into the tank. If a minimal oxygen interaction with the waste is assumed, then the original quantity of air introduced into the sample can be calculated based on normal air composition.

This calculation is performed for the five tank RGS data in Appendix C (see Table C-2); the resulting trapped air volumes generally fall within 1.3 to 4 mL (at STP). Even when the sample argon (assumed to be purge gas) is added to the air, all but one of the "contamination" gas volumes (STP) are less than 4 mL. It appears that not all of the sampler interface gas was released into the sampler during the sampling process or that some oxygen reacted with the waste. This subject will be discussed later in greater detail in Section 4.4 and Appendix C.

4.1 Helium Backfill Technique

In order to minimize the problem of RGS contamination from extraneous gases trapped in the interface volume, a helium backfill technique has been developed. After an RGS sampler has been fabricated, it is placed in a glove box that is evacuated and then backfilled with helium. The RGS piston is then moved forward to its final position through vacuum grease that seals the helium into the interface volume. As an extra precaution, the sampler is enclosed in a hermetic stainless steel cylinder for shipping, also backfilled with helium. This provides a double helium barrier that ensures that the interface volume helium will not leak out (tested to over 1000 hours of storage time).

Helium was chosen for the backfill gas because it is inert, inexpensive, and not found in the Hanford waste tanks. When helium is detected in the RGS sampler gases, it is discarded from the composition analysis as a known and quantified contaminant.

4.2 Helium Backfill Laboratory Verification Testing

The helium backfill concept was initially tested by "aging" backfilled samplers and then recovering the interface volume gas to analyze for composition and quantity. This was done by installing the aged sampler in the Configuration 2 position (see Figure 3). An extra o-ring seal (not shown in Figure 3) was installed over the piston to seal against the interface ring which prevented the interface volume gases from being lost when the attachment chamber, main vacuum chamber and reference canister were evacuated.

Valve B was then closed to isolate the vacuum chamber(s) from the pump, and the RGS piston was pulled back so that the RGS ball valve could be closed (simulating taking a sample). After a few minutes, the ball valve was again opened, allowing the interface gases released (by taking the "sample") to flow into the rest of the system. The piston was again pushed forward to its original position (re-establishing the known system volume). The pressure and temperature were measured to determine the quantity of released interface gas; then Valve C was closed and the reference canister removed so that gas composition could be determined with a mass spectrometer. The raw data from these tests is given in Appendix C, Table C-1. The average quantity of interface gas transferred into the sampler during ball valve operation was 2.64 mL, significantly less than the available 6.1 mL interface volume. These results also demonstrate that the interface volume helium can be retained for over 1000 hours when the sampler is stored in a helium backfilled canister.

4.3 Helium Backfilled RGS Field Results

Development of the helium backfill technique for the RGS was not completed until after testing in the first five tanks was finished. However, helium backfilled samplers were introduced when RGS sampling was restarted in the next set of Hanford waste tanks (241-U-103, S-106 and BY-109). The complete results obtained from the new RGS "three tank" set will be reported elsewhere, but an evaluation of the effectiveness of the helium backfill samplers is made here. The raw data for the quantities of helium and oxygen identified in those samples are given in Appendix C, Table C-4.

The helium backfill (HBF) technique was very effective in replacing interface trapped air and argon with helium in the three tank RGS samples. The oxygen content of these HBF samplers was greatly reduced, as was the resulting calculated air volume (from an average of 2.04 mL to 0.33 mL at STP). These air volumes were consistent with the RGSS measured pretest "leak-rate" extrapolated over the duration of the gas extraction process (see Appendix C, Figure C-1); this implies that the source of the air in the HBF samplers was probably due to extraction system leakage or outgassing rather than the sampler interface volume. The combined air and argon contamination gases were reduced from an average of 2.59 mL to 0.37 mL (at STP) by the helium backfilling technique.

4.4 Oxygen Reaction with RGS Waste

The successful effort to validate the helium backfill technique for RGS samplers also provides the opportunity to compare the "contamination" gas volumes observed from several different types of RGS tests. This comparison is useful in making a qualitative evaluation of the potential oxygen reaction with waste within the RGS sampler. If it can be shown that the oxygen/waste reaction is minimal, then the data from the first five RGS tanks can be more easily adjusted to eliminate contamination effects from the sampler interface volume. (Interface volume contamination is not expected to be a problem for subsequent RGS samples because of the helium backfill technique.)

In Figure 5, a comparison is made of the contamination volumes determined from the first "Five Tank" RGS results, the helium backfill laboratory validation data, and the new helium backfilled sampler data from the 241-U-103, S-106 and BY-109 tanks. As used here, the "contamination" gas volume refers the quantity of gas believed to be released from the RGS interface volume into the sampler when its ball valve is operated, and is the sum of the quantities of air, argon and helium found in the sample.

There are several points that can be made from Figure 5. It is clear that not all of the available interface gas enters the sampler when the valve is closed. Also, it appears that roughly the same range and scatter is observed for all three types of data, although the "Three Tank" results average about 0.8 mL higher than the other two data sets. Since there is no oxygen/waste interaction possible during the helium backfill laboratory testing, and this data for the most part matches the five tank data, it is concluded that oxygen/waste reaction within the RGS sampler over the lag time between taking the sample and testing it is minimal. This conclusion is further supported by examining a plot made by L. A. Mahoney (Shekarritz, 1996) comparing oxygen content with the lag time. This plot has been updated and reproduced here for the reader's convenience as Figure 6. The data presented does not support any significant decrease in RGS oxygen concentration versus lag time.

Although elevated tank temperature would enhance oxygen/waste reaction rates in the RGS sampler, there is no evidence of a significant RGS oxygen level dependence on the "in-tank" hold time (between when the RGS ball valve is closed to obtain the sample and when the sampler is removed from the tank). Data to support this conclusion is provided in Appendix D.

5.0 CONCLUSIONS

The RGS sampler interface "trapping volume" determined experimentally for Sampler PR2 was about 6.1 mL; this value is in good agreement with the calculated value of 6.2 mL based on drawing dimensions. Sampler-to-sampler interface volume variation is expected to be less than ± 0.5 mL.

Although there is a nominal 6.1 mL sampler interface volume which can trap air (and purge gas) as the sampler is lowered through the drill string into the tank waste (or be pre-filled with helium), not all of this contamination gas

Figure 5. Comparison Plot of Contamination Gas Volumes (at STP) for RGS "Five Tank" Data, Helium Backfill Lab Test Data and Helium Backfilled RGS "Three Tank" Data.

Figure 6. RGS Oxygen Concentration Related to Lag Time. The time between sampler removal from the tank and the beginning of the extraction process is the "lag time".

is drawn in with the waste sample; it is concluded that this "draw-in" is almost always less than 4 mL.

It was shown that the helium backfill technique minimizes the effects of RGS interface volume contamination gases on sample gas composition analysis. This conclusion is based on laboratory testing of this technique, and on the RGS field results from Hanford waste tanks 241-U-103, S-106 and BY-109, where helium backfilled samplers were used.

The "Five Tank" RGS data given in the preliminary report (Shekarritz, 1996) can be corrected for interface air contamination using the measured oxygen concentrations and normal air composition. This conclusion can be made because there was no evidence of a significant reaction of entrained oxygen with the sample waste, either during the hold time before the sampler was removed from the tank, or during the lag time after removal and before sample extrusion to begin gas extraction. Also, it is concluded that argon found in RGS samples is purge gas contamination and should also be excluded.

6.0 REFERENCES

A. Skekarritz, et. al., "Preliminary Retained Gas Sampler Measurement Results for Hanford Waste Tanks 241-AW-101, 241-A-101, 241-AN-105, 241-AN-104, and 241-AN-103," PNNL-11450, December 1996.

M. White, Letter Report, "Retained Gas Sampler Lab Tests," PNNL TWSMIT:090596, February 6, 1997.

7.0 ACKNOWLEDGEMENTS

The author wishes to express his appreciation to L. A. Mahoney for providing Figure 6 which compares RGS oxygen levels with lag time. Also, a special thanks is offered to E. R. Sicilano for his initiative and effort in compiling field data gleaned from a variety of sources, including sampling truck logs; this information allowed the correlation of in-tank hold times with RGS oxygen levels.

APPENDIX A Interface Volume Raw Data/Analysis

The raw data for the tests with helium described in Section 2.0 are given in Tables A-1 and A-2.

TABLE A-1			
Date: 7-3-96	V _c = 40.06 mL Gas = Helium	Transducer: 100 T #835-80-02-003	Test Temperature 25 °C
Test Configuration	Charge Pressure P1 (KPa)	Combined Pressure P2 (KPa)	Calculated Vol. V _b (mL)
#1 Blank Flange	99.79	30.21	92.27
	98.50	29.75	92.58
	98.76	29.81	92.66
	100.35	30.28	92.70
	101.81	30.73	92.65
	49.82	15.05	92.55
	53.04	16.01	92.66
	51.69	15.60	92.68
TABLE A-2			
Date: 7-3-96	V _c = 40.06 mL Gas = Helium	Transducer: 100 T #835-80-02-003	Test Temperature 25 °C
Test Configuration	Charge Pressure P1 (KPa)	Combined Pressure P2 (KPa)	Calculated Vol. V _n (mL)
#2 Sampler PR2 (Attached)	101.08	31.38	88.98
	96.75	30.02	89.05
	102.43	31.72	89.30
	51.66	16.03	89.04
	51.55	15.97	89.25
	55.02	17.05	89.21
	99.78	30.89	89.34
	103.04	31.89	89.38

From Table A-1 the average value of $V_b = 92.59$ mL, with a standard deviation of 0.13 mL; for Table A-2 the average value of $V_n = 89.19$ mL with a standard deviation of 0.14 mL.

Calculation of $V_i = 6.08$ mL results from using Equation (3) and the above averages (note that $V_p = 9.48$ mL).

The raw data obtained from the argon tests described in Section 2.0 are given in Tables A-3 and A-4.

TABLE A-3			
Date: 7-15-96	$V_c = 40.06$ mL Gas = Argon	Trans.: 1000 T #679-80-02-023	Test Temperature 25 °C
Test Configuration	Charge Pressure P1 (KPa)	Combined Pressure P2 (KPa)	Calculated Vol. V_b (mL)
#1 Blank Flange	742.6	225.8	91.69
	755.3	229.7	91.67
	760.8	231.4	91.65

TABLE A-4			
Date: 7-15-96	$V_c = 40.06$ mL Gas = Argon	Trans.: 1000 T #679-80-02-023	Test Temperature 25 °C
Test Configuration	Charge Pressure P1 (KPa)	Combined Pressure P2 (KPa)	Calculated Vol. V_n (mL)
#2 Sampler PR2 (Attached)	769.1	240.0	88.32
	754.0	235.4	88.25
	762.6	238.0	88.30

From Table A-3 the average value of $V_b = 91.67$ mL, with a standard deviation of 0.02 mL; for Table A-4 the average value of $V_n = 88.29$ mL with a standard deviation of 0.03 mL.

Again, calculation of $V_i = 6.10$ mL results from using Equation (3) and the above averages.

APPENDIX B

INTERFACE VOLUME CALCULATION

The interface volume is defined as that volume between the RGS sampler insert "interface" surface and the piston double o-rings; this volume can trap contamination gases (see Figures 1 and B-1). The total interface volume was calculated in several steps by determining individual contributions of several different components within the valve housing and summing them. Dimensions used in the calculations are based on drawings H-2-821608 (Rev. 1), H-2-690140 (Rev. 2) and H-2-85345 (Rev. 0).

The annulus volume (V_A) is shown in Figure B-1. The actual length of this volume is determined by how far the insert is screwed into the valve housing; measurements of ten finished samplers showed that about 0.45 inches of the insert remained outside the housing, so that the annulus length is nominally 1.48 inches. The volume can then be calculated as

$$V_A = \pi [R_1^2 - R_2^2] L \quad (\text{B-1})$$

where $R_1 = 0.853$ in., $R_2 = 0.556$ in. and $L = 1.48$ in. When the calculation is made, a result of $V_A = 1.9497 \text{ in}^3$ (31.95 mL) is obtained.

However, the annulus volume is reduced by two "flats" that are machined into the valve housing as shown in Figure B-2. The area one flat occupies can be calculated by determining the angle θ such that $\cos(\theta) = x/R = 0.7775/0.853$; thus, $\theta = 24.36$ degrees. The volume of one flat is

$$V_F = \left(\left[\frac{2\theta}{360} \right] [\pi R^2] - xy \right) L_f \quad (\text{B-2})$$

where $R = R_1 = 0.853$ in., $x = 0.7775$ in., $y = 0.3521$ in. and $L_f = 1.155$ in. This leads to $V_F = 0.0416 \text{ in}^3$. The modified annulus volume ($V_{A'}$) is then

$$V_{A'} = V_A - 2 V_F \quad (\text{B-3})$$

so that $V_{A'} = 1.8665 \text{ in}^3 = 30.59 \text{ mL}$.

The annulus volume is filled with three major components that reduce its volume; these are the Valve Stop, the Rotary Ball Valve and the Viton Seal. The volume of these individual components was determined by weighing five of each component, averaging the component weight and then computing the volume from the known densities of the component's material. Component mass

ANNULUS VOLUME DESCRIPTION

Figure B-1. Detailed Sketch of Geometry Producing the Interface Volume.

RGS VALVE HOUSING

Figure B-2 Simplified Sketch of RGS Valve Housing Showing Ball Valve Mounting "Flats".

measurements were made using a calibrated Sartorius Type 1507 scale, Standards Lab# 677-06-01-024. A summary of these results is given in Table B-1.

TABLE B-1 Component Calculation Summary				
Component	Total of Five Mass (g)	Average Mass (g)	Material Density (g/mL)	Component Volume (mL)
Valve Stop	380.95	76.19	410 SST $\rho = 7.7 \text{ g/mL}$	9.89
Ball Valve	368.60	73.72	304 SS $\rho = 8.0 \text{ g/mL}$	9.22
Viton Seal	51.81	10.35	Viton $\rho = 1.85 \text{ g/mL}$	5.59

The total correction volume due to these components listed in Table B-1 adds up to $V_c = 24.70 \text{ mL}$. The reduced annulus volume ($V_{A''}$) is thus

$$V_{A''} = V_{A'} - V_c \quad (\text{B-4})$$

giving $V_{A''} = 0.359 \text{ in}^3 = 5.89 \text{ mL}$.

Three minor adjustments for the annulus volume are made for the volumes of the cable piston (V_{cp}), the cable (V_{cab}) and the sampler housing sleeve mismatch (V_{sl}).

When the ball valve is in the open position, about 0.3 inches of each of the two cable piston protrudes into the annulus volume, as well as about 2.5 inches of cable; these two dimensions were determined by direct measurement of one assembly. The diameter of the cable piston is nominally 0.136 inches, so that the protruding volume is easily calculated as $V_{cp} = 4.358 \times 10^{-3} \text{ in}^3 = 0.071 \text{ mL}$. The cable is approximately 0.065 inches in diameter, so that treating the cable as a long cylinder, the resulting volume is $V_{cab} = 8.296 \times 10^{-3} \text{ in}^3$, or 0.136 mL.

The sleeve mismatch is the result of the sampler housing insertion into the valve housing falling about 0.025 inches short as shown in Figure B-1. From the dimensions given in Figure B-1, $V_{sl} = 2.818 \times 10^{-3} \text{ in}^3 = 0.046 \text{ mL}$.

The final annulus volume (V_{Af}) is then calculated as

$$V_{AF} = V_{A''} - 2V_{cp} - 2V_{cab} + V_{s1} \quad (B-5)$$

resulting in $V_{AF} = 5.52$ mL.

Finally, the gap volume (V_g) is calculated for the space between the piston and the insert using the dimensions shown in Figure B-1 (and Figure 4). This calculation is performed in three steps; i) the volume for the 0.342 inches to the start of the piston taper is $7.8113 \times 10^{-3} \text{ in}^3 = 0.128$ mL, ii) over the 0.228 inches of piston taper the volume is $0.02883 \text{ in}^3 = 0.473$ mL, and over the last 0.030 inches the volume is $6.727 \times 10^{-3} \text{ in}^3 = 0.110$ mL. Summing these three components of the gap volume gives $V_g = 0.71$ mL.

Since the interface volume is given by

$$V_I = V_{AF} + V_g \quad (B-6)$$

then $V_I = 6.23$ mL. This value is very consistent with the value of 6.1 mL determined experimentally using the ideal gas law.

The interface volume is most sensitive to the distance that the insert is threaded into the valve housing. A 0.010 inch difference in this distance results in a 0.22 mL change in the interface volume, for example.

One volume that has not been considered as part of the interface volume is the "Bit Volume" (V_{BIT}) which exists between the piston and the drill string bit (see Figure 2) over the 0.8 inch piston extension beyond the sampler interface. If the insert o-ring seals properly in the drill bit, then this volume would potentially trap air and possibly contribute to sample gas contamination. This description is complicated by the fact that some of the drill bits have press-in pins that might release some of this trapped contamination gas prior to sampling. Characterizing this potential release mechanism would be difficult, and will not be attempted here.

However, the bit volume is calculated using an average piston diameter of 0.959 inches and the average bit inner diameter of 1.030 inches over the 0.8 inch extension. This results in $V_{BIT} = 0.0887 \text{ in}^3 = 1.45$ mL. Since this quantity represents significantly more air than is determined for the helium backfilled samples taken from U-103 and S-106, it is assumed that the bit does not hold or trap contamination gas. The fact that very little argon was reported for the U-103 and S-106 samples also supports this assumption, since purge gas argon would be expected occasionally as a trapped gas in the bit volume.

APPENDIX C

INTERFACE VOLUME GAS TRANSFER DURING SAMPLING

The RGS sampler interface volume has been measured at 6.1 mL. However, as will be shown, not all of the interface trapped gas is transferred inside the sampler during sampling.

C.1 Lab Tests

A series of laboratory tests were performed to verify the effectiveness of the helium backfill technique in eliminating air contamination of the RGS sample. These results are given in Table C-1. As can be seen from the Table, the volumes of transferred gas were scattered from about 2 mL to less than 4 mL.

TABLE C-1 LABORATORY SIMULATION TESTS - HELIUM BACKFILLED SAMPLERS			
Test #	Total STP Volume (mL)	Helium (%)	Aging Time (hrs)
1	3.44	97.97	2
3	1.98	62.4	335
4	2.21	76.2	145
5	2.11	90.9	73
7	3.38	29.7	984
8	1.49	91.0	21
10	3.52	35.7	1152
11	3.68	92.7*	482
12	1.95	94.6*	1010
AVERAGE	2.64		
STD	0.80		
* Samplers were enclosed in He backfilled (and sealed) PVC containers. The PVC glue outgassed organics - these organics are included as part of the helium when calculating percentage, since they are not due to air in-leakage. The final sampler enclosure canisters will be made out of stainless steel, so that the outgassing problem will be eliminated.			

It should be noted that the primary reason for performing the laboratory tests was to determine helium retention versus time in backfilled samplers. The first ten tests were performed on helium backfilled samplers not enclosed in a helium backfilled canister during aging; the helium concentration remained above 90 percent only for about three days. For the last three tests, the

backfilled samplers were enclosed in helium backfilled containers during the aging period, and the helium (plus organics) concentration remained above 90 percent after 42 days.

C.2 RGS Trapped Air - First 5 Tanks

In Table C-2, the apparent volume of air contamination introduced from the interface volume during RGS sampling in the first five tanks is calculated from oxygen concentration based on normal air composition. These calculations assume that a minimal amount of oxygen was lost to reaction with the waste; additional evidence supporting this assumption will be discussed later. With the exception of five "flyers" (four low, one high - out of the thirty segments evaluated in Table C-2), the calculated volumes of air contamination ranged from 1.3 mL to 4 mL. The high flyer (AN-104/10A/17) had more air (9.47 mL) than is possible from interface volume, and it is assumed that some air in-leakage occurred, either during the sampler hold time or during the extraction process.

Also shown in Table C-2 are the argon volumes found in these samples, and in the last column of the Table, the air and argon volumes are added together. Three of the four low "flyers" are "fixed" (brought to within the 2 to 4 mL range) when argon is included, suggesting that in some cases, argon purge gas may have become a significant part of the trapped interface contamination gas. Averages and standard deviations were calculated for the volume data in Tables C-1 and C-2, and are summarized in Table C-3.

Note that the averages and standard deviations are similar between the lab test helium volumes and the tank RGS air volumes; when tank RGS argon volumes are added to the air volumes, the agreement with the lab test data improves significantly. Again, this result supports the conclusion that some argon purge gas was often trapped with the RGS interface gases, and included with the sample gases.

C.3 RGS Helium Backfilled Sampler Field Results

Valid RGS samples have been obtained from a second set of three Hanford waste tanks (241-U-103, S-106, and BY-109). Helium backfilled RGS samplers (described in Section 4.1) were used in all three of these tanks to minimize air entrapment in the interface volume (and subsequently the RGS sample), and will continue to be used in subsequent RGS tanks. A preliminary evaluation of the effectiveness of the helium backfill samplers is made here based on the quantities of helium and oxygen identified in these samples, as given in Table C-4.

As can be seen from Table C-4, the helium backfill technique was very effective in replacing interface trapped air with helium. The oxygen content of these samplers was greatly reduced, as was the resulting calculated air volume (from an average of 2.04 mL to 0.33 mL at STP). The combined air and

TABLE C-2: RGS TRAPPED AIR VOLUME DETERMINATION - FIRST 5 TANKS
(Assumes no Oxygen Reactivity with Waste)

Tank	Riser	Segment	Oxygen* (μmole)	Calcul. Air @ STP (mL)	Argon* (μmole)	Argon Vol. @ STP (mL)	Air+Argon @ STP (mL)
AW-101	24A	8	17.8	1.90	13.3	0.30	2.20
		17	30.2	3.23	7.7	0.17	3.40
		19	23.1	2.47	7.8	0.17	2.64
		21	18.7	2.00	7.7	0.17	2.17
	24B	18	31.7	3.39	21.8	0.49	3.88
A-101		22	13.8	1.48	13.8	0.31	1.79
		5	12.1	1.29	5.0	0.11	1.40
		8	12.7	1.36	3.0	0.07	1.43
	24	12	17.0	1.82	60.7	1.36	3.18
		9	3.3	0.35 #	90.0	2.02	2.37
		16	8.0	0.86 #	93.8	2.10	2.96
		19	25.1	2.69	93.5	2.09	4.79
AN-105	12A	15	27.6	2.95	2.0	0.04	2.99
		17	23.4	2.50	2.4	0.05	2.55
		19	24.7	2.64	2.6	0.06	2.70
		21	4.7	0.50 #	118.1	2.65	3.15
	7B	4	23.0	2.46	33.3	0.75	3.21
		16	19.7	2.11	27.3	0.61	2.72
		18	16.4	1.75	14.2	0.32	2.07
AN-104	10A	3	32.0	3.42	2.1	0.05	3.47
		13	23.3	2.49	2.6	0.06	2.55
		15	17.6	1.88	2.7	0.06	1.94
		17	88.5	9.47 #	6.1	0.14	9.61
		21	14.7	1.57	43.7	0.98	2.55
	12A	18	24.2	2.59	6.4	0.14	2.73
AN-103	12A	2	21.0	2.25	1.9	0.04	2.29
		5	20.9	2.24	1.4	0.03	2.27
		14	15.2	1.63	2.3	0.05	1.68
		21A	10	29.1	3.11	0.13	3.24
		16	2.8	0.30 #	17.3	0.39	0.69
AVERAGE STD				2.04 0.84		0.54 0.74	2.59 0.81

* (Shekarritz, 1996)

"Flyers"

TABLE C-3
Statistics for RGS "Contamination" Volumes at STP

Statistic	Lab Test - Helium (mL)	Five Tank Cal. Air (mL)	Five Tank Air+Argon (mL)
AVERAGE	2.64	2.04	2.59
STANDARD DEVIATION	0.80	0.84	0.81

argon contamination gases were reduced from an average of 2.59 mL to 0.37 mL (at STP) by the helium backfilling technique.

The air found in the RGS samples obtained with helium backfilled samplers may be due in part to test system "leakage" during the extraction process. For example, at the RGSS maximum allowable pretest measured leak-rate (currently set at 0.003 μ moles/s) as much as 0.48 mL of air could leak (or outgas) into the system over a typical two hour test. In Table C-4, the "Calcul. Leakrate Air" column data is determined by using the pretest measured leakrate multiplied by the actual extraction time (ranging from 1 to 2 hours) for the particular test. The average leakage volume from this column is 0.32 mL which compares favorably with the average air volume calculated at 0.33 mL (STP).

Previously, it has been assumed that the pretest measured leak-rate has been due to mostly outgassing (primarily water vapor) effects, rather than actual in-leakage from outside the RGS extraction system, since the leak-rate is reduced with increased pump-down time. Although the individual test comparisons between sample air and "leakage" air don't correlate in all cases (as can be seen in Figure C-1), the correlation is good enough to suggest that the pretest leakage/outgassing may contain a significant component of air as well as water vapor.

C.4 Contamination Gas Volume Differences between Five and Three Tank Results

The total volume of "contamination" gases shown in Table C-4 for helium backfilled (HBF) samplers range from 2.5 to 4.5 mL, with an average value of 3.42 mL; this average is larger than the 2.59 mL average result obtained from the original five tanks using the non-backfilled (NBF) samplers. It has been suggested that the roughly 0.8 mL difference between these averages might be due to an oxygen reaction with sample waste reducing the apparent air volume calculated for the NBF sampler data. However, examination of the trapped air (oxygen) dependence on sample hold (and in-tank) times provides strong evidence that an oxygen/waste reaction was not significant for RGS samples (see Section 4.4).

TABLE C-4
Effectiveness of Helium Backfill Technique

Segment ID	Helium @STP (mL)	Argon @STP (mL)	Oxygen @STP (mL)	Calcul. Air @STP (mL)	Calcul. Leakrate Air @STP (mL)	Air+Argon @STP (mL)	Total Contamination Gas @STP (mL)
U103-R7-S2	3.04	0.04	0.10	0.46	0.34	0.50	3.54
U103-R7-S5	2.71	0.01	0.15	0.71	0.44	0.72	3.42
U103-R7-S7	3.26	0.01	0.04	0.19	0.40	0.20	3.46
U103-R7-S8	2.95	0.02	0.07	0.32	0.54	0.34	3.29
S106-R7-S3	3.69	0.08	0.04	0.21	0.16	0.29	3.98
S106-R7-S5	3.48	0.02	0.04	0.17	0.39	0.19	3.67
S106-R8-S6	2.92	0.03	0.18	0.85	0.27	0.88	3.80
S106-R8-S10	3.54	0.03	0.03	0.13	0.15	0.16	3.70
BY109-R12C-S4	2.92	0.05	0.07	0.33	0.25	0.38	3.30
BY109-R10B-S5	2.77	0.06	0.04	0.17	0.40	0.23	2.99
BY109-R10B-S6	2.23	0.09	0.03	0.14	0.17	0.23	2.45
AVERAGE	3.05	0.04	0.07	0.33	0.32	0.37	3.42
STD	0.40	0.03	0.05	0.23	0.12	0.22	0.40

SAMPLE AIR vs LEAK AIR

Figure C-1. Comparison of Sample Air (Determined from Oxygen Concentration) with Leakage Air (Calculated from Pretest "Leak-Rate") for Individual Three Tank (HBF) RCS Samples.

The increase in the average contamination gas observed for the field HBF samplers is probably due to the vacuum grease seal that keeps the helium in the interface volume. This seal prevents in-tank gases from diffusing into the interface (and displacing helium) while the sampler is being lowered into position for sampling; for the NBF samplers used in the original five RGS tanks, tank gas that diffused into the interface volume could not be distinguished from genuine sample gas, and thus would not be counted as contamination gas. Also, the seal may have affected the amount of gas transferred from the interface into the sample during the ball valve operation; as previously noted, not all of the available 6.1 mL of interface gas is transferred during the ball valve operation because of effects that are difficult to quantify.

However, neither of these explanations are fully consistent with the HBF sampler laboratory test results which matched the NBF sampler results.

APPENDIX D

IN-TANK HOLD TIME EFFECT ON RGS OXYGEN LEVEL - FIVE TANK DATA

As was discussed in Section 4.4, there was no evidence of an oxygen/waste reaction within the RGS sampler during the lag time between when the sampler was removed from the waste tank and when extrusion of the waste sample was initiated (see Figure 6). However, there remained the possibility that a reaction between oxygen and waste occurred during the in-tank "hold time" after the sample was obtained by closing the sampler ball valve, but before the sampler was removed from the waste tank. During this hold time, the sample would be at the relatively higher tank temperature; the elevated temperature would generally accelerate an oxygen/waste reaction as compared to the ambient temperature conditions that existed during the sampler's storage while awaiting testing. If a significant reaction consumed some of the oxygen during the in-tank hold time, then compensation of interface air contamination for the Five Tank data would be more complicated.

To investigate the possibility of an in-tank RGS sample oxygen reaction, field data assembled by E. R. Siciliano was examined to extract the length of time each sample remained in the tank after the sample was obtained. These in-tank hold time results are compiled in Table D-1; most of the samplers were left in the tank less than an hour, but a few were left overnight providing a good contrast in hold times. In Figure 1, the oxygen levels are plotted versus the in-tank hold time (logarithmic scale). The contrast of in-tank holding times allows a conclusion that the oxygen depletion rate (if any) was low, and not significant for the RGS analysis.

TABLE D-1
Five Tank In-Tank Hold Times

Tank/Riser	Segment	In-Tank Seg. Temperature (°C)	Measured O ₂ (mL)*	In-Tank Time (hrs)	Comments
AW-101/24A	8	40.8	0.40	0.37	Avg. O ₂ 0.51 mL STD 0.15 mL
	17	42.6	0.68	0.45	
	19	43.0	0.52	0.37	
	21	37.5	0.42	0.23	
AW-101/24B	18	43.4	0.71	0.28	
	22	35.8	0.31	21.31	
AN-105/7B	4	39	0.52	0.15	Avg. O ₂ 0.52 mL STD 0.28 mL
	16	44	0.44	5.13	
	18	46	0.37	1.50	
AN-105/12A	15	43	1.12	0.30	
	17	46	0.52	2.83	
	19	46	0.55	0.35	
	21	39	0.11	15.15	
A-101/15	5	46	0.27	4.57	Avg. O ₂ 0.29 mL STD 0.15 mL
	8	57	0.28	0.88	
	12	62	0.38	0.27	
A-101/24	9	63	0.07	0.23	
	16	61	0.18	0.80	
	19	60	0.56	0.33	
AN-104/10A	3	42.2	0.72	0.33	Avg. O ₂ 0.75 mL STD 0.57 mL
	13	42.2	0.52	3.18	
	15	46.7	0.39	0.25	
AN-104/12A	21	40.0	0.33	1.47	
	18	47.8	0.54	0.65	
AN-103/12A	2	37.8	0.47	0.07	Avg. O ₂ 0.75 mL STD 0.57 mL
	5	42.2	0.47	0.08	
	14	42.8	0.34	32.90	
AN-103/21A	10	42.2	0.65	0.20	
	16	41.7	0.06	0.12	

* Given at STP

Figure D-1. Five Tank Data Oxygen Levels (at STP) plotted versus In-Tank Hold Time.

DISTRIBUTION SHEET

To Distribution	From Equipment Development Laboratory	Page 1 of 1			
		Date September 24, 1997			
Project Title/Work Order Retained Gas Sampler Interface Volume		EDT No. 606753			
		ECN No. 643390			
Name	MSI N	Text With All Attach.	Text Only	Attach./ Appendi x Only	EDT/E CN Only
J. M. Bates	K7-15	X			
R. E. Bauer	S7-14	X			
N. S. Cannon (5)	L6-38	X			
A. B. Cockrell	S7-12	X			
P. R. Deichelbohrer	S7-12	X			
D. B. Graves	L6-38	X			
B. E. Hey	T6-07	X			
J. R. Jewett	T6-07	X			
G. D. Johnson	S7-14	X			
C. G. Linschooten	S7-12	X			
L. A. Mahoney	K7-15	X			
A. P. Mousel	S7-12	X			
K. Napora	B1-13	X			
L. R. Pederson	K2-44	X			
J. C. Person	T6-07	X			
D. R. Rector	K7-15	X			
J. S. Schofield	S7-12	X			
A. Shekarriz	K7-15	X			
E. R. Siciliano	H0-31	X			
C. W. Stewart	K7-15	X			
J. R. Thielges	L6-38	X			
Central Files (3) + Orig.	A3-88	X			