MEASUREMENT OF HYDROGEN DIFFUSION RATES THROUGH BOTH "TWIST AND TAPE" AND HEAT-SEALED POLYURETHANE AND POLYVINYL CHLORIDE BAGS

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ABSTRACT

Hydrogen diffusion rates through sealed polyurethane (PU), and polyvinyl chloride (PVC) bags have been measured. The PU and PVC bags are used for safely transferring residue materials from gloveboxes to storage containers at the Rocky Flats Environmental Technology Site (RFETS) and other Department of Energy facilities.

The results of this study contribute to the field of knowledge of hydrogen diffusivity by providing data for improved hydrogen diffusion modeling of various package configurations that include PVC and PU heat sealed and twist and tape 'pig-tail' packages that are in use at RFETS and other DOE sites. Improved modeling of hydrogen gas permeability through layers of confinement of plutonium residues may reduce the need for repackaging. Without the need to repackage residues, efficient use of space, reduced labor, reduced operator radiation exposure, and a significant reduction in costs will be achieved. A goal of any plutonium-residue package decision is to minimize the potential buildup of hydrogen, which is generated radiolytically. Hydrogen generation is proportional to the plutonium loading of a waste container. One way to maximize plutonium loading safely is to model the package using actual measured hydrogen permeability rates, rather than excessively conservative estimates. The hydrogen permeability measurements described in this paper establish the rates of hydrogen diffusion from PU materials, and compares these rates to PVC. PU packages have desirable features for residue bag-out–bag operations. The PU bag is much more flexible, yet is of equal strength when compared to PVC. Another advantage of PU is that it does not introduce chlorides, which are created by radiolytic decomposition of PVC bags and may cause corrosion in waste packages.

The bags are twisted tightly and taped (i.e. pig-tailed), or heat-sealed to close the end of the bag. The resulting package is known as a bag-cut since it is cut from a larger section of a bag-out-bag. This report documents the procedures and results of hydrogen diffusion rates measured through taped or heat-sealed PU and PVC bags.

The average hydrogen diffusion rate through **twisted and taped PU** bag-cut ends is 5.20 E-07 Mol/Second/Mole fraction with a standard deviation of 2.5. The average hydrogen diffusion rate through **taped PVC** bag-cut ends is 4.42 E-07 Mol/Second/Mole fraction with a standard deviation of 0.8. The average hydrogen diffusion rate through **heat-sealed PU** bag-cut ends was 2.32 E-07 Mol/Second/Mole fraction with a standard deviation of 0.6. The average hydrogen diffusion rate through **heat-sealed PVC** bag-cut ends was 1.71 E-07 Mol/Second/Mole fraction with a standard deviation of 0.9. There was no statistically significant difference between the hydrogen permeability of sealed PU and PVC bags. Seven bag-cut ends of each material type, PU and PVC, were hydrogen leak tested over a period of about 7 days. During the test period, the concentration of hydrogen gas inside the test vessel decreased from 4.0% to about 2% by volume.

System leakage through two fully closed test vessels was measured for over 25 days. The vessels used to measure systematic leaks were fully enclosed, except for two plug valves, with ½" thick PVC plate. The hydrogen diffusion rate calculated over this period was about 0.008 E-07 Moles/Second/ per Mole fraction. The losses due to the system, and actual sampling, accounted for less than 1% of the losses through the seal and bag material.

BACKGROUND

Glovebox bag-cuts are made on 14 mil PVC, or 6 mil PU bags, that are sealed at one or two ends by securely twisting the bag segment, wrapping tape around the twisted end, cutting the taped segment at the midpoint, and then adding a second layer of tape to seal off the 'open' end of the bag. The practice is used throughout the DOE complex to seal bags used for transferring radioactive materials from a glovebox into a container such as a drum. For plutonium residue packaging decisions, it is necessary to know the rate at which hydrogen gas leaks from the package. The TRUPACT II SARP Appendix 1.3.7 provides limits that are used to determine hydrogen resistance from each layer of confinement in packages. Computer programs calculate the permissible decay heat of the package based on, among many other variables, the hydrogen resistance, which is the inverse of the hydrogen diffusion rate. The hydrogen diffusion rate must be measured for each layer in a waste package, otherwise estimates of hydrogen diffusivity are used that may be too restrictive. The overall hydrogen leak rate from this type of package is the sum of hydrogen permeability through each layer of the package.

The majority of the bag-cut packages at the Rocky Flats Plant are 14-mil PVC. A new bag-cut package is 6-mil PU. Establishing hydrogen diffusivity rates is necessary to ensure that these bags will be acceptable for use in drums of TRU waste that will be shipped to an off-site disposal facility. The results of this study provide data on hydrogen permeability through both taped and heat-sealed ends for both PVC and PU bags. The results will help determine whether the packages meet transportation requirements. If there is no significant difference in the hydrogen permeability between PU and PVC, then PU may be included as an acceptable layer of confinement at Rocky Flats.

PROCEDURE

The glovebox bag-cuts were twist and tape sealed by operators at RFETS in order to assure that test samples were as similar as possible to the taped ends made during production operations. A test duration was determined, and seven even intervals were scheduled for sampling until about 50% of the initial hydrogen had leaked out of the container.

Each bag-cut was fitted onto a 10" diameter PVC test vessel. Shown in the photographs of **Figure-1** and **Figure-2,** are a PVC heat-sealed bag-cut, and a PU twist-and-taped bag-cut attached to the test vessel. The test vessel was 10" Schedule 40 PVC pipe sealed on the bottom with a 1/2" thick PVC plate. Two O-ring grooves were machined in the outside wall of the pipe in order to seat two bungee cord O-rings. In order to improve the seal, a layer of RTV -732 clear silicone sealant was applied along the lower groove. The cut edge of the bag-cut was secured to the PVC pipe by 2.5" wide yellow vinyl tape wrapped along the lower edge of the bag-cut.

Twenty PVC vessels for glovebox bag-cut testing were specially fabricated to allow gas sampling. Each test vessel was equipped with two brass valves that allowed re-circulation of the test gas and introduction of the NIST certified mixture of 4.0% hydrogen gas. The plug valves (Part # B-4P4T1) were threaded into the PVC vessel and sealed with a 1/8" thick, 70-durometer neoprene washer. The plug valves have proven to be leak tight in other tests conducted at Nuclear Filter Technology. Subsequent helium leak rates for the plug valves have been measured at 1 E-09 cc/second.

After assembly, each vessel was water leak tested to verify a positive seal throughout the container. Helium leak testing of the PVC vessel was not done because when the vessels were tested for leak tightness, Nuclear Filter Technology did not have helium leak test capability. Each bag-cut test vessel was purged for several minutes with the test gas (certified 4.0% hydrogen, balance nitrogen), prior to the first sample injection into the gas chromatograph. Each test vessel was sampled for gas composition on a set schedule. All the PVC and PU bag-cuts were tested at the same time.

Determination of System Leaks

In order to quantify system leak rates at the valves, and the seal around the bag that is attached to the test vessel, a separate test was conducted by measuring the hydrogen leak rates from a fully enclosed PVC vessel (see **Figure-3**, below of test vessel #19). System leakages through two fully enclosed test vessels were measured for over 25 days. The hydrogen diffusion rate calculated over this period was about 0.008 E-07 Moles/Second/ per Mole fraction. The losses due to the system, and actual sampling, accounted for less than 1% of the losses through both the seal and bag material.

The system leak rate through the test vessel, connective tubing, and valves was measured for over 25 days. The hydrogen diffusion rate calculated over this period was about 0.008 E-07 Moles/second/ per mole fraction. The losses due to the system, and sampling, accounted for less than 1% of the losses through the seal and bag material.

Figure-1 Polyvinyl Chloride Bag **(**PVC) bag-out-bag with heat-sealed end attached to test vessel

Figure-2 Polyurethane **(**PU) bag-out-bag with twist-and-taped end attached to test vessel.

Equipment and Operating Parameters

The gas chromatograph used is a Shimadzu GC 14A equipped with a 6 port “Event 91” valve and the column was a MS-5 A, 2.5 meter 80 X 100 molecular sieve. The detector was a thermal conductivity detector (TCD). Operating parameters of the GC were 100°C detector temperature, 110°C column and injector temperature, and 150°C TCD temperature. The current across the TCD was set at 70 milliamps. The data acquisition software used was Shimadzu EzChrome.

QUALITY ASSURANCE

The gas chromatography analysis for hydrogen gas determination was conducted in accordance with DOE/WIPP Procedure 520.1, “Gas Chromatography Determination Of Hydrogen And Methane in Waste Container Headspace,” which is based on ASTM Method 1946-82. The key quality assurance elements, derived from Procedure 520.1 and applied to the test described here, were the use of National Institute of Standards and Technology (NIST) traceable gases for establishing a three-point calibration curve. Calibration curves were run at the start of each day that analyses were conducted. The minimum detection limit (MDL) of the thermal conductivity detector was measured in accordance with 40 CFR Pt. 136, app. B. The chromatograph peak area was measured 14 times for a certified hydrogen gas concentration of 1.5 Vol% hydrogen. The MDL was estimated at 230 parts per million. The precision and accuracy of the test equipment were measured at less than 100 parts per million.

To validate the test data, cell formulas were printed and manually reviewed. Manual calculations verified that the spreadsheet was transforming the data as expected. Finally, the spreadsheet calculations had been used in previous studies that have been published and subjected to peer review.

Determination of Test Period

Since there was no preliminary estimate of hydrogen permeability through twisted and taped bag-cut packages in this exact configuration, a three-day trial run was conducted. The trial test determined an estimate of the time required to obtain reliable test results. The experiment was designed such that the hydrogen gas concentration would be measured at regular intervals through its decay to 50% of its initial concentration. It was determined that the test duration should be about 8 days. Samples were taken about every 30 hours.

Figure-3 Fully sealed PVC vessel used to measure “system” leak rates.

Two Test Cycles

After the first test cycle, during which the first seven PVC and PU taped and the two heat-sealed bag-cuts were measured for hydrogen permeability, a second series of tests was conducted
The schematic diagram in Figure-9 shows the test set-up. A certified mixture of 4.0 Vol% hydrogen gas with a balance of nitrogen was circulated by a peristaltic pump through the gas-chromatograph injection valve and returned to the test vessel. An initial gas sample was taken, and then again at even intervals determined by the estimate described in the section, "Determination of Test Period". Seven samples were taken over the test period. A sample of the gas was injected into the detector for analysis by a six-port valve actuated by the programmed control panel of the gas chromatograph. The concentration of hydrogen in the test vessel decreased over time due to diffusion through the bag. The hydrogen diffusivity losses through tubing and connections was measured and quantified.

The chromatogram peak area is proportional to the concentration of hydrogen in the container. The decay rate, or hydrogen diffusivity, D, through the assembly is given by:

$$\mathbf{D = PV/t\ RT\ ln(H_o/H_t)}$$

Where P is atmospheric pressure, V is the volume of the vessel with connective tubing, t is elapsed time in seconds, R is the Ideal Gas Constant, and T is the temperature in Kelvin. The diffusion rate, D, is in Mol/Second/ Mole fraction (M/S/ M frac). The initial concentration of hydrogen given by the chromatogram peak area is Ho and the concentration of hydrogen after time t is Ht.

These diffusion tests were conducted at the Nuclear Filter Technology Laboratory in Golden, Colorado, which is at an elevation of 6000 feet. Pressure, therefore, is adjusted down from 1 atmosphere to 0.81 atmospheres. The volume of the test container was determined by measuring the inside height and diameter of each vessel and calculating the volume. The volume of the Test vessel was about 12.2 liters. The vessel dimensions, and vessel volume calculations, are included in Attachement-1. The ideal gas constant is 0.08206 L-Atm / Mol-Kelvin. The tests were conducted in a temperature-controlled room that was maintained at between 23 and 27 degrees centigrade. Temperature corrected values to 25.0 centigrade have been shown in the results Table -2.

Peak area data were transferred to a spreadsheet where the diffusion coefficient was calculated at each data point. An average of six calculated diffusion coefficients was taken and reported as the diffusion rate, D'. The standard deviation of the mean was also calculated and reported.

RESULTS -- Hydrogen Diffusivity Through PU and PVC Bags With Taped Ends

The two-run average hydrogen diffusion rate through taped PU bag-cut ends was 5.20 E-07 Mol/Second/mole fraction with a standard deviation of 2.5. The two-run average hydrogen diffusion rate through taped PVC bag-cut ends was 4.42 E-07 Mol/Second/mole fraction with a standard deviation of 0.8.

Given the average hydrogen diffusion rate for the taped PU and PVC bag-cuts, a statistical test of two independent means yielded a deviate of 0.7. The results allow the conclusion that at a 95% confidence level, the two average hydrogen diffusion rates for the two materials are not statistically significantly different.

Hydrogen Diffusivity through PU and PVC Bags With Heat-sealed Ends

The two-run average hydrogen diffusion rate through heat-sealed PU bag-cut ends was 2.32 E-07 Mol/Second/Mole fraction with a standard deviation of 0.6. The two-run average hydrogen diffusion rate through heat-sealed PVC bag-cut ends was 1.71 E-07 Mol/Second/Mole fraction with a standard deviation of 0.9.

For the average hydrogen diffusion rate for the heat-sealed PU and PVC bag-cuts, a statistical test of two independent means yielded a deviate *t* of 1.4. The results allow the conclusion that, at a 95% confidence level, the two average hydrogen diffusion rates for the two heat-sealed materials were not statistically significantly different.

Differences between Seal Types – Twist and Tape Vs. Heat-sealed

Between either bag type, PU or PVC, but given the different *seal techniques*, twist-and-taped or heat-sealed, there does exist a statistically significant difference in the average hydrogen diffusion rates. Given the average hydrogen diffusion rate for the heat-sealed PU and twist and taped PU, a statistical test of two independent means yielded a deviate *t* of 2.7. Given the average hydrogen diffusion rate for the heat-sealed PVC and twist and taped PVC, a statistical test of two independent means yielded a deviate *t* of 5.5. In either case, both deviates indicated at the 99% confidence level that a statistically significant difference exists between seal techniques.

Table-1 below summarizes the test results for the PU and PVC bags with twisted and taped ends and heat-sealed ends.

TABLE-1

	Twist and Taped PVC Bag Diffusion Rate Mol / S/ Mol Frac (Stdrd Dev.) X 10^{-7}	Twist and Taped PU Bag Diffusion Rate Mol / S/ Mol Frac (Stdrd Dev.) X 10^{-7}		Heat-sealed End PVC Bag Diffusion Rate Mol / S/ Mol Frac (Stdrd Dev.) X 10^{-7}	Heat-sealed End PU Bag Diffusion Rate Mol / S/ Mol Frac (Stdrd Dev.) X 10^{-7}
RUN 1 AVERAGE	4.21 (0.6)	4.83 (0.7)		1.63 (0.9)	2.31 (0.5)
RUN 2 AVERAGE	4.63 (0.5)	5.57 (2.4)		1.80 (0.3)	2.33 (0.4)
TWO RUN AVERAGE	4.42 (0.8)	5.20 (2.5)		1.71 (0.9)	2.32 (0.6)

DIFFUSION RATES CORRECTED TO 25.0 C

The WIPP SARP section 1.3.5 requires measurements of hydrogen diffusion tests to be at 25.0°C (298.15 K). In order to normalize test results to 25.0 °C, a temperature corrected rate was calculated. The table below shows the temperature-corrected hydrogen diffusion rates. The room temperature was recorded daily. The average of the temperature recordings taken at the start of each set of samples for test Run-1 was 22.9°C. The average of the temperature recordings taken at the start of each set of samples for test Run-2 was 23.9°C. See Attachment #2 for the temperature correction equation used to normalize data to 25°C.

TABLE –2 Diffusion Rated Corrected to 25°C

	Twist and Taped PVC Bag Diffusion Rate Mol / S/ Mol Frac X 10^{-7}	Twist and Taped PU Bag Diffusion Rate Mol / S/ Mol Frac X 10^{-7}		Heat-sealed End PVC Bag Diffusion Rate Mol / S/ Mol Frac X 10^{-7}	Heat-sealed End PU Bag Diffusion Rate Mol / S/ Mol Frac X 10^{-7}
RUN 1 AVERAGE	4.18	4.79		1.62	2.30
RUN 2 AVERAGE	4.60	5.53		1.79	2.33
TWO RUN AVERAGE	4.39	5.16		1.70	2.31

During the second test run, when the second sample was being taken from test vessel #5, a 1 millimeter tear occurred in the bag-cut. The final calculations did not include this sample. A review of Figure #6 (below), shows how rapidly the hydrogen leaked from the test vessel as a result of the tear.

CONCLUSION

The hydrogen diffusion rates through both sealed polyurethane and polyvinyl chloride bag-cuts used in containing residue materials at the Rocky Flats Environmental Technology Site were measured by Nuclear Filter Technology**.** The average hydrogen diffusion rate through twist and taped PU bag-cut ends was 5.20 E-07 Mol/Second/Mole fraction with a standard deviation of 2.5. The average hydrogen diffusion rate through taped PVC bag-cut ends was 4.42 E-07 Mol/Second/Mole fraction with a standard deviation of 0.8. The average hydrogen diffusion rate through heat-sealed PU bag-cut ends was 2.32 E-07 Mol/Second/Mole fraction with a standard deviation of 0.6. The average hydrogen diffusion rate through heat-sealed PVC bag-cut ends was 1.71 E-07 Mol/Second/Mole fraction with a standard deviation of 0.9. There was not a statistically significant difference between the hydrogen permeability of sealed PU and PVC bags.

System leakage through a test vessel, measured for over 25 days, was about 0.008 E-07 Moles/Second/ per mole fraction, which accounted for less than 1% of the losses through the seal and bag material.

The results of this study provide required data on hydrogen permeability through twist and taped or heat-sealed ends, of both PVC and PU bags. Since there is no difference in the hydrogen permeability between PU and PVC, then PU may be included as an acceptable layer of confinement. Additionally, the work presented here contributes to the field of knowledge by providing data for improved modeling of various package configurations including PVC and PU twist and tape 'pig-tail' packages that are in use at RFETS and other DOE sites. Improved modeling of hydrogen gas permeability through layers of confinement of plutonium residues may eliminate the need for repackaging. Without the need to repackage residues, efficient use of space, reduced labor, reduced operator radiation exposure and a significant reduction in costs will be achieved.

This report documents work conducted under Rocky Flats Environmental Technology Site, Safe Sites of Colorado subcontract # SSOC 0000667BS1.

Hydrogen Concentration for PU and PVC Covers Run -1

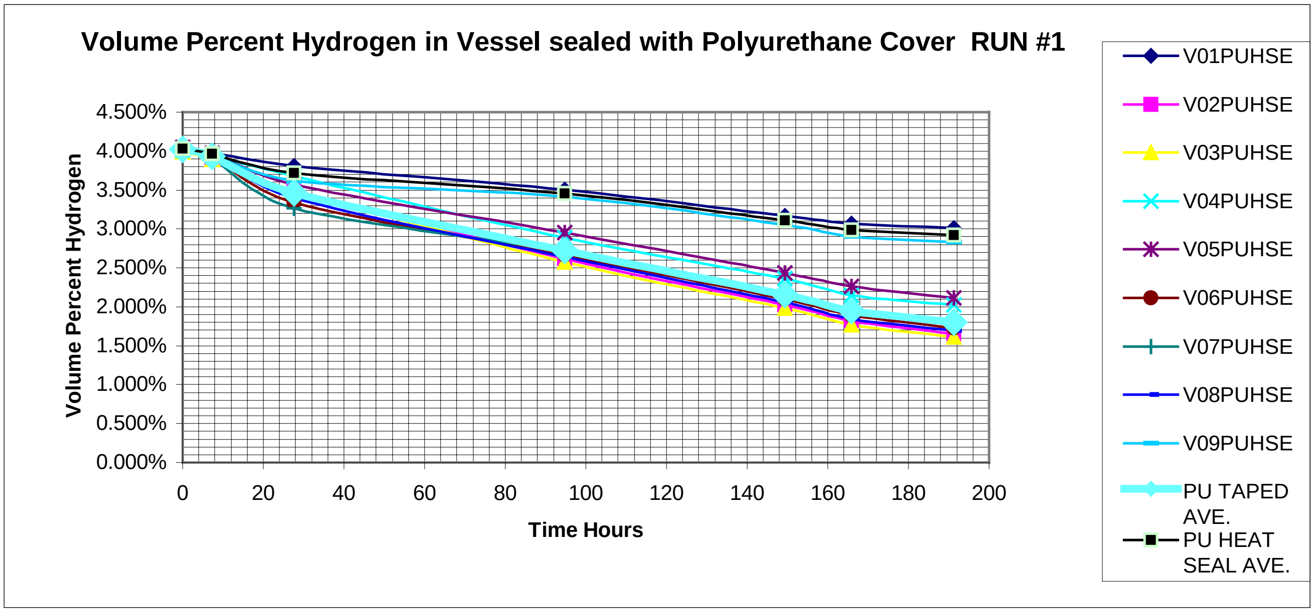


Figure –4 PU Run -1

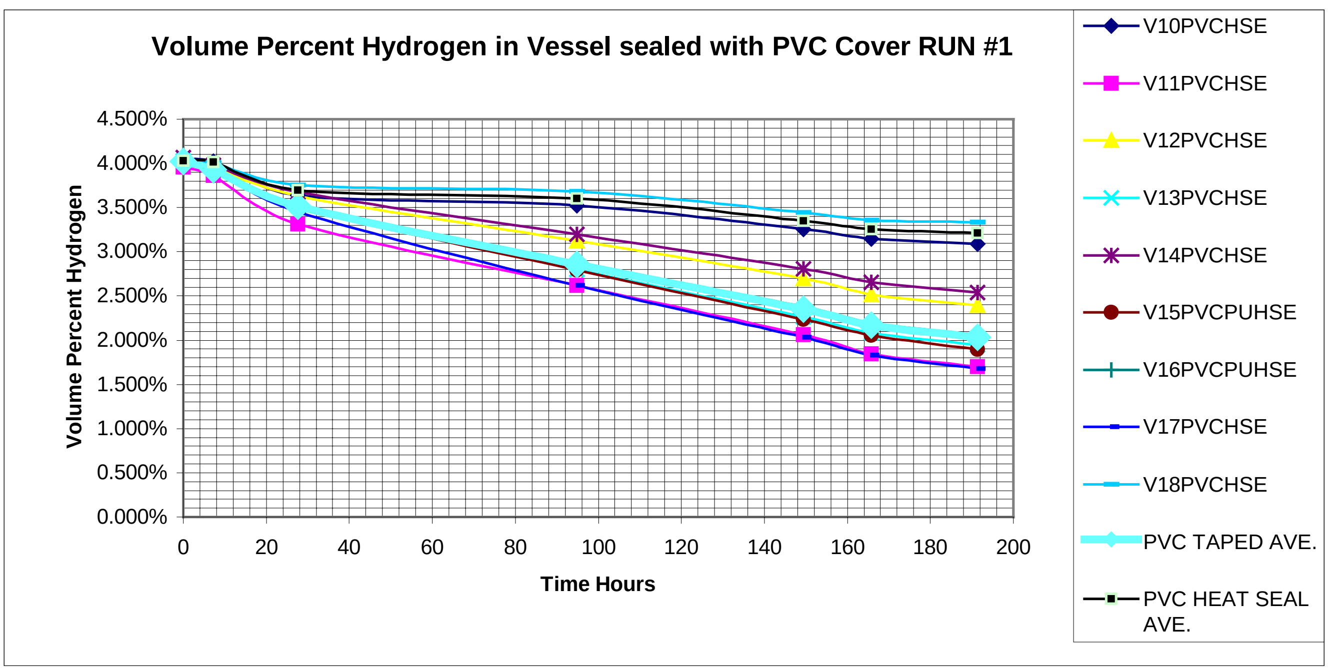


Figure-5 PVC Run-1

Hydrogen Concentration for PU and PVC Covers Run –2

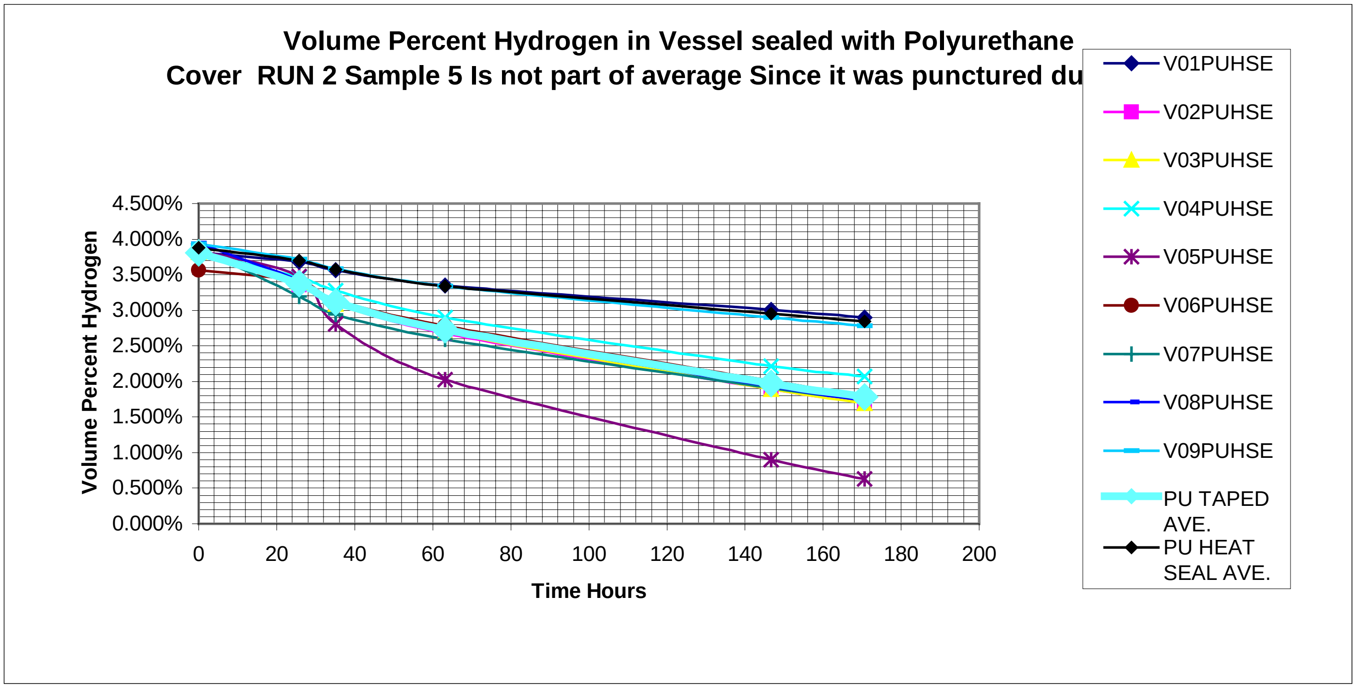


Figure-6 PU Run -2

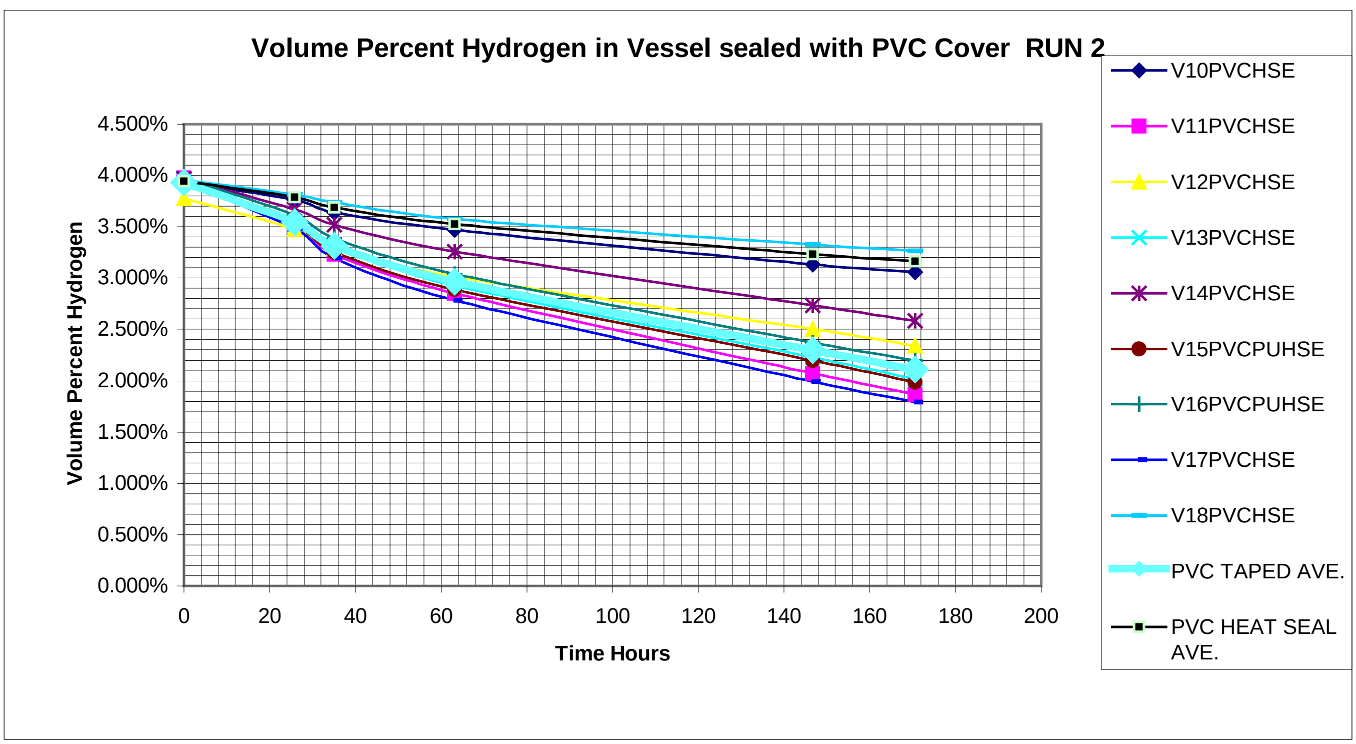


Figure –7 PVC Run-2

Hydrogen Losses Through the "System"

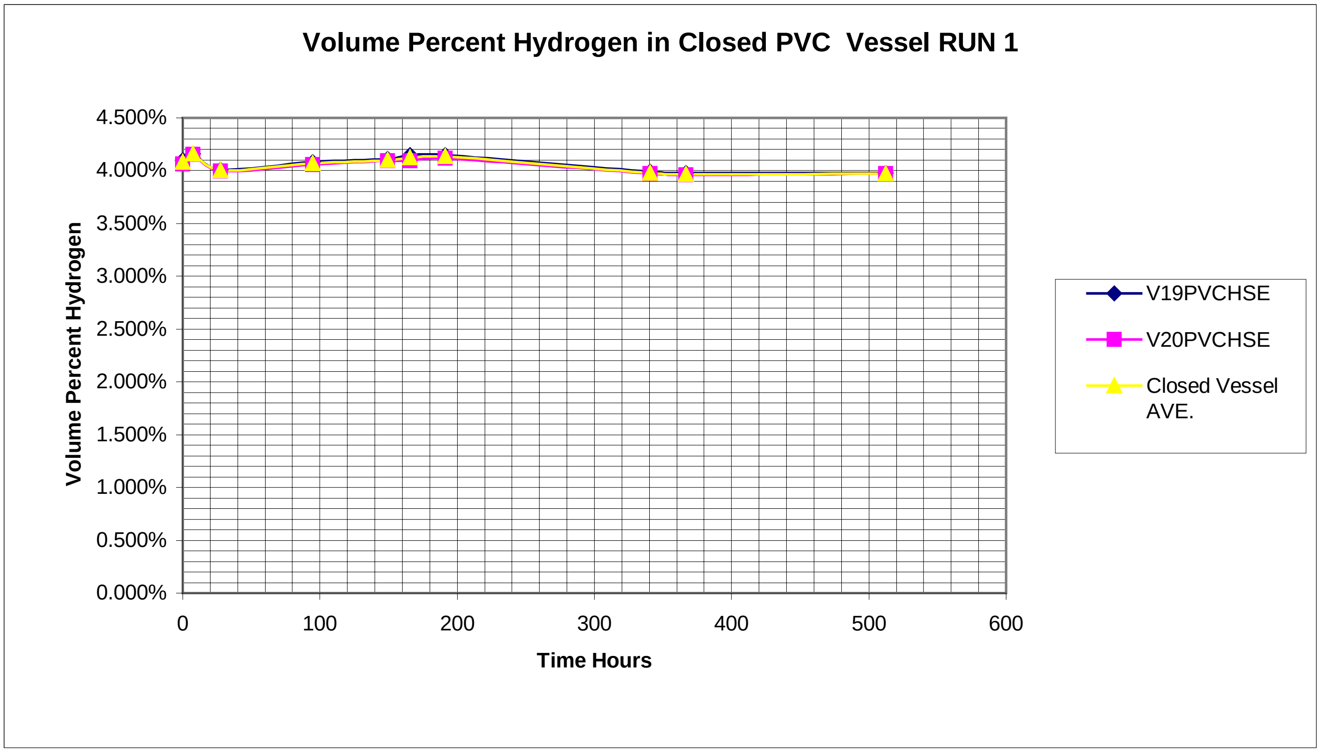
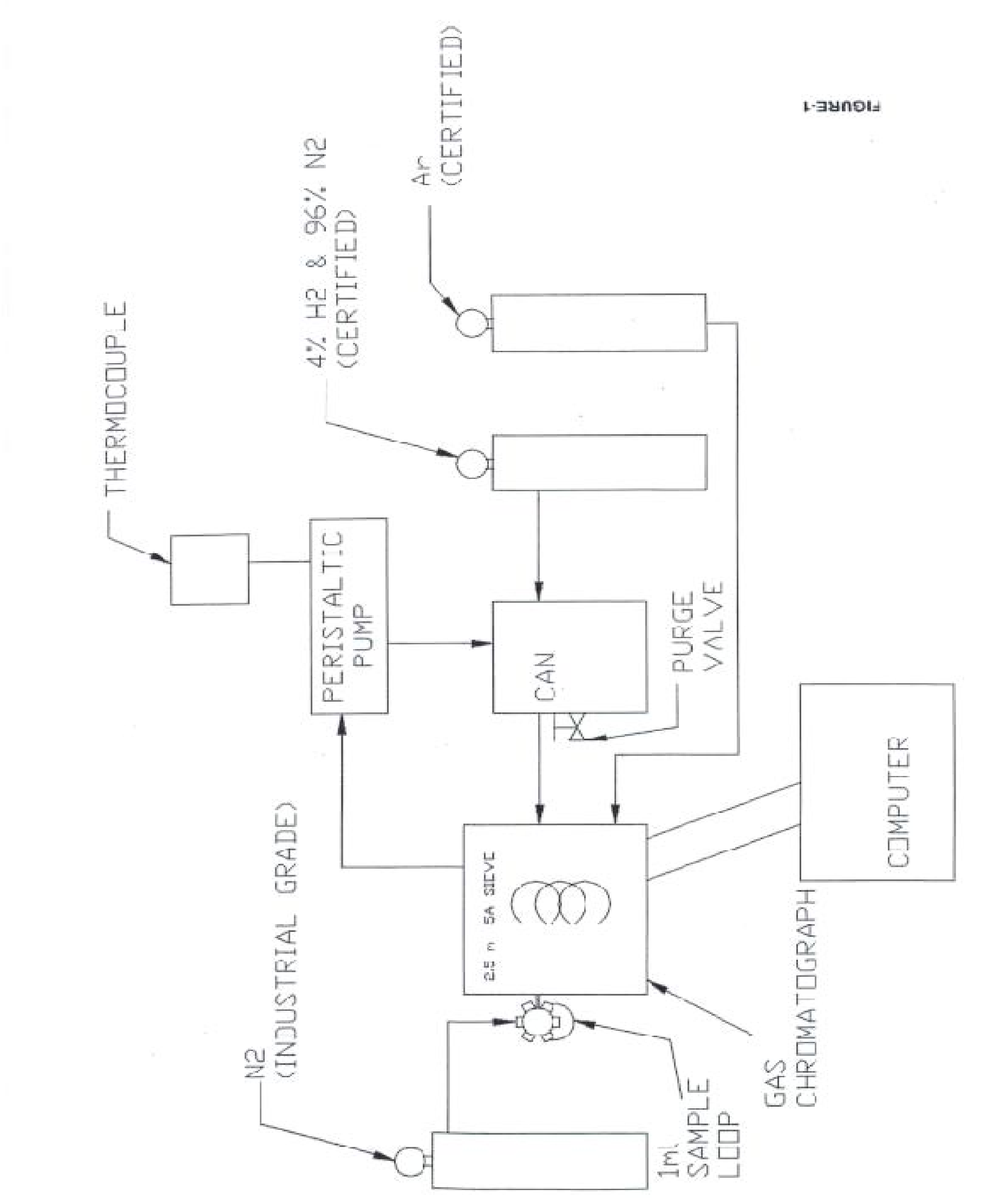


Figure –8 Hydrogen Losses Through the "System"

Figure –9 Schematic Diagram of Hydrogen Gas Test Apparatus



ATTACHMENT –1

TEST VESSEL VOLUME CALCULATIONS

Vessel #	Height	Diameter	Calculated Volume liters
1	24.23	25.36	12.2
2	24.23	25.36	12.2
3	23.90	25.36	12.1
4	24.77	25.36	12.5
5	24.26	25.36	12.3
6	24.25	25.36	12.2
7	24.20	25.36	12.2
8	24.10	25.36	12.2
9	25.37	25.36	12.8
10	24.11	25.36	12.2
11	24.40	25.36	12.3
12	22.80	25.36	11.5
13	23.94	25.36	12.1
14	24.30	25.36	12.3
15	24.25	25.36	12.5
16	24.36	25.36	12.3
17	24.13	25.36	12.2
18	24.85	25.36	12.6
19	23.50	25.36	11.9
20	23.60	25.36	11.9
		AVERAGE	**12.2**
		STDEV	**0.3**

ATTACHMENT –2

TEMPERATURE CORRECTION TO 25 °C

TEMPERATURE CORRECTION OF HYDROGEN DIFFUSION RATES

The WIPP SAR indicates that diffusion measurements shall be conducted at 25 degrees centigrade. The laboratory where diffusion measurements were conducted was maintained at between 23.0 and 27.0 degrees centigrade. The transformation of diffusion rates corrected to 25 degrees centigrade is presented below:

Diffusion rate D' is,

$$D' = \frac{PV}{tRT} \ln \frac{H_o}{H_t}$$

Where: **R** is the ideal Gas constant, 0.082 liter-Atm/ K mol
P is atmospheric Pressure in Atm, adjusted to 6000' altitude to 0.81 atmospheres (atm)
V is the test chamber volume equal to 12.2 Liters
t is elapsed sample time in seconds
T is actual test chamber temperature, Kelvin, ranges from 296.15 K (23.0 C) to 300.15 K (27.0 C)
$\mathbf{H_o}$ is the initial concentration of hydrogen gas
$\mathbf{H_t}$ is the concentration of hydrogen gas at time t

Therefore, the Diffusion Rate Adjusted to 25°C (298.15 K), D'_{25C} is then:

TEMP. TRANSFORMATION EQN. $$D'_{25C} = \frac{D'\,T}{298.15\ K}$$