Tritium Stripping in a Nitrogen Glove Box Using FAES ST 198 (U)

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SUMMARY

Six tritium stripper experiments which mock-up the use of a SAES St 198 stripper bed for a full-scale (10,500 liter) nitrogen glovebox have been completed. Experiments consisted of a release of a small quantity of protium/deuterium spiked with tritium which were scaled to simulate tritium releases of 0.1 g., 1.0 g., and 10 g. into the glovebox. The tritium spike allows detection using tritium ion chambers. The St 198 stripper system produced a reduction in tritium activity of approximately two orders of magnitude in 24 hours (6-8 atmosphere turn-overs) of stripper operation.

INTRODUCTION

SAES metal getter material St 198 was chosen for glovebox stripper tests to evaluate its effectiveness of removing tritium from a nitrogen atmosphere. The St 198 material is unique from a number of other metal hydride-based getter materials in that it is relatively inert to nitrogen and can thus be used in nitrogen glovebox atmospheres.

Metal hydride based-getters have the advantage over traditional catalytic oxidation methods for glovebox tritium removal in that no tritium oxide is formed. Previous work in CHTS was performed on the St 198 material to evaluate its deuterium absorption and material phase characteristics[1] and its ability to remove deuterium from a flowing nitrogen stream[2]. This work is to complete the initial testing of the St 198 material by using it in a tritium environment. Also, recent work in the SRTC Materials Test Faciltiy[3] has involved

the use of a St 198 stripper on a system for analyzing source gas from exit signs. In this system, the source tubes are opened in an atmosphere of Ar/4% protium. Following gas analysis, the hydrogen isotopes are gettered on a St 198 column prior to stacking the gas through the vacuum pump. This system has been operated at room temperature with periodic high temperature activation occuring every 2-3 weeks. Only a slight increase in the hood activity level is normally observed when the tube sampler is evacuated and the gas is pumped to the stack.

The stripper tests described here were conducted at glovebox pressures and at elevated bed temperatures. Glovebox tests were conducted in the MTF Metal Hydride Research Inert Glovebox to simulate tritium releases within a full-scale (10,500 liter) glovebox and the clean-up capabilities of the St 198 material. This report describes the results of these tests.

EXPERIMENTAL

MTF Inert Glovebox

The MTF Metal Hydride Research Inert Glovebox is a Vacuum/Atmospheres Corporation model HE-43 stainless steel glovebox. The glovebox was operated with an inert atmosphere of nitrogen for glovebox testing of tritium stripping of SAES St 198 using deuterium spiked with a very small amount of tritium. The tritium spike will allow detection of the gas using tritium ion chambers and cleanup rate of the glovebox atmosphere. Maximum gaseous inventory in this glovebox is limited to 50 curies of tritium. The glovebox was operated at a pressure of approximately -0.5" of water (with respect to atmospheric pressure) during these tests.

Figure 1 shows a piping schematic for the glovebox. Bubblers are used for positive/negative pressure protection while the pressure controller is used to control the glovebox pressure. A liquid nitrogen Dewer is used to supply nitrogen for pressure control and for glovebox purging. A vacuum pump is used for pressure control and evacuation of the Ante-chamber. A blower located in the room hood is used for purging the glovebox. The glovebox is nominally 620 liters with the Ante-chamber nominally 72 liters. Two gloveports are installed in the front panel of the glovebox.

The active chamber of a Femto-Tech Model 224-DU ion chamber (IC) is installed in the side of the glovebox for measuring glovebox activity. This IC gives direct activity readings in $\mu Ci/m^3$. A Teledyne model A0-316-C fuel cell oxygen detector was used to determine glovebox oxygen levels. A diaphragm pump located in the glovebox was used to supply the glovebox atmosphere to the oxygen sensor.

Figure 2 shows a schematic of the stripper system installed inside the glovebox. The glovebox atmosphere is drawn through the stripper system by a blower at the end of the stripper system. The atmosphere passes through a filter, through a mass flow meter and then to Ion Chamber #1 (IC#1). The flow from IC#1 can either flow through or by-pass the stripper column before flowing to Ion Chamber #2 (IC#2). The flow from IC#2 passes through a surge volume and then onto the inlet of the blower. The blower exhausts to the glovebox atmosphere.

Ion chambers #1 and #2 were constructed by EES. These chambers were cylindrical, stainless steel chambers having an active volume of 1.0 liters. A potential of 600 VDC was supplied using a Fluke high voltage power supply, and the ion currents were measured using Keithley model 617 electrometers. The currents from these two chambers as well as the activity from the femto-TECH glovebox ion chamber were logged using a data acquisition system using the IEEE488 interface on these instruments. Data acquisition consists of a Macintosh computer using National Instruments, Inc. labVIEW® version 2.2.1 software and NB-DMA2800 (IEE488) and NB-MIO-16L (A/D) boards. The data logged are the time, glovebox activity, IC#1 current, IC#2 current, the glovebox differential pressure (differential to atmospheric pressure), and the flow rate.

The flow rate through the stripper system is controlled by adjusting the position of a needle valve between the surge volume and the blower, a Fuji VFC084P Ring Compressor, and is measured using a 20 SLPM Tylan mass flow meter (MFM). The inlet of the MFM is fitted with a 2μm filter to prevent introduction of particulates into the stripper system. A 2μm filter is also attached to the outlet of the column to trap any fines generated by the bed and to prevent particulate contamination of IC#2. A copper cooling coil follows this filter and is to cool the hot stripper gas stream before it reaches the 3-way ball valve.

The design size of the full-scale glovebox is a nominal 10,500 liters with a 5 CFM stripper flow rate while the MTF glovebox is 620 Liters -- roughly a 17:1 ratio on glovebox volumes. To match the glovebox atmosphere turn-over times for the two gloveboxes, a flow rate of 0.291 CFM or 8.25 LPM (7.65 SLPM) is needed for the MTF stripper flow rate to have the same 74 minute turn-over time as the full-scale glovebox. Previous tests of the stripper system, with a different bed design and stripper material, showed the system capable of developing flows up to 15.6 SLPM through the system (Ref. 4, p. 37).

Test Stripper Bed and Heater Block Design

The reactor vessel used for the tests was an existing reactor vessel and a sketch is shown in Figure 3. The reactor is fabricated from 1-1/4" schedule 40 stainless steel pipe. A metal screen is soldered into the bottom of the vessel and is used to contain the getter material. The bottom is a flat end-cap fitted with a 4-VCR gland and nut for flow out of the reactor. The top of the vessel is a 2-3/4 inch Conflat flange welded to the pipe. The inlet fitting is a commercially fabricated 4-VCR gland with nut welded to a 2-3/4 inch Conflat fitting.

The reactor internal length is 5.85 inches and has an external length of 7.0 inches from the flat bottom to the top Conflat flange. The internal volume of the reactor bed was estimated geometrically to be 143 cm^3. The vessel was proof check at 300 psia and and leak-checked with helium before being put into service.

To heat the reactor, a brass heater block was machined and a sketch is also shown in Figure 3. The block is drilled through its center where the bed can be lowered into it. Six 0.25 inch holes are drilled through the block for insertion of heater cartridges and thermocouples. The block was wrapped with insulation and aluminum foil to reduce heat losses to the glovebox from the block.

Two 200 watt or two 300 watt heater cartridges were wired in parallel and placed into positions 1 and 4 or positions 3 and 5 for heating the block. The power to the heater cartridges was controlled using a variable voltage power supply (variac). The temperature of the block was adjusted by manually varying the voltage to the heater cartridges.

Temperature measurements of the heater block were made using a Type K thermocouple (TC) enclosed in a 1/8 inch OD stainless steel sheath placed in position 2 of the heater block. The TC temperature was read from a TC display placed in the glovebox and recorded manually in a laboratory notebook. This temperature is the only temperature measurement reported for these tests. Future reactor designs will have a thermowell positioned in the reactor bed to more accurately monitor the temperature of the getter material.

Bed Loading and Activation

One bed, Bed #4, was used for all tests and was filled with 427 grams of SAES St 198. The material was evacuated at approximately 460°C for over 24 hours. During activation, the evacuation manifold pressure was less than $3x10^{-6}$ torr, as indicated by a cold-cathode ion gauge. Also, a Pirani gauge attached to the inlet fitting of the bed was below its resolution, $1x10^{-3}$ torr, by the end of the material activation. The bed was back-filled with 1 atm of nitrogen, capped, and passed into the glovebox for installation into the glovebox stripper system.

Tritium Release Samples

In order to maintain low gas phase tritium inventories in the Metal Hydride Research Inert Glovebox, the tests were conducted using protium/deuterium spiked with 0.3-4.0 curies of tritium. The tritium spike allowed detection of the gas using the tritium ion chambers. The basic assumption in these tests is that St 198 getter material has the same affinity for tritium as it has for protium and deuterium.

A standard mixture of nominally 1% tritium and 99% protium was used for preparing tritium mixtures for release into the glovebox. A predetermined pressure of the standard was filled into an evacuated sample cylinder and then deuterium added to obtain the desired total pressure of hydrogen isotopes. The sample cylinder would then be placed in the glovebox and the sample released into the glovebox via an air actuated valve: the air actuated valve was opened for 10 to 30 seconds to allow only the gas above atmospheric pressure to be released into the box. The valve was then closed for the duration of the test.

The total amount of hydrogen isotopes to be released was scaled to simulate pure tritium releases into the full-scale glovebox of 0.1 g., 1.0 g., and 10 g. Initial oxygen control was obtained by purging the glovebox with nitrogen before the start of the of the first test to 34 ppm oxygen. Subsequent oxygen levels were maiintianed by the oxygen gettering rate of St 198.

RESULTS

Bed Flow Rate and Glovebox Turn-over Time

It was discovered during the course of testing that the maximum flow rate through the bed was 6.5 SLPM at 26°C and that the flow rate through the bed decreased as the temperature of the heater block was increased. For the tests conducted, the maximum flow rate varied between 2.1 to 3.4 SLPM, depending on the test temperature, and no attempt was made to reduce the gas flow from its maximum rate. It is uncertain if the decreased flow rate is due to swelling of the getter material or the porous frit of the bed or increased flow resistance of the heated gas.

The flow rates of 2.1 to 3.4 SLPM would give residence times in the bed of 1.7 to 1.0 seconds at 22°C and much shorter actual residence times due to the temperature increase of the gas as it flows through the bed. These flow rates give glovebox turn-over times of 273 minutes (4.6 hours) and 169 minutes (2.8 hrs), respectively. The desired flow rate of 7.56 SLPM would have given a bed residence time of less than 0.5 seconds at 22°C. It is hoped that future tests can be conducted at this flow rate for evaluation of the getter material at shorter residence times.

Ion Chamber Scale Factors

To convert current measurements from IC#1 and IC#2 to tritium activity, IC current data were compared to glovebox activity data. IC data were collected with the stripper in the by-pass position with a nominal glovebox activity of 16,000 $\mu Ci/m^3$ as measured by the low range scale of the femto-TECH glovebox ion chamber. The glovebox activity was divided by the IC current measurement and tabulated. These data were averaged and used to convert IC current data to

activity. The average and standard deviations for IC#1 are $1.020x10^{+15}$ and $1.149x10^{+12}$ $\mu Ci/m^3$/amp and for IC#2, $9.972x10^{+15}$ and $1.943x10^{+12}$ $\mu Ci/m^3$/amp, respectively. These values were used for all computations unless stated otherwise.

Initial Stripper Results

Figure 4 shows the activity data for the first St 198 test: Glovebox Test #10. The block was heated to approximately 420°C with the stripper in the by-pass position before valving in the column and releasing the "0.1 gram" tritium sample (0.29 Ci, 25.4 STP-cc hydrogen isotopes).

As can be seen in Figure 4, the glovebox and the calculated IC#1 activity data are in quite good agreement. IC#2 shows an initial increase in measured activity in the first 5 hours of the test and then decreases as IC#1 activity decreases. Oxygen levels in the glovebox also decreased rapidly as the test proceeded. Both glovebox activity and oxygen levels decreased until the background activity level, approximately 10,000 $\mu Ci/m^3$, was reached and the oxygen level stabilized near 10 ppm. A failure of the data acquisition system resulted in a loss of data between 14 and 24 hours into the test.

"1 Gram" Release Results

The second test on Bed #4, Glovebox Test #11, showed that at suitably low temperatures, the St 198 material will getter oxygen in a glovebox, but not hydrogen isotopes under these conditions. Furthermore, the test also showed that the gettering ability of the material can be recaptured by heating the bed to a sufficient temperature to start the gettering of hydrogen isotopes.

Figure 5 shows the results of Test #11 and Test #11 Clean-Up Test (C-U)-- the clean-up due to failure of the heater cartridges. For Test #11, the initial glovebox oxygen content was 160 ppm and after releasing the "1.0 g" tritium sample (0.49 Ci, 217 STP-cc hydrogen isotopes), the glovebox activity was at 678,000 $\mu Ci/m^3$. After 2.7 hours, the oxygen level has dropped to 35 ppm while the tritium activity had not decreased appreciably (618,000 $\mu Ci/m^3$). To aid gettering of the tritium, the power to the heater was increased and the tritium activity of IC#2 dropped greatly at the elevated temperatures.

Unfortunately the power increase used to increase the gettering rate also caused the heater cartridge to fail and thus stop the oxygen and tritium gettering of the material. Initially, the block temperature had exceeded 515°C during this heating and the power to the heaters decreased. At 7.5 hours into Test #11, the block temperature was at 485°C, IC#2 was indicating 5644 $\mu Ci/m^3$, the oxygen level of the glovebox was 24 ppm, and the flow rate down to 2.1 SLPM. The increase in IC#2 activity after this time was used to infer that this was the approximate time that the heaters had failed. The glovebox activity did not change after 8 hours until data logging was stopped after 27 hours, indicating athat the heater failed at after 8 hours.

A new set of heater cartridges was installed and a "clean-up" of the glovebox initiated: Test #11 Clean-Up Test. The data from the clean-up test is shown to arbitrarily start at 10 hours; although, the actual test did not start until approximately 49 hours after the initial sample release (time = 0).

The Test #11 Clean-Up Test started at a block temperature of 29°C, an oxygen level of 47 ppm, and a flow rate of 6.5 SLPM. The power to the heaters was increased to initiate the test. Figure 5 shows that with the getter starting at ambient temperature, heat can be applied to the material to initiate the tritium gettering reaction -- vacuum evacuation of the material is not required to regenerate its activity. After approximately 20 hours, the glovebox was stripped to near background tritium levels and the oxygen level was down to 11 ppm. The final block temperature was 354°C and the flow stabilized at 2.8 SLPM.

Figure 6 shows the stripping results of 3 additional "1 g" releases (all 0.4 Ci, 217 STP-cc hydrogen isotopes) plotted along with Test #10 results for comparison: the final block temperatures are shown with the test number.

Test #12 was conducted to see if a greater gettering rate could be obtained by heating/reactivating the bed without flow for greater than 16 hours and then operating the bed at a temperature higher than the Test #11 Clean-Up Test. Test #13 was a repeat of Test #12, with no change in operating conditions, to determine the repeatability of the stripper run and the change in performance of the material with an additional loading of hydrogen isotopes. Test #14 was conducted at a temperature lower than Test #12 to determine the temperature effect

on the gettering rate and if a lower background tritium activity would be obtained in the glovebox.

Figure 6 shows little if any difference in the gettering performance of the material for the four tests. There is little noticeable difference in stripping ability between a "0.1 g" test and the "1.0 g" tests, minimal temperature affect, and minimal affect on the continual increase in hydrogen isotope loading of the material. Increasing the flow rate or lowering the block temperature would probably show some decreased clean-up performance.

"10 Gram" Release Results

To determine the capacity of the St 198 getter material, Test #15 was conducted where a simulated "10 g" sample was release into the glovebox. (4.0 Ci, 2206 STP-cc hydrogen isotopes). The glovebox activity as a function of time is shown in Figure 7. At a block temperature of near 300°C, the tritium removal rate is moderately slow, but still occurs. After 65 hours, the power to the heaters is increased and then increased again to see if the gettering rate can be increased by increased temperature.

It was discovered that after increasing the heater power the second time, IC#2 activity significantly exceeded the IC#1 activity and the activity of the glovebox was increasing. When this was discovered, the heater power was decreased and the bed initially showed improved gettering kinetics. This improved stripper rate lasted only a few hours before bed returned to its previous performance levels.

Decontamination Factors

Glovebox decontamination factors (DFs) for the tests, the ratio of the maximum glovebox activity to the minimum glovebox activity, were calculated for tests. A summary of the test results are shown in Table 1. The values for Test #15 were calculated for the last values shown in Figure 7.

Table 1. Selected Summary of Test Data

Test =	#10	#11	#11 C-U	#12	#13	#14	#15
Simulated Tritium Release (g)	0.1	1.0	N/A	1.0	1.0	1.0	10.1
Initial Block Temp. (°C)	418	296	26	449	429	366	316
Final Block Temp. (°C)	278	29	354	429	435	337	231
Initial O_2 (ppm)	34	160	47	60	21	9	18
Final O2 (ppm)	10	21	11	12	12	8	5
Initial Flow (SLPM)	2.6	3.3	6.5	2.2	2.2	2.6	2.9
Final Flow (SLPM)	3.4	6.6	2.8	2.2	2.3	2.8	3.4
DF	125	3	139[a]	112	75	85	43

[a]Calculation based on maximum concentration at start of Test #11

DISCUSSION

The St 198 showed good gettering ability for controlling oxygen levels in the glovebox despite the glovebox operating pressure of -0.5 inches of water (with respect to atmospheric pressure). At a heater block temperature above 278°C for these tests, the St 198 material will getter hydrogen isotopes in the presence of oxygen at a sufficient rate for glovebox clean-up operations. At lower temperatures, the oxygen gettering of the material does not allow absorption of the hydrogen isotopes to proceed at a sufficient rate for glovebox clean-up operations. At these lower temperatures the oxide formation on the surface of the material is thought to inhibit hydride formation; higher temperature are thought to cause the oxides to diffuse into the bulk of the material, leaving a surface capable of hydride formation.

Stripper tests performed with block temperatures between 278°C and 435°C and at the relatively low flow rates of 2 to 3 SLPM showed virtually identical glovebox clean-up performance. DFs of approximately 100 were obtained in 24 hrs (6 to 8 glovebox turn-overs). Higher flow rates should show an increased dependence on flow

rate and getter temperature. It is believed that the persistent background activity level on the order of 10^4 $\mu Ci/m^3$ prevented higher DFs from being realized. This background activity results from tritium being absorbed into the glovebox materials (seals, gloves, electrical insulation, etc.) during the initial phase of the tests and then slowly being released when the activity decreased toward the background limit (<15,000-20000 $\mu Ci/m^3$). It is also likely that some of the high background results from internal contamination of the tritium ion chambers. Background tritium activities had also been observed in previous stripper tests in this glovebox using a Pd/zeolite oxidative stripper material.[4] In these tests a background activity of 5,000-12,000 $\mu Ci/m^3$ was commonly observed.

CONCLUSIONS

The tritium getter material, SAES St 198, is a promising candidate for further investigation related to its use in tritium stripping applications. The fact that it is relatively inert to nitrogen gas makes it one of the few getter materials available for decontamination of nitrogen atmospheres without conversion of elemental tritium to tritium oxide. For a small glovebox such as the MTF Metal Hydride Research Inert Glovebox, it is an ideal material for tritium stripping operations and glovebox oxygen control for low oxygen level operations. The ability to maintain a negative pressure glovebox at oxygen levels near 10 ppm and be able to strip tritium in one compact stripper unit is highly desirable when limited space is available in the glovebox and external stripper systems are not practical due to cost or space limitations.

Additional testing should be conducted with an oxygen getter preceding the St 198 material so the impact oxygen has on the gettering rate can be eliminated as a variable. SAES markets a suitable alloy (ST 909) which is able to absorb oxygen and to crack water, methane, and ammonia. Alternate materials such as uranium-238 might also serve well in this function. The oxygen getter would allow the capacity of the actual St 198 to remain constant. The gettering of oxygen will lower the hydrogen isotope capacity of the stripper material through the formation of stable metal oxides.

The tests described in this document were scoping in nature. A number of unanswered questions remain, such as our ability to recover stripped

tritium from the getter material. In principle, hydrogen isotopes absorbed by the metal hydride-based stripper can be desorbed and recovered on a tritium manifold. This has yet to be demonstrated, however, it is apparent that high temperatures (>550°C) and high vacuum are needed to accomplish this.

A number of improvements and design changes are suggested as a result of this study. A bed design with a thermowell in the getter material and tests conducted at shorter residence times are needed to better characterized the stripping performance of the material. Furthermore, ion chambers fabricated to eliminate high activity backgrounds should be used for future tests to determine the actual DFs for the material (fabricate ICs with ceramic insulators and electropolished surfaces and operate them at elevated temperature).

This study tested the effectiveness of St 198 in a small-scale, but fully operational inert-atmosphere tritium glovebox. While tests using flowing gas streams are useful, a number of other factors such as high backgrounds activity levels and oxygen permeation are encountered with actual negative-pressure gloveboxes. In this situation the material was shown to perform satisfactorily.

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5. J. R. Wermer, J. E. Klein, "Testing of Pd/Zeolite in a Tritium Glovebox," USDOE Report SRT-HTS-94-0125 (Draft).

Figure 1. Glovebox Piping Schematic

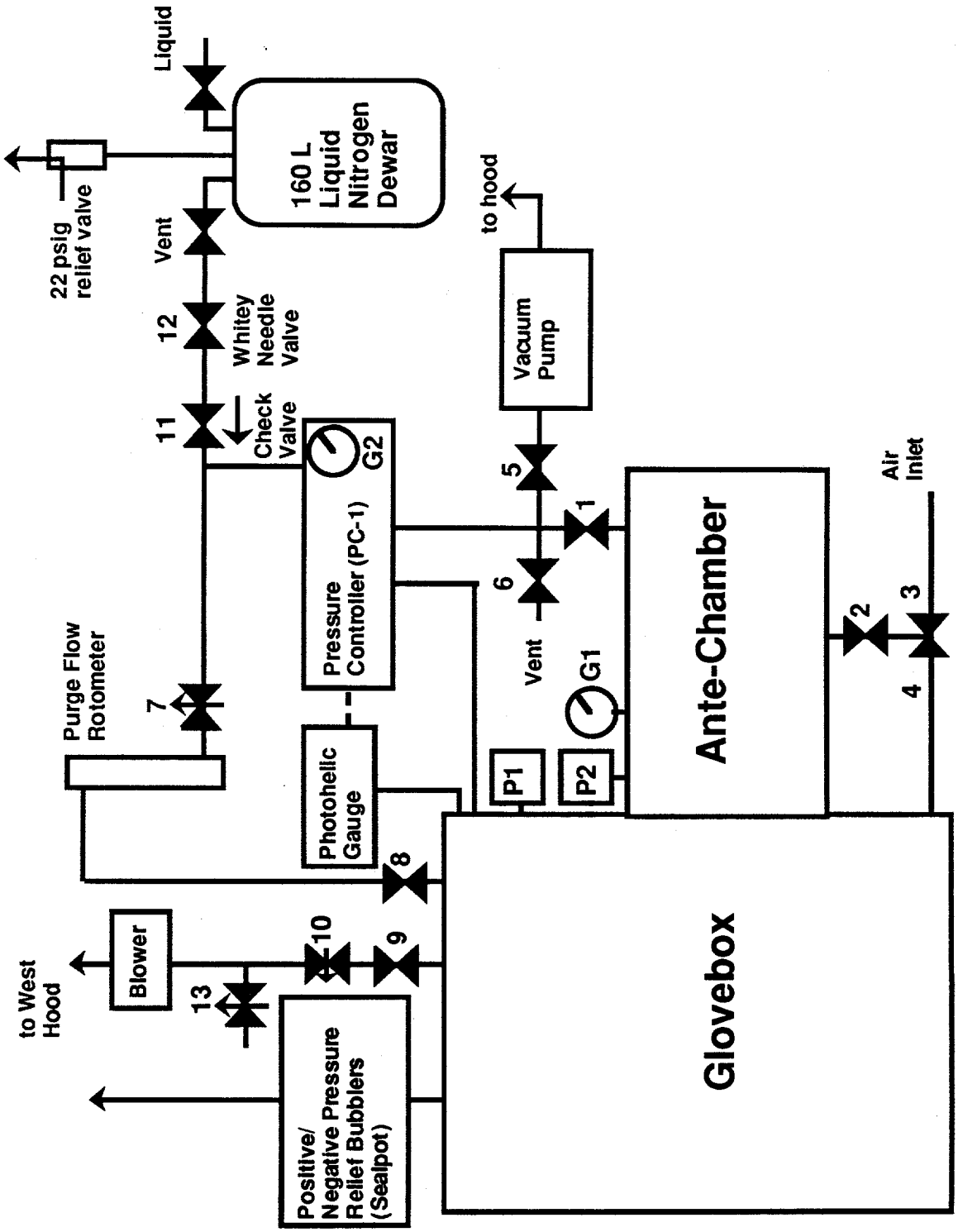

Figure 2. Stripper Flow Schematic

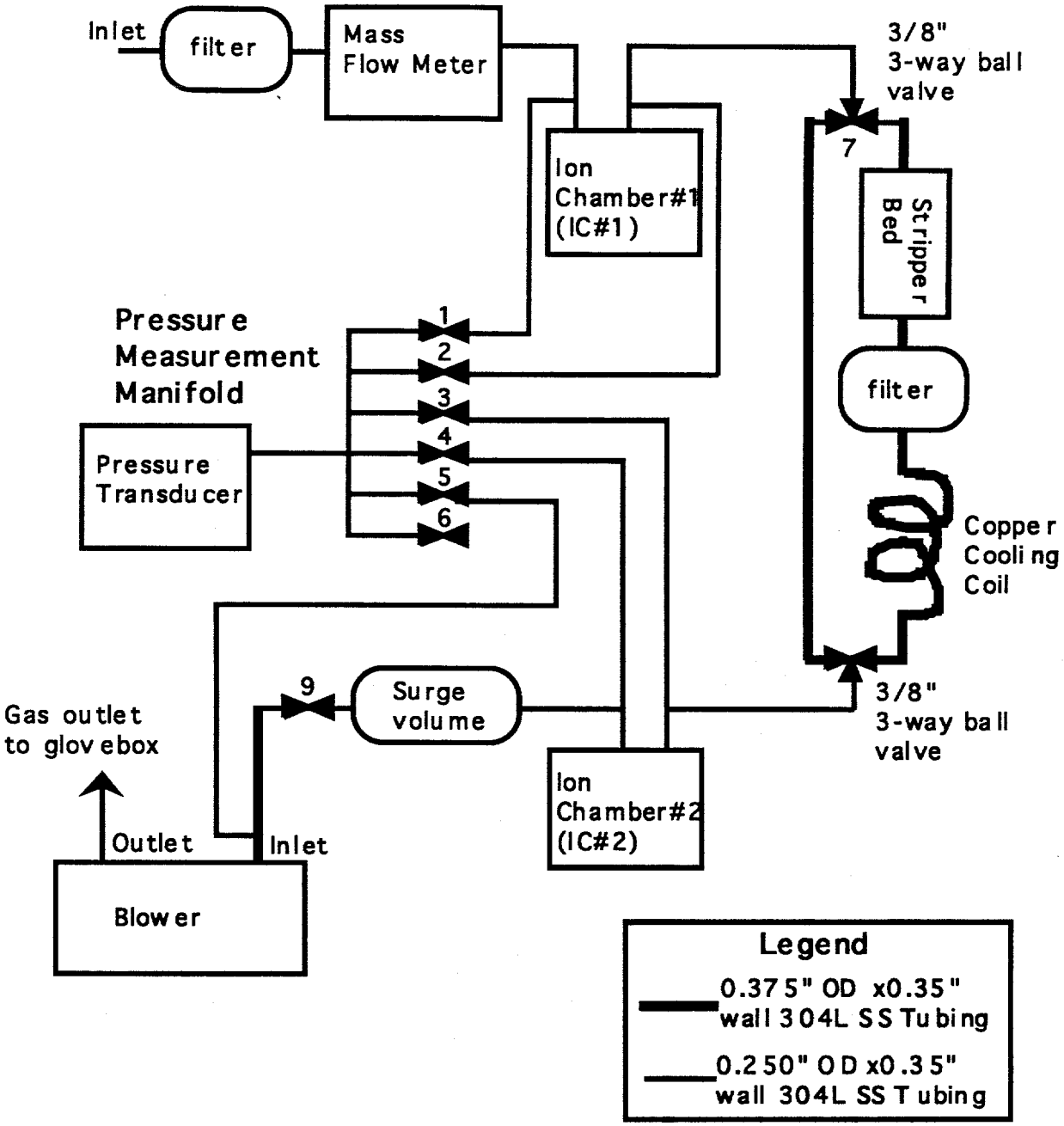

Figure 3. Bed and Heater Block Sketches.

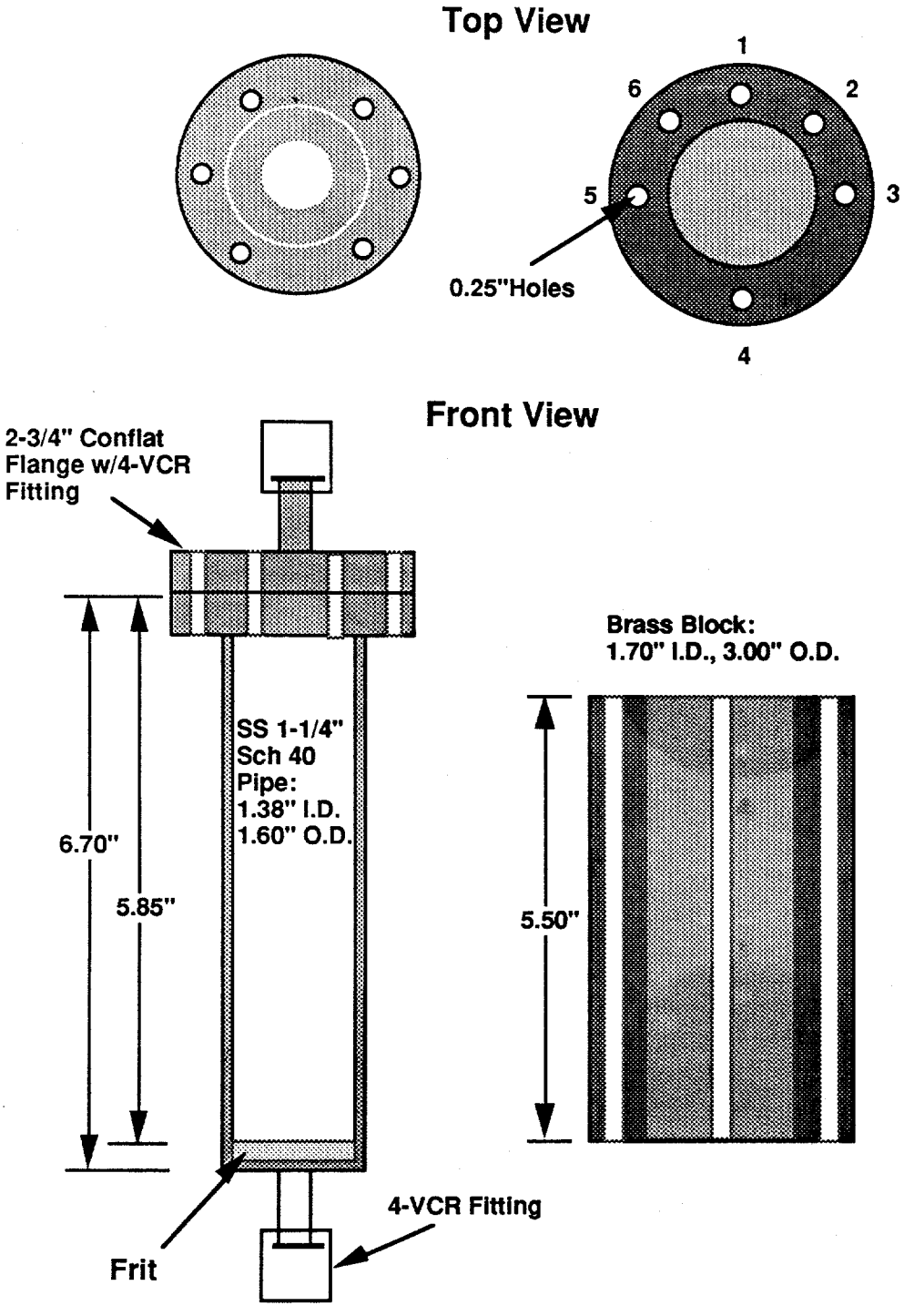

Figure 4. Test #10 Results

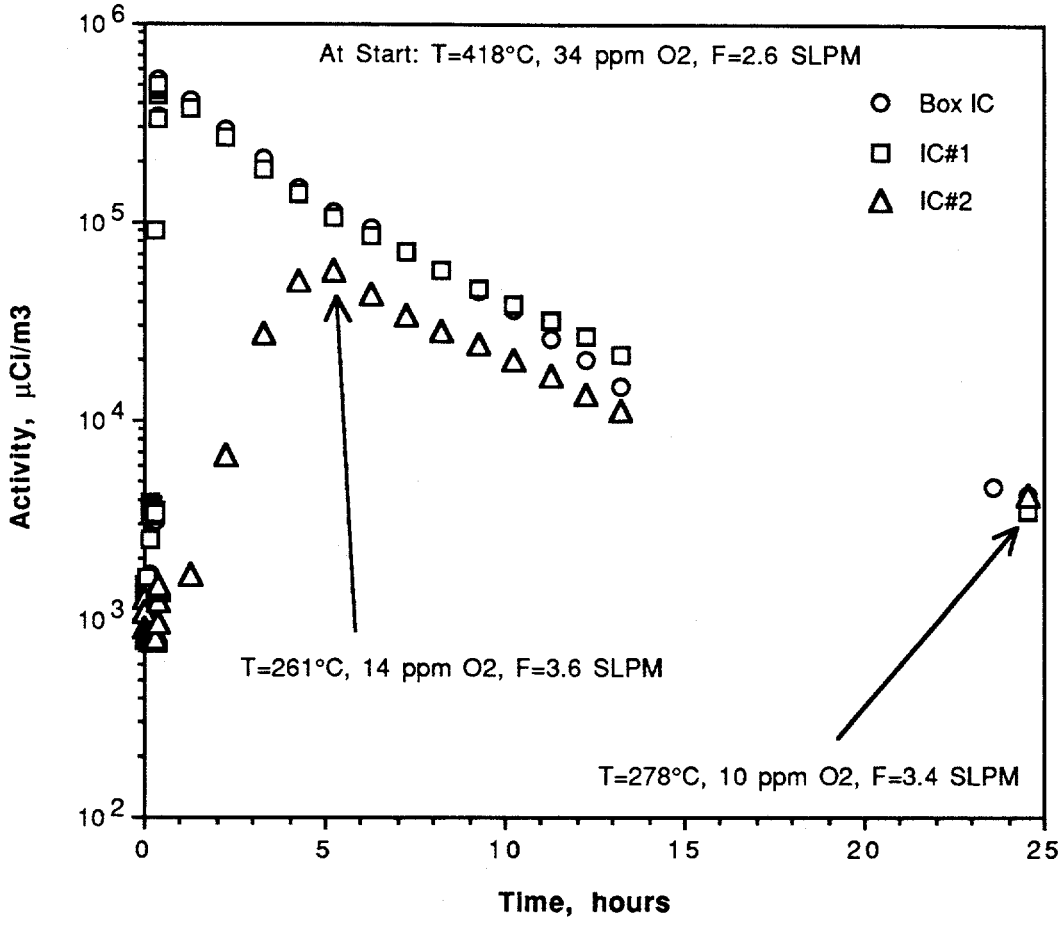

Figure 5. Test #11 and Clean-Up Results

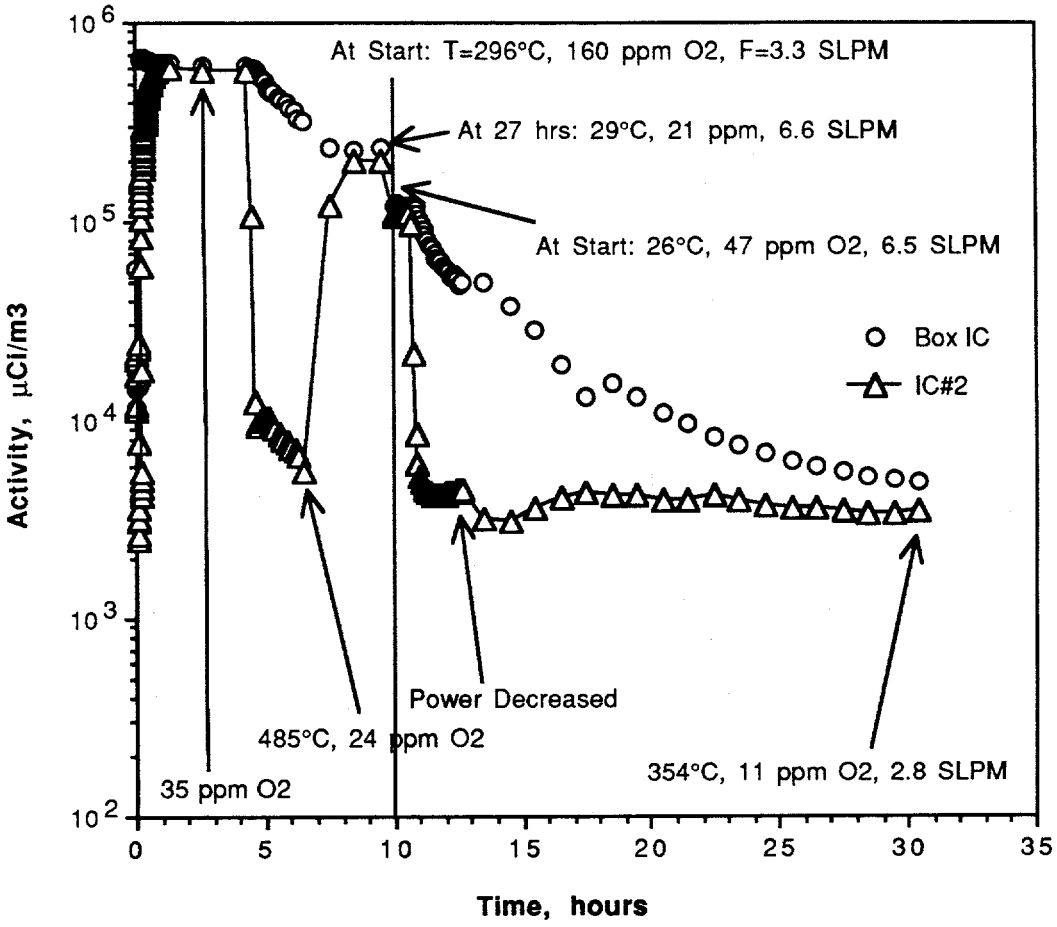

Figure 6. Comparison of Stripper Runs

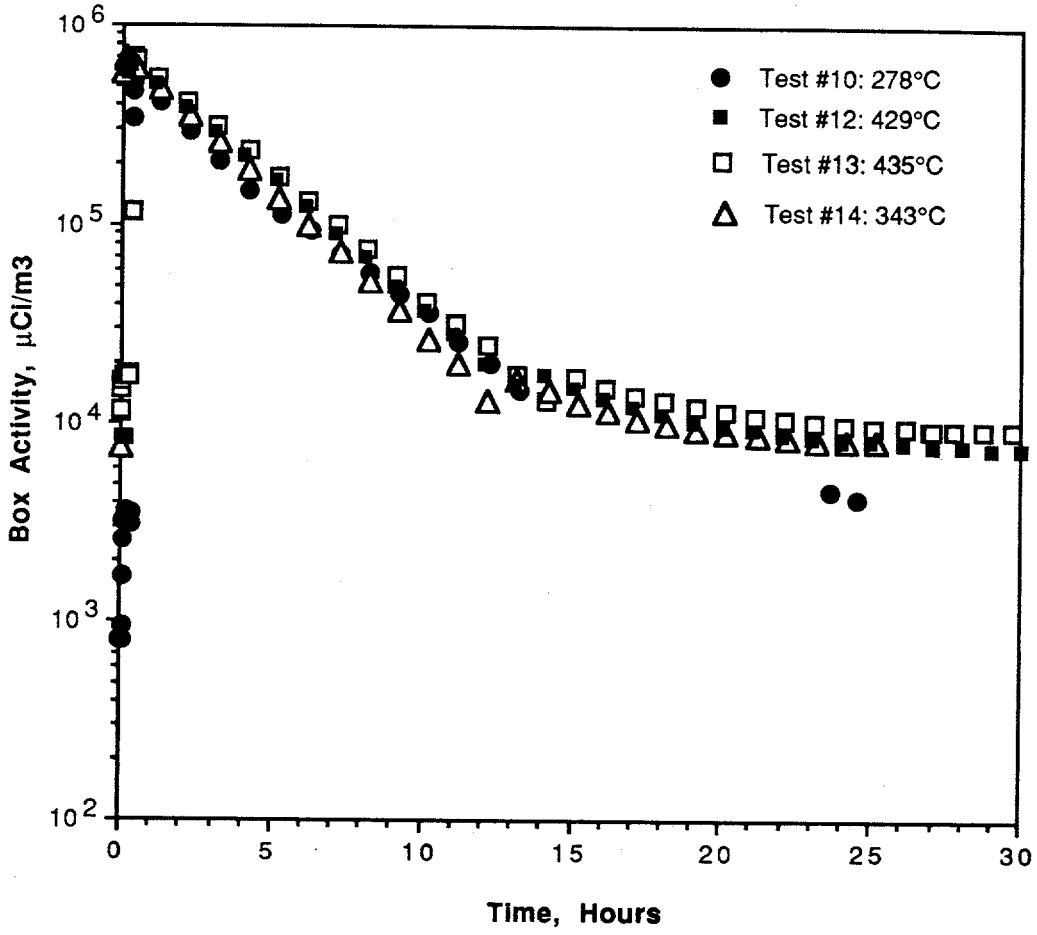

Figure 7. Test #15 "10g" Test