

**This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.**

**DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

WSRC-MS-2004-00573

August 12, 2004

Keywords: TCAP  
Detritiation  
Process Stripper

**NEW SYSTEMS FOR WASTE PROCESSING OF TRITIUM-CONTAINING GASES  
AT THE SAVANNAH RIVER SITE**

A. S. Poore and W. D. Jacobs

Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC 29808 USA  
[anita.poore@srl.doe.gov](mailto:anita.poore@srl.doe.gov) and [william.jacobs@srl.doe.gov](mailto:william.jacobs@srl.doe.gov)

Paper prepared for  
Tritium 2004: 7th International Symposium on Tritium Science and Technology  
Baden-Baden, Germany  
September 12 – 17, 2004

And to be published in the proceedings.

Peer review comments incorporated 1/18/05

# NEW SYSTEMS FOR WASTE PROCESSING OF TRITIUM-CONTAINING GASES AT THE SAVANNAH RIVER SITE

A. S. Poore and W. D. Jacobs

Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC 29808 USA  
[anita.poore@srnl.doe.gov](mailto:anita.poore@srnl.doe.gov) and [william.jacobs@srnl.doe.gov](mailto:william.jacobs@srnl.doe.gov)

*A project to relocate and consolidate tritium processing activities from old, second generation buildings to newer buildings was initiated in the late 1990's at the Savannah River Site. The new waste gas processing systems located in the newer facility utilize recent technology, including metal getters, an innovative permeator design, and TCAP (Thermal Cycling Absorption Process) technology for removal of residual tritium prior to releasing the effluent to the environment. Startup testing results (using protium and deuterium) and corresponding lessons learned for these systems are presented. These systems have since successfully completed tritium startup testing and are operational.*

## I. INTRODUCTION

The Tritium Facilities at the Savannah River Site (SRS) were built to process tritium. Older buildings and their process systems are being decommissioned by relocating or replacing process systems into newer buildings.

A project to relocate and consolidate tritium processing activities from older second generation buildings to newer buildings was initiated in the late 1990's at SRS. The consolidation of the tritium gas processing activities into the newer tritium facilities improves safe operations, reduces environmental releases, improves productivity, and significantly reduces future operating costs.

One of the key aspects of the "tritium consolidation" project was to replace two gaseous process waste detritiation systems from an older facility. The two tritiated gaseous process waste streams are (1) a non-hydrogen stream (containing primarily nitrogen and inert gases) and (2) a hydrogen (primarily protium) stream from the glovebox cleanup regeneration system. These new waste processing systems have been installed, placed in negative pressure gloveboxes and utilize recent

technology for removal of residual tritium from the process waste gas stream prior to releasing the effluent to the environment. This paper focuses on the startup results of protium-deuterium testing and their lessons learned for the two new gaseous process waste detritiation systems.

## II. DETRITIATION OF NON-HYDROGEN PROCESS WASTE GASES

Tritiated non-hydrogen process waste gases are currently processed through a conventional oxidative catalytic stripper system and molecular sieve beds. The new Tritium Process Stripper (TPS) utilizes a metal getter and permeator system<sup>[1]</sup>. This is the first large-scale, industrial application of a metal getter system in tritium processing. The primary duty of the TPS is to remove hydrogen isotopes from gas streams containing non-hydrogen process waste gases (nitrogen and inert gases) prior to their release to the stack. The TPS is also used to remove nitrogen or inert gases from hydrogen-rich streams prior to further processing by the TCAP (Thermal Cycling Absorption Process) system.

### II.A. TPS System Design and Performance Requirements

The major components of the TPS shown in Figure 1 include:

- An oxygen getter consisting of a zirconium-manganese-iron alloy (SAES ST-909<sup>®</sup>) removes oxygen and reduces hydrogen compounds to elemental hydrogen.
- Standard palladium/silver diffusers (also known as permeators) and a custom-built low pressure diffuser<sup>[2]</sup> remove hydrogen isotopes.
- A hydrogen getter consisting of a zirconium-iron alloy (SAES ST-198<sup>®</sup>) cracks water and removes residual hydrogen isotopes.

Individually, these components were demonstrated in bench- or pilot-scale testing but they have not been integrated in a production system prior to the operation of the TPS.

The typical TPS feed stream contains process waste gases containing 1% to 3% hydrogen isotopes (<1% tritium), balance nitrogen or inert gases. The hydrogen-rich TPS feed gas stream contains >90% hydrogen isotopes (protium and/or tritium) in nitrogen and is necessary to purify hydrogen isotopes (nitrogen- and inert-free) prior to further processing in the TCAP system. Contaminants in either TPS feed stream may include small amounts of oxygen, ammonia, and carbon compounds. The feed flow rates are designed to be  $2.5E-4 \text{ m}^3\text{s}^{-1}$  (15 standard liters per minute, slpm) for the non-hydrogen feed stream and less than  $1.7E-5 \text{ m}^3\text{s}^{-1}$  (1 slpm) for the hydrogen-rich feed stream. The TPS design basis output requires a hydrogen isotope gas stream that contains greater than 99.9% hydrogen isotopes and a stackable non-hydrogen gas stream that releases less than 5 ppm tritium to the environment.

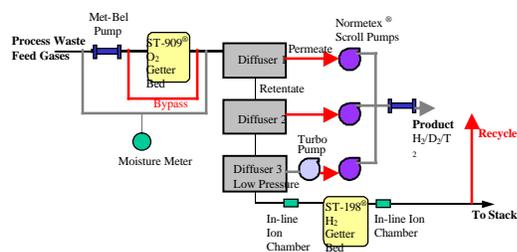


Figure 1 Tritium Process Stripper (TPS) Schematic

## II.B. TPS Startup Testing Results

Integrated system testing for the TPS began with non-tritiated feed streams to evaluate the system's performance and capabilities. Initial test results with a nitrogen carrier feed gas containing 2% protium showed diffuser stage flooding (high permeate-side pressures) at  $3.3E-6 \text{ m}^3\text{s}^{-1}$  (0.2 slpm), where flow rates up to  $2.5E-4 \text{ m}^3\text{s}^{-1}$  were expected. Modifications to the system's vacuum lines were made to improve conductance, particularly for the third stage low pressure diffuser.

Further testing indicated problems with the flow control for the hydrogen-rich feed gas, and ammonia was observed at the exit of the ST-909<sup>®</sup> and each of the diffuser stage retentate exits. It was suspected the nitrogen holdup in the ST-909<sup>®</sup> getter bed and hot catalytic surfaces caused the ammonia formation during processing. Tests using argon as the carrier gas and bypassing the ST-909<sup>®</sup> getter bed show the ammonia formation was decreased, confirming the ST-909<sup>®</sup> getter bed in combination with a high nitrogen hold-up and hydrogen-rich feed gas was the

cause of the ammonia formation. Design modifications to add a bypass line around the ST-909<sup>®</sup> getter bed and the use of ammonia-compatible flow control valves, along with administrative controls, were implemented. A recycle line was also added at the exit of the ST-198<sup>®</sup> getter bed to allow reprocessing of any gas that does not meet the stackable criteria for tritium.

Final cold startup tests at typical feed compositions were performed to evaluate the design modifications and to determine the system response. During this test, the diffuser tube pressures were held constant, as were the temperatures in the getter beds and diffuser stages. The ST-198<sup>®</sup> getter bed was on-line at all times. The results of these tests are given in Table 1<sup>[3]</sup>.

Table I Final TPS Cold Startup Test Results at  $6.6E-5 \text{ m}^3\text{s}^{-1}$  (4.0 slpm) Feed Rate

Feed Gas Composition, vol%		ST-909 <sup>®</sup> By-passed?	Exit Concentration at 3rd DI stage (retentate), ppm		ST-198 <sup>®</sup> Exit Concentration, ppm	
H <sub>2</sub>	N <sub>2</sub>		H <sub>2</sub>	NH <sub>3</sub> (max)	H <sub>2</sub>	NH <sub>3</sub>
5	95	No	0.2	20-30	<1	0
10	90	No	0.4	100-200	0	0
95	5	Yes	0.4	5-10	0	0

The test showed excellent removal of the hydrogen by the three-stage diffuser train. The performance criteria for the hydrogen stream purity and stackable effluent were achieved. Ammonia formation in the ST-909<sup>®</sup> getter bed and in diffuser retentate streams were observed, confirming previous observations. One unexpected, but favorable, result was the apparent cracking of ammonia by the ST-198<sup>®</sup> getter bed. These results suggest that the TPS should be able to achieve the project objective of less than 5 ppm tritium for stack discharges for feed gases containing elemental tritium, tritium oxide and tritiated ammonia. Tritium removal from tritiated methane contaminants remains problematic and is being addressed separately<sup>[4]</sup>.

## III. DETRITIATION OF HYDROGEN-CONTAINING PROCESS WASTE GASES

Hydrogen (protium [H], deuterium [D], and tritium [T]) -containing waste gases have been detritiated using cryogenic distillation for more than 30 years at SRS that is being decommissioned. The new detritiation process for hydrogen-containing process waste gases utilizes the Thermal Cycling Absorption Process (TCAP) technology and is

designed to handle all hydrogen isotopes (H, D, T), unlike the original TCAP which only processed deuterium-tritium (D/T) feed gas mixtures for more than ten years [5]. These hydrogen-containing process waste gases primarily result from regenerating molecular sieve beds in the glovebox tritium stripper system. Typically, these gases contain high concentrations of protium and very little tritium (nominally 0.1%); deuterium may also be present. The new TCAP system, designated “HT-TCAP” to distinguish its function from the older “D/T” processing TCAP unit, primarily separates tritium (T) from protium (H) or protium-deuterium mixtures.

### III.A. HT-TCAP System Design and Performance Requirements

The HT-TCAP system consists of the following major components, shown in Figure 2:

- Metal hydride ( $\text{LaNi}_{4.25}\text{Al}_{0.75}$ ) storage beds store feed and product gases. Large storage tanks are used for stackable raffinate gases.
- The TCAP column and Plug Flow Reverser (PFR) provide hydrogen isotope separation with associated components.

Hydrogen process waste feed gases are stored on  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  metal hydride beds and generally contain less than 1% tritium, balance protium and/or deuterium. The TCAP unit provides hydrogen isotope separation and its technology has been described previously [5]. Stackable raffinate gases, containing less than 5 ppm tritium, are released to the environment. Deuterium gas may be present in both tritium product and stackable raffinate streams.

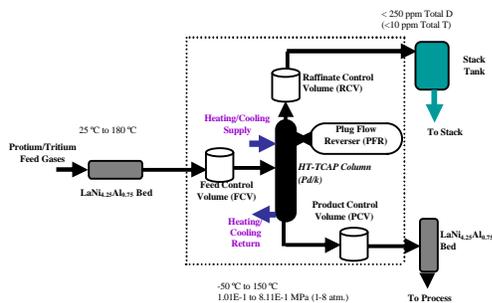


Figure 2 HT-TCAP System Schematic

The quantity of gaseous hydrogen isotopes recovered from the facility’s molecular sieve bed regeneration system is a few hundred thousand liters (STP) per year. To meet this throughput requirement, the HT-TCAP units were designed to contain larger quantities of Pd/k (nominally 50 wt. % palladium deposited on kieselguhr) than previous TCAP columns and to have improved heat transfer characteristics. Aluminum foam was placed in the

interior of the Pd/k column, offsetting the heat transfer limitations obtained by increasing the column’s diameter.

### III.B. HT-TCAP Startup Testing Results

Integrated system testing with hydrogen isotopes was performed using protium-deuterium (HD) feed gas mixtures in advance of tritium testing to evaluate the HT-TCAP system capabilities. Early results from these separation runs showed the raffinate (protium) purities did not meet expectations at several HD feed compositions and feed rates. It was found that decontamination factors (i.e.,  $[\text{D}]_{\text{feed}} / [\text{D}]_{\text{raffinate}}$ ) were less than expected (<10 vs. 50-100 predicted) at the design-basis feed rates. Adjustments to operational parameters were unsuccessful in improving separation performance, though lower feed rates resulted in improved separation.

Evaluation of the unexpected results led to continued facility testing and independent laboratory testing to analyze material and component characteristics. As a result, the Pd/k in the HT-TCAP columns was unloaded and re-loaded with improved packing methodology and radiographic examination criteria.

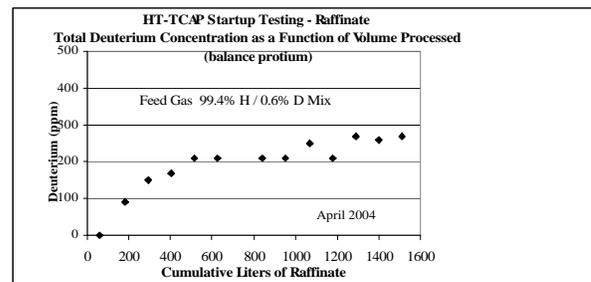


Figure 3 HT-TCAP HD Separation Test Results

The reloaded HT-TCAP columns were then tested with the protium-deuterium feed gases, as shown in Figure 3. Performance tests on the HT-TCAP column with a nominal 99.4% H / 0.6% D feed gas met acceptance criteria for total deuterium in the raffinate (260 – 280 ppm) at reduced feed rates [6].

Additional laboratory testing showed that increasing diameter for a given length reduced the number of separation stages in the Pd/k column, resulting in decreased separation performance. These results contribute to further understanding of the HT-TCAP column’s separation performance [7]. Tritium testing for the HT-TCAP system demonstrated greater separation performance than the protium-deuterium testing, meeting expectations for system operation.

#### IV. LESSONS LEARNED

TPS and HT-TCAP systems startup testing provided challenges due to unexpected system performance. Key lessons learned are highlighted.

##### 1. Late additions to the process flow sheet.

The original feed streams for the TPS were limited to less than 2% total hydrogen isotopes in a nitrogen carrier gas. Bench- and pilot-scale testing at SRS, and work performed at Los Alamos National Laboratory, were used as the basis for the TPS system design. The getter bed had not been tested in the region of hydrogen-rich feed gases added to the TPS flow sheet. Testing showed hydrogen-rich TPS feed stream resulted in ammonia formation that could result in higher than expected tritium releases to the environment. A bypass line was installed and administrative controls for bypassing the ST-909<sup>®</sup> getter bed during processing the hydrogen-rich feed stream will be implemented to minimize ammonia formation in the TPS system.

##### 2. Capability for recycling unacceptable product.

The baseline TPS system design was a once-through operation, where the detritiated effluent was delivered directly to the environment. The Pd/Ag diffusers were expected to provide sufficient hydrogen removal for the TPS process waste feed streams based on their previous process history and the ST-198<sup>®</sup> getter bed would remove any residual hydrogen isotopes. However, contaminants in the process feed gases were found to increase potential tritium releases. A recycle line for the TPS system was added at the exit of the ST-198<sup>®</sup> getter bed for reprocessing unacceptable product, minimizing tritium releases to the environment.

##### 3. Prototype units provide critical information.

TCAP technology has been used in production operations at SRS successfully for more than ten years. However, the new TCAP columns were required to process primarily protium-tritium feed gases at a much higher annual throughput. Due to space limitations in the facility and glovebox, a larger TCAP column was designed. Pre-production testing was limited to heat-transfer and Pd/k packing tests. Uncertainties relating to separation performance were considered an acceptable project risk since TCAP was a "proven" technology. However, the affects of column design changes (e.g. the addition of metal foam and diameter increase) on hydrogen isotope separation performance should have been tested. Full-scale prototype unit testing is recommended for future projects or alternatively, comprehensive laboratory bench-scale experiments should be

employed to determine if significant issues with the design exist.

#### V. CONCLUSION

The new tritium-containing waste gas processing technologies, the tritium process stripper (TPS) and HT-TCAP systems, provided some initial challenges during startup testing. These issues were successfully addressed and the systems have recently started full facility operations.

#### ACKNOWLEDGMENTS

The authors thank L. K Heung, D. W. Howard, R. H. Hsu, and J. E. Klein of the Savannah River National Laboratory, and P. B. Moore, K. L. Sessions, J. M. Horn, and M. L. Autry of the Defense Programs division for their valuable assistance and contributions to this paper.

This report was prepared by Westinghouse Savannah River Company (WSRC) for the United States Department of Energy under Contract No. DE-AC09-96SR18500 and is an account of work performed under that contract.

#### REFERENCES

- [1] R. S. WILLMS, D. TUGGLE, S. A. BIRDSELL, J. PARKINSON, B. PRICE and D. LOHMEIR, "Comparison of Methods for Separating Small Quantities of Hydrogen Isotopes from an Inert Gas," *17th IEEE/NPSS Symposium on Fusion Engineering*, San Diego, CA, October 6-10, 1997, p. 304, IEEE Operations Center (1999).
- [2] D. W. HOWARD, R. S. WILLMS, and S. A. BIRDSELL, "Testing of a Practical Low Pressure Permeator," *18th IEEE/NPSS Symposium on Fusion Engineering*, Albuquerque, NM, October 25-29, 1999, p. 323.
- [3] M. L. AUTRY, "Tritium Process Stripper Startup Performance Tests," *U. S. DOE Report WSRC-MS-2003-00701* (2003).
- [4] J. E. KLEIN, "SAES ST909 Bench Scale Methane Cracking Tests," *Fusion Sci. and Technol.*, **41**, 998 (2002).
- [5] J. H. SCOGIN and A. S. POORE, "Startup and Operation of a Metal Hydride Based Isotope Separation Process," *Fusion Technol.*, **28**, 736-441 (1995).
- [6] K. L. SESSIONS and J. M. HORN, private communication.
- [7] L. K. HEUNG, "Hydrogen Isotope Exchange Tests in Support of HT-TCAP," *U. S. DOE Report WSRC-TR-2004-00402* (2004).

WSRC-MS-2004-00573

August 12, 2004

Keywords: TCAP  
Detritiation  
Process Stripper

**NEW SYSTEMS FOR WASTE PROCESSING OF TRITIUM-CONTAINING GASES  
AT THE SAVANNAH RIVER SITE**

A. S. Poore and W. D. Jacobs

Savannah River National Laboratory, Westinghouse Savannah River Company, Aiken, SC 29808 USA  
[anita.poore@srl.doe.gov](mailto:anita.poore@srl.doe.gov) and [william.jacobs@srl.doe.gov](mailto:william.jacobs@srl.doe.gov)

Paper prepared for  
Tritium 2004: 7th International Symposium on Tritium Science and Technology  
Baden-Baden, Germany  
September 12 – 17, 2004

And to be published in the proceedings.

Peer review comments incorporated 1/18/05