

Comparison of Methods for Separating Small Quantities of Hydrogen Isotopes from an Inert Gas

R. S. Willms^a, D. Tuggle^a, S. Birdsell^a, J. Parkinson^a, B. Price^a, D. Lohmeir^b

^aLos Alamos National Laboratory, Los Alamos NM 87545

^bSavannah River Site, Aiken SC

Abstract — It is frequent within tritium processing systems that a small amount of hydrogen isotopes (Q_2) must be separated from an inert gas such as He, Ar and N_2 . Thus, a study of presently available technologies for effecting such a separation was performed. A “base case” and seven technology alternatives were identified and a simple design of each was prepared. These technologies included oxidation-adsorption-metal bed reduction, oxidation-adsorption-palladium membrane reactor, cryogenic adsorption, cryogenic trapping, cryogenic distillation, hollow fiber membranes, gettering and permeators. It was found that all but the last two methods were unattractive for recovering Q_2 from N_2 . Reasons for technology rejection included 1) the method unnecessarily turns the hydrogen isotopes into water, resulting in a cumbersome and more hazardous operation, 2) the method would not work without further processing, and 3) while the method would work, it would only do so in an impractical way.

On the other hand, getters and permeators were found to be attractive methods for this application. Both of these methods would perform the separation in a straightforward, essentially zero-waste, single step operation. The only drawback for permeators was that limited low-partial Q_2 pressure data is available. The drawbacks for getters are their susceptibility to irreversible and exothermic reaction with common species such as oxygen and water, and the lack of long-term operation of such beds. More research is envisioned for both of these methods to mature these attractive technologies.

I. INTRODUCTION

It is common in tritium facilities to need to separate tritium from inert gases with a very high efficiency so that the inert gases can be vented to the atmosphere without excessive radioactivity. This is frequently accomplished by oxidizing the tritium (and other hydrogen isotopes) in all forms to water and collecting the tritiated water on an adsorbent such as molecular sieve. While this process is highly effective, it has certain drawbacks if most of the hydrogen isotopes are in the diatomic form (i.e. Q_2 , where Q is protium, deuterium or tritium). In this case the tritium is converted from its useful form, Q_2 , to tritiated water which is general useless. Also, the tritiated water is tens of thousands of times more hazardous than Q_2 . Thus, a study was undertaken to determine what other technologies could be used to effect this separation and to determine which technologies are the most attractive alternatives. Seven technology

alternatives were identified. Herein each technology is described as it applies to this application. Advantages and disadvantages are identified and the technologies are compared. The most attractive technologies are identified.

A. The “Base Case” — Flush Nitrogen Processing

An example of the traditional oxidation/adsorption process exists at the Savannah River Site’s Replacement Tritium Facility (RTF) where nitrogen used to flush tritium lines is collected and processed. This “base case” process is shown on Figure 1. As shown, the tritium-contaminated nitrogen is collected in holding tanks. From these the gas is transferred to a catalyst bed where the tritium is oxidized. The resulting tritiated water is collected on a molecular sieve bed, and the clean nitrogen is sent to the stack. Subsequently, the water is reduced by reaction with hot magnesium. The tritium is purified from the resulting hydrogen isotopes by cryogenic distillation.

The characteristics of the nitrogen flush gas stream are:

- Predominately N_2
- <0.25 mole % T_2
- <2.00 total H
- <0.15 molar % O_2
- Small amount of He
- Negligible water and hydrocarbons

Processing of a tank is only begun after its contents have been well characterized by mass spectrometry. The N_2 is cleaned to <10 ppm T_2 so that it can be stacked.

While effective, there are a number of deficiencies associated with this process. These are:

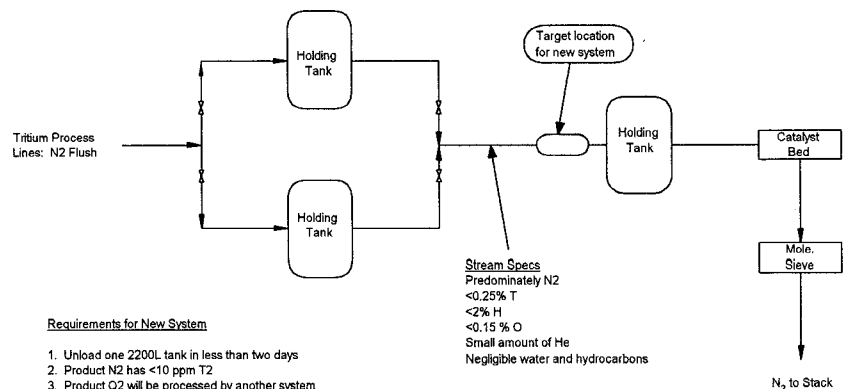


Fig. 1. Schematic of Existing SRS Nitrogen Flush Gas System

- Free tritium gas is converted to the water form which is >20,000 times more hazardous than the Q₂ form;
- While the original stream has tritium in the Q₂ form, this is converted to water, only later to be reduced back to the desired Q₂ form. It would be preferable to maintain the tritium as Q₂;
- The multistep process is cumbersome, somewhat complicated and occupies considerable space; and
- The magnesium bed process generates tritiated, metal oxide waste comparable to the amount of water processed. Consumption of magnesium beds is not only expensive, but the resulting tritiated waste is also an environmental hazard.

B. Technology Alternatives

The primary goal of this study was to identify processing techniques which are simpler, avoid water formation and are essentially waste free. Opportunities for improvements to the present flush nitrogen processing system were considered rather broadly. Seven technologies were identified which could potentially form the basis for such an improved process. These technologies are summarized in Table 1. In the next section each technology will be described and evaluated.

II. TECHNOLOGY DESCRIPTIONS

A. Cryogenic Distillation

Description: Distillation separates materials based on differences in boiling points. Cryogenic distillation is required to separate nitrogen and hydrogen isotopes because of their low boiling points.

For this separation the bottoms product would be recovered at about 96.5 K and the top product would be recovered at about 71.5 K. The top temperature was chosen to be above the freezing point of pure nitrogen, which is approximately 63.2 K. Using these conditions the column top product would be composed of 91.3% hydrogen isotopes and about 8.7% nitrogen. The liquid nitrogen product (the column bottoms) contains a mole fraction of hydrogen isotope of about 8×10^{-13} . This distillation column is operated at about 1300 torr. The column employs fourteen theoretical trays. The column, including a surge volume, will be two and one-half feet tall.

Evaluation: The advantages and disadvantages of this method are:

Advantages

- Large boiling point differences resulting in relatively easy separation
- Relatively small distillation column (2.5 feet)

Disadvantages

- Startup/Shutdown of cryogenic equipment

Table 1
Nitrogen Flush Gas Processing Technologies Considered

Technology
Cryogenic Distillation
Oxydation-Adsorption-Palladium Membrane Reactor
Hollow Fiber Membrane
Getters
Permeators
Cryogenic Adsorption
CryoTrap

- Potential plugging especially in product stream which is near N₂ freezing point
- Top product requires further processing

The primary consideration for distillation is that the freezing point of nitrogen is higher than the dew point of the hydrogen isotopes at the desired top operating conditions. Therefore the desired top product composition, essentially pure hydrogen isotopes, cannot be obtained. Additionally, it is somewhat difficult to work with cryogenic equipment. Thus, this technology is not recommended for the stated application.

B. Oxydation-Adsorption-Palladium Membrane Reactor

Description: For the "base case" process the tritium is oxidized and collected as water. Subsequently the tritium is recovered by reducing the water in the presence of Mg. This latter process produces substantial tritium-contaminated magnesium oxide waste. Alternatively this water could be processed with an essentially waste-free Palladium Membrane Reactor (PMR). This device uses the water-gas shift reaction, $Q_2O + CO \leftrightarrow Q_2 + CO_2$, in concert with a Pd/Ag membrane to recover hydrogen isotopes from water. The performance of PMR technology has been demonstrated at LANL over the last several years. This technology is very similar to permeator technology, with the exception that catalyst is loaded in the high-pressure side of the permeator and gas addition (CO) is required. The system is similar to the two-stage permeator design described elsewhere in this paper, with the exception that the permeators have a catalyst to promote the reaction of Q₂O and CO. The pumping requirements are the same.

Evaluation: The advantages and disadvantages of this system are:

Advantages

- Provides waste-free water processing system

Disadvantages

- Unnecessarily oxidizes tritium to water which is harder to transport (condenses) and is much more hazardous
- Multistep process

The two-stage PMR system would appear to be well suited for the Q₂/N₂ separation application if the Q₂ were already con-

verted to Q_2O at the source. However, it does not seem appropriate to do this conversion as part of the stream processing. Not only does the conversion to Q_2O result in an extra processing step, but the tritium then exists in the more dangerous oxide form. Furthermore, compared to the closely related two-stage permeator system, the PMR system is not as easy to operate nor does it have a comparable demonstrated long-term reliability. Therefore it is considered that the PMR system is not the most appropriate system for the stated application.

C. Hollow Fiber Membrane

Description: Hollow fiber polymer membranes have been used in industry for the past thirty years for the separation of gas mixtures. Species dissolve into the membrane material (usually on the outside of the fiber), and then diffuse through the material to the bore of the fiber, where the permeating gases are pumped away. A separation is effected when species have different permeabilities. Unlike certain metals, such as palladium, polymer membranes allow essentially all gases to permeate, but certain polymers can selectively allow hydrogen and its isotopes to permeate at rates up to 600 times faster than nitrogen.

The typical percent removal of hydrogen (or tritium) from the feed stream is in the range of 50-80% per stage. A system designed to remove 99% of the tritium in the feed stream would employ multiple stages. For instance at 50% removal, 7+ modules in series would be required, and 70% removal would require 4-5 modules [1]. Modules are staged by sending the retentate from one stage to the feed of the next stage. The gas, which permeates to the fiber bores of each module, is collected and pumped away as product.

A 5-stage system was evaluated. If the feed to such a system is 2% hydrogen isotopes in nitrogen, the permeate product would be about 5% of the feed flowrate and would have a composition of 38% hydrogen isotopes and 62% nitrogen. The retentate product would be 95% of the feed and be composed of 0.02% hydrogen isotopes in nitrogen. Thus, both product streams are expected to require further processing.

Off-the-shelf membrane modules are designed for industrial uses and the number of fibers in even the smallest available modules require flowrates of around 50 SLPM which is larger than that required for most tritium processing systems.

Presently the tritium compatibility of polymer membranes has not been established. Further descriptions of these membranes can be found in [2].

Evaluation: The advantages and disadvantages of this system are summarized as follows:

Advantages

- Resistant to most "poisons"

Disadvantages

- Not proven for tritium service
- Both product streams require further processing
- Susceptible to high moisture, oils
- Off-the-shelf components require too high throughput

This method does not provide a perfect separation between N_2 and hydrogen isotopes. Both product streams require further processing. Also the hollow fibers have not been proven in tritium service. Thus, this system is not recommended for the present application.

D. Getters

Description: Metal getters will react with tritium in a flowing nitrogen gas stream to remove and collect the tritium. Hydride getters have long been based on a number of pure metals such as uranium and palladium, and more recently on intermetallics such as those prepared by the SAES getters company. Such systems have been used to remove and recover tritium from glovebox atmospheres [3].

The system proposed to remove and collect hydrogen isotopes from the flush nitrogen gas is a series of metal getter beds. The first bed, filled with SAES St909 getter material, reacts with water to form a metal oxide ($M+Q_2O \rightarrow MO+Q_2$) and with methane to form a metal carbide ($M+CQ_4 \rightarrow MC+2Q_2$). The diatomic hydrogen isotopes from such molecules are released to the gas phase and exit the bed. Other feed gases such as nitrogen, hydrogen, helium, and other rare gases are not retained in this bed [4]. Once this bed is used up, it must be replaced.

Next, the gases are sent to a SAES St198 getter bed where the Q_2 is collected as a metal hydride. The hydrogen isotope partial pressure exiting the St198 bed should be in the 10^{-6} to 10^{-4} torr range.

The hydrogen isotopes collected on the SAES St198 beds are recovered by heating. It is not presently known whether or not further processing of the regeneration gas will be needed (e.g. with a permeator) before these hydrogen isotopes are separated, for instance, with a cryogenic distillation system.

An important consideration for getter-based separation systems is that they must not be fed a stream containing large quantities of oxygen, such as air. If this is done the hot metal will react exothermically with the oxygen, the bed will overheat, the hydrogen isotopes will be evolved and, in an extreme case, the bed will melt.

The only waste that will routinely be generated by this system will be that resulting from oxygen (e.g., O_2 , H_2O) and carbon (e.g., CH_4).

Evaluation: The advantages and disadvantages of this system are summarized as follows:

Advantages

- Relatively simple, one-step separation (followed by regeneration)
- Essentially no further processing required
- Minimal waste generated

Disadvantages

- Limited long-term experience
- Limited breakthrough data
- Potential for failure if inadvertently fed considerable oxygen
- Consumed if impurities concentration is elevated

A showstopper for getter-based systems is their susceptibility to oxidation (e.g., air in-break). However, for the application in question, this should not be an issue. Thus, the getter-based system appears to be attractive due to its relatively simple, straightforward operation. Little waste will be generated. It is recommended that this system be considered for the nitrogen flush gas processing application.

E. Permeators

Description: Pd/Ag permeators have been used to separate hydrogen isotopes from other gases for almost 40 years [5]. This technology is well suited for the separation of deuterium and tritium from an inert gas, such as N_2 , because essentially no hydrogen isotopes are chemically bound to molecules and, therefore, the hydrogen isotopes are free to pass through the membrane. Vacuum pumps are required to separate the hydrogen isotopes from the inert to the degree required in this application (>99%). Many years of tritium experience have been logged with these types of pumps.

To accomplish the required separation a two-stage permeator system is used. The first stage permeator, backed by a scroll pump, removed the bulk of the hydrogen isotopes. The second stage, backed by a turbomolecular pump, removes hydrogen isotopes to trace levels. The system is a steady state "once-through" system with no recycle or batch operations. The basis for this separation can be found in experiments on a related technology, the Palladium Membrane Reactor [6,7].

Evaluation: The advantages and disadvantages of this system are summarized as follows:

Advantages

- Simple, one-step separation
- No further processing required
- Long-term experience with permeators
- Unaffected by common impurities

Disadvantages

- Limited low-pressure permeator data

The two-stage permeator system appears to be well suited for the Q_2 /Inert separation application. The system will achieve much better than required performance and is reliable and easy to operate. While there are years of experience with permeators, there is only limited experience with low partial pressure permeators. However, initial data in this respect is very promising. There are numerous advantages associated with this process. It is recommended that this process be considered for the present application.

F. Cryogenic Adsorption

Description: Cryogenic molecular sieve has been used for many years to process tritium-containing streams. It has been used to adsorb nitrogen and methane from a stream of hydrogen isotopes and helium. The latter two components exit the bed in ultra-pure form [8].

Molecular sieve at liquid nitrogen temperature strongly adsorbs essentially all gases except He (which is adsorbed very weakly). Of the gases normally encountered, hydrogen isotopes are the least strongly adsorbed. Next come the other "permanent gases" such as argon, oxygen, nitrogen, methane, carbon monoxide and carbon dioxide. Thus, this material can be used to separate hydrogen isotopes from He and "impurities" from hydrogen isotopes (as mentioned above). The bed can be used until the adsorbing material saturates the bed and "breaks through" the end of the bed. Then the bed must be warmed to regenerate the adsorbate and prepare the bed for another adsorption cycle.

When nitrogen and trace hydrogen isotopes are fed to a liquid nitrogen-cooled molecular sieve bed, the desired separation could be effected. However, this separation method is not appropriate for this application for the following reason. As gas is fed to the bed, hydrogen isotopes (Q_2), which are the least strongly adsorbed component, are pushed in front of the N_2 . As this progresses, the unused portion of the bed shrinks (and nothing exits the bed) until the Q_2 , and ultimately the N_2 , break through the end of the bed. If the amount of Q_2 is large relative to the N_2 , this is a practical system. However, for the present application there is only a small amount of Q_2 in N_2 . This would make the thickness of the Q_2 front very narrow and impractical.

For reference it should be noted that if He, rather than N_2 , were used for the flush gas then this system would be practical and should be considered.

Evaluation: While cryogenic molecular sieve-based separations are very effective for certain applications, it is impractical for the present application. This is because the concentration ratio of Q_2 to N_2 would result in an unusable adsorption front. This system is not recommended for nitrogen flush gas processing.

G. CryoTrap

Description: Cryotrap are devices which separate components based on differences in freezing points. These are commonly used in laboratory systems to remove, for instance, water from air by lowering the temperature of the air to the point where water freezes. This is effective since the frozen component, water, is the trace quantity. However, for the present application, O_2/N_2 separation, the frozen component would be nitrogen which is the dominant component. For this reason a cryotrap would be impractical for this separation.

Evaluation: Since N_2 is the dominant component in the feed stream and this is the component that would have to be frozen, cryotrap are not recommended for the present application.

III. SUMMARY AND RECOMMENDATIONS

From each of the seven process descriptions, a set of process characteristics can be determined. These are summarized in Table 2. The column headings are worded so that an entry of "yes" is considered good. More explanation of these characteristics is given in the detailed write-ups.

The two systems found to be attractive for this application were permeators and getters. As shown in Table 2, permeators have all "yes" entries and getters have only one "no." However, for the present application the "no" for "Oxygen resistant" is not an important consideration.

Thus, it is recommended that permeators and getters be considered for an improved flush gas nitrogen processing system. Both of these systems would be substantial improvements over the base case system.

While both getters and permeators are appropriate systems, there are nuances which distinguish them from each other. As an example, getters are by nature batch processes, i.e., the beds go through cycles of filling and regeneration. By contrast, permeators operate continuously. Once turned on they continue to perform the desired separation without accumulation of hydrogen isotopes and without interruption. Which type of process is preferred depends on other system considerations.

IV. REFERENCES

- Price, B., "Purification of Tritium Contaminated Nitrogen Using Hollow Fiber Polymer Mem-

- branes," Master's Thesis, University of Texas at Austin, August 1994. Available from author upon request.
- Ito, H., T. Suzuki, T. Takanaga, Y. Matsuda, S. Konishi, Y. Naruse, and S. Hirata, *Fusion Technol.*, **21**, 988 (1992).
- Nobile, A., T. Bieniewski, K. Frame, R. Little and K. Fisher; "Design Optimization of Metal Getter Reactors for Removing Tritium from Flowing Gas Streams," *Fusion Technol.*, **28(3)**, 1558 (1995).
- Baker, J. D., D. H. Meikrantz, R. J. Pawelko, R. A. Anderl and D. G. Tuggle, "Tritium Purification via Zirconium-Manganese-Iron Alloy Getter St 909 in Flow Processes," *J. Vac. Sci. Technol.*, **A 12(2)**, 548 (1994).
- Clark, D., A. Dauchess, L. L. Heung, R. L. Rabun and T. Motyka, "SRS History and Operating Experience With Palladium Diffusers, Westinghouse Savannah River Company, Aiken, South Carolina," *WSRC-TR-94-0412*, August 11, 1995.
- Birdsell, S. and R. S. Willms, "Ultra-High Tritium Decontamination of Simulated Fusion Fuel Exhaust using a two-Stage Palladium Membrane Reactor," to appear in *Fusion Technol.*
- Birdsell, S. and R. S. Willms, "Tritium Recovery From Tritiated Water With A Two-Stage Palladium Membrane Reactor," to appear in *Fusion Engineering and Design*.
- Willms, R. S., J. L. Anderson, J. R. Bartlit, Y. Naruse and K. Okuno, "Fusion Fuel Purification During the Tritium Systems Test Assembly Three-Week Loop Operation," *Proceedings of the Thirteenth Symposium on Fusion Engineering*, Knoxville, TN, p. 795, October 2-6, 1989.

Table 2
Comparison of Nitrogen Flush Gas Processing Technologies

Technology	Water-free	Waste-free	Oxygen resistant	Cryo-gen-free	Simple	Requires no further processing	Appropriate (Size, will work, etc.)	Batch/Cont.
Permeators	yes	yes	yes	yes	yes	yes	yes	Cont.
Getters	yes	~yes	no	yes	yes	yes	yes	Batch
Cryogenic Adsorption	yes	yes	yes	no	yes	no	no	Batch
Cryogenic Distillation	yes	yes	~no	no	no	no	yes	Cont.
Cryotrap	yes	yes	yes	no	yes	no	no	Batch
Stripper/PMR	no	yes	yes	yes	no	yes	yes	Batch
Hollow Fiber Membrane	Yes	yes	yes	yes	yes	no	no	Cont.