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Design Options to Minimize Tritium Inventories at Savannah River

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Large quantities of tritium are stored and processed at the Savannah River Site (SRS) Tritium Facilities. In many design basis accidents (DBAs), it is assumed a vessel's entire tritium inventory is released from the facility and the site for public radiological dose calculations. Pending changes in public dose calculation methodologies are driving the need for smaller tritium releases during DBAs. One option is to reduce the in-process tritium inventory to reduce the unmitigated source term for public dose calculations. This paper discusses process design options to reduce in-process tritium inventories. A Baseline process is defined to illustrate the impact of removing or replacing La-Ni-Al alloy tritium storage beds with palladium (Pd) or depleted uranium (DU) storage beds on facility tritium inventory needs. Elimination of La-Ni-Al alloy beds for tritium storage can reduce process tritium needs by over 1.5 kg, but alternate technology may need to be installed in the process to replace the function of removed storage beds.

Keywords: Tritium; Hydride; Tritide; Aging; Tritium Storage

1. Introduction

The tritium supply for US defense program applications is part of an integrated program to ensure adequate supplies of tritium (and other nuclear materials) for current and future stockpile needs. Facilities such as the Savannah River Site (SRS) were constructed to produce tritium for defense programs. Development programs in the 1980's were initiated to reduce the size of tritium process systems through the use of metal hydride technology [1]. The hydride-based process systems were small enough to be affordability placed in inerted gloveboxes to minimize tritium releases to the environment [2]. The use of metal hydride technology also allowed elimination of many oil and mercury based pumps used for tritium processing and the delivery of tritium nearly free of He-3 [3].

One of the metal hydrides developed for use in the tritium facilities was $LaNi_{5-x}Al_x$ ("LANAx") where x represents the atomic substitution of aluminum for nickel in the base $LaNi_5$ alloy. The pressure-composition-temperature (PCT) properties of the La-Ni-Al alloy can be altered by varying the amount of Al substituted for Ni in the alloy [4].

Tritium aging effects from storing tritium in La-Ni-Al ("LANAx") based alloys have been studied [5]. The desire to perform tritium inventory measurements without removing tritium from a storage vessel, especially from a vessel with long-term tritium exposure, lead to the development of the In-Bed Accountability (IBA) or In-Bed Calorimetry (IBC) method for process hydride bed tritium inventory measurements [6].

As part of development efforts to modify the SRS tritium processes, one topic for examination is the reduction of in-process tritium inventories [7,8]. Fig. 1 illustrates tritium aging effects on the PCT properties for $LaNi_{4.25}Al_{0.75}$ (LANA0.75) where T/M is the tritium-to-metal ratio (T/M), T is the number of tritium atoms, and M is the number of metal atoms for the alloy.

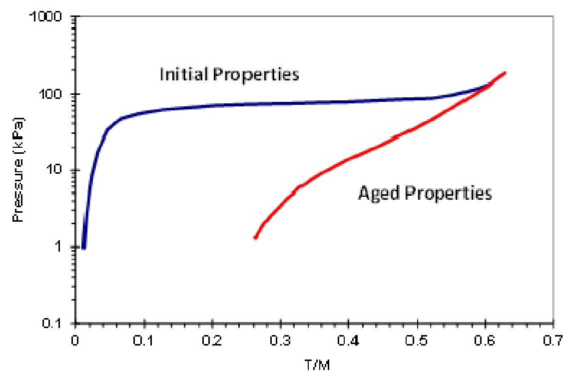

Fig. 1. Typical tritium aged LANA0.75 isotherm.

Fig. 1 illustrates that as LANA0.75 alloy is exposed to tritium, the useable or reversible capacity of a tritium storage bed is decreased. The purpose of this paper is to examine different process options and hydride technologies to reduce total and inaccessible tritium process inventories.

2. Background

For the purposes of this paper, comparisons will be made between storing tritium on LANA0.75, palladium (Pd), and depleted uraninum (DU), He-3 is not significantly retained in DU and has little impact on its PCT properties [9]. He-3 retention in Pd has a slight impact on PCT properties, but significantly less than for LANA0.75 [5]. For comparison purposes of this paper, it is assumed only the PCT properties of LANA0.75 are impacted by tritium storage.

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Fig. 2 illustrates the minimum and maximum storage capacities of a hydride material in terms of the Q/M ratio where Q is the sum of protium (H), deuterium (D) and tritium (T) atoms in the hydride. The Working Capacity of a hydride bed (ΔQ/M) will be its maximum capacity, Q/M_{max}, less its minimum capacity, Q/M_{min}. These capacities can vary for "new" (absent tritium exposure) metal hydride material and tritium "aged" (tritium exposed) materials and are based on bed performance under process operating conditions. For this paper, only Q/M_{min} for the LANA0.75 alloy will be assumed to vary due to tritium aging.

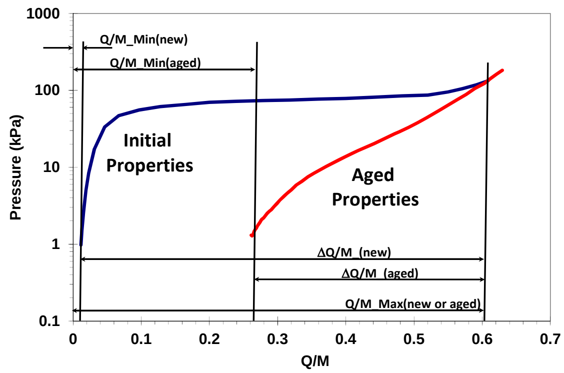

Fig. 2. LANA0.75 capacities

2. Baseline process

Fig. 3 illustrates the baseline process to be evaluated for this paper. The gas input stream first goes through a series of separation and absorption processes before the tritium undergoes isotopic separation and is stored on a Product bed. The process analyzed is for illustration purposes only and does not imply current or projected facility inventories.

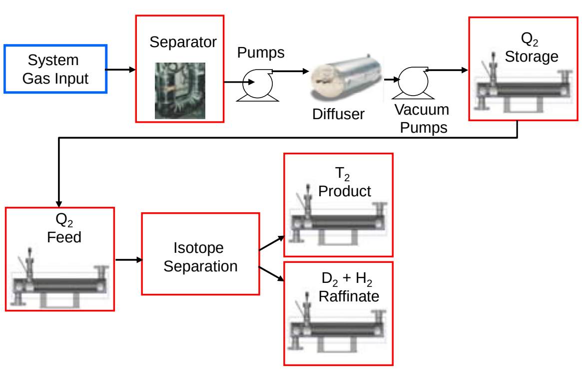

Fig. 3. Baseline process illustration

Table 1 contains some information for the Fig. 3 baseline process for calculation of an initial tritium basis. The capacity of a Storage and Feed beds was taken to be 1500 STP-L (standard liters of gas referenced to 0°C and 760 torr) each, the Separator bed to be 1/3rd the capacity of a Storage bed (500 STP-L), and the Product bed to be 5000 STP-L. For calculation purposes, the composition in the Separator, Storage, and Feed beds will be 50% tritium and 100% tritium in the Product bed.

Table 1. Baseline process information.

	Separator	Storage	Feed	Product
Hydride	Pd	LANA 0.75	LANA 0.75	LANA 0.75
Q/M_{min} (new)	0.050	0.080	0.080	0.080
Q/M_{min} (aged)	0.050	0.355	0.355	0.355
Q/M_{max}	0.720	0.800	0.800	0.800
ΔQ/M (new) STP-L	500	1500	1500	5000
# of Beds	2	4	2	2
% T	50	50	50	100

Table 2 contains the mass of hydride materials needed to have "new" working capacities of 500, 1500, and 5000 STP-L. The molecular weights for Pd, DU, and LANA0.75 were taken as 106.4, 238.06, and 408.66 grams per mole, respectively. The Q/M_{min} and Q/M_{max} values for DU were taken as 0.250 and 2.80, respectively.

Table 2. Mass of hydride (grams) for listed working capacity.

ΔQ/M (STP-L)	Pd	DU	LANA 0.75
500	7,085	4,165	4,221
1500	21,255	12,495	12,662
5000	70,851	41,651	42,205

2. Process tritium inventories

Using the mass of hydride from Table 2 along with the hydride Q/M_{min} and Q/M_{max} values, the minimum and maximum hydride bed gas inventories can be calculated. Table 3 shows the various beds inventories for 1500 STP-L Working Capacity beds. Similar tables can be created for 500 and 5000 STP-L Working Capacity beds.

Table 3. Bed inventories (STP-L) for 1500 STP-L beds.

	Pd	DU	LANA 0.75
Q/M_{max}(new)	1612	1647	1667
Q/M_{min}(new)	112	147	167
Q/M_{min}(aged)	112	147	740
ΔQ/M(new)	1500	1500	1500
ΔQ/M(aged)	1500	1500	927

To calculate in-process tritium inventories, the quantity of gas in each bed must be specified. The capacity of a hydride bed is finite and to operate a batch process in a continuous mode, a pair of beds will need to be operated out-of-phase, e.g. one bed on-line and the other in regeneration mode. To calculate what is defined as the Operational Inventory, one-half of the beds in each process location will contain the minimum bed inventory while the other beds in the same process location will contain the maximum bed inventory. For example, the contribution to Operational Inventory for the Storage beds will be two beds at their minimum inventory and the two beds at their maximum inventory. For new LANA0.75 Storage beds, the Operational Inventory contribution is two-times 167 STP-L plus two-times 1667 STP-L: 3,337 STP-L. At a gas composition of 50% tritium, the tritium inventory for these four beds is 493 grams.

The Useable Inventory will be defined as the sum of the Working Capacity of all the beds in the process. For example, the Useable Inventory for four new LANA0.75 Storage beds is four-times 1500 STP-L: 6,000 STP-L or 807 g tritium. The Maximum Inventory for the Storage beds is four-times 1667 STP-L: 6667 STP-L or 897 g tritium.

2.1 Baseline process inventories

The tritium inventories for the baseline process using the information from Table 1 and Table 2 are summarized in Table 4 where "Ops" is an abbreviation for Operational Inventory. The table shows the new minimum facility inventory as 0.444 kg tritium with a new Useable Inventory of 4.04 kg. As the LANA0.75 beds age, the minimum facility Inventory rises to 1.93 kg tritium while the Useable Inventory is reduced to 2.55 kg.

2.2 Reduced bed process inventories

One method to reduce process tritium inventory is to reduce the number of hydride beds in the process. One option is to rely on different technologies to replace the function of the beds removed from the process. For example, the Separator beds and the Feed beds could be eliminated from the baseline process to produce a "Reduced Bed" Baseline Process. For this process, all the Input gas would be processed through diffusers and the ISS Feed gas would be supplied by a pump. The pros and cons of replacing hydride bed functions with other technologies will not be discussed other than the impact on tritium inventory.

Table 5 is a revised version of Table 4 with the contributions from the Separator beds and the Feed beds eliminated. The table shows the new minimum facility inventory as 0.389 kg tritium with a new Useable Inventory of 3.50 kg. As the LANA0.75 beds age, the minimum facility Inventory rises to 1.73 kg tritium while the Useable Inventory is reduced to 2.16 kg.

2.3 Alternate hydride process inventories

The next comparison will examine the impact on facility inventory by replacing LANA0.75 beds with either Pd or DU beds which have less tritium aging effects. Direct replacement of LANA0.75 beds with either Pd or DU beds with the mass of materials specified in Table 2 (e.g. the same initial Working Capacity) would produce results similar to those presented in Table 4 for new LANA0.75 beds.

An alternate comparison will be to use Pd and/or DU beds that have Working Capacities equal to the LANA0.75 beds at the end of their service life. The concept is if the facility can operate with LANA0.75 beds with a reduced operating capacity, designing a process without LANA0.75 beds should be able to operate with this initial operating capacity.

Table 4. Baseline process inventories (g tritium).

	Separator	Store plus Feed	Prod.	Total
Hydride	Pd	LANA 0.75	LANA 0.75	
Min. (new)	10.0	135	299	444
Min. (aged)	10.0	597	1327	1934
Ops (new)	773	740	1645	2462
Ops (aged)	773	971	2159	3207
Useable (new)	135	1211	2691	4037
Useable (aged)	135	749	1663	2546
Max.	145	1346	2990	4480

Table 5. Reduced bed process inventories (g tritium).

	Storage	Product	Total
Hydride	LANA0.75	LANA0.75	
Min. (new)	89.7	299	389
Min. (aged)	398	1327	1725
Ops (new)	493	1645	2138
Ops (aged)	648	2159	2806
Useable (new)	807	2691	3499
Useable (aged)	499	1663	2162
Max.	897	2990	3887

The end-of-life LANA0.75 beds had a Working Capacity of 927 STP-L for the Storage and Feed beds while the Product bed Working Capacity was reduced to 3090 STP-L. The mass of Pd and DU needed for a 927 STP-L Working Capacity is 13,136 g and 7,720g, respectively, and for a 3090 STP-L Working Capacity is 43,786 g and 25,734 g, respectively. Table 6 shows the Minimum and Maximum gas capacities of these beds while Table 7 shows the Baseline process with DU beds replacing the LANA0.75 beds.

2.4 Minimum process inventories

As was done in Section 2.2, relying on alternate process technologies to replace the function of some of the hydride beds can reduce the total number of beds. Eliminating the Separator bed and the Feed bed contributions to the values in Table 7 are shown in Table 8 which is taken as the minimum facility inventory.

Table 6. Inventories (STP-L) for 927 and 3090 STP-L beds.

	Pd	DU
Q/M_{min}: $\Delta Q/M$ = 927 STP-L	69	91
Q/M_{max}: $\Delta Q/M$ = 927 STP-L	996	1018
Q/M_{min}: $\Delta Q/M$ = 3090 STP-L	231	303
Q/M_{max}: $\Delta Q/M$ = 3090 STP-L	3090	3393

Table 7. Alternate hydride process inventories (g tritium).

	Separator	Store plus Feed	Prod.	Total
Hydride	Pd	DU	DU	
Min.	10	73	163	246
Ops	77	448	995	1520
Useable	135	748	1663	2546
Max.	145	822	1826	2793

Table 8. Minimum process inventories (g tritium).

	Storage	Product	Total
Hydride	DU	DU	
Min.	48.9	163	212
Ops	298	995	1293
Useable	499	1663	2162
Max.	548	1826	2374

3. Discussion

The selection of Q/M_{min} and Q/M_{max} values for the different hydride materials was mostly qualitative and these values alone would not be used as hydride material selection criteria. Actual values would be determined based on actual operating process parameters which were beyond the scope of this paper.

The tritium inventory results for the different scenarios presented are summarized in Fig. 4. As anticipated, the tritium induced (aging) effects of LANA0.75 hydride beds produces 1) an increase in the minimal tritium inventory to fill an "empty" process, 2) an increased amount of tritium needed to operate the process, and 3) a reduction in the Useable tritium in the process. The "Reduced Bed" scenario where the Pd-based Separator beds and the two Feed beds were removed from the baseline process produces some benefit relative to minimum facility inventory use of process inventory, the majority of the tritium is still stored on LANA0.75-based beds which experience tritium aging effects and produce significant amounts of inaccessible tritium.

The Reduced Capacity scenario, where the Useable Inventory for a DU/Pd bed based processes was set equal to the Baseline process Useable Inventory after tritium aging effects, represents a significant reduction in tritium needed to operate the facility. Even though the Baseline process starts out with a Useable Inventory of 4.037 kg, the Useable Inventory reduces to 2.546 kg creating about 1.5 kg tritium that is inaccessible for use by the process.

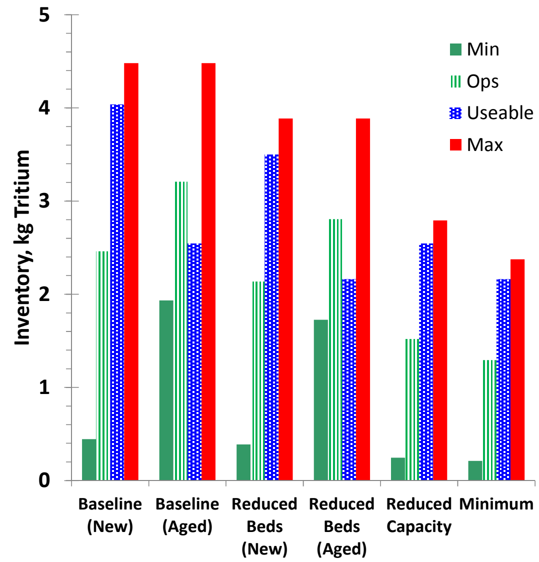

Fig. 4. Inventory option summary

If minimization of the facility inventory is desired, removal of additional hydride beds from the Reduced Capacity scenario can future decrease facility tritium needs. As stated previously, removal of the function of these hydride beds would likely require the addition of other components or processes. A trade study would likely be needed to determine the cost-benefit of a reduced tritium inventory facility with a likely larger glovebox/process equipment footprint and a more compact/smaller footprint facility.

4. Conclusions

The use of LANAx alloys offer many advantages for use in tritium processes including delivery of He-3 free tritium, the ability to tailor the alloy to have desirable PCT properties, and to use the beds in a thermal swing absorption-desorption mode to act as vacuum vessels when cooled (absorption) and to act as pumps when heated (desorption). The major disadvantage of the use of LANAx alloys is the reduced Working Capacity of these beds due to tritium aging effects experienced by the alloy. Strategic replacement of LANAx hydride beds with other hydrides, such as Pd or DU, can reduce facility tritium inventory demands, but may also require additional process equipment to meet the functional requirements of the tritium process.

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References

[1] M. S. Ortman, T. J. Warren, and D. J. Smith, Use of metal hydrides for handling tritium, Fusion Technol. 8 (1985) 2330-2336.

[2] L. K. Heung, J. H. Owen, R. H. Hsu, R. F. Hashinger, D. E. Ward, and P. E. Bandola, Tritium Confinement in a new tritium processing facility at the Savannah River Site, Fusion Technol. 21 (1992) 594-598.

[3] M. S. Ortman, L. K. Heung, A. Nobile, and R. L. Rabun III, Tritium processing at the Savannah River Site: present and future, J. Vac. Sci. Technol. A 8 (3) May/Jun (1990) 2881-2889.

[4] H. Diaz, A. Percheron-Guegan, J. C. Achard, C. Chatillon, and J. C. Mathieu, Thermodynamic and structural properties of $LaNi_{5-y}Al_y$ compounds and their related hydrides, Int. J. Hydrogen Energy 4 (1979) 445-454.

[5] A Nobile, J. R. Wermer, and R. T. Walters, Aging effects in palladium and $LaNi_{4.25}Al_{0.75}$ Tritides, Fusion Technol. 21 (1992) 769-774.

[6] J. E. Klein, M. K. Mallory, and A. Nobile Jr., Tritium measurement technique using “in-bed” calorimetry, Fusion Technol. 21 (1992) 401-405.

[7] J. E. Klein, A. S. Poore, and D. W. Babineau, Development of fusion fuel cycles: large deviations from US defense program systems, Fusion Eng. Design, in press.

[8] J. E. Klein, A. S. Poore, X. Xiao, and D. W. Babineau, A new hydrogen processing development system, Fusion Sci. Technol. in press.

[9] R. Li, Y. Sun, Y. Wei, and W. Guo, Aging effects in uranium tritide, Fusion Eng. Design 81 (2006) 859-862.