SEPARATION OF TRITIUM FROM WASTEWATER

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ABSTRACT

A proprietary tritium loading bed developed by Molecular Separations, Inc. (MSI) has been shown to selectively load tritiated water as waters of hydration at near ambient temperatures. Tests conducted with a 126 µCi tritium/liter water standard mixture showed reductions to 25 µCi/L utilizing two, 2-meter long columns in series. Demonstration tests with Hanford Site wastewater samples indicate an approximate tritium concentration reduction from 0.3 µCi/L to 0.07 µCi/L for a series of two, 2-meter long stationary column beds. Further reduction to less than 0.02 µCi/L, the current drinking water maximum contaminant level (MCL), is projected with additional bed media in series. Tritium can be removed from the loaded beds with a modest temperature increase and the beds can be reused. Results of initial tests are presented and a moving bed process for treating large quantities of wastewaters is proposed. The moving bed separation process appears promising to treat existing large quantities of wastewater at various U. S. Department of Energy (DOE) sites. The enriched tritium stream can be grouted for waste disposition. The separations system has also been shown to reduce tritium concentrations in nuclear reactor cooling water to levels that allow reuse. Energy requirements to reconstitute the loading beds and waste disposal costs for this process appear modest.

INTRODUCTION

Since 1940, tritium in wastewaters has been discharged at various U. S. DOE sites at concentrations greater than the drinking water MCL. Because an economical separation technology was not developed for removal of tritium from wastewaters, isolation, dilution, and hold up time have been the means of partial mitigation in the past. To comply with the MCL requirement, the DOE is currently seeking an economically acceptable method for removal of tritium from wastewaters. The status of current tritium removal technologies are reported in recent technology reviews (1,2,3). Traditional methods of separation such as water distillation, electrolysis, catalytic exchange, and the Girdler Sulfide process are costly or present major safety concerns for the large quantities of wastewaters to be treated.

Tritium is a radioactive soft beta emitting isotope of hydrogen with an atomic weight of 3.0. It exists mainly as tritiated water (HTO) in wastewaters discharged from nuclear facilities. A tritium concentration of 1 µCi/L in water is equivalent to a tritium-to-hydrogen atom ratio of 3.12×10^{-13}. Deuterium, another isotope of hydrogen with a atomic weight of 2.0, is also present in water at a natural concentration of about 150 ppm or at a deuterium-to-hydrogen atom ratio of 6.75×10^{-4}.

At the U.S. DOE Hanford Site, tritium was generated as a reactor by-product from 1944 to 1989 as part of the U.S. Defense Program. The bulk of this tritium was released to the ground as HTO condensates from fuel reprocessing facilities on the 200 Area plateau. Tritium in these previously discharged liquid effluents has migrated to groundwater flowing toward and into the Columbia River. Because tritium decays with a 12.3-year half-life; it is estimated that the present tritium inventory at the Hanford Site is about 2.0×10^5 Ci.

Significant tritium inventories exist in Hanford Site facilities, such as in the underground waste storage tanks, spent-fuel storage basin waters, and water stored at the Liquid Effluent Retention Facility. Since 1995, a state-approved land disposal site (SALDS) has received effluents from the Hanford Site Effluent Treatment Facility (ETF) that are free of all contaminants except tritium. This tritium comes from: (1) process condensates from the 242-A Evaporator when it is processing wastes from underground storage tanks, (2) Hanford N Reactor Basin water stored at the Liquid Effluent Retention Facility, and (3) other miscellaneous wastes.

The U.S. Department of Energy, Richland Operations Office (DOE-RL) Site Technology Coordination Group (STCG), has documented the need to reduce tritium concentrations in Hanford Site wastewaters from 2-3 µCi/L to less than 0.02 µCi/L (RL-MW023, *Technology Needs/Opportunities Statement* [HST 1991]). Implementation of a process to address this need is scheduled during the next several years to correspond with the startup of the Hanford Site high-level waste vitrification process.

Separation technology development for removal of tritium from wastewaters to meet environmental release limits is being conducted in several countries. Work is currently being done in Canada by Ontario Hydro and Atomic Energy of Canada, Limited (AECL), in Japan by Nagoya University and the Japan Atomic Energy Research Institute, and in the United States by MSI, Oak Ridge National Laboratory (ORNL), and the Savannah River Site. One of the more promising technologies is selective tritiated water collection on an adsorption bed.

A cooperative effort is currently under way to demonstrate the effectiveness of the adsorption bed to reduce tritium concentrations in wastewaters to less than the MCL. DOE-RL has provided process and ground water samples through its Hanford subcontractors (Lockheed Martin Hanford Corporation and Pacific Northwest National Laboratory) to MSI in cooperation with Clemson University. COGEMA Engineering Corporation has instigated and coordinated this sampling and testing effort.

TRITIUM ADSORPTION BED SEPARATION TESTING

The tritium concentration in water effluents can be reduced to acceptable discharge levels by processing the water through an adsorption bed process. Under the direction of MSI at Clemson University, extensive pilot-plant testing with fixed-bed ion-exchange media has been conducted with both simulated and process feeds. Demonstration testing has been conducted in the laboratory with actual reactor cooling water and is scheduled for onsite testing with a stationary column at a nuclear reactor in early 2000.

Description of Demonstration Testing

After a series of bench tests at Washington State University that confirmed the selective adsorption of tritiated water (HTO), a pilot plant was constructed to define process operating conditions, define improved adsorption materials, and test representative field samples. The pilot plant operated at the Clemson Environmental Technology Laboratory has four columns, each 2 meters tall and 2 cm in diameter. The columns can be used in series or individually. The flow rate is typically 0.5 L/h, with a velocity on the order of 2 cm/min, definitely laminar. The regeneration vessel is a 7-cm diameter glass column approximately 1 meter tall and is operated in an air fluidized mode.

Typical adsorption materials included custom loaded commercial exchange resins such as sulfonated polystyrene/ divinylbenzene. The commercially available adsorber material is pretreated by loading selective sites, removing exchangeable hydrogen, and thorough drying. The resin was first loaded with aluminum sulfate to form an Al^{+3} site bonded to at least one sulfonated group on the media. Aluminum in this form has a high number of waters of hydration and has a greater affinity for tritiated water over light water. Adsorption was typically run at 30°C; pressures varied with adsorption material, ranging from 70-140 kPag (about 2 bar absolute). The feed solution was deionized in a mixed bed system to remove all potential interfering ions. The bed media can be occluded with colloids and adsorbs certain organic compounds if they are present in the feed stream. The adsorption material was added dry from the top and the feed was pumped vertically upward through the column(s). Water outlet samples were collected in vials for subsequent scintillation counting in a Packard Instrument Model 2300.

Results

Over 80 runs have been conducted using standard test solutions, samples from Hanford and Brookhaven, and coolants from various PWR nuclear power plants. Selective tritium removal has been consistently demonstrated as shown by the results in the Table I.

Table I. Selective Tritium Adsorption Results

HTO Feed Conc. μCi/L	Source	Number Of Columns	Maximum Decrease %	Normalized[a] HTO Adsorption
1000	CP&L (PWR)	1	69	5.8
245	CP&L (PWR)	4	97	6.1
125	MSI Standard	2	93	6.0
2	BNL Groundwater	2	83	3.7
0.3	Hanford ETF Sample	2	78	1.6

[a]Integrated adsorption per unit volume of media adjusted for the initial feed concentration.

Table I shows the maximum percentage decrease in tritium content from the feed concentration. Five feeds and differing volumes of resin were used in these runs. The reductions were significant for all feed concentrations but were smaller for the feeds with lower tritium concentrations. For all feed concentrations the percent decrease increases with resin volume. This result allows design of systems to achieve varying separation targets. In all cases the resin saturates relative to the feed and must be regenerated for the next cycle. This is illustrated in the Figure 1 adsorption curve, which shows percent decrease of tritium as a function of the total water processed for the four-column run. The first water exiting the columns is 97% reduced in tritiated water relative to the feed. Thus, in the case with the 245 µCi/L feed, the outlet water was at 6 µCi/L. The outlet tritium concentration increased until the resin was saturated, as indicated by the s-curve approaching the zero axis at the top. The resin requires regeneration for reuse after loading.

Figure 2 shows the selective removal of tritiated water from a Brookhaven National Laboratory (BNL) groundwater sample. The sample was first deionized with a mixed bed ion exchange resin. The initial tritium level was 2.1 µCi/L and the maximum removal was 83%, achieving 0.36 µCi/L. Additional resin columns would be required to reach the drinking water standard.

Figure 2 also shows tritium removal from Hanford's ETF effluent. This effluent was sufficiently free of other contaminants and was fed to the demonstration column in the as-received condition without performing a pre-deionization step. Significant tritium reduction was achieved, but somewhat less than expected. The feed was at an initial concentration of 0.3 µCi/L and maximum removal was 78%, achieving 0.07 µCi/L. The data were not corrected for background radiation and it is also possible that relative heavy water concentration is a factor at these low tritium levels. Again, additional adsorption media volume would be required to achieve the drinking water standard.

The greater fraction of tritium removal for the first liquid through the column followed by the decreased removal fraction in later water suggests a need for a moving bed column for efficient operation. A proposed moving bed system is described in the following section.

In all cases, the adsorption media must be regenerated to remove all waters and to concentrate the tritiated water for disposal or storage. This prepares the resin for the next adsorption cycle. The regeneration can be accomplished either in the adsorption vessel or a separate system that allows the media to be easily fluidized. In the current pilot unit, the media is fluidized and transferred to a glass column for regeneration. Regeneration is accomplished in three phases. First, the void water is removed with air in a downflow mode. Second, the remaining free water is removed by hot gas in an upflow mode. This gas is typically air or nitrogen and is heated to 100-110°C. As the resin dries, it is fluidized in the column thereby improving heat and mass transfer.

Tritium Adsorption Curve using 4 Teflon Columns in Series
245µCi/L CP&L Feed Concentration
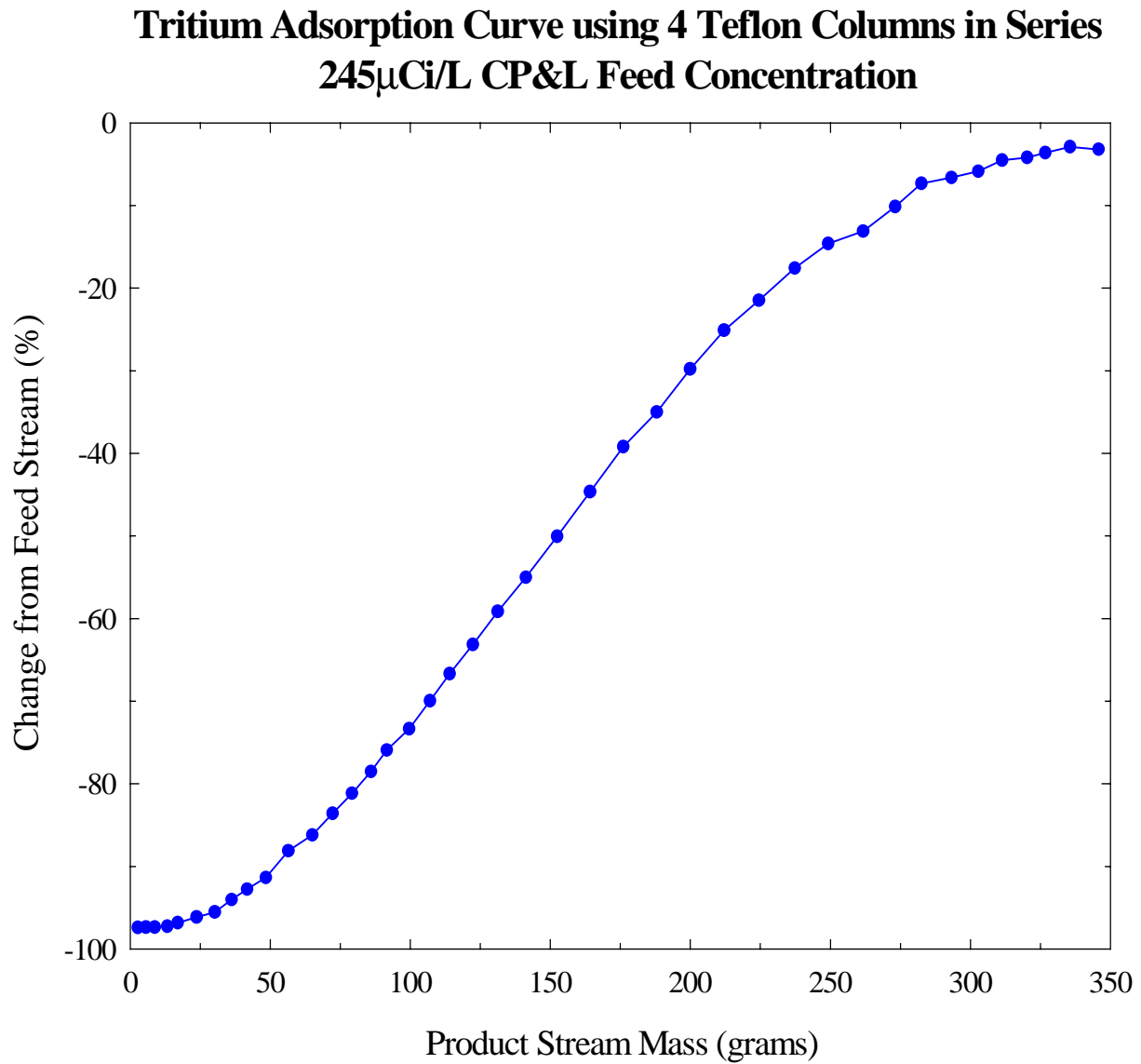
Figure 1. Tritium Adsorption Curve using 4 Teflon Columns in Series for 245µCi/L Carolina Power and Light (CP&L) Feed Concentration

**Tritium Adsorption Curve using 2 Teflon Columns
in Series, 2.1μCi/L Ground Water from Brookhaven
and 0.3μCi/L Hanford Process Sample (ETF effuent)**
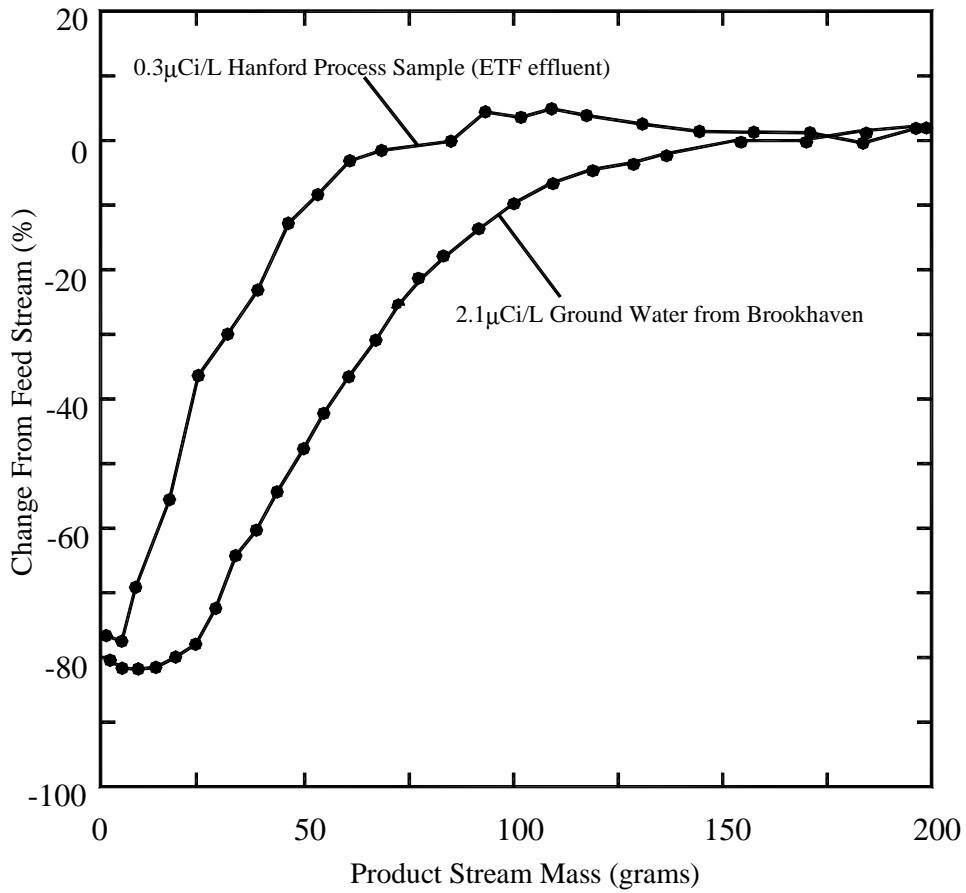
**Figure 2. Tritium Adsorption Curve Using 2 Teflon Columns in Series - 2.1μCi/L Ground
Water from Brookhaven and 0.3μCi/L Hanford Process Sample (ETF Effluent)**

The tritium level of the free water removed from the media during the first phase was near the feed concentration. At the end of phase two, the tritium level drops as the light waters of hydration begin to be driven off. At this stage, the selectively adsorbed tritium remains on the media. The third stage of regeneration is illustrated in Figure 3 and was typically carried out at 140-150°C to remove the bulk of the tritium from the media. The results shown in Figure 3 show a 60% and 90% degree of regeneration. Improving regeneration and shortening regeneration times is a current focus of the MSI technology program.
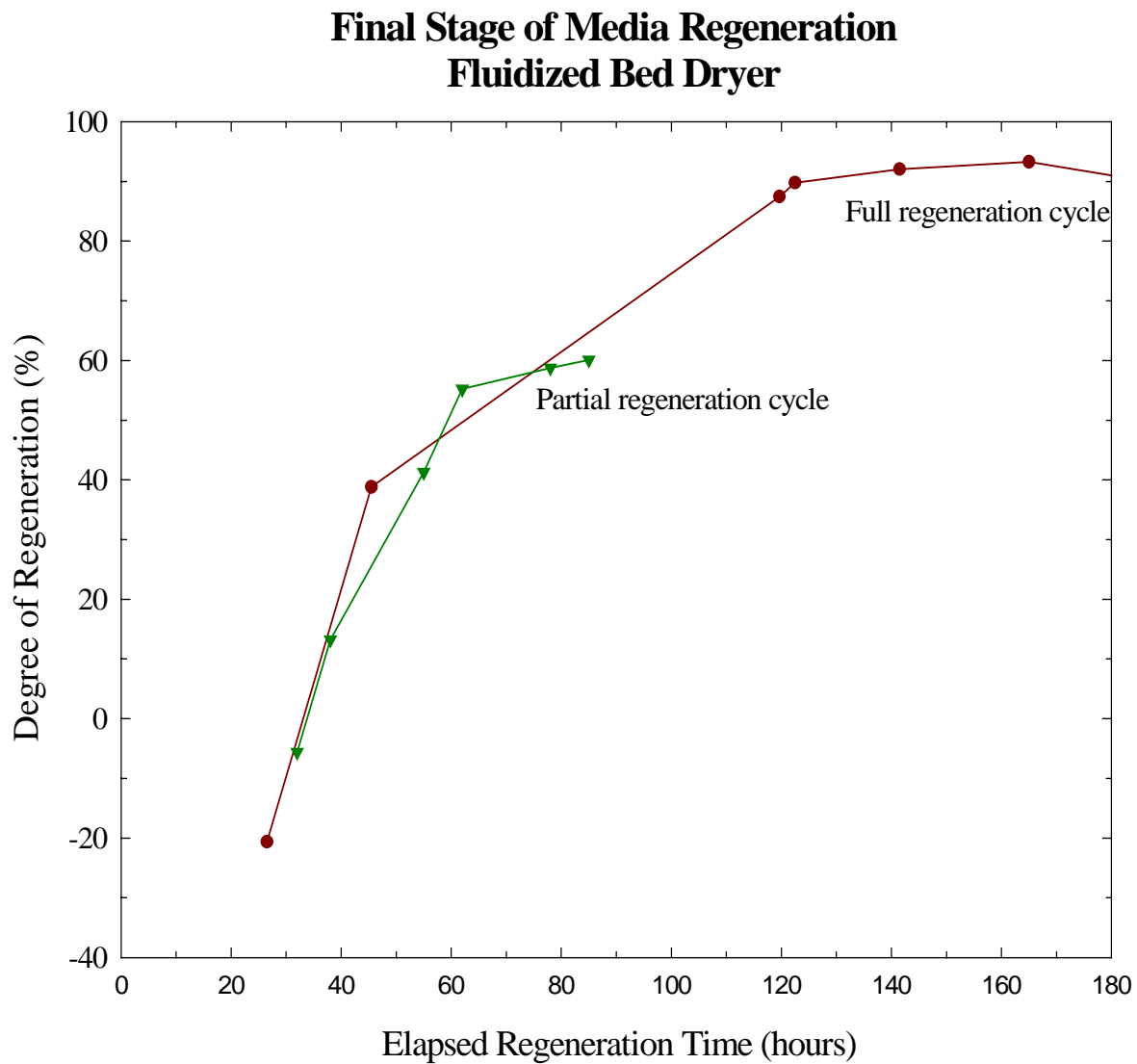

Figure 3. Final Stage of Media Regeneration in a Fluidized Bed Dryer

PROPOSED LOADING BED FOR HANFORD OPERATIONS

Process Description. Tritiated water at low concentrations in light water is preferentially loaded on a proprietary adsorption bed as hydrated water, allowing the tritium-depleted stream to pass through the bed. Cation sites attached to the bed media are employed to preferentially hydrate the tritiated water. This loading process is conducted at about 303 K (30°C). The tritiated water feed stream is introduced at the bottom of column#1, as shown in Figure 4. The water flows up through the bed where it is removed from the top of the column as a depleted tritiated water stream. The bed media material is introduced at the top of column #1 and flows downward to form a countercurrent flow through the column. Tritiated water adsorption on the bed was found to be directly proportional to feed concentration and bed volume. Depleted tritiated water streams with a tritium concentration below the MCL are possible by using the appropriate bed length and residence time to accomplish the necessary exchange. The appropriate bed length and residence time to obtain target tritium concentrations will be determined from demonstration tests.

As the media moves down through the column and becomes loaded, it is removed from the bottom of the column to a tritium-removal and media-regeneration system. Free water is drained from this removed media and recycled back to the column's tritiated water feed tank. More than one media-receiving tank will be used to provide the capability of continuous processing through the column. The removed media is then heated to a moderate temperature of about 378 K (105°C) to remove the remainder of the interstitial water and the lightly held hydration water. These waters are returned to the column's feed tank for reprocessing and constitute approximately 50% of the feed-flow stream. The media-bed material is then heated to about 418 K (145°C) and the more strongly bonded hydrated water (including the bulk of the tritiated water) is swept off the media as water vapor with a heated nitrogen gas flow and is passed through a condenser. The condensate from the condenser, containing the bulk of the tritiated water, is collected as liquid in a receiving tank. The volume of condensed water amounts to 0.25 to 0.5 percent of the original volume of feed and contains about 99 percent of the tritiated water. The gas from the condenser is recycled to a heater for reuse. The regenerated adsorber material is then recycled to the top of the column for reuse.

This smaller volume of tritiated water is then pumped to the bottom of column #2. This column is smaller, has a moving bed similar to column #1, and receives media at the top of the column. The tritium is loaded on the bed media, and the tritium-depleted stream is removed from the top of the column and recycled back to the feed tank of column #1. This recycled stream constitutes only a small fraction of the volume of the feed stream to column #1.

The media is removed from the bottom of the column to the #2 media-recovery system, where it is drained and the tritium is removed the same as for the #1 media-recovery system. The drained water is pumped back to the #2 column feed tank. The tritiated water in the gas stream is loaded on a molecular sieve and then grouted for disposition. The gas from the molecular-sieve bed is recycled and reheated for reuse. The dehydrated media is recycled to its respective column for reuse to load additional tritiated water with no detrimental effects.
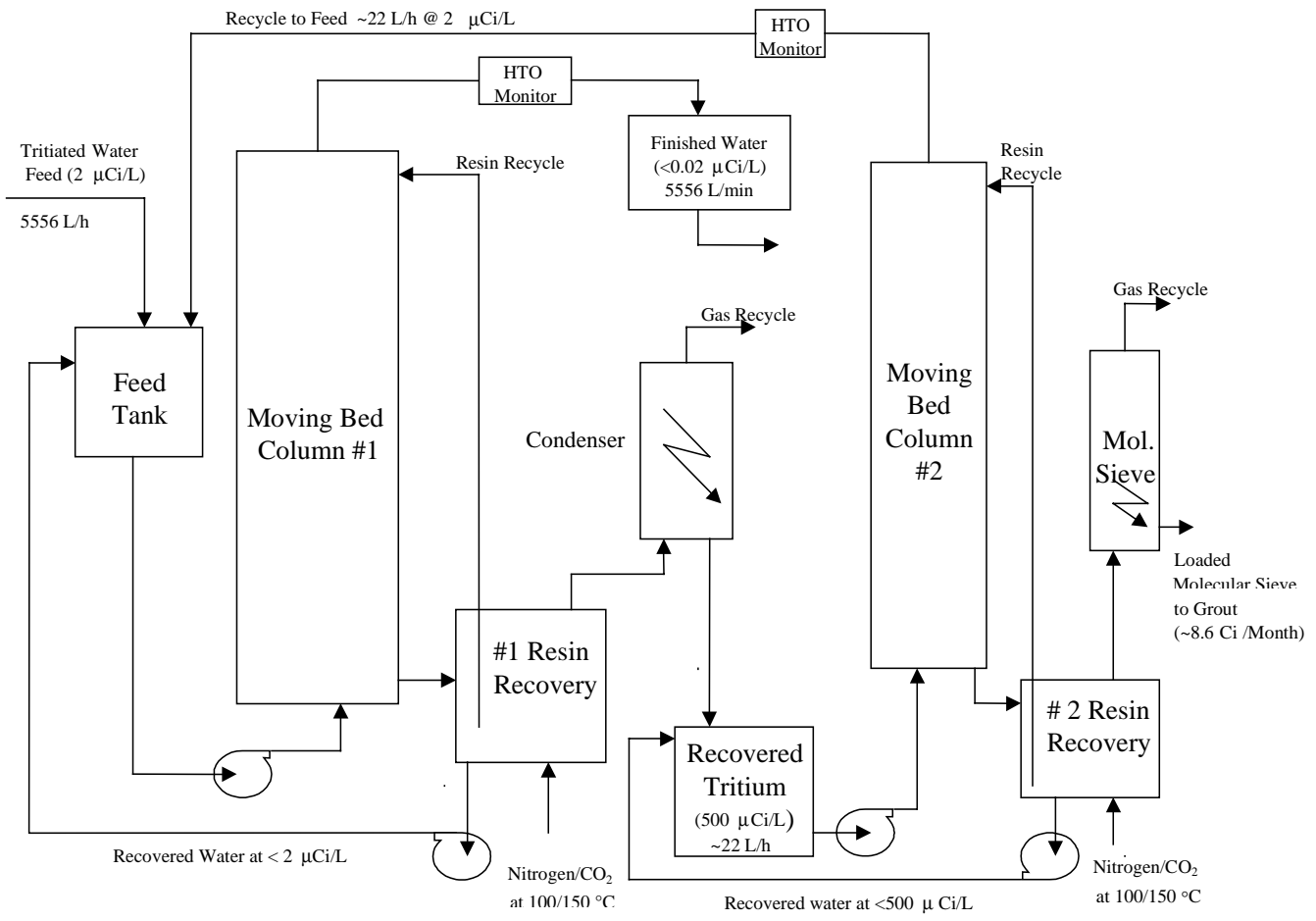
Figure 4. Moving-Bed Tritium Resin Separation Process

Recycle to Feed ~22 L/h @ 2 µCi/L

HTO Monitor

HTO Monitor

Tritiated Water Feed (2 µCi/L)

5556 L/h

Resin Recycle

Finished Water (<0.02 µCi/L) 5556 L/min

Resin Recycle

Gas Recycle

Feed Tank

Moving Bed Column #1

Condenser

Moving Bed Column #2

Mol. Sieve

Gas Recycle

#1 Resin Recovery

Recovered Tritium (500 µCi/L) ~22 L/h

2 Resin Recovery

Loaded Molecular Sieve to Grout (~8.6 Ci /Month)

Recovered Water at < 2 µCi/L

Nitrogen/CO₂ at 100/150 °C

Recovered water at <500 µ Ci/L

Nitrogen/CO₂ at 100/150 °C

SUMMARY

The MSI media used in the loading bed process is thermally and chemically robust. However, if the feed contains active cations such as sodium in groundwater, the media is susceptible to competing ion exchange. The feed stream must be essentially clean of other contaminants, such as other radionuclides, sodium, and organics, or must be cleaned before it is processed for tritium removal. The Hanford Site ETF effluent stream appears to be an acceptable feed, without pretreatment, for this process.

The Hanford Site fuel-basin waters are expected to be processed through the ETF, and the resulting effluent should also be acceptable feed for this loading bed process.

Groundwater at the Hanford Site will need prior treatment to remove soluble cations or organics. Modular loading bed units could be set up at various locations, as needed, to pump and treat groundwaters at the Hanford Site.

This process appears promising and is available for a demonstration-phase application. The process requires a phase change of a major portion of the stream during media reconstitution. Chemical conversion of the tritium to a different compound is not required for this separation process, and this process should be economically competitive. The process is safe and does not require handling flammable or explosive gases or the use of high pressure as do conventional tritium separation processes such as electrolysis, catalytic exchange or the Girdler Sulfide process. This process is new and would require further demonstration of a moving bed system at the Hanford Site and favorable detailed cost estimates to implement. Scale-up to meet operational requirements is also needed.

REFERENCES

1. Fulbright, H. H., A. L. Schwirian-Spann, K. M. Jerome, B. B. Looney, and V. Van Brunt, 1997, *Status and Practicality of Detritiation and Tritium Reduction Strategies for Environmental Remediation,* WSRC-RP-96-0075, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina.

2. Miller, A. I., 1999, *Tritium Treatment Technologies for Groundwater Remediation at Savannah River Site*, WSRC-OS-98-00127, prepared by Chalk River Laboratories and Atomic Energy of Canada, Limited, for Westinghouse Savannah River Company, Aiken, South Carolina.

3. Jeppson, D. W., 1999, *Evaluation of Technologies for Removal and Mitigation of Tritium in Hanford Site Wastewaters,* DOE/RL-97-54, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington

4. HST, 1991, RL-MW023, *Technology Need/Opportunities Statement, DOE/RL-98-01, Rev. 1,* Hanford Science and Technology for the U. S. Department of Energy, Richland Operations Office, Richland, Washington.