Evaluation of Low Level Waste Technology - " A Media Based Tritium Removal Process"

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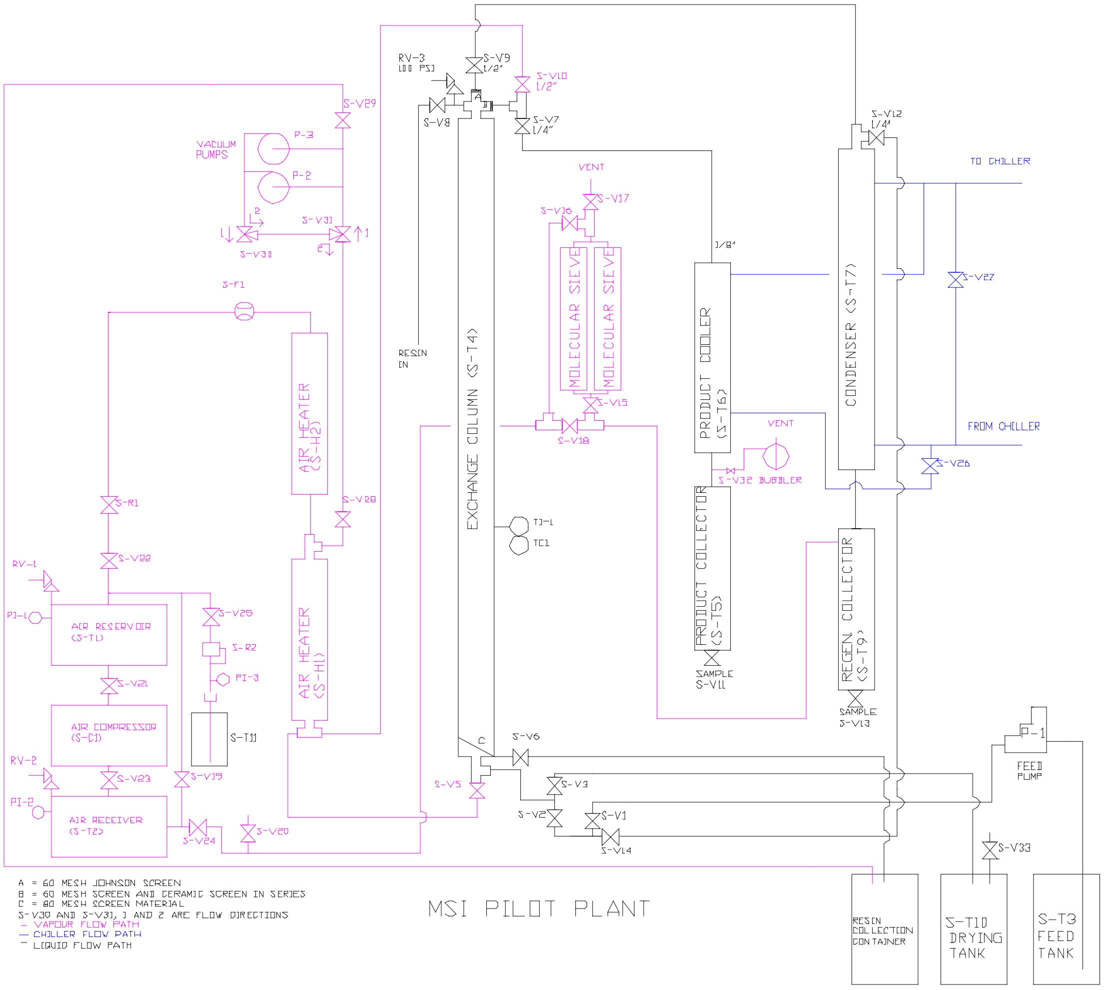

Evaluation of a Low Level Waste Technology – “A Media Based Tritium Removal Process”

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Final Report, January 2002

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REPORT SUMMARY

Existing technologies for removal of tritium liquids require a large capital investment which utilities cannot justify based on the extremely low dose values experienced. For this reason, the potential for a media based process under development by Molecular Separation Inc. (MSI) has generated considerable interest within the nuclear industry. EPRI directed this project to enhance understanding of the process and assess its viability as a nuclear plant radwaste processing technology.

Background

Several nuclear plant operators have expressed an interest in achieving “zero” activity release from their liquid waste systems. From a practical standpoint, 0.1 curies of fission product and activation activity represents a fraction of one percent of that allowed under present regulations. Similarly, the dose associated with the discharge of radioactive tritium is less than one tenth of one percent of the annual dose allowable to a member of the public in an unrestricted area (10CFR20.1301). For this reason, tritium release is not an item of concern for the majority of nuclear plants. However, a few utilities have expressed interest in tritium removal due to unique features at their nuclear sites (e.g. discharges into small bodies of water).

Objectives

To perform a comprehensive evaluation to determine if the media based process is commercially viable for large scale processing.

Approach

Project managers structured the study into distinct tasks. The goal was to extend earlier laboratory experiments to allow reasonable scale up to commercial processing. Additionally, the project team designed various tests to define key process parameters and uncover limiting conditions that would adversely affect the process. These included:

- Assessing the affect of common nuclear plant ionic species on the media’s tritium removal performance.
- Defining key characteristics related to removal media processing.
- Quantifying the removal of tritium from nuclear plant liquids.
- Assessing basic economics associated with the technology.

Based on achieving favorable results in this initial phase, the project team planned additional work to demonstrate the tritium removal process in an actual plant application.

Results

The project team has clearly demonstrated tritium removal with the TRS Process in the test work performed to date. Initial laboratory data showed significant reduction in the tritium concentration in wastewater samples. However, further testing strongly suggests that commercialization of the current process is unlikely. The project team based this conclusion on the exceedingly low capacity of the media and the need for complete media drying. Both the drying requirement and the low capacity translate into major hardware capital expenditures.

EPRI Perspective

Over the past decade, utilities have achieved major reductions in radioactive discharge from nuclear plant operations. The vast majority of plants release less than 0.1 curies of fission product and activation activity annually, well within present regulations. As our utility members continually strive to drive these discharges even lower, EPRI will investigate and develop the latest technologies needed to meet these challenging goals. This project assessed a unique media based process under development by Molecular Separation Inc. Earlier laboratory testing suggested an effective low capital investment tritium removal technology. EPRI directed this work at assessing its viability as a commercial process for nuclear plant wastewater.

Keywords

Low level radioactive wastes
Liquid processing
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Radioactive waste processing

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INTRODUCTION

Over the past decade, major reductions in the radioactive discharges from nuclear plant operation have been achieved. The vast majority of plants release less than 0.1 curies of fission product and activation activity annually. Several Boiling Water Reactor (BWR) plants have moved to “zero” liquid release and eliminated plant liquid discharges completely. Similarly, Pressurized Water Reactor (PWR) plants have optimized their liquid processing programs to minimize waste generation and by applying advanced processing strategies and technologies.

Several nuclear plant operators have expressed an interest in achieving “zero” activity release from their liquid waste systems. From a practical standpoint 0.1 curies of fission product and activation activity represents a fraction of one percent of that allowed under present regulations. Similarly, the dose associated with the discharge of radioactive tritium is less than one tenth of one percent of the annual allowable dose to a member of the public in an unrestricted area (10CFR20.1301). For this reason, the vast majority of nuclear plants tritium release is not an item of concern. However, a few utilities have expressed interest in tritium removal due to unique features at their nuclear sites (e.g. discharges into small bodies of water).

However, existing technologies for removal of tritium liquids require a large capital investment. Such investments cannot be justified based on the extremely low dose values being experienced. For this reason, the potential for a media based process under development by Molecular Separation Inc. (MSI) has generated a considerable interest within the nuclear industry. Initial laboratory data showed significant reduction in the tritium concentration of a wastewater. Commercialization of the process will require a comprehensive evaluation of a number of details relating to the process to determine if it is viable for large scale processing. This project is directed at enhancing the understanding of the process and assessing its application and viability to nuclear plant radwaste processing.

1.1 Nuclear Plant Tritium Production

Tritium is produced in light water reactors by both neutron activation and fission. However, the predominant mechanism of tritium production is thermal and fast neutron activation of boron-10.

$$^{10}B(n,2\forall)\rightarrow T \qquad \text{[Eq. 1-1a]}$$

$$^{10}B(n,\forall)\rightarrow {}^{7}Li(n,n\forall)\rightarrow T \qquad \text{[Eq. 1-1b]}$$

Boron-10 is a naturally occurring isotope representing approximately 20% by weight of chemical boron. Boron-10 is a very efficient neutron absorber and as such is used for chemical shim and reactivity control in PWRs.

Tritium production via reaction 1-1a is from fast neutron activation of boron-10. For this mode of production, tritium generation follows the concentration of boron-10 in the reactor coolant. At the start of the fuel cycle the boron concentration is around 1,000 ppm. The boron concentration is then steadily reduced over the course of the fuel cycle to essentially zero at the end of the year-long fuel cycle. Thus, tritium production via this mechanism will initially be high and then decline linearly over the course of the fuel cycle.

Tritium formation by the duplex reaction (equation 1-1b) is by thermal neutron activation of boron-10 to lithium-7 and then fast neutron activation of lithium-7 to tritium. Thus, tritium production via this reaction constantly builds up over the course of the fuel cycle as the lithium-7 concentration increases.

The overall formation of tritium from boron-10 is the sum of that produced from reaction 1-1a plus 1-1b as shown in Figure 1-1 for a 1,000 MW_e reactor(1). Tritium produced by these mechanisms represents approximately 95% of the total tritium released from the plant each year.

Less important mechanisms of tritium production include neutron activation of lithium-6 (equation 1-2) and neutron activation of hydrogen gas (equation 1-3).

$$ {}^{6}\mathrm{Li}(n,\forall)\rightarrow \mathrm{T} \qquad [\mathrm{Eq.}\ 1\text{-}2] $$

$$ \mathrm{H}_2(n,\gamma)\rightarrow \mathrm{T} \qquad [\mathrm{Eq.}\ 1\text{-}3] $$

Together, these two mechanisms for tritium production represent less than about 5% of the total tritium produced by a commercial nuclear generating plant each year.

Tritium is also a ternary fission product of power reactors. Tritium is produced at a rate of 8.7 x 10^{-5} triton per fission in U-235 fueled reactors. Due to the energy of these fission products and normal fuel cladding thickness of 16.5 to 33 mils, essentially none of these tritons will recoil through the cladding. Also, there is little evidence of diffusion of this tritium through the cladding into the reactor coolant[1]. Thus, barring fuel leaks, this tritium source is of no significance.

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[1] Radbench, Version 1.0 "Technical Benchmarking of Industry Wide LLW Process." 2001. EPRI, Palo Alto, CA. 1001003

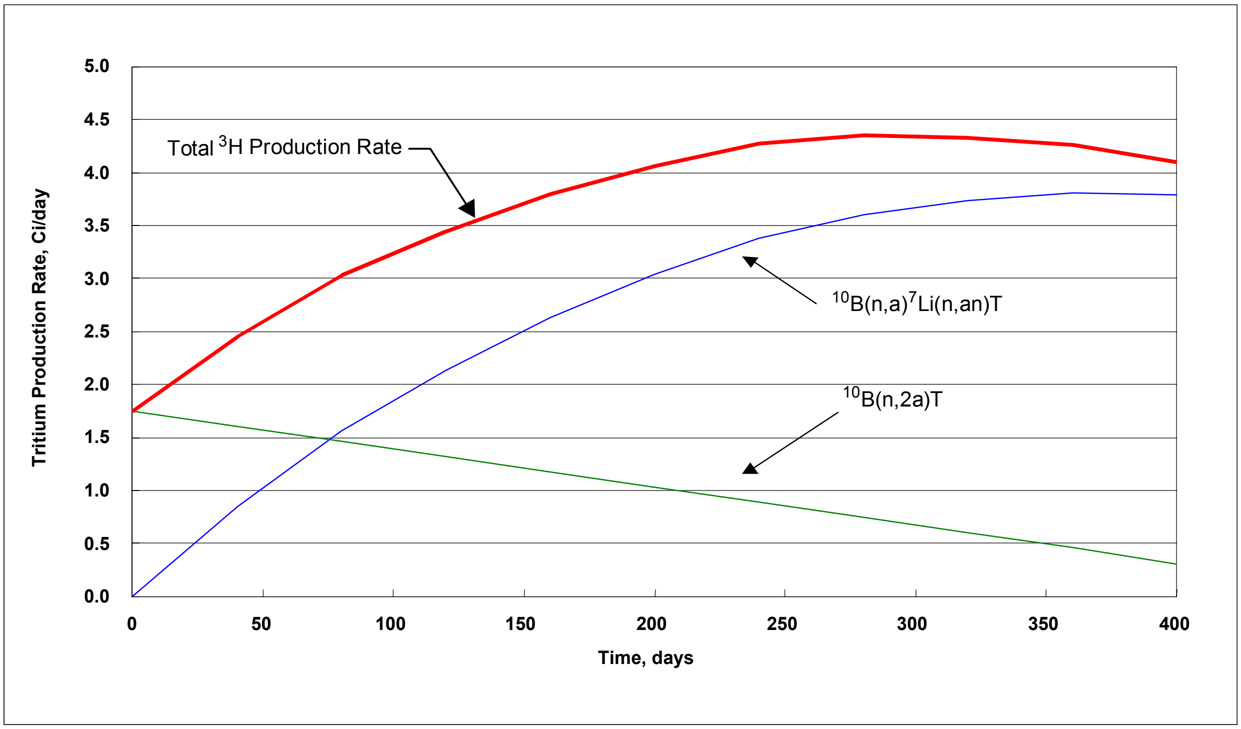

Figure 1-1
Tritium production rate per day for a typical 1,000 MWe pressurized water reactor.

1.2 Nuclear Plant Tritium Release

Tritium is released from nuclear plants via two major pathways. First, as a gaseous water vapor release through the plant air ventilation system. Second, as a liquid discharge through various plant release points, the major being the plant radwaste processing system. Figure 1-2 graphically shows the breakdown of tritium release between these two pathways for BWRs and PWRs.

This data shows that the liquid pathway is the dominant tritium release mechanism for both BWRs and PWRs. Additionally, due to the use of boron as a reactor chemical control the tritium released by PWRs is approximately an order of magnitude larger than that of BWRs.

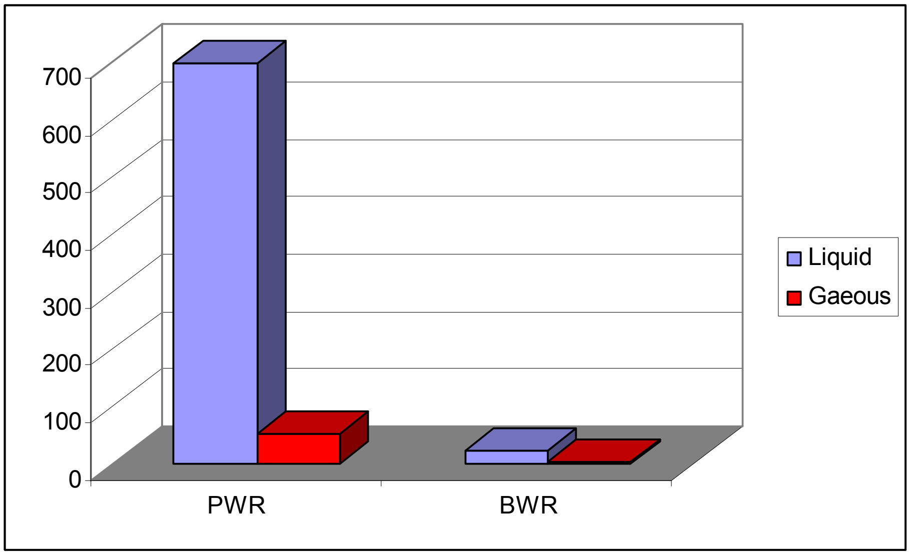

Figure 1-2
Annual Gaseous and Liquid Tritium Release, Curies

Source – NUREG 51581 Volume 14, Radioactive Materials Release from Nuclear Power Plants 1993.

Tritium is a low energy beta emitter (B – 5.7 Kev) with a 12.3 year half-life. For this reason, the resulting dose to an individual member of the public via the liquid release pathway is quite low. Figure 1-3 shows the calculated annual whole dose along with the tritium portion of the dose to a member of the general public for a typical BWR and PWR plant. In both cases the dose is less than 0.1 mRem, which represents less that 0.1% of the value allowed under existing regulations.

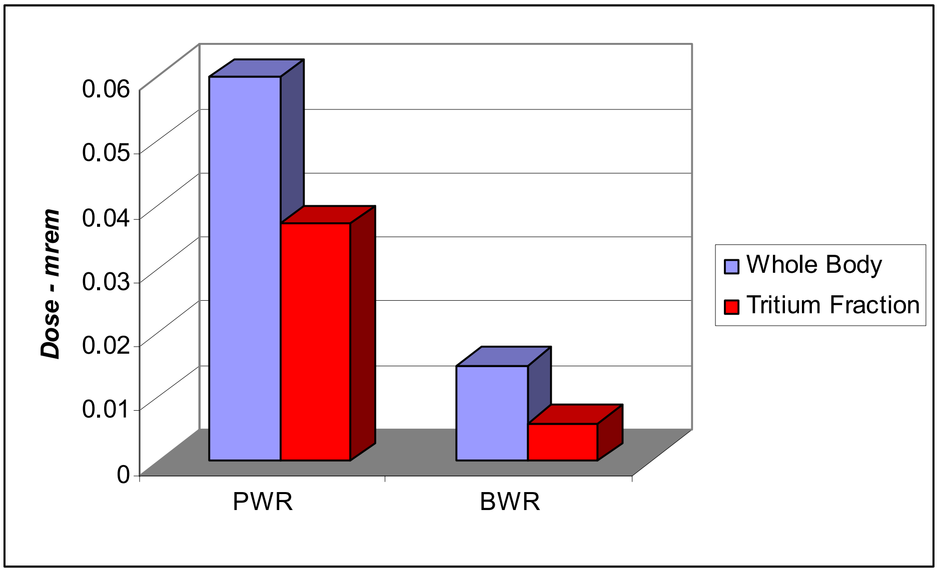

Figure 1-3
Annual Environmental Dose

2

MSI TRITIUM RESIN SEPARATION (TRS) PROCESS

2.1 Discussion of the TRS Process

The TRS Process is a proprietary method for the preferential removal of tritium from liquids. The process has been shown to selectively adsorb tritiated water (HTO) through the hydration of ions loaded onto a conditioned resin media. Typical adsorption materials include commercial exchange resins such as sulfonated polystyrene/divinylbenzene (cation) resin. Prior to use the resin is pretreated by loading the ion exchange sites with aluminum sulfate to form an Al^{+3} site bonded to at least one sulfonated group in the media structure. Aluminum in this form has a high number of waters of hydration and due to the energy associated with the hydration the resin has a greater affinity for tritiated water (HTO) over light water (HOH). The tritium removal is conducted at near ambient temperatures (87^0 F, 30^0 C) and low pressure (30 psi, 2 bar absolute). Preconditioning is required to remove competing cations from the feed stream. Their presence would adversely affect the process by removing the aluminum ions from the resin media.

Once removed from the wastewater, the captured tritium is released from the media by a stepwise drying process. The first drying stages remove interstitial and adsorbed light water from the media. This water is returned to the inlet stream for reprocessing. The last stage of the process involves subjecting the media to high temperature air (300^0 F, 150^0 C) to completely dehydrate the media. The liquid removed in this step is elevated in tritium and is ultimately captured for disposal on a molecular sieve.

2.2 Early Testing of the TRS Process

A series of laboratory bench tests conducted at Washington State University confirmed the selective adsorption of tritiated water (HTO) by means of a TRS media. Based on this confirmation, a pilot plant was constructed at Clemson Environmental Technology Laboratory. The unit consisted of four (4) test columns each 2 meters (79 in) tall by 2 cm (.8 in) in diameter. The connecting piping allowed the columns to be operated individually or in series. System flow entered at the bottom of the columns and was maintained at 0.5 L/hr (0.13 gph), which corresponded to a linear flow through the bed of 2 cm/min (.8 in/min). Media was added to the system in a dry form. Media regeneration was accomplished by means of fluidizing the media with heated air in an external glass vessel with a diameter of 7 cm (2.8 in) and a height of approximately 1 meter (39 in).

A test program was designed to define optimum process conditions and various exchange media using representative field samples of tritiated water. Over 80 test runs were conducted using standard solutions, samples from the DOE Hanford site, Brookhaven National Laboratory and various PWR nuclear power plants. Typical results of this testing are shown in Table 2-1 below.

Table 2-1
Summary of Clemson TRS Process Testing

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

(a) Maximum Tritium Decrease is experienced at the beginning of the test run.

(b) Integrated adsorption per unit volume of media adjusted for the initial feed concentration.

(c) 1000 μci/L equals 3.7 E+7 Bq/L

Figure 2-1 shows the tritium removal for the Hanford and Brookhaven test runs. In these cases, the Maximum Tritium Decrease (value at the very beginning of the service run) for both samples was in the range of 78 to 83%. The Hanford media (2 columns) was essentially fully exhausted after passing 85 ml of feed solution. The Brookhaven media (2 columns) exhaustion was reached after passing 150 ml; this difference is believed to be related to the higher concentration of tritium in the feed water.

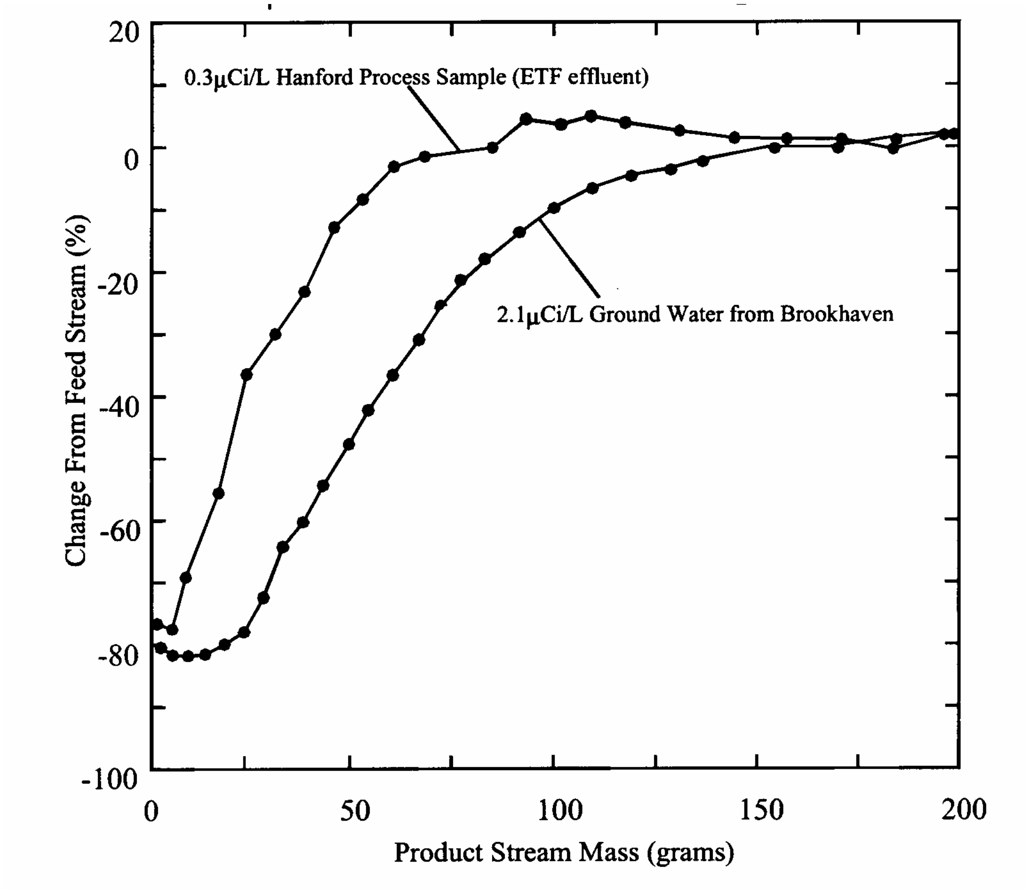

Figure 2-1
Tritium Adsorption Curves from Clemson Testing

Analysis of the test results concluded that the <u>total tritium micro curies removed</u> during the service run (integration of the removal during the run) was:

1. Directly proportional to the amount of media used for processing.
2. Directly proportional to the tritium concentration in the feed stream.

The term Maximum Tritium Reduction refers to the percent reduction at the start of the run, the test work showed that for dilute tritiated streams the initial reduction is independent of feed concentration.

3

PROJECT TEST PROGRAM

3.1 Overall Test Program Discussion

The project was structured into distinct tasks. The initial work was directed at assessing the tritium removal process as it relates to nuclear power plant liquids. The goal was to extend earlier results of laboratory experiments to a size that would allow reasonable scale up to commercial processing. Additionally, various tests were designed to define key process parameters and uncover limiting conditions that would adversely affect the process. Based on achieving favorable results in this initial phase, additional work was envisioned to demonstrate the tritium removal process in an actual plant application.

The project's intended objectives were to provide the industry with the following information related to the TRS removal process:

1. Assessing the affect of common nuclear plant ionic species on the removal media's performance in the processing of radioactive liquid waste streams.
2. Defining key characteristics related to removal media process.
3. Quantifying the removal of tritium from nuclear plant liquids.
4. Assessing basic economics associated with the technology, as it would be applied to nuclear plant liquid processing.

Beaker tests were used to address items 1 and 2. The media was repeatedly exposed to ionic contaminants and organic compounds commonly found in nuclear power plant waste streams. Since the media of choice was cation resin pre-loaded with aluminum ions, loss of aluminum due to exposure would indicate no loss of tritium removal capacity. Similarly, loss of sulfur would indicate deterioration of the resin structure. Beaker tests where the resin was exposed to pure tritiated water provided a measurement of the resin media's distribution coefficient K_d value, a measurement of the media's ultimate removal capacity.

Pilot plant column testing addressed Item 3 by focusing on quantifying the tritium removal capacity in a column larger than that used on earlier laboratory tests. Additionally, operation of the pilot plant system would provide significant data on the process parameters, e.g., time, temperatures, media physical performance and tritium capture.

The information generated in this test program would be used to assess the process viability and basic economics related to a nuclear power plant processing application.

3.2 Beaker Tests

The work was performed by Duratek in a radiological controlled area (RCA) at the ChemNuclear Consolidation Facility (CNCF), Barnwell, South Carolina.

Beaker tests to determine media effectiveness were performed prior to pilot plant testing. The media used included P26I (organic) prepared at the Clemson Technical Center, I20A, and I20B (both inorganic) media prepared at CNCF. The tests involved placing 10 ml of each media formulation in a beaker. 20 ml of tritiated water was then added to each beaker. The beakers were then stirred on a magnetic stir plate for 2 hours. Liquid was decanted from each beaker for tritium analysis. A scintillation detector located at CNCF was used to analyze the samples taken during bench testing. The decrease in tritium concentration was a measure of media capacity under pure water conditions.

The results of the media after exposure to tritiated water are found in Table 3-1.

Table 3-1
Base Case Tritium Removal Tests

Media	HTO Feed Concentration µCi/ml	Concentration of Decant µCi/ml	Percent HTO removal
P26I	5.44	4.23	22.23%
I20A	5.44	3.32	38.87%
I20B	5.44	5.40	0.79%

Note: 1)Tritiated liquid sample provided by Carolina Power & Light.

2) 1000 µci/L equals 3.7 E+7 Bq/L

The results from the media beaker capacity tests demonstrated positive tritium removal for P26I (organic) media and I20A (inorganic) media. The organic media P26I was selected for use in the pilot test based on its effective removal of HTO in previous tests. The media effectiveness bench test did not indicate this, but the research group believed that the pilot plant process would be more effective because of the height of the media (bed height) in the column.

3.3 Contaminant Beaker Tests

Media contamination beaker tests were then performed using the P26I media. Four wastewater surrogates were prepared containing common impurities found at nuclear plants. These surrogates included solution containing 400 ppm of boron, a solution of 1.5 ppm lithium, a solution containing 150 ppm silica, and one of 4 ppm turbine oil.

Four 5 ml samples of media were placed in separate beakers. Next, 20 ml of one surrogate was added to each beaker. Each test exposed the media to only one impurity. These beakers were then placed on a heated stir plate. Temperature of the samples was raised to 50^0C (120^0F) and mixed for two hours. The beakers were then decanted and ten beads of media were removed from each beaker for a Electron microprobe analyses (EMPA). Each media was then exposed to the surrogate four more times. After the fifth exposure, another ten pellets were removed from each sample for EMPA analysis. Ten pellets of unexposed media were prepared as a blank for analysis. EMPA work was performed at the University of South Carolina.

The percent of media aluminum and sulfur remaining after repeated exposures to the impurities can be found in Table 3-2.

Table 3-2
Media Beaker Contamination Test Results

Sample	**Aluminum**	**Percent Aluminum Remaining % After Exposure**	**Sulfur**	**Percent Sulfur Remaining % After Exposure**
Sample (Blank) Clean P26I media	2.6	N/A	15.99	N/A
Sample - 150ppm Silica 1 exposure	2.63	100%	16.54	100%
Sample - 150ppm Silica 5 exposures	1.87	71.92%	10.54	65.92%
Sample 400ppm boron 1 exposure	2.64	100%	16.00	100%
Sample 400ppm boron 5 exposures	0.47	18.08%	2.21	13.82%
Sample 1.5ppm lithium 1 exposure	2.35	90.38	14.92	93.31%
Sample 1.5ppm lithium 5 exposures	1.27	48.85%	6.96	43.53%
Sample 4ppm Turbine Oil 1 exposure	2.15	82.69%	12.97	81.11%
Sample 4ppm Turbine Oil 5 exposures	1.51	58.08%	8.49	53.10%

The media contaminant beaker tests indicated that after five exposures to common impurities, large portions of the aluminum and sulfur were lost. The sample exposed to 400 ppm boron lost 81.92 % aluminum and 86.18% sulfur. The loss of aluminum and sulfur is directly proportional to the sites of hydration and deterioration of the media. Samples exposed to lithium and turbine oil also experienced aluminum and sulfur loses. Although not as extreme as exposures to boron, the impurities would reduce the sites of hydration by approximately one half. Tests verified that impurities would have to be removed first to increase media effectiveness and reduce waste generation.

3.4 Pilot Plant Column Tests

Description of Equipment and Pilot Plant Operation

Equipment

A pilot plant was constructed by Duratek which would allow adsorption and regeneration phases to be performed in the same column. Figure 3-1 shows a schematic of the Pilot Plant System and Table 3-3 gives a summary of the Pilot Plant components. This simplified the size and complexity of the system because the media would only have to be sluiced once during initial loading. The main column (S-T4) was 3 inches (7.6 cm) in diameter with a height of 68 inches (173 cm). Working volume of the column was 6 liters (1.6 gal) of hydrated media. Dry media, previously weighed, was sluiced into the column by creating a vacuum using vacuum pumps P-3 and P-4. Media was sluiced out in the same manner. The column was wrapped with heating strips and insulated. Temperature was controlled with a programmable logic controller (PLC). Column temperature was held at 50^0C (120^0F). The feed tank S-T3 was filled with 15 liters (4 gal) of tritiated water and weighed. Airflow was established at a flow rate of 20 SCFH (0.6 SCMH) via the air compressor to prevent column blockage during media hydration. A peristaltic pump was used to feed tritiated water into the column. Samples were cooled and collected during the adsorption phase via product cooler S-T6 and product collector S-T5 respectfully.

Sampling Schedule

When five liters of tritiated water from the feed tank had been pumped into the column, media hydration was completed and airflow secured. The feed pump continued to pump tritiated water from the feed tank into the column. After seven liters were pumped from the feed tank into the column, treated water flowed down to the product collector. Five 100 ml samples were taken. Next, ten 250 ml samples were taken and five 1 liter, samples were taken until the feed tank was empty. All samples were weighed. The adsorption phase was complete at this point.

Pilot Plant Operation

The regeneration phase dehydrated the media. The column temperature was raised to 80^0C (176^0F). Water in the column was gravity drained to the drying tank S-T10. When water flow stopped, air was supplied to the top of the column via the air compressor to force freestanding liquid from the column. The drying tank had approximately 4.5 liters of water in it. The water was weighed and a sample was taken. The column temperature was then raised to 120^0C (250^0F). Air was recirculated through the column from bottom to top. Using the air heaters, the air temperature was held at 120^0C (250^0F). The flow rate was set at 250 SCFH (7 SCMH).

Moisture removed from the media was collected in the regeneration collector S-T9. The temperature and recalculating airflow rate were maintained for four to five hours. Approximately 2.5 liters (7 gal) of condensate was collected in the regeneration collector and weighed. When no more condensate was captured in the regeneration collector, the column and air temperatures were raised to 160^0C (320^0F) and airflow was directed through the molecular sieve. The remaining moisture (elevated tritium concentration) was removed from the media due to the elevated temperature and captured on the molecular sieve. This took approximately 4 hours. At this point the media was regenerated and ready for the next operating cycle.

Table 3-3
Summary of Pilot Plant Components

Component	**Description**
Feed Tank (S-T3)	15 Liters capacity (4 gal)
Peristaltic pump	Flowrate of 125 ml/min. (0.03 gpm)
Primary Column (S-T4)	Approximately 6 Liter capacity (1.6 gal) with dimensions 3 in. (7.6 cm) dia. X 68 inch (1.7 m) long, media normal loading approx. 2000-2100 g. (4.4-4.6 lb) Equipped with a wrap heater capable of holding the water temperature within the column at a set point in the range of 50 to 120^0 C (120-250^0F).
Air supply with heater system.	Delivery/recirculation – 20 to 250 SCFH (0.6-7 SCMH)
Product Collector Tank (S-T5)	7 Liter (1.8 gal) capacity equipped with a pre- product cooler (S-T6)
Dry Tank (S-T10)	4.5 Liter (1.2 gal) capacity
Regeneration Collector (S-T9)	2.5 Liter (0.7 gal) capacity equipped with a pre-condenser (S-T7)
Molecular Sieve	Silica Gel

Simplified summary of the processing steps

Processing – Time 2 hours

- Tritiated feed is pumped to the bottom of the primary column (125 ml/min., 0.3 gpm).
- In some of the tests air was supplied to the bottom of the column at 20 SCFH (0.6 SCMH) to prevent media plugging.
- Primary column temperature is held 50^0C (122^0F).
- The process water is collected in the Product Tank.

Drying – Time 4 to 5 hours

- Primary column is drained to the Dry Tank.
- Heated Air is introduced to the primary column from the top to blow the remaining moisture from the media.

Regeneration – Time 4 hours

- Primary column temperature is raised to 120^0C (250^0F)
- Air is recirculated through the column from the bottom @ 250 SCFH (7 SCMH) and the air temperature is maintained with the air heaters.
- After leaving the column the air is cooled and the moisture is condensed into the Regeneration Tank.
- As a final step, the air temperature is raised to 160^0C (320^0F) and routed through the molecular sieve for removal of the tritium remaining in the air stream.

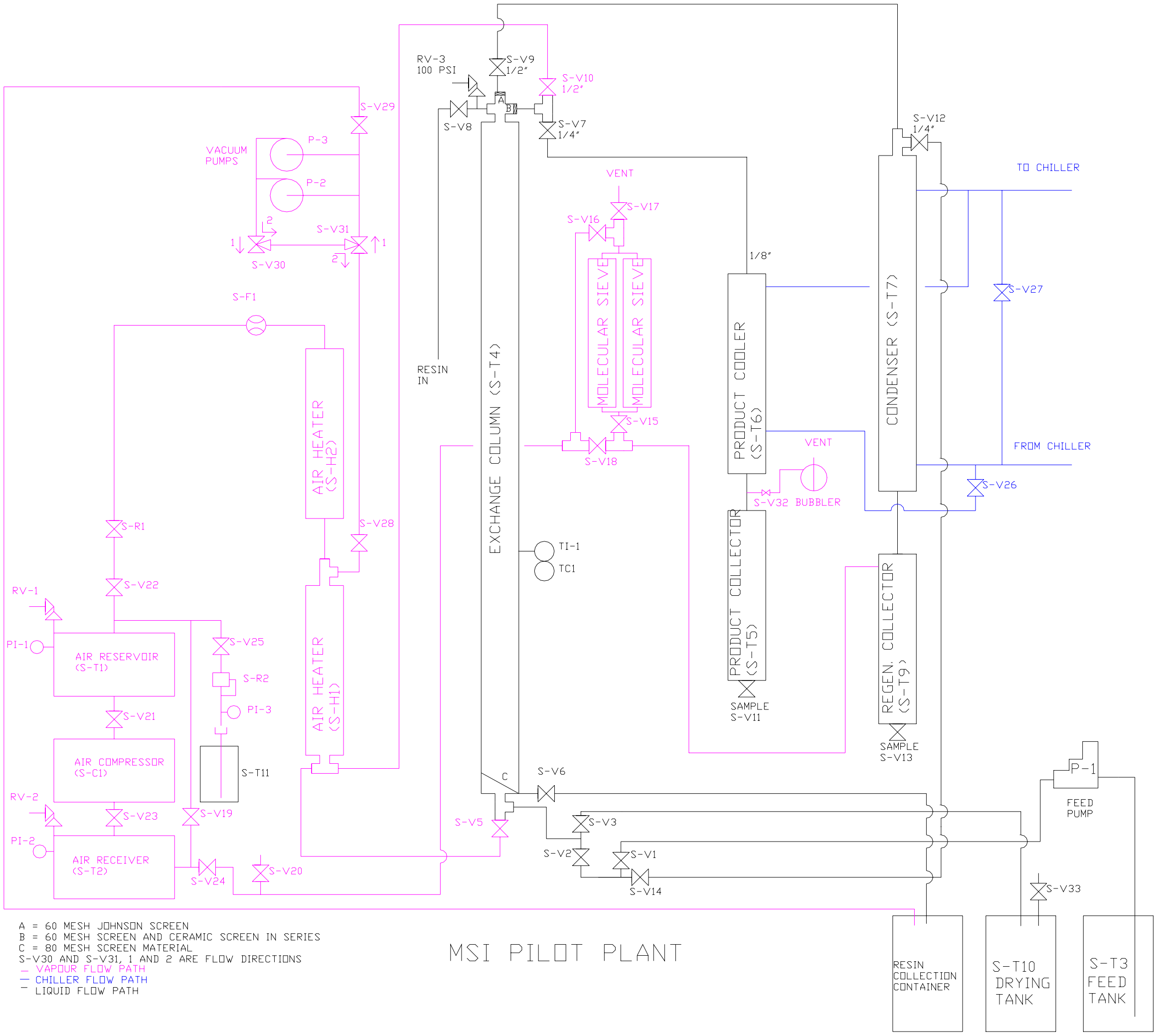

Figure 3-1
Pilot Plant System Schematic

Column Test 1. – Media P26I, Cycle 1

Discussion Column Test 1. – Media P26I, Cycle 1

The column was loaded with P26I media. The feed tank S-T3 was filled with tritiated water provided by CP&L and the column temperature was raised to 50^{0}C (122^{0}F). An airflow of 20 SCFH (0.6 SCMH) was established through S-V5. The feed pump was started at 125 ml/min (0.03 gpm). After pumping 2.5 liters (0.7 gal) into the column it was noted that column temperature had risen to 104^{0}C (220^{0}F). Airflow was secured after 5 liters (1.3 gal) had been pumped into the column. The temperature began to fall as more feed water was pumped into the column. When a total of 7 liters (1.8 gal) was in the column, the column temperature had returned to 50^{0}C (120^{0}F).

The next day, samples were then taken as reported in Table 3-4 and analyzed for tritium concentration. The samples were severely colored and contained solids less than 120 micron in size.

The temperature of the column was raised to 80^{o}C (175^{0}F). The water was drained from the column and collected in the drying tank S-T10. The pilot unit was then aligned for intermediate drying phase. Column temperature was raised to 120^{o}C (250^{0}F) and airflow through the column was established and was set at 250 SCFH (7 SCMH) and the air temperature raised to 120^{o}C (250^{0}F) to match the column temperature. After 4 hours, 2,473.4 grams (5.4 lb) of condensate was collected. The system was aligned for the final drying phase. Air and column temperatures were raised to 160^{o}C (320^{0}F). Airflow was now directed through the molecular sieve for final removal of the tritium. The process was complete after 4 hours. The total cycle took approximately 12 hours to complete.

The results in Table 3-4 indicate that the media, after processing 15 liters (4 gal) of water with a tritium concentration of 6.35 µCi/ml, was never fully depleted. Each sample showed a reduction in tritium concentrations except for two samples (4 and 20). The higher concentrations could be due to instrument error or randomness associated with counting. Air was required for agitation and mixing to prevent column blockage during the media hydration. The result was a uniform and consistent tritium removal rate, but the media was not exhausted at the termination of the cycle. If processing could be performed without agitating and mixing the media, it is possible that higher removal rates could have been obtained. In this case, the feed would have encountered less depleted media as it traveled up through the column.

Another processing anomaly was the exothermic reaction encountered during hydration of the media. The actual temperature of the media could not be obtained since the column thermocouple was above the media on the outer wall. The column temperature reached >100^{0}C (212^{0}F) before enough feed could be pumped in to lower the temperature. It is believed that this caused the media to breakdown causing lower performance. While collecting samples, it was noted that there was severe coloration and solids in the product water.

Test 1 Results

Column Loading Media g. - 2097 g (4.6 lb)

Feed Tank Volume ml, µCi - 14,956 g, 94,969 µCi (32.9 lb, 3.5 E+9 Bq)

Product Tank Volume ml, µCi - 7,111 g, 42,567 µCi (15.7 lb, 1.6 E+9 Bq)

Drying Tank Volume ml, µCi - 4,671 g, 4,671 µCi (10.3 lb, 1.7 E+8 Bq)

Regeneration Tank Volume ml, µCi - 2,473 g, 15,006 µCi (5.4 lb, 5.6 E+8 Bq)

Total Process Time hrs. - 12 hrs.

Table 3-4
Cycle 1 using P26I media

	grams	•Ci/g	•Ci
Feed	14,955.78	6.35	94969.2
Samples			
1	99.02	5.84	578.08
2	96.05	5.86	562.76
3	98.37	5.674	558.15
4	98.09	12.30	1206.12
5	100.87	5.75	580.00
6	251.7	5.81	1462.88
7	253.88	5.45	1383.9
8	248.68	5.81	1444.09
9	250.87	5.75	1441.25
10	249.51	5.87	1463.88
11	253.1	5.80	1468.74
12	253.85	5.70	1446.69
13	253.27	5.97	1511.01
14	254.98	5.91	1507.44
15	249.28	5.71	1424.39
16	997.94	5.47	5454.74
17	997.2	5.94	5921.37
18	1003.9	6.19	6218.16
19	994.18	5.81	5771.22
20	106.86	10.87	1161.89

Note: 1000 µci/L equals 3.7 E+7 Bq/L
Shaded area denotes suspect data

Column Test 2. – Media P26I, Cycle 2

Discussion Column Test 2. – Media P26I, Cycle 2

The descriptions will only address changes in operation and occurrences worth noting apart from normal operations detailed above. The exothermic reaction occurred again in this test. The column temperature reached 102°C (216°F). The feed was continuous until the feed tank was emptied. Samples taken were colored and contained solids. The condition of the samples when compared with cycle 1 was worse. Samples contained approximately 1/16 to 1/8 inches (0.16 to 0.32 cm) of sediment in the bottom of the sample bottles. The results from cycle 2 are shown in Table 3-5.

Upon completion of the two cycles, media performance was questioned because it did not perform the same as previous MSI studies. The media was sluiced out of the column and weighed. The original weight was 1,813.46 grams; the new weight indicated 283.17 grams of media were lost. The lost media was assumed to be the sludge in the sample bottles.

Test 2 Results

Column Loading Media g. - 2,097 g (4.6 lb) (previously used in Cycle 1 test)

Feed Tank Volume ml, µCi - 14,944 g, 87,226 µCi (32.9 lb, 3.2 E+9 Bq)

Product Tank Volume ml, µCi - 7,437 g, 40,901 µCi (16.4 lb, 1.5 E+9 Bq)

Drying Tank Volume ml, µCi - 4,704 g, 27,455 µCi (10.4 lb, 1.0 E+9 Bq)

Regeneration Tank Volume ml, µCi - 2,790 g, 15,544 µCi (6.1 lb, 5.8 E+8 Bq)

Process Time hrs. - Not Reported

Table 3-5
Cycle 2 using P26I media

	grams	•Ci/g	•Ci
Feed	14,943.56	5.837	87225.56
Samples			
1	97.82	5.709	558.45
2	98.36	5.66	556.72
3	102.7	5.66	580.77
4	107.57	5.47	588.41
5	104.02	5.77	600.40
6	250.28	5.38	1347.26
7	251.33	5.76	1447.91
8	254.2	5.67	1441.57
9	251.54	5.66	1423.97
10	251.85	5.69	1432.27
11	249.29	5.57	1389.54
12	251.24	3.96	995.92
13	252.3	3.85	972.12
14	251.67	5.80	1460.44
15	252.23	5.89	1464.95
16	995.37	5.48	5454.63
17	995.38	5.74	5715.47
18	988.96	5.68	5612.35
19	987.73	5.46	5392.02
20	444.03	5.55	2466.14

Note: 1000 µci/L equals 3.7 E+7 Bq/L

Column Test 3. – Media P26I, Cycle 1A

Discussion Column Test 3. – Media P26I, Cycle 1A

New P26I media from the same prepared batch used in Cycles 1 and 2 was loaded into the column. Column temperature was not raised to 50°C (120°F) to minimize the effects of the exothermic reaction during hydration of the media. The column temperature reached 103°C (217°F) during hydration of the media. Results are found in Table 3-6. The media was depleted after processing 6.5 liters of feed water as indicated by tritium concentrations higher than the initial feed. The media appear to be releasing tritium thereby increasing the tritium concentration in the treated water. The overall process performance was poor. It was decided that Duratek should prepare a new batch of P26I to verify the results obtained by the media prepared at Clemson (refer to Test 5).

Test 3 Results

Column Loading Media g. - 2096 g (4.6 lb)

Feed Tank Volume ml, μCi - 15,259 g, 87,261 μCi (33.6 lb, 3.2 E+9 Bq)

Product Tank Volume ml, μCi - 7,439 g, 40,901 μCi (16.4 lb, 1.5 E+9 Bq)

Drying Tank Volume ml, μCi - 5,370 g, 30,326 μCi (11.8 lb, 1.1 E+9 Bq)

Regeneration Tank Volume ml, μCi - 2,027 g, 8,183 μCi (4.5 lb, 3.0 E+8 Bq)

Process Time hrs. - Not Reported

Table 3-6
Cycle 1A using P26I media

	grams	•Ci/g	•Ci
Feed	15,259.06	5.39	82261.59
Samples			
1	95.23	4.77	454.34
2	98.14	4.80	470.88
3	100.9	4.82	486.64
4	99.64	4.65	463.62
5	95.58	5.01	478.57
6	246.69	5.02	1238.38
7	248.94	5.26	1310.42
8	240.96	5.40	1300.94
9	249.03	5.53	1376.64
10	247.85	5.65	1399.11
11	247.08	5.59	1381.42
12	253.25	5.52	1397.69
13	244.2	4.63	1130.65
14	239.7	5.42	1298.22
15	248.94	5.66	1409.75
16	996.06	5.59	5567.98
17	985.81	5.57	5487.02
18	1005.19	5.65	5681.33
19	986.48	5.60	5519.36
20	903.24	5.54	5000.34

Note: 1000 µci/L equals 3.7 E+7 Bq/L

Column Test 4. – Media I20A, Cycle 1

Discussion Column Test 4. – Media 120A, Cycle 1A

The column was loaded with I20A media prepared at CNCF. Difficulties were encountered loading the media. Due to its large size, the media would clog valves and bends in the system piping. This new media required no air during waste processing. During the final drying phase, the column and air temperatures were raised to 200^{0}C (320^{0}F). The total time required to complete a cycle was 8 hours. Looking at the results in Table 3-7, it was noted that the tritium concentration in the dry tank was the lowest. The column was then refilled with water with a tritium concentration of 5.737 µCi/g. The system was then left overnight. The column was drained to the drying tank and a sample was taken that contained 4.75 µCi tritium (tritium removal was 17.2 % from overnight contact).

I20A media was performed with this inorganic media prepared by Duratek. The results concluded that a long residence time was needed to remove tritium. The media did not break down during the cycle. The samples were clear and free of solids. From a processing standpoint, the media does not shrink, swell or break down during processing.

Test 4 Results

Column Loading Media g. - 2,227 g

*Feed Tank Volume ml, µCi - 13,453 g, 68,515 **µCi** (29.6 lb, 2.5 E+9 Bq)*

Product Tank Volume ml, µCi - 7,700 g, 47,666 **µCi** (17.0 lb, 1.8 E+9 Bq)

Drying Tank Volume ml, µCi - 5,106 g, 19,920 **µCi** (11.2 lb, 7.4 E+8 Bq)

Regeneration Tank Volume ml, µCi - 2,027 g, 8,183 **µCi** (4.5 lb, 3.0 E+8 Bq)

Process Time hrs. - 8 hrs.

Table 3-7
Cycle 1 using I20A media

	grams	•Ci/g	•Ci
Feed	13,452.87	5.093	68515.47
Samples			
1	107.19	5.34	572.29
2	95.16	5.23	497.40
3	104.48	5.46	569.94
4	105.46	5.21	549.34
5	97.2	5.29	513.90
6	254.88	5.11	1302.95
7	255.02	5.38	1370.99
8	246.01	5.43	1336.82
9	248.04	4.62	1145.20
10	244.6	5.11	1250.64
11	244.86	4.84	1186.10
12	241.4	5.38	1298.97
13	250.66	5.42	1358.58
14	240.03	5.55	1330.97
15	235.51	5.17	1218.53
16	1000.55	5.55	5553.05
17	1009.73	5.58	5637.32
18	992.68	5.54	5503.42
19	1008.82	11.71	11814.29
20	717.36	5.10	3654.95

Note: 1000 µci/L equals 3.7 E+7 Bq/L
Shaded area denotes suspect data

Column Test 5. – Media P7, Cycle 1

Discussion Column Test 5. – Media P7, Cycle 1

P7 media was sluiced into the column. This media did not swell as much as the P26I media. No air was required during hydration of the media. Heaters on the column were not turned on. A slight exothermic reaction was noted when column temperature rose to 31°C (88^{0}F). As more feed was introduced to the column, the temperature began to drop indicating that heat generation was complete. The heaters on the column were turned on to raise the column temperature to 50°C (120^{0}F). Samples were clear and no solids were found. Results can be seen in Table 3-8.

Duratek prepared this organic based media for the test. P7's performance was similar to cycle 1 using P26I media. Ease of processing with this media was as good as the inorganic media I20A. The samples were clear and no solids were found indicating the media did not break down during hydration. Of the two organic media, overall performance was best with P7. Unfortunately, no media contaminant beaker testing was performed on this media.

Test 5 Results

Column Loading Media g. - 1,936 g (4.26 lb)

Feed Tank Volume ml, µCi - 15,175 g, 81,097 µCi (33.4 lb, 3.5 E+9 Bq)

Product Tank Volume ml, µCi - 6,894 g, 34,589 µCi (15.2 lb, 3.5 E+9 Bq)

Drying Tank Volume ml, µCi - 5,399 g, 27,085 µCi (11.9 lb, 3.5 E+9 Bq)

Regeneration Tank Volume ml, µCi - 2,027 g, 8,183 µCi (4.5 lb, 3.5 E+9 Bq)

Process Time hrs. - Not Reported

Table 3-8
Cycle 1 using P7 media

	grams	•Ci/g	•Ci
Feed	15,175.38	5.34	81097.23
Samples			
1	95.71	4.90	468.98
2	98.58	5.13	505.62
3	99.45	4.88	485.32
4	100.79	4.76	480.06
5	110	4.98	548.24
6	250.36	4.90	1227.77
7	254.03	5.32	1351.19
8	251.97	4.82	1213.49
9	252.01	4.91	1236.19
10	254.54	5.08	1293.83
11	252.28	5.07	1277.80
12	251.01	4.71	1181.76
13	249	4.72	1175.03
14	246.27	4.76	1171.26
15	249.58	4.18	1042.00
16	939.78	5.28	4962.04
17	988.54	5.22	5162.16
18	967.92	4.55	4403.07
19	983.02	5.50	5403.66

Note: 1000 µci/L equals 3.7 E+7 Bq/L

Column Test 6. – Media P26I, Cycle 1B

Discussion Column Test 6. – Media P26I, Cycle B

Duratek prepared this P26I media. Large amounts of DI water were required during the preparation to rinse the media to a conductivity of >3 µS/cm. Rinse water contained no coloration or solids. Air was required during hydration of media to prevent column blockage. The airflow rate was set at 20 SCFH (0.6 SCMH). The column heaters were not energized until the exothermic temperature rise began to drop. The column temperature was then set at 50^{o}C (120^{0}F). All the samples collected were colored and contained solids. The results are found in Table 3-9. Cycle 1B using P26I was the only cycle performed on this new batch of media due to continued poor performance.

Test 6 Results

Column Loading Media g. - 2,164 g (4.8 lb)

Feed Tank Volume ml, µCi - 14,914 g, 67,320 µCi (32.8 lb, 2.5 E+9 Bq)

Product Tank Volume ml, µCi - 7,577 g, 34,096 µCi (16.7 lb, 1.3 E+9 Bq)

Drying Tank Volume ml, µCi - 4,868 g, 21,893 µCi (10.7 lb, 8.1 E+8 Bq)

Regeneration Tank Volume ml, µCi - 2,457 g, 10,708 µCi (5.4 lb, 4.0 E+8 Bq)

Process Time hrs. - Not Reported

Table 3-9
Cycle 1B using P26I media

	grams	•Ci/g	•Ci
Feed	14,913.59	4.51	67319.95
Samples			
1	117.99	7.57	892.95
2	117.07	4.35	508.67
3	111.85	4.46	499.19
4	116.66	4.32	503.74
5	108.52	4.33	469.67
6	257.22	4.54	1166.75
7	261.24	4.48	1170.62
8	260.1	4.43	1151.98
9	260.99	4.54	1185.16
10	266.31	4.12	1098.00
11	266.58	4.52	1205.21
12	267.39	4.41	1178.39
13	264.61	4.46	1180.16
14	265.2	4.58	1215.68
15	267.01	4.24	1132.92
16	995.92	4.45	4434.83
17	982.33	4.48	4403.79
18	972.04	4.55	4418.89
19	967.77	4.43	4288.19
20	450.28	4.42	1992.04

Note: 1000 µci/L equals 3.7 E+7 Bq/L
Shaded area denotes suspect data

4

ASSESSMENT TRS TEST RESULTS

The project's intended objectives were to provide the industry with the following information related to the TRS removal process:

1. Assessing the affect of common nuclear plant ionic species on the removal media's performance in the processing of radioactive liquid waste streams.
2. Defining key characteristics related to removal media process.
3. Quantifying the removal of tritium from nuclear plant liquids.
4. Assessing basic economics associated with the technology, as it would be applied to nuclear plant liquid processing.

4.1 Beaker Testing

Objective: The beaker tests had as its objective to identify the most promising media (tritium removal capacity) for detailed pilot plant column testing. Additionally, beaker testing provided an assessment of the affect of common ionic wastewater contaminants on TRS media.

Assessment of Media Capacity (Distribution coefficient K_d) Testing Results

1. Program testing clearly showed significant tritium removal for two test media, P26I and I20A. P26I was selected as the prime candidate for pilot plant testing based on the favorable results achieved in earlier MSI testing. In hindsight, this appears to have been a poor choice, since the P26I was an organic resin and highly questionable for repeated exposure to high temperature drying cycles. I20A on the other hand being an inorganic compound would be expected to withstand such osmotic shocks from drying operations. Unfortunately, Tests 1 and 2 confirmed this projection and P26I experienced major deterioration after the first cycle of operation.
2. Beaker testing did produce noticeable reduction in tritium reductions with a liquid to media ratio was approximately 2:1. It should be pointed as a reference that similar tests using ion exchange media for such ions as cobalt and cesium produce K_d values in the range of several thousands.

Assessment of Beaker Contaminant Testing Results

1. The impurities did have a major negative affect after repeated exposures. Contaminant removal prior to the TRS is required. Such preconditioning for the TRS process will add to the cost and further make this process unattractive from a cost/benefit standpoint. Breakdown products during the TRS process may require further processing to reclaim product water. Exposure of P26I to all of the common contaminants (silica, boron, lithium and turbine oil) resulted in major loss of aluminum and sulfur from the media. Since the testing was limited to an organic media, the effect of such materials to an inorganic media is open to conjecture.

2. Although the contaminant testing was performed and some interesting conclusions were made, the testing did not address key questions that would apply to a plant process. These include such questions as:
    - Is the fouling irreversible, i.e. does the regeneration process restore active sites or is a chemical treatment step required to recover the media performance, or is it more cost effective to trash the media once fouled? The thermal regeneration process may concentrate the impurities on/in the media and render the media useless. It is not surprising that oil would cover the active site and that repeated applications of oil increased the degree of fouling. The affect of high temperature regeneration remains a question.
    - If the media is fouled (to any degree), how are kinetics affected? Does the process flow rate need to be decreased to meet effluent target concentrations, does the top part of the media need to be sluiced and replaced with fresh media, does the contaminant uniformly foul the media charge or follow a chromatographic front similar to ion exchange?
    - Do cations/anions interfere with the adsorption process under full process conditions experienced in column operation? This remains to be evaluated should additional column tests be performed. Questions also remain concerning affects of the regeneration process, such as, would it drive the impurities off of the media or does the thermal process and subsequent concentration of the impurities make the media unusable?

4.2 Pilot Plant Column Testing

Objective: To define key characteristics related to removal media process. Additionally, the column testing would quantify the removal of tritium from nuclear plant liquids. This testing would then allow an assessment of basic economics associated with its application to nuclear plant liquid processing.

General Assessment of Pilot Plant Column Test Results

1. Column testing did not establish the tritium removal capacity for the media being tested. The practice of mixing air within the column to prevent media blockage resulted in a greatly diminished tritium removal percentage and produced a flattening of the performance curve. Operation of a fluidized bed would be expected to be lower due to the contact of the liquid with partially depleted media throughout its residence within the column. A fixed bed would

produce a higher efficiency since the media would operate more as a chromatographic column. It should be noted that no air mixing was used in Tests 4 and 5. However, for some unexplained reason, the results were surprisingly similar to those achieved with air mixing of the column. Unfortunately, use of air completely masked the media exhaustion endpoint and prevented the determination of the media tritium removal capacity. The flat tritium removal performance combined with data gained in earlier tests strongly suggests that the amount of media used for the test had far more capacity than could be exhausted by the 15 Liters (4 gal) of feed water.

2. The preferred media (P26I), a cation organic based resin, was not capable of withstanding the regeneration process. The temperatures of the drying cycle combined with the osmotic shock of the rewetting produced massive degradation of the resin within 2 operating cycles. It should be pointed out that the media used in Test 5 was an organic material and did not show signs of degradation during its only operating cycle.

3. Numerous tritium measurements in the product stream exceed the concentration of the feed tank value. This raises questions regarding the degree of precision of those determinations and the test protocol.

4. Tritium removal rate of 25 percent could not be attained in Duratek's pilot unit. Pilot Plant Column testing showed that with P26I media, numerous columns would be required to effectively lower the tritium concentration. Each column placed in series would remove a small fraction of the tritium. The effluent water quality required would determine how many columns would be needed. The media would have to be discarded after two cycles. This would generate large quantities of waste. Duratek concluded that the TRS Process is not a cost effective solution for tritium removal technology.

5. Six column tests were performed under this TRS Testing Program. Even with this limited number of tests considerable variation in the operating conditions were experienced. Table 4-1 summarizes the key operating conditions and observations for each of the tests.

Table 4-1
Summary of Pilot Plant Operating Conditions

Condition	*Test 1*	Test 2	*Test 3*	*Test 4*	*Test 5*	*Test 6*
Media	P26I	P26I	P26I	I20A	P7	P26I
Media Type	Organic	Organic	Organic	Inorganic	Organic	Organic
Cycle	1	2	1A new same batch	1	1	1 new batch
Air Fluidized Batch	Yes	Yes	?	No	No	Yes
Exothermic Reaction (max. temp)	Yes (104 C)	Yes (102 C)	Yes (102 C)	?	Slight (31 C)	Yes (?)
Column Heaters Used						
At start	Yes	?	No	?	No	No
After Exothermic Spike	-	-	-	?	Yes	Yes
Media Breakdown seen	Yes	Yes	?	?	?	Yes
Regeneration Temp	80 C 120 C 160 C			200 C		
Total Cycle Time	12 hr	?	?	8 hr	?	?

Assessment of Pilot Plant Column Processing Efficiency

Figure 4-1 presents a simplified schematic for the pilot column test system. Note that the Drying Tank is recycled back to the Feed Tank at the conclusion of the processing cycle. The liquid in this tank had only limited contact with the media and therefore the tritium concentration is assumed to be essentially equivalent to the input stream. Since the liquid in the Regeneration Tank is assumed to have an elevated tritium concentration produced by the first stage of high temperature drying, the liquid is either recycled back to the Feed Tank or considered as a waste product. Therefore, the final process liquid is only that contained in the Product Tank.

Table 4-2 provides a tritium radioactivity balance across the major system components for each of the pilot column tests. Similarly, Table 4-3 presents the liquid balance across the major components and the unidentified quantity determined for each of the tests. The “effective input volume" is then calculated using Eq. 4-1. Finally, Eq. 4-2 is used to calculate the process efficiency and the results are given in Table 4-4. Only three of the tests (Test 1, 2 and 5) yielded significant tritium removal results. The remaining three tests either produced negative results (Tests 3 and 4) or only slight tritium removal (Test 6). Once again, the test results raise a question regarding the test accuracy and protocol.

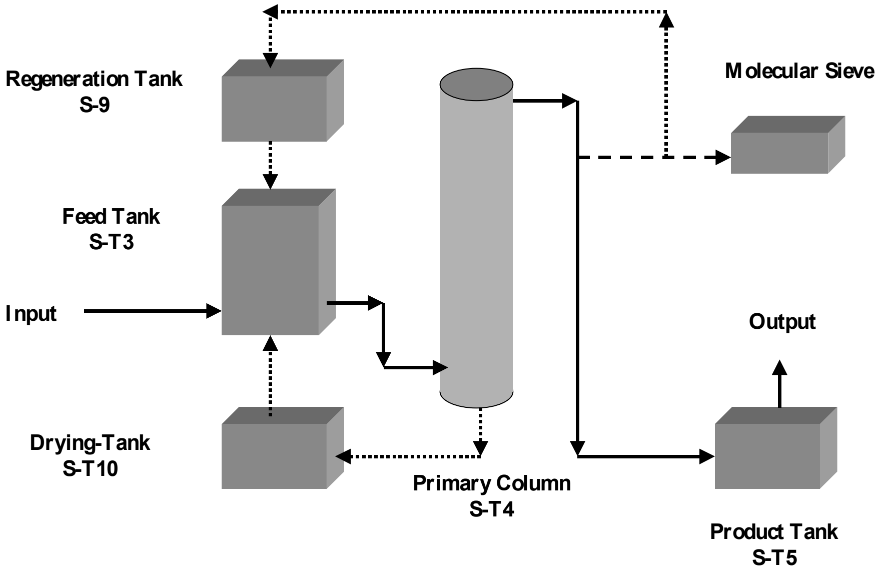

Figure 4-1
Pilot Column Simplified Schematic

Table 4-2
Tritium µCi Balance within TRS Process

Test	Feed Tank	Product Tank	Drying Tank	Regeneration Tank	Molecular Sieve[a]
1	94,969	42,567	28,018	15,006	9,377
2	87,225	33,043	27,455	15,544	11,183
3	82,262	40,901	30,327	8,183	2,851
4	68,515	47,666	19,620	8,183	(-6,953)
5	81,097	34,589	27,085	8,183	11,240
6	67,320	34,097	21,893	21,893	622

Note. a) Molecular Sieve value calculated as the difference of Feed Tank less other tank values.
b) 1000 µci/L equals 3.7 E+7 Bq/L

Calculation 1- Effective Process Volume for the TRS Process

Assumptions:

- The Drying Tank will be recycled to the Feed Tank for reprocessing due to inadequate contact with the process media prior to draining of the column.
- The Regeneration Tank will be recycled to the Feed Tank for reprocessing due to elevated tritium levels from the drying process.
- Process water has a mass of 1g/ml.

Calculation:

System Input Volume = V_{Input}

Drying Tank Volume = V_{Drying}

Regeneration Tank Volume = $V_{Reg.\ Tk}$

$$V_{Input} = V_{Feed\ Tk} - V_{Drying\ Tk.} - V_{Reg.\ Tk} \qquad \text{[Eq. 4-1]}$$

Table 4-3
Pilot Testing Volume of Processed Water - ml

Test	Feed Tank	Drying Tank V_{Drying}	Regen. Tank $V_{Reg.\ Tk}$	Calculated Input V_{Input}	Product Tank	Unaccounted
1	14,956	4,671	2,473	7,812	7,112	-700
2	14,943	4,704	2,790	7,449	7,438	-11
3	15,259	5,370	2,027	7,862	7,438	-424
4	13,452	5,106	2,027	6,319	7,700	+1,381
5	15,175	5,399	2,027	7,749	6,895	-854
6	14,914	4,868	2,457	7,589	7,577	-12

Note: 1000 ml equals 0.26 gal.

Calculation 2 TRS Process Removal Efficiency

Assumptions:

- The Product Tank Input Concentration was equal to the Feed Tank Concentration.

Calculation:

System Input Concentration μCi/ml = C_{input}

Product Tank Concentration μCi/ml = $C_{Product}$

$$\text{TRS Removal Efficiency } \% = (C_{input} - C_{Product}) / C_{input}) * 100 \qquad \text{[Eq. 4-2]}$$

Table 4-4
TRS Process Removal Efficiency

Test	Input Conc. C_{input}	Product Conc. $C_{Product}$	Process Removal Eff. %
1	6.35	5.99	5.7
2	5.84	5.5	5.8
3	5.39	5.50	-
4	5.09	6.19	-
5	5.34	5.02	6.0
6	4.51	4.50	0.2

5

ASSESSMENT OF TRS FOR A FIELD APPLICATION

Unfortunately, the data derived from this Test Program does not provide the information needed to scale the TRS process to a field application. It does however provide considerable information concerning the process parameters, e.g., flow, temperature and process times. A review of the Clemson Environmental Technology Laboratory data shows that it provides the best quantification of the process capacity and efficiency. Therefore, the approach taken to provide a first order assessment of a TRS field application is to combine the test data from the earlier Clemson testing with process information generated under pilot test program.

Clemson results were reproducible and show significant correlation between tests of liquid of varying tritium concentrations and quantity of media used. Figure 5-1 shows the tritium removal from liquid streams of three concentrations (i.e., 1028 µci, 245 µci and 125 µci). The data presented is normalized in terms of µci of tritium removed per kilogram of dry media verses the service run. It is important to note that the media capacity is directly related to the tritium concentration. Processing 1,028 µci of liquid resulted in a media capacity of ~ 150 µci /Kg of media, and processing 125 µci of liquid resulted in the media capacity of ~ 15 µci /Kg of dry media).

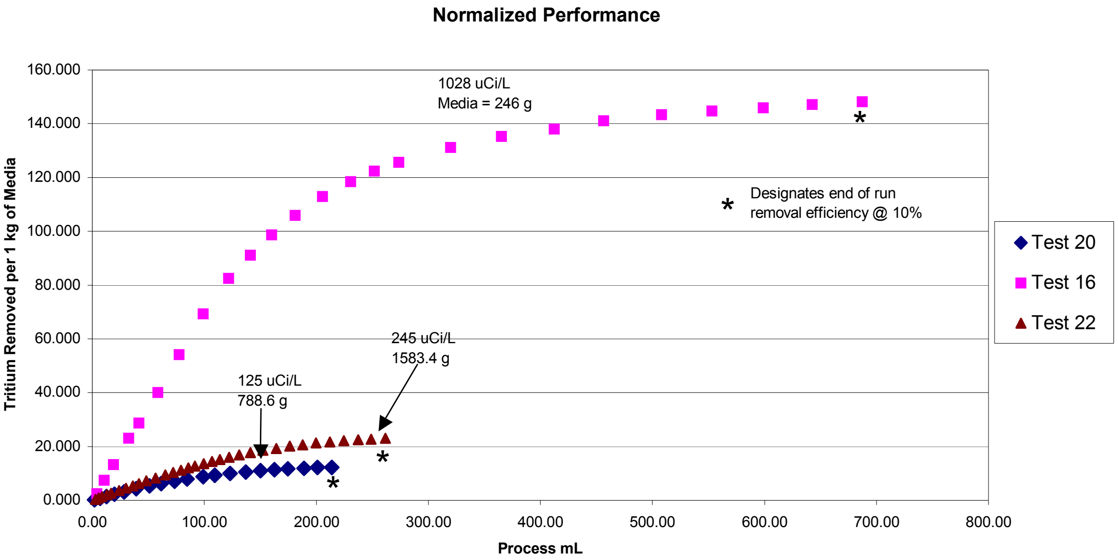

Figure 5-1
Clemson Tests - Capacity Determination

Figure 5-2 used Clemson data to show a typical media's tritium removal capacity and removal efficiency verses the throughput. This figure illustrates the rapid decrease in tritium removal that takes place during the service run. In this test, the removal efficiency dropped from an initial value of ~70% to 38% during the first quarter of the service run.

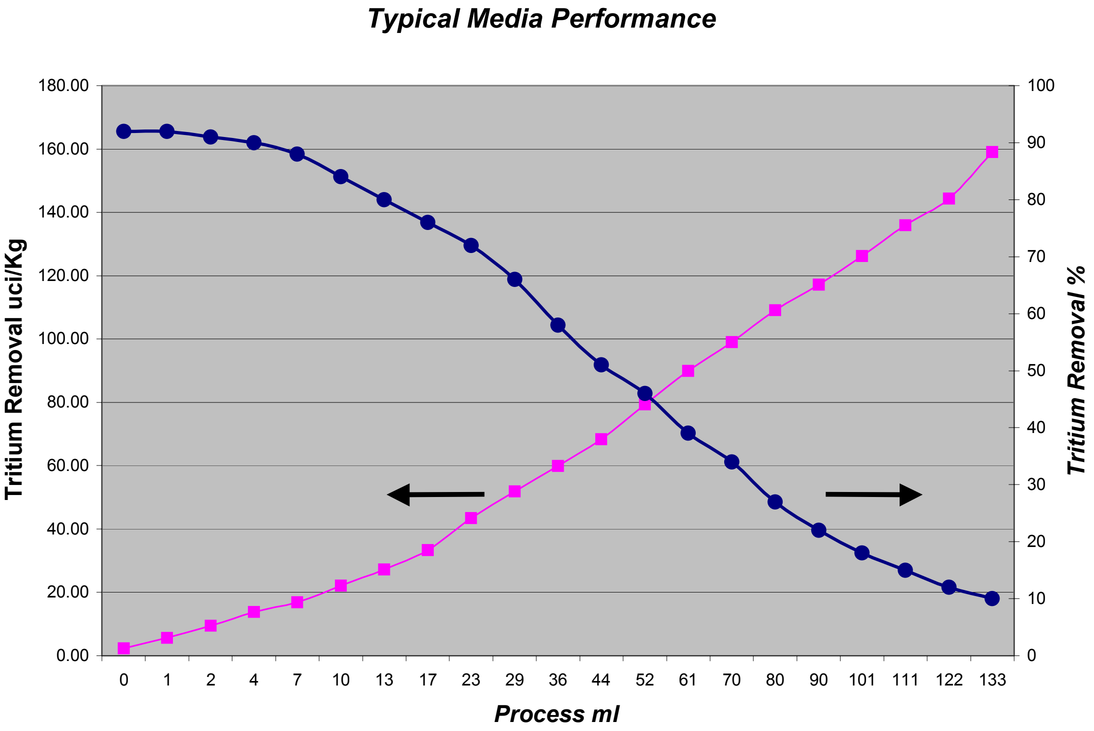

Figure 5-2
Typical Tritium Removal – Total uci and Removal Percent

Table 5-1 summarizes the dry media tritium capacity and removal efficiency for the tests reported from the Clemson Environmental Technology Laboratory test program.

Table 5-1
Summary of Clemson Test Results

Test	*Columns*	*Media Dry g*	*Input •ci/L*	*Service Run[a] Removal 10%*			*Service Run[b] Removal ~1%*		
				Run g[c]	*•ci removed*	*Efficiency %*	*Run g[c]*	*•ci removed*	*Efficiency %*
16	1	246	1000	78	34.7	44	169	38.9	23
20	2	789	125	169	9.6	44	301	10.3	26
21	2	802	125	159	8.9	45	292	9.6	28
22	4	1583	245	273	38.1	57	382	39.5	42

Note. a "Service Run Removal 10%" refers to the termination of the service run at an tritium removal efficiency of approximately 10%.

b "Service Run Removal 1%" refers to the termination of the service run at an tritium removal efficiency of approximately 1%.

c. Run g. is a weight measure of the liquid processed.

5.1 Estimate of TRS Full System Performance Characteristics

The information presented above was used in developing a set of assumptions for estimating the performance characteristics of a commercial size application. The following assumptions were made:

Assumptions

1) Vessel size	Dia. 2 ft. X Height 8 ft. (25 ft^3), (0.6 m X 2.4m)
2) Media bed (dry) depth, volume	4 ft. depth (1.2m)
3) Media volume	12.6 ft^3, (0.35 m^3)
4) Media Density	45 lb (20 Kg)
4) Process Flow	2 gpm (7.57 L/min)
5) Input Liquid	1,000 µci/L
6) Media Tritium Capacity	77µci/ lb dry media, (170 µci/Kg dry media)
7) Service Run End Point	10% Tritium Removal
8) Tritium Removal Efficiency	25%
9) Service Run Volume	0.08 gal/lb dry media (0.69 L/kg dry media)
10) Cycle Time	8 hrs.

Cycle Throughput

Media lb = Media Volume X Media Density

= 12.5 X 45 = 560 lb

Product gallons = Media lb X Throughput gal/lb

= 560 X 0.08 = 45 gal per cycle

Tritium Reduction = Input Tritium X Tritium Removal Efficiency

= 1000 X .25 = 750 µci/L

Time Require to Process 1000 gallons

Time = (1000 gal / Product gallons per cycle) X 8

= (1000 / 45) X 8 = 180 hours (requiring 22 operating cycles)

This simplified processing example shows that a 25% reduction in 1000 gallons of wastewater containing 1000 µci/L would require approximately 20 operating cycles. Based on a very optimistic assumption concerning the time required to regenerate the media (8 hr) it would require approximately one months time (8hr/day/20 days/mo). Industry experience with air-drying of radwaste processing media suggests that the time could easily be in the range of 24 to 72 hours.

Even more important, the following operating cycles would require additional time due to the decrease in operating capacity as the tritium concentration decreases in the wastewater (refer to Figure 5-1). This time factor is reflected in Figure 5-3, which shows the number of operating cycles required to meet a specific percent reduction in the wastewater tritium value.

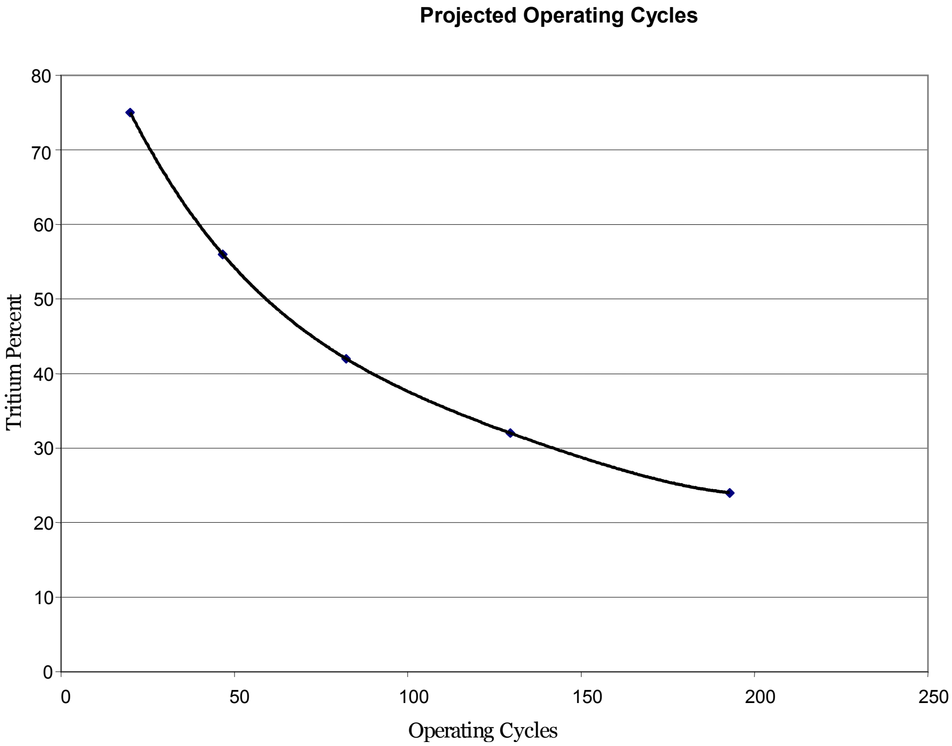

Figure 5-3
Relationship of Number of Cycles to Tritium Reduction

6
CONCLUSIONS

Major Finding

Tritium removal with the TRS Process has been clearly demonstrated in the test work performed to date. However, the existing data strongly suggests that the commercialization of the process, as it is presently defined, is unlikely. This conclusion is based on the exceedingly low capacity of the media and the need for complete media drying. Both the drying requirement and the low capacity translate into large major hardware capital expenditures.

General Conclusions

A review of the process and data leads to the following general conclusions:

Media

1. The principal organic media (P26I) tested in this program underwent catastrophic deterioration as a result of the process temperatures and osmotic shock tied to the wetting and drying process. Therefore, a substitute material is required. This may require the use of an inorganic media capable of withstanding the demands of process conditions. Once such a material has been identified, further testing would be required to quantify its performance. Column test results achieved under this program do not provide insight to alternate materials. Limited beaker tests did show that an inorganic media (120A) possessed similar tritium removal properties as P26I (organic cation media). However no column tests were performed with this material.

2. Earlier testing established the media capacity for an organic cation media at approximately 140 µci/Kg dry media when processing 1000 µci/L wastewater. It is important to note that the media's capacity decreases to 12 µci/Kg dry media when processing 125µci/L wastewater, a ten fold reduction.

3. Earlier test work showed approximately a 25% reduction in tritium concentration for various tritiated liquids. Testing conducted under this program failed to duplicate these results, which is believed to be due to the test protocol.

4. Beaker testing clearly demonstrated a significant loss of performance of the media due to the presence of ionic contaminants. A media sample exposed to 400 ppm boron lost 81.92 % aluminum and 86.18% sulfur. The loss of aluminum and sulfur is directly proportional to the sites of hydration and deterioration of the media. Samples exposed to lithium and turbine oil

also experienced aluminum and sulfur loses. Although not as extreme as exposures to boron, the impurities would reduce the sites of hydration by approximately one half.

Overall TRS Process

1. The TRS Process, as it is presently defined, presents challenges in terms of demands on the media and operating steps. The media must undergo a complete dehydration/hydration after each operating cycle. Additionally, the media is exposed to elevated temperatures up to 160°C (320°F). From an operating standpoint, the media transfers and flow distribution requirements are a concern. Finally, the design of the media drying system will be a formidable problem. All of these difficulties were experienced in the test program using one small column of approximately 6 Liter capacity (1.6 gal) with dimensions 3 in. (7.6 cm) dia. X 68 inch (1.7 m) long, media normal loading approx. 2000-2100 g.
2. The process as it is presently defined will require full demineralization pretreatment for removal of the ionic species in the wastewater prior to the TRS processing. This will add complexity and significant cost to the process.
3. Earlier testing established a direct proportional relationship between the wastewater tritium concentration and the media performance in terms of media removal capacity. This means that as the tritium concentration is lowered, the effective media capacity is also reduced. Under this principal, succeeding operating cycles will have decreasing service runs hindering major reduction in the wastewater's tritium concentration.

Field Application of the TRS Process

1. An assessment of a field application suggests that, even assuming optimum performance, processing of major quantities of wastewater with the TRS is impractical. Processing of 1000 gallons of wastewater containing 1000 µci/L will require 20 cycles of a relatively large vessel of media (vessel size - dia. 2 ft. X height 8 ft. (0.6 m X 2.4m); media bed (dry) depth - 4 ft. depth (1.2m), volume - 12.6 ft^3, (0.35 m^3)).
2. Testing to date has not established the quantity of waste resulting from the TRS Process. The process as presently defined could have three waste streams; exhausted molecular sieve media, regeneration liquid waste and spent media and fragments resulting from attrition. This aspect of the process would need to be addressed prior to proceeding with a large-scale application.

Canadian Tritium Removal Process

Canadian reactors operate on a heavy water cycle producing significantly higher levels of tritium during plant operation. This has led them to be leaders in the field of tritium removal based on their experience and technology development programs. Appendix A discusses their latest development in this area. Ontario Power Technologies has developed a Tritium Removal Plant (TRP) that incorporates both a flexible and simple design into a smaller, more compact system. However for a U.S. nuclear plant, this tritium removal process would be considered to represent a large capital investment. Such investments cannot be justified based on the extremely low dose values being experienced.

Additional research and development related to novel tritium removal technologies is currently being studied in a number of other countries.

A

CANADIAN TRITIUM REMOVAL DEVELOPMENT PROGRAM

Technological innovation in the field of tritium removal continues to be a topic of interest in the US nuclear industry. To date, no cost effective technology has been found to remove tritium from the liquid waste stream. It should be stressed that present tritium levels found in the discharge from US plants are well within all regulatory requirements. Utilities operating Pressurize Water Reactors that utilize small bodies of water as their primary outlet for release are particularly interested in reducing tritium from their discharge water. This interest lies in the hope of finding a low cost removal method capable of processing liquid containing very low tritium concentrations. Since Canadian reactors operate on a heavy water cycle, this has led them to be leaders in the field of tritium removal based on their experience and technology development programs. The following sections discuss their latest development in this area.

More promising, novel methods of removing tritium are currently being studied in a number of other countries. Ontario Power Technologies has developed a Tritium Removal Plant[1] (TRP) that incorporates both a flexible and simple design into a smaller, more compact system. The CANDU-6 TRP "consists of a low inventory, leak-tight electrolysis cell or group of cells in the front-end to convert the D_2O (mixed with HDO and DTO) from the moderator system to D_2, HD, or DT." (Sood, S.K. et al., 13). A Cryogenic Distillation (CD) system follows the electrolysis section "to enrich the moderator tritium to between 50% and 80% DT while detritiating the bulk of the D_2 gas which is then converted back to heavy water by recombining the D_2 with oxygen." (Sood, S.K. et al, 13). This CD system is smaller than the traditional one found in the Darlington Tritium Removal Facility (TRF) and is much simpler than the Princeton Tritium Purification System (TPS). Consequently, this new, compact system has the potential for modularity and may reduce costs for tritium decontamination equipment for CANDU-6 reactors.

The researchers at Ontario Power Technologies compared their existing tritium removal systems (Darlington TRF and Princeton TPS) to the CANDU-6 TRP and found many technical advantages to using this new system.

1. Detritiation is done onsite, thus costs associated with off-site processing are avoided.
2. Its simple design denotes fewer components and an easier process control implementation, which in turn will result in lower maintenance and lower operating costs.

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[1] Sood, S.K., C. Fong, K.M. Kalyanam, and K.B. Woodall. "A Compact, Low Cost, Tritium Removal Plant for CANDU-6 Reactors".

3. The design allows for modularity and customization to fit the unique processing demands of each plant.

4. In addition to detritiation, the CANDU-6 TRP can reduce carbon-14 (C-14) production and release by up to 30% to 40%. C-14 is produced when neutrons bombard oxygen-17 (O-17) nuclei in the reactor moderator. The CANDU-6 TRP will reduce O-17 nuclei in the moderator by using oxygen in the TRP recombiner to displace the enriched O-17 in the moderator heavy water. A reduction in O-17 nuclei will decrease the rate of C-14 production.

5. The CANDU-6 TRP requires less space than the original Darlington TRF and its low deuterium and tritium levels makes it possible to be situated in the reactor building rather than in a separate building.

Unlike some of the other removal systems currently being investigated, the CANDU-6 TRP is a proven system. Pilot studies have been performed in several CANDU plants, and the results are promising. Mr. Martin Carney of Ontario Hydro Technologies explained an essential advantage and disadvantage of the CANDU-6 TRP. He pointed to the CANDU-6 TRP's compact design. This quality allows the system to be configured as a mobile unit capable of moving between sites whenever tritium removal is necessary. Although there are many technical advantages to using the CANDU-6 TRP, the process rests on advanced technology and is seen as capital intensive with respect to the desires expressed in the US for a low cost simplified process. It is important to note, that it is not necessarily cost effective for the low tritium concentrations seen in U.S. nuclear power plants.

Targets:

Nuclear Power

Low-Level Waste Management

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