

The Use of Cryogenically Cooled 5A Molecular Sieves for Large Volume Reduction of Tritiated Hydrogen Gas

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ABSTRACT

A commercial hydrogen isotope separation system based on gas chromatography (AGC-ISS) has been built. The system operates in two modes: stripping and volume reduction. The purpose of the stripping mode is to reduce a large volume of tritiated hydrogen gas to a small volume of tritium rich hydrogen gas. The results here illustrate the effectiveness of the AGC-ISS in the stripping and volume reduction phases. Column readiness for hydrogen isotope separation is confirmed by room temperature air separation tests. Production runs were initially carried out using natural levels of deuterium (110-160ppm) in high purity hydrogen. After completion of the deuterium/hydrogen runs the system began operations with tritiated hydrogen. The paper presents details of the AGC-ISS design and results of tritium tests. The heart of the AGC-ISS consists of two packed columns (9 m long, 3.8 cm OD) containing 5A molecular sieve material of 40/60 mesh size. Each column has 5 individually controlled heaters along the length of the column and is coiled around an inverted inner dewar. The coiled column and inner dewar are both contained within an outer dewar. In this arrangement liquid nitrogen, used to cryogenically cool the columns, flows into and out off the annular space defined by the two dewars, allowing for alternate heating and cooling cycles. Tritiated hydrogen feed is injected in batch quantities. The batch size is variable with the maximum quantity restricted by the tritium concentration in the exhausted hydrogen. The stripping operations can be carried out in full automated mode or in full manual mode. The average cycle time between injections is about 75 minutes. To date, the maximum throughput achieved is 10.5 m³/day. A total of 37.8 m³ of tritiated hydrogen has been processed during commissioning. The system has demonstrated that venting of >99.95% of the feed gas is possible while retaining 99.98% of the tritium. At a maximum tritium concentration of ~ 7 GBq/m³ (190 mCi/m³), processing tritiated hydrogen gas at a rate of 8.1 m³ (NTP)/day results in an average tritium concentration in the process effluent line of 1.4 MBq/m³ (37 µCi/m³). The average process exhaust flow, split between helium and hydrogen, is 10.6 litre/min. Product from the stripping phase is stored on a 5 kg depleted uranium bed. A 250 g depleted uranium bed is available for storage of enriched product. Several, ionization type, tritium sensors are located throughout the process to control emissions, control valve switching, and monitor evolution of tritiated species from the columns.

INTRODUCTION

While cryogenic distillation has been known and used for the purpose of separating isotope mixtures of hydrogen, this technique is mainly suitable for large scale processes. Distillation

suffers from the disadvantages of providing a low separating efficiency as well as requiring the retention of a fairly large inventory of material in the distillation system [1, 2]. Gas chromatography has many advantages when applied to separation of hydrogen isotopes. It is simple, reliable, inexpensive, easy to operate, and provides a high separation efficiency with low inventory.

The mechanism of separation in gas chromatography is based mainly on the varying degrees of physical adsorption of the different hydrogen isotope species on the packing material, in this case 5A molecular sieve. Cheh [1] previously investigated the retention times of various hydrogen isotopes by 5A molecular sieves, 7.6 m, 2 cm diameter molecular sieve column. Kawamura [2] experimentally measured the adsorption isotherms on liquid nitrogen cooled 5A molecular sieve.

An industrial AGC-ISS system, based on previous work [1, 3], was designed, built and commissioned. This paper describes the system, its' operation and presents results from the tritium commissioning phase.

ADVANCED GAS CHROMATOGRAPHIC ISOTOPE SEPARATION SYSTEM

The AGC-ISS separates various isotopes of hydrogen to facilitate stripping radioactive species from inactive hydrogen and thereby reducing the volume of tritium-containing gas to less than 1% of its original volume. Concentrated tritiated gas is collected and stored, while inactive hydrogen is vented to stack.

The AGC-ISS is highly automated, with computer control algorithms for most routine operating functions. The system is designed to be highly reliable, using welded stainless steel tubing with minimum fittings. All components are high quality and tested before installation. The control computer monitors all critical process parameters and provides warnings if parameters deviate from normal values. If any parameter exceeds acceptable preset trip values, the AGC-ISS automatically shut down and is placed in a safe mode. The high degree of automation provided minimizes the need for manual operation and so reduces the possibility of human error. For additional operator protection, the AGC-ISS is fully enclosed in a glove box whose atmosphere is exhausted directly to stack, preventing the backflow of any gas into the room. The exhaust from the AGC-ISS is continuously monitored for the presence of tritium.

The AGC-ISS has two modes of operation: stripping and volume reduction. The stripping mode processes large quantities of contaminated hydrogen gas, stripping the inactive hydrogen from the gas mixture and releasing it to the stack. Any tritium-containing species are retained in the system. The volume reduction mode further reduces the gas inventory in the system by performing the stripping operations with no external tritiated gas feed into the system.

System Description

The heart of the AGC-ISS consists of two coiled columns, each 9.1 m long and 3.8 cm in diameter, containing 5A molecular sieve. Each coil has five individually controlled heaters along its length, located on the shell of the columns, to allow the sequential heating of each section of the column. Each section also has its own thermocouples, to allow independent control of the heaters. This permits the progression of temperatures along the column needed to enhance the separation of tritium from other hydrogen isotopes.

The molecular sieve material is 40/60 mesh size with a packing density ~0.7 g/cc. Each column contains ~7.2 kg of molecular sieve. The sieve, prior to testing, was conditioned by heating it in an inert gas flow, to 250°C for ~12 hrs and then at 350°C for another ~12hrs.

To minimize the amount of liquid nitrogen needed for the alternate cooling and warming required during the various processes, the molecular sieve coils are mounted in a concentric dewar assembly. Each of the coils is mounted inside a large dewar. Concentrically mounted in the middle of the coil is a second dewar that is inverted and open at the bottom. Both the inner and outer dewars are connected to a nitrogen pressurizing system and can be independently pressurized or vented as required to control liquid nitrogen level. This arrangement allows the liquid nitrogen to be forced either into the annular space between the inner and outer dewars, immersing the columns in liquid nitrogen, or into the inner dewar, draining the annulus and exposing the columns.

When the columns are operating in either stripping or volume reduction modes, the helium carrier flow is once-through, i.e. helium flows from a pressurized external supply, through the column(s) as required, and then to stack. When operating in transfer mode helium carrier is circulated by a metal bellows compressor. In both cases constant carrier flow into the columns is maintained by a mass flow controller. This flow provides the driving force to move the hydrogen through the system.

Valving is provided to allow the flow to go from either Column 1 to Column 2 or stack and vice versa, so each column can serve as either the stripping column or the receiving column. In once-through mode, there is always a flow path to stack to vent the helium carrier gas. As long as there is no tritium in the gas flow exiting a column, the flow can be routed directly to stack. When active hydrogen is detected in the exhaust of one column, the flow is directed through the second column to trap all hydrogen, allowing only the helium carrier to go to stack. If tritium, above a preset limit, is detected downstream of the second column, the stack isolating valves are closed to completely isolate the system and prevent any release of radioactivity to the environment.

All transfers to and from the uranium hydride storage beds are performed in the transfer mode. The system is designed that when flowing through the Uranium hydride beds, there is no path to

the stack. This removes any chance of inadvertent releases to the environment. The overall system gas inventory is adjusted before commencing these modes of operation, so that neither venting nor helium addition is required during the transfer process.

The AGC-ISS also has a vacuum/recovery system in addition to the process loop. This system is capable of evacuating all sections of the process loop to pressures of 10^{-3} mbar or less. This allows part of the process loop to be evacuated and backfilled with air prior to opening it for maintenance. The ability to reduce the tritium inventory in the process loop prior to being maintained minimizes tritium exposure to maintenance staff. The vacuum system is also used to evacuate those parts of the system that have been opened to air during maintenance to prevent air and moisture from contaminating the columns or uranium beds before the system is restored to service.

In addition to the vacuum pumps, a recovery pump and associated valving has been provided to recover gas from various parts of the system and to return the gas to the columns. This allows gas to be recovered from the expansion tank or from other parts of the process loop after an upset that may have put contaminated hydrogen into parts of the system where it is normally not present.

Mass flow controllers are used to regulate the tritiated gas feed and the inert carrier gas. Pressure gauges are available throughout the system to monitor operations. Tritium ionization monitors are installed at various points in the system to track tritium in the process effluent, the transfer of tritium to the hydride storage beds and in the main exhaust of the glovebox. A residual gas analyzer is available to analyze in real time the gas composition at the exhaust of columns 1 or 2.

Stripping Mode

In automated stripping operation, the AGC-ISS processes a tritiated hydrogen feed in a batch. The tritium from the incoming hydrogen feed is retained within the system, while the inactive hydrogen is exhausted to the environment; trace quantities of tritium in the exhaust remain below emission guidelines.

Fig. 1. schematically illustrates the AGC-ISS principle of operation.

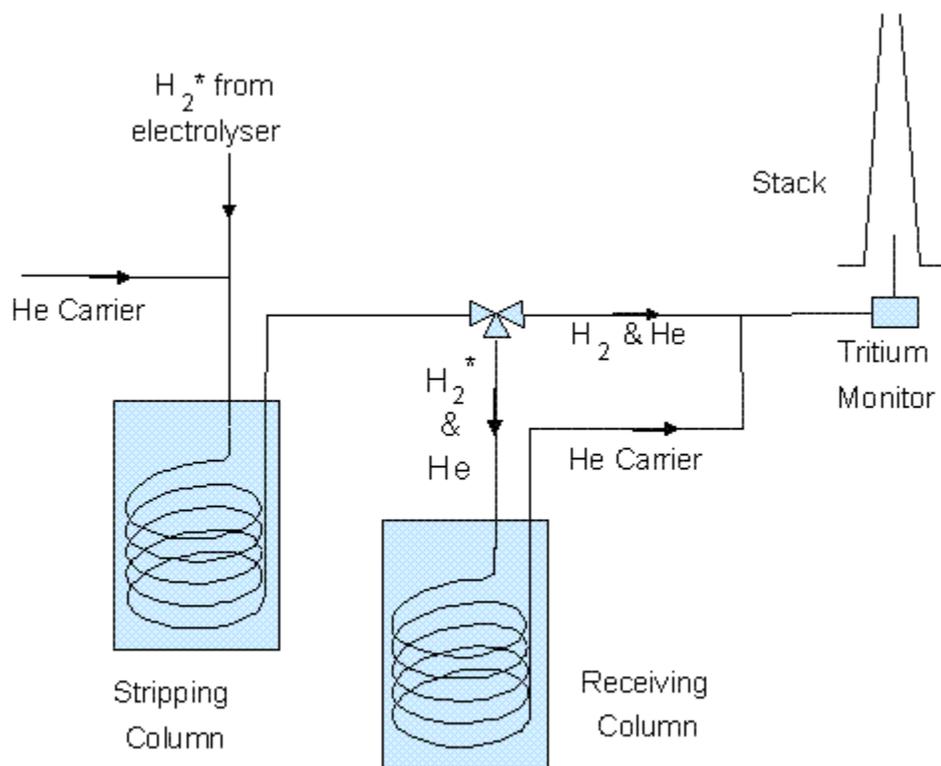


Fig. 1. Schematic illustrating AGC-ISS principle of operation. H₂^{*} represents tritium containing hydrogen gas

A helium carrier gas flow is established through the molecular sieve stripping column that has been cooled to -196° C. A batch of tritium (100-450 sL) contaminated (H₂^{*}) hydrogen is then injected into the column, displacing a like amount of hydrogen isotopes from the downstream end of the column. The lighter, more mobile, isotope, H₂, interacts less strongly with the 5A packing than the heavier tritiated isotopes. As a result hydrogen is trapped further downstream into the column than tritiated species. When additional hydrogen is added to the column, this uncontaminated hydrogen is pushed out and is carried to the stack by the helium carrier.

When the addition of the batch is complete, the carrier flow is routed through the stripping column to the receiving column before going to stack. The stripping column is then warmed progressively releasing all the hydrogen which moves it to the cold (-196° C) receiving column where it is trapped again. This operation further segregates the heavier and lighter isotopes, moving the lighter isotopes to the downstream end of the column. This second (receiving) column is identical to the first (stripping) column, so it now can perform the stripping operation. The first column is cooled, becoming the receiving column in the next cycle of the operation.

A stripping cycle comprises the following steps:

1. Set flow path from helium supply through stripping column to exhaust
2. Inject fixed quantity of tritiated hydrogen into the stripping column and displace an equivalent quantity of tritium-free hydrogen to the process exhaust
3. Place receiving column into flow path downstream of stripping column so that helium flow path is from the helium supply into the stripping column through the receiving column to the process exhaust
4. Empty the liquid nitrogen from the annulus region of the stripping column
5. Heat stripping column to move tritiated hydrogen from stripping to receiving column
6. After pre-set time, determined during tritium commissioning, stop heating
7. Cool stripping column by filling annulus region with liquid nitrogen
8. Return to step 1 where now the receiving column becomes the new stripping column and the former stripping column becomes the new receiving column
9. Continue steps 1 through 8 until operator terminates operation or no further feed material is available.

Valving is provided to reverse the roles for the two columns to permit continuous stripping for long periods of time. Thus very large volumes of lightly contaminated hydrogen are processed, releasing large amounts of uncontaminated hydrogen and retaining the tritium.

Volume Reduction Mode

The predominant operating mode of the AGC-ISS is the stripping mode that operates at constant gas inventory. This operation will continue for long periods, releasing hydrogen that is added but retaining all the tritium. Once a sufficient inventory of tritium has built up, the system hydrogen inventory is reduced as much as practical to minimize the gas remaining that is sent to the uranium storage bed for temporary storage. Volume reduction is identical to stripping with one difference that there is no tritiated hydrogen feed.

In this mode of operation, the column containing the gas is warmed as previously, but instead of the released gas all being sent to the receiving column, the inactive gas released from the column is sent to the stack. As soon as tritium is detected in the gas stream, the stream is diverted to the second (cold) column to be trapped. The volume of gas in the system is now significantly reduced. This process is repeated as needed to reduce the hydrogen inventory in the system to the desired level. The remaining gas can now be transferred to the Uranium hydride bed for temporary storage.

Gas stored in the uranium bed can be transferred back to the columns to undergo further volume reduction as required.

Basis for Separation of Hydrogen Isotopes

A gas chromatographic column can separate two gaseous species depending on the retention time of each gaseous species within the column. Retention time—the time it takes a gas species to traverse the column length—is a measure of how strongly a particular species interacts with the column packing material. The longer the retention time the stronger the interaction. The difference in retention times allows a column to separate components.

Retention time studies conducted at Ontario Hydro [1] on a 5A molecular sieve column of 7.6 m length and 2 cm ID yielded the results presented in Fig. 2.

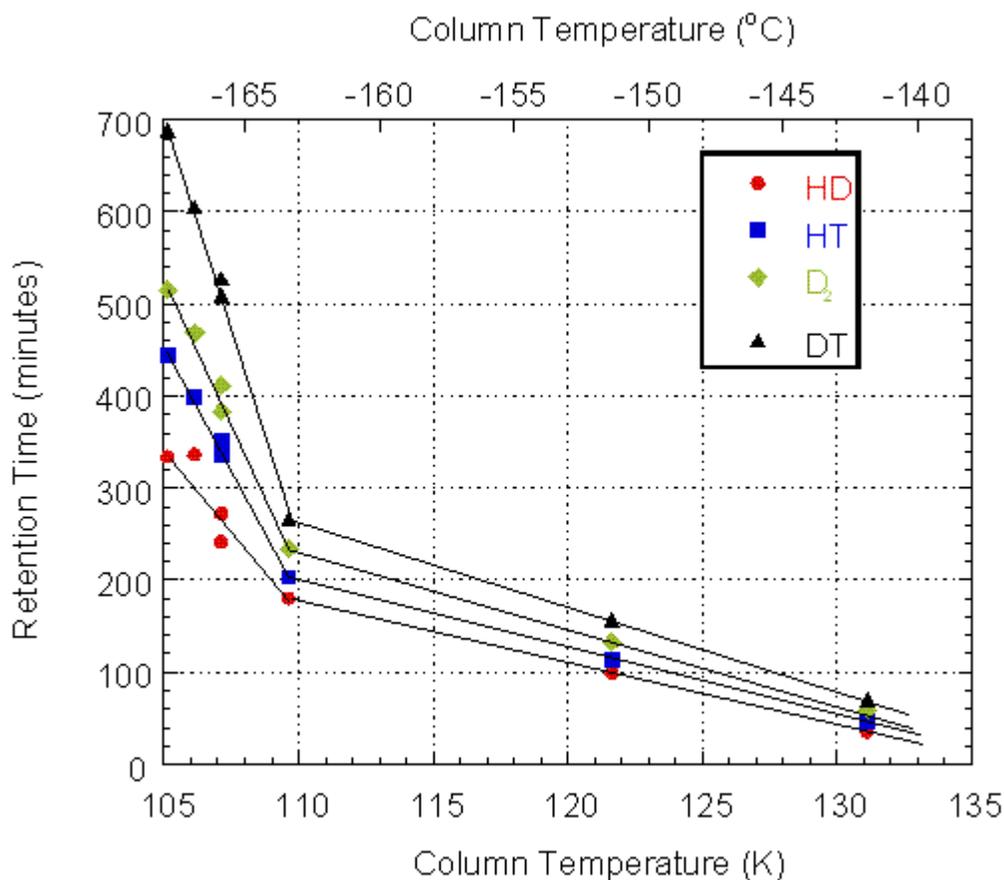


Fig. 2. Retention time of various isotope species as a function of operating temperature in a 7.6 m x 2 cm ID column

For a column temperature of < 110 K (-163° C), the retention times for the various hydrogen species increase significantly as the temperature decreases. Extrapolation of the data to liquid nitrogen temperatures 77 K (-196° C) gives the following retention times: HD – 1392 min; HT – 1975 min; D₂ – 2315 min; DT – 3348 min.

The longer column length of the AGC-ISS over that of the study [1] 10 m vs 7.6 m, increases the retention times, improving separation capabilities.

A relative measure of efficiency of separation is the ratio of retention times. This relative term is independent of column length, column cross-section and carrier gas flow and depends only on the adsorbent (5A mole sieve) and temperature. Table I. presents the ratio of retention times for the gas species shown in Fig. 2. at two temperatures, 105 and 77 K.

Table I. Efficiency of Separation

	Column Temperature (K)	
	105	77
Species	Ratio	
HT/HD	1.41	1.42
D ₂ /HT	1.13	1.17
DT/D ₂	1.35	1.45

From the table it appears that it is easier to separate HD from HT and DT from D₂ than HT from D₂.

For the molecular sieve columns to effectively separate they must be conditioned, that is, adsorbed water present on the molecular sieve is removed by heating the columns (>300°C) in a flowing nitrogen gas stream. Adsorbed water reduces the available surface area for interaction with the hydrogenic species thereby reducing the retention time of the hydrogen isotopes. The effectiveness of the molecular sieve column conditioning is confirmed by injecting an O₂/N₂ mixture and measuring the temporal separation of O₂ from N₂. This test is carried out at ambient temperatures.

RESULTS AND DISCUSSION

Column Hydrogen Capacity

The 'capacity' of each column was measured by injecting hydrogen at a continuous rate of 25 lpm along in addition to the carrier gas flow of 5 lpm of helium. As the liquid nitrogen cooled column is filled by hydrogen the mass transfer zone moves downstream along the column [4]. Each column has approximately 840 litre (STP) stoichiometric capacity. The mass transfer zone is determined by the time difference between the 5 and 95% of the steady state outlet pressure. For both columns this time is around 2.5% of the time required to fill the column indicating a short mass transfer zone.

Tritiated Hydrogen Feed

The tritiated hydrogen used for the testing of the AGC-ISS was provided by an electrolyzer. The tritium concentration in the electrolyzer varied through the course of the testing as the tritium concentration in the electrolysis cell increased to match the concentration in the feed tank. Initially the tritium concentration was of the order of 0.74 GBq/m^3 (20 mCi/m^3) and reaching a maximum of $\sim 7 \text{ GBq/m}^3$ (190 mCi/m^3). The form of tritium was mainly HT in H_2 with DT as negligible prior to stripping and volume reduction. The amount of deuterium was the naturally occurring levels found in water of 110-160 ppm [5]

System Cycle Time and Throughput

The total time for one cycle (defined as the time between two batch injections) is the sum of times taken for the following actions:

Injection time: Δt_{inj}

Time for emptying annulus: Δt_{an}

Time for heating column: Δt_h

Time for cooling column: Δt_c

Total cycle time: $\Delta t_{total} = \Delta t_{inj} + \Delta t_{an} + \Delta t_h + \Delta t_c$

Using test data from stripping operations: $\Delta t_c = 8.2$ minutes and $\Delta t_{an} = 5.4$ minutes for column 1. For column 2 the values are: $\Delta t_c = 8$ minutes and $\Delta t_{an} = 9.6$ minutes. The times taken to empty the annulus and to cool the column are physical constraints of the system and cannot be altered. The injection time can be varied because the mass controller can vary the injection flow from 0 to 100 slpm. The length of time for injection is then dictated by the maximum batch size the column can process without significantly increasing emissions from the injection side breakthrough. For this system this quantity is ~ 450 litres; therefore, Δt_{inj} for the maximum batch

is $450/100 = 4.5$ minutes. The time to heat the column is a variable of the system constrained by throughput and tritium emissions. A physical limit, dictated by the rate of heat transfer into the molecular sieve columns, prevents the heating time from being less than ~35 minutes. For a throughput of 8.1 m^3 (STP)/day the combined time of column 1 and 2 cycles is 148 minutes.

Throughput and Tritium Emissions

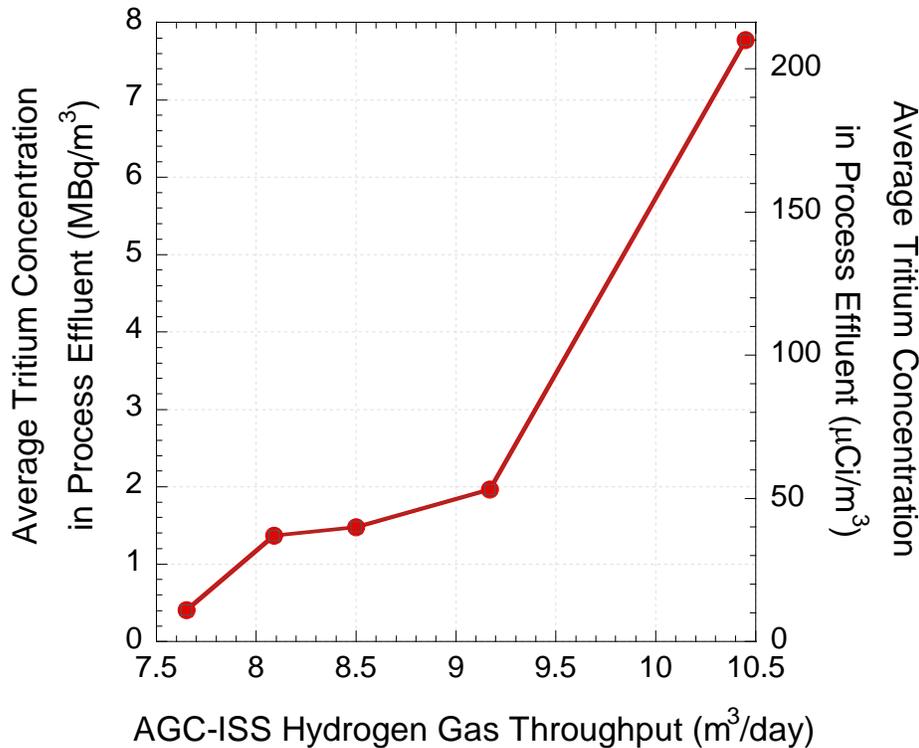


Fig. 3. Variation in the average tritium concentration in the process effluent with hydrogen gas processing rate

For a fixed tritium concentration in the feed gas and column heating rates the tritium emissions to the environment increases with throughput. Fig. 3. presents the tritium concentration in the process effluent as a function of throughput. A significant increase in the tritium concentration in the effluent is seen to occur for throughputs of >9200 litres/day. A throughput of 9200 litres/day corresponds to approximately 470 litres/batch; greater than 50% of the column capacity. This indicates that breakthrough of tritium occurs at such large batch sizes.

The temperature to which the outlet of the stripping column is heated during a column-to-column gas transfer affects tritium emissions. Increasing the temperature reduces the tritium in the

process effluent but decreases the processing throughput. The decrease in throughput occurs because a longer time is required to achieve the final temperature resulting in a longer cycle time.

Column Temperature and Emissions

The quantity of hydrogen isotopes adsorbed on the molecular sieve depends strongly on sieve temperature[6]. It is not surprising that the tritium concentration in the effluent depends on the temperature to which the column is heated during the transfer phase. A direct measure of the molecular sieve material was not available. In the AGC-ISS the thermocouples used to measure column temperatures are located on the shell of the columns, underneath the heaters, and do not reflect the true molecular sieve temperature. Because of the poor thermal conductivity of the molecular sieve material, the sieve material does not reach the temperature at the shell during cycling operations. The following example provides an indirect assessment of the molecular sieve temperature on tritium emissions. For a fixed throughput, the terminal temperature to which the shell at the column outlet was heated was set to -75°C . The heater duty cycle, however, was varied. The result was in one situation the end temperature was reached in 34 minutes while in the second situation the end temperature was reached in 49 minutes. This extra time to reach the same terminal shell temperature resulted in a reduction in the peak tritium concentration seen in the process effluent, from ~ 19 to 5 MBq/m^3 (500 to $140 \mu\text{Ci/m}^3$). This clearly demonstrates both the poor thermal conductivity of the column and, indirectly, the effect of molecular sieve temperature on the tritium emissions.

Thus, the operation of the AGC-ISS is bounded by the allowable tritium emissions, the rate of throughput and the physical constraints of the system imposed by design. Low tritium in the effluent can be achieved but at a cost to throughput for a given system design.

AGC-ISS Performance during Automated Stripping Operations

Fig. 4. presents typical profiles (column driving pressure, tritium concentration in process effluent), over one cycle and 5 batch injections, observed during the operation of the AGC-ISS in the stripping mode. The different operations the AGC-ISS performs during one cycle are observable in the pressure profile. The rise in column head pressure in the 0 to 10 minute time period is a result of injecting a batch of hydrogen gas. Here the injection rate was 50 slpm. Increasing the injection rate to 100 slpm results in a peak pressure of $\sim 0.42 \text{ MPa}$ (47 psig). During the time interval defined by the sudden drop in column pressure beginning at the 10 minute time period and before the next pressure rise (~ 20 minute interval) the following sequence of events are occurring in the AGC-ISS. First, the injection stops resulting in an immediate pressure drop. Second, the receiving column which was maintained at liquid nitrogen pressures during the injection is prepared for heating. Preparation for column heating entails: draining the liquid nitrogen surrounding the column, switching flow path from 'stripping (full) column to process exhaust' to one of 'stripping column to receiving (empty) column to process exhaust', and initiation of stripping column heating. Third, the rising driving pressure beginning at roughly the 20 minute interval and ending at the 85 minutes interval is a result of a combination of two effects: the increase in resistance to gas flow due to a warmer column and, an increased volume of gas in the process lines due to the desorption of hydrogen from the

stripping column on its way to the receiving column. The peak pressure, in this time interval, represents the peak in the hydrogen desorption rate. Last, the decrease in pressure at the 85 minute interval represents cooling the stripping column back to liquid nitrogen temperature in preparation for the next cycle.

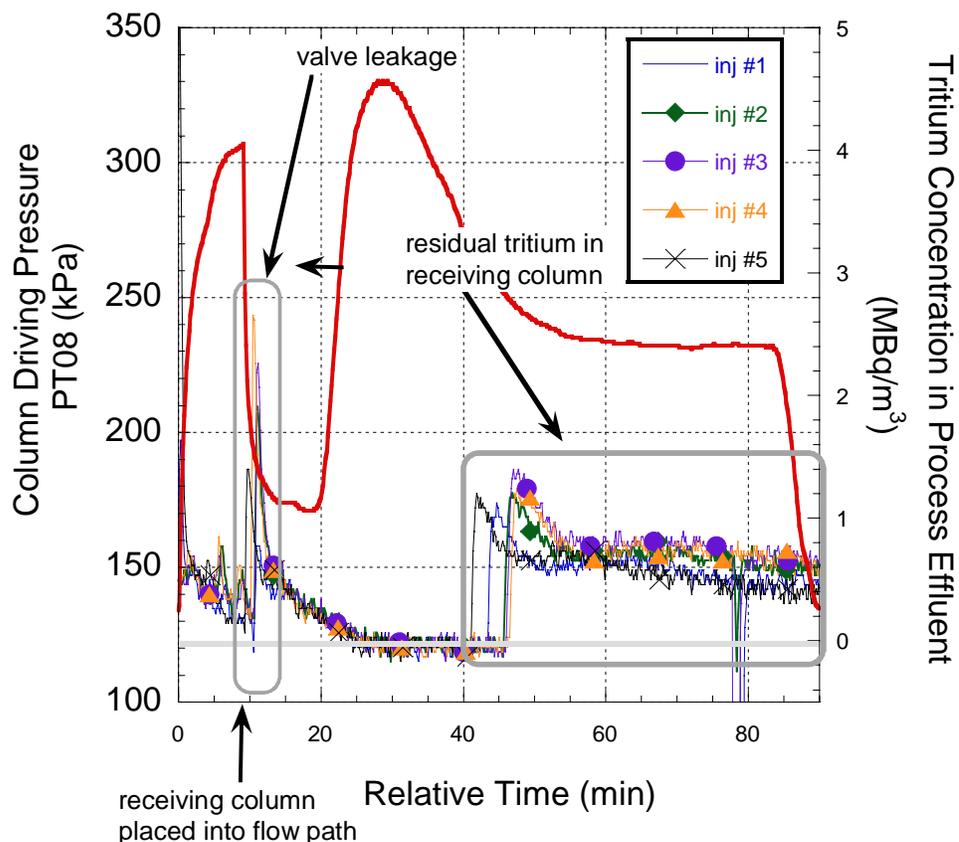


Fig. 4. Tritium concentration in effluent stream and column driving pressure profiles during one cycle for several batch injections

The tritium concentration profile in the process effluent is indicative of the performance of the molecular sieve columns and of leaks in process valving. During the injection period (0-10 minute interval) the tritium concentration in the effluent decreases. Here the tritium in the exhaust is the residual tritium remaining in the outlet side of the stripping column from a previous cycle. As the injection ends there is a sudden rise in tritium concentration. This is found to be a result of leaking seats in valves which are being actuated to change flow path. From about the 15-minute time interval to around 40 minutes the receiving (cold) column has been placed in line resulting in a gradual drop of the tritium concentration to zero. At about the 40 to 45 minute time interval the tritium concentration rises as a result of the receiving column saturating. Any residual tritium at the outlet of the molecular sieve column is pushed out as the hydrogen mass transfer zone moves to the receiving column outlet. The same residual signal

observed at the 90-minute interval will be observed when this column is again in the stripping position.

Two extended stripping operations were carried out with the following results. A throughput of $7.65 \text{ m}^3 (\text{H}_2) / \text{day}$ with a tritium feed concentration of $\sim 4.6 \text{ GBq/m}^3$ (125 mCi/m^3) yielded an average tritium concentration of 0.44 MBq/m^3 ($12 \text{ } \mu\text{Ci/m}^3$) in the process effluent. Processing at $8.1 \text{ m}^3 (\text{H}_2) / \text{day}$ with a tritium feed concentration of $\sim 7 \text{ GBq/m}^3$ (190 mCi/m^3) yielded an average tritium concentration of 1.4 MBq/m^3 ($37 \text{ } \mu\text{Ci/m}^3$) in the process effluent.

CONCLUSION

The AGC-ISS during tritium commissioning processed 37.8 m^3 (NTP) of tritiated hydrogen (28 litres of water) while retaining <20 litres. These numbers indicate the AGC-ISS vented greater than 99.95% of the hydrogen gas fed into the system. Approximately 174 GBq (4.7 Ci) of tritium was injected during this time. At a tritium concentration of $\sim 7 \text{ GBq/m}^3$ (190 mCi/m^3), processing at a rate of 8.1 m^3 (NTP)/day tritiated hydrogen gas resulted in an average tritium concentration in the effluent line of 1.4 MBq/m^3 ($37 \text{ } \mu\text{Ci/m}^3$). At this inlet concentration 56 GBq (1.5 Ci) of tritium is injected per day with $\sim 21 \text{ MBq}$ ($570 \text{ } \mu\text{Ci}$) released and 99.96% of the tritium is retained.

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