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Author(s):
Nobile, Arthur Jr.
Reichert, Heidi
Hollis, William Kirk
Taylor, Craig Michael
Gordon, John Cameron
Dale, Gregory E.

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Pre-Conceptual Design for Northstar ^{99}Mo Process Tritium Removal System

Arthur Nobile(1), Heidi Reichert(1), W. Kirk Hollis(2), Craig Taylor(2), John Gordon(2) and Greg Dale(3)

(1)Weapon Systems Engineering Division
(2)Chemistry Division
(3)Accelerator Operations and Technology Division

Los Alamos National Laboratory, MS A114
Los Alamos, NM 87544

Abstract

The Northstar-proposed accelerator-based ^{99}Mo production process uses the photonuclear reaction ^{100}Mo(γ,n)^{99}Mo in an enriched ^{100}Mo target. The ^{99}Mo production facility concept under consideration involves 8 target irradiation systems. Seven targets are under irradiation at any one time, with one target being off-line for maintenance. Each target is irradiated in a target vessel that has a recirculating helium flow loop to maintain cooling of the target. In a photonuclear reaction, a total of 36-38 mCi/yr of tritium is produced in the ^{100}Mo targets. This tritium will accumulate in the helium flow loops. The resulting tritium levels in the flow loops are not a concern from a perspective of environmental release or radiation exposure to a member of the public. Rather, the concern is one of gradual increase in surface contamination levels in process equipment due tritium permeation into steels and tritium exchange with of hydrocarbon oil, surface moisture, and other system contaminants. During maintenance and weekly target replacement when process systems are accessed, exposure to atmospheric air will result in tritium outgassing which could be a concern for worker exposure, and spread of contamination. While these hazards can be mitigated with common worker protections such as local ventilation and contamination control methods, the preferred approach would be to maintain low tritium levels in the system by use of an engineered system.

In this report we describe a preliminary concept for a Tritium Removal System (TRS) to remove tritium that is generated in the ^{99}Mo production process. Preliminary calculations have been performed to evaluate an approximate size for the system. The concept described utilizes well established detritiation technology based on catalytic oxidation of tritium and tritiated hydrocarbons to water in a high temperature (400 °C) reactor and capture of water in a molecular sieve bed. The TRS concept involves use of a single system that would cycle through each of the seven online target systems and remove tritium that has been accumulated after one week's run time. The TRS would perform cleanup operations on each target system for a period of approximately 24 hours. This would occur while the system is still online and just prior to target replacement, so tritium levels would at their minimum values for target replacement. In the concept, during normal operation a small fraction (1%) of the helium recirculating in the system would be diverted through the TRS and returned to the flow loop. With this approach sufficient levels of detritiation can be accomplished in a 24 hour period. In the study it was found that because of the need to maintain low oxygen levels in the system (<100 ppm) this increases the size of the catalytic reactor. As a result of this finding, consideration should be given to other methods for removing tritium from the system. Other methods such as catalytic exchange of tritium with an unsaturated organic compound and subsequent trapping on activated carbon or molecular sieve could offer advantages of reducing reactor size and operation at lower reactor temperature. However the most significant advantage of such an approach would be the ability to operate in very low oxygen environments, which would eliminate any concerns for oxidation of the target.

1.0 Introduction

In the ^{99}Mo production process under development by Northstar, ^{99}Mo is produced through the photonuclear reaction ^{100}Mo(γ,n)^{99}Mo. This reaction is accomplished by accelerator irradiation of a ^{100}Mo enriched target. The facility concept under consideration for ^{99}Mo production involves irradiation of seven targets that are each maintained under helium cooling in recirculating loops. The photonuclear (γ,n) reaction produces a very small quantity of tritium that will be released in the helium flow loop. In the facility concept under consideration 36-38 mCi/yr are produced. This is well removed from any concern associated with environmental impact or radiation exposure of a member of the public. However, if no provisions are made to remove tritium from the system, concentrations will increase and eventually pose concerns associated with radiation exposure of workers and spread of tritium contamination.

While concerns on radiation exposure and spread of contamination can be mitigated by common contamination control practices, a more reliable means of dealing with these is through implementation of an engineered system that would ensure overall tritium level in the system are minimized.

In this report a Tritium Removal System (TRS) concept for control of tritium in a ^{99}Mo facility is described. The TRS concept utilizes well-established and understood technology for tritium removal that involves oxidation of tritium and tritiated organics to tritiated water in a relatively high temperature (400 °C) catalytic reactor. Water produced is collected on a fixed molecular sieve bed. This water on molecular sieve is then periodically disposed of as low-level waste.

An important consideration in this system is the concentration of oxygen that will be present in the recirculating helium loops. Some oxygen must be present for the oxidation reactions that occur in the TRS reactor. However, oxygen is a concern for the Mo target and must be minimized to avoid oxidation of the target as it is at high temperature. It is estimated that the target can tolerate oxygen levels of 100 ppm. The rates of oxidation of tritium and tritiated organics in the TRS catalytic reactor are a function of this oxygen concentration. This value thus influences the size of the catalytic reactor.

To arrive at the TRS concept being proposed, the material balance and reaction kinetics equations for the system were developed and solved. The analysis involved solution of the equations in their unsteady state form in order to understand the transient aspects of the system. The analysis was performed using Wolfram SystemModeler. The unique aspect of this software is its ability to handle the interactions that occur between the individual unit operations in the system.

Once the appropriate analysis routine was developed for the proposed TRS concept, a number of operating scenarios for the ^{99}Mo plant were run, and from these a proposed operating scenario developed.

In this report we summarize the TRS concept and the proposed operating scenario for the system to maintain low tritium levels during sustained operation of the plant. While the detritiation technology chosen is well-established and has been used in tritium facilities for many years with high reliability, we point out the limitations of this technology in this application and discuss options for use of alternate technologies that could offer advantages over the conventional technology.

2.0 System Operating Approach and Parameters

System Operating Approach

The ^{99}Mo production facility will have a total of eight target systems. A target system consists of the target under irradiation and a supporting helium flow loop that passes helium over the target in a recirculating fashion for cooling. During normal operations seven of the eight target systems will be under irradiation and producing ^{99}Mo, and one target system will be offline for maintenance. During one calendar year operating period, each target system will operate for 45 weeks and be offline for 7 weeks.

Each helium flow loop irradiates 1 target for 6.5 days. After this irradiation period the target is removed from the system and is replaced over a 12 hour period, after which the next irradiation cycle begins.

System Operating Parameters

The target operates at a temperature of 600 °C or higher due to the energy deposition from the beam. The helium flow loop operates at a pressure of 400 psi and a flow rate of 200 g/s. Helium pumping in each flow loop is accomplished by an industrial positive displacement roots blower. Normal operating pressures for roots blowers are well below 400 psi. In order for the roots blowers to function at such high pressure, the blower is contained within a pressurized blower vessel having volume of approximately 1 m^3.

The blower vessel consists a 3 ft. diameter steel pipe with one end of the pipe terminated with a 3 ft pipe cap, and the other end terminated with a 3 ft. pipe flange. This flange mates to another blank flange which provides the closure for the vessel. The roots blower is held by a support structure that is welded to the blank flange. The blank flange and roots blower remain in a fixed location. All gas, electrical and instrument services for the blower and other equipment inside the vessel pass through the blank flange. The portion of the vessel consisting of the 3 ft. pipe, pipe cap and flange slide back and forth to allow access to the roots blower.

With this approach the blower experiences a pressure differential across the its housing of only a few psi which is equal to the differential pressure necessary to provide the required flow through the system.

Helium supply to the roots blower enters the blower vessel via a feedthrough through the blank flange that is open to the blower vessel. From the vessel, helium enters the inlet plenum of the blower which is open to the vessel. Helium exiting the vessel is discharged to a pipe that passes through the blank flange and continues to the rest of the flow loop.

Materials of construction for the blower vessel and recirculation piping are conventional carbon steel. To keep costs low, no attempt has been made to specify that these materials be stainless steel, or that any special cleaning or surface treatment specifications be applied to the piping.

Oxygen concentration during when the system is operating and under irradiation is kept to levels less than 100 ppm. This provides some oxygen for the oxidation reactions in the TRS catalytic reactor, but is believed to be sufficiently low to not cause significant oxidation of the target.

3.0 TRS Concept Description

The TRS concept is simple. The system consists of catalytic reactor and molecular sieve bed. The catalytic reactor would contain commercial catalyst designed for oxidation of elemental hydrogen and hydrocarbons to water and carbon dioxide in a low-oxygen atmosphere. Water would then be adsorbed on the molecular sieve bed.

This is the method that has been used in tritium facilities for the past forty years. It is simple, low cost and very reliable. The facility would have a single stationary system that would service all of the target systems in the facility. Each target loop would have piping connecting to the TRS.

Each of the target systems would operate for a defined period of time without being valved to the TRS. During this time tritium concentrations would increase in a linear fashion. Near the end of the defined operating time interval, the target system would be valved to the TRS. The TRS would be operated such that a side stream of the main system flow consisting of approximately 1% of the total system flow rate would be sent through the TRS. The total system flow rate is 200 g/s (1.12 m^3/s), thus approximately 2 g/s (0.0112 m^3/s) would pass through the TRS.

Figure 1 shows the system configuration of the TRS as shown in SystemModeler connected to a single target system. A side stream of helium passes through the TRS where tritium is removed and the stream is then sent back to the main flow loop. With this approach the system can operate while target irradiation is in progress. Diverting 1% of the main flow loop out of the system is an advantage, as it does not pose a significant change to the flow characteristics of the system.

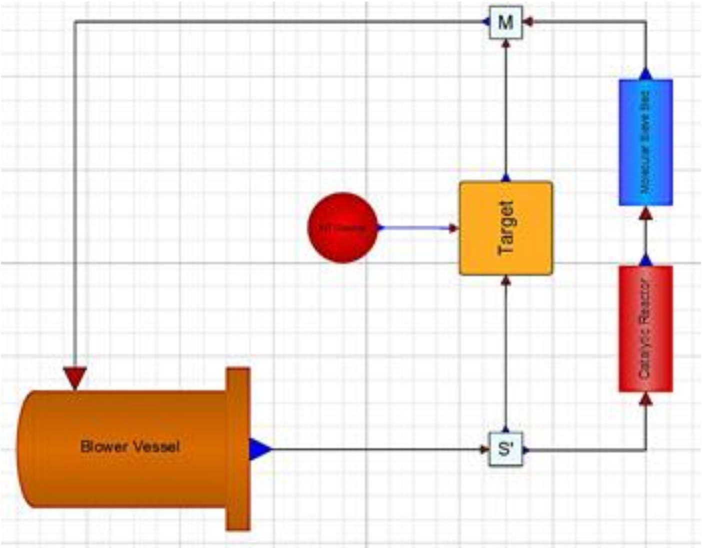


Figure 1. Configuration of TRS as it is online with a single target irradiation system.

In the configuration shown in Figure 1, the TRS is connected in parallel with flow passing through the target. It is thought that with this approach the pressure drop across the target may be sufficient to drive 1% of the stream through the TRS. If this can be accomplished this would eliminate the need for an additional blower to drive flow through the TRS. Further analysis of the flow characteristics of the system will determine whether a flow balancing device such as a metering valve or flow controller can be placed in one of the streams to achieve the desired flow rate through the TRS. If this can be done, all flow through the TRS can be accomplished with blowers already in place as part of the target system.

Flow through the TRS would continue until the tritium concentration in the target system is brought to a desired lower level. The TRS is then taken off line and system valves are repositioned to bring the TRS on line with the next target system. The TRS would be continuously cycled through the seven operating systems. With this approach the overall tritium levels in each target system are kept at low values.

4.0 Development of System Model and Sizing of Components

Analysis Approach

The material balance and reaction kinetics equations for the system in Figure 1 were developed and solved using Wolfram SystemModeler software. In the analysis, the differential equations were solved numerically in their unsteady state form to allow analysis of transient aspects of the system. The unique aspect of this software is its ability to handle the interactions that occur between the individual unit operations in the system. The ability for the outlet response of any unit operation to be provided as input to the downstream unit operation is provided by the SystemModeler software.

Tritium generation is modeled as evolving from the target in the form of HT. The target is modeled as a continuous stirred tank reactor (CSTR) as it is assumed to be well mixed.

The output stream from the blower vessel is the feed for the TRS. Due to its large volume, the blower vessel will behave as a CSTR. Its outlet concentration will be governed by the CSTR equation. This outlet concentration is the input concentration for the TRS catalytic reactor.

The catalytic reactor operates as an ideal plug flow homogeneous reactor where terms for convective transport, axial dispersion and chemical reaction are included. The reactor equations have as their inlet boundary condition the outlet concentration response of the blower vessel. The model provides fundamental reactor design information such as reactor physical dimensions, weight of catalyst, operating temperature and flow rate.

The output stream from the catalytic reactor is the feed for the molecular sieve bed. Models are based on fundamental transport equations with terms for convective transport, axial dispersion and adsorption. This model will allow sizing of catalyst bed to achieve desired decontamination factor.

Analysis Assumptions

- **It is assumed that tritium is released from the target into the flowing helium stream as elemental T_2.** Since the stream has oxygen concentration of approximately 100 ppm, it is likely that significant oxidation of T_2 to water will occur. However, without understanding the extent of oxidation that will occur, the conservative assumption is made that full oxidation of T_2 to tritiated water occurs.

- **The blower being used is considered to provide oil-free pumping since the gas has no direct contact with the blower lubricating fluids**. The blower impellers revolve without making contact with each other and the housing, therefore no lubrication is required in the conveying chamber. However, oil is present in the system as the blower shaft bearings are oil lubricated and typical vapor pressures for ISO oils are very low (~10^{-3} torr). The degree of oil contact with the bearings is small, so large concentrations of oil are not expected in the system. An effort is now underway at LANL to measure the degree of oil vapor content in the system. While these levels should be small, there is likely to be sufficient hydrocarbon concentration in the system to competitively undergo exchange reaction with tritium. Whether tritium is present as elemental tritium or tritiated water, significant hydrogen exchange is expected to occur.

  It should be noted that the blower vent ports are open to the interior of the blower pressure vessel where oil can enter process flow loop, posing a risk of oil vapor entering the process per manufacturer. Rapid depressurization of blower will result in gross compromise of seals and exposure of oil to the process; compressed process gas inside the oil sump will expand through the piston ring seals and into the seal vent chamber. Aerzen manufacturers do offer another line of blowers with housings that are designed as pressure vessels, separate forced oil system that ensure oil-free conveying, but this has been deemed cost prohibitive option. Thus, it is possible that there will be some oil contamination of the interior of the blower vessel.

- **For robust catalytic reactor design, it is conservatively assumed that all tritium present in the helium flow loop is in the form of tritiated methane (CH_3T).** There is a high probability that tritiated longer chain hydrocarbons originating from blower oils are present which participate in exchange reactions. Thus, the most conservative assumption is that tritium will be exchanged with hydrocarbons. Oxidation of tritiated methane has higher catalytic oxidation activation energy than longer chain hydrocarbons. Thus, without knowledge of the distribution of hydrocarbon species in the system, the assumption is made that all hydrocarbons are present as tritiated methane. CH_3T that is not oxidized in the reactor is assumed to pass through the molecular sieve bed.

Governing Equations

The goal of the analysis is to develop the governing equations for each unit operation in the system and solve in an integrated fashion using SystemModeler. This produces a model that can analyze system performance characteristics as a function of equipment size and operating parameters.

Target Volume

The Target Volume has volume of approximately 1 L. It can be modeled as a CSTR with a generation source, g_T, consisting of the elemental tritium that is generated in the ^{99}Mo target. Tritium is generated at approximately 5.4 mCi/target/year. The Target Volume model is shown in Figure 2.

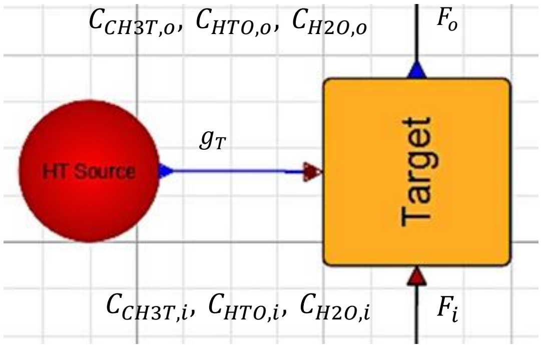


Figure 2. Model for Target Volume showing inlet and outlet stream variables and tritium source.

$C_{CH3T,i}$, $C_{HTO,i}$ and $C_{H2O,i}$ are the Target Volume inlet concentrations of CH_3T, HTO and H_2O, respectively, and $C_{CH3T,o}$, $C_{HTO,o}$ and $C_{H2O,o}$ are the outlet Target Volume concentrations of these species. F_i and F_o are the inlet and outlet flow rates.

The Target Volume is modeled as indicated above using the CSTR equations. An equation is written for each of the above mentioned species as follows,

$$V_T \frac{dC_{CH3T,o}}{\partial t} = F_i C_{CH3T,i} - F_o C_{CH3T,o} + g_T \qquad [1]$$

$$V_T \frac{dC_{HTO,o}}{\partial t} = F_i C_{HTO,i} - F_o C_{HTO,o} + g_T \qquad [2]$$

$$V_T \frac{dC_{H2O,o}}{\partial t} = F_i C_{H2O,i} - F_o C_{H2O,o} + g_T \qquad [3]$$

V_T is the volume of the Target Volume. The initial conditions are written for the condition at startup of the system where all concentrations are zero. So at initial time, $t = 0$,

$$C_{CH3T,o}(0) = 0 \qquad [4]$$

$$C_{HTO,o}(0) = 0 \qquad [5]$$

$$C_{H2O,o}(0) = 0 \qquad [6]$$

Blower Vessel

The Blower Vessel has volume of approximately 1 m^3. It can also be modeled as a CSTR. No tritium is generated in this volume. The Blower Vessel model is shown in Figure 3.

$C_{CH3T,i}$, $C_{HTO,i}$ and $C_{H2O,i}$ are the Blower Vessel inlet concentrations of CH_3T, HTO and H_2O, respectively, and $C_{CH3T,o}$, $C_{HTO,o}$ and $C_{H2O,o}$ are the outlet Blower Volume concentrations of these species. F_i and F_o are the inlet and outlet flow rates.

The Blower Vessel is modeled using the CSTR equations. An equation is written for each of the above mentioned species as follows,

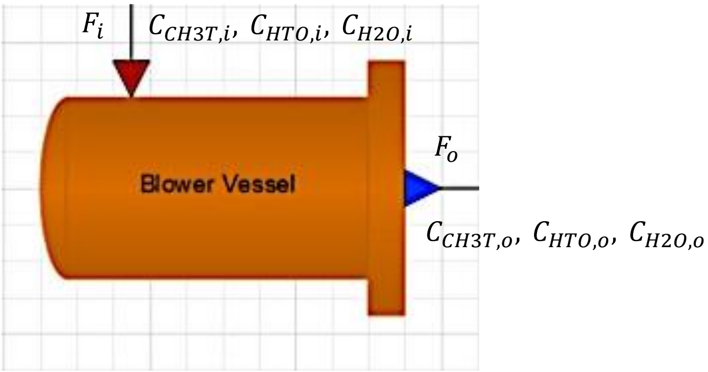


Figure 3. Model for Blower Vessel showing inlet and outlet stream variables.

$$V_{BV}\frac{dC_{CH3T,o}}{\partial t} = F_i C_{CH3T,i} - F_o C_{CH3T,o} \quad [7]$$

$$V_{BV}\frac{dC_{HTO,o}}{\partial t} = F_i C_{HTO,i} - F_o C_{HTO,o} \quad [8]$$

$$V_{BV}\frac{dC_{H2O,o}}{\partial t} = F_i C_{H2O,i} - F_o C_{H2O,o} \quad [9]$$

V_{BV} is Blower Vessel volume. Similar to the Target Volume, initial conditions are written for the condition at startup where all concentrations are zero. So at initial time, t=0,

$$C_{CH3T,o}(0) = 0 \quad [10]$$

$$C_{HTO,o}(0) = 0 \quad [11]$$

$$C_{H2O,o}(0) = 0 \quad [12]$$

Splitter

The Splitter performs the simple function of splitting the single inlet stream into two outlet streams. No chemical separation, chemical reaction, heat removal or heat addition occurs in this device. The Splitter has no volume so any change to the inlet stream flow rate or composition is immediately observed in the outlet streams. The only variable specified is the split fraction, η_S, which is the fraction of the minor stream that is split away from the major stream. For operation of this system, we are using split fractions of 1%.

With no separation or reaction occurring in the Splitter, outlet concentrations for both streams are equal to the inlet concentrations. Figure 4 shows Splitter variables.

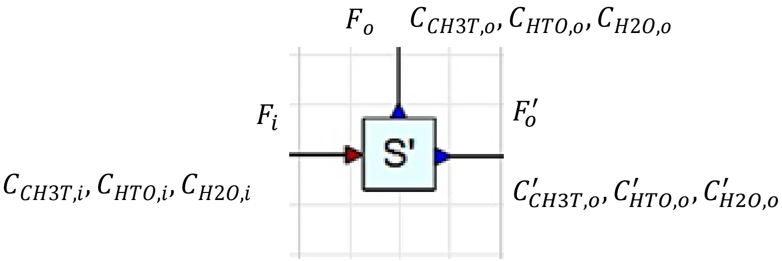


Figure 4. Model for Splitter showing inlet and outlet stream variables.

The governing equations for the Splitter are the following,

$$F_i = F_o + F'_o \qquad [13]$$

$$F'_o = \eta_S F_i \qquad [14]$$

Mixer

The Mixer performs the function of combining two streams into a single stream. No reaction or heat addition/removal occurs in this device. Mixing is assumed to be ideal, so no heat of mixing effects are the case. The Mixer has no volume, so any change to an inlet stream flow rate or composition is immediately observed in the outlet stream.

Figure 5 shows Mixer variables.

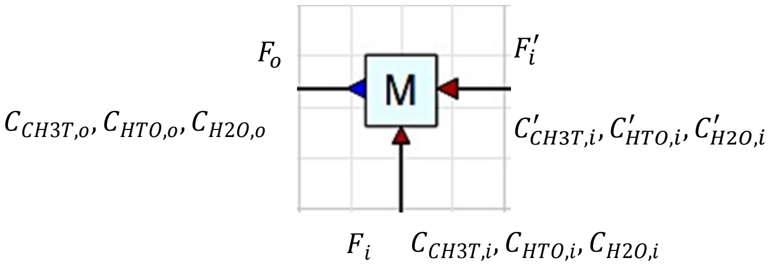


Figure 5. Model for Mixer showing inlet and outlet stream variables.

The governing equations for the Mixer are the following,

$$F_i C_{CH3T,i} + F'_o C'_{CH3T,i} = F_o C_{CH3T,o} \qquad [15]$$

$$F_i C_{HTO,i} + F'_o C'_{HTO,i} = F_o C_{HTO,o} \qquad [16]$$

$$F_i C_{H2O,i} + F'_o C'_{H2O,i} = F_o C_{H2O,o} \qquad [17]$$

Catalytic Reactor

The Catalytic Reactor functions to oxidize all chemical forms of tritium to tritiated water. Tritium can be present in elemental form (T_2 and HT) and in other chemically-bound forms such as in water form or bound to hydrocarbon molecules. As indicated above there will be small quantities of hydrocarbon vapor from oils in the system we. Exchange reactions between tritium and these oils will occur either at the hot surface of the Mo target, in the catalytic reactor or by radiolysis of tritium.

In this initial scoping effort we make the conservative assumption that all tritium is in hydrocarbon form. We don't know the types of hydrocarbons that will be in the system. There is likely to be oil vapor, but due to presence of the hot ^{99}Mo target, there is likely to be some cracking of hydrocarbons resulting in species with lower molecular weight. Without prior knowledge of the extent of the cracking reactions occurring, we assume all hydrocarbons are present as methane. Since methane is the most difficult hydrocarbon to oxidize, this will be the most conservative assumption for design of the catalytic reactor.

For design of the catalytic reactor we assume that the primary reaction occurring is the following:

$$CH_3T + 2O_2 \rightarrow HTO + H_2O + CO_2 \qquad [18]$$

This will be catalyzed by a noble metal catalyst such as palladium. Measurements of the reaction rate of this reaction in air according to the rate expression,

$$-r_{CH_3T} = k_d C_{O_2} C_{CH_3T} \qquad [19]$$

were studied by R. Ellis et al., *Fusion Technol.* **21**, 566 (1992). In the Northstar system oxygen will be held at levels at or below 100 ppm. Given these oxygen concentrations and very low tritium concentrations it is a safe assumption that $C_{O_2} \gg C_{CH_3T}$. Thus the quantity $k_d C_{O_2}$ in Eq. [19] is a constant value across the catalytic reactor since C_{O_2} does not significantly change. Eq. 19 can then be stated as,

$$-r_{CH_3T} = k'_d C_{CH_3T} \qquad [20]$$

where $k'_d = k_d C_{O_2}$. Since the reaction does not occur in air as studied by R. Ellis et al., rate constants provided by Ellis et al. are not valid. Since, per Eq. [19] rate is proportional to oxygen concentration, we simply scale the rate constant per the ratio of oxygen in the Northstar system and oxygen in air (0.0001/0.21). Figure 6 shows an Arrhenius plot of the rate constant for the oxidation of methane in 100 ppm oxygen.

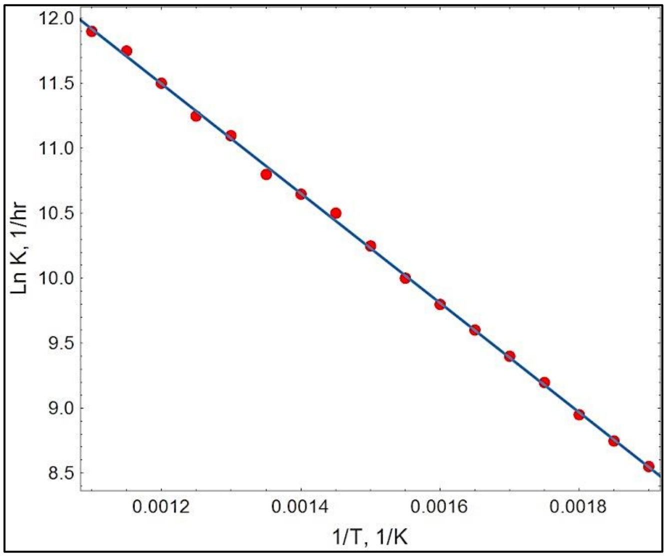


Figure 6. Arrhenius plot for rate constant of methane oxidation in 100 ppm oxygen.

Now that the methane oxidation rate constant has been determined, we can write the transport equations for the catalytic reactor and develop solutions to the behavior of methane oxidation in the reactor as a function of reactor geometric parameters and operating conditions. The solutions will study of the performance of the system as a function of geometry and operating parameters with goal of establishing a design for the particular application.

The transport equations are written in the unsteady state form to provide capability to assess transient behavior of the system. The reactor is modeled as a plug flow system with chemical reaction occurring along the reactor length. Included in the reactor equations are axial diffusion effects along the reactor length. As with the unit operation models above, we track the species CH_3T, HTO and H_2O.

The governing transport equation for tritiated methane is as follows,

$$\frac{\partial C_{CH_3T}}{\partial t} = -U_z \frac{\partial C_{CH_3T}}{\partial z} + D_{e,CH_3T} \frac{\partial C_{CH_3T}}{\partial z} + r_{CH_3T} \qquad [20]$$

where U_z is the gas velocity in the reactor. It is assumed that flow in the reactor is plug flow, so gas velocity is easily calculable from volumetric flow rate. D_{e,CH_3T} is the effective diffusivity in the catalyst packed bed. For this differential equation we define one boundary condition which is the tritiated methane concentration at the reactor inlet, z=0,

$$C_{CH_3T}(t,0) = C_{CH_3T,i}(t) \qquad [21]$$

In the SystemModeler code, $C_{CH_3T,i}(t)$ will be the time-dependent outlet concentration of the unit operation upstream of the reactor, which is the splitter. We also define one initial condition which is the tritiated methane concentration profile along the length of the reactor at time=0,

$$C_{CH_3T}(0,z) = C_{CH_3T,0}(z) \qquad [22]$$

In a similar fashion, the transport equation defining tritiated water concentration along the reactor length is as follows,

$$\frac{\partial C_{HTO}}{\partial t} = -U_z \frac{\partial C_{HTO}}{\partial z} + D_{e,HTO} \frac{\partial C_{HTO}}{\partial z} + r_{HTO} \qquad [23]$$

The boundary condition is the tritiated water concentration at the reactor inlet, which is the time dependent outlet concentration of the splitter,

$$C_{HTO}(t,0) = C_{HTO,i}(t) \qquad [24]$$

The initial condition is the tritiated water concentration profile along the length of the reactor at time=0,

$$C_{HTO}(0,z) = C_{HTO,0}(z) \qquad [25]$$

Finally, the concentration profile of water along the reactor is governed by,

$$\frac{\partial C_{H_2O}}{\partial t} = -U_z \frac{\partial C_{H_2O}}{\partial z} + D_{e,HTO} \frac{\partial C_{H_2O}}{\partial z} + r_{H_2O} \qquad [26]$$

which has boundary condition,

$$C_{H_2O}(t,0) = C_{H_2O,i}(t) \qquad [27]$$

and initial condition,

$$C_{H_2O}(0,z) = C_{H_2O,0}(z) \qquad [28]$$

Each of the above equations contains the rate of production or decomposition of the species whose concentration is being calculated. Eq. [20] defines the rate of decomposition of tritiated methane, $-r_{CH_3T}$. Rates of production of tritiated water and normal water are still needed. From the stoichiometry of Eq. [18] we can write,

$$r_{HTO} = -r_{CH_3T} \qquad [29]$$

and,

$$r_{H2O} = -r_{CH_3T} \qquad [30]$$

Eqs [20]-[28] are solved to determine the time-dependent concentration profiles of the three species along the reactor. The equations are solved using the Mathematica NDSolve differential equation solver.

The solver simultaneously solves the equations and produces a solution consisting of the time dependent concentration profiles of the three species in the reactor.

The Mathematica NDSolve code is fed to the SystemModeler code and is used as a subroutine within SystemModeler. By doing this, SystemModeler can create integrated system models which allow full understanding of system dynamics and interactions between individual components. Mathematica is a very advanced modeling code, so the ability to use this code within SystemModeler allows the ability to quickly address complex integrated systems.

Before using the Mathematica reactor code within SystemModeler, some calculations were performed with the reactor in Mathematica outside of SystemModeler to understand its dynamic and steady state behavior. This provided us the ability to understand reactor performance as a function of its geometric parameters (reactor length and diameter) as well as operating parameters (temperature, flow rate and inlet concentrations of the species being tracked).

Calculations were performed for the baseline reactor design, which has length and diameter of 2 m and 0.3 m, respectively. Its operation is at 600 °C temperature and 400 psi pressure. Calculations were performed for a reactor packed with oxidation catalyst having void fraction of 0.20, which is typical for packed catalyst beds. Flow rate through the reactor is a function of the split fraction in the Splitter, which is assumed in this study to be 1%. Thus, flow rate through the reactor is 1% of the full 200 g/s system flow rate or 2 g/s.

In fully operating systems, inlet reactor concentration will be unsteady-state in nature. The system is expected to operate in a cleanup mode where tritium contaminated portions of the system are brought online and flow is passed through the reactor until cleanup is achieved. For initial study of reactor performance we keep inlet concentration constant to allow study of performance in the absence of changing inlet concentration. This value was arbitrarily set to 0.30 pmol/m^3

To understand dynamic performance of the reactor, the calculation is started with no tritiated methane in the reactor. At t=0, a step change is made to the inlet tritiated methane concentration to 0.30 pmol/m^3. This concentration value is the steady state concentration that would result with the baseline helium flow rate in the system (200 g/s) flowing past target that is generating the baseline tritium generation rate in the target (38 mCi/yr). This does not necessarily represent any particular concentration value in the system, but was chosen as a constant value to assess the reactor performance.

Figure 7 shows tritiated methane concentration along the reactor length for several times after step increase in inlet tritiated methane concentration. The plots show progression of the front through the bed. At 5 s the front has progressed 0.5 meters into the bed, and at 20 s the front is nearly broken out of the bed. At 40 s the reactor is at steady-state. At steady-state it is seen from the plot that the methane conversion across the reactor is small. Inlet concentration is 0.30 pmol/m^3, and at the exit of the reactor the concentration has dropped to approximately 0.22 pmol/m^3. Thus tritiated methane conversion across the reactor is not large (~27%). Later in the report we will show that the fact that this conversion is small is not a problem or issue for operation of the system due to the large circulation rates in the system.

Figure 8 shows tritiated and normal water concentrations in the reactor for several times for same conditions as calculation in Figure 7. Inlet tritiated water concentration was zero. Inlet normal water concentration was 0.015 pmol/m^3. Some inlet water was added to the stream only for purposes of offsetting of curves so each set of curves could be visualized. If inlet water concentration was zero, curves would have exactly the same values. The curves in Figure 8 show a front of water and tritiated water progressing through the reactor. The front exits the reactor at about 20 s and is at steady-state operation at less than 40 s.

These results indicate that the reactor response to changes in inlet concentration is fast. The reactor will respond to inlet changes and reach steady-state in less than 40 s. Tritiated methane conversion across the reactor for each pass is not large (~27%). Because of the first order behavior of the reaction, this conversion value will not be a function of the inlet concentration. So for fixed reactor size and operating conditions this conversion expressed in percent value will be independent of inlet concentration value. Integrated calculations discussed below use this reactor model to evaluate overall system performance.

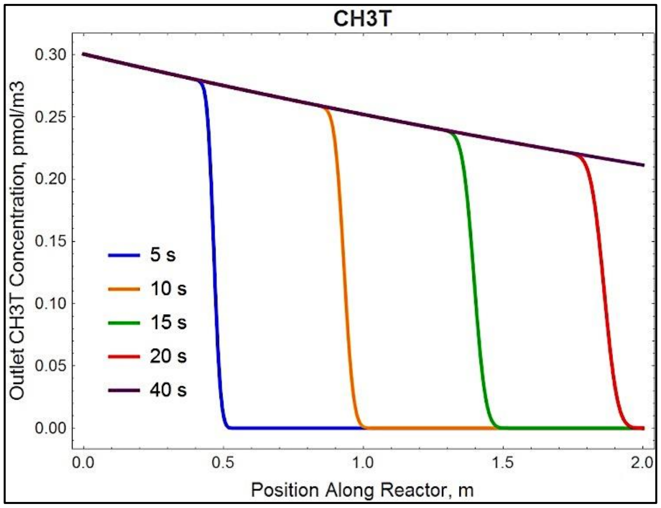


Figure 7. Tritiated methane concentration along reactor length for several times after step change in tritiated methane inlet concentration from 0 to 0.3 pmol/m^3.

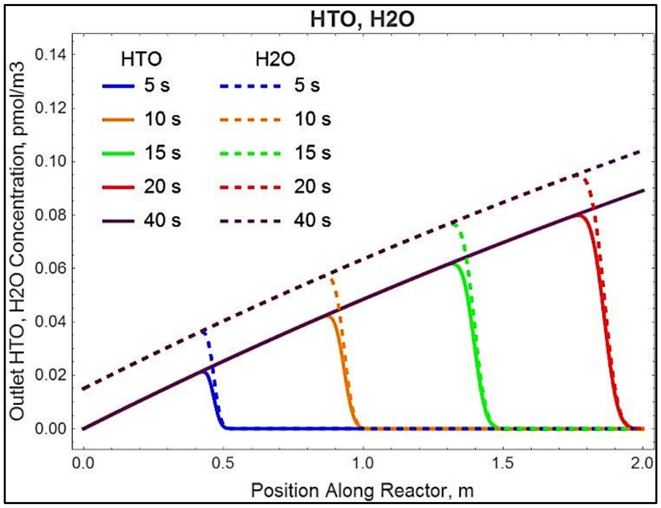
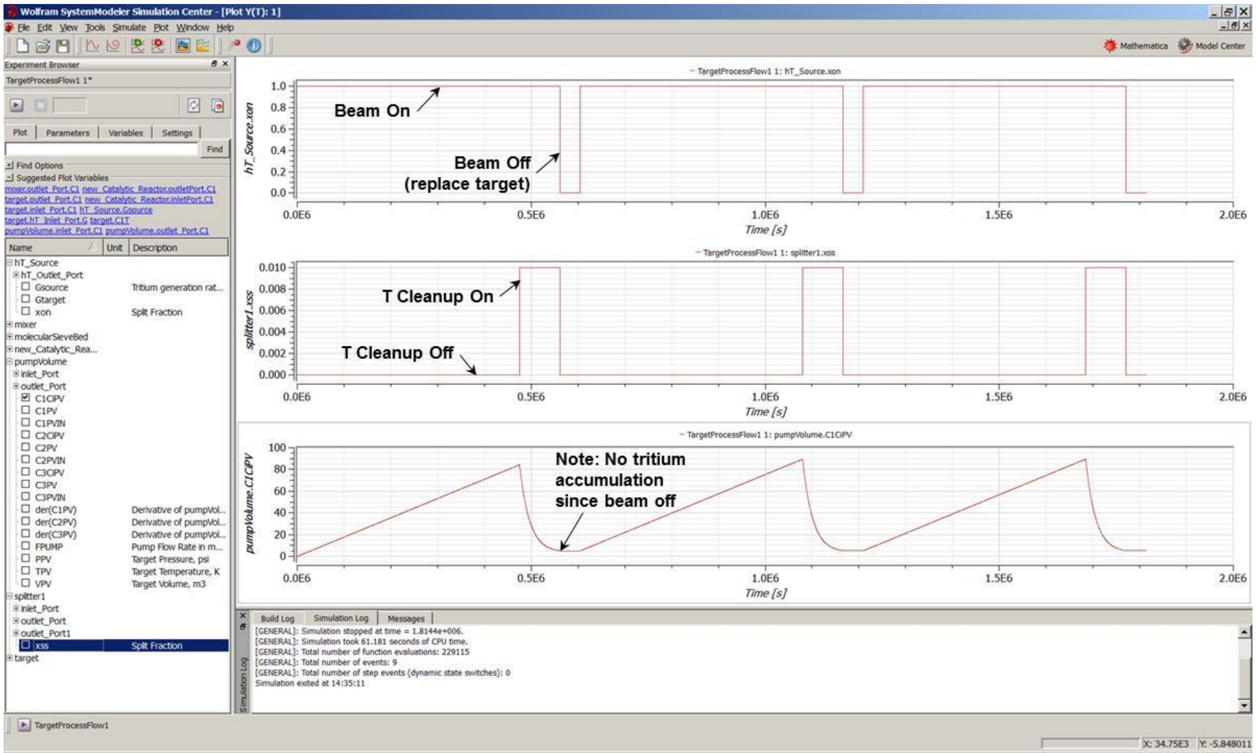


Figure 8. Tritiated and normal water concentration along reactor length for several times after step change in tritiated methane inlet concentration from 0 to 0.3. Inlet value of tritiated water is zero. Inlet normal water concentration is 0.015 pmol/m^3, only for purpose of offsetting curves so each curve could be seen.

Integrated System Performance

The goal of this effort is to model performance of the system shown in Figure 1. Above the models for each of the unit operations were defined. During operation of the system the individual unit operations will interact. The Mathematica SystemModeler software solves each of the unit operations equations simultaneously, and in doing this is able to capture the full dynamic behavior of the system. Figure 9 shows three plots that illustrate behavior of the system.



Name	Unit	Description
hT_Source		
hT_Outlet_Port		
☐ Gsource		Tritium generation rat...
☐ Gtarget		
☐ xon		Split Fraction
mixer		
molecularSieveBed		
new_Catalytic_Rea...		
pumpVolume		
inlet_Port		
outlet_Port		
☑ C1CiPV		
☐ C1PV		
☐ C1PVIN		
☐ C2CiPV		
☐ C2PV		
☐ C2PVIN		
☐ C3CiPV		
☐ C3PV		
☐ C3PVIN		
☐ der(C1PV)		Derivative of pumpVol...
☐ der(C2PV)		Derivative of pumpVol...
☐ der(C3PV)		Derivative of pumpVol...
☐ FPUMP		Pump Flow Rate in m...
☐ PPV		Target Pressure, psi
☐ TPV		Target Temperature, K
☐ VPV		Target Volume, m3
splitter1		
inlet_Port		
outlet_Port		
outlet_Port1		
☐ xss		Split Fraction
target		

```
[GENERAL]: Simulation stopped at time = 1.8144e+006.
[GENERAL]: Simulation took 61.181 seconds of CPU time.
[GENERAL]: Total number of function evaluations: 229115
[GENERAL]: Total number of events: 9
[GENERAL]: Total number of step events (dynamic state switches): 0
Simulation exited at 14:35:11
```

Figure 9. Results from dynamic model calculation showing behavior of one ^{99}Mo target as a function of time. Calculation represents operation for three weeks. (a) Beam flux on target (1.0 = beam on, 0.0 = beam off), (b) fraction of total flow entering TRS (0.010 = 1% of total flow through the TRS, 0.00 = no flow through TRS), (c) tritium quantity in the pump volume in μCi.

The calculation starts at time=0 by turning on the beam. The beam status (on or off) is shown in Figure 9(a). Figure 9(b) shows the fraction of the system flow entering the TRS. Initially no flow enters the TRS. Figure 9(c) shows the tritium quantity in the Blower Vessel in μCi. Irradiation of the target continues for 6 days at which point the tritium quantity in the Blower Vessel has reached 85 μCi. At this point, beam is turned off and the TRS is valved into the system. One percent of the total system flow flows through the TRS. Operation of the system in this manner continues for 24 h, after which the tritium concentration in the Blower Vessel is reduced to approximately 5 μCi. Flow to the TRS is stopped and the beam is turned back on. This completes the seven day operating cycle and a new cycle begins.

After cleanup of one target system is completed, the TRS is valved into the next target system which will be at the end of its seven day operating cycle. Thus, each target system operates out of phase for a period of one day. This allows the system to continue to operate in an ongoing manner with tritium cleanup service provided by a single TRS.

5.0 Advanced Concepts

The above description represents the baseline proposed concept. Below are potential other technology options that could be considered for the system.

Due to the low tritium generation rates and high flow rates present within the system, tritium concentrations are low (ppb levels). Thus a very large surface area getter is potentially required (in order to compete with possible helium blanketing effects), or the use of a large amount of a "regular" getter may be necessary, representing a potentially high cost issue. The low tritium concentrations may also limit the application of catalytic approaches towards chemically converting the tritium into a suitable form for disposal (e.g. via tritiation of an appropriate unsaturated organic compound). Oxygen concentrations are scant and therefore efficient (catalytic) oxidation of gaseous tritiated species into tritiated water capable of then being captured on a molecular sieve may be a challenge as well. Note that as tritium decays into ^{3}He, this should be accounted for in terms of helium bubble/pressure formation within any material/storage system.

In order to assess some possible approaches, a few scenarios are assumed:

(a) The tritium, as either at HT or T_2 (likely the former), might be *removed as close to the source (target) as possible*, i.e. before it reaches the blower vessel. This would potentially negate the need for tritiated hydrocarbon species removal via post blower vessel oxidation chemistries at all (see c below). In this scenario, the loop may need to be reconfigured, so that any now non-tritiated hydrocarbon vapor may simply be trapped out (i.e. no need for a catalytic reactor). Alternatively in the absence of an oil vapor trap, by placing the catalyst bed and molecular sieve beds in series with the target and blower, rather than in a parallel configuration, catalytic oxidation of now non-tritiated hydrocarbon species (via the use of for example, a Pd/Al_2O_3 catalyst) into H_2O would then simply be required. Some other direct tritium removal possibilities are alluded to below.

(b) Direct oxidation of tritium into tritiated water using a catalyst and molecular sieve bed capture *before it reaches the blower*. An analogous approach is taken in the purification/regeneration of a glovebox catalyst bed where heated copper metal (or some other finely divided metal) is commonly used to remove oxygen. This oxygen removing column is normally regenerated by passing a hydrogen/nitrogen mixture through it while it is heated: the water formed is passed out of the box with the excess hydrogen and nitrogen. It is common to use molecular sieves to remove water by adsorbing it in the molecular sieves' pores (https://en.wikipedia.org/wiki/Glovebox).

(c) If in the current scenario, tritiated hydrocarbon species do result from reactions with the pump oil, hydrocarbon oxidation chemistries will need to be applied at low O_2 concentrations within the loop. Assuming that there are ppb levels of tritium and ppm levels of oxygen (on a molar basis), there should be enough oxygen in the system to be able to facilitate the complete oxidation of e.g. CH_3T (i.e. via $CH_3T + 2O_2 \rightarrow CO_2 + HTO + H_2O$). This of course will depend on the efficacy of the oxidation catalyst (e.g. Pd/Al_2O_3 or other metal oxide supports; *e.g.* P. Gélin, M. Primet *Applied Catalysis B: Environmental* **2002**, *39*, 1) at low levels of substrates. Other catalytic materials are used in the high temperature oxidative combustion e.g. the use of Cr_2O_3 and Co_3O_4 + Ag (to bind sulfur and halogens if this is a need) in elemental analyzer isotope ratio mass spectrometry (http://www.forensic-isotopes.org/assets/IRMS Guide Finalv3.1_Web.pd). CO_2 that may be formed upon carbon based oxidation (or the presence of other impurities present in the stream) could be also be a competitive species for tritiated water with respect to capture on the molecular sieve. Perhaps this could simply be dealt with by suitably scaling the amount of molecular sieve to be used.

Direct Tritium Removal at the Target

Scenarios b and c above suggest ways to catalytically remove tritium pre-blower and post-blower. This remainder of this report focuses on approaches of removal close to the point of generation other than catalytically converting tritiated compounds into water. Rather than focus on detailed engineering aspects for the configuration of the helium loop(s) in this regard, this effort simply considers some known technologies and classes of materials that might potentially be used to scavenge tritium within an inert gas stream. One of the challenges lies in the fact that the tritium is present at ppb levels in the He diluent, so efficient tritium sequestration is needed.

Any getter/catalyst material would obviously need to be tested for efficacy towards the levels of tritium that are present in the system either at the “ambient” temperature present in the helium flow loop

(100-120^{o}C), or perhaps within an engineered scenario designed to alter gas pressure or temperatures into a regime where the getter or tritiding material could optimally operate.

Lab scale experiments using H_2 and/or D_2 might also be undertaken in "feasibility studies" in order to select the most promising materials candidates under these conditions. Due to the large volume of literature of potential materials phase space, the various areas below are only briefly touched on. Some references are provided for further reading and interrogation of the subject matter.

Getter materials. Note that the electronic configuration of tritium is the same as protium and deuterium. The chemical properties of the isotopes are also the same. Rates of reaction may vary for the different isotopes due to the difference in the atomic masses. Additionally, the energy provided by the radioactive decay of tritium (to ^{3}He) can provide the activation energy required so that some reactions will occur with tritium that will not occur with deuterium or hydrogen (DOE Handbook: Tritium Handling and Safe Storage (DOE-HDBK-1129-99, March 1999)). If tritium scavenging can be achieved close to the point of target irradiation before it gets to the pump system (and assuming that radiolytic effects do not do anything deleterious to the scavenging material – probably not an issue as the beta decay to ^{3}He varies from 0 to 18.6 kiloelectron-volts (keV) with an average energy of 5.69 keV (DOE Handbook: Tritium Handling and Safe Storage (DOE-HDBK-1129-99, March 1999)), this may represent a better alternative than (oxidative) catalytic conversion of carbonaceous species containing tritium (formed for example by subsequent reactions with pump oil/pump oil vapor). Multiple getter/tritiding samples may have to be placed within the He loop between the target and the blower in order to deal with the low tritium concentrations present. The literature on hydrogen uptake in materials is vast, so only a few references are made below to some possible areas of interest.

Metal based getters. Since tritium in such a system is present at low concentrations and would not be subject to recycle, sequestration of the tritium by a getter that can then be disposed of safely, or its conversion into another material of suitable form for storage/disposal may indeed be desirable. Various getter materials include metals such as uranium, cerium, scandium, erbium, palladium, titanium, zirconium, etc. (J. L. Maienschein *Nuclear Technology* **1978**, *38*, 387). These materials have various advantages and disadvantages. Advantages include reaction with only hydrogen isotopes in some cases, but not other impurities (in fact some of these metals are used as materials to purify gas streams containing hydrogen isotopes). Disadvantages include the possible pyrophoricity of the metal powder itself (therefore requiring inert atmosphere handling) as well as the potential pyrophoricity of the resulting hydride phase that may be formed (again requiring appropriate consideration). Mischmetal getters are commercially available and these might be applicable here (http://vacaero.com/information-resources/the-heat-treat-doctor/1166-getter-materials.html). Ce based mischmetals have been used to get hydrogen from helium streams (W. Q. Dong, W. Jing, C.-C. Ping, Y Zhou *Journal of the Less-Common Metals,* **1987**, *131*, 321 and references therein). Consideration of potential mischmetal pyrophoricity should also be given as mischmetals are used in lighter flints, so spark when struck with steel (http://www.thefreedictionary.com/misch+metal).

Other commercial getter materials are also available (see e.g. https://www.saesgetters.com/suisorb.) As alluded to above, a challenge for a getter material in this kind of scenario is the potentially high surface area that would be required to deal with the small amount of tritium present in the large amount of He feed gas. In order to address the issue of high surface area, perhaps a "nanogetter"/nanomaterial could also be considered (vide infra).

Hydrogen (and possibly Tritium) Storage Materials Hydrogen storage materials pertinent to transportation and power generation may also represent options for the sequestration of hydrogen isotope such at tritium. Hydrogen storage follows two approaches; physical storage where compressed hydrogen gas is stored under pressure or as a liquid and; chemical storage, where the hydrogen is bonded with another material to form a hydride and released via a chemical reaction or by the use of temperature. In terms of material properties, hydrogen storage density generally increases in going from physical (surface) adsorption, to intermetallic hydrides, to complex hydrides to chemical hydrides (M. U. Niemann, S. S. Srinivasan, A. R. Phani, A. Kumar, D. Y. Goswami, E. K. Stefanakos *Journal of Nanomaterials* **2008**, *Article ID 950967, doi:10.1155/2008/950967*).

Perhaps we can we can draw some analogies for tritium from the storage of hydrogen within chemical compounds or by adsorption onto solid state materials. If recycle of tritium is not going to be an issue, but rather long term storage of a tritiated material is the goal (again the issue of ^{3}He formation over time in any potential tritium storage medium should be considered and mitigated for), then we essentially want to utilize a material where, once tritium is captured, the tritium uptake/bonding is "irreversible" or requires a large amount of energy for release to occur (e.g. occurs within a temperature regime way above that where the tritium containing material would be handled/stored). Chemically bound tritium is likely better than adsorbed forms for disposal/storage purposes.

Carbon Based Materials Carbon based materials have been widely studied as hydrogen storage media. *(Chem. Eng. Technol.* **2010**, *33*, 213 and references therein). These include activated carbons (where high adsorption capacity typically occurs at cryogenic temperatures and under high gas pressures), carbon nanotubes, graphite nanofibers and more recently graphene and graphene oxide.
Nanomaterials such as graphenes represent intriguing materials in terms of their hydrogen (and perhaps tritium) storage characteristics. Graphene has been shown to convert into graphane under a stream of hydrogen atoms (*Chem. Eng. Technol.* **2010**, *33*, 213 and references therein). The graphane can be reversibly converted back into graphene, albeit it at 350°C (D. C. Elias et al. *Science* **2009**, *323*, 610). Whether or not these classes of materials are of practical utility as tritium getters in the presence of low tritium concentrations and under the temperatures and pressures in operation within this kind of system remains to be seen, but may be worth investigating. If so, an interesting question also arises as to the fate of the tritiated graphene when the tritium atoms decay into ^{3}He – does the graphane revert back into graphene upon ^{3}He release? Polyaniline-based nanocomposite materials for hydrogen storage have also been investigated (*International Journal of Hydrogen Energy* **2007**, *32,* 1010).

Organic based getters have also been investigated for scavenging hydrogen from TRU waste containers. Good performance has been achieved with 1,4-bis(phenylethynyl)benzene (DEB). It has a capacity of 240-330 cm^{3} (STP) hydrogen per gram DEB. DEB is a non-toxic, non-mutagenic, crystalline solid. Because it is a di-alkyne (containing two triple bonds), one mole of DEB reacts with 4 moles of hydrogen. It melts at 179°C; whereas the fully hydrogenated product melts at 87°C. The standard formulation for the DEB getter is a mixture of 75% DEB and 25% palladium-carbon catalyst (5% Pd on carbon). The production process involves mixing the two materials together in a ceramic jar mill for several hours, after which the DEB getter is ready for use. It has been shown to be stable in the absence of hydrogen for up to 18 months (at 70°C, under N_2). The DEB formulation has been successfully incorporated into several forms including powder, pellets, shaped polymer composite, a urethane adhesive film a castable RTV silicone (http://www.wmsym.org/archives/1997/sess23/23-02.htm; http://www5vip.inl.gov/technicalpublications/Documents/2670755.pdf; http://www5vip.inl.gov/technicalpublications/Documents/3480248.pdf)

Carbon Nanotubes (CNTs) and Boron Nitride nanotubes including doped, single-walled and multi-walled species have been investigated for their hydrogen storage capacities. (A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature*, **1997**, *386*, 377; P. M. F. J. Costa, K. S. Coleman; M. L. H. Green, *Nanotechnology*, 2005, *16*, 512, 2005; T. Das; S. Banerjee, K. Dasgupta, J. B. Joshi; V. Sudarsan *RSC Adv.,* **2015**, *5*, 41468; X.-F. Jiang, Q. Weng, X.-B. Wang X. Li J. Zhang, D. Golberg, Y. Bando *Journal of Materials Science & Technology* **2015**, *31,* 589). Although much promise has been demonstrated, more progress is still required in terms of gas storage capacities at ambient temperatures and pressures.

Porous Polymer Frameworks have also received a lot of attention for their hydrogen storage characteristics (e.g. K. Sakaushi, M. Antonietti *Acc. Chem. Res.*, **2015**, *48*, 1591 and references therein). Again improvement is needed in H_2 uptake under "practical" temperatures and pressures.

Metal Organic Frameworks (MOFs) and Zeolites Metal organic frameworks (MOFs) and zeolites have also been used as solid state media for the storage of hydrogen (H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi Science **2013**, *341*, 974 and references therein). The disadvantage that these materials possess in the context of this application is their need to be cooled to cryogenic temperatures for the uptake of appreciable amounts of gas.

Hollow Glass Microspheres These have been considered in the context of hydrogen storage (*Chem. Eng. Technol.* **2010**, *33*, 213 and references therein) and in fact have actually been used to contain D/T mixtures in fusion applications.

Metal hydrides The literature on the hydriding of metals upon reaction with hydrogen is vast. We would like the formation of the hydride (tritide) phase to happen within the temperature and pressure ranges within the loop, or for a promising material to be readily engineered into the loop somehow, so that optimal conditions for its irreversible hydride (tritide) formation could be realized. Examples of commonly studied metal hydride systems for processing hydrogen isotopes in power plant scenarios have been highlighted elsewhere (Yu. F. Shmal'ko, V. V. Solovei, M. V. Lotots'kyi, E. V. Klochko, Yu. Zavalii, O. B. Ryabov, V. A. Yartys' *Materials Science* **2001**, 37, 689). Again, consideration of the reactivity/pyrophoricity of the resulting hydride phase and/or its precursor(s) should be given here.

Metal nitrides and imides are also known to uptake hydrogen with hydrogen desorption occurring at reasonably high temperatures (e.g. P. Chen, Z. Xiong, J. Luo, J. Lin & K. L. Tan *Nature* **2002**, *420*, 302). Some of the resultant metal amide phases that are possible upon H_2 uptake may not be desirable for this application, due to their potential reactivity with H_2O or oxygen.

Some concluding statements. There are materials that are potentially capable of effecting the desired catalytic transformations of tritium or hydrocarbons to water, or forming some form of chemically bound tritide species. The challenge here is to invoke a method that is not limited in efficiency (rate) by the low reactant concentrations in the helium gas stream. The helium loop system may need to be reconfigured to achieve reasonable catalytic rates or getter uptake rates, given that the concentrations of tritium and oxygen are very low. Multiple passes over a suitable tritium or hydrocarbon oxidation catalyst or getter may need to be achieved. Alternatively, the loop may need to be reconfigured so that the tritium can be "syphoned" off to help levels build up to a point where it can be reasonably catalytically reacted with suitable oxygen levels also introduced into the system in such a way that it doesn't cause target oxidation issues. In any storage scenario, an evaluation of the decay of tritium into ^{3}He should be made in order to assess any issue due to helium pressure build up.

Use of electrochemical membrane sensors. An electrochemical membrane sensor can be employed to measure and remove hydrogen (i.e., H, D, T) simultaneously. This sensor is comprised of a proton conducting ceramic with electrodes (Yb-doped Sr-Ce-O tubes with Pt electrodes) that selectively permeates hydrogen while chemically reducing tritiated hydrocarbons and water at the surface of the membrane at 600 C. No mechanical pumping is required and sensor operation is compatible with the high flow rate of the process stream. This electrochemical pumping technology can be inserted after the heated target, where it can maintain a concentration and pressure differential across the ceramic membrane (ratio on the order of 10^{20}) where the gas remains segregated in the sensor until it is emptied. A separate electrochemical membrane sensor can also be employed to measure oxygen. For the oxygen sensor, a yttria stabilized zirconia based sensor monitors oxygen concentration which is also capable of electrochemically pumping out oxygen. Since this version of a “TRS” does not require oxygen as a reactant, this technology can also scavenge oxygen in the system as it is measured.

Although this technology requires further experimental testing to gather empirical separation data, it is a viable option as it has been proven suitable for trace tritium removal including tritium associated with hydrocarbon or water. The ceramic material and sensor development is mature, and further testing can be performed to aid in process modeling and concept development.

6.0 Conclusion and Recommended Process Optimization Activities

A concept has been proposed for maintaining low tritium levels in the Northstar ^{99}Mo production system. The concept is based on conventional low cost reliable technology which has been used in tritium facility for several decades. The baseline concept provides cleanup of 7 operating target systems on an ongoing basis with each target system operating for a period of 6 days with one day of cleanup by the TRS. Initial sizes of the catalytic reactor and molecular sieve bed are estimated. Further work is necessary to establish final specifications for procurement of such a system. The system utilizes off-the-shelf technologies, so a system design can be developed and the system can be fabricated by vendors with capability to fabricate conventional chemical processing systems.

A number of other options are considered as potential longer term solutions for tritium cleanup of systems such as this. These are higher risk options which would require further development, but could offer advantages in a number of areas.