Design of Laboratory System to Recover Tritium from Zirconium Recycle and Plan to Test System

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SUMMARY

The objective of the tritium separations task is to develop a viable process to separate tritium from the zirconium recycle off-gas stream. In support of this long-term objective, the goal of the present work is to design a test system and prepare a test plan for an alternate tritium capture method suitable for, and compatible with, recycle of the reactive gas (i.e., chlorine) in the zirconium recycle process. The zirconium recycle process is under development to recover zirconium from the Zircaloy® cladding component of used nuclear fuel. Small quantities of all isotopes of hydrogen (^{all}H) are trapped in the Zircaloy as zirconium hydride. Processing releases and converts this hydrogen to hydrogen chloride, including tritium-substituted hydrogen chloride, ^{3}HCl (a.k.a., TCl). This compound of tritium must be removed from the zirconium recycle process off-gas and sequestered to satisfy regulations governing emissions of tritium.

Nine distinct dry processes were identified as potentially viable for capturing tritium from the zirconium recovery/recycle process off-gas. Processes that would produce large amounts of secondary waste or require additional non-simple separations steps were eliminated from further consideration. Three process technologies were identified as promising candidates for further study and evaluation. One technology avoids the introduction of tritium into the chloride volatility step. It uses high-temperature pretreatment of the cladding in an inert gas to release all isotopes of hydrogen, which are subsequently converted to water and removed from the inert gas stream with 3A molecular sieves. Details of the process and its implementation are described in this report.

The other two technologies involve removing TCl (and HCl) from the off-gases of the chloride volatility step. Chemisorption of HCl by agents that are known to produce hydrogen bonds, such as NaF and BiOF, were considered, but no data on the sorption capacity of these agents were found. Information was available on the selective physisorption of HCl using 5A molecular sieve. The available data in chart form do not adequately cover the low HCl concentration range expected in the zirconium recycle off-gas (<4 v/v%). Experimental conditions are provided in the report for obtaining the data on the capacity of these molecular sieves at HCl concentrations of interest.

Tests are suggested to evaluate each of the three promising technologies. A thermogravimetric analysis (TGA) technique is suggested to obtain the equilibrium mass of HCl adsorbed on 5A molecular sieve at various gas-phase HCl concentrations. Flowing gas mixtures of various compositions can be prepared using highly accurate mass flow controllers. The volume fraction (readily related to partial pressure) of the sorbate gas and the weight gained by the sorbent at equilibrium provide a data pair. Additional data pairs can be obtained by increasing the flow of the sorbate gas and allowing the weight gained by the sorbent to re-equilibrate at a higher value. Sufficient data to obtain adsorption isotherms for HCl mixed with an inert gas at different temperatures are recommended. Repeating the measurement of the isotherms in the presence of about 10% Cl_2 in the gas mixture will determine the effect, if any, by Cl_2 on the sorption capacity. The effect of regeneration of the sorbent on subsequent measurements of capacity should also be evaluated. Following desorption of HCl at an elevated temperature, the amount of HCl remaining on the sorbent should be ascertained and the loading of the regenerated sorbent should be measured.

The same testing protocols and equipment may be used to test one of the chemisorption reagents. It is suggested that bismuth oxyfluoride (BiOF) be evaluated. Data for one isotherm would be useful for ascertaining if chemisorption is competitive, or not, with physisorption on molecular sieves. If the results are promising, additional isotherms should be determined and desorption tests should be completed similar to those done for the molecular sieve.

Pretreatment of the cladding to remove tritium depends primarily on temperature as the rate determining variable. Measurement of the removal rate at a up to three different temperatures are recommended.

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ACRONYMS

DF	decontamination factor
HCl	hydrogen chloride (implicitly, hydrogen isotopes are of natural abundance)
^{all}HCl	hydrogen chloride (implicitly, all hydrogen isotopes of artificial abundances)
MRWFD	Materials Recovery and Waste Forms Development (campaign)
NTRD	Nuclear Technology Research and Development Program
ORNL	Oak Ridge National Laboratory
ppm	parts per million
ppmv	parts per million by volume
sccm	standard cubic centimeters per minute
TCl	tritium chloride
TGA	thermogravimetric analysis
UNF	used nuclear fuel

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DESIGN OF LABORATORY SYSTEM TO RECOVER TRITIUM FROM ZIRCONIUM RECYCLE AND PLAN TO TEST SYSTEM

1. INTRODUCTION

1.1 Objectives

The objective of the tritium separations task is to develop a viable process to separate tritium from the zirconium recycle off-gas stream. In support of this long-term objective, the goal of the present work is to design a test system and prepare a test plan for an alternate tritium capture method suitable for recycle of the reactive gas in the zirconium recycle process. Tritium exists in the zirconium recycle process as tritium-substituted hydrogen chloride, ^{3}HCl (a.k.a., TCl). The process for which an alternate is sought is aqueous scrubbing of HCl from a gas stream composed predominantly of chlorine (Cl_2) and an inert carrier gas [e.g., argon (Ar)]. Aqueous scrubbing effectively removes the highly soluble HCl from the less soluble Cl_2, but it humidifies the gas stream. Drying of the gas stream is required to recycle the Cl_2 and inert gas because of the deleterious effects of water in the zirconium recycle process. An alternate method that separates ^{all}HCl while avoiding the complications of a drying step will be beneficial because of the simplifications it imbues (where ^{all}HCl refers to hydrogen chloride containing any combination of hydrogen isotopes, including tritium).

1.2 Background

Zircaloy® cladding makes up about 25% of the mass of used nuclear fuel (UNF) assemblies. Approximately 98 wt% of the Zircaloy is high-value, hafnium-free zirconium. As part of the Materials Recovery and Waste Forms Development (MRWFD) campaign [within the Nuclear Technology Research and Development (NTRD) Program] to develop technologies for processing UNF, zirconium recycle is being developed as a technology to further reduce the amount of waste destined for disposal in a geologic repository. Recovered zirconium could be either recycled or disposed as low-level radioactive waste. Because irradiated zirconium contains a small fraction of radioactive ^{93}Zr activation product, zirconium recovered from UNF might be limited to reuse in nuclear applications, such as making new cladding. Should reuse be uneconomical, it may be possible to decontaminate the recovered zirconium sufficiently from other fission and activation products to qualify it for much less expensive low-level waste disposal.[1]

Cladding from UNF may be contaminated with residual adherent fuel, fission recoil fuel fragments embedded in the metal, and gaseous fission products that can diffuse into the metal. In particular, part of the tritium produced during irradiation of the nuclear fuel is trapped in the metal of the cladding as zirconium hydride. Other isotopes of hydrogen, e.g. ^{1}H and ^{2}H, will be similarly trapped in the metal. Treatment of the cladding with hydrogen chloride (HCl) or chlorine (Cl_2) at temperatures around 400°C converts the zirconium to volatile zirconium tetrachloride ($ZrCl_4$), thereby releasing the tritium.[2,3] Treatment of the cladding with HCl releases the tritium (and other isotopes of hydrogen that may be present) in the form of molecular hydrogen, whereas treatment with Cl_2 releases the tritium, and other isotopes of hydrogen, as hydrogen chloride (e.g., ^{all}HCl). The off-gas treatment methods to sequester the tritium depend on the choice of chlorination agent.

The *current baseline* process to recycle zirconium utilizes chlorine gas to convert the metals in the Zircaloy cladding to chlorides. The gaseous $ZrCl_4$ separates from the nonvolatile fuel fragments and nonvolatile metals (e.g., nickel), effecting a significant radiological decontamination.[4] After separation, cooling of the gas stream condenses (or desublimes) the $ZrCl_4$ as a solid salt. In addition to zirconium, some chlorides of the alloy components of Zircaloy are volatile, e.g., tin tetrachloride ($SnCl_4$) and niobium pentachloride ($NbCl_5$) or niobium oxychloride ($NbOCl_3$), which may be condensed along with the zirconium.[1,5] Any tritium or tritiated zirconium hydride in the alloy will react to produce TCl, which remains in the gas stream. The off-gas treatment system will be required to capture and retain a large portion of this TCl to meet regulatory requirements. The system may also be required to tolerate low concentrations of uncondensed metal chlorides.

1.3 Tritium Gettering Options

Generally, the vapor pressure of the metal chlorides and oxychlorides that arise from chlorination of Zircaloy are very low at ambient temperatures. Most have vapor pressures around 10^{-7} Torr at 21°C, while the vapor pressure of tin tetrachloride ($SnCl_4$) is around 10^{-2} Torr at 0°C.[4] Although traces of $SnCl_4$ will remain in the off-gas following condensation of the $ZrCl_4$, the remaining gas stream consists primarily of the inert carrier (Ar), Cl_2, HCl, and TCl, the latter two being at low concentration. Potential options to treat the off-gases from the recycle process have been previously described,[2,3,6] and additional information was found during the preparation of this report. A brief summary with assessment is provided here.

- *Condensation*—The boiling points of Ar, HCl, and Cl_2 are -189.3°C, -84.9°C, and -34.6°C, respectively. Chlorine solidifies at -101.0°C and together these data indicate the need to run a cryogenic condenser at around -100.0°C. Because the very small mass of hydrogen and tritium in the cladding leads to very low concentrations of HCl and TCl in the gas phase, their partial pressure may not exceed their vapor pressure at the condenser temperature; condensation of these species may not occur. However, a significant fraction of the HCl/TCl may be soluble in liquid Cl_2. Concentrations can be increased by recycle of the unseparated process gas, and treatment of a small slip stream may be more effective. Although further separation by fractionation is feasible, is an undesired complication.

  Assessment: Recovery of HCl/TCl with condensation requires expensive cryogenic processes. Additional separation steps may be required to recycle the chlorine, making the recovery more complicated. Development of this technique is considered low priority.

- *Chemical Conversion and Trapping*—Both HCl and Cl_2 react with metals, such as copper, to produce the metal chloride. In the case of HCl-TCl, the reaction releases H_2-HT. The chloride content of the gas is converted to nonvolatile metal chlorides. The H_2 can be oxidized to produce water, and the water is readily trapped on molecular sieves. Only the inert carrier gas then would be available for recycle. Previous scoping studies conducted by the authors using this methodology have been reported.[2,3] Although such a method may be useful for sample analysis, it eliminates the straightforward recycle of the Cl_2 and produces large quantities of metal chloride waste.

  Assessment: The production of large quantities of secondary metal chloride wastes disqualifies this technology from further consideration.

  As another option, a regenerable sorption technique utilizing manganese oxide (MnO), has been patented.[7] The MnO chemically reacts with HCl at temperatures between about 315°C and 500°C, trapping the chlorine as $MnCl_2$ and releasing water. Heating the $MnCl_2$ above 700°C in the presence of oxygen converts the manganese back to the oxide form while releasing the chlorine. Our thermodynamic calculations performed using HSC version 9 indicate that Cl_2 does not react with the MnO at the reported HCl sorption temperatures.[8] Issues to consider in this approach are the drying of an inert gas-Cl_2 stream and reactions of H_2O-HTO with Cl_2 at the sorption temperatures (i.e., 315°C and 500°C). Our thermodynamic calculations using HSC version 9 indicate an equilibrium of low HCl concentration in H_2O-Cl_2 mixtures maintained above 400°C.[8] If the kinetics are favorable, the HCl-TCl would be rapidly reformed from reactions of H_2O-HTO with Cl_2, so the regenerable sorbent may be ineffective this specific application.

  Assessment: A MnO-based regenerable sorbent will be ineffective in the presence of excess chlorine. This disqualifies this technology from further consideration.

- *Aqueous Liquid Scrubbing*— Aqueous scrubbing effectively removes the highly soluble HCl from the less soluble Cl_2, but it humidifies the gas stream. This method is used in the industrial production of Cl_2, where concentrated sulfuric acid (H_2SO_4) solutions are used to dry the Cl_2. Aqueous scrubbing was implemented for laboratory-scale zirconium recycle tests, but the moist chlorine stream was neutralized to produce a waste.[1] At commercial scale where recycle of the Cl_2 and inert gas is needed for economy, drying of the gas stream is required because of the deleterious effects of water in the zirconium volatilization step.

  Assessment: Both drying operations and aqueous hydrochloric acid handling operations result in additional costs. This is the process for which an alternative is sought. Further work is not recommended.

- *Chemisorption*—Hydrogen bonding is exploited in the adsorption and separation of some halides from gas streams. For example, sodium fluoride (NaF) beds are used to sorb hydrogen fluoride (HF) while allowing fluorine (F_2) to pass. Adsorption occurs at low temperature (25°C–40°C) to produce sodium bifluoride (NaF·HF), and the bed can be regenerated by heating (~150°C) to decompose the bifluoride into its constituent parts.[9] Little information on analogous separations for HCl was found in the literature. Reported spectroscopic data indicate cesium halides such as CsCl may bond with HCl.[10] By extension, CsF and NaF may also be useful sorbents. Another potential sorbent is bismuth oxyfluoride (BiOF). In separating HF from UF_6, it is reportedly a better sorbent than NaF. At 22°C the BiOF sorbs HF, while UF_6 is not adsorbed at all.[9,11] Data are not available on the sorption of HCl on BiOF.

  Assessment: Sorbents that function via hydrogen bonding are very selective and can have high loading capacity. Use of a sorbent such as BiOF represents a new and speculative approach to remove HCl from a chlorine bearing gas stream. It is recommended that scoping tests be performed to ascertain whether HCl is chemisorbed by BiOF (or other agents such as NaF and CsF) and adsorption isotherms obtained as appropriate.

  A sorbent composed of Y zeolite and activated alumina has been developed for removing HCl from hydrogen streams produced during catalytic reformation of petroleum products.[12] Reportedly the mixture is more effective than either of the two sorbents used independently, loading to a capacity of around 7 wt% at gas-phase HCl concentrations as low as 5 ppm at 25°C. The alumino silicate–based zeolite physisorbs the HCl, and the activated alumina scavenges it by a chemisorption process. The chemisorption occurs by two paths, one in which the HCl forms both an Al–Cl bond and an Al–OH bond and one in which an Al–Cl bond is formed along with the release of water.[13] There was no mention of the rejection of Cl_2 in the reference, but our thermochemical calculations (using HSC Chemistry version 9)[8] indicate that alumina and silica are unreactive with Cl_2 when water or hydroxyl groups are completely absent.

  Assessment: The evidence suggests that sorption of TCl will result in the release of the tritium as tritiated water. Removal of water from a chlorine bearing stream requires drying operations similar to those required for the aqueous scrubbing option. Consequently, evaluation of this sorbent is of low priority and may be reconsidered in the future.

  Two alumina-based commercial sorbents (specific composition not identified) have been shown to remove HCl from an inert N_2 carrier gas. The sorbents were loaded to capacities of up to 10 wt%, with loadings of 7 wt% to 17 wt% at breakthrough HCl concentrations of 1 ppmv.[13] This type of metric is dependent on the dimensions of the sorbent bed, gas flow rate, and gas concentrations. The experimental work did not include Cl_2 in the gas mixture[13]; thus, the data do not address the potential for either rejection or co-adsorption of Cl_2.

  Assessment: This sorbent is of low priority for the same reasons as the preceding sorbent.

- *Physisorption*—Activated carbon and zeolites are used to sorb a variety of halide-bearing compounds from gas streams. Activated carbon does not show selectivity between Cl_2 and HCl. Zeolites have a greater affinity for polar molecules than does activated carbon. Limited data are available in the literature on the HCl sorption capacity of type 5A and type 13X molecular sieves[14] (see Figure 1). These data illustrate good sorption capacity at high concentrations of HCl. Data on the capacity at lower concentrations (lower partial pressures) are needed to ascertain if these zeolites are practical for removing HCl (TCl) from zirconium recycle off-gas.

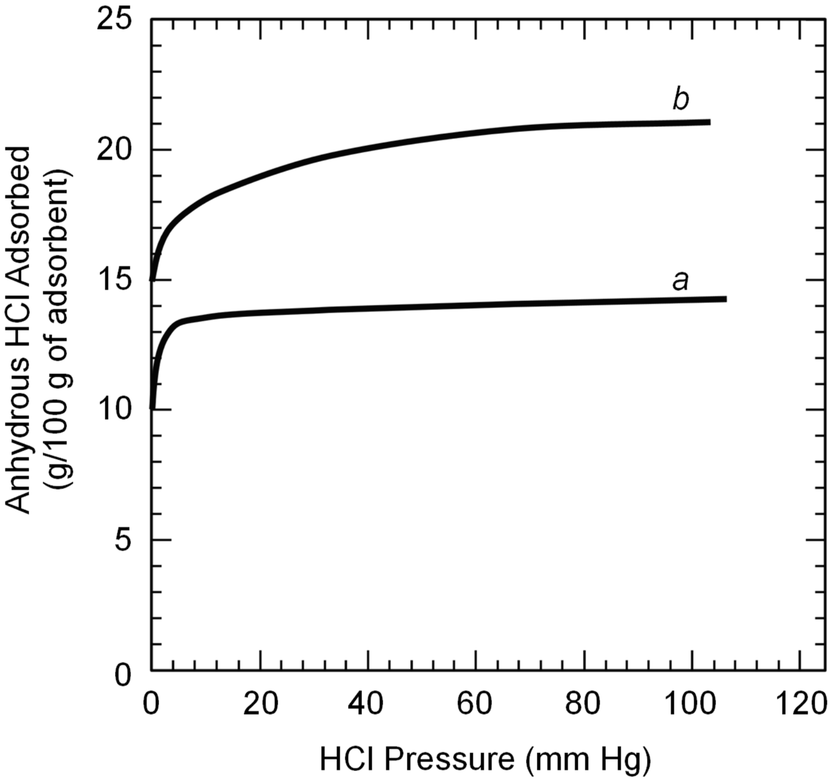

Figure 1. Adsorption capacity of molecular sieves (a) type 5A and (b) type 13X to trap HCl as a function of the partial pressure of gaseous HCl at 25°C (adapted from reference 14).

A separation process to purify a chlorine gas stream by using 5A molecular sieves to selectively remove HCl has been patented.[15] The separation was developed to avoid water scrubbing to remove HCl from a gas stream while permitting purified Cl_2 to be recycled to a hydrocarbon chlorination process. The process had the advantage that the anhydrous gas stream to be treated would remain dry throughout the plant system. Details are found in the reference for preparation of the molecular sieve, including converting the sodium alumino-silicate to the magnesium form. Hydrogen chloride was reported to be selectively adsorbed from a mixture of HCl and Cl_2 gases. Adsorption of the HCl was best at temperatures of 24°C to 65°C, with a noticeable heat of sorption. Desorption to regenerate the sorbent used an inert gas to purge the bed as it was heated at temperatures between 425°C and 540°C. Freshly prepared zeolite adsorbed up to 14 wt% HCl, but the amount adsorbed decreased to a nearly constant 3.5 wt% on subsequent loading-desorption cycles. This particular process appears to be the most proven method that would be applicable to removing HCl and TCl from Ar-Cl_2 gas mixtures encountered in the zirconium recycle process.

Detailed sorption isotherms of HCl loading as a function of its gas-phase partial pressure were not found in the literature. The partial pressure of HCl in the zirconium recycle process off-gas, arising from all isotopes of hydrogen associated with the cladding, will be less than 4 mm Hg, a value below which the curves of Figure 1 do not provide adequate resolution of the sorption capacity. Data on the capacity at lower concentrations (lower partial pressures) are needed for confident design of systems for removing HCl (TCl) from zirconium recycle off-gas.

Assessment: The 5A molecular sieve has been shown to be selective for removing HCl from gas streams containing Cl_2. The sorption capacity is high when the partial pressure of HCl is over around 4 mm Hg. It is recommended that sorption isotherms be obtained at HCl partial pressures below 4 mm Hg to extend the existing data and permit design of an absorber appropriate for treating the zirconium recycle off-gas.

1.4 Cladding Pretreatment Approach

Another approach is to avoid introducing tritium into the zirconium recycle process. Such an approach requires a pretreatment step to remove the tritium before reactive gases are used to volatilize the zirconium.

Experiments have been performed to measure the amount of tritium trapped in Zircaloy cladding, including cladding that was previously processed through the voloxidation process at temperatures around 500°C.[16,17] Heating the cladding to temperatures up to 700°C released the tritium to a flowing, dry, inert gas stream. Tritium deposited within the metal matrix of the cladding diffuses to the surface where it is swept away by the gas stream. The process is slow, requiring around 48 h or longer to release 99+% of the tritium at 700°C. The released hydrogen and tritium may be converted to water by the addition of oxygen and use of a catalyst (e.g., CuO). The tritiated water may then be removed from the gas phase with molecular sieves (e.g., type 3A molecular sieve). Using this approach, there are several design issues that must be addressed.

Equipment Size—In tests with Zircaloy cladding in laboratory equipment, chlorination rates have been reported to range from 10% to 40% per hour.[18] More rapid chlorination rates could likely have been achieved if the reactor had been equipped with a means to remove the heat produced by the exothermic reaction.[18] The chlorination rate has also been reported as 30%/h.[19] Chlorination (reaction) times of 3–8 h may be expected. In comparison, a pretreatment step (as above) to remove tritium will require 48 h at an operating temperature of 700°C. Based on reaction times alone, the pretreatment vessel will require 6–12 times the volume of the chlorination reactor if the Zircaloy throughput is to remain unchanged. Because the pretreatment step requires higher temperatures than chlorination, additional time will be required for heat-up, and both the process vessel and cladding charge will have to be cooled following treatment. Both the pretreatment and chlorination could be completed in the same reactor (vessel) by piping the proper gases to and from the system at the proper times. Nonetheless, the reactor volume will need to be much larger than one used only for chlorination. Because it must reside in shielded facilities, the effect on cost of shielded space must also be considered.

Tritium Capture Efficiency—Oxygen must be added to the pretreatment exhaust stream to convert the released hydrogen and tritium to water. To improve the decontamination factor (DF) using molecular sieves to capture the tritiated water, the addition of water vapor may be required. Recycle of the inert carrier gas is not recommended because any residual oxygen or water will react with the Zircaloy, leading to losses of zirconium as oxide wastes. Although the inert gas could be conditioned for recycle, the cost of doing so very likely far exceeds the value of the gas.

Reactant Gas Control—As already mentioned, process gases should be free from oxygen and water vapor, to the extent possible, to avoid further oxidation of the cladding. The effect of oxidation is to increase the Zircaloy's resistance to chlorination.[20] Use of the same reaction vessel to implement both pretreatment and chlorination will require purging the gases in the system following chlorination to achieve an inert gas environment. Chlorine and other reactive gases should be neutralized before the purge gas can be vented to the stack.

Assessment—Pretreatment of the cladding at elevated temperature to remove the tritium from the cladding prior to chlorination is attractive because there are fewer unknowns in the design of the off-gas treatment system. Studies should be conducted to obtain better data on the release rate of tritium/hydrogen as a function of temperature.

2. SELECTION AND DESIGN OF PROCESS

2.1 Selection of Process to Remove Tritium from Zirconium Recycle

Three dry methods for separating removing tritium from the zirconium recycle process were identified for further consideration and experimental verification. Two methods involve removal of HCl (TCl) from Cl_2-Ar bearing off-gases arising from the chlorination process and one method involves pretreatment of the cladding to remove HCl (TCl) before the chlorination step.

1. *Chemisorption*—Chemisorption of HCl (TCl) on a halide-bearing salt could be attractive because such salts are unreactive to Cl_2. Compounds such as NaF, BiOF, and CsCl are known to participate in hydrogen bonding, the first two having been used in separation of HF from other reactive gases. The BiOF contains two atoms (oxygen and fluorine) that are known to produce hydrogen bonds. Because there are no data on the effectiveness of these compounds to sorb HCl, the chemisorption approach is the most uncertain of the three approaches. Because small amounts of hydrogen and tritium are trapped in the cladding, the low concentrations of HCl and TCl arising from chlorination of the cladding could lead to very low sorbent loadings or poor tritium DFs. Adding more HCl as a diluent could improve the overall tritium DF (see additional related remarks in physisorption section below). Nonetheless, the trapping system is expected to be small relative to the size of the chlorination process. Specific proof-of-principle experiments are recommended to ascertain whether this method represents a potentially viable and new approach for the subject separation. Regeneration and reusability should also be evaluated.

   Alumina-based sorbents have a strong affinity for HCl and can reduce the concentration of HCl in an inert gas stream to very low concentrations (e.g., < 1 ppm). Rejection of Cl_2 is not explicitly quantified, but thermochemistry calculations indicate that such sorbents are not reactive with Cl_2 when the alumina is sufficiently dried and water is not present in the gas stream. Regeneration temperatures and reusability of the sorbent are considerations deserving evaluation in the future. Currently it is of lower priority.

2. *Physisorption on Molecular Sieves*—Type 5A and type 13X molecular sieves are known to adsorb HCl up to loadings of 14% and 21% by weight, respectively, at HCl partial pressures around 100 mm Hg. Use of 5A molecular sieves has been proven to selectively remove HCl from Cl_2-bearing streams.[15] It has been estimated that the HCl concentration (including all isotopes of hydrogen) in zirconium recycle off-gas will be about 4 ppmv (parts per million by volume) without recycle of the processing gas.[2] This is equivalent to an HCl partial pressure of about 0.003 mm Hg for a process operating near atmospheric pressure, far below the values shown in Figure 1. The volume fraction of HCl in the off-gas can be increased by recycle of the chlorination gas and by adding HCl. This will have the tendency to improve TCl recovery while reducing the TCl concentration in the product. The potential for HCl in the recycled gas to react with cladding to release hydrogen, or tritium, is mitigated by the large excess of Cl_2 that should react with H_2 (or HT) in the chlorination process. A process could be engineered to use one of these molecular sieves, but additional data on the sorption capacity at low partial pressures of HCl are needed. Designs will need to consider the amounts of

tritium-contaminated HCl to be handled and disposed of and the deterioration rate of the molecular sieves (e.g., reusability and replacement frequency). Again, the trapping system is expected to be small in relation to the size of the chlorination process.

3. *Pretreatment*—Treatment at high temperature in an inert atmosphere to release hydrogen and tritium from the cladding has been demonstrated. Oxidation of hydrogen and tritium over a heated CuO catalyst is a known effective means to obtain tritiated water, which can be captured by type 3A molecular sieves. DFs can be increased by the addition of water vapor. As described in Section 1.4, the long residence time in pretreatment requires a system 6–12 times larger in volume than the chlorination process. There is the potential that pretreatment and chlorination may be performed in the same vessel, although different gases and operating temperatures will be used for each phase of processing. The advantage of this approach is that there are fewer unknowns in design of the off-gas treatment system. An important unknown is how high temperature treatment in an inert gas affects the release of tritium from the cladding—does it hinder the release or improve the release.

2.2 Pre-Conceptual Design of Systems for Tritium Removal

The preceding assessments identify three potential processes to abate tritium release from the zirconium recycle process. Simplified implementation diagrams showing how the tritium removal process interfaces with the zirconium recycle process, along with identification of gaseous species and first order estimates of gas compositions, can help in identifying issues that could reduce the effectiveness of the tritium removal process. If solutions to these impediments exist, then there is no show stopper for the tritium removal process. For example, low concentrations of volatile salts could neutralize a sorbent; combinations of temperature reduction and filtration could ameliorate this problem.

Two concepts for implementation are presented in this section. The two solid sorbents represented by chemisorption reagents and molecular sieves would be implemented in much the same fashion, although details such as bed height and diameter might differ. Thus, one concept for use of the solid sorbents is presented. A second concept for the very different pretreatment process is also presented.

2.2.1 Solid Sorbents for HCl and TCl

The concept for implementing a process to remove TCl from the zirconium recycle process off-gas using molecular sieves is shown in Figure 2. The use of chemisorbents may be implemented by a similar process; essentially the molecular sieve bed is replaced with a chemisorbent bed (e.g., pellets of BiOF or activated alumina). In the figure, the zirconium recovery process is shown as a chlorination reactor and a condenser to collect the crude $ZrCl_4$ product. The crude product may be subject to further purifications not shown here. The off-gas from the condenser will consist primarily of the inert carrier gas (e.g., argon), residual chlorine, and very low concentrations of metal chlorides, HCl, and TCl. The metal chlorides (noted as MCl_4 for convenience) are present in the off-gas because there is a finite vapor pressure of these compounds at condenser temperatures around 50°C–100°C. Combined concentrations of HCl and TCl are estimated to be 5 ppm for systems wherein the process gas is used in once-through mode. An optional bypass line could be used to allow the HCl and TCl to accumulate in a recirculating loop before treating the off-gas to remove these acid gases. The off-gas treatment system consists of an off-gas temperature adjustment step to obtain conditions close to optimal for removal of HCl and TCl with the 5A molecular sieve. This should result in additional condensation of small amounts of metal chlorides, so a filter is used upstream of the molecular sieve. The molecular sieve bed selectively removes the HCl and TCl, allowing the inert carrier gas and chlorine to be recycled to the zirconium volatility reactor. In practice, a second molecular sieve bed could be used so that one bed is in off-gas treatment mode while the other is in regeneration mode. Regeneration consists of heating the bed to high temperatures while a very small flow of inert carrier gas moves through the bed. Aqueous scrubbing may be used to strip the HCl and TCl from the regeneration carrier gas, and the aqueous phase can be neutralized and converted to a waste form. As previously discussed, information on the HCl loading of the molecular sieve as a function of concentration in the gas phase and operating temperature of the sorbent bed are gaps that need to be filled. Because sorption on molecular sieves may be reversed by increasing temperature, data are required on the thermal regeneration of the sorbent. Unknowns include fraction of adsorbate removed and reduction in sorbent capacity following each regeneration cycle. Similar data gaps exist in the understanding of the chemisorption reagent.

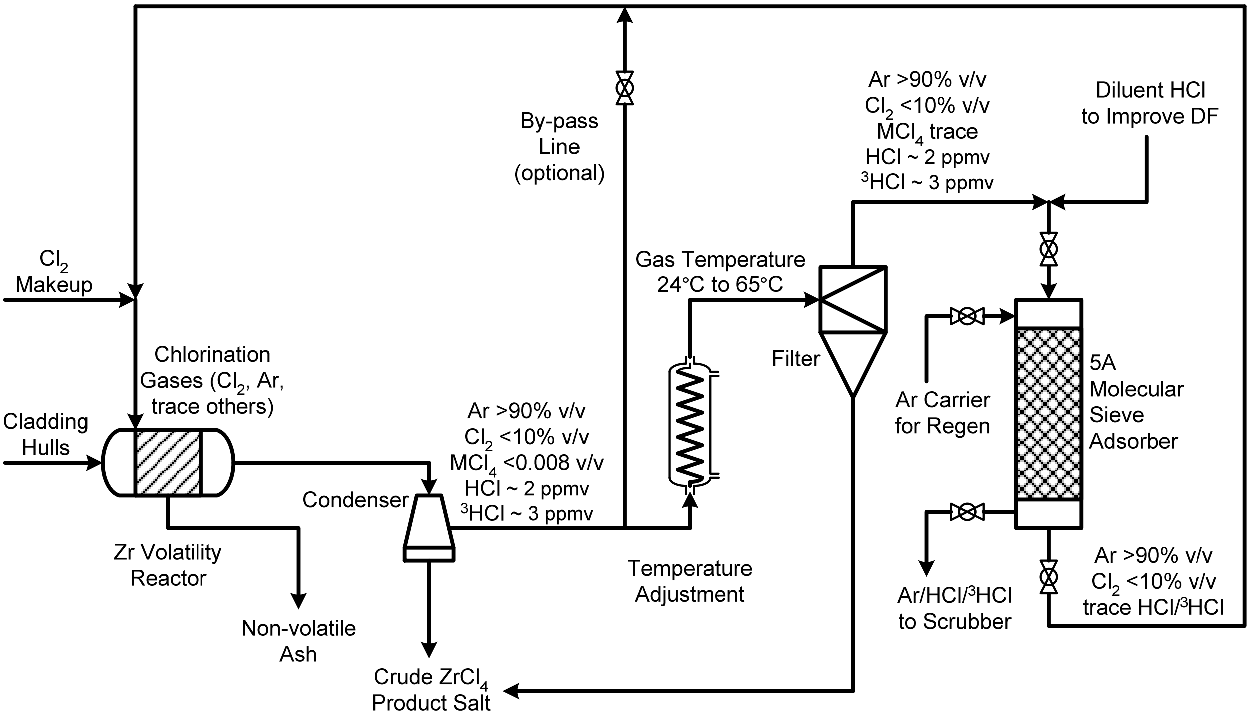

Figure 2. Flowsheet illustrating concept of tritium removal from zirconium recycle process off-gas using solid sorbents.

2.2.2 Pretreatment to Remove Tritium before Chlorination

A concept for pretreatment of the cladding to remove tritium before the chlorination step is illustrated in Figure 3. As discussed in Section 1.4, heating the cladding to 700°C under an inert gas (e.g., argon) removes the hydrogen isotopes without oxidizing the cladding. Based on previous studies to determine the temperatures at which tritium was released from the cladding, the removal rate is relatively slow, requiring about 48 h to remove 99+% of the tritium. A low flow of inert gas sweeps the released hydrogen and tritium away from the cladding and into a treatment system. Catalytic oxidation of the released tritium and hydrogen requires oxygen be added to the gas to produce water. The water can then be removed from the inert gas stream with 3A molecular sieve to very low concentrations. Because the amount of hydrogen, of all isotopes, arising from the cladding is very small, diluent water may need to be added to improve the DF for tritium. Recycle of the carrier gas is not recommended because excess oxygen and/or water vapor will travel back to the reactor and oxidize the surface of the cladding, which will lengthen the induction period for the subsequent chlorination of the cladding. In addition, the volumetric flow rate of the inert gas during pretreatment can be very low, so releasing the stream to the stack avoids complications that recycle would cause. Unknowns in the process include the effects of exposure of the cladding to inert gases at high temperature. For example, could a physical change in the cladding hinder the chlorination process. Do changes, if any, depend on the type of inert gas used (e.g., argon versus helium). Additional data on the rate of tritium removal from the cladding are needed to design a process implementation of the proper size and holding time.

After the tritium removal step, chlorination of the cladding can be completed in the same reactor. Hardware are shown to enable gas recycle in this mode to avoid production of large amounts of chloride wastes. The pretreated cladding would be cooled to about 400°C and chlorine introduced to the inert gas in the recycle circuit. The portions of the circuit used to collect tritium would be bypassed. Salt product would be collected in the condenser and routed to further purification steps as required. The inert gas, excess chlorine, and any residual volatile chloride salt would be recycled to the chlorination reactor. At the end of the chlorination step, no radiological gases should be present, but an off-gas treatment to remove chlorine from the circuit will be required before another batch of cladding is introduced and the tritium removal step begins. Design needs to consider that metal chlorides in the system, including the chloride corrosion product film on the internal surfaces of the equipment, are hygroscopic and very corrosive in the presence of moisture. Effects of chlorine residues in the circuit that may revolatilize and reach the molecular sieve represents a future research area if the dual use reactor is considered as a means to reduce equipment and costs. An inert atmosphere processing cell to house the equipment is an option to mitigate corrosion. Another option is to use a separate reactor for the chlorination step. Both considerations are beyond the scope of the present experimental plan.

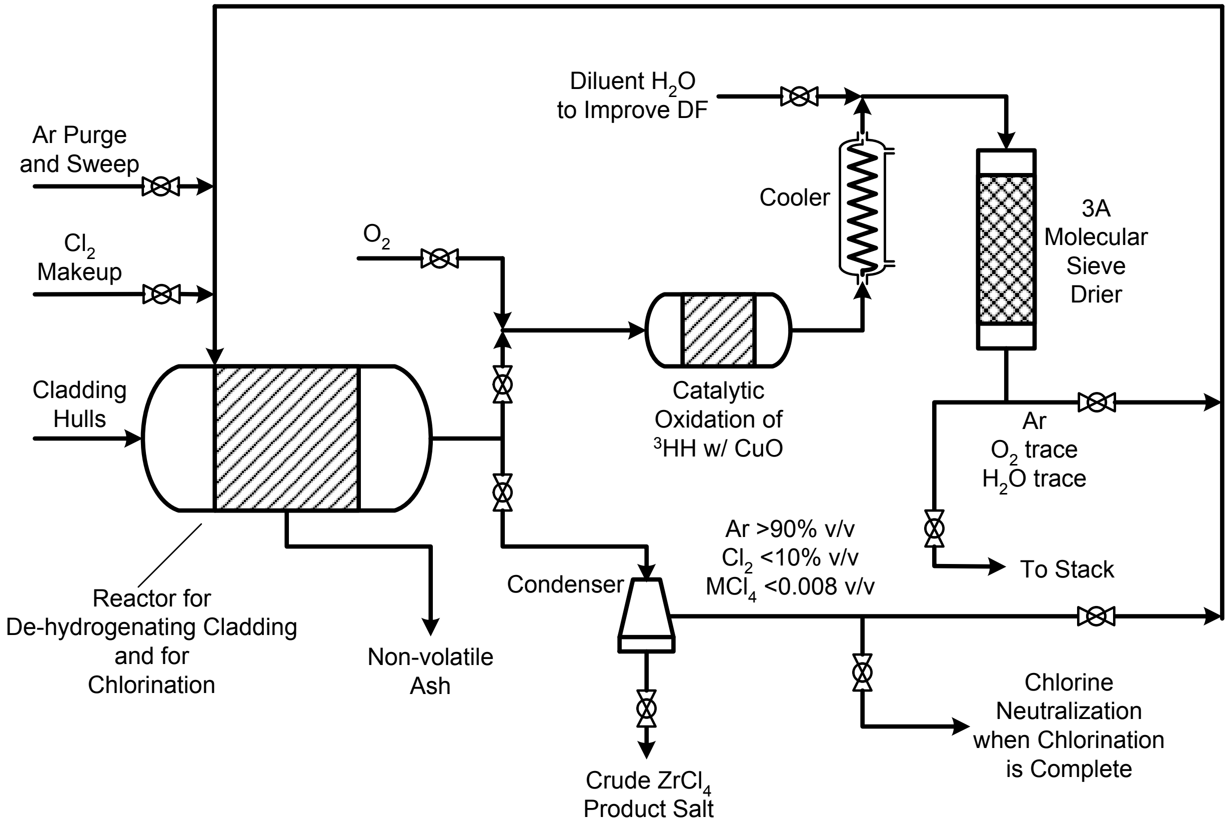

Figure 3. Pretreatment process to remove tritium and chlorinate cladding can be done sequentially in one vessel.

3. TEST PLAN FOR CONDUCT OF LABORATORY EXPERIMENTS

3.1 Sorption on Molecular Sieve and Chemisorbent

The tritium removal system that meets the requirements of the milestone is selective sorption on a solid sorbent. Use of 5A molecular sieves has been proven to selectively remove HCl from Cl_2-bearing streams. Experiments to determine its sorption capacity as a function of HCl partial pressure, particularly at partial pressures less than about 10 mm Hg, are needed. It should be noted that the same testing protocols and equipment may be used to test one of the chemisorption reagents (e.g., BiOF).

3.1.1 Methodologies

The primary data required to effectively use the 5A molecular sieve for removal of TCl from the zirconium recycle off-gas stream is the capacity of the sorbent as a function of ^{all}HCl partial pressure. A gasometric technique has been used for corrosive gases (e.g., HF), and it relies heavily on calibrated vessel volumes, temperature measurement, and pressure measurement.[21] At the low partial pressures of HCl in equilibrium with the sorbent, anticipated for the present system, pressure measurements may not be sufficiently accurate. The higher pressures measured in the vessels either before adsorption or after desorption could be used to infer quantities of HCl adsorbed, and precise temperature measurement and control will be required. Simpler method might weighing a sorption cell charged with sorbent and/or desorbing the HCl from a sample into an aqueous solution and titrating the solution for acid content.

Another measurement technique involves the rate of pressure reduction in a closed system as the sorbent removes the sorbate from the gas phase.[22] This is accomplished with vessels of calibrated volume with, for example, the sorbent in a small vessel and the gas in a larger vessel, the two being connected with a pipeline and valve to allow isolating the two vessels. The technique is based on the principle that the capacity of the sorbent is inversely proportional to the time required to sorb a gas to a low pressure (e.g., 10^{-2} mm Hg). This seems to be a rapid and simple technique to implement, but as a relative method it requires a known standard molecular sieve to which the sorption time can be compared. In the present case, no highly characterized standard is available. Pressure measurements to low values are required. Once one sorbent is characterized, this could be a useful technique for obtaining data on other sorbents.

A common method recently used by researchers for measuring sorption capacity is thermogravimetric analysis (TGA).[23,24,25] Flowing gas mixtures of various compositions can be prepared using highly accurate mass flow controllers, as illustrated in Figure 4. The volume fraction (readily related to partial pressure) of the sorbate gas and the weight gained by the sorbent at equilibrium provide a data pair. Additional data pairs can be obtained by increasing the flow of the sorbate gas and allowing the weight gained by the sorbent to reequilibrate at a higher partial pressure. In a flow-through system, as illustrated in Figure 4, keeping ambient moisture-containing air from back-flowing into the system and maintaining the temperature of the gas phase and sorbent will be important. In a variation of this technique, one manufacturer recommends a test procedure using an adsorption bulb (or cell) filled with sorbent and fitted with isolators (potentially valves) at either end, which is periodically removed from the gas circuit and weighed.[26] When further weight gain by the bulb no longer occurs, the sorbent is equilibrated with the gas stream. Accurate measurements of small weight gains are readily achievable. Desorption takes place at higher temperatures, 425°C to 540°C. TGA equipment of the type illustrated in Figure 4 will not be suitable for the desorption process. Regeneration of sorbent contained in sample cells can be done in a separate furnace, and the entire cell weighed before and after a regeneration cycle. Regenerated sorbent will be reloaded to ascertain the effect of regeneration on the capacity and equilibrium isotherm.

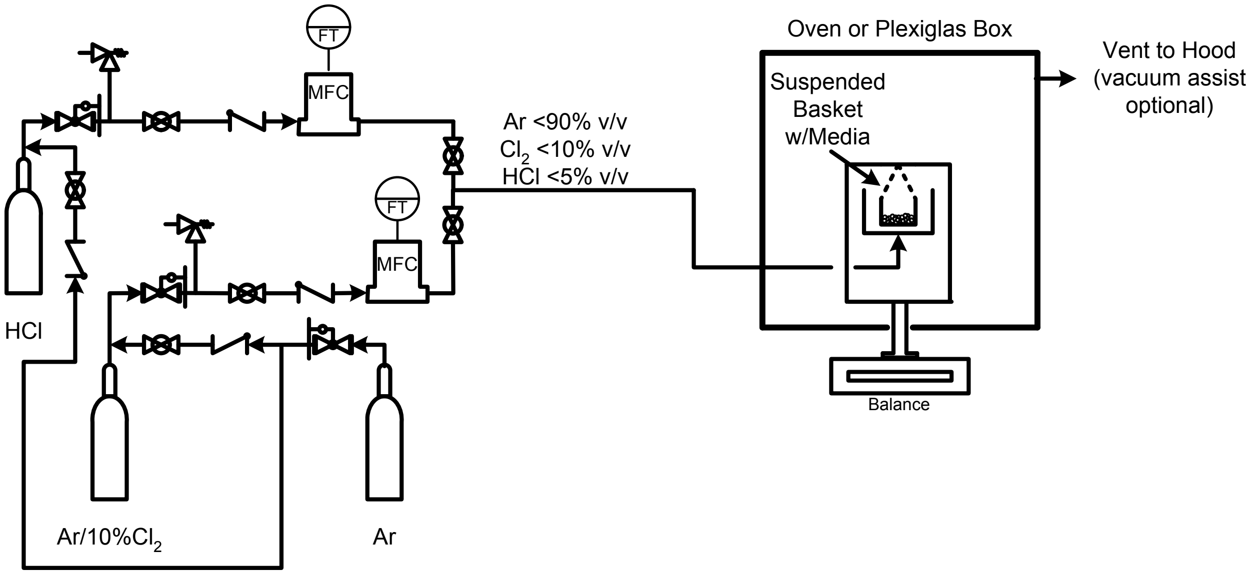

Figure 4. A thermogravimetric analysis technique for measuring sorption capacity.

3.1.2 Proposed Tests of Molecular Sieve

The equilibrium weight gain of 5A molecular sieve caused by sorption of HCl should be measured at several partial pressures of HCl in both an inert gas and in an inert gas containing Cl_2. An appropriate range of HCl concentrations is 5 ppmv to 500 ppmv. Concentrations of about 5, 10, 20, 50, 100, 200, and 500 ppmv should be selected. With appropriate selection of mass flow controllers, two or three gas mixtures of HCl will be sufficient. Certified mixtures of 5 ppm to 10% HCl in N_2 are available commercially,[27] and one vendor offers mixtures with a selection of balance gas other than N_2.[28] Because the carrier gas could have an effect, it is recommended that the carrier gas be the same as specified in the zirconium chlorination step (specifically argon).

The amount of HCl adsorbed also is expected to be dependent on the temperature, so measurements at a minimum of two temperatures should be made. Construction of isotherms at the two temperatures will provide information on how strongly temperature affects the adsorption of HCl from inert argon gas. Repeating the measurement for one temperature and with about 10% Cl_2 in the feed gas will provide information on the effect, if any, by Cl_2. A summary of proposed tests is shown in Table 1.

Table 1. Summary of minimum conditions at which weight gain of the 5A molecular sieve will be measured (use same matrix for BiOF or other chemisorbent)

Temperature (°C)	Balance Gas	HCl Range (ppmv)[a]
25	Ar	5–500
50	Ar	5–500
74	Ar	5–500
25	$Ar\text{-}10\%Cl_2$	5–500
75	$Ar\text{-}10\%Cl_2$	5–500

[a] Selected nominal values: 5, 10, 20, 50, 100, 200, and 500 ppmv

Regeneration tests should be conducted with 5A molecular sieve loaded with HCl. In an initial scoping test of desorption, the most highly loaded sample (presently assumed to be the sample loaded at 25°C and gas composition of 500 ppmv HCl in argon) should be purged with the inert gas while being heated to 550°C in 50°C increments. At each new temperature the measured weight of the sample should decrease to a new value (or the weight-time curve should flatten considerably). The data will provide a guide for whether there is value in heating above a certain temperature (e.g., would 300°C be adequate?).

Consideration must also be given to damage to the sorbent when temperature is increased. Samples from the same batch should be heated to a specific temperature and held for 30 min to inflict thermal damage to the sorbent. Separate samples should be tested at each of the following temperatures: 250°C, 275°C, 300°C, 325°C, 350°C, 400°C, 450°C, 500°C and 550°C. After cooling, each sample will be loaded at the highest HCl concentration (500 ppmv) and the saturation weight gain measured. Results will indicate maximum temperatures at which regeneration should occur.

For every loading test condition shown in Table 1, the final loaded sample will be regenerated at the recommended temperature. A repeat of the sorption test will be run on the regenerated sample, and the sorption isotherm compared to the original. A second regeneration and sorption test will be run to ascertain if further changes in the adsorption isotherm occurs.

Data for one isotherm would be useful for ascertaining if chemisorption is competitive, or not, with physisorption on molecular sieves.

3.1.3 Proposed Tests of Chemisorbent

It is proposed that BiOF be tested as a chemisorbent for HCl. To use it as a sorbent media, the compound needs to be manufactured into structurally sound pellets. Techniques used to prepare NaF pellets are well known, and these will be used to prepare BiOF pellets. If pellets can be successfully manufactured, a test matrix similar to that used for the molecular sieve will be followed, albeit with different upper temperature ranges to be determined during structural testing of the pellets. If the pellets cannot be successfully fabricated, tests with BiOF end. As a fallback, the sorption tests will be performed with NaF pellets to obtain data to compare with the performance of the molecular sieve.

3.2 Pretreatment

Gaps in the information required to design an effective pretreatment process fall into two broad areas. First, the effect of prolonged high temperature exposure of the cladding to an inert gas (e.g., Ar, He) on the subsequent chlorination process is unknown. Second, there is insufficient data on the rate of tritium release from the cladding as a function of temperature, and none at temperatures above 700°C. The pretreatment process appears to be highly dependent on temperature. Temperatures above 700°C could significantly reduce the processing time, which could reduce the size of the processing equipment. Temperatures should be limited to about 850°C, because of safety concerns. [Failure modes of the process implementation will, at some point, be considered. One potential failure mode could involve a vessel breach or valve failure, permitting cell air to enter the process. At temperatures of 900°C, or more, Zircaloy burns in air and the reaction is highly exothermic. Keeping temperatures below an ignition point is one potential precaution to address safety concerns. Further analysis is beyond the scope of this report.]

3.2.1 Experimentally Determine Effect of Pretreatment on Chlorination Process

Tests to determine the effect of pretreatment on chlorination of cladding may be performed with unirradiated Zircaloy cladding material. Normally there is an oxide layer on the external surfaces of irradiated cladding, deposited while the fuel was in the power reactor and while the fuel was in post-irradiation storage (both wet and dry storage). The recommended tests will be performed with unused cladding to avoid the cost of working with radioactive materials and to ascertain the effect of pretreatment alone. Tests include treating the cladding at temperatures ranging from 700°C to 850°C for time intervals ranging from 24 h to 72 h in both argon and helium gases. A treatment matrix is summarized in Table 2.

It is recommended that the treatments of long duration be done first because if no significant effect on chlorination is measured, there would be no need for the shorter duration tests.

Table 2. Matrix of pretreatment conditions to prepare cladding for chlorination tests.

Temperature (°C)	Gas	Time Range (h)[a]
700	Ar	24–72
800	Ar	24–72
850	Ar	24–72
700	He	24–72
800	He	24–72
850	He	24–72

[a] Selected nominal values: 24, 48, and 72 h.

Cladding samples will be of uniform composition (e.g., all Zircaloy-4 or other selected alloy) and cut to uniform lengths and weighed). After samples of cladding have been treated at the specified conditions, each sample will be subjected to controlled chlorination. Chlorination conditions for each sample will be the same and the time for complete chlorination will be measured. Specific chlorination conditions are a temperature of 400°C, chlorination gas composition of 50%Ar—50%Cl_2, and a total gas flowrate appropriate to the selected size of the Zircaloy sample (to be determined).

3.2.2 Experimentally Determine Effect of Temperature on Tritium Release

The release of tritium from the cladding is primarily influenced by the temperature. The inert gas used as a carrier should have no measurable effect on the tritium release rate. Determination of tritium in the cladding and release of tritium as a function of time at three different temperatures should be measured. Residual tritium remaining in the cladding at the end of the test can be removed by oxidizing the cladding at 1200°C. Capture and measurement of the tritium may be completed using techniques previously reported.[17] Tests should be completed on cladding from two different fuel burnups, preferably with the cladding being of the same type (e.g., Zircaloy-2 or Zircaloy-4). It is also preferable that the fuel be removed from the cladding by a low temperature operation, such as leaching in nitric acid at around 100°C. Cladding subjected to high temperature processing, such as voloxidation, could bias the results.

Table 3. Matrix of pretreatment conditions to measure tritium release from irradiated cladding.[a]

Temperature (°C)	Gas	Time Range (h)[a]
700	Ar	8–72
800	Ar	8–72
850	Ar	8–72

[a] After the final timed sample is taken, the cladding should be oxidized at 1200°C to remove any remaining tritium for measurement.

[b] Selected nominal values: 8, 24, 48, and 72 h.

4. CONCLUSIONS

Nine distinct dry processes were identified as potentially viable for capturing tritium from the zirconium recovery/recycle process off-gas. These were down-selected to three process technologies for further study and evaluation. Two technologies involve removing TCl (and HCl) from the off-gases of the chloride volatility step; physisorption using 5A molecular sieve and chemisorption using either BiOF or NaF. A third technology avoids the introduction of tritium into the chloride volatility step. It uses high-temperature pretreatment of the cladding in an inert gas to release hydrogen and subsequently converted it to water and recover the water with 3A molecular sieves.

Tests are suggested to evaluate each of the three promising technologies. A thermogravimetric analysis (TGA) technique is suggested to obtain the equilibrium mass of HCl adsorbed on 5A molecular sieve at various gas-phase HCl concentrations. The same testing protocols and equipment may be used to test one of the chemisorption reagents. It is suggested that bismuth oxyfluoride (BiOF) be evaluated, with NaF as a backup in the event that BiOF pellets do not have appropriate mechanical properties (e.g., should be able to support themselves in a packed bed without crushing).

Pretreatment of the cladding to remove tritium depends primarily on temperature as the rate determining variable. Measurement of the removal rate at a up to three different temperatures are recommended. Tests are also recommended to determine if high temperature treatment with inert gas affects the subsequent chlorination step.

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