



## ORAU TEAM Dose Reconstruction Project for NIOSH

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### Locations of Stable Metal Tritide Use at the Savannah River Site

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## ACRONYMS AND ABBREVIATIONS

|             |  |
|-------------|--|
| CFR         | Code of Federal Regulations  |
| Ci          | curie  |
| cm          | centimeter   |
| DOE         | U.S. Department of Energy  |
| dpm         | disintegrations per minute   |
| g           | gram   |
| GI          | gastrointestinal   |
| HSV         | hydride storage vessel   |
| HT          | elemental tritium (tritiated gas)  |
| HTO         | tritiated water vapor  |
| HTV         | hydrogen transport vessel  |
| in.         | inch   |
| kBq         | kilobecquerel  |
| keV         | kiloelectron-volt (1,000 electron-volts)                                       |
| kg          | kilogram   |
| L           | liter  |
| LANA        | lanthanum-nickel-aluminum alloy (LaNi <sub>4.25</sub> Al <sub>0.75</sub> only) |
| LSC         | liquid scintillation counting  |
| LWR         | light-water reactor  |
| mol         | mole   |
| MPa         | megapascal   |
| MPD         | multistage palladium diffuser  |
| NIOSH       | National Institute for Occupational Safety and Health                          |
| ORAU        | Oak Ridge Associated Universities  |
| ppm         | parts per million  |
| psia        | pounds per square inch absolute  |
| PUREX       | plutonium-uranium extraction   |
| PWR         | pressurized-water reactor  |
| RSI         | Resource Services Incorporated   |
| R&D         | research and development   |
| SAF         | self-absorption factor   |
| SMT         | stable metal tritide   |
| SRDB Ref ID | Site Research Database Reference Identification (number)                       |
| SRL         | Savannah River Laboratory  |
| SRNL        | Savannah River National Laboratory   |
| SRP         | Savannah River Plant   |
| SRS         | Savannah River Site  |

|        |   |
|--------|---|
| SRTC   | Savannah River Technology Center        |
| STC    | special tritium compound                |
| SUF    | serum ultrafiltrate                     |
| TCAP   | thermal cycling absorption process      |
| TPBAR  | tritium-producing burnable absorber rod |
| TVA    | Tennessee Valley Authority              |
| U.S.C. | United States Code                      |
| UREX   | uranium extraction                      |
| wt%    | weight percent                          |
| μCi    | microcurie                              |
| μm     | micrometer                              |
| °C     | degrees Celsius                         |

## 1.0 SUMMARY

**NOTE: Because of the sensitive nature of some of the processes at the U.S. Department of Energy (DOE) Savannah River Site (SRS), this report does not provide a comprehensive list of metal tritides SRS has used. Rather, this report provides a representation of the types and uses of metal tritides that might have been encountered at the site. Evaluation of other metal hydrides is conducted in a set of classified notes associated with this document.**

Various metal tritides are encountered at SRS Tritium Facilities. In the early 1980s, the Savannah River Laboratory began a major program to develop and use metal hydrides in its tritium production facilities. Metal hydrides turned out to be ideally suited for tritium handling and processing. These metals include uranium, palladium, titanium, lanthanum-aluminum-nickel tritide, mischmetal, and zirconium. Evaluations of the physical and chemical properties of these compounds have shown that uranium and palladium do not bind tritium in a manner significantly different from tritium oxide. Therefore, they are not considered as special tritium compounds (STCs). The remaining metals form compounds that cannot be adequately assessed using the tritium oxide urine bioassay model and are therefore classified as STCs.

## 2.0 INTRODUCTION

At SRS, several metals have been used as a means of separating and storing tritium. These metals include uranium, palladium, titanium, lanthanum-aluminum-nickel tritide, lithium tritide, tritiated mercury, mischmetal, and zirconium. Tritium can form metal tritides with the relative ease of tritium exchange. Metal tritides have been used and researched at SRS, other DOE sites, and commercial sites for many years.

These compounds can be created by intentional combination of tritium with the desired materials or by inadvertent contamination of a material that has been subjected to the presence of tritium over time. Metal tritides are essentially tritium in a particulate form, which can present dose reconstruction problems that are distinctly different from those of the more commonly encountered tritiated water vapor (HTO).

The primary objective of this document is to provide information on the potential sources of stable tritium compounds at SRS. The source documents that were reviewed for this report consist of those in the Site Research Database (SRDB) as well as documents available in the open literature. This document reports information about tritium compounds that has been found by the document review process to date only.

### 2.1 GENERAL PROPERTIES OF TRITIUM

Tritium undergoes decay by emission of a low-energy beta particle and has a half-life of approximately 12.3 years. Due to their low penetrating ability, tritium emissions are not readily detectable through the use of instruments that are commonly used to monitor for other common radionuclides that can contaminate the workplace (e.g., pancake Geiger-Müller detectors connected to count rate meters).

The most common technique used for tritium air sampling (for both HT and HTO) is the flow-through ionization chamber. Removable tritium surface contamination can be detected through liquid scintillation counting (LSC), and this analytical method is in widespread use for analysis of workplace (contamination smears) and biological (urine) sample media.

Because it decays by emission of low-energy beta particles that cannot penetrate human skin, tritium is not typically considered a significant external radiation exposure hazard. However, inhalation,

ingestion, or skin absorption of tritium can result in internal radiation doses. Because tritium in its prevalent oxide form behaves chemically identically to water, it undergoes fairly rapid uptake by, and elimination from, the human body. These biological processes make tritium oxide relatively easy to detect in bodily excretions (primarily urine) at very low levels, which simplifies the radiobioassay, dose assessment, and exposure control processes.

Hydrogen atoms (including those that exist in the form of tritium) tend to diffuse through materials with which they come into contact and can be released at a later time. While this property of hydrogen atoms can complicate measures to contain tritium, it has been well characterized and appropriate materials can be specified to minimize unintended adverse effects. This property can also be used to practical advantage because hydrogen atoms can be diffused through other materials and stored within the matrix for subsequent storage, transportation, release, and use. The diffusion processes can be accelerated through application of heat.

## 2.2 STABLE METAL TRITIDES

Other than HT and HTO, tritium can form metal tritides with the relative ease of tritium exchange. The property of interest of these materials is that they react with hydrogen isotopes to form stoichiometric hydrides, where the hydrogen isotope is contained in interstitial sites in the metal lattice, rather than occupying binding sites of the metal itself (Nobile and Motyka 1991).

The hydriding/dehydriding reaction of various metals can be used as a basis for the storage, pumping, compression, purification, and separation of hydrogen isotopes. One advantage of using hydride technology in tritium processes is the compact size of hydride equipment. This is due to the fact that the volumetric density of hydrogen in typical hydrides is greater even than that of liquid or solid hydrogen. The compact size of hydride beds allows installation in process hoods and gloveboxes at locations where only minimal space is available. For example, use of these materials at SRS has allowed for the reduction of the number of gloveboxes in use and the overall size of some of the facilities. Other benefits of using hydride technology for tritium handling applications are improved safety during storage of tritium in the hydride form at below atmospheric pressure and simple, reliable pumps and compressors with valves as the only moving parts (Ortman et al. 1989).

Metal tritides are classified as either stable or unstable depending on their ease to release tritium. The unstable metal tritides pose no problems because they dissociate themselves with ease in the environment and biologically form the more conventional water vapor tritium. Stable metal tritides (SMTs), however, maintain their original form with a stable metal-tritium bond. Traditionally, SMTs have not been well understood in terms of biokinetics, bioassay, workplace monitoring techniques, and characterization and identification in the workplace.

Particulate SMTs can be ingested or inhaled and result in radiation dose. After ingestion, these particles lose some fraction of their tritium as HTO in stomach digestive fluids. Some SMTs lose essentially all of the tritium, and others lose very little, depending on the solubility of the specific material in the gastrointestinal (GI) tract. In any case, the only significant dose from ingestion of SMTs is due to the resulting HTO that is released. Because HTO is rapidly assimilated physiologically, this dose component is readily assessed via urine bioassay. After inhalation, however, particulate SMTs can be deposited in the lung. Once deposited, the tritium bound to the particulate is removed from the body via two mechanisms:

1. Dissolution of tritium from the particulate and absorption into the body as HTO and removal through urine, expired air, and perspiration; and

2. Mechanical transport of the particulate itself to the GI tract and removal through feces. (Inhaled SMTs removed to the gut will cause dose in the same manner as ingested SMTs, as described above.)

The behavior of SMTs can present a variety of challenges to the reconstruction of doses based on records from a facility's radiation protection program. For example:

- It can be difficult to differentiate between SMTs and the more common forms of tritium using routine workplace monitoring techniques.
- The physical and chemical behavior of SMTs can render commonly used tritium bioassay and available internal dose models ineffective.
- Difficulties in identifying and quantifying contamination can cause significant delays between performance of workplace monitoring and completion of analyses.

Although the DOE radiological protection community has been aware of SMTs for many years, to date their impact has been limited by the design features that are incorporated into DOE facilities that handle significant quantities of tritium. These design features include various forms of material containment and control, such as gloveboxes and high-efficiency particulate air filtering ventilation systems that effectively prevent significant releases of SMTs to occupied areas of the workplace or the environment. In recent years, sensitivity to SMT contamination has increased as a result of DOE decontamination and decommissioning of older facilities. These activities can compromise the effectiveness of the installed design features and allow releases of SMT contamination to the surrounding areas.

NIOSH has established a method for assigning doses due to intakes of STCs. This process provides recommendations for the calculation of doses based tritium bioassay. These recommendations vary depending on what is known about the STC that is contributing to the urinary excretion of tritium (ORAUT 2007).

### **3.0 USE OF METAL TRITIDES**

**NOTE: Because of the sensitive nature of some of the processes at SRS, this report does not provide a comprehensive list of metal tritides SRS has used. Rather, this report provides a representation of the types and uses of metal tritides that might have been encountered at the site. Evaluation of other metal hydrides is conducted in a set of classified notes associated with this document.**

The SRS Tritium Facilities have used a variety of metal hydride materials in process vessels or beds for the safe processing and storage of tritium. Due to the sensitive nature of the work at SRS, information such as the quantities of material and the details of the work on metal hydrides and tritides at SRS are still classified. However, a qualitative breakdown of the metal hydride work is presented here. At SRS, these materials are used in tritium processes as storage media and are the subject (or byproduct) of research activities (Moxley 2002).

At SRS, the determination as to whether a compound is classified as an STC is based on the degree to which the tritium atoms are held in the compound. The tritium in STCs is bound more tightly than the tritium in tritium oxide. Using this designation, uranium tritide and palladium tritide are not considered SMTs because they do not bind tritium in a manner significantly different from tritium oxide (Moxley 2002). To develop a complete picture of the use and production of SMTs at the site, this report includes discussion of these two materials.



A program was initiated in 1981 by the Savannah River Laboratory in cooperation with the Tritium Facilities with the goal of implementing metal hydride technology in the SRS Tritium Facilities. This program was initiated to take advantage of the discovery in 1969 of intermetallic compounds, such as  $\text{LaNi}_5$  and  $\text{FeTi}$ , that would rapidly and reversibly absorb and desorb hydrogen under moderate conditions of temperature and pressure. Since then the processes described below have gone through bench-scale, pilot-scale and, in some cases, full-scale testing.

### **3.1 ZEOLITE**

For approximately 64 years, SRS has isolated tritium from its process streams by catalyzing the formation of tritiated water (from process streams) and then sorbing that water on a 3A zeolite molecular sieve (molsieve) bed. This requires converting elemental tritium to tritium oxide and capturing the oxide on zeolite moisture absorber rods, which can then be processed to recover tritium. The tritium is recovered by regenerating the saturated bed into a magnesium-based water-cracking unit (Hsu and Heung 1997).

The SRS Tritium Facilities use 30 nitrogen gloveboxes and 2 primary stripper systems that support normal tritium removal from the nitrogen atmosphere. A third identical system named the secondary stripper handles accidental tritium release in any of the gloveboxes. Each of these three systems has three zeolite beds, with each of these beds holding 104 kg of zeolite type 3A. A fourth stripper system named the purge stripper, which controls the purge of nitrogen from the gloveboxes to the atmosphere, has three smaller zeolite beds. Each of these smaller beds holds 27 kg of zeolite type 4A (Heung et al. 2004).

Experience from the stripper system at SRS shows that more than 99.9% of the moisture on zeolite beds is nontritiated water. About half of the water appears to come from moisture leaking into gloveboxes, with about half due to negative pressure operation and half to glove permeation (Hsu and Heung 1997).

Because zeolite molsieves rely on strong physical forces rather than chemisorption to retain adsorbates, their adsorption is characterized by a non-linear isotherm (the amount of a given compound adsorbed increases rapidly to a saturation value as its pressure or concentration increases in the external bulk phase). Any further increase in pressure at constant temperature causes no further increase in the amount adsorbed. With zeolite molsieves, this equilibrium saturation value typically corresponds to a complete filling of the internal void volume with the adsorbate. When adsorbed molecules are desorbed via heat or by displacement with another material, the crystal's chemical state remains unchanged (EPA 1999).

Because the tritium is adsorbed on the zeolite rather than forming an alloy with the metallic components, zeolite is not considered a metal tritide in this report.

### **3.2 STAINLESS STEEL**

Austenitic stainless steels are extensively used in the nuclear industry because of their good corrosion resistance and mechanical properties. Prolonged use of tritium in process plants results in a tritium burden in steel and other metals (Richardson and Hong 2001). A typical 1020 steel component exposed to hydrogen gas at 1 atmosphere of pressure at room temperature will dissolve far less than 1 ppm of hydrogen. However, when the same component is corroded by acid cleaning, exposure to hydrogen sulfide, or simple exposure to moisture, the concentration of nascent hydrogen on the surface can become quite high and the hydrogen solubility during the exposure can exceed several parts per million, but might not lead to the formation of a hydride (Louthan 2008).

The equilibrium solubility of hydrogen in iron at a hydrogen pressure of 1 bar is small. Theoretical concentrations of interstitial hydrogen in solid iron vary from an atomic ratio of about  $1 \times 10^{-6}$  at room temperature to approximately  $1 \times 10^{-3}$  near the melting point of iron. The preparation of bulk, composition, crystal structure, and physical properties, however, is possible only under equilibrium conditions in an atmosphere of hydrogen at pressures of several gigapascals (Antonov et al. 2002).

At first glance this solubility determination contradicts the observed behavior of tritium retention in steel. However real solids are not perfect crystals, but rather they contain defects that can play a crucial role in the uptake and transport of hydrogen in metallic materials. The absorbed hydrogen in a metal can be present in either of two locations in the microstructure: interstitial sites in the lattice or extraordinary sites typically associated with crystalline defects. Hydrogen absorption causes the iron lattice to expand because the effective size of the nascent hydrogen atom is larger than the size of the interstitial site. This size difference causes hydrogen to prefer extraordinary sites where the site size within the lattice is expanded and the incoming hydrogen is more readily accommodated. Examples of extraordinary sites include grain boundaries, vacancies, dislocations, and any other volume where the sites within the lattice structure are dilated.

The concentration of hydrogen at the extraordinary sites in body-centered cubic (ferritic) or body-centered tetragonal (martensitic) steels can greatly exceed the concentration of hydrogen at the normal inter-lattice sites. Frequently, the hydrogen at extraordinary sites is termed "trapped hydrogen," and the hydrogen at the normal inter-lattice sites is termed "dissolved or diffusible hydrogen." The mobility of hydrogen increases as temperature increases, and the difference in residence time at the various sites eventually becomes negligible at high temperatures. Further, at temperatures much below room temperature the mobility of hydrogen decreases to the point that relocation cannot occur and local equilibrium cannot be maintained (Louthan 2008).

Iron and steel hydrides are not considered further in this report because the high temperatures and pressures that are required for formation make it very unlikely that these materials would be encountered at the SRS.

### **3.3 URANIUM**

As previously mentioned, metal tritides can be created either by the intentional combination of tritium with the desired materials or by inadvertent contamination of a material that has been subjected to the presence of tritium over time. Before 1981, metal hydrides were used to process tritium at DOE sites, such as uranium storage and purification beds at Mound Laboratory and Los Alamos National Laboratory, a vanadium compressor bed at Los Alamos National Laboratory, and uranium beds at the Savannah River Laboratory for a short time in the 1950s to store and transport deuterium and tritium during experimental work.

Depleted uranium has a long-standing history in tritium activities. This metal is used to store tritium, transport tritium gas and, in special applications, selectively remove tritium from flowing gas streams. Uranium offers a very high storage capacity; 120 standard  $\text{cm}^3$  of gas per gram of uranium can be easily accommodated without compromising the reaction kinetics. It is well suited to removing tritium from clean inert gas streams with high tritium concentrations and offers uniform reaction kinetics over a very broad range of tritium-to-uranium atom ratios. It is possible to charge uranium with tritium up to an atom ratio of nearly 3 (tritium atoms per uranium atom), although the operating range is usually restricted to a ratio of 1.5 so sufficient tritium storage capacity remains for unforeseen events (Shmayda 2005).

At room temperature, tritium in the presence of uranium powder forms uranium tritide. The tritium partial pressure in the bed is very low. As a result, at room temperature the bed acts as a vacuum pump that getters all of the hydrogen isotopes. The impurity gases that might be present, such as

$^3\text{He}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , or argon, either remain in the overpressure gas in the bed or react with uranium to form stable compounds.

Uranium has a theoretical maximum storage capacity of 1.26 wt% and bonds with tritium to form a tritide at room temperature and pressure. However, uranium as a storage material has drawbacks for various operations. Tritide formation in uranium is an exothermic reaction meaning the system needs to be actively cooled to maintain the fast kinetics of the tritiding process. There is also a significant volume expansion as the reaction takes place, which limits the size and orientation of storage beds. At SRS, high temperatures were required to desorb the tritium from the metal, which led to concerns about tritium permeation through the stainless-steel bed and process inefficiencies due to long heating and cooling times. In addition, the pyrophoric nature of uranium led to safety concerns with respect to its potential use at SRS (Ortman et al. 1989).

In the fourth quarter of 1991, a program to develop a hydrogen transport vessel (HTV) using depleted uranium with capacity for up to 18 g of tritium was initiated. An experimental transport vessel was fabricated and tested in the laboratory before the final design was completed (Heung 1994a). The vessel body is fabricated from two 4-in. schedule 40 stainless-steel pipe caps. This vessel contains 0.5 kg of depleted uranium in the form of 0.5- to 1.0-in.-diameter bar stock in lengths not greater than 0.5 in. Before first use, the depleted uranium in a new HTV must be activated. During activation, hydrogen gas reacts with the uranium bar stock to decompose the bar stock into powder. Heating during activation accelerates penetration of any uranium oxide layer by the hydrogen isotopes. Port filters with a maximum pore size of 2  $\mu\text{m}$  were designed to contain all uranium powder within the HTV. This hydride transportation bed has been in service since 1995 (Heung 2001).

SRS has also used uranium as a decomposer to crack tritiated water from various streams into oxygen and hydrogen isotopes. These isotopes can then be separated from any helium isotopes present by permeation through a palladium-silver alloy diffuser (Ortman et al. 1989). Because the decomposer is operated at high temperatures, it is unlikely that the exothermic hydriding reaction would occur to an appreciable degree as a result of this process.

### 3.4 MAGNESIUM

The regeneration and recovery of hydrogen isotopes from zeolite beds is accomplished by a zeolite bed recovery system. The system consists of magnesium beds, a furnace, circulation pumps, pressure regulators, mass flow meters, and recycle tanks. The magnesium bed is a 25-cm diameter vessel and holds 20 kg (823 mol) magnesium turnings supported by a porous plate at the bottom. The magnesium container is heated in a furnace equipped with resistant electric heaters. Inlet gas containing water moisture flows through a standpipe to the lower side of the porous plate. As the gas mixture rises through the magnesium bed, the moisture reacts with the magnesium to irreversibly form  $\text{MgO}$  and elemental hydrogen. The hydrogen gas exits the top of the bed and circulates in the loop. During operation the magnesium bed is maintained between 450°C and 500°C. Twenty kilograms of magnesium can reduce a maximum of 823 mol of water and generate 18,000 L of  $\text{H}_2$  (Heung et al. 2004).

When the magnesium is consumed, the bed is removed and disposed of as low-level radioactive waste. The hydrogen isotopes are collected in recycle tanks and later separated to recover the tritium (Heung et al. 2004). It is unlikely that the magnesium would have been able to form a hydride, however. The hydrogenation/dehydrogenation reaction for pure magnesium is very slow and occurs only at high temperature (350°C to 400°C) under a hydrogen pressure of more than 3 MPa. Further, the surface oxidation of magnesium ( $\text{MgO}$ ) exposed to air would significantly hinder the rate of hydrogenation (Stier et al. 2005).

### 3.5 LANTHANUM-NICKEL-ALUMINUM ALLOY

The first metal hydride vessel designed for tritium service at SRS was a 6-mol capacity storage/compressor. It started tritium storage in 1984 and was removed from service in 1986. The vessel was used to store tritium at ambient room temperature and pressure and to produce up to 300 psia by heat. The container volume was filled with 1 kg of lanthanum-nickel-aluminum alloy (LANA; specifically  $\text{LaNi}_{4.7}\text{Al}_{0.3}$  in this instance), which occupied about 75% of the volume. The remaining 25% of volume was left for volume expansion of the hydride particles. Inside the inlet/outlet port of the vessel was a cylindrical, sintered, porous stainless-steel filter with a nominal pore size of 5  $\mu\text{m}$  (Heung 2001).

An experimental tritium gas handling manifold was installed in 1985 in support of the development of metal hydride technology. The manifold uses a small  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  metal hydride storage bed to store about 10 g of tritium for experimental work. As tritium is needed in the manifold, this storage bed is heated to deliver it at the required pressures. When tritium is no longer needed, it is reabsorbed by cooling the storage bed. This minimizes the amount of tritium that must be pumped through mechanical vacuum pumps, which prolongs the life of the pumps (Ortman et al. 1989).

Twenty LANA hydride samples in a controlled matrix study were charged with tritium and placed in storage in March and April 1987. The interaction of tritium with these samples was investigated by collection of equilibrium desorption isotherms at time intervals generally on the order of several months (Ortman et al. 1989).

After the success of the 6-mol beds, larger beds with capacities up to 70 mol were designed for isotope storage and pumping. These beds are used to store tritium and its isotope mixtures among purification and separation processes. The body of the vessel is a horizontal container fabricated from schedule 40 stainless-steel pipe with a volume of about 4.4 L. The vessel is filled with  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  to approximately 70% full. The container is fully enclosed in a 4-in. schedule 10 stainless-steel jacket (Heung 2001).

For separating hydrogen isotopes from inert gases such as helium and nitrogen, a flow-through type of vessel was used. The U-shape column was built out of stainless-steel pipes up to 8 cm in diameter. The metal hydride for this application was palladium deposited on kieselguhr, a siliceous sedimentary mineral (otherwise known as diatomaceous earth). This packing material was chosen because of its ability to withstand hundreds of absorption and desorption cycles without decrepitation. The column had an inlet port and an outlet port on top of the legs of the U. Both ports were fitted with porous metal filters on top of the packing material to reduce the chances of clogging by fine particulates. After the column became saturated, it could be heated to desorb the hydrogen isotopes, which would then be collected as purified product (Heung 2001).

To separate the hydrogen isotopes from each other, a metal hydride chromatographic column is applied in a thermal cycling absorption process (TCAP) (Bradley 1983). This TCAP used the isotopic effect of palladium to separate the isotopes in a long column filled with palladium deposited on kieselguhr. The column is designed to minimize the height of the unit so it can be easily installed inside a glovebox. Multielement porous stainless-steel filters are fitted in the inlet/outlet ports to confine the packing material (Heung 2001). The feed and the outputs from the system are stored in metal hydride beds using LANA. Initial prototype TCAP testing using protium and deuterium was performed in the Advanced Hydride Laboratory at the SRTC.

Development of the TCAP began in 1980, and production-scale operation began in 1994 (Scogin and Poore 1994).

### 3.6 TITANIUM

Tritium is periodically removed from process streams but might not be needed for several years. Therefore, SRS recognized a need for additional tritium storage that exceeded convenient transfers of gas to tanks or process hydride beds. With this need in mind, a hydride storage vessel (HSV) was developed for long-term (more than 5-year) storage of tritium. Several hydrides were investigated for use in the HSV. Titanium was chosen over depleted uranium, a  $\text{LaNi}_{4.15}\text{Al}_{0.85}$  alloy, and zirconium. Depleted uranium has the undesirable characteristics of being pyrophoric, slightly radioactive, and does not retain  $^3\text{He}$  in the metal matrix as well as other materials. Helium retention within the metal matrix is important because it permits storing tritium at high concentration without outgassing of helium leading to increased pressure on the vessel walls. Titanium hydrides are not pyrophoric in air and are stable in both air and water at ambient temperatures (Heung 1994a).

By weight, titanium has a greater storage capacity than the  $\text{LaNi}_{4.15}\text{Al}_{0.85}$  alloy and a lower tritium equilibrium pressure. Titanium was chosen over zirconium because the desorption temperature for tritium recovery from titanium is lower than that for zirconium (Klein 2001). The basic design of the HSV is an upright vessel about 17 cm in diameter and 30 cm high of 6-in. schedule 40 stainless steel. Two pieces of stainless-steel tubing penetrate the top cap of the container body and serve as inlet and outlet for the flow of gases. The open ends of the tubes are welded on with porous stainless-steel filters (2- to 5- $\mu\text{m}$  pore size) to prevent titanium particles from escaping the container (Heung 2001).

The vessel contains about 4.5 kg of titanium and can store 67 mol of tritium for 4 years before helium release occurs. When part of the tritium is replaced by deuterium or protium, its storage time can be increased proportionally. The HSV is designed to stay in storage up to the time when helium decay reaches the 0.3-atom ratio. If permanent storage is the objective, the assumption must be made that all the helium will come off in the gas phase. The ultimate helium pressure limits this vessel to storage of 10 mol of tritium indefinitely (Heung 2001). The vessel is designed for one-time use only because, after heating to 600°C in the presence of tritium, the stainless-steel wall of the vessel will most likely be saturated with tritium at the equilibrium level with the tritium pressure. This can cause surface contamination and weaken the vessel wall as well (Heung 1994a).

### 3.7 PALLADIUM

Production-scale separation of tritium from other hydrogen isotopes at SRS has been accomplished by several methods. These methods include thermal diffusion (1957 to 1986), fractional absorption (1964 to 1968), cryogenic distillation (beginning in 1967), and TCAP (beginning in 1994). In each of these processes, confinement systems have been used to minimize tritium release to the environment and to protect workers from tritium exposure. These systems typically consist of a primary containment system such as the material vessel, a secondary confinement such as a glovebox, and accessory systems for removing contaminants from the secondary containment atmosphere in the event of a leak from the primary containment. Depending on the process, these accessory systems can include stripper systems, getter systems, or some combination of the two.

The primary functions of a stripper system are to concentrate and recover the tritium, reduce the background level of tritium in the confinement system, and reduce worker exposure. The conventional and most widely used method of removing tritium from confinement atmosphere gas is catalytic oxidation followed by absorption in a drying agent such as zeolite. The baseline zeolite molsieve recovery technology at SRS uses a magnesium bed to decompose water. In conventional oxidation-absorption stripping technology, the feed gas is processed through a heated catalyst bed (350°C to 500°C) to convert elemental hydrogen to oxides (water). The gas is then cooled to 20°C to 30°C to absorb the waters in a dessicant, moisture-absorbing material, typically a synthetic zeolite. Tritium in the form of oxide is thus removed from the gas and trapped in the zeolite (Birchenall 1992).

To reclaim the tritium, the zeolite is heated, evolving the trapped water, which is then passed over an elevated temperature uranium bed. The uranium bed oxidizes, cracking the water released from the zeolite bed. The oxygen from the water is retained on the uranium bed, and the resulting hydrogen isotope mixture can be reprocessed (Birchenall 1992). At SRS, the catalyst bed has typically been a palladium-aluminum or palladium-silver alloy. However, because this material is only used as a high-temperature catalyst in the oxidation of elemental tritium, metal hydrides are not formed unless inadvertent cooling of the diffuser membrane occurs in the presence of hydrogen (Clark et al. 1995).

The earliest diffusers at SRS were single-stage, water-cooled units designed specifically for the Tritium Facilities by DuPont. Palladium is able to store a large atomic percentage of hydrogen at room temperature and allows hydrogen to diffuse with a high mobility. However, one drawback of palladium is that, as it is for many metals, the addition of hydrogen to a metal adversely affects the material's mechanical properties by reducing ductility and increasing susceptibility to fatigue and corrosion, which necessitates the backing of palladium with a hydrophobic solid such as kieselguhr or the development of a palladium alloy. An application in which palladium that requires mechanical resilience is useful is as a hydrogen diffusion membrane. By filtering hydrogen gas through a membrane of palladium, high-purity hydrogen can be obtained because the palladium allows for high diffusion of hydrogen atoms while blocking the transmission of impurities (Hale et al. 2013).

After 1958 these units were redesigned to be a "multistage palladium diffuser" (MPD). Each stage of the MPD consisted of one pure palladium diffuser tube wound in a coil supported by a ceramic core in its own flanged section, and the stages were connected by stainless-steel jumpers. Each stage was contained by a water-cooled stainless-steel shell and cooling jacket, and the stages were connected using O-ring seals. Water-cooling of the shell reduced diffusion losses through the shell and prevented heat damage to the O-rings. The last of the MPD stages was taken out of service in 1985 (Motyka et al. 1995).

Diffusers manufactured by Resource Services Incorporated (RSI) came into service around 1983. These commercially available units used a 75% palladium, 25% silver alloy for the diffusion coil (Motyka et al. 1995). Alloying palladium with another metal offers the opportunity to alter the properties of the hydride and improve its overall performance. For instance, additions of silver greatly improve the mechanical resilience of palladium hydrides by suppressing the miscibility gap at room temperature. This gap results in the separation of the material into a low hydrogen ( $\alpha$ ) phase, and a high hydrogen ( $\beta$ ) phase. The lattice mismatch between these phases results in considerable strain and plastic deformation within the material. Depending on the silver composition, the hydrogen diffusion rate can also be increased in relation to pure palladium. However, the addition of silver also decreases the hydrogen solubility and results in a trade-off of properties with changing compositions (Hale et al. 2013).

The RSI diffuser consisted of five coiled palladium-silver permeation tubes mounted in parallel in a single chamber to reduce the pressure drop associated with high tube-side gas flows (Motyka et al. 1995).

Early in the 1990s, concerns about the cost of maintenance of palladium silver diffusers, the production of tritiated water by the use of catalytic stripper systems, and the need for disposal of uranium beds as waste prompted investigations into the use of metal hydride getter beds for tritium removal. Aside from the production of tritiated water, the problem with the uranium bed cracking system is that the uranium bed is consumed in the process and cannot be regenerated because the temperatures necessary to decompose the stable uranium oxide would result in a sintered uranium product with greatly reduced surface area for subsequent water cracking (Birchenall 1992).

In January 1994, consolidation of operations from some of the older buildings into newer facilities began. Part of the gas purification process in this new facility was a flow-through bed using a U-shaped column filled with palladium on kieselguhr. These beds allowed hydrogen to be absorbed

and desorbed without the heat necessary to decompose uranium, which permitted the beds to be reused (Clark et al. 1995).

Assuming occasional inadvertent cooling of the palladium, failure of the coils due to hydride formation might be anticipated. No record of such a failure at SRS has been found. Heaters, heater controllers, and thermocouples have all failed on occasion, but apparently insufficient hydrogen was present in the palladium coils to cause hydrating at the lowest temperatures it reached. Multiple thermocouples are normally used, so that the control function of a failed thermocouple can be replaced by a backup (Motyka et al. 1995).

### **3.8 INTENTIONALLY FORMED ZIRCONIUM**

A newer system, the Tritium Process Stripper, uses metal hydride getters and diffusers to remove tritium from process waste streams without the formation of tritium oxide. To strip tritium from a process stream, two getters are used in series: a sacrificial getter that reacts with oxygen and cracks water to convert all hydrogen isotopes to the elemental form, followed by a second getter that getters hydrogen as a hydride (Hsu and Oji 1997). A commercially available zirconium-manganese-iron alloy getter material, SAES St 909, is used in a bed as the sacrificial getter to absorb oxygen and reduce hydrogen-containing compounds to elemental hydrogen. The primary getter chosen for the process was SAES St 198 after testing indicated that the material could strip hydrogen from nitrogen or inert streams down to the desired part per million level (Clark et al. 1995). When the St 198 bed becomes saturated, it is heated to desorb the hydrogen isotopes, which then undergo isotopic separation (Hsu and Oji 1997).

SAES St 909 was originally developed for dissociating (cracking) tritiated water for the recovery of tritium. Various zirconium alloys were tested for water vapor sorption rates and hydrogen "pick-up" rates, and the zirconium-manganese-iron alloy was chosen as the material with the best combination of water-cracking rate and low hydrogen pick-up. The zirconium-manganese-iron alloy was combined with an aluminum binder for pellet formation and sold as SAES St 909. St 909 was shown to crack methane, carbon monoxide, carbon dioxide, ammonia, and oxygen in helium streams.

In 1999, SRS started testing St 909 to determine its methane-cracking performance with different methane concentrations, with different impurities, and in carrier gases of helium, hydrogen, and nitrogen. Test programs using bench-scale (6-gram), pilot-scale (500-g), and full-scale (5,300-g) St 909 beds were conducted (Klein and Holder 2005).

The St 198 metal getter, having a reported composition of 76.5% Zr and 23.5% Fe, is unique from a number of other metal hydride-based getter materials in that it is reactive with hydrogen isotopes, oxygen, water, and other gases, while remaining relatively inert to nitrogen. This property allows the St 198 to be used in nitrogen glovebox atmospheres (Nobile et al. 1994).

### **3.9 ZIRCONIUM TRITIDES FROM FUELS**

The most important movement of tritium in a light-water reactor (LWR) is diffusion of a portion of tritium from the fuel into the Zircaloy cladding, where it is trapped as a hydride. The portion of tritium trapped in the cladding is typically 15% to 60% of the tritium produced in the fuel (IAEA 2004). To recover target components from the zirconium or thorium-based hydride fuels by solvent extraction, the fuel and Zircaloy cladding must be dissolved and suitable feed solution prepared. Because zirconium resists dissolution by nitric acid, the choice of reagents to dissolve hydride fuels is limited (Mozin 2008). In an LWR fuel reprocessing plant using the plutonium-uranium extraction (PUREX) process, after chopping the fuel elements and fuel dissolution in nitric acid, about 60% of the total amount of tritium is retained in the cladding. The bulk of the remainder is in the form of HTO and nitric acid, which is distributed through the various streams in the process (IAEA 2004).

Alloys of zirconium (i.e., Zircaloy) have been used as cladding for nuclear fuel because of their low thermal neutron absorption cross section and their relatively good resistance to corrosion and radiation damage. Zircaloy cladding makes up roughly 25% by mass of used nuclear fuel in the United States (Crowder et al. 2010). The alloying elements and composition are varied to provide the proper corrosion resistance while maintaining strength and ductility to prevent failures during reactor operations. For example, it was discovered that the presence of nickel in Zircaloy-2 (Zr-2) promoted absorption of hydrogen. Because pressurized-water reactors (PWRs) use an overpressure of hydrogen in the reactor coolant, Zircaloy-4 (Zr-4) was developed in which the nickel was replaced with additional iron to maintain corrosion resistance. Zr-2 is used exclusively for boiling-water reactors (BWRs) and has as its major constituents 97.963% Zr, 1.6% Sn, 0.15% Fe, 0.1% Cr, and 0.05% Ni. In the major BWR fuel rod types, the thickness of the cladding ranges from 0.03 to 0.037 in. Zr-4 is used in PWR fuel rods and has as its major constituents 97.911% Zr, 1.6% Sn, 0.225% Fe, 0.125% Cr, and 0.002% Ni. In the major PWR fuel rods types, the thickness of the cladding ranges from 0.0225 to 0.03 in. (Bond, Mailen, and Michaels 1992).

Zirconium alloy cladding materials resist attack by nitric acid, which is the most widely accepted solvent for recovery of uranium and plutonium from fuels. To overcome this resistance, the cladding must be removed or altered in such a way that the fuel can be dissolved and used in a process feed stream. The chop-leach process has been employed in commercial reprocessing plants for the recovery of uranium and plutonium from spent LWR fuels. In these plants, the fuel is dissolved from short segments of chopped fuel rods by an aqueous nitric acid solution, then the uranium and plutonium are recovered by solvent extraction, using the PUREX process at first and later the uranium-extraction UREX process, as a solution of their nitrate salts (Bond, Mailen, and Michaels 1992). In this process, tritium that is bound in the cladding in the form of zirconium tritide follows the cladding to its eventual disposal site.

Electrolytic dissolution of Zircaloy in nitric acid was recognized as a possibility with the virtue of allowing solvent extraction by conventional means in conventional stainless-steel equipment. A 5,000-ampere dissolver was installed at the Semiworks in early 1961. The design was based on the "metal contact" concept in which the fuel assemblies to be dissolved were placed in an anodic niobium basket inside a niobium cathode. In late 1961, the dissolver was converted to a "liquid contact" system in which the fuel assemblies to be dissolved were suspended between a platinum-clad niobium anode and a niobium cathode (Caracciolo and Kishbaugh 1964).

Under electrolysis, the majority of the Zircaloy cladding is converted to an oxide that falls to the bottom of the dissolver as a sludge, with 15% remaining in solution. Two methods of sludge removal were investigated at SRS and found satisfactory. In the first method, a trough was installed below the electrodes to catch the sludge. The sludge and dissolver solution were continuously pumped from the trough to a decanter or a 200-mesh screen canister where the sludge settled and the solution returned by gravity to the dissolver. In the second method, the sludge was allowed to collect in the dissolver and, at the completion of the run, was rinsed with dilute acid to remove absorbed uranium. The sludge was then flushed toward the jet suction by water sprays in the bottom of the tank and removed as a slurry. The electrolytic dissolver operated through 1979, when most of the processable fuel was exhausted (Bebbington 1990).

Several research groups have measured the tritium content of irradiated fuels and Zircaloy hulls by various methods with varying results. Measurements of 0.5- to 0.6-g Zr-2 samples made at SRS showed a range of 67 to 99  $\mu\text{Ci}$  tritium/g hull with an average of 86  $\mu\text{Ci/g}$  (Crowder, Laurinat, and Stillman 2010).

The use of Zircaloy as a cladding for fuel rods protects the fuel from corrosion by the cooling water, but it can degrade over time as a result of the hydrogen that permeates the crystalline structure of the metal. Helium is a product of the decay of tritium and, in contrast to tritium, is a very stable atom that



shows an extremely low solubility in metals. Due to its insolubility, accumulation of helium atoms can produce highly pressurized bubbles (Laesser 1989). Metal tritide films of five different elemental tritides were observed by Beavis and Miglionico (1972) at Sandia National Laboratories over a 5- to 6-year period.

Once a critical ratio of helium to metal (0.25 to 0.35) is reached, the rupture of pressurized bubbles near dislocation networks with continuous paths to the surface results in sudden helium release. Abrupt increases in helium released from tritides are accompanied by flaking or blistering of the surface. This damage from helium buildup can cause small particles to break off the tritide surface (Schober, Tinkaus, and Lasser 1986; Schober 1988; Schober and Farrell 1989). Studies have shown a considerable detachment of tritide particles due to the formation and rupture of the bubbles. Detached particles varied in size from 1 to 50  $\mu\text{m}$  in diameter (Beavis and Miglionico 1972).

While the production of hydrides in fuel cladding is generally considered undesirable due to hydride-induced fracturing, researchers have sought to capitalize on the storage capacity of tritium in zirconium hydrides by placing the hydride in contact with the tritium as soon as it is produced. In December 1998, DOE announced that commercial reactors would be the source for new tritium production. Assemblies of tritium-producing burnable absorber rods (TPBARs) are irradiated in a commercial LWR to produce tritium. TPBARs are similar in size and nuclear characteristics to standard, commercial LWR, stainless steel-clad burnable absorber rods. The internal components have been designed and selected to produce and retain tritium. Within the stainless-steel cladding is a metal "getter" tube that encircles a stack of annular ceramic pellets of lithium aluminate. The pellets are enriched with  $^6\text{Li}$  (DOE 2016).

When irradiated in the LWR, the  $^6\text{Li}$  pellets absorb neutrons, which simulates the nuclear characteristics of a burnable absorber rod, and produce tritium. The tritium chemically reacts with the metal getter, which captures the tritium as a metal hydride. The irradiated TPBARs are removed and shipped to SRS. At SRS, the tritium is extracted from the irradiated TPBARs and purified through a number of chemical and physical separation steps (Hsu and Heung 1997).

In October 2003, the first TPBARs were inserted into the Tennessee Valley Authority (TVA) Watts Bar Unit 1 reactor for irradiation. The first shipment of irradiated TPBARs arrived at SRS in August 2005 and was stored, awaiting completion of the processing facility. The first extraction of tritium from TPBARs was successfully completed in January 2007.

To meet design limitations on rod internal pressure and burnup of the lithium pellets, the amount of tritium production per TPBAR is limited to a maximum of 1.2 g over the full design life (less than 495 equivalent full-power days). The potential release rate of tritium into the reactor coolant is subject to a design limit of less than 1,000 Ci/1,000 TPBARs per year. This is achieved by the combined effects of the metal getter tube surrounding the lithium aluminate pellets and an aluminide barrier coating on the inner surface of the cladding.

#### **4.0 STABLE METAL TRITIDE HANDLING AREAS**

STCs have been present in several SRS facilities. These materials are used in tritium processes as storage media and are the subject (or byproduct) of research activities and fuel processing.

##### **4.1 F-AREA**

In 1950 the U.S. Atomic Energy Commission authorized the Savannah River Project principally for the production of tritium for weapons use. Tritium processing operations have been performed at SRS since October 1955. Process equipment and designs were drawn from experience at the Hanford

Site, and tritium process flows were extrapolated from the initial tritium production conducted at the Los Alamos National Laboratory.

The process equipment was enclosed in a stainless-steel cabinet with panels (sometimes called a hood). The panels were framed and held glass windows for visual inspection of equipment. The panels were mounted on tracks to permit opening for access to equipment for maintenance or replacement. This early design proved to be ineffective in containing contamination within the cabinet. Soon after startup, contamination problems were evident within the process room, sometimes spreading to other adjacent rooms (Blackburn 1994).

This area processed its final charge in October 1958 (DuPont 1973), after which all of the process lines and equipment were flushed with inert gas (Blackburn 1994). A characterization of the building in 1994 indicated that tritium was extracted in the facility from LiAl slugs. Mercury is known to have been used in the pumps, and the process piping was assumed to be contaminated with mercury (Scallon and England 1994). However, hydrogen is fairly insoluble in mercury, forming a hydride or dihydride only at extremely low temperatures, which makes the presence of mercury hydride at SRS extremely unlikely. The facility had made use of palladium-silver diffusers and zeolite beds, but there are no indications that metal tritides were fabricated or used in this area (Scallon and England 1994).

## 4.2 H-AREA

In H-Area, tritium processes started in 1957 (Buley et al. 1995) and continued until approximately 2002. Processing in this area included vacuum heating of reactor targets for the extraction of tritium, purification by palladium diffusion, and separation by thermal diffusion and cryogenic separation (Rabun 2000).

The first HSV was loaded on April 3, 1996, delivered to H-Area, and installed in a monitoring manifold. Temperature and pressure data have been recorded from this apparatus since late May 1996. Nine samples were originally prepared with varying tritium and deuterium loadings for use in a long-term storage program. One sample has been used to collect pure tritium isotherm data on an annual basis (Shanahan 1998).

After 2004, personnel from SRTC performed experimental work to develop tritium processing and handling techniques. Tritium was pumped, compressed, purified, dissolved in, and reacted with various materials. A variety of STCs were deliberately made such as uranium tritide, palladium tritide, titanium tritide, and LANA tritide. Tritiated vacuum pump oils are known to have been formed during processing.

All metal hydrides used in tritium production and in research and development (R&D) are contained in stainless-steel vessels, which are referred to as metal hydride beds, equipped with sintered metal frit filters. These beds usually consist of horizontal cylindrical vessels, with the metal hydride powder filling about 70% of the volume. The powder occupies the lower portion of the horizontal cylinder, allowing some free volume above the powder for normal expansion and contraction of the powder. There are some applications that involve flow through the metal hydride powder. In these applications, the metal hydride is palladium supported on kieselguhr, the cylindrical cavity is fully packed, and the bed configuration is a coiled tube or a U-tube (Nobile and Motyka 1991). All tritium operations were performed in air-ventilated hoods. Kanne tritium air monitors were used to indicate airborne tritium activity in hoods and rooms. Work areas and adjacent areas that had the potential for contamination were monitored by smearing with filter paper and counting with liquid scintillation counting on a regular basis and immediately after completion of any job.

All tritium process equipment in H-Area is secondarily confined in gloveboxes or jacketed piping, the first large-scale tritium handling facility in the DOE complex to do so. These operations included

hydrogen isotopic separation, loading and unloading of tritium, shipping and storage recovery from zeolite beds, and stripping of nitrogen flush gas to remove tritium before stack discharge (Hsu and Oji 1997).

Additional operations conducted in this area include purification of tritium by palladium diffusion, storage of gaseous tritium, and small-scale storage of tritium using storage beds.

A  $^3\text{He}$  purification process in H-Area involves slowly passing the gas through a cold gold trap, then through an ambient zeolite bed to remove any moisture from the gas stream, and finally through two liquid nitrogen-cooled zeolite beds connected in series to condense out the inert gases and nitrogen. Purified helium-3 is stored in a feed tank that is loaded via a compressor into a gas cylinder. The cold zeolite beds are regenerated after each transfer by allowing them to slowly warm to ambient temperature, allowing the inert gases and nitrogen trapped in them to be released to the waste tank (Hsu and Oji 1997).

In December 1998, DOE announced that commercial reactors would be the primary source for tritium production. In May 1999, DOE selected TVA's Watts Bar Unit 1, Sequoyah Unit 1, and Sequoyah Unit 2 commercial LWRs for irradiating the DOE-supplied TPBARs. In October 2003, the first TPBARs were inserted in TVA's Watts Bar reactor for irradiation. The SRS was tasked by the DOE to design and construct a Tritium Extraction Facility to process irradiated tritium-producing burnable absorber rods (TPBARs) from a commercial LWR. The intent is for the rods to provide tritium to support DOE requirements. DOE started funding the conceptual design for the project in 1996. The TPBAR was designed by Pacific Northwest National Laboratory. The TPBAR assemblies are irradiated in a commercial utility LWR and transported to SRS for tritium extraction and processing (DOE 2016).

A staff of approximately 600 workers was employed during peak construction phase of this project, and the facility has an operations staff of approximately 100 permanent employees. Within the project area, the TPBARs are unloaded and the tritium gas extracted. It has a truck receiving area, cask decontamination area, TPBAR and waste preparation area, furnaces, and hot maintenance area, along with the associated gloveboxes for extraction pumps and tanks. It also includes an overhead crane and remote handling equipment. Another facility provides preliminary purification of the extracted gases.

This project celebrated completion of the nonradioactive startup testing program on February 28, 2006. Over 700 different systems and components were successfully tested. In November 2006, the project successfully began radioactive operations. In February 2007, SRS completed the startup of the project and made the first transfer of new tritium gas to the nation's tritium inventory.

### **4.3 A-AREA**

Current tritium handling practices in this area are limited to relatively small quantities of tritium. With one exception, no SMTs are intentionally formed or handled. Quantities inadvertently formed or incidental to handling are expected to be very small and might be mixed with other alpha and beta/gamma emitters, which are a much more severe radiological hazard. Operations in this area fall into three categories: (1) chemical analyses of materials that contain tritium, (2) mechanical testing of metals that contain dissolved elemental tritium, and (3) metallographic preparation and examination of materials that contain tritium. Of these, only the metallographic preparation appears likely to present any credible hazard from respirable SMTs (Howard 2000).

Several laboratories within the buildings are used or have been used for tritium work in the past. Most of the metal hydride development work was done "cold" with protium and deuterium (Howard 2000). In about 1954, bench-scale experimental work was done to investigate the use of electrolysis to

remove tritium from heavy water. It is conceivable that tritiated rust could have been formed on steel exposed to heavy-water moisture. However, tritium was present only at tracer levels in the heavy water used for the experiments. The project was terminated because of practical difficulties, and all equipment was removed shortly thereafter.

In the mid-1970s, experimental work was done in gloveboxes and hoods to develop processes for handling tritiated materials. The glovebox ventilation systems used heated uranium metal and copper metal stripper beds to remove tritium and oxygen from the containment atmosphere. It is conceivable that metal tritides could have been formed in these beds. Mercury diffusion pumps, backed by mechanical roughing pumps, were employed in the processing equipment.

All equipment, including the gloveboxes, hoods, pumps, and other process equipment was removed sometime in the early 1980s and sent to the burial ground. Monitoring of this area after removal of this equipment has revealed no indication of residual tritium contamination.

In 1987, an experimental program was initiated to study the effects of tritium exposure on the absorption-desorption characteristics of metal hydrides. In this program, samples of  $\text{LaNi}_{4.15}\text{Al}_{0.85}$ ,  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  (LANA),  $\text{LaNi}_{4.15}\text{Al}_{0.3}$ , and palladium were loaded with tritium and placed in dormant storage. At periodic intervals samples were taken from storage, and the tritium absorption-desorption characteristics were measured. The experimental program has produced information on these characteristics for the materials as a function of tritium exposure (Nobile and Motyka 1991).

A "cold" process demonstration facility began operation in November 1987. Materials that were used in the cold process included protium and deuterium but not tritium (Posey et al. 1987). The purpose of the cold process area was to demonstrate the metal hydride technology by integrating the various unit operations into an overall process (Motyka 1989). The cold process area was automatically controlled, with the equipment designed to be operated as an integrated process to simulate production, and as a series of one or more unit processes to prove out equipment. The continuous presence of an operator was not required during routine operations (Posey et al. 1987).

A variety of analytical measurements have been conducted on samples that have contained tritium. These samples have been, variously, liquids such as heavy-water reactor moderator, reactor cooling water, high-level waste tank supernate, or solids contaminated with the aforementioned liquids. While it is conceivable that tritiated solids could have been present in these samples, or that tritiated rust could have been formed from exposure of steel to the tritiated water, the tritium constitutes only a minor fraction of the radionuclides present. These other radionuclides represent a far more severe hazard from penetrating radiation, such as  $^{137}\text{Cs}$ , or from inhalation or ingestion, such as  $^{239}\text{Pu}$ .

When the overall activity levels have exceeded the limits for handling in the other laboratories, tritium-bearing materials were handled in shielded cells. These materials have included pieces of equipment contaminated with reactor moderator or coolant such as tubes or fittings that have been processed to decontaminate them to the point where they can be handled in other laboratories. Such decontamination has been accomplished by washing, rinsing, or degassing. Other materials that have been processed in these cells include high-level waste tank sludge and supernate. While it is conceivable that tritiated solids could have been present in these samples, or that tritiated rust could have been formed from exposure of steel to the tritiated water, the tritium constitutes only a minor fraction of the radionuclides present in these cells, either from these materials or from contamination with nontritiated materials processed in other jobs.

Mechanical testing (tensile strength, fracture toughness, yield strength, etc.) of metal samples that have been exposed to tritium is currently conducted. The samples are bulk samples (dimensions on the order of inches), and no particulates are generated or handled in this laboratory. Tritium is

present in the samples in the form of dissolved elemental tritium. Monitoring capabilities are present and detailed procedures are used to conduct all tests.

Metallographic techniques are currently used to prepare samples for, and to conduct, both scanning and transmission electron microscopy examinations. The metallographic preparation techniques involve cutting, sectioning, mounting, and polishing of the samples. It is conceivable that the cutting or sectioning could generate particulates with dissolved tritium. The polishing preparation is performed wet (with water) and does not generate any airborne particulates. The water is disposed of to a low-level drain. Mounting embeds the samples in a liquid plastic that hardens and holds the sample and the process generates no particulates.

Other current analyses in this area include the preparation of air samples from SRS facilities for analysis of tritium and  $^{85}\text{Kr}$ . The samples are received in a stainless-steel cylinder that contains a molsieve to trap the radionuclides. The sieve is baked to capture the moisture that could contain the tritium. The captured moisture is analyzed by LSC, after which it is disposed of to the low-activity waste tank. Only very low quantities of tritium are present. Presence or formation of significant quantities of tritiated solids is not considered credible.

## **5.0 POTENTIAL FOR METAL HYDRIDE EXPOSURE**

In general, readily dispersible or respirable-sized particles of metal tritides were not handled at SRS. With the exception of the metal hydrides that were examined within the SRTC, these materials were not handled outside their process containment vessels (Rabun 2000). Process beds containing tritium-exposed metal hydride powder were disposed of without removal of the powder from the bed. On rare occasion, however, it was necessary to remove some metal hydride powder from the process vessel in which it was originally contained (Nobile and Motyka 1991). For instance, a number of metal hydrogen absorbers were placed into tritium exposure to study the effect of tritium decay on the thermodynamics of the metal hydride system. Removal of the material from their respective process vessels was to be completed in a chemical hood and only after repeated cycles of evacuation, heating, and backfilling of the vessel with air (Nichols 1996). When these samples reached the end of life, they were discontinued in the program but retained for additional study. To make the samples available for further study, the metal powders must be removed from the sample vessels after procedures to remove as much tritium as possible and to passivate the metal surface with air (Walters 2006).

### **5.1 ENGINEERING CONTROLS**

Because tritium is classified as a byproduct material arising from the production of a special nuclear material, periodic inventories must be undertaken and the material must be accounted for as a waste product from any nuclear fuel processing operation (Baumann and MacMurdo 1977). Therefore, analytical determination of tritium in process streams is an integral part of the developmental program for alternate fuel cycle technology at SRS. All tritium inventories in process and product tanks, hydride and other beds, and process piping must be accounted for, which reduces the potential for an undocumented exposure.

As fine metal particles, metal hydrides can be very reactive to oxygen in air. Excessive air exposure for most metal hydrides leads to rapid oxidation that can reach red-hot temperatures. Based on this, it is reasonable to surmise that efforts would have been taken to limit air exposure to avoid reduction of the reactivity and the capacity for hydrogen absorption, as well as mitigating the potential for fire hazards (Heung 2001).

According to DOE, the primary condition that must be met for the potential exposure to STCs to exist is that tritium contamination is present at levels greater than one-tenth of the value in Appendix D of

10 CFR Part 835 (1,000 dpm/100 cm<sup>2</sup>). DOE guidance states that at levels less than one-tenth of this value, the potential for significant exposures is minimal and does not warrant action beyond standard practices (DOE 2015). Typically, the practices that are used to prevent release of tritium gas to the processing areas and to the environment have also served to prevent release of tritiated particulates and tritiated organics. Similarly, protection of the worker from contact with tritium gas and tritiated water also provides a high degree of protection from tritiated particulates (Rabun 2000).

For example, when handling those materials containing tritium as the only significant radionuclide, work was done in air-ventilated hoods dedicated to the handling of radioactive materials. Alternatively, work involving limited quantities could be conducted within a radiobench, an enclosure with the same shape as a glove box except that in there is an open area in place of the glove panel. For sufficiently low levels of tritium, work could be performed on an open benchtop. If the materials contain other radionuclides in quantities sufficient to present a hazard from penetrating radiation, then the work was done in the High Level Cells. These are highly contaminated with other beta/gamma materials. The ventilation systems for these hoods, radiobenches, and cells might also be contaminated (Howard 2000).

All metal hydrides SRS has used in tritium production and R&D have been contained in stainless-steel vessels. These process beds would have been disposed of without removal of the metal-exposed powders. Rather, the bed would be largely purged of residual tritium by repeatedly heating and evacuating the chamber and by isotopic exchange with deuterium (Nobile and Motyka 1991). In addition, all tritium operations in H-Area took place in one of 30 nitrogen-filled gloveboxes (Heung 1994b).

To reduce tritium loss to the environment, the production area uses a multilayered confinement system (Heung et al. 1991):

- Gloveboxes provide secondary containment. All tritium processing equipment is installed in sealed gloveboxes; tritium transfer lines outside the gloveboxes are contained in stainless-steel jackets; both the gloveboxes and the transfer line jackets are filled with a recirculating nitrogen atmosphere (Horen et al. 1993).
- Primary and secondary strippers clean up the glovebox atmosphere. The nitrogen is continuously circulated through a primary stripper system during normal operation to remove any tritium that might have escaped the process equipment; in the event of an accidental tritium release the nitrogen in that specific glovebox is circulated through a secondary stripper system to speed up the cleanup.
- Purge stripper further cleans up the purge gas. Nitrogen purge from the gloveboxes is further stripped of tritium in a purge stripper before it is released to the environment.
- Zeolite bed recovery system recovers the tritium. All the tritiated water accumulated in the stripper system is recovered through a zeolite bed regeneration system.

## 5.2 SHORTFALLS OF EXISTING CONTROLS

In May 2007, there were 30 containers of legacy tritium exposure samples of several metal tritides, limited to palladium, LANA, titanium, and a single gram-quantity sample of a zirconium alloy hydride. A small sample was removed from each for further analysis and the remainder was disposed of. This work was performed in a glovebox, but due to the particulate form of these materials it was recognized that the routine job coverage practices for gaseous tritium might not be adequate. For example, portable tritium air monitoring instruments are not capable of detecting the particulate tritides

because the filter should remove almost all of them before they reach the chamber (Moxley 2007). This shortfall can be largely overcome by counting the filters using LSC.

There are additional shortfalls for monitoring air samples using LSC, however, that are not specific to SRS. True activity intakes can be uncertain due to self-absorption of the weakly penetrating beta particles by the hydride material itself. In addition, activity collected and measured on filters tends to overrepresent the intake because of capture of nonrespirable particulates and dissolution in scintillation cocktail. The final shortfall to consider is self-absorption of tritium beta radiation due to dust loading of the filter (BWXT 2000).

## **6.0 DOSIMETRY CONSIDERATIONS**

Particulate SMTs can be ingested or inhaled and result in radiation dose. After ingestion, SMTs lose some fraction of their tritium as HTO in stomach digestive fluids. Some SMTs lose essentially all of the tritium and others lose very little, depending on the solubility of the specific material in the GI tract. In any case, the only significant dose after ingestion of SMTs is due to the released HTO. Because HTO is rapidly assimilated physiologically, this dose component is readily assessed via urine bioassay.

After inhalation, however, metal tritides can be deposited in the lung. Once deposited, the tritium bound to the particulate is removed from the body via two mechanisms:

1. Dissolution of tritium from the particulate and absorption into the body as HTO and removal through urine, expired air, and perspiration.
2. Mechanical transport of the particulate itself to the GI tract and removal through feces. Inhaled SMTs removed to the gut cause dose in the same manner as ingested SMTs as described above. Removal of these materials from the lung through mechanical transport can be slow depending on the solubility of the individual tritide. SMTs can therefore reside in the lung for a considerable amount of time and result in lung dose.

## **6.1 SOLUBILITY**

The dissolution rate of particles that are deposited in the respiratory tract is a major factor governing retention and translocation of their constituents to other organs in the body. Radioactive particles that dissolve slowly in lung fluid tend to remain in the lung tissue for long periods, and the biological effects of the particles are usually confined to the region near the deposition site (i.e., the lung tissue). On the other hand, highly soluble materials, such as HTO, that deposit in the respiratory tract are translocated to other organs and body fluid more readily and might therefore have a shorter retention time in the body.

The current understanding of some metal tritides is incomplete because the rate at which the material dissolves in the human respiratory tract is not known. DOE guidance is applied for the few metal tritides that have been studied. However, all the other metal tritides are currently grouped together and assumed to have "slow" dissolution behavior. This assumption might lead to overly conservative estimates of the dose an individual would receive in the event of an intake, which makes it desirable to characterize the dissolution rate of metal tritides of interest (Farfan et al. 2011).

Dissolution rates of some metal tritides have been measured by immersing the particles in various aqueous solutions and by determining the amount of dissolved radionuclides in the solution. For example, a sample of tritiated  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  similar to that used at the SRS Tritium Facilities was analyzed to estimate the particle size distribution of this metal tritide powder and the rate at which it dissolves in the human respiratory tract after inhalation. Samples were placed in serum ultrafiltrate

(SUF), an aqueous solution that contains various salts, and were enclosed in a static dissolution system to determine the dissolution rates. The in vitro dissolution apparatus measured the tritium in HT and in solution to account for the fact that the dissolved tritium in metal tritide could exist in HT or could exchange with protium in the water to form HTO.

The results of this experiment indicate that more than 99% of the tritium was released in 10 days as a result of the LANA matrix dissolving in the SUF and the tritium diffusing or offgasing from the matrix. This behavior is consistent with a dissolution type F (Farfan et al. 2011).

In a similar experiment, titanium tritide samples were ground into powders that were examined in an optical microscope, and particle size was determined using an image analyzer. SUF was used to determine the dissolution rates of metal tritides within a static dissolution system. The in vitro dissolution apparatus was designed to measure the tritium in the gas phase and in solution.

Retention of tritium in the lung in animal studies followed a bi-phase exponential decay with half-lives of 0.81 and 66 d. In rats, 37%, 29% and 16% of the tritium were excreted by urine, feces, and expired air after 121 d, respectively. Tritium associated with titanium tritide was eliminated in this study with an average biological half-life of 50 d, suggesting that titanium tritide may be classified with an ICRP absorption type of M (Cheng et al. 1999). Subsequent research confirmed that the dissolution rate of metal tritides can be expressed as a two-component decay curve representing the fast and slow phases of retention. The updated fast phase for titanium tritide was found to yield a 1-day biological half-time, with the slow phase yielding a 33-day half time. These values correspond to an ICRP absorption type of somewhere between F and M (Zhou 2004).

There is some disagreement over the solubility of zirconium hydride. Using the same experimental procedure, zirconium powder was purchased and ground to respirable sizes (1 to 3  $\mu\text{m}$ ) in a ball mill at Lovelace Respiratory Research Institute. A sample of the material was then tritiated at the Pinellas Plant, after which the fine powders were examined and electron photomicrographs were taken under a transmission electron microscope to determine the activity median aerodynamic diameter of the particles. Similar to the procedures in the LANA solubility studies, samples of the hydride were placed in SUF and enclosed in a static dissolution system to determine the dissolution rates. The in vitro dissolution apparatus measured the tritium in the gas phase (HT) and in solution (Zou et al. 2010).

The dissolved pattern was characterized by an initial fast-rate release of tritium that slowed with time. Total dissolved tritium in 71 days accounted for 37.2%  $\pm$  1.3% of the initial tritium present in the particles; 65% of the total dissolved tritium was released after the first month of dissolution. The retention half-times for tritium as calculated from the dissolution rate constants are 42 and 385 days for the fast and slow phases of the retention function, with an overall half-time of 114 days. The results indicate that the ZrT is a poorly soluble material (Zou et al. 2010). A similar study by Zou and Cheng (2004), however, concluded that the dissolution rate of ZrT ranked between Types M (moderate) and F (fast) materials.

For materials that have not explicitly been tested for solubility, the tendency for tritium to desorb from the material can be estimated with knowledge of the enthalpy of the material. Very stable hydrides have a large negative reaction enthalpy and dissociate only at high temperatures. A summary of the absorption types of the metal tritides considered in this paper is presented in Table 6-1. Note that none of the materials considered have an ICRP absorption type of S, indicating a very insoluble material.



Table 6-1. Absorption types of representative metal tritides.

| SMT                     | Absorption type |
|-------------------------|-----------------|
| LANA                    | F               |
| Palladium               | F               |
| Palladium-aluminum      | M               |
| Palladium-silver        | F               |
| Titanium                | M               |
| Uranium                 | F               |
| Zirconium               | M               |
| Zirconium-iron-chromium | M               |

## 6.2 SAMPLE SELF-ABSORPTION

The radiation dose to tissue from metal tritide particles depends on their solubility and retention in the body. In each tritide particle, a portion of the beta particles from decay of tritium is absorbed by the metal matrix and therefore cannot contribute to absorbed radiation dose to tissue. The betas originating inside a particle can be absorbed before reaching the particle surface, a phenomenon referred to as self-absorption (Lantz and Steward 1988). To determine dose to the lung from metal tritide particles imbedded in the lung, and to correct LSC of bioassay samples that contain metal tritide particles, the self-absorption of the tritium betas by the tritide particle should be considered. Because the tritium betas are of such low energy (average 5.7 keV), self-absorption in a metal tritide particle even as small as 1  $\mu\text{m}$  is significant. The self-absorption factor (SAF), the fraction of beta particles that escapes from a particle, can be found for spherical particles by numerical integration (Tsoulfanidis 1991, as referenced in Kropf et al. 1998). Similarly, when analyzing air monitoring samples for metal tritide using LSC, it is necessary to consider SAF because STCs do not dissolve appreciably and release tritium to LSC cocktail. Only beta radiation that escapes the particles in LSC cocktail is available for detection. The SAF is used to estimate the "true" STC activity that would be "observed" when samples are counted via LSC.

Research has suggested that bremsstrahlung photons, created when beta particles are self-absorbed, are not expected to be a significant contribution to dose from tritiated particulates (DOE 2004).

## 6.3 DETERMINATION OF INTAKES FROM EXISTING DATA

To determine an individual's dose from tritium, an intake assessment usually relies on bioassay. However, due to the insoluble nature of SMTs and the fact that an established fecal bioassay protocol is not currently available for these materials, the intake amount can better be determined from measurements of SMT concentration in the air or from assumed resuspension of surface contamination.

### 6.3.1 Air Sampling Data

Air monitoring can be used to estimate intake directly, as opposed to the indirect bioassay methods. Particle size and dissolution rate variabilities have minor effects on intake determination via air monitoring. Intake is considered to be proportional to the true activity captured on the filter of an air sampling device. Particulates tend to shield their tritium beta activity by self-absorption of the beta radiation within the mass of particulate. Observed activity on a filter sample, measured by suspending particulates from the filter into LSC solution, therefore underrepresents the true activity available for deposition to the lung (i.e., intake). However, when tritiated particulate intake is defined in terms of observed activity (and when the dose conversion factor is correspondingly defined in terms of observed activity intake), the uncertainty in that observed intake essentially disappears because self-absorption is no longer a concern.

### **6.3.2 Surface Contamination Data**

Removable surface contamination can produce elevated airborne contamination due to resuspension. The fraction of surface contamination that can be resuspended is highly dependent on the type of activities in the contaminated area. The most widely used method for quantifying tritium contamination on smear and air samples is LSC. Although this technique gives acceptable results for tritium forms that are soluble in LSC cocktail (e.g., HTO), it generally underestimates the true tritium activity if STCs are present. Therefore, consideration of sample self-absorption is necessary.

## **7.0 CONCLUSION**

Various metal tritides are encountered at SRS Tritium Facilities. In the early 1980s, Savannah River Laboratory began a major program to develop and use metal hydrides in tritium production. Metal tritides are metals that absorb and store tritium atoms in the crystalline structure of the metal. When a metal tritide is inhaled, the lungs retain the material, which slowly releases tritium. This release of tritium occurs as the metal tritide particles dissolve and the tritium diffuses out. Once the tritium is released from the metal tritide particle, it is assumed to be converted to HTO and subsequently behave according to the HTO biokinetic model.

Metal hydrides turned out to be ideally suited for tritium handling and processing. These metals include uranium, palladium, titanium, lanthanum-aluminum-nickel tritide, mischmetal, and zirconium. In general, tritides at SRS can generally be characterized as readily soluble metal tritides. Evaluations of the physical and chemical properties of these tritium compounds have shown that uranium and palladium do not bind tritium in a manner significantly different from tritium oxide. Therefore, they are not considered STCs. The remaining metals form compounds that cannot be adequately assessed using the tritium oxide urine bioassay model and therefore are classified as STCs.

As stated in OTIB-0066, in the vast majority of occupational exposures to tritium it is not possible to identify the tritium compound taken into the body based on the observed urinary excretion. Therefore, the selection of the appropriate tritium compound in an intake evaluation must usually be based on process knowledge of the source terms in the workplace. The material presented in this paper, and the classified notes associated with this paper, describes the types of SMTs used at SRS, the locations at which these materials could be encountered, and the time frames during which these materials were handled. This information, when coupled with existing tritium bioassay data and the methods presented in OTIB-0066 should be sufficient to bound metal hydride doses at SRS.

## REFERENCES

- Antonov, V. E., M. Baier, B. Domer, V. K. Fedotov, G. Grosse, A. Kolesnikiv, E. G. Ponyatovsky, G. Schneider, and F. E. Wagner, 2002, "High-Pressure Hydrides of Iron and its Alloys," *Journal of Physics: Condensed Matter*, volume 14, number 25, pp. 6427–6445. [SRDB Ref ID: 163825]
- Baumann, E. W. and K. W. MacMurdo, 1977, *Determination of Tritium in Solutions from Nuclear Fuel Reprocessing*, DP-MS-77-36, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, South Carolina, January 1. [SRDB Ref ID: 163826]
- Beavis, L. C., and C. J. Miglionico, 1972, "Structural Behavior of Metal Tritide Films," *Journal of the Less Common Metals*, volume 27, issue 2, pp. 201–211. [SRDB Ref ID: 90498]
- Bebbington, W. P., 1990, *History of du Pont at the Savannah River Plant*, E. I. du Pont de Nemours and Company, Wilmington, Delaware. [SRDB Ref ID: 11249]
- Birchenall, A. K., 1992, *RTF Glovebox Stripper Regeneration Development*, WSRC-TR-92-530, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 83981]
- Blackburn, G. W., 1994, *History of 232-F, Tritium Extraction Processing*, WSRC-IM-94-39, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 12094]
- Bond, W. O., J. C. Mailen, and G. E. Michaels, 1992, *Evaluation of Methods for Decladding LWR Fuel for a Pyroprocessing-Based Reprocessing Plant*, ORNL/TM-12104, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October. [SRDB Ref ID: 163827]
- Bradley, R. F., 1983, *Metal Hydride/TCAP Program at Savannah River*, DP-MS-84-9, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, South Carolina, November. [SRDB Ref ID: 84822]
- Buley, R. D., D. J. Green, and J. Metzler, 1995, *Tritium Processing and Containment Practices at the Savannah River Site*, WSRC-MS-95-0083P, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 59922]
- BWXT (Babcock & Wilcox Technologies of Ohio), 2000, *Mound Technical Basis Document for Stable Tritiated Particulate and Organically Bound Tritium*, MD-10516, Issue 0, Miamisburg Environmental Management Project, Miamisburg, Ohio, March 23. [SRDB Ref ID: 32921]
- Caracciolo, V. P., and A. A. Kishbaugh, 1964, *Electrolytic Dissolver for Power Fuels*, DP-896, E. I. du Pont de Nemours and Company, Savannah River Plant, Aiken, South Carolina, October 1. [SRDB Ref ID: 163829]
- Cheng, Y., 1993, "Dissolution Rate and Radiation Dosimetry of Metal Tritides," p. K-15, *Department of Energy 1993 Radiation Protection Workshop Proceedings, Las Vegas, Nevada, April 13-15, 1993*, Office of Health and Nevada Field Office, Las Vegas, Nevada, December. [SRDB Ref ID: 45955]
- Cheng, Y., Snipes, M. B., Wang, Y., Jow, H. 1999, "Biokinetics and Dosimetry of Titanium Tritide Particles in the Lung," *Health Physics*, volume 76, number 2, pp. 120–128.

- Clark, E. A., D. A. Dauchess, L. K. Heung, R. L. Rabun, and T. Motyka, 1995, *SRS History and Experience with Palladium Diffusers*, WSRC-TR-94-0412, Rev. 1, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 163830]
- Crowder, M. L., J. E. Laurinat, and J. A. Stillman, 2010, *Measurement of Tritium During Voloxidation of Zircaloy-2 Fuel Hulls*, SRNL-STI-2010-00608, *Nuclear Technology*, October 14. [SRDB Ref ID: 163832]
- DOE (U.S. Department of Energy), 2015, *DOE Standard: Radiological Control Programs for Special Tritium Compounds*, DOE-STD-1129-2015, Washington, D.C., September. [SRDB Ref ID: 164261]
- DOE (U.S. Department of Energy), 2016, *Final Supplemental Environmental Impact Statement for the Production of Tritium in a Commercial Light Water Reactor*, DOE/EIS-0288-S1, National Nuclear Security Administration, Washington, D.C., March. [SRDB Ref ID: 163623]
- DuPont (E. I. du Pont de Nemours and Company), 1973, *Savannah River Plant History: Separations Areas, July 1954 through December 1972*, Savannah River Plant, Aiken, South Carolina. [SRDB Ref ID: 48560]
- EPA (U.S. Environmental Protection Agency), 1999, *CATC Technical Bulletin: Choosing an Adsorption System for VOC: Carbon, Zeolite, or Polymers?*, EPA-456/F-99-004. Clean Air Technology Center (MD-12) Information Transfer and Program Integration Division Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, North Carolina, May. [SRDB Ref ID: 165205]
- Farfan, E. B., T. R. LaBone, G. C. Staack, Y. S. Cheng, Y. Zhou, and T. P. Varallo, 2011, *Determination of In-Vitro Lung Solubility and Intake-to-Dose Conversion Factor for Tritiated Lanthanum Nickel Aluminum Alloy*, SRNL-STI-2011-00587, Savannah River Nuclear Solutions, Savannah River National Laboratory, Aiken, South Carolina. [SRDB Ref ID: 128544]
- Hale, L. M., B. M. Wong, J. A. Zimmerman, and X. W. Zhou, 2013, "Atomistic Potentials for Palladium-Silver Hydrides," *Modeling and Simulation in Materials Science and Engineering*, volume 21, number 4, 45005. [SRDB Ref ID: 163833]
- Heung, L. K., 1994a, *Titanium for Long-Term Tritium Storage*, WSRC-TR-94-0596, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 84122]
- Heung, L. K., 1994b, *Stripper System Performance in the Replacement Tritium Facility*, WSRC-MS-94-0470, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 87644]
- Heung, L. K., 2001, *Design of Metal Hydride Vessels for Processing Tritium*, WSRC-MS-2001-00179, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 45954]
- Heung, L. K., R. H. Hsu, J. L. Rice, and T. S. McGee, 2004, *Performance Improvements of a Tritiated Water Recovery System*, WSRC-MS-2004-00088, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 163834]

- Heung, L. K., J. H. Owen, R. H. Hsu, R. F. Hashinger, D. E. Ward, and P. E. Bandola, 1991, *Tritium Confinement in a New Tritium Processing Facility at the Savannah River Site*, WSRC-MS-91-049, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 84075]
- Horen, A., S., T. Motyka, M. J. Montini, and R. F. Hashinger, 1993, *Startup Status of the Replacement Tritium Facility at the Savannah River Site*, WSRC-MS-93-282, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 83989]
- Howard, D. W., 2000, "Special Tritium Compounds in the Savannah River Technology Center," memorandum to N. D. Johnson, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina August 3. [SRDB Ref ID: 94505].
- Hsu, R. H., and L. K. Heung, 1997, *Confinement and Stripping Systems for APT Tritium Processing*, WSRC-RP-97-00887, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 79410]
- Hsu, R. H., and L. N. Oji, 1997, *Tritium Facilities Modernization and Consolidation Project Process Waste Assessment, Project S-7726, Waste Assessment and Treatment and Disposal Option Assessment*, WSRC-TR-97-00368, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina, November 14. [SRDB Ref ID: 83973]
- IAEA (International Atomic Energy Agency), 2004, *Management of Waste Containing Tritium and Carbon-14*, Technical Report Series No. 421, Vienna, Austria.
- Klein, J. E., 2001, *A 1600 Liter Tritium Hydride Storage Vessel*, WSRC-MS-2001-00247, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 84023].
- Klein, J. E., and J. S. Holder, 2005, *SAES St 909 Getter Testing at the Savannah River National Laboratory: Bench, Pilot and Full Scale Tests*, WSRC-MS-2005-00450, Savannah River National Laboratory, Aiken, South Carolina. [SRDB Ref ID: 163835]
- Kropf, R. F., Y. Wang, and Y. S. Cheng, 1998, "Self-Absorption of Tritium Betas in Metal Tritide Particles," *Health Physics*, volume 75, number 4, pp. 398–404. [SRDB Ref ID: 76828]
- Laesser, R., 1989, *Tritium and Helium-3 in Metals*, Springer-Verlag Berlin, Berlin, Germany.
- Lantz, M. W., and J. B. Steward, 1998, "Accounting for the Self-Absorption of Betas in Cobalt-60 Hot Particles," *Radiation Protection Management*, volume 5, pp. 25–29.
- Lindner, C. N., R. E. Burnham, C. Chiappetto, B. T. Snider, and R. N. Lutz, 2004, *Transport & Disposal of Tritium Producing Burnable Absorber Rods at the Tritium Extraction Facility*, WSRC-MS-2004-00840, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina. [SRDB Ref ID: 84051]
- Louthan, M. R., 2008, "Hydrogen Embrittlement of Metals: A Primer for the Failure Analyst," *Journal of Failure Analysis and Prevention*, volume 8, issue 3, pp. 289–307. [SRDB Ref ID: 163807]
- Motyka, T., 1989, *Advanced Hydride Laboratory*, WSRC-RP-89-69, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina. [SRDB Ref ID: 163837]

- Motyka, T., E. A. Clark, D. A. Dauchess, L. K. Heung, and R. L. Raburn, 1995, *Experience with Palladium Diffusers in Tritium Processing*, WSRC-MS-95-0048, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina. [SRDB Ref ID: 84124]
- Moxley, J., 2002, "Radiological Control Program for Special Tritium Compounds," memorandum to D. P. Potocik, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina June 27. [SRDB Ref ID: 45992]
- Moxley, S. J., 2007, "Radiological Controls for Handling Legacy Tritium Exposure Samples from the Metal Hydride Test Cell," memorandum to D. P. Potocik, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina, May 15. [SRDB Ref ID: 84856]
- Mozin, V., 2008, "Options for Hydride Fuels Reprocessing," *Joint International Workshop: Nuclear Technology and Society – Needs for Next Generation*, University of California-Berkeley, Berkeley, California. [SRDB Ref ID: 163838]
- Nichols, G. S., 1996, *Procedure for Removing of Used Metal Hydrides*, Westinghouse Savannah River Company, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina, October 7. [SRDB Ref ID: 84854]
- Nobile, A., and T. Motyka, 1991, *Disposal of Tritium-Exposed Metal Hydrides*, WSRC-TR-91-391, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, South Carolina. [SRDB Ref ID: 84117]
- Nobile, A., W. C. Mosley, J. S. Holder, and K. N. Brooks, 1994, "Deuterium Absorption and Material Phase Characteristics of  $Zr_2Fe$ ," *Journal of Alloys and Compounds*, volume 206, issue 1, pp. 89–93. [SRDB Ref ID: 163805]
- ORAUT (Oak Ridge Associated Universities Team), 2007, *Calculation of Dose from Intakes of Special Tritium Compounds*, ORAUT-OTIB-0066, Rev. 00, Oak Ridge, Tennessee, April 26.
- Ortman, M. S., L. K. Heung, A. Nobile, and R. L. Rabun, 1989, "Tritium Processing at the Savannah River Site: Present and Future," *Journal of Vacuum Science & Technology A*, volume 8, number 3, pp. 2881–2889. [SRDB Ref ID: 76826]
- Posey, W. N., A. R. Moche, T. Motyka, and W. A. Roberson, 1997, "Safety Evaluation of the Advanced Hydride Laboratory in Building 773-A," memorandum to T. L. Capeletti, Technical Division, Westinghouse Savannah River Company, Savannah River Laboratory, Aiken, South Carolina, July 10. [SRDB Ref ID: 84833]
- Rabun, R. L., 2000, "Special Tritium Compounds in the SRS Tritium Facilities," memorandum to D. P. Potocik, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina, August 25. [SRDB Ref ID: 94447]
- Richardson, R. B., and A. Hong, 2001, "Dose to Lung from Inhaled Tritiated Particles," *Health Physics*, volume 81, number 3, pp. 313–324. [SRDB Ref ID: 163839]
- Rudisill, T. S., and J. L. Mickalonis, 2006, *Decontamination of Zircaloy Spent Fuel Cladding Hulls*, WSRC-TR-2006-00321, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina, September 27. [SRDB Ref ID: 163804]

- Scallon, K. L., and J. L. England, 1994, *D&D Characterization of the 232-F Old Tritium Facility at the Savannah River Site*, WSRC-TR-94-0545, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 45952]
- Schober, T., H. Trinkaus, and R. Lasser, 1986, "A TEM Study of the Aging of Zr Tritides," *Journal of Nuclear Materials*, volumes 141–143, Part I, pp. 453–457.
- Schober, T., 1988, "Aging Induced Property Change in Metal Tritides," *Fusion Science and Technology*, volume 14, number 2P2A, pp. 637–642.
- Schober, T., and K. Farrell, 1989, "Helium Bubbles in  $\alpha$ -Ti and Ti Tritide Arising from Tritium Decay: A TEM Study," *Journal of Nuclear Materials*, volume 168, issues 1–2, pp. 171–177.
- Scogin, J. H., and A. S. Poore, 1994, *Startup and Operation of a Metal Hydride Based Isotope Separation Process*, WSRC-MS-94-0488, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 83958]
- Shanahan, K. L., 1998, *FY97 Status Report on the HSV and Titanium Tritide Samples*, WSRC-TR-98-00067, Westinghouse Savannah River Company, Savannah River Site, Aiken, South Carolina. [SRDB Ref ID: 83940]
- Shmayda, W. T., 2005, "Technologies for Mitigating Tritium Releases to the Environment," *Laboratory for Laser Energetics Review*, University of Rochester, volume 103, pp. 142–154. [SRDB Ref ID: 163840]
- Stier, W., L. G. Camargo, F. Oskarsson, and H. Jonsson, 2005, "Hydrogen Storage in Magnesium-Based Alloys," *American Chemistry Society*, volume 50, number 1, p. 15. [SRDB Ref ID: 163808]
- Walters, R. T., 2006, *Estimating the Hazard from Inhaling the Resuspendable Fraction of a Metal Tritide Powder*, WSRC-TR-2006-00337, Westinghouse Savannah River Company, Savannah River National Laboratory, Aiken, South Carolina, September 26. [SRDB Ref ID: 84859]
- Zou, Y., and Y. S. Cheng, 2004, "Dosimetry of Metal Tritide Particles as Evaluated by the ICRP 66 Model and a Biokinetic Model from Laboratory Rats," *Health Physics*, volume 86, number 2, pp. 155–160.
- Zou, Y. and Y. S. Cheng, 2010, "Dissolution Rate and Biokinetic Model of Zirconium Tritide Particles in Rat Lungs," *Health Physics*, volume 98, number 5, pp. 672–682. [SRDB Ref ID: 163806]