SAFE AND COMPACT STORAGE AND TRANSPORTATION OF TRITIUM AS TITANIUM TRITIDE

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ABSTRACT

The development program carried out at Chalk River Nuclear Laboratories (CRNL) on the immobilization of separated tritium from the heavy water of CANDU reactors for long-term storage has been completed. The program included the construction and operation of a laboratory facility to handle, immobilize and package tritium, an investigation of the properties and release of tritium from the titanium metal chosen to immobilize the tritium, and the design and testing of a transport container for licensing as a Type B package. The results of this experimental and testing program are summarized. They demonstrate the suitability of titanium for long-term storage and transportation of tritium.

INTRODUCTION

Atomic Energy of Canada Limited and Ontario Hydro are presently constructing plants to remove tritium from heavy water and concentrate it to T_2. These plants will reduce operator exposure and tritium emissions from operating reactors. The recovered tritium must be safely packaged for long-term storage. Packaging tritium as a solid metal tritide is preferred over gaseous tritium because of the concern for leakage of the gas. Uranium has been used extensively for short-term storage and transportation of tritium; however, it has the disadvantage of producing very fine particles upon hydriding and dehydriding which are pyrophoric in air. For long-term storage, titanium and zirconium were the prime metal candidates because the hydrides are easily prepared yielding a high hydrogen (tritium) density, stable in air and water, and the hydrogen (tritium) can be recovered, if required. Titanium metal was selected over zirconium primarily because the tritium could be recovered at a somewhat lower temperature.

PREPARATION OF TITANIUM TRITIDE

The development program has centred on the use of titanium metal sponge for long-term storage of tritium with the potential to recover the tritium for future use. Because the handling of concentrated tritium requires special safety precautions, the program has focused on developing a fast and simple reaction procedure. The sponge form of titanium metal is used instead of a massive solid (bar) because of the large available surface area. Powders have not been used because of safety concerns for the small metal tritide particles which could be more easily dispersed.

The titanium tritide sponge product is prepared by first activating the sponge surface by vacuum annealing, and then reacting the tritium gas directly with the sponge initially at room temperature (1). Tests carried out with titanium sponge contained in a prototype reaction vessel designed for use in the CRNL Tritium Extraction Plant have demonstrated a fast reaction (order of minutes) between tritium and activated titanium sponge. The sponge has maintained its activity throughout a 28 month test period as four aliquots of tritium, totalling 148 TBq (4000 Curies), have been added over this period without any additional heating of the sponge. A similar batch-type process will be used to fill the storage vessels in the Tritium Extraction Plant.

The CRNL Tritium Laboratory (2) has been designed and constructed as part of this program. It has been used to prepare various titanium tritide samples and to demonstrate the packaging of tritium in a prototype storage vessel. The laboratory has also been used to develop the technical skills necessary for handling pure T_2. All operations with concentrated tritium are carried out in a high integrity stainless steel vacuum system located inside of an inert atmosphere glove box. Various tritium analysis techniques and an extensive tritium monitoring system are also used. The operating procedures developed have demonstrated the safe preparation of high specific activity titanium tritides.

REACTIVITY IN AIR

For long-term storage of titanium tritide, the consequences of container failure must be addressed. In this event, the tritide would be exposed to air and moisture. The potential for release of tritium in these circumstances has been examined (3).

The titanium sponge used for immobilization of tritium (nominal particle size 2-6 mm) is stable in air at normal temperatures. Typically ignition occurs at 600-650°C. However, the reactivity of metal hydrides in air increases with decreasing particle size and increasing temperature. Because the hydriding procedure results in volume expansion of the metal and a brittle product, the possible production of fine particles was investigated. Production of fine particles by multiple hydriding-dehydriding cycles (up to 10 cycles), showed only a very slight increase in fine particles. This is illustrated in Figure 1. Most of the observed change was due to manually breaking up the samples between hydriding and dehydriding. The fragmentation of titanium hydride ($TiH_{1.0}$) was investigated by subjecting a sample to four weeks on a wrist-action shaker to simulate vibration that may be received during transportation. Some size reduction was observed, primarily in the first week, after which the particle size distribution remained unchanged. Only about 10 weight percent of the particles were reduced to less than 38 μm after the testing procedure.

The ignition temperature of both titanium sponge and its hydride in air was measured for each particle size fraction obtained from sieve analysis of a typical sponge sample using a technique developed by Evans (4). These results showed a reduction in ignition temperature from 600-650°C to 400-450°C over the particle size range from 9.5 mm to less than

38 μm. There was no evidence of spontaneous ignition at room temperature for any of the samples of either titanium sponge or titanium hydrides prepared from the sponge with stoichiometric compositions in the range from $TiH_{0.6}$ to $TiH_{1.4}$.

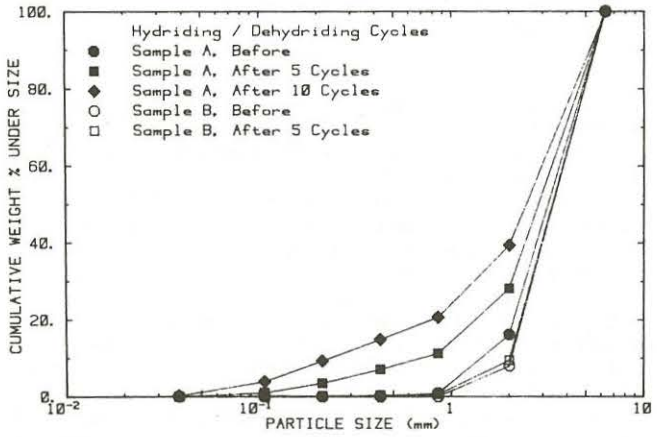

FIGURE 1: EFFECT OF MULTIPLE HYDRIDING/DEHYDRIDING CYCLES ON PARTICLE SIZE DISTRIBUTION OF Ti SPONGE. SAMPLE A WAS MANUALLY BROKEN UP BETWEEN HYDRIDING AND DEHYDRIDING.

To determine how fine the particle size must be for room temperature ignition, more severe mechanical size reduction techniques were used. Manual crushing of $TiH_{1.7}$ using a mortar and pestle resulted in only 30 weight percent under 10 μm, as determined by a Sedigraph Particle Size Analyser. The ignition temperature of this sample was 445°C. The ignition temperature decreased as the particle size was reduced in a Shatterbox, in which the sample was spun with a hardened steel puck and ring at 900 rpm. A titanium hydride sample ignited spontaneously after 10 minutes of testing in the Shatterbox. Subsequent particle size analysis showed the sample had 80% by weight of the particles under 10 μm. This severe action is not likely to occur in handling and transportation of the titanium tritide product.

REACTIVITY IN WATER

The leaching behaviour of high specific activity titanium tritide was examined to assess the chemical stability of this product in an aqueous environment. Complete details of the test program are documented in References 5 and 6. Specially prepared titanium tritide sponge samples were placed in deionized water at room temperature in closed vials and the release monitored for ~180 days.

The cumulative fractional release of tritium into the leachant (as HTO) is shown in Figure 2, and that into the atmosphere above the leachant (as HT) is shown in Figure 3. The major difference in the Series A and B samples, identified in the figures, was in the set-up of the tests. The Series A samples were transferred directly to the leach test vessels after they were prepared while the Series B samples were left exposed to atmosphere in a special air atmosphere glove box to promote the release of tritium adsorbed on the sponge surface prior to beginning the leach tests. The effect of this surface-adsorbed tritium on the cumulative fractional release is evident in Figures 2 and 3 (compare Series A and B $TiT_{1.0}$ samples).

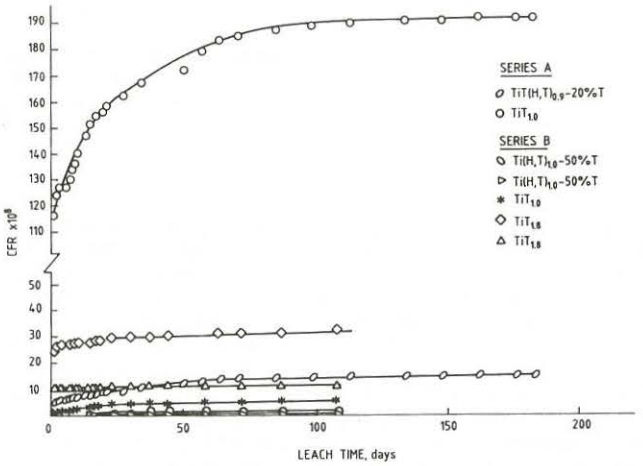

FIGURE 2: CUMULATIVE FRACTIONAL RELEASE (CFR) OF ^3H (AS HTO) FROM TITANIUM TRITIDE

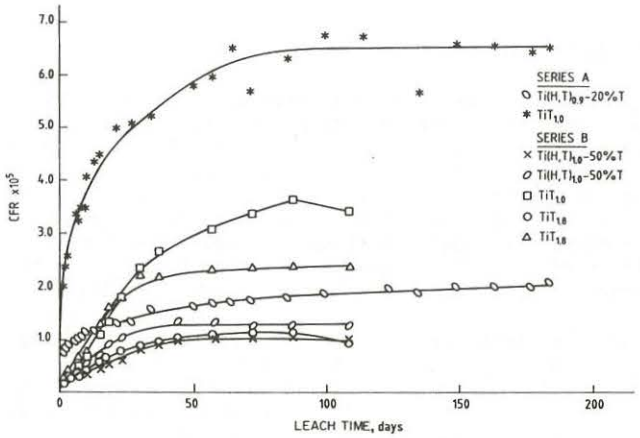

FIGURE 3: CUMULATIVE FRACTIONAL RELEASE (CFR) OF ^3H (AS HT) FROM TITANIUM TRITIDE

A cumulative fractional release of tritium as HTO of the order of 10^{-5} was obtained after 100 days of testing with tritium/titanium ratios up to $TiT_{1.8}$. The cumulative fractional release of tritium in the elemental form into the air atmosphere above the leachant was in the order of 10^{-6} - 10^{-8} for the same test period and samples. The variability observed in the results from samples hydrided to the same final ratio and/or with the same gas composition was likely due to different surface characteristics and the amount of surface adsorbed tritium. The elemental tritium resulted from the release of either adsorbed tritium and/or from the corrosion reactions which produce titanium oxide and/or hydroxide and tritium gas. Because the tritium release into the water was much higher, the indication was that isotopic exchange was the predominant release path for tritium from titanium tritide samples in an aqueous environment. However, the samples were discoloured from an original silver-gray to dark brown/black indicating formation of a surface oxide. This surface oxide (or hydroxide) and/or a decrease in the amount of surface-adsorbed tritium was likely responsible for the decrease in the release rate of both species with time.

STORAGE AND SHIPPING PACKAGING

The titanium tritide will be stored in a stainless steel vessel which will serve both as a reaction vessel and a storage vessel. The vessel is designed to contain the tritium and the helium-3 produced from total decay of the tritium. It also provides for retreival of the tritium and helium-3 at some future date. The vessel is fabricated from 316 L stainless steel, which was chosen for this application after evaluation by Ells and co-workers (7,8). It is an all-welded construction and equipped with two all-welded bellows sealed valves to provide a flow path during hydriding and during recovery. Stainless steel filters (20 μm) are included on the inlet and outlet to prevent transfer of any fine titanium tritide particles. A schematic of the ~6.5 L vessel is shown in Figure 4. The volume of the titanium tritide is only 1.5 L, with the remaining volume being required to contain the helium-3. The vessel will contain up to 18.5 PBq (500 000 Curies) of tritium in 850 g of titanium sponge, at an average tritium/titanium ratio of 1.0 ($TiT_{1.0}$). At normal storage conditions, loss of tritium from this vessel by leakage or permeation will be negligible because of the low equilibrium pressure of tritium ($\sim 10^{-12}$ Pa) and the low temperature (25°C). The shipping package, which has been designed to the Type B (u) shipping requirements of the Canadian Transport Regulations, consists of this primary containment vessel, a flanged stainless steel secondary containment vessel and a drum type overpack that provides impact and fire resistance for the radioactive contents. The total mass is approximately 200 kg. This assembly is shown schematically in Figure 5.

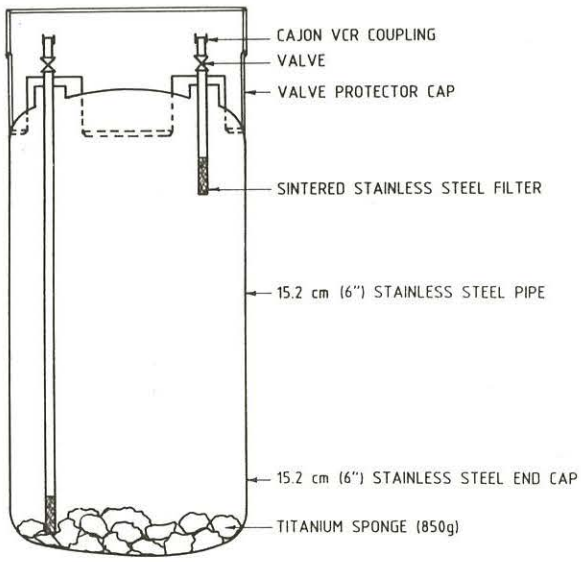

FIGURE 4: SCHEMATIC OF REACTION/STORAGE VESSEL

Because the radioactive material will generate a decay heat of up to 17 W, temperature profiles across the package have been established. With a 17 W heater inserted into the titanium sponge, the wall temperature of the primary containment vessel ranged from 46°C near the bottom to 62°C near the top (a distance of 25 cm). A temperature of 41°C was recorded at the centre height of the secondary vessel wall, and decreased to 25°C in the thermal/impact absorbing material, 4 cm from the outer wall of the overpack.

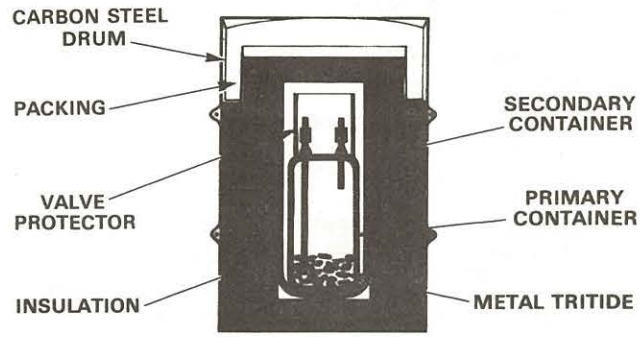

FIGURE 5: TRITIDE TRANSPORTATION PACKAGE

The destructive testing program is the last phase of testing being carried out to obtain a transportaation license. Two prototypes will be tested destructively to demonstrate that both the inner and outer containment vessels will remain helium leak tight (10^{-8} Pa·m³·s⁻¹). The first has been subjected to a "crush test", in which a 500 kg steel plate is dropped from 9 m onto the package sidewall, and a 1 m drop test onto a 15 cm diameter steel pin. It will now be subjected to the thermal test, i.e. 800°C for 30 minutes, at the CRNL Fire Test Facility which burns kerosene in an open fire. Similarly, the second prototype will be dropped onto its top rim from 9 m, then onto the steel pin and finally fire tested.

CONCLUSIONS

The development program on the immobilization of tritium has demonstrated that titanium sponge metal is a safe and compact storage and transportation medium for tritium.

Safe handling techniques have been developed and demonstrated for the preparation of the titanium tritide product. Leach testing and reactivity in air studies have indicated that titanium tritide is a stable compound under normal storage conditions and in the event of failure of the primary containment vessel and exposure to air and water. Tests on a transportation package for 18.5 PBq (500 000 Curies) are being completed in order to obtain a Type B license.

ACKNOWLEDGEMENT

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