Tritium Recovery From Mixed Waste - 17004

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ABSTRACT

Nuclear Sources and Services (NSSI) in Houston, TX houses a unique infrastructure to recover tritium from a variety of different streams for re-use. NSSI accepts gaseous, aqueous, and tritiated-solid feedstock. For example, titanium-tritide foils from spent neutron generator sources are detritiated at 1000 °C. Tritium gas is recovered from a variety of metal getter beds. Tritiated liquid that is desorbed from zeolite drier beds or generated while reconditioning nickel beds is transferred to a Combined Electrolysis Catalytic Exchange (CECE) system to concentrate the tritium fraction before the gas is transferred to a hydrogen isotope separator for enrichment. Mixed-waste liquids, typically generated in the pharmaceutical industry, are converted to tritiated water and inactive gaseous effluents using a high-temperature, two-stage, catalytic-oxidation destruction process. The destruction efficiency of solvents is extremely high, typically in the 99.9999% to 99.99999% range. The resultant water containing tritium is also directed to the CECE subsystem. At present, liquid activities ranging from the 0.37 MBq/L (10 µCi/L) to 740 GBq/L (20 Ci/L) can be processed economically. The CECE subsystem has detritiated 2 metric tons of heavy water per year and is designed to detritiate up to 30 metric tons of light water per year. NSSI is licensed to operate within a 2-gram tritium inventory limit.

Recently the Mixed-Waste Oxidation Facility that can process up to 40 liters of liquid per day has been upgraded to reduce the corrosive effects of halogen-based mixed wastes on the effluent scrubbing system. This paper will outline the key features of this system and discuss the effectiveness of the upgrades and the operational parameter space.

INTRODUCTION

The tritium facility at NSSI in Houston, Texas shown in Figure 1 below was designed with the philosophy of recycling tritium back into the research community instead of ground disposing. In order to achieve these ends a variety of systems were installed to handle the wide variety of tritiated wastes that were in the disposal market. The NSSI facility is currently operating under a commercial recycling license for all processes except for the mixed waste oxidation system (MWOS) which is undergoing the last stages of research and development with the treatment of real world waste to characterize the process for final approval.
The first process installed in 1999 is a high temperature thermal desorption system (TiT2) that is able to desorb, process and capture tritiated gas from a variety of metal hydrides such as titanium. These foils are generally used in neutron sources.

The next process installed in 2000 was a hydride bed unloading station that is able to recover tritium from a broad array of getter beds. This includes metal hydride beds containing depleted uranium (DU), zirconium-iron alloy (ZrFe), copper and copper alloys and nickel that contain elemental tritium. Regenerable desiccant beds containing 4A and 5A molecular sieve that contains tritiated water are also processed in this facility. The system is able to process both elemental and water feed streams: by unloading the tritiated species to regenerate the beds and when required, chemically passivate the beds to prepare the residual metals for disposal as low level waste.

In 2001 three new processes were installed to handle tritiated liquids. A mixed waste oxidation system (MWOS) uses high-temperature, two stage catalytic oxidation to convert solvents into tritiated water and carbon dioxide at efficiencies in the 99.9999% to 99.99999% range [1-5]. The second process is a tritium compatible alkaline electrolyzer which converts tritiated light or heavy water from feed stock, the MWOS, or the bed unloading station into a tritiated hydrogen gas stream and a non-tritiated oxygen effluent. The final process was an isotopic separation system (ISS) that is able to separate the hydrogen isotopes from the elemental tritiated gas streams leaving the electrolyzer, TiT2, or the bed unloading station into a purified (5%-10%) tritium gas product and a non-tritiated (<0.37 MBq/m³ (10 µCi/m³)) hydrogen-deuterium gas effluent. The upgraded tritium
elemental gas can then be loaded onto a storage bed and recycled back to the research community for fusion experiments.

Finally in 2005, to increase the facility throughput of low activity water, a liquid phase catalytic exchange (LPCE) column was added to the electrolyzer to create a combined electrolysis and catalytic exchange (CECE) system that is able to concentrate low levels of tritiated water from an activity of 0.37 MBq/L (10 µCi/L) up to a maximum of 740 GBq/L (20 Ci/L). This allowed the ISS, which was the rate limiting process, to always operate at the improved throughput when processing any low activity tritiated light water, heavy water, or MWOS feed streams.

By 2010 the NSSI tritium facility was able to process and recycle a large variety of tritiated materials with a wide range of activities from light water to heavy water, elemental tritium on foils or getter beds, and mixed waste. But by 2011 experience demonstrated that the feed stock for the mixed waste was poorly characterized and often had higher halogen contents than reported. The high chlorine content in the feed stock caused corrosion in the system which halted further testing of real world feed stock.

This paper will detail the results from the 2015 upgrade of the MWOS with the purpose of handling a larger variety of mixed waste from the real world feed stock.

DESCRIPTION and DISCUSSION

Mixed waste is hazardous waste, as defined by the Resource and Conservation & Recovery Act, which is ignitable, corrosive, reactive or toxic liquid that is also radioactive, as defined by the Atomic Energy Act in 1984, which in this case is tritium. Taken separately, each type of waste has a ground disposal path but when combined, mixed waste becomes expensive and difficult to dispose. NSSI identified the need for mixed waste treatment in the market and built a mixed waste oxidation system that would break the feed into its atomic constituents and then recombine the elements into tritiated water, solids and carbon dioxide. This process would thereby remove all of the hazardous waste EPA codes and leave only tritiated water. The process, which uses a high temperature two stage catalytic oxidation furnace, has demonstrated solvent destruction efficiencies of 99.9999% to 99.99999%. [2, 4]

The MWOS is housed in a 1.2 m x 2.4 m x 2.4 m (4’ x 8’ x 8’) air box shown in Figure 2 below for both tritium and liquid containment. The system can process up to 40 L/day, but throughput is very dependent on the thermal energy of the feed stock. In 2015 the system was upgraded to handle tritiated gas feeds as well as liquid feed.
The process is illustrated in the flow diagram provided in Figure 3 below. Feed stock from tank 1 is mixed with water from tank 2 and is co-injected into the bottom of the furnace with an oxygen gas stream. The high temperature furnace decomposes the liquid to form water and CO₂. The hot gas from the furnace is then passed through a low temperature water scrubber to condense the water vapor as tritiated water and to separate the water vapor from the carbon dioxide. Metal ions precipitate with the water to create salts. The resultant water is collected in tank 5 as the product. A portion of that product is pumped from the tank through a heat exchanger, to maintain the low liquid temperature, back to the condenser to continue the condensation process. Caustic is co-injected to neutralize the water. The carbon dioxide effluent gas is passed through a moisture trap to capture any remaining tritiated water vapor and is then vented to the stack through a carbon monoxide detector. The carbon monoxide detector is used to monitor the destruction efficiency of the process.
The central component of the system is the two stage oxidation furnace which is detailed in Figure 4 below. The first volumetric oxidation stage is located in the void space at the bottom of the furnace where the solvent/water/oxygen feed is co-injected. The majority of the disassociation of the molecules occurs in this region. Heavy elements, such as sulfur, will sublime onto the void space surfaces or collect as debris at the bottom of the furnace. The second catalytic oxidation stage is located at the top of the furnace where the hot gas passes over a platinum on alumina catalyst. Hydroxyls created from the dissociation of water in the first stage participate in radical oxidation over the platinum catalyst thereby achieving very high destruction efficiencies. The temperature in the furnace is controlled between 800 °C and 850 °C in order to maintain both the high destruction efficiency and remain within metallurgical safety limits of the furnace.

The graph in Figure 5 demonstrates the oxidation of tritiated solvent at different flow rates. The plot of furnace temperature against time shows that for this particular feed stock a flow rate of 17 sccm keeps the furnace within the 800 °C to 850 °C target band. When the flow rate was increased to 20 sccm the furnace temperature exceeded the upper limit and had to be reduced.
Experience indicates that hydroxyls are vital to attaining high destruction efficiencies. It is important to determine the best water-to-solvent ratio for each feed stock composition. Too much water in the mix causes the reaction to run cooler and create more product that needs to be treated in the CECE and ISS process afterwards. Too little water results in an insufficient number of hydroxyls and degrades the high destruction efficiencies.

The solvent to water is not the only ratio of concern. The solvent-to-oxygen ratio is also important in maintaining high destruction efficiencies. The production of carbon monoxide in the effluent gas stream is a very good indicator of insufficient oxygen in the process and therefore degraded destruction efficiencies. The graph in Figure 6 shows a plot of the concentration of carbon monoxide in the effluent gas during the processing of solvents discussed in Figure 5 above. In this particular case, there was not enough oxygen for the chosen solvent flow rate at the start of the run and so the carbon monoxide content increased with time. Once the oxygen flow rate was increased, carbon monoxide production quickly decreased to background levels in favor of making CO$_2$. The two carbon monoxide peaks observed in this figure coincide with two short duration shut down events indicating that the oxygen management is important during startup and shut down evolutions.
In summary, three parameters, solvent feed, water feed and oxygen flow, must be balanced in order to maximize throughput, minimize final product, remain within temperature safety limits and maintain high destruction efficiencies. The feed flow increases system throughput but generates furnace heat that can exceed the safety limits. The water flow provides hydroxyls for efficiency and cools the furnace but creates more product that needs to be treated by subsequent energy intensive systems. The oxygen maintains high efficiencies but also increases heat carry over into the water scrubber and represents an operational cost. A model is being developed to optimize these conditions for the broad variety of feed compositions. This model will continue to be tested and updated against the varied feed stock provided by generators.

CONCLUSIONS

Commissioning runs using simulated feed stocks were completed prior to 2015. During 2016 the feed stock provided by generators was processed in the system. Batch 1 comprised thirty liters of 37 GBq/L (1 Ci/L) liquid, consisting of acetonitrile, methanol and toluene. Batch 2 comprised 2 liters of 1,036 GBq/L (28 Ci/L) liquid, containing methanol, ethly acetate and acetone.

Batch 2 was visually clear, oxidized easily and presented no unique challenges. Batch 1 was visually brown, opaque, contained sediment (see Figure 7 below) and was more difficult to process.
Three major lessons were learned during the processing of Batch 2. The first is that typical feed stock provided by generators may be poorly characterized. A pre-filter stage is required before the liquid can be pumped into the system to deal with unexpected sediment. The unidentified elements contained in Batch 2 precipitously decreased the pH of the condensate over the course of the processing run as can be seen in Figure 8. As the condensate acidified, the water attacked copper gaskets within the system. Caustic was added to the product to increase the pH and minimize system damage. A solution of 30% by weight of potassium hydroxide (KOH) was added to the condensate to balance the pH four times during the run. As the KOH was added, a precipitate developed as shown in the samples illustrated in Figure 9 and collected as dried precipitate filtered from the product in Figure 10. This precipitate will have to be filtered from the product in-situ in order to prevent damage to pumps and clogging of the heat exchangers.
Fig. 8. PH of the Product with KOH Additions

Fig. 9. Example of Precipitate in the Samples from the MWOS Product

Fig. 10. Dried Precipitate from MWOS Product
The processing of feed stock provided by generators has provided an insight into the future challenges that can be expected during the transition from research and development activities using simulated mixed waste feed to the processing of generator feed. The system will be upgraded in early 2017 to pre-filter the feed stock before introduction in the MWOS and to filter the condensate in-situ during processing to protect the system components.

Overall the Mixed Waste Oxidation System has demonstrated to be very robust with the ability to handle poorly characterized feed stock and large PH swings while maintaining system integrity and high destruction efficiencies. The proposed minor upgrades of filtering will further increase system robustness to ensure a high processing-to-maintenance duty cycle. The model to balance and optimize the feed, water and oxygen flows will continue to evolve as the spectrum of generator feeds expands, allowing for higher system throughputs.

REFERENCES


