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RECENT ADVANCES IN SRS ON HYDROGEN ISOTOPE SEPARATION USING THERMAL CYCLING ABSORPTION PROCESS (TCAP)

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The recent TCAP advances at Savannah River Site (SRS) include compressor-free concept for heating/cooling, push and pull separation using an active inverse column, and compact column design. The new developments allow significantly higher throughput and better reliability from 1/10th of the current production system's footprint while consuming 60% less energy. Various versions are derived in the meantime for external customers to be used in fusion energy projects and medical isotope production.

I. INTRODUCTION

Palladium and other materials were found to have hydrogen isotopic effects^{1,2} soon after the discovery of deuterium in 1931 and tritium in 1934. Developing an efficient isotopic separation process based on this property proved to be a significant technical challenge due to the burden of maintaining radioactive confinement. Batch palladium chromatography for hydrogen isotope separation dates to the 1950's.³ A "continuous" process using Pd chromatographic separation did not appear for half a century until SRNL invented the concept of TCAP and successfully developed a working unit in 1980's.⁴ Because TCAP demonstrated unequivocal advantages, it has gradually replaced all other separation processes for hydrogen isotope production at SRS: thermal diffusion, fractional absorption, and batch cryogenic distillation. TCAP is currently the sole process of purifying tritium at SRS.

Since the 1st generation TCAP systems are approaching design life, considerable effort has been spent at SRS developing, testing, and evaluating new innovative concepts to advance the technology, reduce the footprint to conserve glove box space, and increase efficiency.⁵⁻⁸ As a result of the successful demonstration of these innovations, external customers have approached SRNL to acquire TCAP units for tritium purification.

II. TAKE INNOVATIONS TO THE NEXT STEP

II.A. TCAP Working Principle

TCAP is a gas chromatograph in principle using palladium in the column packing, but it is unique in the fact that the carrier gas, hydrogen, is being isotopically separated and the system is operated in a semi-continuous

manner. TCAP consists of a column packed with palladium coated on kieselguhr (Pd/k), a plug flow reverser (PFR) packed with plain kieselguhr, and a single valve connecting the two together, as illustrated in Figure 1.

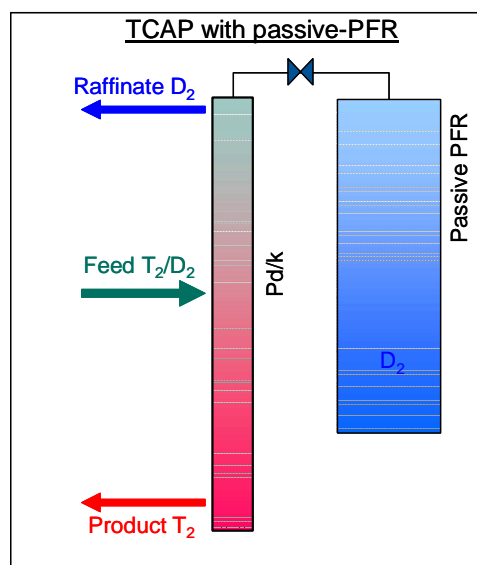


Figure 1. Illustration of TCAP Working Principle with a Pd/k Column and Plug Flow Reverser (PFR).

The aspects of hydride technology which provide interim hydrogen storage, generate pressure, and create vacuum have been innovatively applied to create the TCAP process. During operation, the Pd/k column is heated to desorb hydrogen gas and generate pressure, to transfer gas to the PFR, and cooled to absorb hydrogen gas and create a vacuum which pulls gas back into the Pd/k column. Palladium has a very large isotope effect at low temperature and prefers the lighter hydrogen isotope. The PFR allows gas to flow in and out of the column without mixing, thus maintaining the concentration profile created by the Pd/k column. By applying heating and cooling in each cycle, temperature swing as well as pressure swing is created, which is the driving force within a TCAP system. By moving gas back and forth in the Pd/k column, hydrogen isotopes are separated at each of the column's separation stages. The number of theoretical separation stages in a Pd/k column varies based on column length and diameter. The Pd/k column's

effective number of theoretical stages is enhanced by the fact that the gas can be repeatedly reprocessed in the same column, thus achieving efficient isotope separation. During each cycle, a gas mixture is fed into the Pd/k column and pure product and raffinate are withdrawn from the two ends of the column. The TCAP invention is an engineering achievement with simple design and advanced control logic and is suitable for radioactive confinement. A simple on/off valve is the only mechanical moving part. The robust design presents features of inherent safety and extra long life. It can be scaled from very small to large with plenty of versatility depending on throughput. Testing has demonstrated that TCAP can easily separate the naturally occurring 150 mole ppm deuterium in a standard hydrogen cylinder, thus producing pure protium.

II.B. TCAP Development for SRS Tritium Plant

The world-leading technology for hydrogen isotope separation advances continuously in the directions of compact, modular, more efficient and enhanced safety. The next generation CTC-TCAP concept was developed at SRNL in 2008. LN₂ cooling/electric heater was used instead of hot/cold N₂ gas. This advanced concept will reduce the footprint of the TCAP system to about 1/10th through eliminating the refrigeration/compressor in the hot/cold nitrogen circulation system, which is bulky and requires a high level of maintenance. Push and pull separation using an active inverse column was fully developed in 2010. The inverse column prefers heavier isotope and is used to replace PFR. It works complementary with the Pd/k column that likes lighter isotope. Isotopes are separated twice in each cycle: once in Pd/k column and once in inverse column. Throughput doubled with the inverse column at otherwise identical experimental conditions. On the other hand, at the same throughput the T₂ inventory in this TCAP with inverse column would be ½ of the original TCAP with PFR. The raffinate impurity was below detection limit in laboratory test using H₂/D₂. We expect the raffinate impurity would be reduced significantly for tritium emission to the environment but has not yet determined if this reduction is going to be in fractions or orders of magnitude. Extremely compact column design was tested with excellent performance in heating/cooling characteristics and isotope separation efficiency. By eliminating heavy metal shell and using aerogel insulation, the column heat load is reduced to about 25% of the 1st generation TCAP. Figure 2 shows a prototype TCAP being tested for implementation in SRS tritium production. Due to compact column assembly and improved balance construction, the unit is identified as mini-TCAP. The plant-configured columns represent the same material, dimension, throughput and inventory but not the physical configuration, nor is it tritium certified (paperwork on tritium certification is excluded in the scope in order to

save time and cost since only H/D testing has been planned).

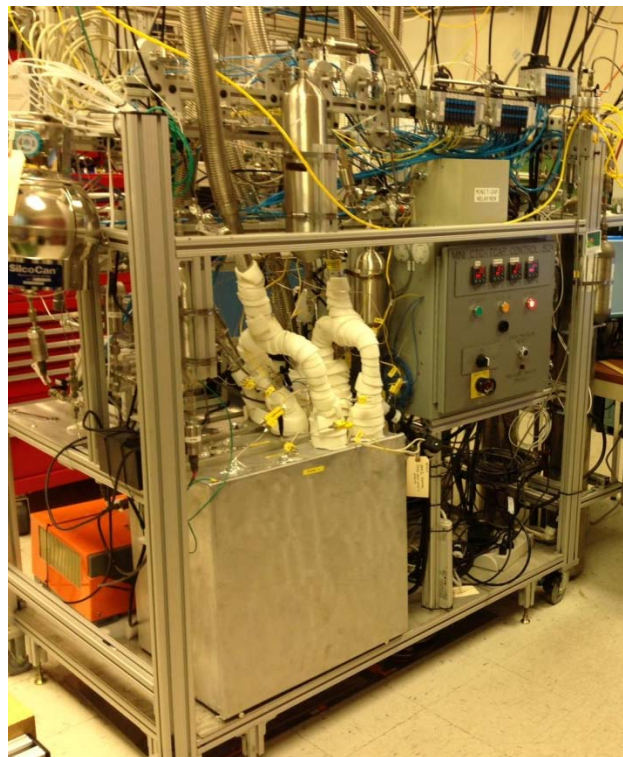


Figure 2. Plant Configured TCAP for SRS Tritium Implementation.

II.C. SHINE H/D TCAP

SHINE Medical Technologies, a US based company, is proposing a new process for US production of the medical isotope Mo-99. The process involves neutron generated by D-T fusion in a linear accelerator without need of a nuclear reactor, which aligns with the mission of Global Threat Reduction Initiative (GTRI) in the US DOE NNSA Office of Defense Nuclear Nonproliferation. SRNL is supporting the mission by providing one or more TCAP units for tritium-deuterium separation. A H/D TCAP demonstration unit has been designed and constructed for SHINE (Figure 3). The unit adopted all of the latest enhancements from the mini-TCAP plus a few more advanced features in column construction and cryogenic insulation. The demonstration unit uses tritium compatible material/construction but will not have tritium certification paperwork. The analytical instruments are also different due to the different nature of H/D versus T, e.g., no ion-chamber will be installed in this unit. It has lower throughput than the needed tritium units. Upon successful demonstration of the performance and customer satisfaction, two or more tritium TCAP units have been planned in the future.



Figure 3. SHINE H/D TCAP Constructed.

II.D. LLE H/D and Tritium TCAP's

Laboratory for Laser Energetics (LLE) at University of Rochester, an NNSA facility engaged in fusion energy research, requires a low throughput automatic batch TCAP system for tritium separation. A miniature version, designated as micro-TCAP, was developed that will fit inside a small glovebox. The development was carried out in two stages: a prototype H/D micro-TCAP was constructed and demonstrated successfully in 2012. After exceeded customer expectation with successful demonstration for H/D separation, a tritium ready unit has been delivered. Figure 4 shows the team during performance acceptance evaluation.



Figure 4. LLE D/T TCAP during Performance Acceptance Evaluation (from left to right: John Reid, Walter Shmayda, H. Tommy Sessions, Sharon Redd, and Steve Xiao. The screen shows the pressure changes due to thermal cycling in the Pd/k and MS columns.).

Since the beginning of the prototype development, frequent communications have been held between SRNL and LLE to align the micro-TCAP development with the glovebox radioactive clean up system being developed in parallel by LLE. A mockup of the LLE glovebox, complete with feed through, was constructed and the prototype micro-TCAP was mounted inside this mockup to verify functional fit. In the 1st startup run the prototype micro-TCAP produced higher than 99% (up to measurement limit) purity of D₂ from a 45:55 H₂/D₂ feed mixture. Since the TCAP operating parameters interact with each other, parameter optimization was obtained using Taguchi's orthogonal arrays, which provide means of obtaining 100% optimization while only testing 50% of the possible variables. The optimized parameters further reduced the required time to about half for the same product purity.

The study in prototype micro-TCAP indicated some unique features that differentiate it from a semi-continuous TCAP system. For example, at both the product and raffinate ends, a small amount of gases are stagnant which requires a few more cycles to reach 99% purity, while in a conventional TCAP system with continuous feeding per cycle, high purity product and raffinate purge out through both ends eliminating stagnancies. A valve was added to the prototype between the Pd/k and inverse columns to transfer the stagnant portion back to the column middle, which solved the issue without any negative impacts. It was further learnt that the valve could be used to generate pure H₂ in the raffinate end through inverse column. In the typical TCAP operation raffinate end is loaded with H₂ from a gas cylinder, which carries 150 mole ppm deuterium from natural abundance.

II.E. TCAP Component Selection

Extensive evaluation was conducted for component selection in regard to material tritium compatibility, pressure rating, performance and durability. A new type of LN₂ valve was installed and evaluated which demonstrated satisfactory performance. The valve has better cryogenic thermal insulation property and faster response time than the one used previously. Thermocouples were tested and the types identified to read LN₂ temperature correctly. A type of MKS pressure transducer with accuracy specified as percent of reading, not full scale, was evaluated and tested for TCAP application. The transducer has high pressure rating, small dead volume, stable zero drafting, and tritium compatible internal wetted materials. A special valve was jointly developed with Swagelok using copper stem tip for tritium application. It benefits from small actuator, high pressure rating and low cost. These components have been selected for the TCAP projects.

II.F. SRS TCAP Development at a Glance

TCAP technology at SRS continues in miniature design for diversified applications. Figure 5 shows representation of TCAP technology footprint reduction. The CTC-TCAP represents 1/10th footprint of the 1st generation TCAP currently is approaching end of design life. The mini-TCAP incorporated an inverse column that doubles throughput and improves raffinate purity. The micro-TCAP has compact column design and is simplified that can be readily installed in a small inert glovebox. Micro-TCAP processes small quantities of tritium, deuterium, and protium mixtures to recover high purity tritium. Regardless of the capacity or throughput of a TCAP design, the cycle time is about the same since heating or cooling capacity is selected to match the need. In other words, TCAP can be scaled up or down straightforward. The equipment process is relatively simple to start up, operate, and shut down. In Nomenclature summary,

CTC-TCAP

- Lab prototype with LN₂ cooling/electric heater
- Reduces footprint to 1/10 by eliminating need for hot/cold nitrogen gas system

Mini-TCAP

- Lab prototype with inverse column
- Two versions have been tested with columns at respective 1/25th and 1:1 of the CTC-TCAP scale

Micro-TCAP

- Ultra-compact column design
- Small batch version



Figure 5. New TCAP technology continues in miniature design for diversified applications.

III. CONCLUSIONS

New TCAP development in SRS has incorporated a series of major improvements initially for SRS Tritium plant. The technology has attracted external customers from tritium community: LLE (Rochester, NY) and SHINE (Monona, WI). The co-development is benefited from synergies with the following implementations: new compact column design, push and pull separation using an active inverse column, optimized configuration and control, electrical heating/LN₂ cooling without refrigeration/compressor, state of the art components

meeting ASME B31.1 and compatible with tritium, miniature version for diversified applications, etc.

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