Thermal Cycling Absorption Process—A New Way to Separate Hydrogen Isotopes

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Abstract

The thermal cycling absorption process (TCAP) is a semi-continuous chromatographic process for hydrogen isotope separation developed at the Savannah River Technology Center (SRTC) of the Savannah River Site (SRS) to support the tritium production and recycling operations for the national defense program. Hydrogen has three isotopes—protium, deuterium, and tritium. Among these, protium is known as normal hydrogen. Deuterium and tritium are heavier isotopes and are used in weapon systems. Deuterium and tritium fuse to form helium plus a free neutron, then releasing huge amounts of energy (1.7 trillion joules per mole). This is the source of energy for boost weapons. Fusion also serves another vital national interest—energy security. The problem is that the separation process required to supply tritium is costly, cumbersome, and inefficient. The TCAP method is compact, safer, and more efficient and an important technology for supporting the weapons program as well as for future fusion reactor fuel processing.

Introduction

Hydrogen has three isotopes—protium, deuterium, and tritium. Among these, deuterium and tritium are used in weapon systems, which requires the separation of deuterium and tritium in high purity. Isotopes have very similar chemical properties. Therefore, isotope separation is, in general, more difficult than chemical separation. Deuterium is relatively cheap because it occurs in nature in 150 parts per million. The rest is hydrogen. In nature, tritium is produced by cosmic bombardment and is only found in trace level. As a result, tritium is essentially a man-made isotope.

Tritium is radioactive and disintegrates to helium-3 and beta rays. A tritium nucleus has two neutrons and one proton while helium-3 has two protons and one neutron. During the radioactive decay of tritium, one neutron turns into a proton and beta rays. This decay half-life is 12.3 years (Souers 1985). (If the neutron were free, the half-life would be 12 minutes. The presence of two other nuclear particles stabilizes the neutron in tritium.) Because tritium reduces by half every 12.3 years, tritium can continually be produced and reprocessed to maintain defense capabilities.

Several technologies exist to separate gaseous hydrogen isotopes (Lee 1993). Cryogenic distillation uses liquid hydrogen (at −265°C). This operates at high density with high capacity. Thermal diffusion uses high temperature gas at 800°C. It is not an economical system for hydrogen, but a good system for purifying inert gas as such as helium, argon, or krypton. Both systems are large and occupy a three-story building. Another method uses the batch sorption columns based on gas chromatograph. This method has low capacity. A better method is desired, and TCAP meets that need.

Thermal Cycling Absorption Process Achievement

Development History

In 1981, TCAP-I was built at SRS. It consisted of a 5-ft column heated with electricity and cooled with cold glycol liquid, which was in turn cooled by dry ice. Tests proved the concept. A year later, TCAP-II, a 20-ft column, was built to generate scale-up parameters, with heating and cooling from a Freon™ compressor. The process control was further developed and plug flow reverser (PFR) was added to the system. PFR allows gas to flow out of the column without

mixing and reverse the direction of gas flow back into the column again without mixing, maintaining the concentration profile. In 1982, a project was set up to replace the thermal diffusion column with TCAP (Lee 1982; 1983). To support the project, TCAP-III, a 40-ft column, was designed and tested at the Savannah River Technology Center using hydrogen and deuterium mixtures. Test results demonstrated the purity and capacity, which met the requirement of plant operation. In parallel to TCAP-III, an aluminum-block design was proposed by the engineering group. After a long study, the aluminum-block design was terminated because of fabrication difficulty.

In 1985, the Replacement Tritium Facility (RTF) (the current Building 233-H) was proposed. In this new facility, processes were all based on metal hydride. The thermal diffusion column (a three-story building) and storage tanks were replaced by TCAP and metal hydride storage beds, respectively (Heung 1985). SRTC built the Advanced Hydride Lab (AHL) to test new metal hydride technologies for the Replacement Tritium Facility, each unit operation, and interactions among units. TCAP-IV (stainless steel coil design) was installed in the AHL (Horen 1991). The heating and cooling system here was based on nitrogen gas. Since TCAP-III, no change has been made on the column length and the diameter that determines the product purity and the throughput capacity.

Thermal Cycling Absorption Process Principle

TCAP is a gas chromatograph in principle using palladium, but is operated in a semi-continuous manner. TCAP consists of a column packed with palladium coated on kieselguhr and a PFR packed with plain kieselguhr. Kieselguhr helps to reduce the pressure drop along the column and provides a large surface area of the palladium metal to get a fast isotope exchange reaction. One end of the column is connected to a PFR. A thin layer of palladium on kieselguhr readily absorbs hydrogen gas. It absorbs more hydrogen at lower temperatures then at higher temperatures. The equilibrium pressure at a given hydrogen concentration in palladium (in atomic ratio of hydrogen to metal, H/M) and at given temperature is known as “isotherm”.

Palladium also has a very large isotope effect (Lee 1983; 1985; 1991) and preferentially absorbs the lighter isotope. This isotope effect is quantified by a separation factor, as defined by the ratio of the heavier to lighter isotopic concentration in the gas phase to the same ratio in the solid phase. In another words, it is a ratio of those two ratios. The separation factor is larger at lower temperatures. This separation factor is sometimes called the “single stage “ separation factor. A column can have many stages. The overall enrichment factor of a given column is approximately the single-stage separation factor powered by the number of stages. Therefore, a larger separation factor and a longer column length give a better separation.

Thermal Cycling Absorption Process Operation

A mixed gas stream is fed at a fixed location in the middle of the column. The PFR is connected at one end of the column. An enriched stream is withdrawn at the opposite end of the column, and the depleted stream is withdrawn at the PFR end of the column. The column is thermally cycled by the heating and cooling system. During the heating in the regeneration cycle, the hydrogen gas is desorbed from palladium, and the pressure in the column increases. Then, the desorbed gas is transferred into the PFR. During the cooling separation cycle, the hydrogen gas is absorbed into palladium, and the column pressure decreases. At this point, the gas in the PFR is transferred back into column. As the gas flows through the column, the isotopic exchange occurs between the gas and the solid (Pd) phases. By the isotope effect described above, the heavier isotope is released from the solid and exchanged for the lighter isotope. The heavier isotope (tritium) migrates toward the far end of the column. The heavier isotope is enriched here and depleted at the PFR end of the column. During every cold

cycle, separation takes place with the lighter isotope preferentially absorbing onto the palladium. During the desorption cycle, some of the separation gained is lost, and the column is regenerated. But since the separation factor is greater at colder temperatures, net separation is obtained after each complete absorption-desorption cycle. This net separation produces the product and raffinate purity.

In the total reflux mode, the gas is moving back and forth between column and PFR (no feed, no withdraw). After many cycles, a relatively sharp boundary is formed in the middle of the column. High purity isotopes are at the both ends. In the production mode of the operation, a small fraction of the mixture is fed. The product (heavy isotope) and raffinate are withdrawn. The fraction of the product stream to the total withdraw is determined by the concentration at the feed point.

TCAP has been operated in Tritium Operations. It achieved higher purity products. TCAP will replace cryogenic distillation in the near future. Los Alamos National Lab has planned to build TCAP for their tritium operations.

Design Consideration

The throughput capacity is proportional to the total column inventory of the hydrogen isotope and inversely proportional to the cycle time. The column inventory is directly proportional to the column length and to the cross-section area of the column. By increasing the column diameter by two, the system capacity increases four times.

The purity of the product and raffinate depends on the column length, the temperature difference between hot and cold, the throughput rate, and the feed concentration. Higher purity can be achieved by a longer column, smaller feed rate, or larger delta temperature. But the longer column has a higher pressure drop and longer time for gas transfer.

The separation factor of protium to tritium is much larger than that of deuterium to tritium. Shorter columns can achieve the same purity for tritium-protium separation as that of tritium-deuterium separation. With the same column length, the feed rate can be larger for tritium-protium separation than tritium-deuterium separation.

Process Models and Simulation

SRTC developed mathematical models and computer simulation programs for TCAP operation (Lee 1984). Quantitative relationships between column length, cold and hot temperatures, and feed rate to the product/raffinate purity could be calculated. This simulation package has been a valuable resource for design calculation and optimization of the operation. For example, the product and raffinate purities for D-T and H-T separations as a function of the feed rate could be calculated. Two operational temperature sets are in a nominal range (-40 to 150°C). The purity of product (tritium) and raffinate (deuterium) depends on the temperature set, feed rate, and the isotopic mixture. In addition, other variables are the feed location, the column length (number of stage), and the feed concentration. For engineering reasons, the high and low temperatures are limited. The capability of the simulation program serves well for project design.

Based on the given requirements such as throughput capacity and the purity of product and raffinate, the design parameters such as (1) column length, (2) column diameter, (3) feed location, and (4) hot and cold temperatures of heating/cooling system can be determined using the program. Some of the requirements can be achieved by adjusting the operational control parameters such as feed rate for a fixed TCAP system. The acceptable ranges of hardware and control parameters are essential pieces of information for the system design and can be obtained by the process simulation (Lee 1999).

TCAP Advantage

TCAP has a very small footprint. It fits into a glove box (the first barrier for radiation release), thus providing a safer method of handling radioactive materials. It is operated in a nominal temperature range. In the semi-continuous operational mode, TCAP can have a very large throughput rate. The process control is very simple. It is based on the mid-column concentration rather than desired product or raffinate purity. It has one feed stream and two output streams, one for product and one for raffinate. Therefore, TCAP requires no tank for intermediate cuts. Because of these advantages, TCAP is the choice of technology in the tritium process.

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Biography

Myung W. Lee received his Ph.D. in physical chemistry from Brown University. He has more than 30 years of experience in chemical dynamic, isotope separation, quantum chemistry, and material science areas. He published 30 technical journals and over 100 reports ranging of basic quantum mechanics to practical applications. He holds eight patents and over a dozen invention disclosures. His current interest is in areas of metal hydride and molecular modeling of materials.