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METAL HYDRIDE BASED ISOTOPE SEPARATION -- LARGE-SCALE OPERATIONS (U)

by

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ABSTRACT

A program to develop a metal hydride based hydrogen isotope separation process began at the Savannah River Laboratory in 1980. This semi–continuous gas chromatographic separation process will be used in new tritium facilities at the Savannah River Site. A tritium production unit is scheduled to start operation in 1993. An experimental, large–scale unit is currently being tested using protium and deuterium. Operation of the large–scale unit has demonstrated separation of mixed hydrogen isotopes (55% protium and 45% deuterium), resulting in protium and deuterium product streams with purities better than 99.5%.

INTRODUCTION

Hydrogen isotopes have been purified by several methods at the Savannah River Site. These methods include thermal diffusion (1955 – 1986), fractional absorption (1964 – 1968), and cryogenic distillation (1967 – present). The Replacement Tritium Facility (RTF), a new reservoir loading and unloading facility scheduled for startup in 1993, will use a Thermal Cycling Absorption Process (TCAP) for isotopic separation. TCAP is a semi–continuous gas chromatographic separation process, under development at the Savannah River Laboratory since 1980. The key feature of TCAP is its compact size, allowing the process to be placed in a glovebox. TCAP's separative capacity is comparable to a 2–story batch cryogenic distillation column.[1]

TCAP development during the past ten years has evolved from research and development units to the plant–configured stainless steel (SS) coil unit. A Savannah River Laboratory pilot plant, the Advanced Hydride Laboratory, has demonstrated the operation of a prototype SS coil TCAP unit. The Advanced Hydride Laboratory is a "cold" process demonstration facility that demonstrates the RTF's metal hydride technology by integrating various unit operations into an overall process.[2] Metal hydride storage beds ($LaNi_{4.25}Al_{0.75}$) are used for hydrogen isotope storage as part of the TCAP system.

In this paper, the performance of the large–scale SS coil TCAP unit under production operation using protium and deuterium will be presented. Plant operating parameters and throughput are classified and will not be discussed in this paper.

EXPERIMENTAL

TCAP uses palladium coated on kieselguhr (Pd/k) as the active packing material. Kieselguhr is a diatomaceous earth with a large surface area. Palladium is deposited on the kieselguhr granules by a chloride deposition process. Palladium chloride is then reduced to

the metal by hydrogen at high temperature. The Pd/k used in these studies was made by Ionex Research Corp. The material in the large–scale SS coil TCAP column contains about 40 weight percent palladium coated on kieselguhr, sieved to remove particles less than 50 mesh (300 microns).

The prototype TCAP unit consists of two parts: a Pd/k packed column, and a larger column filled with kieselguhr called the Plug Flow Reverser (PFR). The Pd/k packed column is a 2.54 cm diameter 304L stainless steel coil that is contained within a 304L stainless steel shell. Hot or cold nitrogen gas passes through the shell surrounding the Pd/k packed coil to heat or cool the metal hydride, which desorbs or absorbs hydrogen isotopes. The PFR is a 12.7 cm diameter 304L stainless steel column which allows internal gas transfer to or from the Pd/k column with minimal gas mixing. The top end of the Pd/k column is connected in series with the PFR. Raffinate, consisting of the light isotopes, is withdrawn from the top end of the Pd/k column and product, consisting of the heavy isotope, from the bottom end. The feed, containing a mixture of hydrogen isotopes, is introduced at the midpoint of the Pd/k column. A schematic of the TCAP unit is shown in Figure 1. The prototype TCAP was operated initially in total reflux, a mode of operation in which there is no withdrawal of product or introduction of feed, to develop the concentration profile along the length of the Pd/k column. TCAP production operation is a semi–continuous mode of operation during which product and raffinate are withdrawn equal to the amount of feed introduced to the Pd/k column each cycle. The TCAP unit was then operated in a production mode for approximately 80 hours. The product, raffinate and feed gases were sampled to determine TCAP's separative ability. Product and raffinate samples were taken approximately every two hours, and were analyzed by mass spectrometry. The midpoint column concentration, which is an important control parameter, was sampled approximately every hour and analyzed using a Leybold Quadrex 100® residual gas analyzer.

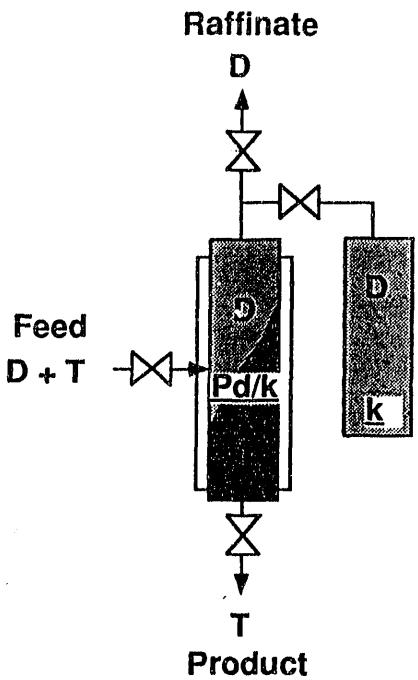

Figure 1. TCAP Schematic

RESULTS

Results from a typical production run are shown in Figure 2. Elapsed time of the run is plotted against hydrogen (protium) concentration. The feed rate, a parameter which affects the production rate of the TCAP unit, can be described as a percent of the total hydrogen inventory in the Pd/k column that is introduced per cycle. Higher feed rates give higher production rates. The two feed rates examined in this study were 3% of column inventory and

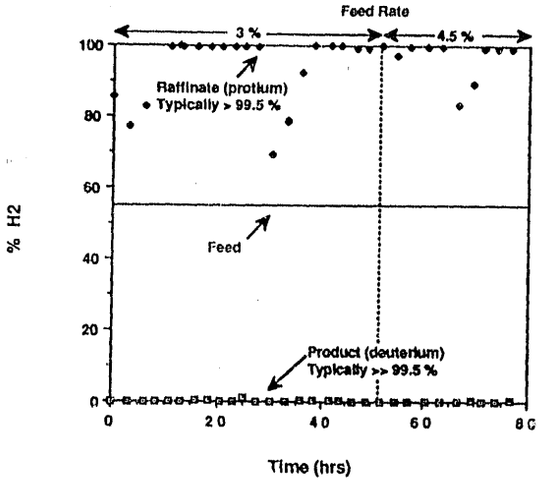

Figure 2. Prototype TCAP results with protium and deuterium

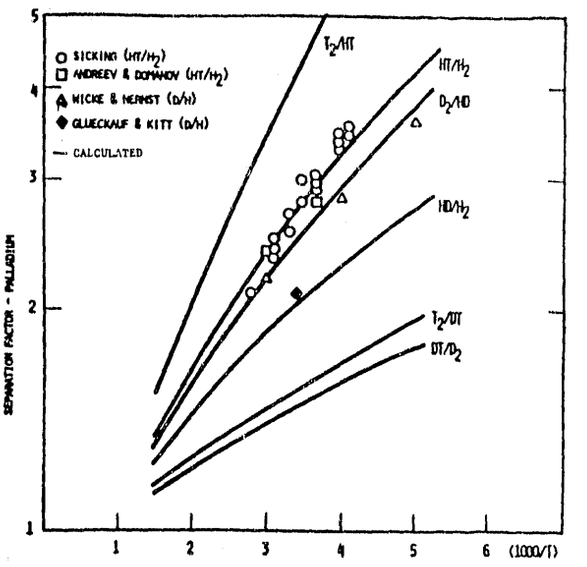

Figure 3. Separation Factor (Palladium)

4.5% of column inventory. The mixed isotope feed concentration was constant at 55% protium and 45% deuterium. The resulting product purity during production operation was typically much greater than 99.5% deuterium, and was generally greater than 99.9% deuterium. The raffinate purity was typically better than 99.5% protium.

DISCUSSION

I. Isotopic Separation

The TCAP unit takes advantage of palladium's very large isotopic effect. Palladium preferentially absorbs the lighter hydrogen isotope over the heavier isotopes. This effect increases as temperature decreases. Separation factors of the hydrogen isotopes to metal hydride are defined by the ratio of the gas phase isotopic ratio to the solid phase isotopic ratio. The separation factors for hydrogen isotopes to palladium for a range of temperatures are shown in Figure 3.[3]

Operation of the Pd/k column may be divided into a cold half–cycle and a hot half–cycle. During the cold half–cycle, the cooled Pd absorbs the hydrogen isotopes flowing from the PFR through the raffinate end of the Pd/k column toward the product end. Due to the preferential absorption of the lighter isotopes by Pd, the heavier isotope is effectively traveling much faster than the lighter isotopes. As a result, a concentration profile develops along the length of the Pd/k column, with the heavy isotope concentrated at the product end, and light isotope(s) remaining at the raffinate end. During the hot half–cycle, the gas is desorbed from the Pd and flows from the Pd/k column toward the PFR. Again, due to the isotopic effect, the heavier isotope travels faster than the lighter isotope(s), which partially negates the separation gained in the cold half–cycle. However, the hot half–cycle does not completely negate the separation gained in the cold half–cycle since the preferential absorption of lighter isotopes by Pd is significantly reduced at high temperatures. As a result, the concentration profile is reduced somewhat but is still present at the end of the hot half–cycle. Therefore, a net gain in separation is realized after

each full cycle. In this way, high purity product and raffinate are produced after repeated cycling.

II. Semi–Continuous Operation

A semi–continuous isotopic separation process can be created by withdrawing small portions of the column's hydrogen inventory as product from each end of the Pd/k column during the heating half–cycle equal to the amount of feed supplied during the cooling half–cycle to maintain a constant column profile and inventory.[3] TCAP cycling steps are shown schematically in Figure 4. The production rate depends on the desired purities of the product and raffinate. Another mode of operation for startup and non–production periods is total reflux in which there is no introduction of feed or withdrawal of product and raffinate from the Pd/k column, only gas transfer to and from thePFR. Total reflux develops or maintains the column's concentration profile during these periods.

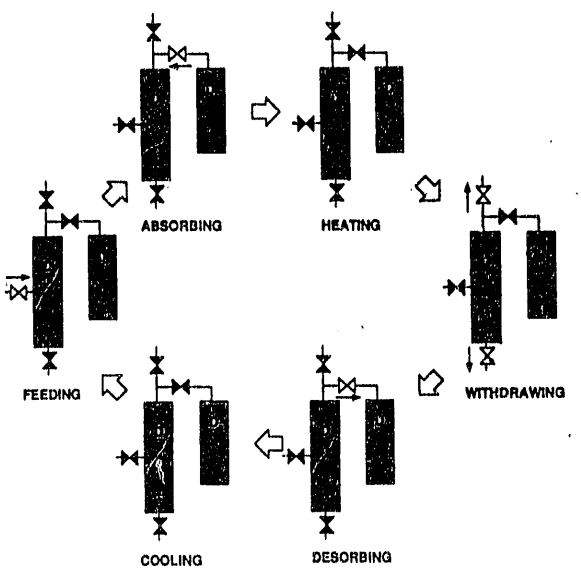

Figure 4. TCAP Process Cycling Steps

Control of TCAP's production operation is dependent on two factors: the total Pd/k column's hydrogen gas inventory, and the midpoint column concentration. The total Pd/k column inventory is used to determine the total amount of product and raffinate that will be withdrawn each cycle. The column inventory is measured by the pressure in the PFR at the end of the cold half–cycle. If the PFR pressure at this point is greater than some target value, more product and raffinate are withdrawn during the next hot half–cycle which returns the Pd/k column inventory to its target quantity. The relative amounts of product and raffinate withdrawn are determined by the concentration of the gas at the midpoint of the Pd/k column at the end of the hot half–cycle. The feed is introduced to the Pd/k column at a constant feed rate each cycle. This feed rate may be changed during experimental runs to study its effect on product purities and production throughput.

III. Large–scale Operation

Experimental objectives for the large–scale TCAP operations in the Advanced Hydride Laboratory were: identifying possible operating problems, evaluating control logic, and demonstrating separation and long–term performance.

Prototype TCAP testing revealed certain operating limitations due to the mechanical breakdown of the Pd/k particles at high gas flow rates. Without the discovery and resolution of this problem, the RTF would have lost its operability shortly after startup. Additional studies at the Savannah River Laboratory identified a solution to this Pd/k breakdown problem. Heat treatment to strengthen the Pd/k material was found to reduce the effects of mechanical breakdown at high gas flow rates.[4]

The TCAP cycling steps shown in Figure 4 are sequenced automatically by the control scheme based on process parameters. During prototype TCAP testing, the control of TCAP was modified from a temperature to a pressure based process. Temperature was found to be less sensitive to the process operation than pressure due to the design of the thermowells in the Pd/k column. This modification significantly improved the process efficiencies and product purities since the control scheme is an integral part of TCAP operation.

Isotopic separation was demonstrated in the prototype TCAP from a mixed protium and deuterium feed, giving product and raffinate purities better than 99.5%. Variation in process parameters such as feed rate and midpoint column concentration were found to affect the raffinate (protium) purities more significantly than the product (deuterium) purities. Separation and long–term tests with the prototype TCAP are ongoing to evaluate its performance during startup, transients, and upsets.

SUMMARY AND CONCLUSIONS

The development and operation of a metal hydride based hydrogen isotope separation process has been described in this paper. The prototype TCAP unit's operation and separation capability has been demonstrated using protium and deuterium. Benefits of prototype TCAP testing include: determining operating limitations before production is impacted, evaluating various control schemes to optimize operating conditions, and demonstrating isotopic separation. TCAP's separation capability with tritium and deuterium will be determined upon startup of the RTF at the Savannah River Site.

ACKNOWLEDGEMENT

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