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NEXT-GENERATION TCAP HYDROGEN ISOTOPE SEPARATION PROCESS

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A thermal cycling absorption process (TCAP) for hydrogen isotope separation has been in operation at Savannah River Site since 1994. The process uses a hot/cold nitrogen system to cycle the temperature of the separation column. The hot/cold nitrogen system requires the use of large compressors, heat exchanges, valves and piping that is bulky and maintenance intensive. A new compact thermal cycling (CTC) design has recently been developed. This new design uses liquid nitrogen tubes and electric heaters to heat and cool the column directly so that the bulky hot/cold nitrogen system can be eliminated. This CTC design is simple and is easy to implement, and will be the next generation TCAP system at SRS. A twelve-meter column has been fabricated and installed in the laboratory to demonstrate its performance. The design of the system and its test results to date is discussed.

I. INTRODUCTION

Separation of hydrogen isotopes at the Savannah River Site started in the 1950s. The technology for this application has evolved from thermal diffusion (1955-1986) to fractional absorption (1964-1968), to cryogenic distillation (1967-2004) and to TCAP (1994-present). TCAP stands for Thermal Cycling Absorption Process. It was invented by Dr. Myung Lee of Savannah River National Laboratory in 1980 (Ref. 1 & 2). The invention was followed by about 10 years of development before a production unit was installed. Tritium and deuterium separation was accomplished in 1994. TCAP is now the preferred process at Savannah River Site for enriching tritium to high purities and for removing tritium from waste hydrogen streams. TCAP in effect is a semi-continuous chromatographic process using a packed column of palladium supported on kieselguhr (Pd/k) and a plug flow reverser (Figure 1). Its operation requires heating and cooling to cycle the temperature. Design of the heating and cooling system has always been a challenge because short cycle time and wide temperature swing, from below the freezing point to above the boiling point of water are desired. During the initial development phase different heating and cooling options were considered. A hot/cold nitrogen system was eventually selected. Nitrogen gas is a poor heat transfer fluid and requires the use of large size equipment which includes compressors, heat exchangers, valves and pipes, but it is clean and is non-hazardous. On the contrast liquid is a more efficient heat transfer media, but liquid heat transfer fluids are usually hazardous chemicals and once contaminated with tritium become mixed wastes. Mixed wastes are costly to dispose off, and the equipment contaminated with mixed wastes is difficult to maintain. For these reasons the nitrogen system has been used since 1994. However, effort to seek a better hot/cold system than the hot/cold nitrogen system continues. Note that a change in the hot/cold system will most likely change the column design, and potentially the separation efficiency also.

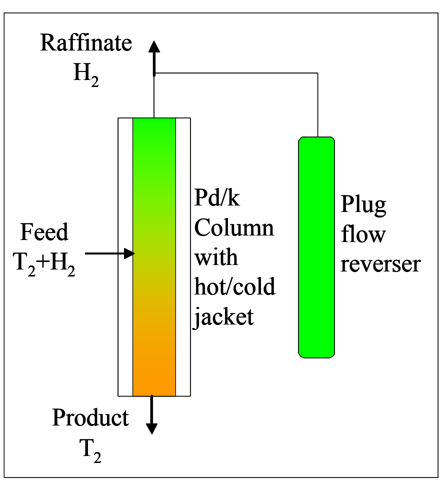

Figure 1. Schematic of the TCAP.

II. COLUMN DESIGN FOR THE HOT/COLD NITROGEN SYSTEM

TCAP was designed to fit inside gloveboxes. To be compact and thermally efficient, a tube coil design was used. A 12-

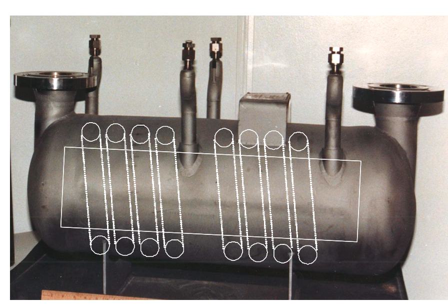

Figure 2. TCAP coil design.

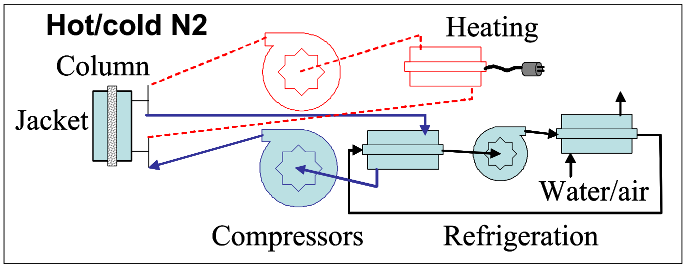

Figure 3. Schematic of the hot/cold nitrogen system.

meter long column is formed into a coil like a spring. The coiled column is placed in an annular space formed by two sections of concentric shells. The outer shell has an inlet and an outlet for the circulating hot/cold nitrogen. The inner shell is closed that forces the nitrogen to flow through the annular space where the coiled column is located. See Figure 2. With this design the column is compact and can fit into a glovebox easily. In addition, the column coil can expand and contract during thermal cycling and thus avoids thermal stress problems. Thermal cycle time of about 45 minutes is achievable. However, with nitrogen as the heat transfer fluid large volume of it has to be circulated since the heat content per volume is low. This requires the use of large pipes and valves, large heat exchangers, heaters, refrigeration and compressors for circulation. As shown in Figure 3 this system has many components and is large and complex. Maintenance and thermal insulation to prevent condensation in a tritium area are persistent issues.

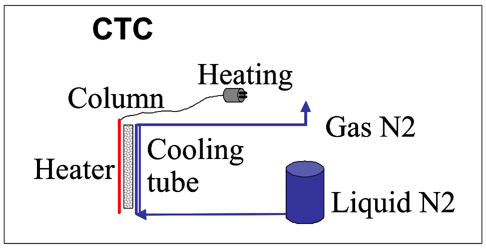

Figure 5. The new CTC thermal system.

III. THE NEW CTC DESIGN

The goals of the new design are 1) Replace the hot/cold nitrogen system with a simper system, 2) Keep the compact size to fit existing glovebox and 3) Maintain or improve the separation efficiency.

The new design is called the CTC design. CTC stands for compact thermal cycling. Its unique feature is that it does not use any heat exchangers or circulation fluids. The Pd/k column is directly heated by electric heaters and cooled by liquid nitrogen tubes. The column in U-shape sections is assembled in close contact with the heaters and liquid nitrogen tubes. A layer of copper wool is used to improve thermal distribution among the column, the heaters and the cooling tubes. The components are hold snuggly together with thermal insulation, clamps and an outer box, so that the components are free to expand and contract during thermal cycling, and the heat capacity of the system is kept at a minimum. Small heat capacity facilitates thermal cycling and reduces energy consumption. This column assembly is illustrated in Figure **4**. Thermal cycling of this Pd/k column requires only electric power and liquid nitrogen. The compressors, heat exchangers and the piping and valves of the hot/cold nitrogen system are all eliminated. This greatly reduces the equipment requirements of the thermal system and eliminates the maintenance issues associated with the circulating fluid system. The simplicity of this new heating/cooling system is illustrated in Figure 5, as compared to the hot/cold nitrogen system in Figure 3.

IV. EXPERIMENTAL CTC-TCAP SYSTEM

An experimental system was installed in the laboratory to test the performance of the new CTC design. The system consists of a Pd/k column assembly, a plug flow reverser, 3 calibrated volumes for metering feed,

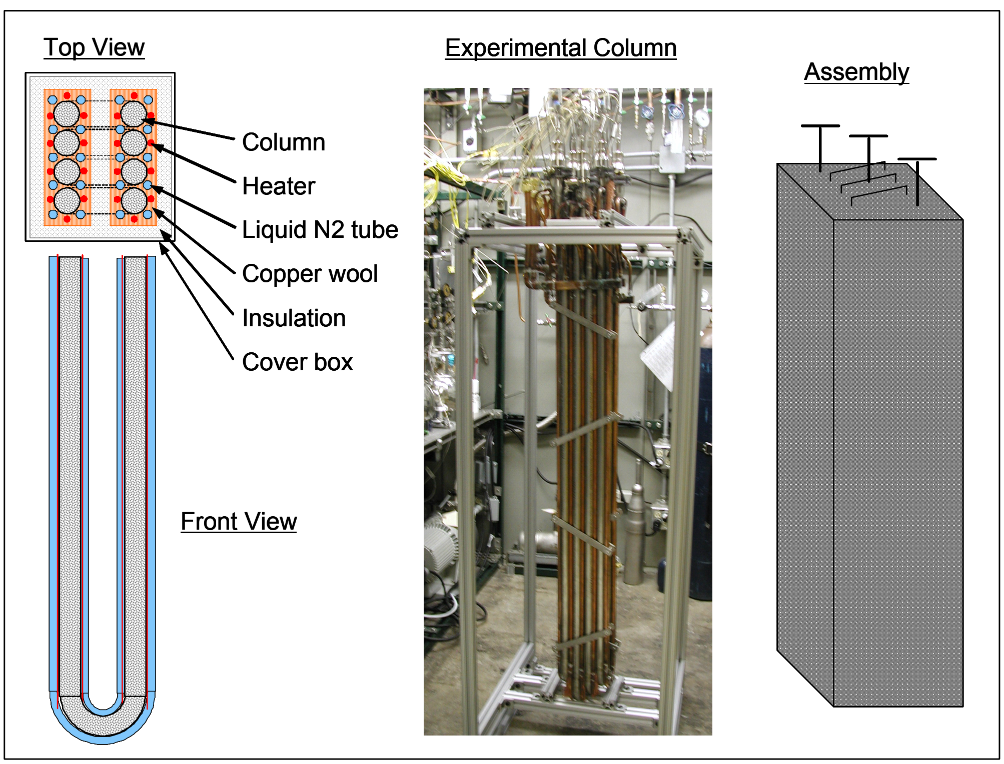

Figure 4. The new CTC-TCAP column design.

product and raffinate and three 100-liter tanks for feed preparation and product recycle. The column assembly includes a 12-m long, 3.2-cm diameter column in four U-shape sections assembled as shown in Figure 4. Twenty AeroRod® 0.32-cm diameter electric heaters (ARi Industries Inc, part # BXX13B62-4T) for heating and ten U-shape 0.95-cm diameter copper tubes for liquid nitrogen cooling are used. The plug flow reverser is a 7-meter long 11.4-cm diameter column filled with kieselguhr. The connections of the gas components are shown in a schematic diagram in Figure 6. Not shown in the figure are the mass spec system, the H_2 and D_2 supply gas cylinders, the vacuum system, the liquid nitrogen tank and the computer control and data logging system. A picture of the equipment is shown in Figure 7**.**

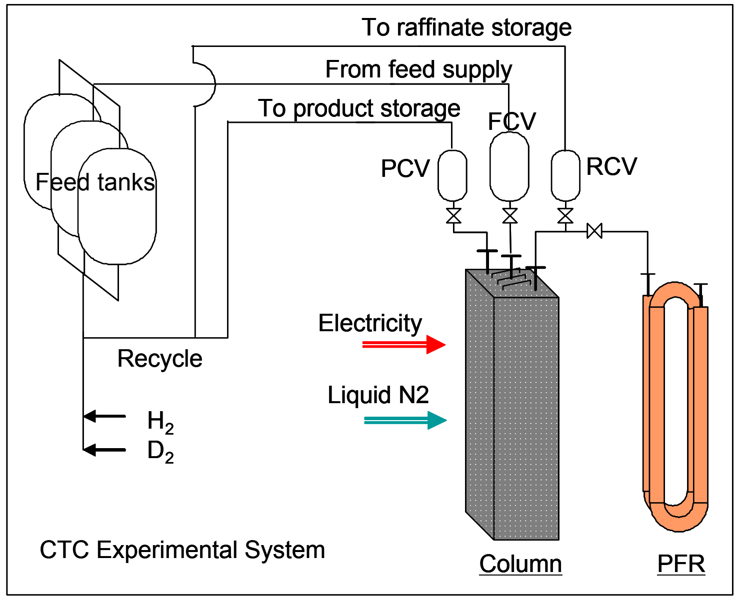

Figure 6. Schematic of CTC-TCAP experimental system.

V. EXPERIMENTAL RESULTS

Testing of the experimental system is in progress. Preliminary tests conducted to date are discussed below.

V.A. Thermal Cycling Test

The objective of this test was to see how quickly the column can be heated and cooled. The design target is to cycle the column temperature between -30 and 120 °C in less than 45 minutes. The column was filled with helium gas to about 1500 torr. Liquid nitrogen from a dewar was fed to the cooling tubes to begin the cooling cycle. Once the target temperature of -30 °C was reached the liquid nitrogen was stopped and the heaters were turned on to heat the column to 120 °C. The trends of temperature and pressure of the column were recorded. There were 24 thermocouples attached to the outside surface of the column at different locations. As expected these thermocouples did not give the same temperature at the same time. The spread is up to about 80 °C. Achieving uniform temperature over a 12-meter long column is always a challenge. The temperature spread is expected to have some negative effect on the separation efficiency of the column. The average temperature in the column was calculated from the pressure data using the ideal gas law. The results of this calculated temperature and the readings of four thermocouples located at the mid points of the straight legs of the U-shape sections are shown in Figure 6. The average cycle time was 37 minutes, meeting the design target of 45 minutes. The test was repeated at a higher helium pressure of 5,000 torr. The results were practically the same.

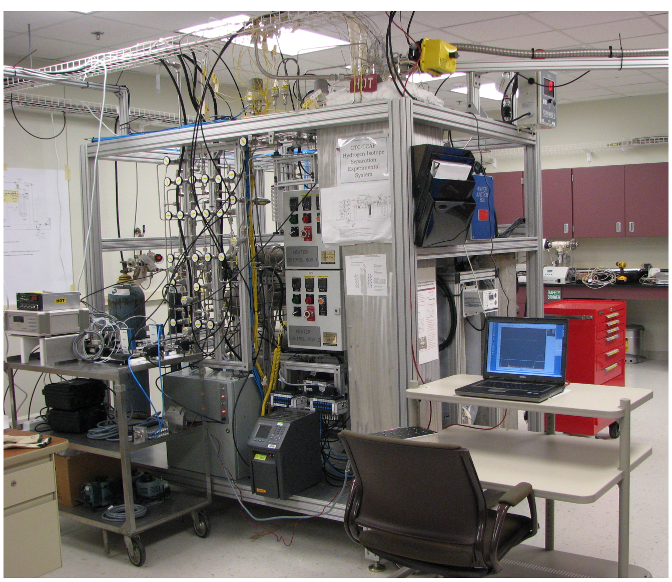

Figure 7. Photo of CTC-TCAP experimental system.

V.B. Staging Test

Staging calculation is a method used to measure the efficiency of a packed column for separation. In this method the column is conceptually divided into a number of stages. Fluid entering each stage will mix and react with the contents in the stage and will reach equilibrium before exiting the stage. If a change is made in the feed to the column, the response to the change measured at the exit end of the column will be a function of the number of stages that the column actually provided. A large number of stages indicate high efficiency. A method to identify the number of stages of a given column is to make a pulse change in the feed. The pulse will appear at the exit as a peak. The height of the peak will be a measure of the number of stages. To do this the peak height is first calculated as a function of the number of stages. Comparing the calculated peak height with the actual

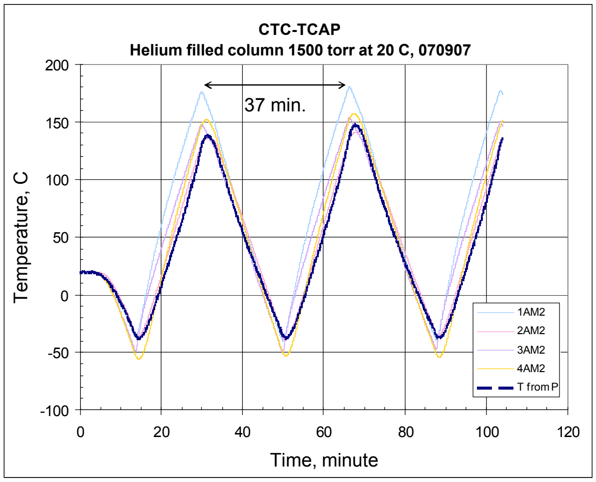

Figure 8. Thermal cycle data.

peak height will identify the number of stages of the column (Ref. 3).

This method was applied to the Pd/k column with Argon as the flowing gas and helium as the pulse gas. A typical test involves the following steps. Argon gas is fed to the column at a constant rate using a mass flow controller. The outlet is open to atmosphere. At time 0 Argon flow is switched to helium flow at the same rate for 30 seconds before it is switched back to argon. The helium peak coming out of the column is measured by a RGA (Dycor Dymaxion by Ameteck Process Instruments) and recorded. The height of this helium peak is compared with those calculated. The number of stages that gives the same peak height is the number for the column. This process is repeated for various flow rates. The results are summarized in Figure 7 which shows the number of stages for the 12-meter column and also as the height of a stage for different flow rates. The flow rate has a significant effect on staging. The number of stage decreased from 340 to 140 as the flow rate increased from 1 to 4 STP liters per minute. The target number of stages is 120 (Ref. 1). This column appears to have sufficient number of stages. This test will be repeated with H_2 and D_2 to include the effect of isotopic exchange.

VI. SUMMARY

A new design concept has been developed for the thermal cycling absorption process for hydrogen isotope separation. The new design uses electric heaters and

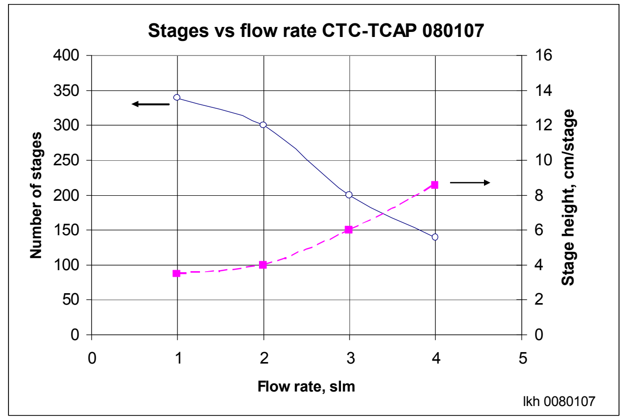

Figure 9. Staging test data.

liquid nitrogen tubes to cycle the column temperature, so that a thermal fluid (gas or liquid) circulation system is eliminated. The new design greatly simplifies the equipment requirements of the thermal cycling system. Once demonstrated it will be the next generation TCAP hydrogen isotope separation system for Savannah River Site. An experimental system to demonstrate this process is in the startup phase. Data generated to date included thermal cycling and staging. Both results indicated that the new design is meeting target performance. Protium and deuterium separation data is expected in a few months.

ACKNOWLEDGMENTS

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