Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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DEMONSTRATION OF THE NEXT-GENERATION TCAP HYDROGEN ISOTOPE SEPARATION PROCESS

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ABSTRACT

The first generation of TCAP hydrogen isotope separation process has been in service for tritium separation at the Savannah River Site since 1994. To prepare for replacement, a next-generation TCAP process has been developed. This new process simplifies the column design and reduces the equipment requirements of the thermal cycling system. An experimental twelve-meter column was fabricated and installed in the laboratory to demonstrate its performance. This new design and its initial test results were presented at the 8th International Conference on Tritium Science and Technology and published in the proceedings. We have since completed the startup and demonstration the separation of protium and deuterium in the experimental unit. The unit has been operated for more than 200 cycles. A feed of 25% deuterium in protium was separated into two streams each better than 99.7% purity.

I. INTRODUCTION

TCAP stands for Thermal Cycling Absorption Process. Its working principle has been published in several places (Ref. 1, 2 and 3). The process consists of a palladium packed column and a plug flow reverser (PFR). The palladium is deposited on a porous support of kieselghur (Pd/k) for reaction kinetics and gas flow. Feed is introduced to the mid point of the column. Product (heavier isotope) and raffinate (lighter isotope) are withdrawn from the ends of the column. The PFR is filled with kieselguhr to increase its plug flow property. It is connected to the raffinate end of the column for moving gas in and out of the column. The column temperature is typically cycled between about -50 to 150 °C. Gas is transferred from the PFR to the column during the cold half cycle and from the column to the PFR during the hot half cycle. Feed is introduced during the cold half cycle and the product and raffinate are withdrawn during the hot half cycle. Since the introduction of feed and the withdrawals of product and raffinate take place once in every cycle, the process is a semi-continuous process. The separation of the hydrogen isotopes is effected by the isotopic absorption and desorption of the palladium. Palladium preferentially adsorbs the lighter hydrogen isotopes than the heavier isotopes. And the effect is more pronounced at low temperatures than at high temperatures. As the gas mixture is transferred back and forth through the column at different temperatures, the heavier isotope is concentrated at the product end of the column and the lighter isotope at the raffinate end of the column.

Cycle time is an important factor in the separation capacity of a given column, since the throughput is proportional to the number of cycles.

Therefore, heat transfer and the design of the heating and cooling system for the column are important. The first generation of TCAP column at Savannah River Site is a coil-in-shell design that uses a hot and cold circulating nitrogen system to cycle the temperature. Nitrogen is clean and without the chemical hazard of liquid heat transfer fluids. However, due to the low heat capacity of nitrogen on a volume basis, this nitrogen system requires the use of compressors, heat exchangers, pipes and valves that are all bulky and difficult to maintain. The coiled column is also difficult to pack evenly. This next-generation TCAP uses a simple CTC (compact thermal cycling) design concept for the heating and cooling system. Electric resistance heaters and liquid nitrogen tubes are used to heat and cool the column directly, thus the hot/cold nitrogen system is eliminated. The column is also changed from a coiled column to a U-shape column which is much easier to pack. The objective of this paper is to present the startup and demonstration results of the experimental unit of this next-generation TCAP.

II. EXPERIMENTAL EQUIPMENT

The details of this experimental TCAP system have been described in Reference 3. Briefly it consists of a Pd/k column assembly, a PFR, 3 feed tanks, 3 calibrated volumes (FCV, PCV and RCV), a control panel that include power supply, temperature controls and power cutoffs for the electric heaters, an online residual gas analyzer (RGA), and a computer system for automatic control and data acquisition. All components, except the computer, the RGA and the liquid nitrogen dewars, are installed on a moveable 1.5 m X 2.1 m (5'X7') rack. See Figure 1 for a photo of the equipment rack and Figure 2 for a schematic of the connection of the main components. The column assembly includes a 12-m long, 3.2-cm diameter column in four U-shape sections connected in series, Twenty AeroRod® 0.32-cm diameter electric heaters (ARi Industries Inc.) for heating and ten U-shape 0.95-cm

diameter copper tubes for liquid nitrogen cooling. The plug flow reverser is a 7-meter long 11.4-cm diameter column filled with kieselguhr. Not shown in Figure 2 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 acquisition system.

III. EXPERIMENTAL PROCEDURES

The demonstration tests were conducted in two steps. In the first step, called the "total reflux operation", a mixture of protium and deuterium was loaded in the column. The column temperature was cycled and the gas was transferred between the column and the PFR. The gas composition at the product end and the raffinate end were measured every cycle. The objective was to demonstrate that the deuterium concentration would increase at the product end and the protium concentration would increase at the raffinate end as the number of cycle increased.

The second step was "online operation". During each cycle, feed was introduced and product and raffinate were withdrawn. The feed, a mixture of protium and deuterium would be separated into a deuterium stream and a protium stream semi-continuously.

III.A. Total Reflux Operation

After a thorough bake out at 150 ^{o}C under vacuum, the column was charged with 104 STP liters of D_2 followed by 105 STP liters of H_2. Both were charged through the mid point (feed point) of the column. Charging the column this way would distribute the D_2 to both ends of the column, making it more difficult for the process to establish a steady state profile of high purity D_2 at the product end and high purity H_2 at the raffinate end, so that a true and hard test was given to the process. The PFR was charged with 159 STP liters of H_2.

The operation started with the cold cycle and a transfer of 50 sl from the PFR to the column. The general steps used are as follows (components shown in Figure 2):

1. Cool column with liquid nitrogen (LN) controller temperature set at -50 ^{o}C
2. When the column pressure is less than 20 torr and the temperature is lower than -20 ^{o}C, open valve to transfer gas from PFR to column.
3. When product end pressure increases to 50 torr, stop gas transfer and switch cooling to heating. Set heater controller temperature at 160 ^{o}C.
4. When the column pressure reaches 1,000 torr, take RGA samples from product and raffinate ends.
5. When the column pressure reaches 6,000 torr and the temperature is higher than 120 ^{o}C, open valve to transfer gas from column to PFR. When the PFR pressure is 2,200 torr, stop gas transfer and switch heating to cooling.
6. Repeat steps 2 to 5.

III.B. Online Operation

For online operation, feed was introduced to the mid point of the column using the FCV, and product and raffinate were withdrawn via the PCV and the RCV. Feed was prepared in feed tank 1 and the product and raffinate were recycled back to feed tank 2. When feed tank 1 became empty it would switch roles with tank 2. In this way the protium and deuterium are recycled and not wasted. The feed composition for this online operation test was 25% D_2 in H_2, and the feed rate was 10 sl/cycle, which was 3.4% of a column inventory of 296 STP liters.

It is impractical to operate the TCAP process manually because the number of steps involved. Before online operation, an automatic control and data logging program was developed using the LabVIEW software. A flow diagram of the operation steps is given in Figure 3. Feed introduction, product and raffinate calculations and withdrawals, switching between heating and cooling are all automated. The key function of the control program is to maintain constant gas inventory in the system. With the feed rate set at constant, the program must decide how much product and raffinate to withdraw for each cycle so that the inventories of deuterium and protium are kept constant. The dependent variables measured for control are 1) the PFR low pressure at the end of a cold gas transfer, and 2) the mid column composition at the end of a hot gas transfer. At steady state the total amount of product and raffinate to withdrawn (TPR) and the mid column composition stay constant.

The equations to calculate the TPR (total product and raffinate), product and raffinate are as follows:

TPR = Feed + (PFR target low pressure – PFR actual low pressure) * (constant 1) * (constant 2)

Where "constant 1" is a conversion factor to convert the pressure to standard liters, "constant 2" is a control parameter having a positive value of 1 or less. When the calculated TPR is negative it is set to 0.

Product = TPR * fraction D_2 at the mid column

Raffinate = TPR – Product.

IV. RESULTS AND DISCUSSIONS

Total 59 cycles were conducted in the total reflux mode. The cycles were accumulated from several runs. A typical run started in the morning and ended in the afternoon. Each run ended at the cold cycle and resumed with the cold cycle.
The product and raffinate compositions were monitored by an online RGA and an offline micro GC (gas chromatograph) on withdrawn samples. Using the micro GC gave much more consistent results on high purity samples.

Recall that the column was charged at the mid feed point with D_2 first and H_2 last. The initial concentration profile was therefore high in D_2 at both ends of the column and high in H_2 at the middle section of the column. As the cycling progressed, the D_2 moved toward the product end of the column, and the H_2 moved toward the raffinate end of the column. An S-shaped concentration profile would gradually be developed. Samples taken from the product and raffinate ends would show an increase in purity as the number of cycles increased. This trend is shown in Figure 4. The data showed that after 20 cycles the product reached 96% D_2 and the raffinate reached 98% H_2. Both purities continued to improve and were better than 99.8% after 59 cycles at the conclusion of the total reflux test. The process separated the mixture of protium and deuterium as expected. Note that the steady concentration profile could be achieved with less number of cycles if at the beginning the column was charged with D_2 from the product end and H_2 from the raffinate end.

The online operation followed the total reflux operation. A total of 21 runs accumulated 138 cycles. Like the total reflux operation, the runs were started in the mornings and stopped for the nights or the weekends. A typical temperature and pressure trend is shown in Figure 5. Their ranges are as follows: column temperature -55 to 155 ^{o}C, column pressure ~0 to 5800 torr, PFR pressure 1000 to 2200 torr. The gas transferred between the column and the PFR was about 80 sl. Total gas in the system was 367 sl. At the end of a cold cycle the pressure left in the PFR was 1000 torr which was 71 sl. That left 296 sl in the column, and the percent of gas transferred between the column and the PFR was 80/296=27%. The cycle time was 64 minutes, of which 38 minutes for the cooling half cycle and 26 minutes for the heating half cycle. The liquid nitrogen consumption was approximately 20 liters/cycle.

At a feed rate of ten standard liters per cycle, the product and raffinate purities were maintained at the same level as those at the end of the total reflux operation. In Figure 6 the product and raffinate concentration data were collected after the process had been online for 100 cycles. The product and raffinate purities based on micro GC results were steady at 99.84% and 99.77%, respectively.

Figure 7 shows the trends of TPR (total product and raffinate to withdraw) and mid column composition. They indicate the stability of the process. The ideal condition would be for both of them to follow a straight line, with the TPR being the same as the feed rate and the mid column composition being the same as the feed composition. During the online runs there were several known process upsets, such as errors in the control program, emptied liquid nitrogen dewars and variations of pressure in the liquid nitrogen dewars causing change in the cooling rate. These were discovered and corrected. By adjusting the TPR equation constant from 1.0 to 0.8 and then 0.7, the process stability was further improved evidenced by less scattering of the TPR and D% data. The extreme data points in Figure 7 were caused by the above process upsets. The importance is that in spite of all these upsets, large and small, the control program was able to bring the process back to steady state.

V. CONCLUSIONS

The experimental next-generation thermal cycling absorption process was successfully started up and demonstrated. The new design functioned as anticipated. The separation of protium and deuterium has been demonstrated. Product (D_2) and raffinate (H_2) better than 99.7% purity were produced at a feed rate of 10 sl/cycle containing 25% D_2 in H_2. The system is easy to start up, operate and shut down since there are no large components of a hot/cold circulation system. Data generated to date indicate that the performance of the process meets expectations. The system is

now ready for systematic testing of the effects of various process conditions on throughput and product quality.

ACKNOWLEDGMENTS

Sharon Redd was a great help in conducting the experiments. Her dedication to the work is highly appreciated.

REFERENCES

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2. A. S. Horen and M. W. Lee, "Metal Hydride Based Isotope Separation – Large-Scale Operations", Fusion Technology, vol. 21, 282 (1992).
3. L. K. Heung, et al, "Next-Generation TCAP Hydrogen Isotope Separation Process", Fusion Science and Technology, vol. 54, 399, August (2008).

Figure 1. Experimental Next-Generation TCAP system for hydrogen isotope separation.
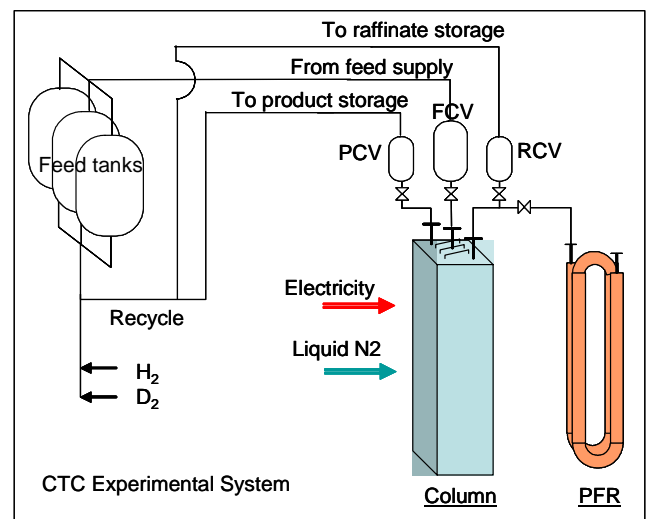
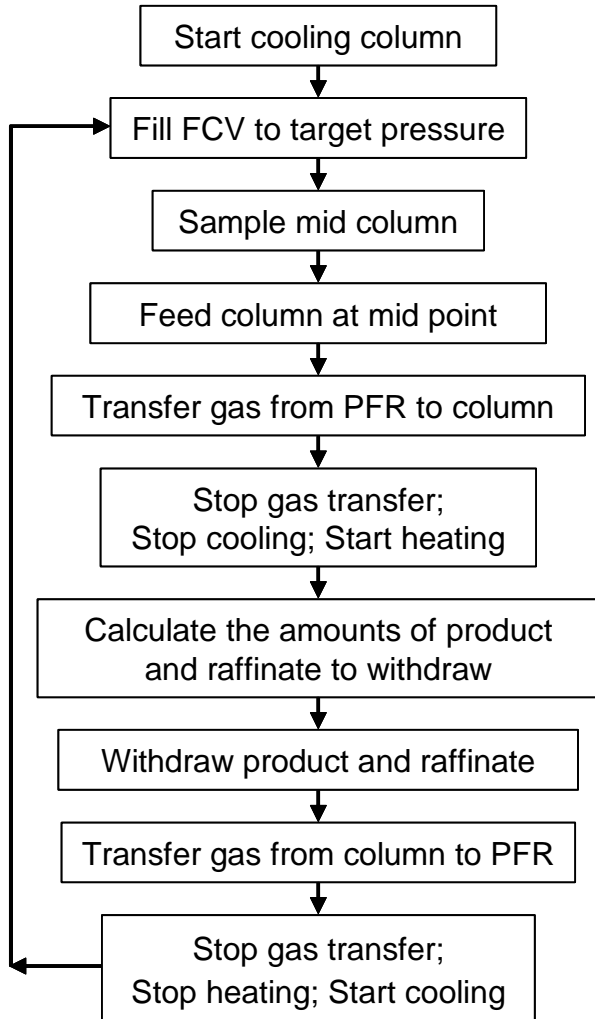**Figure 2. Schematic of the experimental Next-Generation TCAP system.**

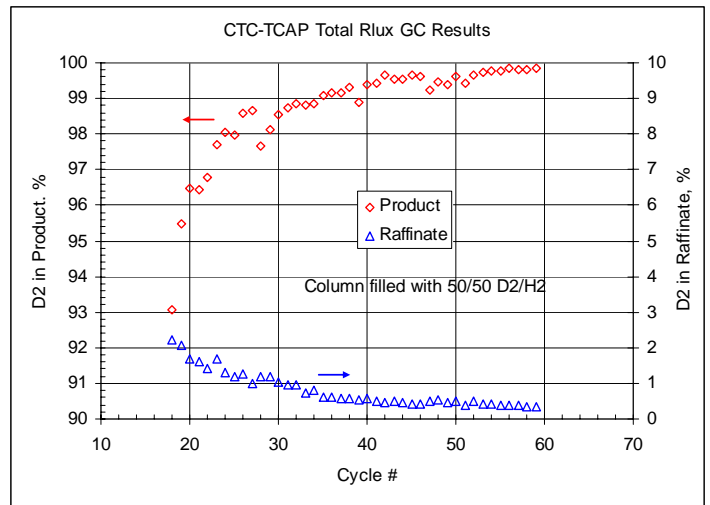**Figure 3. Online operation steps for the experimental Next-Generation TCAP.**

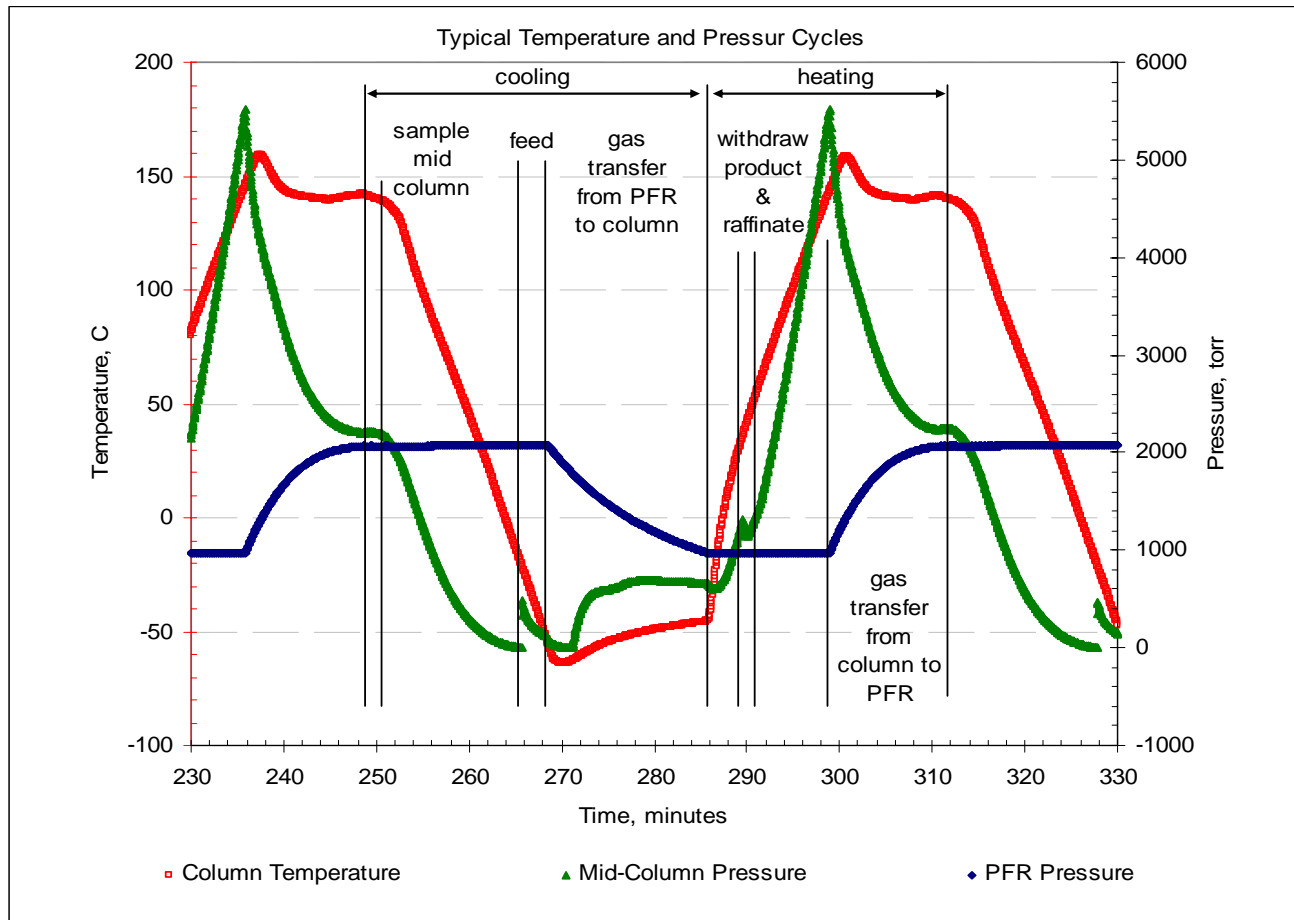**Figure 4**. **High purity of product and raffinate developed during total reflux operation.**

Figure 5. Pressure and temperature trend of the experimental Next-Generation TCAP during online operation at 10 sl/cycle of 25% D_2 in feed.

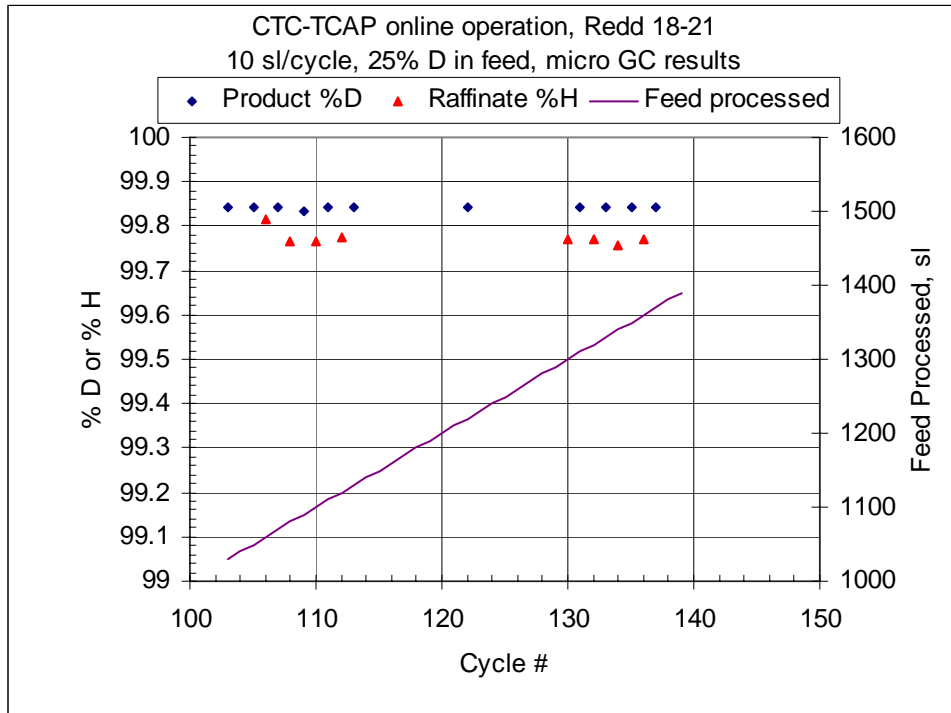**Figure 6**. **Product and raffinate quality maintained during online operation.**
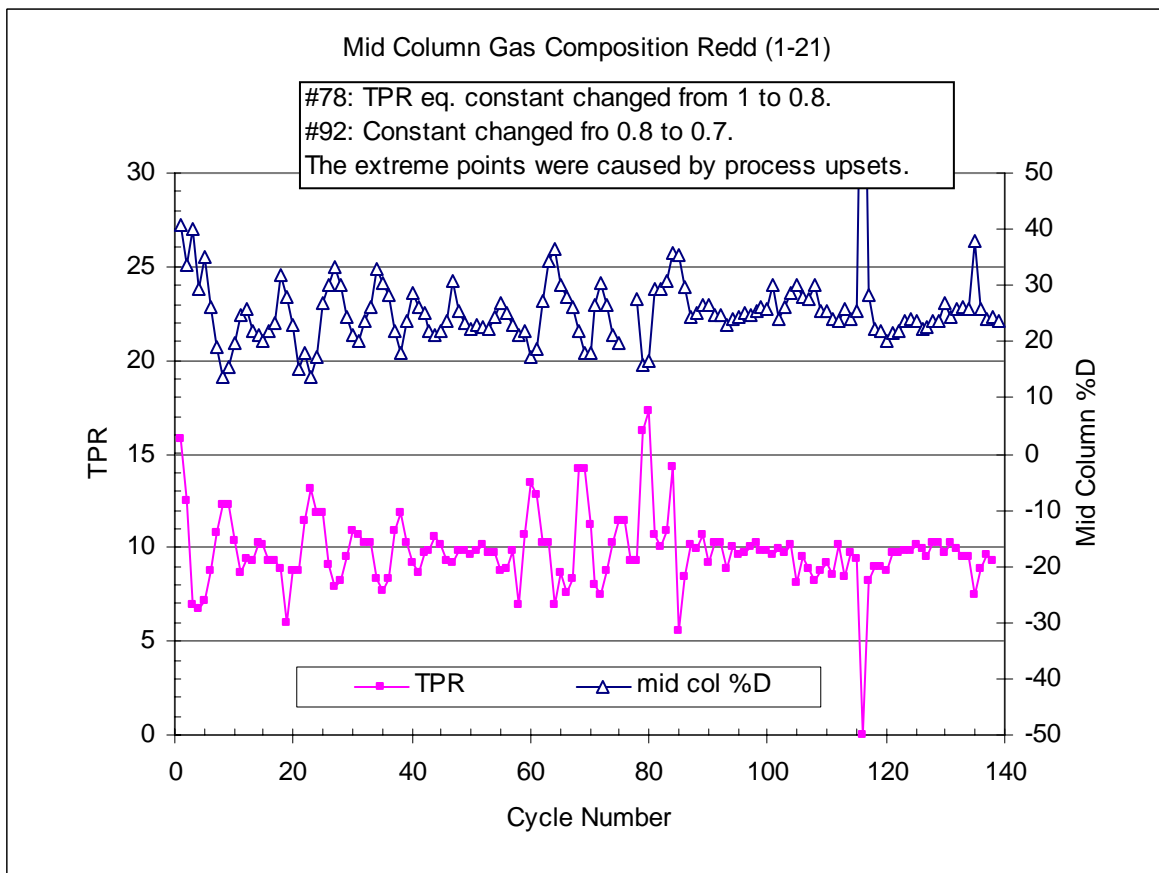

Figure 7. The trends of TPR and the mid column composition during online operation.