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Benchmarking Hydrogen Isotope Separation Efficiency of Pd/k Packed TCAP Columns

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Abstract

By leveraging the large isotope effect in the palladium hydrogen isotope system, the Thermal Cycling Absorption Process (TCAP) provides an efficient and advantageous means to separate protium, deuterium, and tritium. To meet increased future tritium processing demands, such as those needed for fusion power plants, current designs of the separation columns need to be adapted and optimized using the progress made in understanding hydrogen isotope science. One key to this optimization lies in understanding the baseline performance for currently employed separation packing materials. Pd/k and molecular sieves, as commonly used for the separation of hydrogen isotopes, are herein evaluated to establish a baseline for their separation efficiency. Van Deemter plots are formulated, and the influence of each parameter is evaluated to determine areas for improvement.

I. Introduction

The Savannah River Tritium Enterprise (SRTE) has used the Thermal Cycling Absorption Process (TCAP) to separate hydrogen isotopes for 30 years. The working principle behind the success of this process relies on the absorption phenomena of the three hydrogen isotopes on palladium, in which the preferential absorption of the lighter isotopes dominates at low termperatures.[1] Utilizing this behavior, palladium deposited onto a porous kieselguhr support (Pd/k) is supplied as the column packing material. Fundamentally, TCAP functions as a semi-continuous chromatographic process wherein a heating and cooling cycle shuttles feed gas through the separation column and leverages the significant isotopic effect of palladium. In a cycle, gas is transferred from the active column to the passive column (plug flow reverser, PFR), which contains an inert packing material and is used to maintain the concentration profile, and back. (Figure 1) After several cycles, the substantial isotopic preference for lighter isotopes produces a concentration gradient with each respective isotope collected at opposite ends of the column.

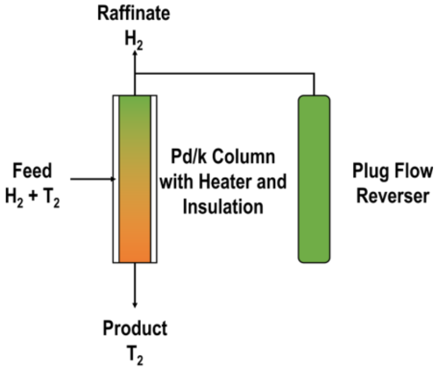

Figure 1: TCAP Process Schematic

Performance data for TCAP has been collected and analyzed to assess routes of system improvement, though is limited in its scope.[2-4] An important factor to consider is the separation efficiency of the TCAP columns and its packing material. Many factors can influence the column efficiency, such as the particle size and homogeneity of the packing material, the packing density, column diameter, and the kinetics of hydrogen sorption for the active material. As with any chromatographic process, the separation efficiency can be evaluated from the number of equivalent stages (N) through which the gas and column material interact. Thus, the goal of this work is to explore some of the factors listed above and determine their effect on the separation process.

II. Methods

A U-shaped, stainless-steel column, with a 0.25” outer diameter and a total length of 2’, is filled with the appropriate packing material for efficiency testing. The column is attached to the apparatus as detailed in Figure 2 with appropriate controls for heating and cooling, along with mass flow controllers to maintain target flow rates and a mass spectrometer to monitor the column effluent.

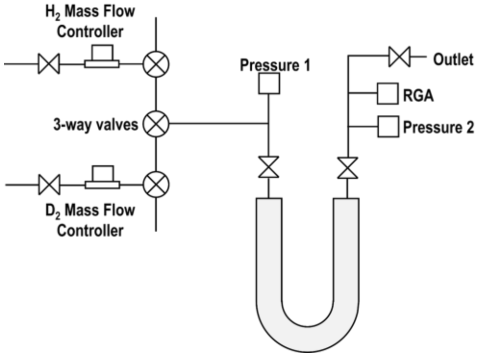

Figure 2: Pulse Test Apparatus

For investigations into the effects of particle size on separation efficiency, molecular sieve samples were crushed using a Fritsch Pulverisette 6 Planetary Mono Mill. The crushed samples were then sieved to the desired particle size distributions with a Fritsch Analysette 3 Pro Vibratory Sieve Shaker.

In a typical experiment, the column of interest is heated or cooled to the desired temperature. A fixed flow of hydrogen gas (H_2) is delivered into the column and a constant profile established on the residual gas analyzer (RGA). The flow is then switched to deuterium gas (D_2) for 30 seconds and promptly switched back to H_2. This creates a D_2 pulse that moves through the column and is measured at the outlet. The D_2 peak profile is obtained for further analysis. Mass flow controllers are used to modify and control the desired flow rates for testing. These varied flow rates are used for calculating the mobile phase linear velocity in the below detailed van Deemter analysis.

III.Results and Discussion

A. Van Deemter Analysis and Factors Influencing Column Efficiency

In chromatography, a marker for an efficient process is determined through calculating the height equivalent to a theoretical plate (HETP). Minimization of the HETP is necessary for efficient chromatographic separations. This parameter is calculated based on the relationship between the plate number (N) and the length of the column (L) as indicated by the following equation:

$$HETP = L/N \quad (1)$$

Basic determination of theoretical chromatographic plates alone cannot give insight into the factors that affect the separation efficiency of a system. With a foundation in liquid chromatography, the van Deemter model worked to deconvolute these factors and is a sufficient means to examine and optimize a separation process.[5] As applied in chromatography, the van Deemter model relates the physical, kinetic, and thermodynamic properties that influence separations into a mathematical equation. (Figure 3) This equation encompasses three parameters as a function of the mobile phase velocity (µ); constant *A* corresponds to eddy diffusion, *B* to longitudinal diffusion, and *C* correlates resistance to mass transfer.[5-7]

$$H = A + \frac{B}{\mu} + C\mu \quad (2)$$

Term *A* is influenced by the quality of column packing due to the size and shape of the packing material. The rate of gas flow in the mobile phase impacts term *B* by altering how long the mobile phase and stationary phase interact. Lastly, term *C* relies on the columns ability to restore of equilibrium as the mobile and stationary phases interact. In understanding how each of these parameters governs the overall separation process, one can improve separation efficiency through targeted column design.

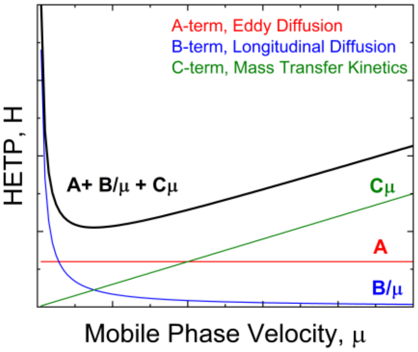

Figure 3: Van Deemter Equation and Curve

B. Data Fitting and Analysis

Gas concentrations measured using the RGA produce a time profile at the outlet of the column. The profile of the relative concentration of deuterium to protium in time is fit using an exponentially modified gaussian[8].

$$C = \frac{hw}{s}\sqrt{\left(\frac{\pi}{2}\right)}\, e^{\frac{w^2}{2s^2}-\frac{t-T}{s}}\left(1-erf\left(\frac{1}{\sqrt{2}}\left(\frac{w}{s}-\frac{t-T}{w}\right)\right)\right) \quad (3)$$

The concentration C at given time t is a function of only 4 variables: The residence time, T, of the pulse within the column, i.e., how long it takes for the pulse to reach the outlet of the column; The width of the pulse, w, in terms of standard deviation; The skew of the pulse away from Gaussian shape, s; And normalization factor h. The number of plates for the column is then determined in a similar manner to Belliveau[9].

$$N = \left(\frac{T}{w}\right)^2 \quad (4)$$

This allows for calculation of the HETP. The exact values for T, w, s, and h are determined by minimizing the RMS difference between the exponentially modified gaussian and output from the RGA. Before the subtraction is performed, the RGA output is smoothed to remove artifacts produced due to the heating and cooling methods.

C. Establishing Baseline Performance

Experimental data is fit to a standard set of equations, modified from previously determined methods[10], to yield the HETP of the column for a given range of flow parameters. At low temperatures, there is evidence of van Deemter behavior showing optimal operating flow rates for each case. (Figure 4a) In this work less focus is given to the impact of the B-term as it is largely impacted by flow rate rather than the nature of the packing material. In their fitting to the van Deemter equation, the A and C-terms present as greatly influencing the separation behavior of the Pd/k under these conditions. The van Deemter fits present negative A-terms for the low temperature extremes that steadily become positive as temperature is increased. Though negative A-terms are a non-physical result, the present trend still emphasizes the influence of the Pd absorption kinetics and H/D preference with respect to HETP. All van Deemter parameters are summarized in Table 1. The data collected at -52°C and a linear velocity of 0.9 cm/s was not included in the data fitting to prevent unreasonable behavior in the fitting program.

Along with the A-term, a significant trend is observed in the C-terms for these low temperature data in response to the hydrogen isotope sorption kinetics inherently present for Pd. At -52°C, a large C-term is observed following a stark inflection point in the van Deemter fitting as indicated by the prompt increase in HETP. For the remaining low temperature data, the influence of this resistance to mass transfer term stays present. This phenomenon highlights the importance of increasing the kinetics of hydrogen sorption onto Pd at low temperatures where the H/D preference is most prevalent.

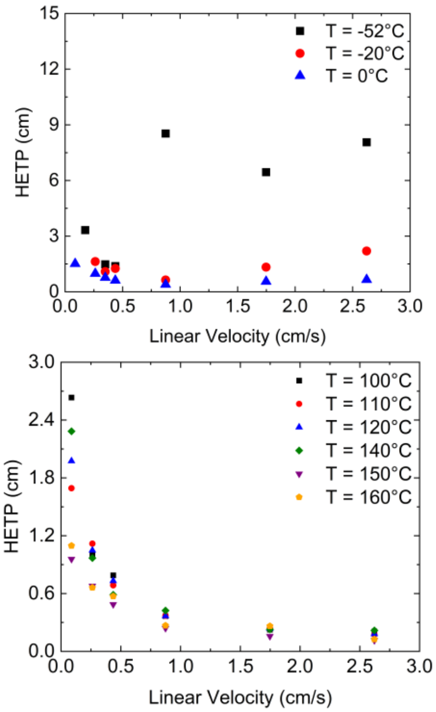

Figure 4: Height equivalent of a theoretical plate (HETP) of baseline pulse test data for a Pd/k packed column at (a) low and (b) high temperatures.

At high temperature extremes the isotopic preference for Pd exists in a non-predictive manner as indicated by the change in absorption for each isotope as a function of temperature.[11] Despite this, experimental fluctuations in *A*-terms (Figure 4b) trend with this relative change in isotope preference as temperature is increased. For separations at each temperature examined, the *C*-terms approach zero with increasing temperature. It is important to note that at these temperatures the hydrogen sorption capacity for Pd is significantly diminished which in turn promotes poor separation factors for the respective isotopes. This gives rise to negative *C*-terms at the higher temperatures, as the adsorption of hydrogen isotopes becomes kinetically fast for Pd. With the presented van Deemter fits improvements can be made with respect to the optimal column packing (A-term) and isotope sorption kinetics (*C*-term).

Table 1. van Deemter Parameters for Pd/k Pulse Test Experiments

Temperature	*A*-term	*B*-term	*C*-term
-52 °C	-1.52 ±1.59	0.69 ±0.35	3.77 ±0.72
-20 °C	-0.82 ±0.42	0.58 ±0.13	1.05 ±0.0.18
0 °C	0.40 ±0.13	0.10 ±0.02	0.06 ±0.08
100 °C	0.24 ±0.08	0.21 ±0.01	-0.06 ±0.04
110 °C	0.56 ± 0.17	0.10 ± 0.02	-0.19 ± 0.09
120 °C	0.45 ± 0.11	0.14 ± 0.01	-0.15 ± 0.06
140 °C	0.24 ± 0.05	0.18 ± 0.01	-0.04 ± 0.03
150 °C	0.41 ± 0.10	0.05 ± 0.01	-0.14 ± 0.06

160 °C	0.42 ± 0.09	0.06 ± 0.01	-0.13 ± 0.05

D. Influence of Particle Size

Following general chromatographic principles, the reduction of particle size translates into an improvement in the efficiency of separation. Particle size reduction namely brings a benefit of increasing the particle surface area and decreases the sorption distance through a particle. This physical change in turn can increase the sorption capacity for the active column material. This improvement in physical sorption behavior can largely impact the eddy diffusion (*A*-term) through the column and aid in minimizing the optimal HETP.

To investigate this phenomenon for the presented system, the above-described pulse tests were again performed using molecular sieves as the packing material. Two columns were packed with samples crushed and sieved to two different particle sizes, 30 mesh and 40 mesh (600um and 425 um) respectively. In accounting for the functional operating conditions for hydrogen isotope separation using molecular sieves, the temperature for the pulse test experiments was -170°C. Presented in Figure 5 are the results from the subsequent experiments.

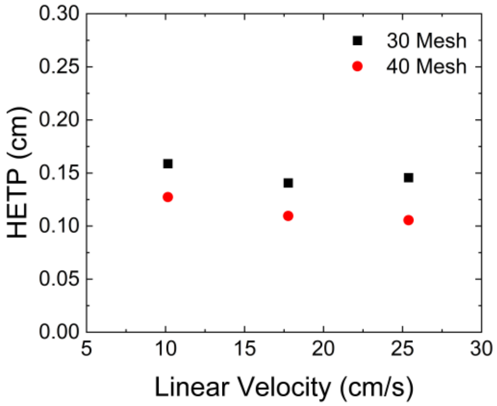

Figure 5: HETP versus gas phase velocity of the molecular sieve columns for two different particle sizes

Accordingly, the decrease in particle size from 30 mesh to 40 mesh afforded a consistent decrease in HETP across all measured flow rates. With this value drop comes a reduction in the A-term for the corresponding van Deemter model and reduction of the HETP, allowing for more optimal operating conditions. See Table 2 for the van Deemter parameters. Additionally, compared to the above presented behavior for Pd/k where there are dominating C-terms at lower temperatures, there is little to no effect from the mass transfer kinetics. This HETP for molecular sieves approaches zero for each sample size because of the fast surface adsorption for molecular sieves at low temperatures. As such, in fitting this data the *C*-term is set to zero to account for this behavior. While minimizing the particle size and distribution is a desirable solution for improving the separation efficiency, limitations are still present. As the particle size is decreased, the tighter packing in the column creates a concern due to the high pressure drop. With this inherent drawback, the column diameter must then be changed to ensure the pressure drop is within appropriate operating conditions.

Table 2. van Deemter Parameters for Molecular Sieves Pulse Test Experiments

Particle Size	*A*-term	*B*-term	*C*-term
30 Mesh	0.13 ± 0.01	0.26 ± 0.16	0
40 Mesh	0.090 ± 0.003	0.38 ± 0.04	0

IV. Conclusions

Several pulse test analyses were performed on Pd/k packed columns to compare the separation stage height versus flow rate, resulting in more accurate van Deemter parameters. The analysis was also performed at various temperatures ranging from LN_2 cooled to elevated temperatures to determine separation limits relative to column temperature. Improving the separation efficiency can also be achieved by decreasing the particle size as observed experimentally on molecular sieve packed columns. The above presented results partially highlight potential routes to improve the separation efficiency of TCAP columns and operating parameters. With this new knowledge more efficient columns and materials can be designed to improve overall performance.

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Month Day, 2023

Dear Editor,

We are writing to submit our original research article titled "Benchmarking Hydrogen Isotope Separation Efficiency of Pd/k Packed TCAP Columns" for consideration by Fusion Science and Technology. We confirm that this work is original and has not been previously published, nor is it currently being considered for publication elsewhere.

In this paper, we present for the first time, expanded baseline data for the separation of hydrogen isotopes on Pd/k. This data serves to determine areas of improvement for the Thermal Cycling Absorption Process (TCAP). TCAP continues its function to separate hydrogen isotopes at SRS and other locations but requires optimization to meet the growing demands in tritium processing, especially for fusion power plants. Examining previously published reports of TCAP performance reveals potential areas of improvement, though this requires further investigation to highlight key areas.

Herein, pulse test analyses are performed on Pd/k packed columns to determine the height equivalent to a theoretical plate (HETP) for a given set of flow velocities. This data is collected at various temperatures and plotted according to the van Deemter equation. By comparing the van Deemter parameters, eddy diffusion (A-term) and resistance to mass transfer (C-term) are found to be key factors in limiting the separation efficiency. Furthermore, improvements are first examined with respect to the A-term by performing pulse tests on molecular sieves of two different particle sizes. This collection of pulse test analyses gives new insight into the performance of Pd/k for TCAP and ways to improve its operation.

We believe this manuscript is appropriate for publication in your journal as it offers avenues for studying and improving TCAP technologies to address an expanded scope in tritium science.

Sincerely,

Kori D. McDonald