This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

METHOD TO TEST ISOTOPIC SEPARATION EFFICIENCY OF PALLADIUM PACKED COLUMNS

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The isotopic effect of palladium has been applied in different ways to separate hydrogen isotopes for many years. At Savannah River Site palladium deposited on kieselguhr (Pd/k) is used in a thermal cycling absorption process (TCAP) to purify tritium for over ten years. The need to design columns for different throughputs and the desire to advance the performance of TCAP created the need to evaluate different column designs and packing materials for their separation efficiency. In this work, columns with variations in length, diameter and metal foam use, were tested using an isotope displacement method. A simple computer model was also developed to calculate the number of theoretical separation stages using the test results. The effects of column diameter, metal foam and gas flow rate were identified.

I. INTRODUCTION

Palladium absorption of the three hydrogen isotopes exhibits a large isotopic effect (Ref. 1). It is an absorbent of choice for use in chromatographic type of columns to separate the hydrogen isotopes. Beginning in 1980, palladium deposited on kieselguhr (Pd/k) has been applied as a packing material in the Thermal Cycling Absorption Process (TCAP) at Savannah River Site for hydrogen isotope separation (Ref. 2). Kieselguhr is a diatomite chiefly composed of amorphous silica in the form of granules of about 0.5 mm size. Palladium is deposited on the porous kieselguhr via a soak-and-dry process using solutions of palladium chloride ($PdCl_2$) or palladium tetraamine nitrate $Pd(NH_3)_4(NO_3)_2$. TCAP is a semi-continuous chromatographic process. The Pd/k is packed in a long column which is thermally cycled to effect the separation of the isotopes. The separation efficiency of the TCAP column can be affected by several factors:

- Pd distribution in the kieselguhr,
- Packing density and uniformity,
- Column diameter,
- Presence of metal foam in the column.
- Gas flow rate (residence time)

The objective of this work is to identify the effects of some of the above factors on the separation efficiency. The separation efficiency of a packed column can be measured by the equivalent number of equilibrium stages. The number of stages can be determined by comparing experimental data with the calculated response curves. The steps taken include:

- Develop calculation models for data analysis.
- Fabricate experimental columns with variation in diameters and metal foam use.
- Test the experimental columns at room temperature with different flow rates.
- Comparing data with calculation results.

II. THE CALCULATION MODELS

Models to calculate response curves were developed for three types of feed change, 1) step change without isotope exchange, 2) step change with isotope exchange, and 3) pulse change with isotope exchange.

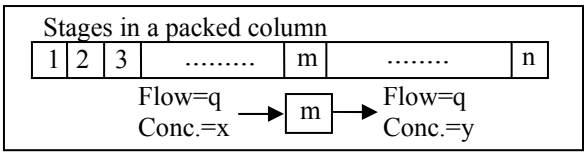

Figure 1. Theoretical stages in a packed column.

II.A. Step Change In Feed Without Isotope Exchange

A packed column is divided into n equal size sections called stages (Fig. 1). The column is filled with non-hydrogen gases and kept at a constant pressure and temperature. The gas composition within each stage is considered to be uniform. Each stage has an inlet rate, outlet rate and capacity. Material balance on a given component around a stage gives:

Inlet rate –Outlet rate = accumulation

or

$$q*x-q*y = C*(dy/dt) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

q = constant total flow rate

x, y = inlet and outlet concentrations
C = capacity of the stage
t = time

To a unit step change in feed equation 1 is solved to yield the following solution

$$Y=1-e^{(-t/\tau)}*[1+(1/1!)*(t/\tau)^1+(1/2!)*(t/\tau)^2+\ldots..+(1/(n-1)!)*(t/\tau)^{(n-1)}] \quad \ldots\ldots\ldots\ldots\ldots(2)$$

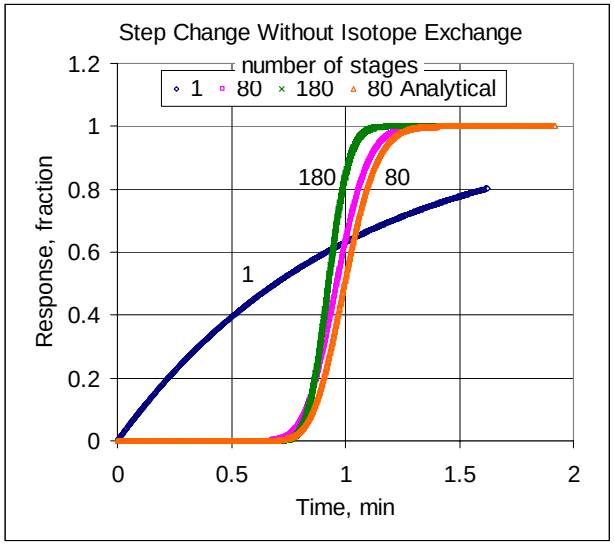

Figure 2. Response to step change in feed.

Where Y is the response to a step change for n equal size stages connected in series. For a small n, equation (2) is easy to calculate in a spread sheet. As n increases, using a Visual Basic program to calculate is much more convenient. The response curves to a step change for different number of stages are calculated and shown in Figure 2.

II.B. Step Change In Feed With Exchange Between H_2 And D_2

When hydrogen isotopes are in the column, absorption and isotope exchange between the solid phase and the gas phase occurs. The capacity is divided into two parts. Gas phase capacity is calculated using the ideal gas law and the solid phase capacity is determined by the absorption capacity of Pd at the test conditions. For stage m in a finite small time step, the inlet gas composition is that of the preceding stage (m-1), and the outlet gas composition is that of the stage at the preceding time step. The new composition in the stage is now different and redistribution between the gas phase and the solid phase must occur to reach a new isotopic equilibrium. This equilibrium is governed by a separation factor equation derived from reference 1:

$$SF = (D/H)_g/(D/H)_s = (-261.25/T + 0.4263) * C_{hs}^{1.6} + (721.15/T + 0.0668) \quad \ldots\ldots\ldots\ldots(1)$$

Where SF = separation factor, $(D/H)_g$ = deuterium to protium ration in the gas phase, $(D/H)_s$ = deuterium to protium ration in the solid phase, T = temperature K, and C_{hs} = fraction of H in solid.

The separation factor is calculated using the C_{hs} from a preceding time step. The new distribution of the isotopes must satisfy this separation factor by exchanging certain amount of D for H between the gas phase and the solid phase. Let this amount be Ed, then:

$$SF=[(D-Ed)/(H+Ed)]_g / [(D+Ed)/(H-Ed)]_s$$

or

$$Ed=\{[-SF*(Hg+Ds)-Dg-Hs]+[(SF*(Hg+Ds)+Dg+Hs)^2-4*(SF-1)*(SF*Hg*Ds-Dg*Hs)]^{0.5}\}/\{2*(SF-1)\} \quad \ldots\ldots\ldots\ldots(2)$$

Where Hg, Dg = amounts of gas phase protium and deuterium and Hs, Ds = amounts of solid phase protium and deuterium

Once Ed is calculated, the new values for Hg, Hs, Dg, and Ds can be calculated. This is repeated for all the stages for one time step. Once that is done a new time step is calculated. The time steps must be small so that the results approximate a real solution. A Visual Basic program was written in Microsoft Excel to do this calculation.

When there is no isotopic effect; that is, when the separation factor is 1, the model is reduced to the same as the inert step change model, represented by equation (2). The calculated results of equation (2) and this model are compared in Figure 2 and they are practically the same. This shows that the finite time step model is a very good approximation for the analytical solution. Another property shown in Figure 2 is that the increase from 80 to 180 stages generates only a small difference between the response curves. It will be difficult to tell the difference for smaller changes in the number of stages. A pulse change method to be discussed next is a better method.

II.C. D_2 Pulse Change In Feed

Pulse change here is defined as "changing the feed from pure H_2 to pure D_2 for a short period of time". In effect this is just like two step changes in series. The step change program is modified to calculate the response to a pulse change with isotopic exchange. A typical calculated result is shown in Figure 3 and 4. The peak height of each response curve is clearly a function of the number of stages and can be fitted by an equation. With this method the number of stages can be better determined.

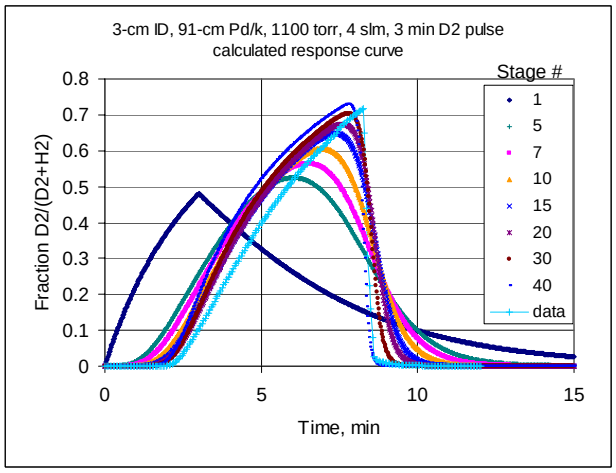

Figure 3. Response to pulse change in feed.

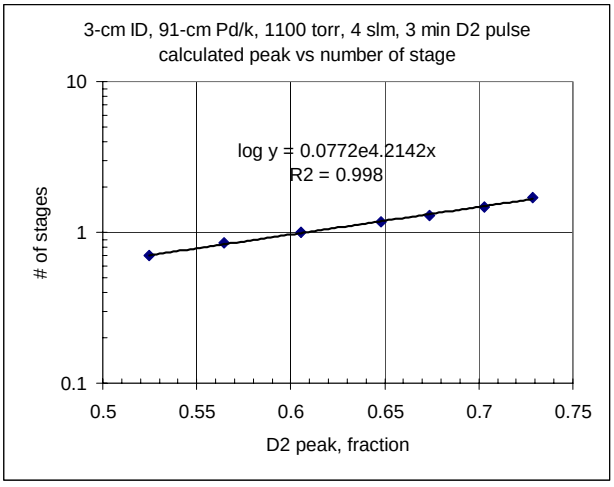

Figure 4. Response to pulse change in feed.

III. TEST APPARATUS AND METHOD

A schematic of the apparatus is shown in Figure 5. It consists of a one-meter long column filled with Pd/k, mass flow controllers (MKS models) to set the target flow rate of H_2 and D_2, a mass spectrometer (Pfeiffer Prisma) to measure the effluent composition, and a computer data logging system to record the flow rates, pressures and mass spec results. The columns were fabricated from stainless steel with inside diameters of 1.37, 3.0 and 4.66 cm. One column was filled with aluminum foam (RGI Duocel®) in the form of 1" tall cylinders of the same diameter as the ID of the columns, then it is filled with the Pd/k. The metal foam was used to improve heat transfer in the column. Palladium content in the Pd/k is 54 wt%. The column properties and the test flow rates are summarized in Table 1. The column with Al foam had a lower Pd density because the foam had taken up part of the column volume. The flow rates were calculated from the volumetric flow rates divided by the actual cross section openings of the columns.

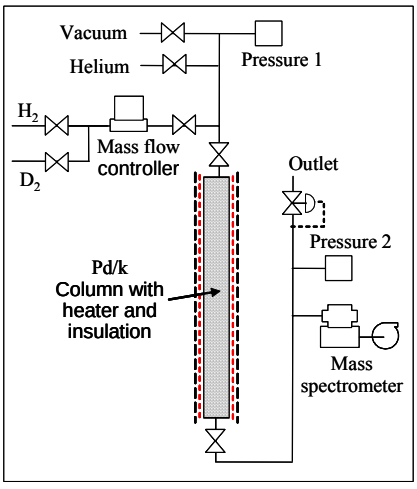

Figure 5. Test apparatus.

Table 1. Column properties and flow rates.

Column	Inside Diameter cm	Metal Foam	Pd density g/cc col	Flow cm/min
1	4.66	No	0.66	263, 558, 1124
2	4.66	Al	0.53	287, 610
3	3.00	No	0.64	567
4	1.37	No	0.67	998

For a typical run, a steady flow rate of H_2 was first established. The flow was then switched to D_2 for 3 minutes before it was switched back to H_2. A D_2 peak would be measured at the outlet. This D_2 pulse could be repeated. The peak height duplicated itself very well (Figure 6). The pulse duration could be varied if desired.

Using the method explained in Section IIC the D_2 peak height is calculated using the test conditions with the number of stages as the variable. The stage number that gives the same peak height as that measured will be the number of stages of the column at the test conditions.

IV. RESULTS AND DISCUSSION

The application of this method is demonstrated with the following test results.

IV.A. Effect of Flow Rate

The column with 4.66 cm diameter was tested at 3 flow rates, 263, 558, and 1124 cm/min.

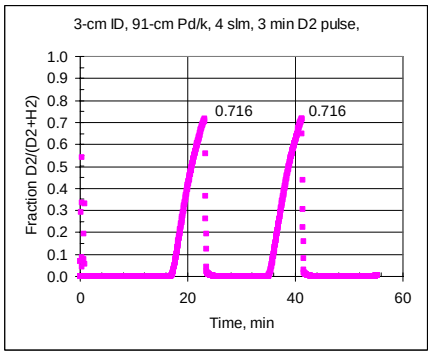

Figure 6. D_2 pulse response repeated.

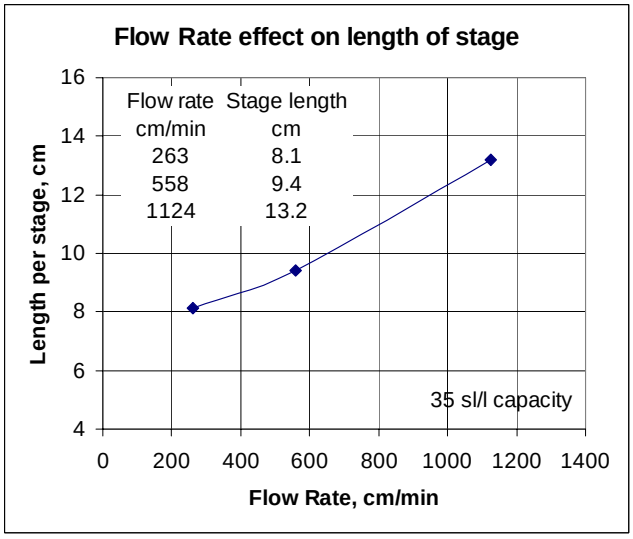

Figure 7. Flow rate effect on staging.

These linear rates were calculated by the volumetric rate divided by the effective cross section of the column. The effective cross section is calculated from the void volume divided by the length of the column. The theoretical number of equilibrium stages for a given flow rate was determined by the method described above. The results show the column length per stage increases from 8.1 cm to 9.4 and 13.2 cm as the flow rate increases from 263, 558 and 1124 cm/min. See Figure 7. High gas flow rate reduced the separation efficiency significantly.

IV.B. Effect of Diameter

Three one-meter long columns with 3 different inside diameters, 4.66, 3.00, 1.37 cm, were prepared and tested the same way as above. The gas flow rates were adjusted so that the linear flow rates were about the same. The results are shown in Figure 8. The column length per stage increased from 1.78 to 2.54 and 4.06 cm when the ID increased. The effect is also very significant.

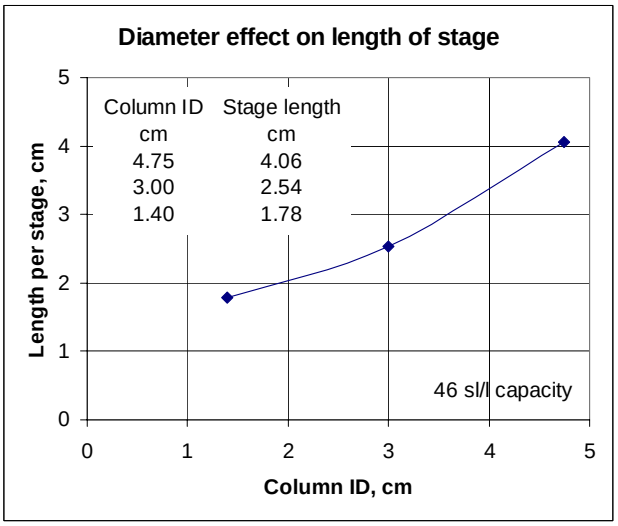

Figure 8. Diameter effect on staging.

IV.C. Effect of Metal Foam

Foam Effect		
Column ID inch	**Al Foam**	**Efficiency inch/stage**
1.87	No	1.6
1.87	Yes	1.6

The use of aluminum foam in the column to improve heat transfer is desired in some applications. To study the effect of aluminum foam in the column on separation efficiency, two one-meter long, 4.66-cm diameter columns, one with aluminum foam, the other without, were tested at a flow rate of 558 cm/min. The numbers of stages in the 1-m column are 22.1 for the one with the foam and 22.8 for the one without the foam. The length per stage is 4.53 and 4.39 cm respectively. The difference is very small. Considering the foam replaced about 20% of the volume for Pd/k, the foam actually improved the staging efficient on a per gram Pd basis.

V. SUMMARY

A mathematical model was developed to calculate the response curve of a palladium packed column when it is subjected to a step change or pulse change in feed. This model can be used to analyze experimental data and identify the effect of design and operating condition on the separation efficiency. One-meter long columns packed with palladium-on-kieselguhr with variation in diameter were used to generate response curve data. The number of stages and the length of a stage for the columns were identified by comparing data with calculated response curves. The results showed that the gas flow rate, the diameter and the use metal foam all have a significant effect on the separation efficiency. This information can be used to design better columns and more efficient operating conditions.

ACKNOWLEDGMENTS

Sharon Redd and Judy Dye carried out the experiments. Their enthusiasm to the work is highly appreciated.

References

1. M. W. Lee, “Tritium Separation Using Metal Hydrides”, Gordon Research Conference, Oxnard, CA (USA) February 10 (1986).
2. A. S. Horen and M. W. Lee, “Metal Hydride Based Isotope Separation – Large-Scale Operations”, Fusion Technology, vol. 21, 282 (1992).