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Hydrogen Isotope Exchange Tests in Support of HT-TCAP (U)

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with contributions from others*

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* See "Acknowledgement" section.

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Abstract

Hydrogen isotope exchange kinetics of Pd/k was tested in laboratory scale columns to help troubleshoot the HT-TCAP performance problem. The main objective was to evaluate the effects of “old” and “new” Pd/k, column diameter, and metal foam on hydrogen isotope exchange efficiency. This efficiency affects the separation performance of the TCAP column.

Three kinds of columns were used in the tests:

1) ¾” pipe, 6” long, U-shape column. This column was used because it was readily available due to a completed PDRD project. This group of tests compared “new Pd/k” and “old Pd/k”, and produced a bake-out recipe for new Pd/k.
2) 3-ft long columns of various diameters: ¾”, 1.25” and 2” with and without foam (aluminum and copper). This group of tests compared the effect of diameter, foam and Pd/k on staging performance.
3) The Jacobs coil, an existing 20-ft coil filled with Al foam identical to HT-TCAP. This group of tests was to see how a plant-type column performed. (See reference 2 for more details.)

The following methods and computer programs were developed to help evaluate the test data:

1) An equation and a visual basic program for calculating response curves to step changes in inert feed concentration.

2) A finite difference method and a visual basic program for calculating response curves to step changes in hydrogen isotope concentration.

3) A finite difference method and a visual basic program for calculating response curves to pulse changes in hydrogen isotope concentration.

The pulse response test and calculation were found most useful for comparing the isotope exchange performance of Pd/k packed columns. Increasing column diameter from 1.25" to 2" reduced the number of equilibrium stages by about 40%. Aluminum foam and copper foam did not reduce the number of stages. The new Pd/k required much more bake-out and absorption/desorption cycles before it could reach the same exchange kinetics as the old Pd/k.

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[*] See "Acknowledgement" section.

1. Introduction

Three new TCAP isotope separation units have been installed in Building 233-H as part of the Tritium Consolidation project. The differences between these new units and the other two existing units in the build include: column diameter increased from 1.25" to 2", aluminum foam used for heat transfer improvement, Pd/k produced by a new vendor with a new procedure, and the PFR diameter increased from 4" to 6". All these were expected to have effects on the performance of the column but were not tested before the columns were designed, built and installed for cost reasons. During cold tests with H_2 and D_2 separation, these new units produced raffinate purity meeting the target of 500 ppm D in H only for feed rates up to 4%. The design target was 8%. A vigorous drive was initiated to define the cause for this less than expected performance and to seek solutions.

The separation efficiency of the TCAP column can be affected by these factors:

- Packing material properties such as the isotope exchange kinetics.
- Packing density, uniformity and etc. of the column.
- Column diameter.
- Aluminum foam in the column.

The objective of this work is to test and analyze the effects of the above factors on the separation efficiency.

The approaches taken include computer modeling and experimental testing:

- Develop calculation models for data analysis. These include step change response without isotope exchange, step change response model with isotope exchange, and pulse change response with isotope exchange.
- Fabricate experimental columns of various diameters, with and without foam, and using different Pd/k packing.
- Test the experimental columns at room temperature with different flow rates.

A mass spec and an experimental manifold used for PDRD projects were adapted for this experimental work.

2. Development of the calculation models

2.1 Step change in feed concentration without exchange (using inert gases)

A packed column is divided into n number of equal size sections called stages. The void space is filled with inert gases at a constant pressure and temperature. The gas in each stage is considered to be completely mixed. Each stage has inlet rate, outlet rate and capacity. Material balance on a given component around a stage gives:

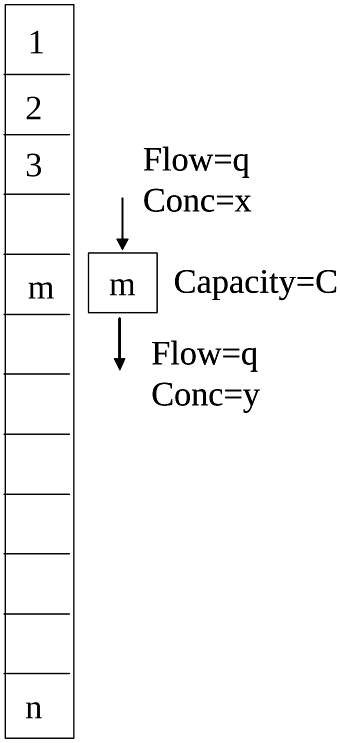
Inlet rate –Outlet rate = accumulation

or

$$q*x-q*y = C*(dy/dt) \qquad \text{……………………………………………(1)}$$

where

q = constant total flow rate
x, y = inlet and outlet concentration of component
C = capacity of the stage
t = time



At steady state, $x_o=y_o$ = constant and $(dy_o/dt)=0$, or

$q*x_o=q*y_o = C*(dy_o/dt)=0$ ……………....……(2)

Equation (1) minus (2) yields

$q*(x-x_o)-q*(y-y_o) = C*[d(y-y_o)dt]$ …………....………(3)

Let $X=(x-x_o)$, and $Y=(y-y_o)$, equation (3) becomes

q*(X-Y)=C*(dY/dt)

or

X-Y=C/q*(dY/dt)=•*(dY/dt) ……………....……(4)

where • =C/q=residence time

Take Laplace transform of equation (4) for a unit step change (X=1) to give

Y(S)=1/[S*(1+ • *S)]

For n stages in series

Y(S)=1/[S*(1+ • *S)^n]

……....……………..…(5)

Inverse Laplace transformation of equation (5) yield

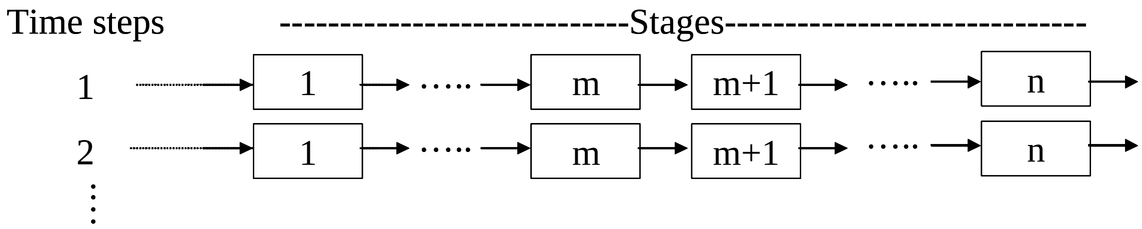
Y=1-e^(-t/ •)*[1+(1/1!)*(t/ •)^1+(1/2!)*(t/ •)^2+…...+(1/(n-1)!)*(t/ •)^(n-1)] ....(6)

Equation (6) is the response to a step change for n number of equal size stages connected in series.

For a small n, equation (6) is easy to calculate in a spread sheet. As n increases, using a Visual Basic program to calculate is much more convenient. Such a program is given in Appendix 1. The response curves to a step change for different number of stages are calculated and shown in Figure 1. This exercise shows that the mathematical solution for a step change of concentration in feed without any exchange reaction in the column is quite complex already. It will be very difficult to develop a mathematical solution for cases when exchange also occurs. To overcome this difficulty, a finite time step method was used to develop a calculation method that can be carried out in an Excel spread sheet using the Visual Basic tool. The development of this method is explained below.

2.2 Step change with exchange (H_2 and D_2)

The column is divided into n number of equal size sections called stages. Each stage has inlet gas, outlet gas and holdup (or called capacity). The capacity is divided into two parts: one part in the gas phase and the other in solid phase. Gas phase capacity is calculated from pressure, temperature and volume using the ideal gas law, and the solid phase capacity is set constant at 0.65 (H+D)/Pd. In a finite small time step, the amount of gas coming into the stage equals the amount of gas going out so that the capacity in the stage stays constant. The inlet gas composition is that of the preceding stage, 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 equilibrium. The new equilibrium is governed by the isotopic correlation of Pd absorbing a mixture of H_2 and D_2. The isotopic correlation is expressed 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) …………(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
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=$[(D-Ed)/(H+Ed)]_g$ / $[(D+Ed)/(H-Ed)]_s$
and
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)} ………………………………….(2)

Where Hg, Dg = gas phase protium and deuterium
Hs, Ds = 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 a 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 is written in Microsoft Excel to do this calculation. The program is shown in Appendix 2.

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 (6). The calculated results of equation (6) and the model are compared in Figure 2 and are practically the same in shape. This shows that the finite time step model is a very good approximation for the analytical model.

The response curves to a step change from H_2 to D_2 and from D_2 to H_2 are shown in Figure 3. These curves show that the difference becomes small and difficult to differentiate when the number of stages becomes large. A better test method needs to be developed.

2.3 Pulse change with exchange (D_2 pulse)

The step change exchange program can be modified to calculate the response to a pulse change with exchange. Pulse change here is defined as "changing the feed to a column from pure isotope A to pure isotope B for a short period of time, then back to A." In effect this is just like two step changes in series. A Visual Basic program for a pulse change in D_2 on H_2 is given in Appendix 3. The feed concentration change and the response curves for different number of stages in a given column are shown in Figures 4 and 5. The heights of the D_2 peaks are depending on the number of stages and can be fitted by an equation.

3. Test Apparatus

The test apparatus for the step change and pulse change tests are similar. A schematic of the apparatus is shown in Figure 6. It consists of a column filled with Pd/k to be tested, a mass flow controller to set the target flow rate of H_2 and D_2, a mass spectrometer to monitor the effluent composition, and a computer data logging system to record the flow rates, pressures and mass spec results.

4. Test Method and Results

4.1 Comparing “new” Pd/k with “old” Pd/k

“New” Pd/k as received was loaded into the U column. The sample volume was 42 cc and the weight was 42.8 g. The Pd/k was activated by H_2 absorption at room temperature and desorption at about 150 ^oC. After the third absorption, step change tests were conducted between H_2 and D_2 flowing through the column at 100, 200 and 500 sccm. After five exchanges, the column was heated to 300 ^oC under Ar purge for 1 hour. Then more exchanges were conducted at 500 sccm.

Another identical column was filled with an “old” Pd/k, measured at 47 cc and 41.1 g. Similar activation and step-change flow tests were conducted. The results were compared with the “new” Pd/k. The comparison showed the new Pd/k did not produce as sharp a breakthrough curve as the old Pd/k before the 300 ^oC heating and purge. After the 300 ^oC heating, the new

Pd/k’s breakthrough curve improved to about the same as that of the old Pd/k. This is shown in Figure 7.

Another set of tests with the new Pd/k was conducted to see how much purge is required to bring the new Pd/k kinetics to the ultimate state by heating at no higher than 180 ^oC. To do this, the used sample in the U-column was replaced with a new sample of the new Pd/k. The new sample weighted 42 g. The column was saturated with H_2 at room temperature and purged with Ar at 170 ^oC for 1.5 hours. This was repeated. It was then subjected to step changes between H_2 and D_2 flow. The time spent on H_2 and D_2 exchange was equivalent to hydrogen purge at ambient temperature. It was a total of 7 hours of hydrogen purge before the exchange kinetics increased to a steady level. The improvement in exchange kinetics was measured by the D_2 concentration at 950 seconds after a change from H_2 to D_2 at 500 sccm. This concentration increased steadily until after about 8 exchanges. This is shown in Figure 8.

The step change method produced breakthrough curves. The sharpness of the breakthrough curve is an indication of the exchange kinetics of the packing material if the column is well packed. A breakthrough curve can be calculated using a height equivalent to a theoretical stage (HETS) method. In the calculation the HETS (or the number of stages) is adjusted until the calculated curve fits the data. Unfortunately this method does not work well when the number of stages is large, when a large change in the number of stages brings a very small change in the shape of the curve. Therefore this method cannot compare the performance of two packing materials well when the number of stages is large. A different method, the pulse method, was later developed, and this method can differentiate the performance much better.

Using the pulse technique, the U column was installed in the apparatus the same way as the step change test. The column was saturated with H_2 at room temperature, and steady flow of H_2 through the column to atmosphere was established. The H_2 flow was switched to D_2 flow for one minute, then back to H_2. The concentration of the effluent gas was measured using the mass spec. The effluent gas would show a D_2 peak. With the height of this peak, the number of separation stages is calculated using the equation of the model.

The D_2 pulse test results of the "old" and "new" Pd/k are shown in Figures 9 and 10. The results of the old Pd/k were generated after 5 cycles of exchanges and that of the new Pd/k were after 20 cycles. The number of stages was 9 for the old Pd/k and 10 for the new Pd/k. Noting the difference in cycle numbers, these results show the two Pd/k's performed about the same, consistent with the step change results discussed earlier.

4.2 Effect of aluminum foam in column

To define the effect of aluminum foam in the column on separation efficiency, two 3-ft long, 2-in diameter columns, one with aluminum foam, the other without, filled with the new Pd/k were tested for the number of separation stages. These columns were first "activated" with H_2 absorption at room temperature followed by helium purge at 150-180 ^oC. The absorption and purge were repeated 2 times before the final evacuation and saturation with

Foam Effect

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

H_2 for D_2 pulse tests. The test procedure is similar to that described earlier for the U-shape column, except that the gas flow rate is higher at 10 SL/min and the pulse size is 3 minutes. The gas flow rate is near the average gas transfer rate of the actual TCAP unit. The results are presented in Figures 11 and 12. The numbers of stages in the 3-ft column are 22.1 and 22.8 for the one with foam and the one without foam, respectively. They are considered the same. The foam did not reduce the number of stages in the column. Note that the column with foam contains less Pd/k than the one without foam, 1592 g versus 1982 g.

4.3 Effect of diameter of column

Three feet long columns with 3 different diameters: 2", 1.25", 0.75" OD (1.87", 1.18", 0.55" ID), were prepared and tested the same way as above. The gas flow rates were adjusted so that the linear flow rates per cross section area were the same. The results are shown in Figures 12, 13, and 14. The results show that the column diameter effect on the number of stages is very significant. The column length per stage increases from 0.7 inch to 1 inch and 1.6 inch when the ID increases from 0.55, 1.18 and 1.87 inch.

Diameter Effect

Column ID inch	**Flow rate** cm/min	**Efficiency** inch/stage
1.87	563	1.6
1.18	567	1.0
0.55	987	0.7

4.4 Effect of gas flow rate

During gas transfer between the column and PFR of the TCAP, the gas flow is high at the beginning of the transfer and decreases as the pressure difference decreases. To quantify this gas flow rate effect on the number of separation stages, the 2-inch diameter column without foam was tested at 3 different gas flow rates: 4.7, 10 and 20 SL/min. The results show the column length per stage increases from 3.2" to 3.7" and 5.2" as the flow rate increases from 4.7, 10 and 20 SL/min. High gas transfer rate reduced the separation efficiency significantly. Considering most of the gas transfer takes place at the high flow range, the TCAP column efficiency can be improved by reducing the high flow range and increasing the low flow range.

2" 3-ft no foam, at 56 sl capacity

Flow, slm	Inch/stg	Ratio
4.7	3.2	0.86
10	3.7	1
20	5.2	1.41

4.5 The demonstration coil and column E from T-CON

A 20-ft long 2-inch diameter column with aluminum foam, used for the Pd/k loading demonstration earlier, was reloaded with Pd/k and tested using both step change and pulse change procedures. Column E of the T-CON TCAP system was removed from the process and transported to Central Shop, where a D_2 pulse test was conducted. The results are compared in Figure 15. Column length per stage for the demonstration column is 4.3 inches, and for the coil 1 and coil 2 of column E, 15 and 11 inches. The staging efficiency of the demonstration coil was significantly better than those of column E. The potential cause for this difference included Pd/k packing condition, residual water in column, and deviation in testing conditions. Schedule at the time did not permit further testing of column E.

5. Summary

This work demonstrated:

- Pulse change model served better than step change model for evaluating column efficiency.
- H_2/D_2 exchange tests defined the effect of column diameter, foam and Pd/k type on staging efficiency.
- “New” Pd/k needs more “exercise” than “old” Pd/k to achieve equal efficiency.
- Increase of column diameter decreases number of stages.
- Foam does not reduce number of stages.
- Dense and uniform packing increase number of stages.
- High gas flow rate reduces the number of stages.
- HT-TCAP column and Pd/k, when properly prepared and operated, should meet operation needs but will probably not meet the original design target due to the effect of low packing density and large column diameter.

Acknowledgements

A large number of people worked diligently for this effort, giving their time on off hours and on weekends. These include Jim Klein, Bob Hsu, Greg Staack, David Jacobs, Martin Scott, Steve Hite, Sharon Redd, Jody Dye, Melinda King, Nancy Wallace and Jackie Johnson. Their contributions are much appreciated.

Reference:

1. M. W. Lee, "A Study Of The Separation Factors For Hydrogen Isotopes On Metal Hydrides", Savannah River Laboratory Quarterly Report, July-September, 1985, DPWD-85-20-3.
2. R. H. Hsu, "Jacobs Coil Testing In C-061", April 21, 2004, SRT-HTS-2004-00033.

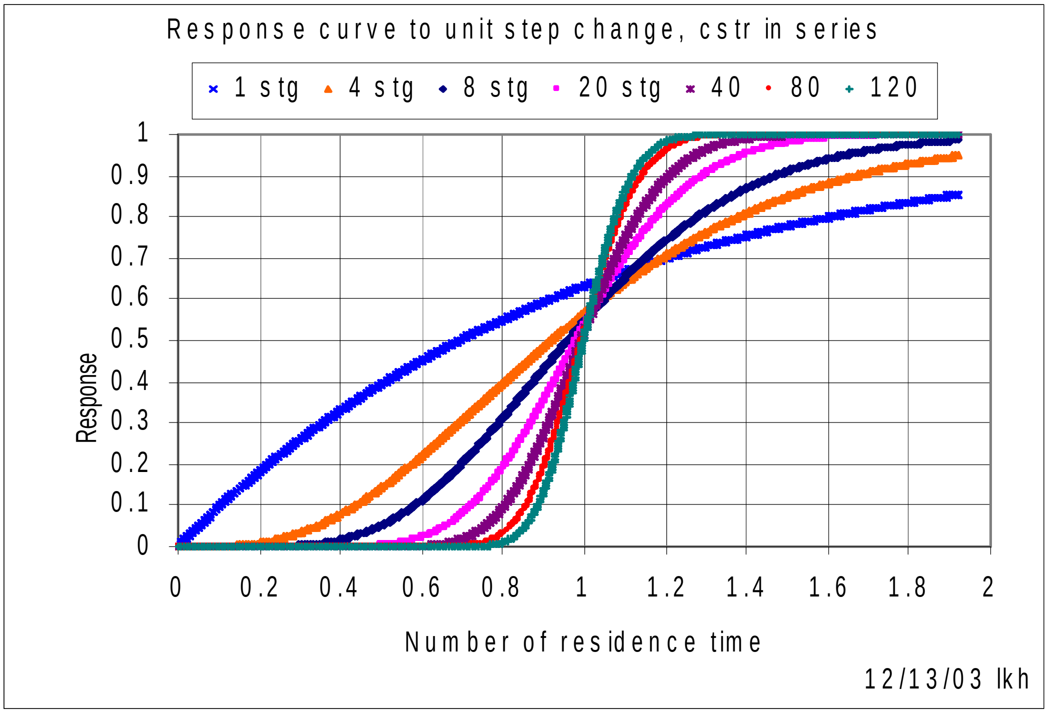


Figure 1 Response curve to unit step change for series of stages.

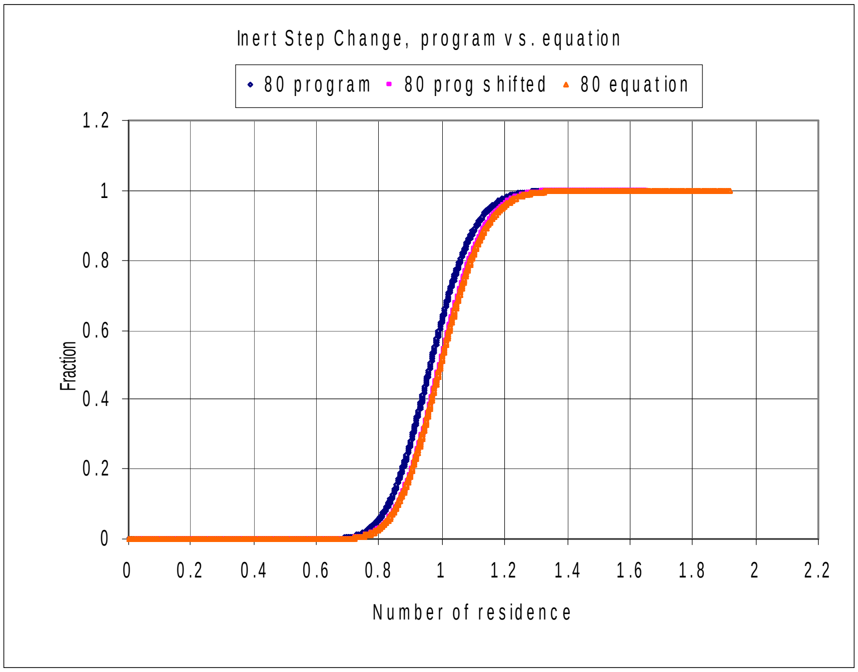
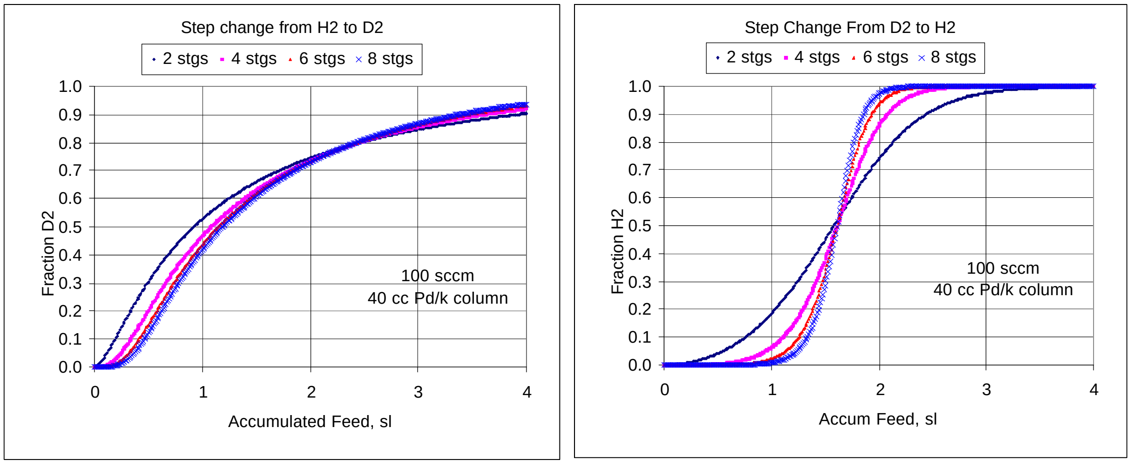


Figure 2 Response curves to unit step change calculated by two different methods.



- Difference is small when # of stages is large

Figure 3 Response curves to step change from H_2 to D_2 and from D2 to H2.

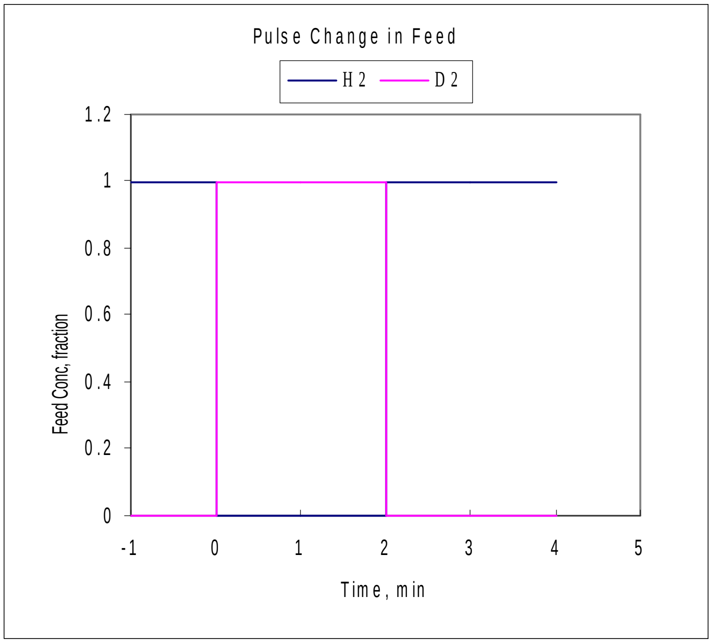


Figure 4 Schematic of a pulse change in feed".

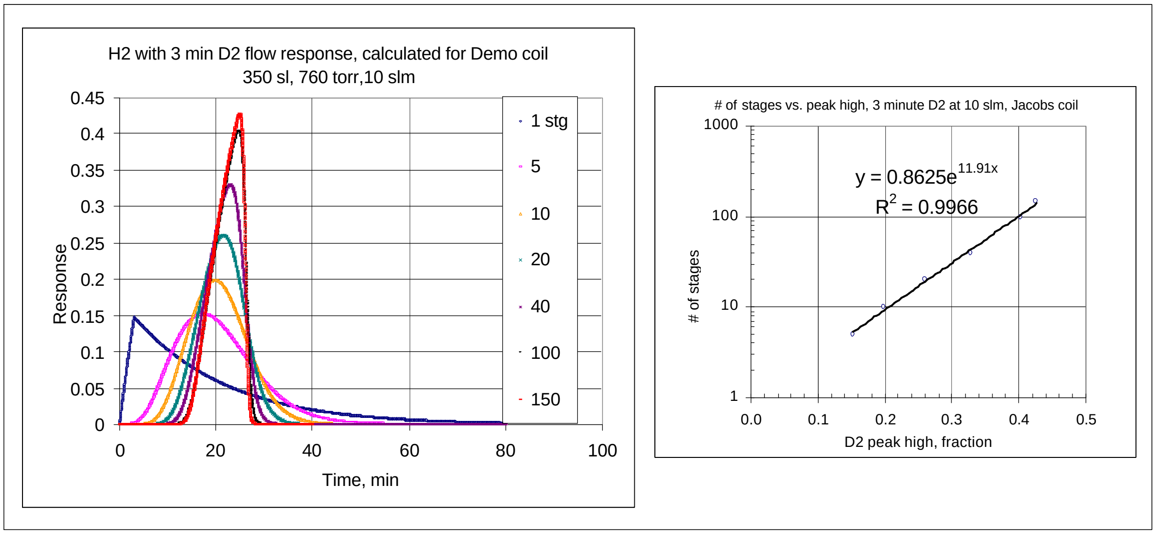


Figure 5 Response curves to a pulse of D_2 depending on the number of stages.

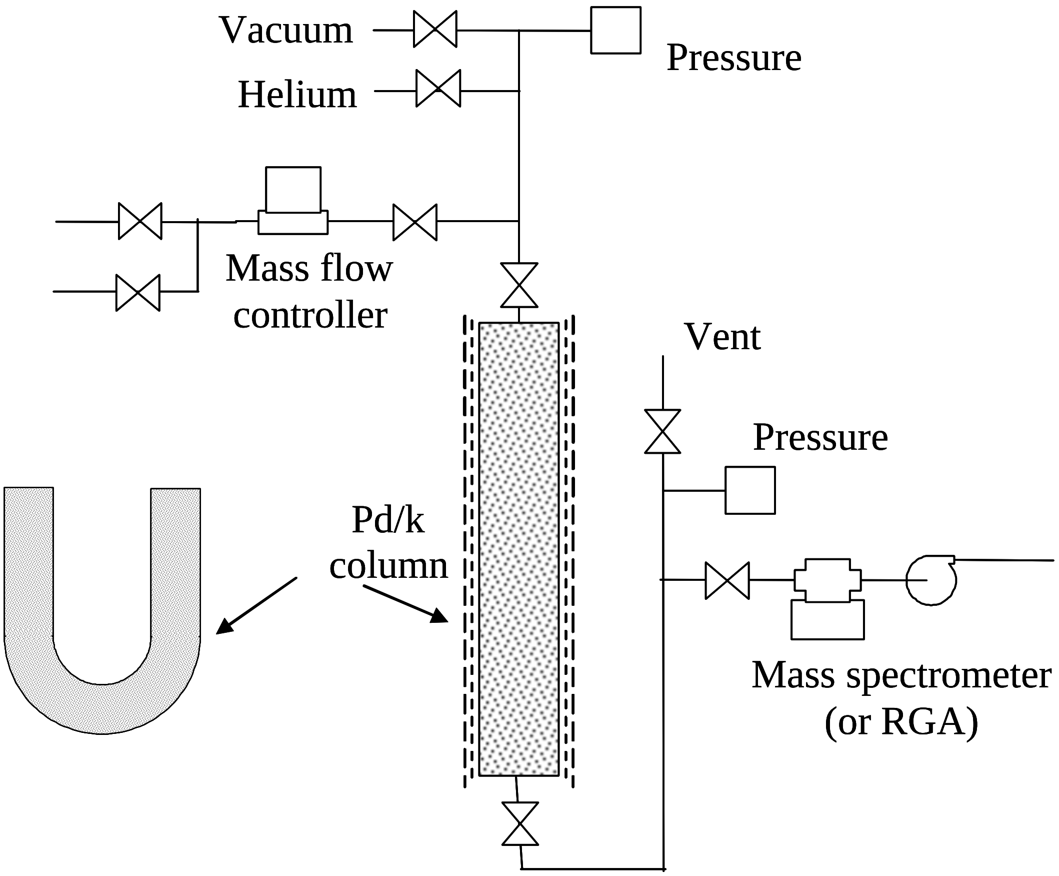


Figure 6 Schematic of experimental equipment for H_2/D_2 exchange tests.

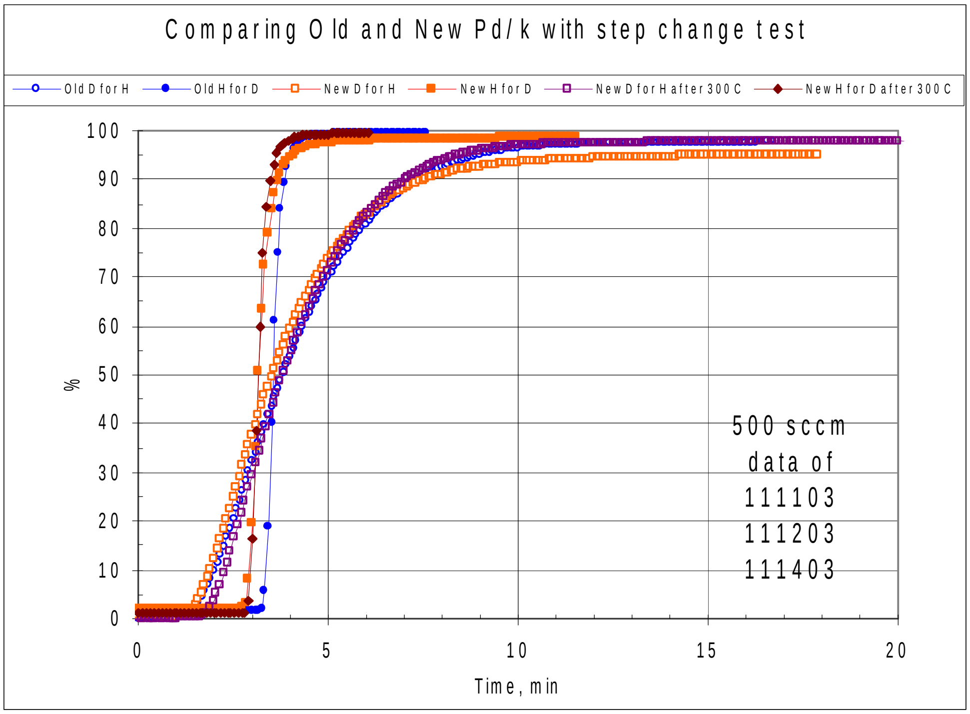


Figure 7 Comparing H and D exchange kinetics of "old" and "new" Pd/k, 300 °C bake out brought the "new" to match the "old".

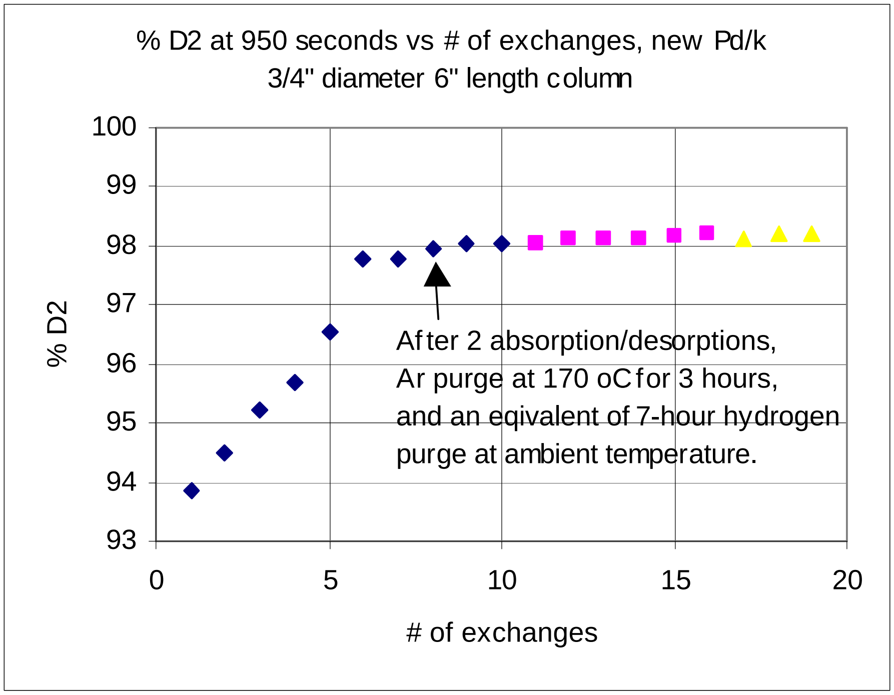
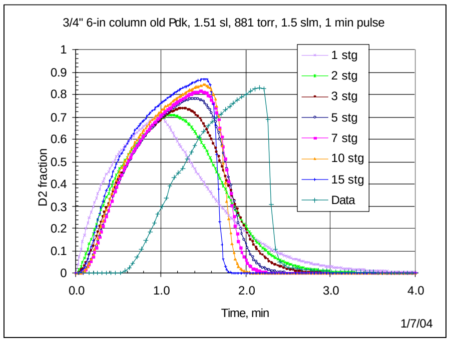
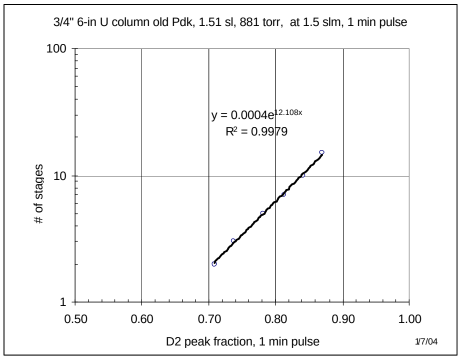
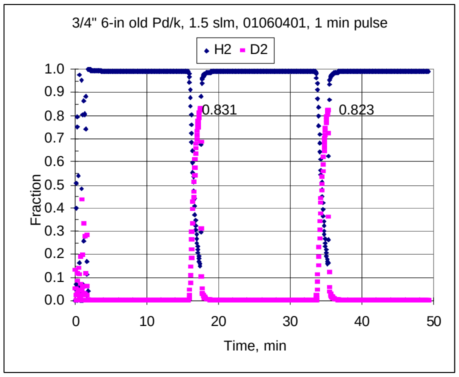


Figure 8 New Pd/k required more heat and purge to improve kinetics.







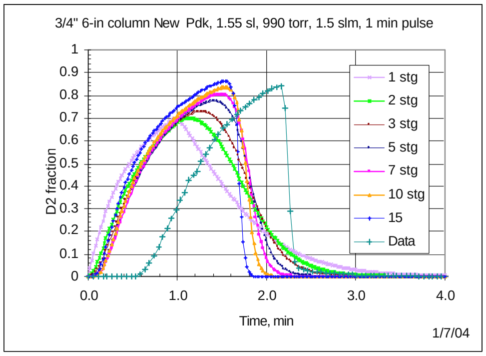
"Old" Pd/k after 5 cycles in U-column:

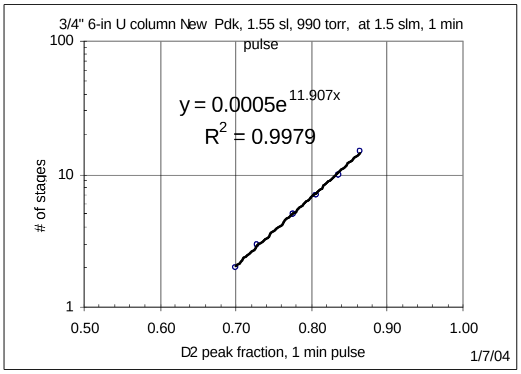
Number of stages: 8.94

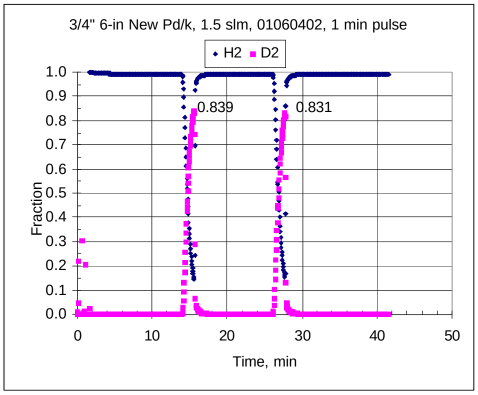
Length per stage: 0.67 inch

stage per g-Pd: 0.41

Figure 9 "Old" Pd/k column response curve to a D_2 pulse.







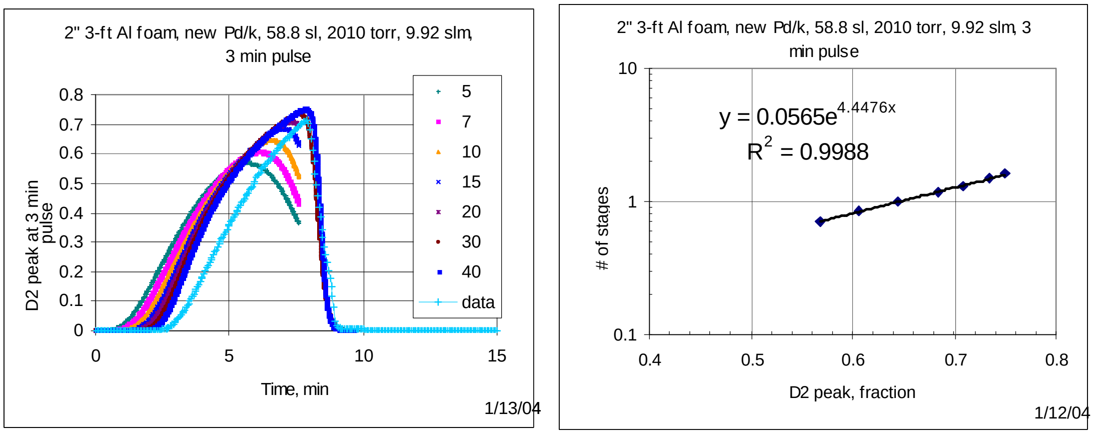
"New" Pd/k after 20 cycles in U-column:

Number of stages: 10.4

Length per stage: 0.58 inch

stage per g-Pd: 0.46

Figure 10 "New" Pd/k column response curve to a D_2 pulse.



2” diameter 3-ft with foam:

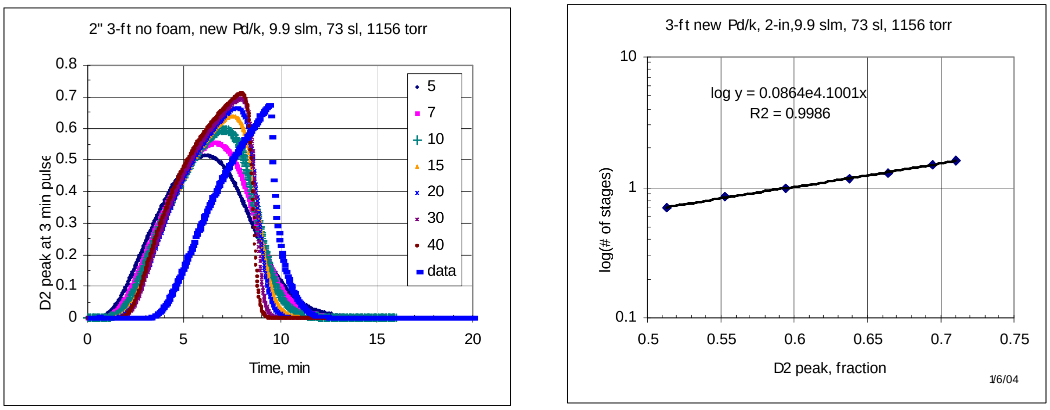
D2 peak: 0.7125

Number of stages: 22.1

Length per stage: 1.6 inch

stage per g-Pd: 0.026

Figure 11. 3-ft long 2-in diameter column with aluminum foam and "new" Pd/k.



2” diameter 3-ft no foam:

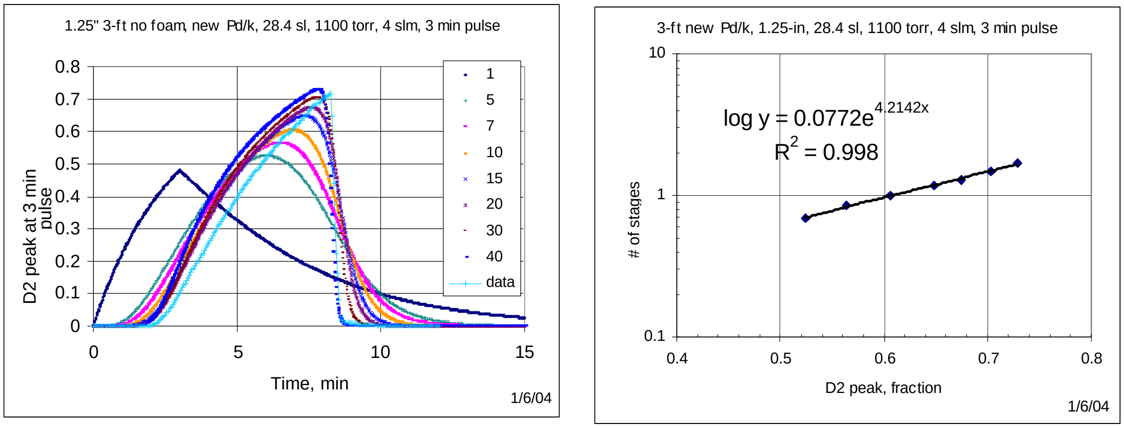
D_2 peak: 0.672

Number of stages: 22.8

Length per stage: 1.6 inch

stage per g-Pd: 0.021

Figure 12. 3-ft long 2-in diameter column without aluminum foam with "new" Pd/k.



1.25” diameter 3-ft no foam:

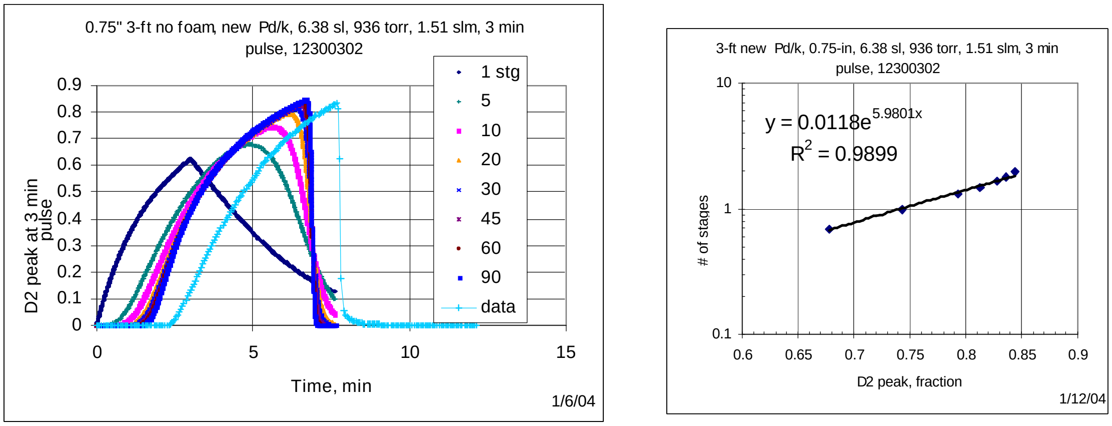
D2 peak: 0.716

Number of stages: 37.8

Length per stage: 1.0 inch

stage per g-Pd: 0.091

Figure 13. 3-ft long 1.25-in diameter column without aluminum foam with "new" Pd/k.



0.75” diameter 3-ft no foam:

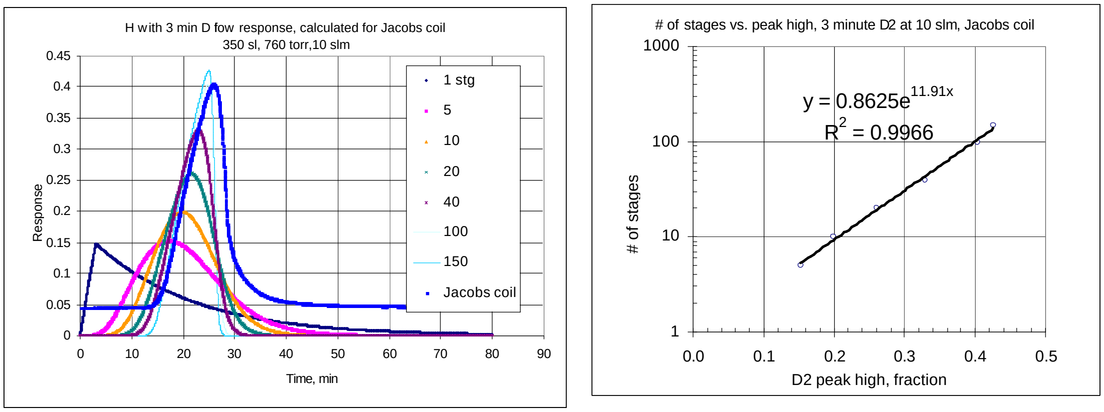
D2 peak: 0.832

Number of stages: 51.1

Length per stage: 0.7 inch

stage per g-Pd: 0.548

Figure 14. 3-ft long 0.75-in diameter column without aluminum foam with "new" Pd/k.



Demo coil (Jacobs coil) at 10 slm:

D2 peak: 0.35

Number of stages: 55.7

Length per stage: 4.3 inch

Column E at 10 slm (coils 1 & 2):

D2 peak: 0.244, 0.267

Number of stages: 16, 21

Length per stage: 15, 11 inch

Figure 15. Demonstration coil and column E coils.

Appendix 1 Visual Basic program to calculate step change response for stages in series.

```
Sub Macro1()
' Program to calculate respose to step change for stages in series.
' Y=1-e^(-t/ t)*[1+(1/1!)*(t/ t)^1+(1/2!)*(t/ t)^2+…...+(1/(n-1)!)*(t/ t)^(n-1)]
' Macro1 Macro
' Macro recorded 11/30/2003 by K Heung
'
' Keyboard Shortcut: Ctrl+b
'
n = 130
Volume = 250
Flow = 8
Restime = Volume / n / Flow * 60
Minutes = 60
seconds = Minutes * 60
For Etime = 1 To seconds
    S = 0
        For sta = 1 To n
        Fact = Application.WorksheetFunction.Fact(n - sta)
        S = S + 1 / Fact * (Etime / Restime) ^ (n - sta)
        Next sta
    Worksheets("HTTCAPPFR").Cells(Etime + 5, 23).Value = Etime / 60
    Worksheets("HTTCAPPFR").Cells(Etime + 5, 24).Value = 1 - S * Exp(-Etime / Restime)
Next Etime

End Sub
```

Appendix 2 Visual Basic program to calculate step change response for stages in series with H2/D2 exchange.

```
Sub StageCalc120903()
'
' StageCalc120903 Macro
' Macro recorded 12/9/03 by t6238, finished 12/14/03 lkh
'
' Keyboard Shortcut: Ctrl+j
'
Dim fhg(0 To 500, 0 To 150) As Variant
Dim fdg(0 To 500, 0 To 150) As Variant
'Inputs:
T = 295 'column temperature, K
P = 760 'column pressure, torr
hc = 1.55   'H2 capacity in column at time 0, sl
dc = 0  'D2 capacity in column at time 0, sl
n = 4   'number of stages
sf = (-261.52 / (T) + 0.4263) * 0.5 ^ 1.6 + (721.15 / (T) + 0.0668)
'separation factor a function of T and composition
hf = 0  'H2 feed rate, sl/min
df = 0.1    'D2 feed rate, sl/min
V = 0.04    'column physical volume, liter
W = 0.042   'packing wt, kg
wp = 0.5    'wt fraction MH in packing
vf = 0.8    'void fraction in column
dt = 0.05    'time step size, min
tts = 500   'total time steps to calculate
'End of inputs
G = P * V * vf / n / (760 * 22.4 / 22.4 / 273) / T
'gas in void per stage, sl
fhiv = 1 'fraction H2 in void at time 0
fhf = hf / (hf + df)    'fraction H2 in feed
fdf = 1 - fhf   'fraction D2 in feed
'
For nn = 1 To n 'nn is stage number
'Time 0 for all stages:
hin = 0
din = 0
Hg = G * fhiv
Dg = G * (1 - fhiv)
Ed = 0
Hs = hc / n
Ds = dc / n
fhg(0, nn) = fhiv
```

```
fdg(0, nn) = 1 - fhiv

'Start from time step 1 for all stages:
   For ts = 1 To tts 'time step
   fhg(ts, 0) = fhf
   fdg(ts, 0) = fdf
   '
   hin = (hf + df) * fhg(ts, nn - 1) * dt 'H2 in, sl
   din = (hf + df) * fdg(ts, nn - 1) * dt 'D2 in, sl
   Hg = G * fhg(ts - 1, nn) + hin - (hin + din) * fhg(ts - 1, nn) 'H2 in gas phase
   Dg = G * fdg(ts - 1, nn) + din - (hin + din) * fdg(ts - 1, nn) 'D2 in gas phase
   'Hs=H2 in solid is the same as the last time step
   'Ds=D2 in solid is the same as the last time step
   'calculate Ed:
   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))
   'calculate new values for next step:
   Hs = Hs - Ed
   Ds = Ds + Ed
   fhg(ts, nn) = (Hg + Ed) / (Hg + Dg)
   fdg(ts, nn) = 1 - fhg(ts, nn)
   Next ts
Next nn
For ncell = 0 To tts
Worksheets("StageWexch").Cells(ncell + 25, 2).Value = ncell * dt
Worksheets("StageWexch").Cells(ncell + 25, 3).Value = fhg(ncell, n)
Worksheets("StageWexch").Cells(ncell + 25, 4).Value = fdg(ncell, n)
Next ncell

End Sub
```

Appendix 3 Visual Basic program to calculate pulse response in an exchange column

```
Sub Pulse()
'
' Pulse Macro
' Macro recorded 12/22/2003 by K Heung for calculating response to a pulse with exchange
'
' Keyboard Shortcut: Ctrl+k
'
Dim fhg(0 To 4000, 0 To 200) As Variant
Dim fdg(0 To 4000, 0 To 200) As Variant
'
'Inputs:
T = 295 'column temperature, K
P = 800 'column pressure, torr
hc = 1.4 'H2 capacity in column at time 0, sl
dc = 0  'D2 capacity in column at time 0, sl
n = 1 'number of stages to calculate
'sf=(-261.52/T+0.4263)*(H fract in s)^1.6+(721.15/T+0.0668)
'D/H separation factor a function of T and composition
H2f = 1.5 'H2 flow rate when on, slm
hf = 0  'H2 feed at time 0, sl/min
df = 1.5 'D2 feed at time 0 for the pulse, sl/min
V = 0.04  'column physical volume, liter
W = 41 'packing wt, kg
wp = 0.53 'wt fraction MH in packing
vf = 0.75 'void fraction in column
dt = 0.02 'time step size, min.
tts = 800 'total time steps to calculate
fhiv = 1 'fraction H2 in void at time 0
td = 1  'minutes of D2 flow
tds = td / dt '# of time steps of D2 flow
'End of inputs, remember to change worksheet name and column # below for outputs
'
G = P * V * vf / n / (760 * 22.4 / 22.4 / 273) / T
'gas in void per stage, sl
fhf = hf / (hf + df) 'faction H2 in feed
fdf = 1 - fhf 'fraction D2 in feed
'
For nn = 1 To n 'nn is stage number
'time 0 for all stages:
hin = 0
din = 0
Hg = G * fhiv
Dg = G * (1 - fhiv)
```

```
Ed = 0
Hs = hc / n
Ds = dc / n
fhg(0, nn) = fhiv
fdg(0, nn) = 1 - fhiv
'
'start from time step 1 for all stages:
    'at time 0, switch from H2 to D2 for td minutes
    For ts = 1 To tds 'time steps for D2 flow
    fhg(ts, 0) = fhf
    fdg(ts, 0) = fdf
    '
    hin = (hf + df) * fhg(ts, nn - 1) * dt 'H2 in, sl
    din = (hf + df) * fdg(ts, nn - 1) * dt 'D2 in, sl
    Hg = G * fhg(ts - 1, nn) + hin - (hin + din) * fhg(ts - 1, nn) 'H2 in gas phase
    Dg = G * fdg(ts - 1, nn) + din - (hin + din) * fdg(ts - 1, nn) 'H2 in gas phase
    'Hs=Hs in last time step
    'Ds=Ds in last time step
    Cs = Abs(Hs / (Hs + Ds)) 'fraction of H in solid, Abs to avoid hangup
    sf = (-261.52 / T + 0.4263) * Cs ^ 1.6 + (721.15 / T + 0.0668)
    'separation factor a function of T and composition
    'calculate Ed, the amount exchanged in one stage:
    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))
    'calculate new values for next step:
    Hs = Hs - Ed
    Ds = Ds + Ed
    fhg(ts, nn) = (Hg + Ed) / (Hg + Dg) 'total gas is constant
    fdg(ts, nn) = 1 - fhg(ts, nn)
    Next ts
    '
    'switch back to H2
    hf = H2f    'H2 flow rate, slm
    df = 0  'D2 pulse ended
    fhf = hf / (hf + df) 'fraction H2 in feed
    fdf = 1 - fhf 'fraction D2 in feed
    '
    For ts = tds + 1 To tts ' time steps
    fhg(ts, 0) = fhf
    fdg(ts, 0) = fdf
    '
    hin = (hf + df) * fhg(ts, nn - 1) * dt 'H2 in, sl
    din = (hf + df) * fdg(ts, nn - 1) * dt 'D2 in, sl
    Hg = G * fhg(ts - 1, nn) + hin - (hin + din) * fhg(ts - 1, nn) 'H2 in gas phase
    Dg = G * fdg(ts - 1, nn) + din - (hin + din) * fdg(ts - 1, nn) 'H2 in gas phase
    'Hs=Hs in last time step
```

```
    'Ds=Ds in last time step
    Cs = Abs(Hs / (Hs + Ds)) 'fraction of H in solid, Abs to avoid hangup
    sf = (-261.52 / T + 0.4263) * Cs ^ 1.6 + (721.15 / T + 0.0668)
    'separation factor a function of T and composition
    'calculate Ed, the amount exchanged in one stage:
    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))
    'calculate new values for next step:
    Hs = Hs - Ed
    Ds = Ds + Ed
    fhg(ts, nn) = (Hg + Ed) / (Hg + Dg) 'total gas is constant
    fdg(ts, nn) = 1 - fhg(ts, nn)
    Next ts
    '
Next nn
For ncell = 0 To tts
'Worksheets("6inPulseCalc").Cells(ncell + 25, 2).Value = ncell * dt
'Worksheets("Pulse3ft").Cells(ncell + 25, 3).Value = fhg(ncell, n)
Worksheets("6inPulseCalc").Cells(ncell + 25, 21).Value = fdg(ncell, n)
Next ncell

End Sub
```