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FLOW IN A METAL HYDRIDE CHROMATOGRAPHIC COLUMN (U)

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ABSTRACT

The flow of hydrogen isotopes in a metal hydride chromatographic column is calculated by a one-dimensional finite difference method. The Ergun equation is used to define the gas flow; and equilibrium pressure isotherms are used to define the column holdup. Solid phase loadings are shown to move as a wave front on absorption, but remain more uniform on desorption.

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INTRODUCTION

The flow of hydrogen between the reflux tank and the packed metal hydride absorber is a limiting time step in the semicontinuous separation of hydrogen isotopes. A computer code was written to help define this flow.

BACKGROUND

Isotopes of hydrogen can be separated chromatographically by many metal hydrides. Since metal hydrides have a change in separation factor with temperature, the separation can be made semicontinuous by thermal cycling[1]. To achieve separation the desorbed gas is collected in a reflux tank to be later returned to the cold column. This stream is analogous to the reflux stream in a distillation column. Separation is achieved each time the hydrogen from the reflux tank flows across the active absorbent. The more volatile isotope is pushed further away from the reflux tank. While the reflux tank is being filled in the hot desorption cycle some separation is lost; but since the separation factor has shifted toward the lighter isotope not all the gain on the cold cycle is lost.

An inert packing in the reflux tank ensures that any heavy isotope that may get to the reflux tank near the end of the desorption cycle will also be the first gas removed on the next absorption cycle.

Feed, as a small fraction of the refluxed gas, can be added while the column is cold; and product and raffinate streams can be withdrawn from each end of the column while the column is hot. Given these thermal conditions, the column becomes a metal hydride pump and external pumps are not required. The process is a series of batch operations that become semicontinuous with computer control of on/off valves. Details of this isotopic separation process are presented by Lee[1].

TYPICAL APPARATUS

The flow scheme for the process is shown by Figure 1. Frits of porous metal (5 micron) were used to contain the packing, and additional frits were used to protect the valves. Even though feed addition and product withdrawal are not included in these calculations, inlet and outlet valves are shown for completeness.

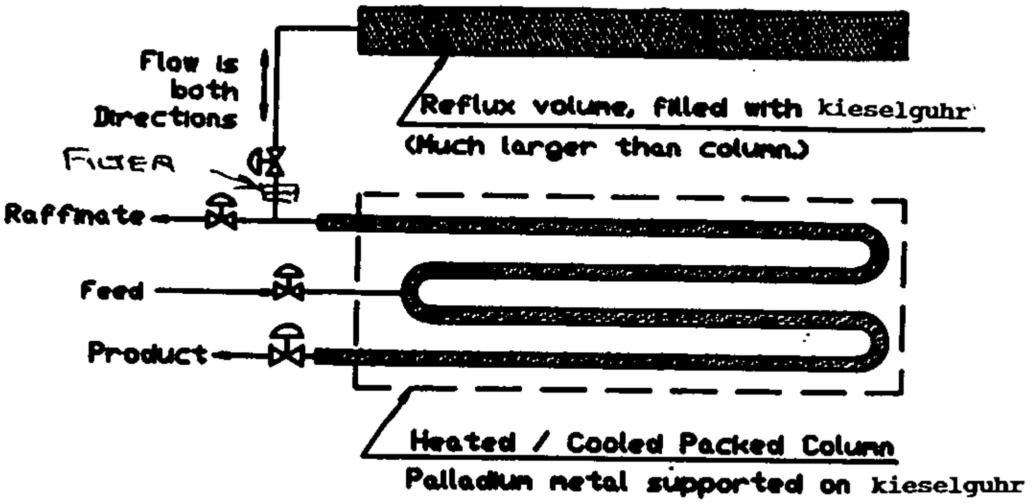

Figure 1. Flow in a Metal Hydride Chromatographic Column

Parameters use in these calculation:

Volume of the reflux tank: 40 liters
Volume of the column: 4 liters
Diameter of column: 2 cm
Length of the column: 12.73 meters
Packing: 30 - 40 mesh kieselguhr
Active coating: 50% palladium
Internal void fraction: 0.8
Temperature Range: -20°C to 120°C
Filters were assumed to increase the length of the first cell to fifty fold
Column hydrogen loadings will cross over beta phase area

MATHEMATICAL MODEL

Calculations were done on a Cray computer using the one-dimensional finite difference method shown in Figure 2, where the individual cell lengths were 1/50th of the total length. The Ergun[2] equation is solved for flow at each cell boundary using the average properties of the gas to calculate the increase or decrease of hydrogen at each cell for a finite time. With these new quantities established for each cell, a new equilibrium pressure was calculated. A material balance determined the amount of gas in the reflux tank.

Specific boundary conditions were required at the first and last cell:

1. A half-cell length provides resistance at the first cell. External resistance can be represented by increasing the length of the half-cell without changing it's capacity. All other cells had half of a cell length from adjacent cells and half of a cell length from the current cell. The resistance for cells inside the two boundaries are therefore one cell length. Accumulation can be thought of as occurring at the line marking the middle of a cell.

2. The closure of the valve to the reflux tank was represented as zero flow into or out of cell 1. The valve is to be closed during heating and cooling between the two temperature levels. The actual computer code allowed additional heating and cooling after the valve was opened.

3. The 50th cell at the product end of the column does not have an outlet while gas is flowing into or out of the reflux tank. There is, however, accumulation and depletion at this cell.

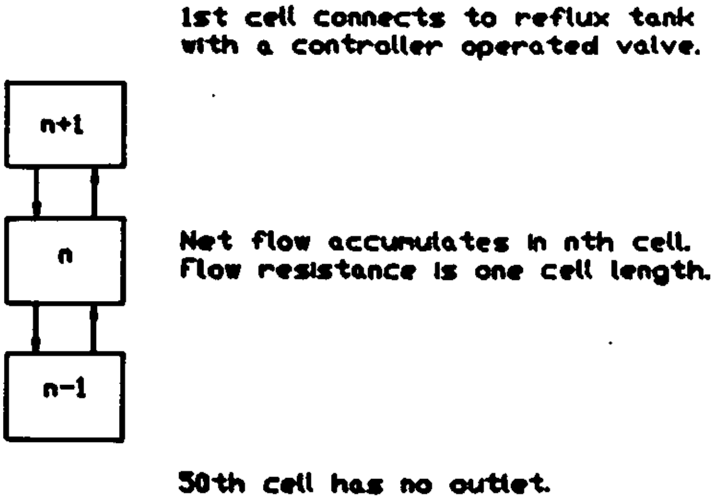

Figure 2. Details of Finite Difference Calculation

Equilibrium pressure equations were taken from Wicke[3]. The alpha phase near the hydrogen free end of the equilibrium data was defined to be linear from the origin and intersect each isothermal plateau at a solid phase concentration of 0.1. Concentrations in the solid phase were defined as atoms of hydrogen per atom of palladium (PD).

Each iteration always started with the previous solid phase concentration at the intersection to the material balance line, then up to an approximate equilibrium pressure solution. The next material balance line crossing was assumed to be straight line to the previous equilibrium trial solution. This procedure converged to the proper solution in at least three trial solutions. Solutions in the alpha phase region were trivial and could be solved analytically.

RESULTS

Typical results are shown by Figure 3 for the solid phase concentrations; and by Figure 4 for the corresponding column pressures. Figure 4 also shows the pressure of the reflux tank where it's pressure is between the high pressure of desorption and the low pressure of absorption. While pressure measurements can be made on a few locations of the column, concentration measurements would be difficult to obtain. Therefore, these profiles of concentrations can be helpful in understanding the process inside the column.

The first 95 seconds show absorption as the column is cooled. The concentration increases and the pressure drops to zero as the column is cooled. From 95 to 325 seconds, the reflux gas is allowed to flow into the cold column, and the cell adjacent to the reflux tank quickly increases in concentration. The concentration proceeds as a wave as each succeeding cell becomes saturated. Finally the 50th cell becomes saturated and the absorption is discontinued. Figure 4 shows that pressures also increase in a wave-like manner. At 325 seconds the 50th cell has become saturated and the pressure in that cell has just increased by a few hundred torr. This rise can be monitored by a control computer to determine the end of the absorption cycle.

At 325 seconds, desorption is started and the column is heated for about 400 seconds. This initial heating period with the valve to the reflux tank closed is not shown and in the calculation code it was assumed that pressure and concentrations become uniformly distributed, and a step to the high temperature can be assumed. At the higher temperature the valve to the reflux tank is opened and the desorbed gas flows from the column. The concentration in cell 1 drops a little faster than in the rest of the cells, but pressures throughout the column are nearly uniform since most of the pressure drop comes from the filter.

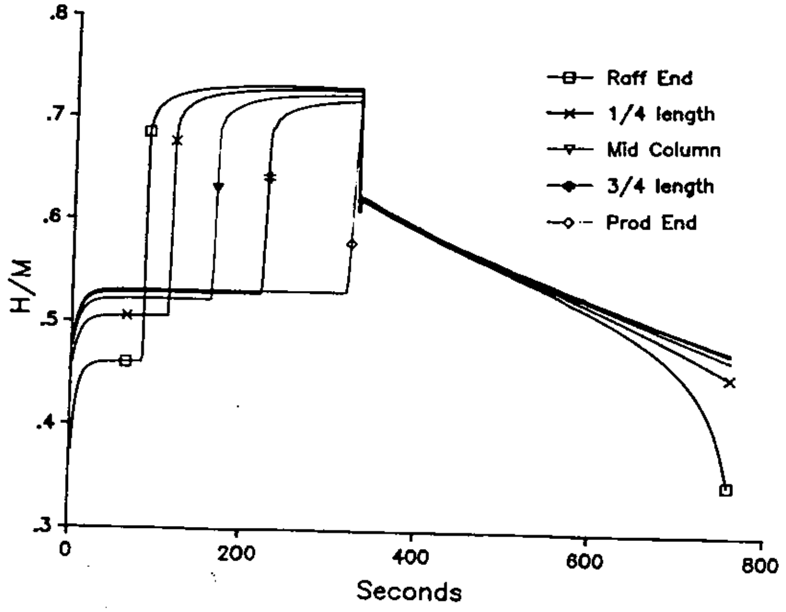

Figure 3. Solid Phase Concentrations

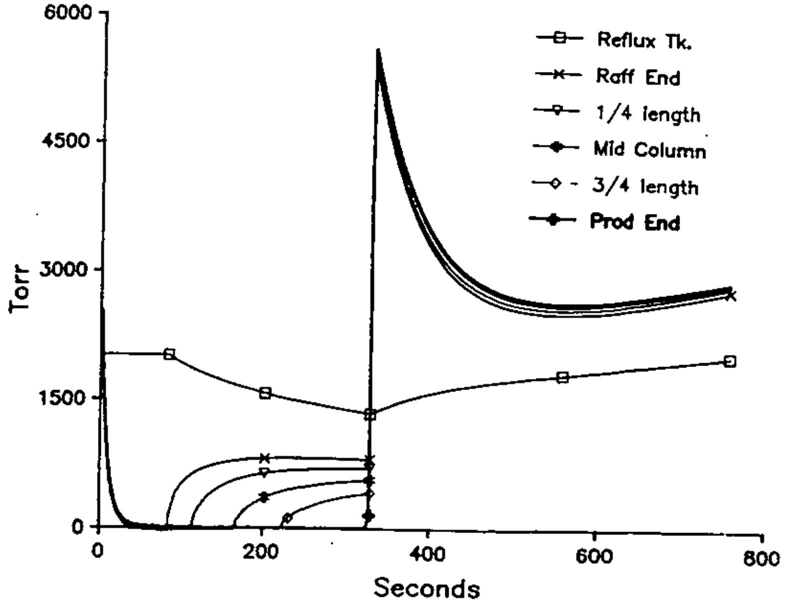

Figure 4. Gas Phase Pressure

CONCLUSIONS

A computer code has been written to define concentration and pressure profiles in a semicontinuous chromatographic column. The results can be made to match both experimental conditions and other configurations investigated as a guide to experimental development.

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