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by

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Summary

A column packed with pellets of copper plated $\text{LaNi}_{4.25}\text{Al}_{0.75}$ has been evaluated for its separation efficiency using a displacement method. Deuterium breakthrough curves were produced experimentally and compared with those calculated with a stage model. The height equivalent to a theoretical plate was attained and its dependence on temperature and gas flow rate was established.

1. Introduction

Metal hydrides usually show some isotopic effect toward the absorption of hydrogen isotopes. The effect is different from one metal hydride to the other. Palladium, for example, preferentially absorbs the lighter protium more than the heavier deuterium and

tritium from a mixture of the isotopes, and the magnitude increases as temperature decreases[1]. $\text{LaNi}_{0.25}\text{Al}_{0.75}$, on the other hand, preferentially absorbs the heavier tritium more than the lighter deuterium and protium at low temperatures, but reverses this effect when the temperature is above about 40°C [2]. The isotopic effect of many metal-hydrogen systems has been investigated, and some of them have been tested for separating hydrogen isotopes[3]. The most commonly applied technique is batch gas chromatography[4].

A new semi-continuous gas chromatography process for separating hydrogen isotopes, called the Thermal Cycling Absorption Process (TCAP), has been developed at Savannah River Laboratory[5]. This TCAP process, compared to a batch process, has much higher separative capacity and is able to produce higher purity hydrogen isotope products. The process has been demonstrated with a single metal hydride, palladium deposited on kieselguhr, as the packing material in the separation column. However, its performance can be significantly improved if the Pd is paired with a hydride of inverse isotopic effect. A hydride is said to have an inverse isotopic effect if it preferentially absorbs heavier isotopes. Vanadium and $\text{LaNi}_{4.25}\text{Al}_{0.75}$ are two examples. $\text{LaNi}_{4.25}\text{Al}_{0.75}$ was chosen as a potential inverse packing material for pairing with Pd, because it also has other desired properties like pressure range and stability.

$\text{LaNi}_{4.25}\text{Al}_{0.75}$ breaks down to a fine powder after repeated cycles of absorption and desorption. The fine powder is not suitable

for use in a packed column because it gives too much resistance to gas flow. To overcome this problem, the $\text{LaNi}_{4.25}\text{Al}_{0.75}$ must be converted to pellets before it is used in a column. An experimental column packed with the pellets was tested for its separation efficiency. The data was needed for the design of an inverse column to pair with the Pd column in the TCAP process.

2. Experimental Details

2.1 Packing material

$\text{LaNi}_{4.25}\text{Al}_{0.75}$ from Ergenics, Inc. was ground and screened to less than 100 mesh ($<149 \mu\text{m}$). The powder was plated with copper to about 30% by weight by a process similar to that described by Ishikawa[6]. The copper plated powder was converted to pellets by a hand operated hydraulic press using 884 atm pressure. The pellets were 0.5 cm diameter and 0.5 cm high, weight about 0.5 gm each.

2.2 Experimental column

The experimental column was fabricated with stainless steel type 304. It is 2.245 cm in diameter, 61 cm long. The column is jacketed with a 3.2 cm diameter pipe. A heat transfer fluid (Fluorinert by 3M) was circulated through the jacket to maintain a constant temperature in the column for experiments below 25°C . A resistance electric heater wrapped around the jacket was used for experiments above 25°C . The jacket was insulated to minimize heat loss. A

thermocouple inserted into the center of the column was used for temperature measurement. A total of 765 gm of pellets was packed in the column for the tests. The pellets contain 70% by weight $\text{LaNi}_{4.25}\text{Al}_{0.75}$.

2.3 Experimental apparatus

A schematic of the experimental apparatus is shown in Fig. 1. It consists of the column described above, two gas analyzers (Gas Chromatograph Series 580 by GOW-MAC Instrument Co.), two pressure sensors (MKS Baratron 390 HA), two mass flow controllers (Tylan), and a temperature control system. The gas manifold was fabricated with 0.635 cm stainless steel tubing and Cajon VCR or swagelok connectors. The column temperature, the pressures, the gas flow rates and the gas compositions were continuously recorded by an IBM PC computer using a Keithley 500 data acquisition system.

2.4 Experimental procedure

A displacement method was used to generate breakthrough curves under different column temperatures and gas flow rates. From the breakthrough curves, the separation efficiency of the column can be calculated.

Before conducting the tests, the column with the pellets was first evacuated under heat (150°C) for about 20 hours to eliminate any volatile impurities. The column was then cooled to room temperature and exposed to hydrogen at a pressure of about 4000 torr. The hydride material would begin to absorb hydrogen after

about 15 minutes, and became saturated after about 60 minutes. The column was then desorbed by heating to 150 °C under evacuation for about one hour. The absorption and desorption were repeated 10 times to get the hydride material fully activated.

For each test, the column was cooled (or heated) to a target temperature, and then saturated with H₂ under a target pressure. D₂ at a controlled rate was fed into the column at time zero. At the same time the outlet valve was opened and adjusted to maintain a constant pressure in the column. The gas compositions at the inlet and outlet of the column were continuously measured by the inline gas analyzers and recorded by the data acquisition system.

3. Results

3.1 Breakthrough curves

When D₂ gas enters the column and exchanges with the H atoms in the solid phase, an S-shape concentration profile will be developed. This concentration profile moves toward the end of the column and eventually exits the column completely. The breakthrough curve is the deuterium concentration measured at the exit of the column against time (or amount of effluent), Fig. 2. Usually the concentration of deuterium stays at zero for a period of time and then gradually increases to 100%. The length of time it stays at zero and the actual shape of the curve depends on column temperature and gas flow rate. In general the longer the time it stays at zero

and the sharper the rise of the curve, the better is the separation efficiency. The efficiency will be described by height equivalent to a theoretical plate (HETP) using the stage theory.

3.2 The stage theory

The column is divided into a finite number of hypothetical stages, in each of which equilibrium is attained. The size of such a stage is the HETP. A high separation efficiency is indicated by a small HETP. The HETP can be affected by a number of variables such as diameter of the column, the size of the packing pellets, the operation temperature, and the gas flow rate. This paper discusses the effects of temperature and gas flow rate only.

The breakthrough curve may be calculated by applying the stage theory. The mathematical model is developed as follows.

Let at time m ,

H_{im}, D_{im} = gas flow rates of H and D into stage n , mol/min

H_{om}, D_{om} = gas flow rates of H and D out of stage n , mol/min

H_{sm}, D_{sm} = H and D in solid in stage n , mol

H_{xm}, D_{xm} = H and D losses to solid in stage n , mol

S = separation factor, dimensionless

C = absorption capacity of the column, mol

N = total number of stages in the column

In our case, $H_x = -D_x$, because $H_{sm} + D_{sm} = C/N = \text{constant}$ due to constant column temperature and pressure; the isotopic effect on absorption

capacity has been neglected. By definition of the separation factor:

$$S = \frac{(D_{im}-D_{xm})/(H_{im}+D_{xm})}{(D_{sm}+D_{xm})/(H_{sm}-D_{xm})} \quad (1)$$

By assuming a value for N , starting with stage 1, the concentration change with time at the exit of each stage may be calculated easily by the use of a personal computer. The concentration profile at the exit of the last stage is the breakthrough curve. By varying the value of N , a series of breakthrough curves may be calculated. By comparing the experimental curve with the calculated curves, the number of theoretical stages of the column may be attained (Fig. 2). With N known, the HETP is just the column length divided by N . The separation efficiency may also be expressed by other units, such as number of stages per STP liter of absorption capacity of the column.

3.3 Temperature effect

The temperature effect on the number of stages per STP liter column absorption capacity (N_c) is shown in Fig.3. At about -50°C the kinetics is so slow that the separation efficiency approaches zero. As temperature increases the number of stages increases due to the increase in exchange kinetics. The temperature effect on N_c follows the following equation:

$$N_c = 0.0035 T + 0.206 \quad (T = ^\circ\text{C}) \quad (2)$$

3.4 Flow rate effect

The number of stages per unit column absorption capacity as a function of gas flow rate is shown in Fig.4. As flow rate increases the number of stages decreases due to the reduction in residence time. The rate of decrease follows an exponential decay curve rather than a straight line, because higher gas flow rate improves the mass transfer which compensates some of the loss of exchange caused by residence time reduction. The following equation describes the flow rate effect rather well:

$$N_c = 0.33 \exp(-3.25 U) \quad (U=\text{STP liter/min/cm}^2) \quad (3)$$

4. Discussion

The displacement tests and the theoretical stage calculation is a useful method for developing correlations to describe separation efficiency of metal hydride pellet columns. With the effects of temperature and flow rate known, one will be able to design an inverse column to pair with the Pd column for the TCAF process.

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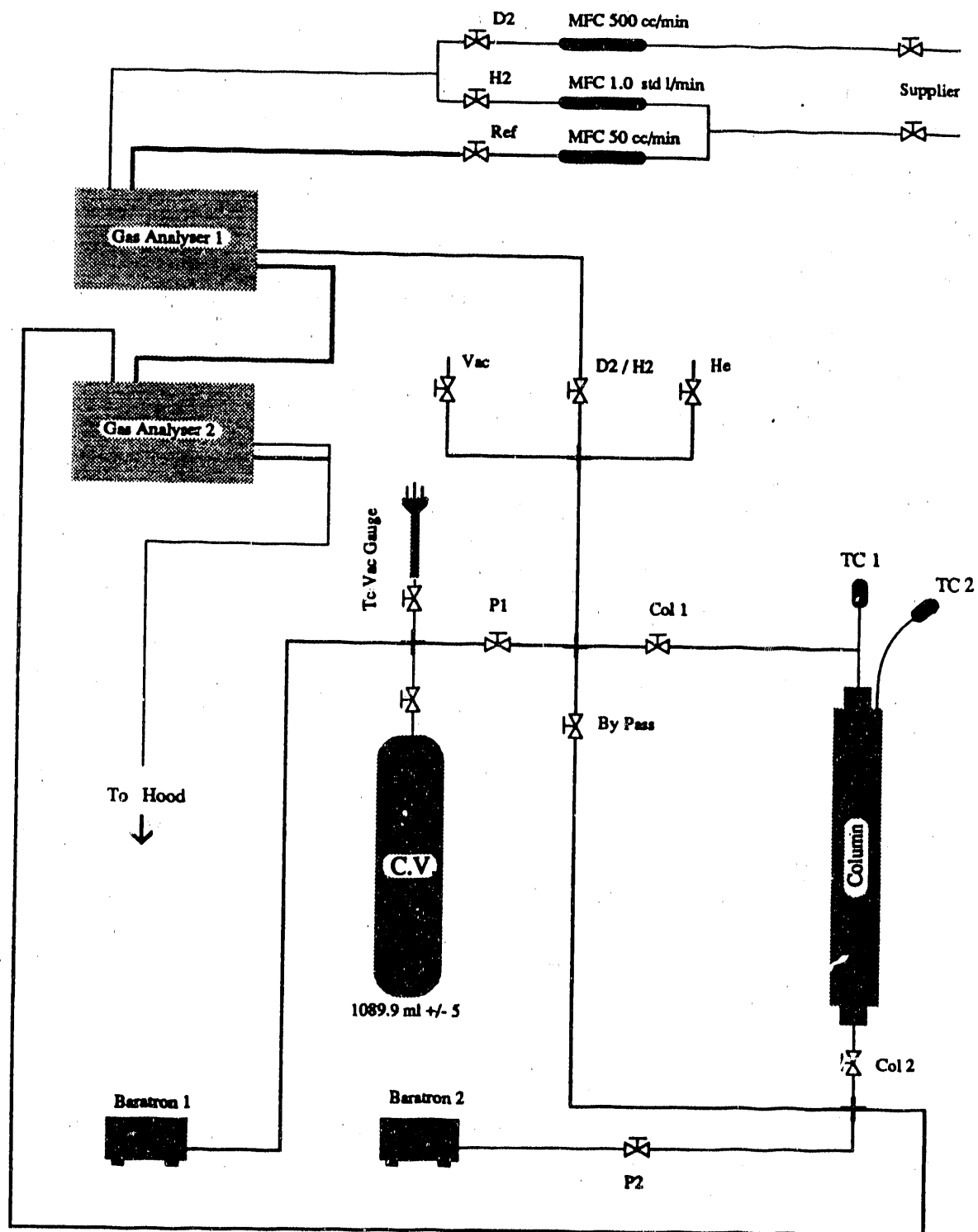


Fig. 1 Experimental apparatus.

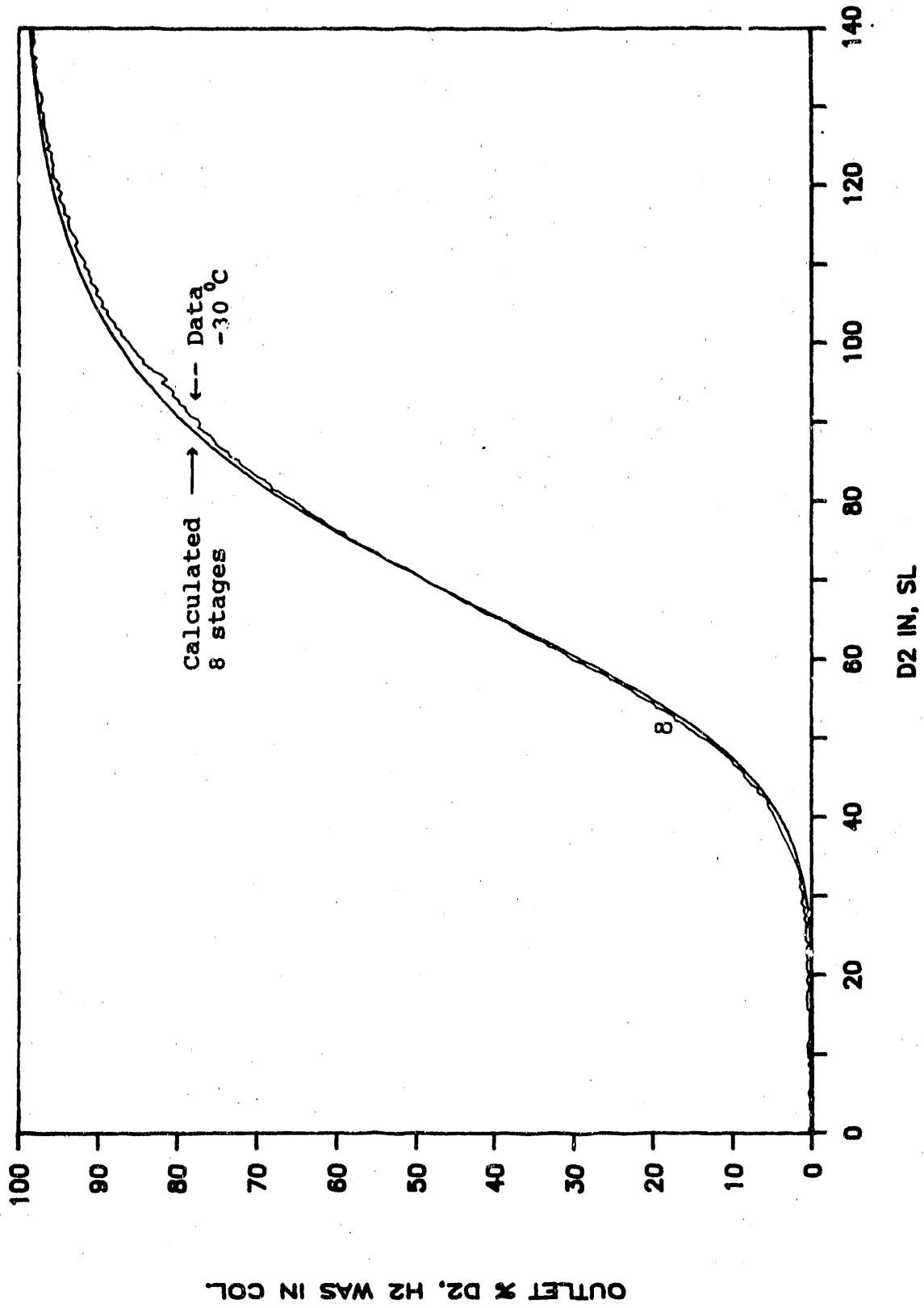


Fig. 2 Typical breakthrough curve.

LANA.75-CU COLUMN, CALC/DATA. 5/2/90

D2 DISP H2, .5 L/MIN, TEMP EFFECT

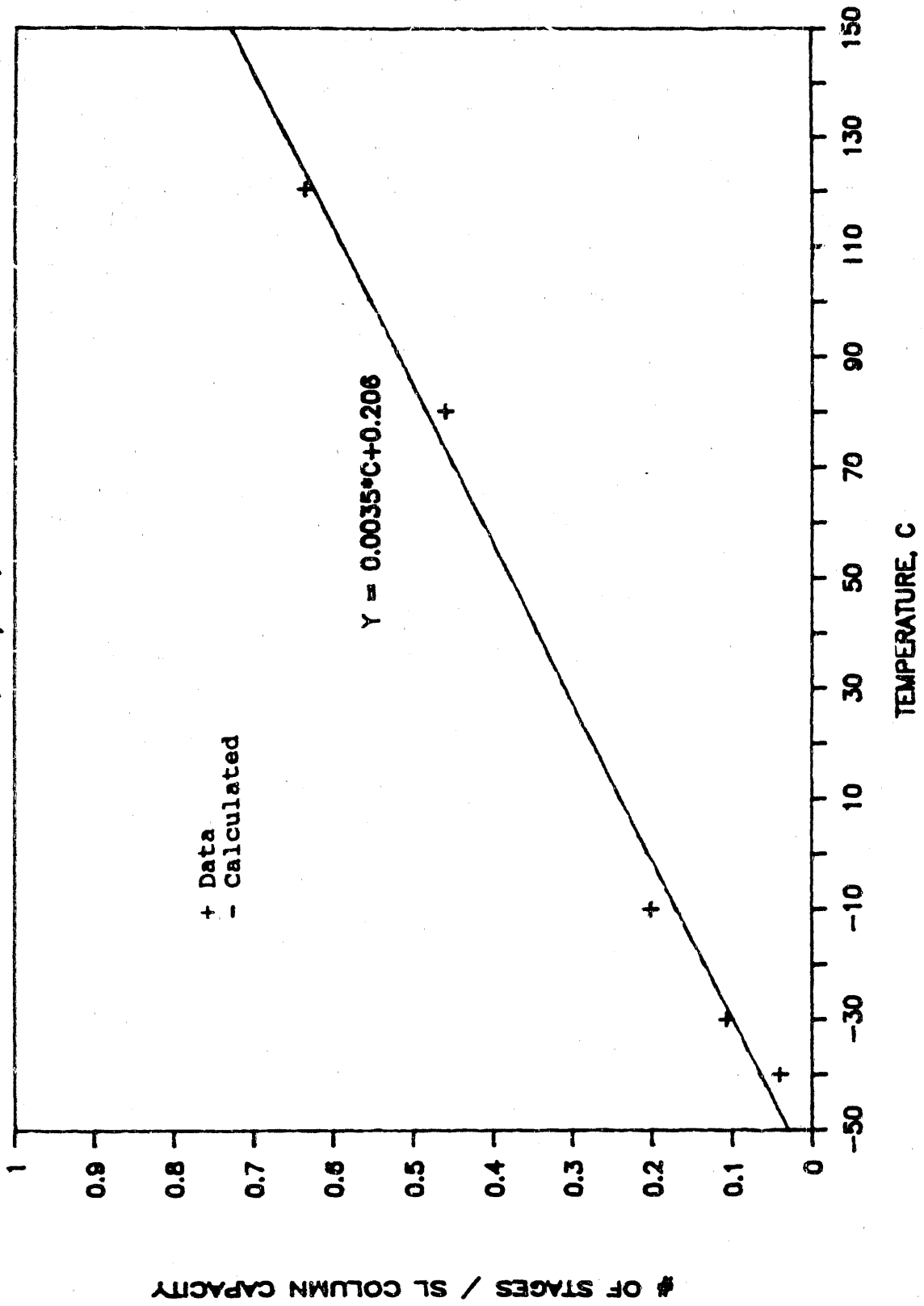


Fig. 3 Temperature effect on separation efficiency.

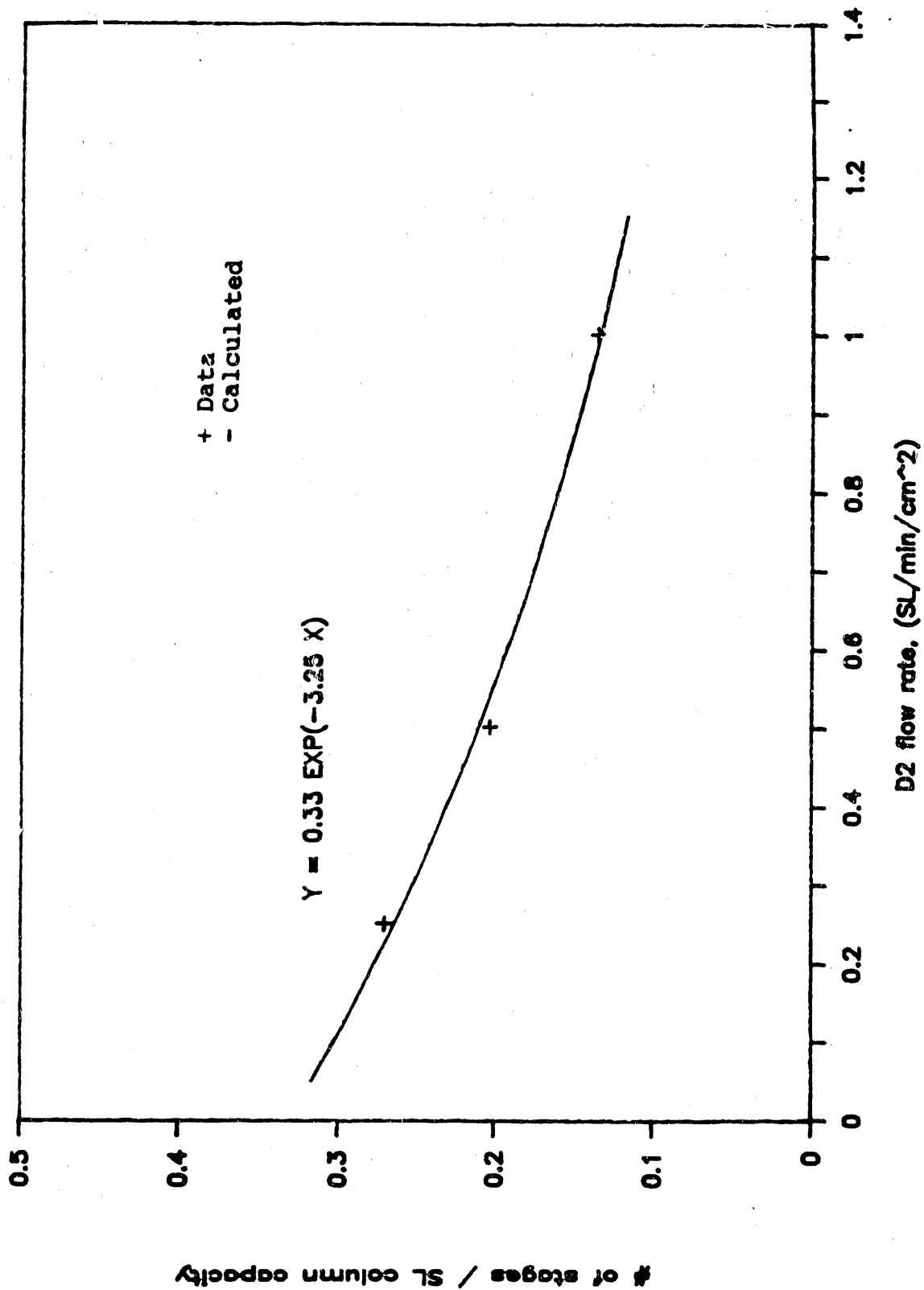


Fig. 4 Gas flow rate effect on separation efficiency.

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