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CASCADES FOR HYDROGEN ISOTOPE SEPARATION USING METAL HYDRIDES*

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ABSTRACT

Designs are presented for continuous countercurrent hydrogen isotope separation cascades based on the use of metal hydrides. The cascades are made up of pressure swing adsorption (PSA) or temperature swing adsorption (TSA) stages. The designs were evolved from consideration of previously conducted studies of the separation performance of four types of PSA and TSA processes.

INTRODUCTION

One of the important applications envisioned for metal hydrides is the separation of hydrogen isotopes. The separations permitted by isotope effects in metal-hydrogen systems are particularly appropriate for applications with a gaseous hydrogen feed, such as in the recovery of deuterium from industrial hydrogen streams or the processing of the fuel of fusion reactors.

The present work deals with the design of cascades for hydrogen isotope separation when using metal hydrides in pressure swing adsorption (PSA) or temperature swing adsorption (TSA) stages. The results of previous studies [1,2,3] on the separation performance of individual stages of these processes are used to develop design principles for such cascades. Illustrative designs are presented for a tritium removal problem.

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PROPERTIES OF PSA AND TSA STAGES

In the earlier studies (op. cit.) on individual PSA and TSA stages a stream of tritiated hydrogen was used as the feed and vanadium was used as the solid phase. In the vanadium-hydrogen system at the temperatures used in these studies an equilibrium isotope effect exists such that tritium is preferentially taken up by the solid from a protium-tritium mixture [4,5]. A kinetic isotope effect also exists and was evident in the earlier work. In the kinetic isotope effect, tritium is taken up and released more slowly than protium during an absorption-desorption cycle. The two effects are opposite in their separation behavior.

The PSA and TSA processes studied are cyclic gas-solid separation processes which are widely used for industrial gas separations. PSA in particular is routinely used for the purification of hydrogen.

The version of PSA principally used in the earlier work was a two-column version known as heatless adsorption. Details of the heatless adsorption cycle are given in Reference 1. When this process was operated with short cycles (2 min. with 45.7 cm long x 0.77 cm i.d. columns containing 60 g V, 200-300 std cm³/min. high pressure feed flow rate), the kinetic isotope effect controlled separation and the process produced a high pressure product enriched in tritium and a low pressure product depleted in tritium. Rapid cycling was achieved by selecting the temperature (373 K) and high (1030 kPa) and low (103 kPa) pressures so that cycling occurred wholly within the monohydride phase. Long cycles (up to 4 hr with the same column and flow rate range as above) led to separations controlled by the equilibrium isotope effect. Long cycles were made not only possible but necessary by lowering the temperature to 298K when using the same low and high pressures. Then cycling occurred between the monohydride and dihydride phases and the process produced a

high pressure product depleted in tritium and a low pressure product enriched in tritium. Thus two versions of the PSA process used in the reference studies were two-column PSA operated in the single phase mode and in the two phase mode [1]. A third version involved a single column process operating in the single phase mode [3]. The single column process is identical to the two column process when the latter was operated with no purge. A fourth cyclic process version involved two columns but temperature was cycled rather than pressure [2]. This TSA process was operated in the single phase mode. Even though this process was operated wholly within the monohydride phase, because the column temperature could not be changed rapidly, the cycles were long (30 min) and the TSA process was controlled by the equilibrium isotope effect.

For each of the process versions studied the stage separation factor, α , was measured as a function of the product cut, θ . The stage separation factor is the average steady state mole fraction of tritium in the enriched product stream divided by the average steady state tritium mole fraction in the depleted product stream. The product cut is the moles of enriched product per cycle divided by the total moles of feed introduced per cycle. These measurements for the four process versions are summarized in Fig. 1.

CASCADES OF PSA AND TSA STAGES

Multiplication of the separation effect of a single stage is accomplished by the use of a series of stages arranged to form a continuous countercurrent cascade as shown in Fig. 2. Each of the rectangles in this figure represents a PSA or TSA stage, and the arrows between stages represent the flow of enriched and depleted streams from stage to stage. The enriched stream from a stage flows upward and the depleted stream downward.

The feed to a given stage is the sum of the depleted stream from the stage above and the enriched stream from the stage below. Although these streams are shown entering a given stage separately, in practice they enter together as shown in Fig. 3. This figure shows the principal items of equipment for each stage. Valves and instrumentation are not shown. Since one of the streams making up the feed will be at low pressure and the feed to the stage must be at the high pressure, a compressor is required for each stage. Also since all flows are intermittent, a surge vessel is required. It is assumed the high pressure and low pressure are constant throughout the cascade. This is a reasonable approximation if the pressure drop through the columns during flow at high pressure is small. This was the case experimentally.

Design of a cascade of the kind shown in Fig. 2 consists for present purposes of determining the number of stages required to accomplish a specified separation and determining certain indices of the size of the cascade and of the power required by the compressors. The design proceeded in the customary way [6] by developing overall material balances and partial (tritium) material balances around the entire cascade and around the stripping and enriching sections. Details are omitted because of space limitations. First order difference equations resulted which could be summed after making two assumptions. These were that the cut and the stage separation factor were constant throughout each section of the cascade although values in the stripping section were different from those in the enriching section. Tapered cascades resulted from the assumption of constant cuts in the two sections. The assumption of stage separation factors independent of tritium mole fraction restricted the design to situations in which the HT mole fraction is small so that the

T_2 mole fraction is negligible. Thus the design method is restricted to a two-component system. To avoid encountering pinches during the summation, restrictions on the ranges of values of cuts in the two sections were necessary. The result was that cuts greater than 0.5 were desirable in the stripping section and cuts less than 0.5 were desirable in the enriching section. One sees from Fig. 1 that equilibrium stages (two-column two phase mode PSA and two-column single phase mode TSA) are therefore appropriate for use in the stripping section, and kinetic stages (one- and two-column single phase mode PSA) are suitable for the enriching section.

Summation of the difference equations for the two sections leads to determination of the numbers of stages required in each section and of the interstage flow rates for each stage.

Indices of the size and power requirements for the cascade are obtained by summing up the high and low pressure flow rates for the entire cascade. The total low pressure flow rate is that which must be compressed from the low pressure to the high pressure and is proportional to the total power requirement for the cascade. The total high pressure feed flow rate is the sum of the total high pressure flows leaving each stage plus the sum of the low pressure flows after compression. The total high pressure feed flow rate is an index of the size (volume) of the cascade.

ILLUSTRATIVE CASCADE DESIGNS

The method outlined above was used to prepare illustrative designs for a specific hydrogen isotope separation problem. The problem involved removal of tritium from hydrogen and had earlier been used by Benenati [7] to illustrate the use of a cascade of dual temperature exchange stages using vanadium hydride for hydrogen isotope separation.

The problem is stated as follows. The hydrogen in 300 kg H₂O/day containing 1 Ci T/kg is to be decontaminated yielding a depleted product containing one percent of the tritium fed and an enriched product reduced in volume by a factor of 30. The present interest is restricted to the hydrogen isotope separation itself and the conversions of water to hydrogen and vice versa are ignored. For the gaseous separation problem the feed and product flow rates and the corresponding compositions (HT mole fractions) are

$$\begin{aligned}
 F &= 1.927 \times 10^{-4} \text{ Kg-mole H}_2/\text{s} & z_F &= 3.1 \times 10^{-7} \\
 P &= 6.42 \times 10^{-6} \text{ Kg-mole H}_2/\text{s} & y_P &= 9.21 \times 10^{-6} \\
 W &= 1.863 \times 10^{-4} \text{ Kg-mole H}_2/\text{s} & x_W &= 3.21 \times 10^{-9}
 \end{aligned}$$

The separation factor-cut relation for the single phase mode processes shown in Fig. 1 was used for the enriching section and the relation in this figure for the two-column two-phase mode PSA process was used for the stripping section. Interest was restricted to this PSA process in the stripping section since it had larger stage separation factors than the TSA process, the only other equilibrium process.

In carrying out the design procedure the number of stages in the stripping section was calculated as a function of θ_S for $0.55 \leq \theta_S \leq 0.95$. Then for each value of θ_S the number of stages in the enriching section was calculated as a function of θ_E where $0.05 \leq \theta_E \leq 0.45$. Extrapolated values of the α - θ relations were used when required. During the course of these calculations the total low pressure flow rate and total feed flow rate were also calculated. The results are shown in Table 1.

Solutions were not obtained for all θ_S - θ_E combinations. For those combinations for which there are no entries in Table 1 convergence of an iterative procedure used for calculation of the enriching section

was not obtained in 50 iterations. Presumably not all combinations are possible, probably because of the pinch phenomena mentioned earlier. The matter was not examined further. Convergent solutions were found for all values of θ_S for large values of θ_E . Convergence was not obtained when θ_E was small.

The number of stages in the stripping section ranges from 3 to 15 and depends only on θ_S . It becomes small as θ_S and hence α_S , becomes large. The number of enriching stages ranges from 11 to 14 and is relatively insensitive to either variable. The total low pressure flow rate and the total high pressure feed flow rate vary with both θ_S and θ_E . They become small as both θ_S and θ_E become small. Thus cascades of small size with small power requirements have many stages and vice versa. An economic optimum may be expected to involve a compromise between number of stages on the one hand and cascade volume and power requirement on the other. The location of this optimum may depend strongly on cost of the hydriding metal or alloy used.

The designs in Table 1 are not optimal for various reasons. Principal among these is the fact that different α - θ relations may be possible and require further experimental exploration. For instance smaller cuts may be possible in the stripping section while maintaining high separation factors. Similarly the possibility of obtaining reasonably high separation factors at larger cuts in the enriching section requires exploration. Also, the pressure range used in the experiments on which the present designs were based is large and would result in large power requirements for the cascade. A smaller pressure range may produce separation factors which are not much reduced from present values and at the same time would reduce power and compressor size requirements.

Because the present designs are not optimal a detailed comparison of them with the design of Benenati [7] would not be significant. It is worthwhile mentioning however that the number of stages in the present design ranges from 14 to 26 whereas the dual temperature exchange design required 48 stages. Further, the PSA stages are actual stages whereas for the dual temperature exchange process they are ideal stages.

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Table 1.
Cascade Parameters for Tritium Removal Problem

| θ_S/α_S | Entries for each θ_S - θ_E combination | | | | |
|---------------------|---|-------------|-------------|-------------|------------|
| | $\left\{ \begin{array}{l} n_S/n_T \\ Q_L/Q_F \end{array} \right.$ | | | | |
| | 0.55/1.42 | 0.65/1.90 | 0.75/2.38 | 0.85/2.86 | 0.95/3.34 |
| θ_E/α_E | | | | | |
| 0.25/1.46 | | | | | |
| | 15/26 | | 5/17 | 4/15 | 3/16 |
| 0.35/1.44 | 0.136/0.236 | | 0.247/0.359 | 0.787/1.108 | 4.34/5.99 |
| | 15/26 | 7/19 | 5/17 | 4/16 | 3/17 |
| 0.45/1.40 | 0.191/0.345 | 0.216/0.371 | 0.439/0.744 | 1.45/2.43 | 8.39/14.09 |

n_S number of stages in stripping section
 n_T number of stages in cascade
 Q_F sum of high pressure feed flow rates, kg-mole/s
 Q_L sum of low pressure flow rates, kg-mole/s
 α_E, α_S stage separation factors in enriching and stripping sections
 θ_E, θ_S cuts in enriching and stripping sections

FIGURE CAPTIONS

- Fig. 1 Stage separation factors for PSA and TSA processes. Two-column PSA [1]: $p_H = 1030$ kPa, $p_L = 103$ kPa. Single phase, $T = 373$ K. Two phase, $T = 298$ K. TSA [2]: $p_H = 689$ kPa, $T_L = 333$ K, $p_L = 620$ kPa, $T_H = 423$ K. Single column PSA [3]: $T = 372$ K, $p_H = 1030$ kPa, $p_L = 103$ kPa.
- Fig. 2 Schematic diagram of continuous countercurrent cascade.
- Fig. 3 Schematic diagram of principal items of equipment associated with a single PSA or TSA stage.

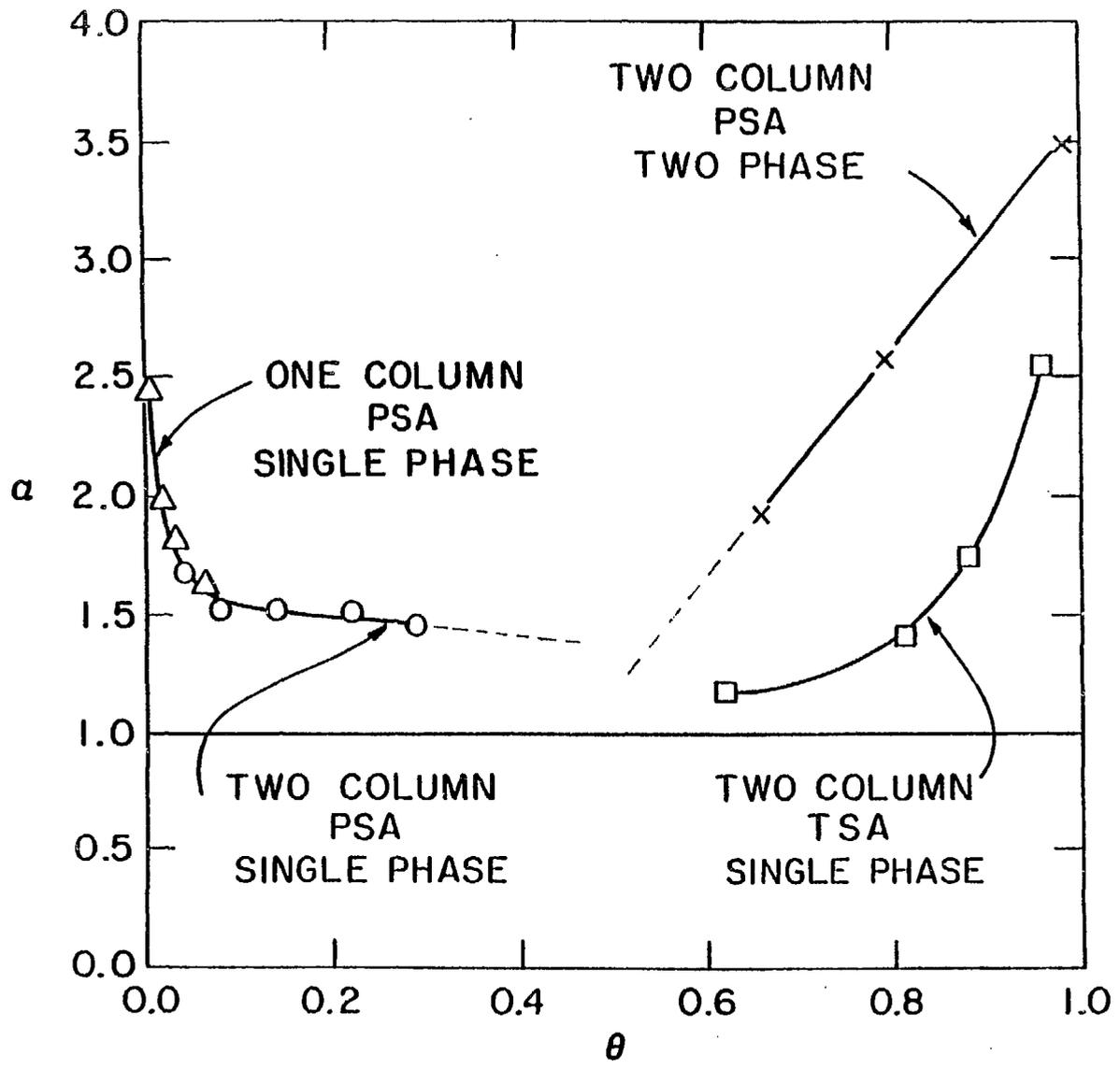


Figure 1

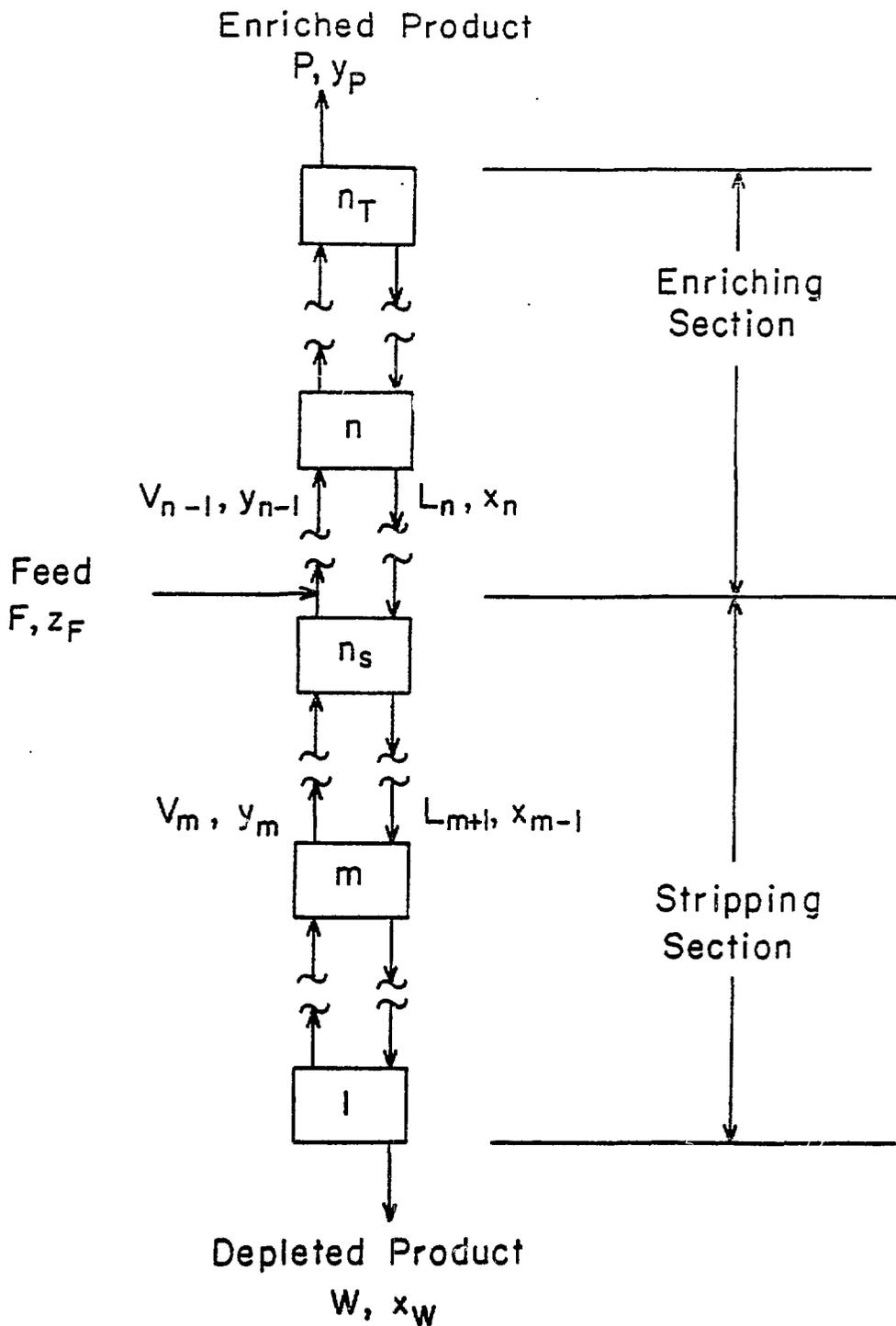
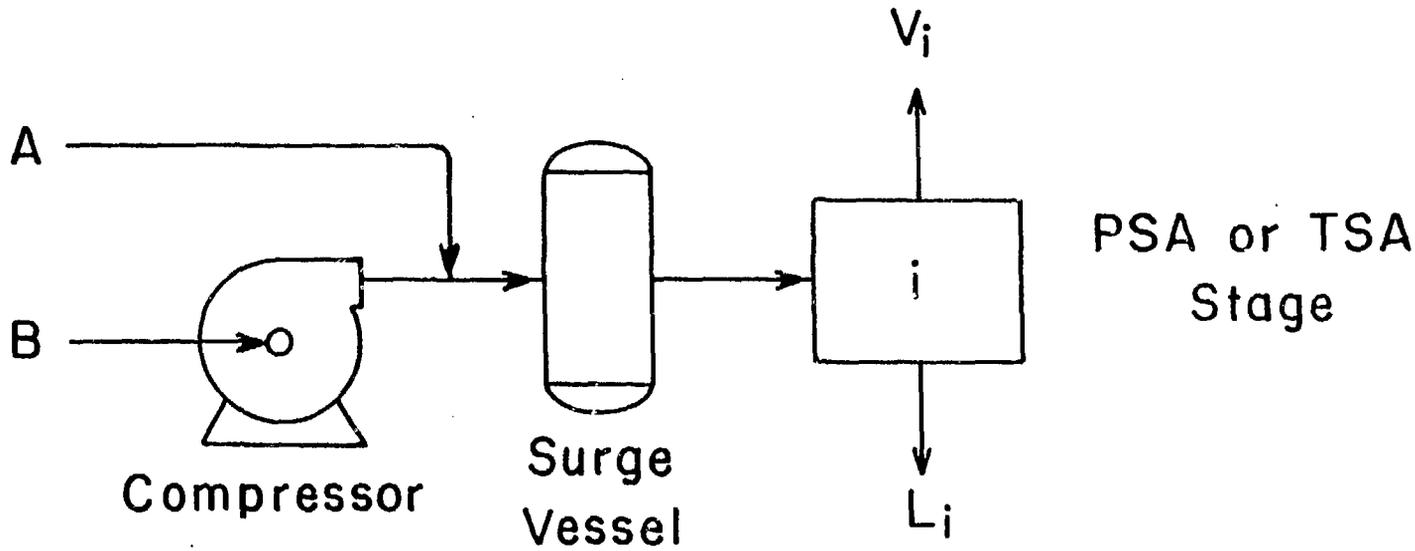


Figure 2



| Location Section | A | B |
|---------------------|-----------|-----------|
| Stripping | L_{i+1} | V_{i-1} |
| Enriching | V_{i-1} | L_{i+1} |

Figure 3