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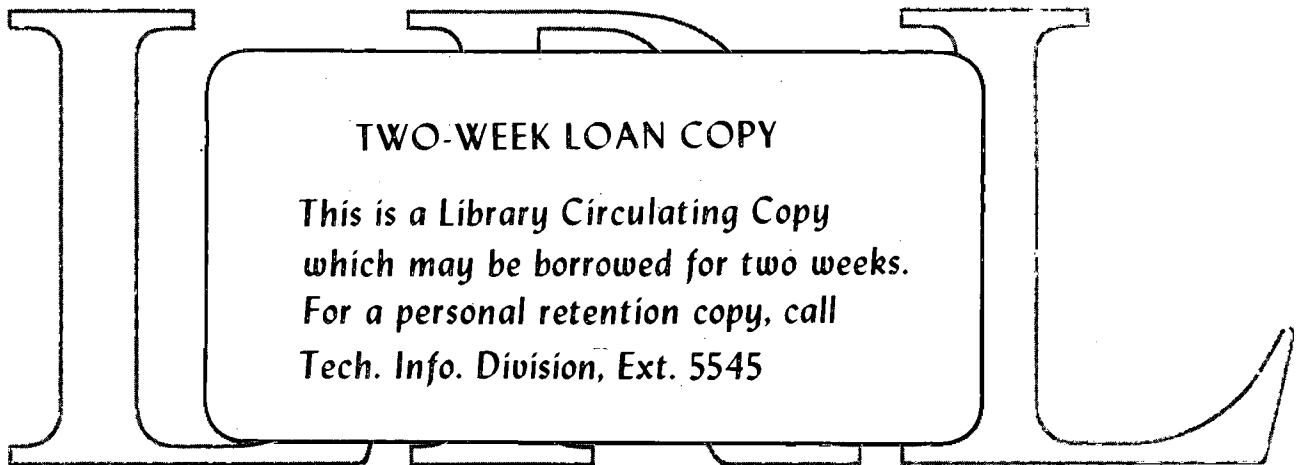
CYCLING ZONE ADSORPTION, A NEW SEPARATION PROCESS

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CYCLING ZONE ADSORPTION, A NEW SEPARATION PROCESS

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ABSTRACT

Cyclic changes in concentration are produced in a fluid which flows

through a fixed bed of solid adsorbent owing to temperature cycling of the

bed. The product stream is collected separately during the periods of posi-

tive and negative deviations from the feed composition. The separation is

increased by using separate zones in series, the temperature changes in

adjacent zones being out of phase. The separation is governed by the wave

propagation properties of the beds.

INTRODUCTION

Development of continuous countercurrent processes for the separation

of gases or liquids by adsorption or chromatography has had only partial suc-

cess owing to the mechanical problems involved in the movement of settled beds

of solid particles. Fixed-bed operation has had to be intermittent owing to

the required regeneration of the solid after it becomes saturated with the

feed mixture.

Recently, attention has turned to cycling operation of fixed beds,

especially in the papers by Wilhelm and his co-workers (1966, 1968) where

"parametric pumping" has been described and shown to lead to large separation

factors. Similar results were described earlier by Bohrer (1965) and

Skarstrom (1959) and more recently by Jenczewski and Myers (1968). In all of

these processes there is a periodic reversal of the fluid velocity in phase

with imposed changes in a thermodynamic potential, usually owing to pressure

or temperature. It has been suggested (Wilhelm, Rice, Rolke, and Sweed, 1968)

that the separation results from a coupling in the equations of transport

between the cycles of flow and temperature or pressure to produce large changes

in fluid composition.

On the other hand, it appears likely that flow reversal is not neces-

sary to produce a separation. Indeed, it may be a disadvantage because of the

limitations on production rates which it imposes. Introduction of pressure or

temperature cycles into a fixed bed without simultaneous flow reversals may

not produce the same steady state gradients of composition along a column as

in parametric pumping but will lead to cycling changes in the composition of

fluid inside and leaving the bed which can be used to advantage. The cycling

changes are propagated through the adsorbent bed as waves and, by setting cycle times and times of passage of fluid through the bed at optimum values the amplitude of the concentration waves can be made large. Because of the ability of different solid materials, such as physical adsorbents, ion exchange resins, or special chromatographic materials, to differentiate between wide ranges of components in gases or liquids, many applications of such processing methods suggest themselves. No batch-type regeneration of solid is needed and the heat requirements may not be excessive.

PROCESS DESCRIPTION

Consider the fixed-bed process illustrated in Fig. 1, in which a fluid having a constant solute concentration, y_f, is passed into a bed of solid particles. The system is held at a constant low temperature, T_C. After a long time, the effluent solute concentration must eventually become y_f. If at this time, the temperature is raised to T_H, solute which was previously stored on the solid is now expelled into the fluid; the effluent has a solute concentration y_h for some time, depending on the relative volumetric ratios of fluid and solid and on the equilibrium distribution coefficient. Finally, the concentration returns to y_f. Now if the temperature is decreased to T_C, the solid takes up solute from the fluid, and the depleted effluent solute concentration becomes y_ℓ. After a certain period, the concentration again returns to y_f and the cycle must repeated. If parallel twin columns are used, as in Fig. 2, one exactly one-half cycle out of phase with the other, a separation can be achieved by periodically switching the output of each column as shown in the figure. The result is continuous production of two streams of different concentrations, one higher and one lower than that of the feed.

It can be shown that the process has an optimum cycle time which

depends on the time of passage of a wave of fluid concentration through the

bed; this is analogous to the optimum flow-temperature phase relationship of

parametric pumping.

The type of operation illustrated in Fig. 1 will be referred to as a

single-stage or single-zone process. The separation factors which can be

achieved may be interesting if the change in the adsorption equilibrium dis-

tribution coefficient is great enough between the low and the high temperatures,

but the separations are not as great as can be obtained after several repeated

cycles with a parametric pump.

The separation can be improved considerably, however, by operating

two or more single zones in series, the temperature changes in each zone being

a half cycle out of phase with those in the adjacent zones, as illustrated in

Fig. 3. The increase in the separation factor obtained in this way can be

calculated by methods analogous to those used by Pigford, Baker, and Blum (1969).

The result shows that the separation factor for n zones should be the same

as that obtained after n batch cycles in the direct mode of parametric

pumping. The advantage of the cycling zone adsorber is, however, that it

operates without flow reversal and therefore produces enriched and depleted

products continuously. The theory shows that operation of a parametric pump

with positive feed and continuous withdrawal will severely impair the separa-

tion factors.

The question of heating and cooling these adsorbent beds is an important

one. The direct mode of operation illustrated in Fig. 1 is one in which there

is a standing temperature wave within the bed. Such operation may not be

practical on a commercial scale, however, owing to the thermal resistance of

the packed bed itself. There is another method of heating and cooling the

solid in which there occurs a travelling wave of temperature changes that

moves through the bed owing to the fluid velocity. This occurs when the

column is insulated and the input fluid stream is alternately heated and

cooled in ordinary heat exchangers located outside the packed bed, as in

Fig. 4. Wave fronts separating hot and cold fluid travel through the bed at

a speed determined by the ratio of the volumetric heat capacities of the flowing

and stationary phases. For a liquid-solid system this speed is about one half

the fluid velocity; for a gas-solid system the thermal velocity may be three

orders of magnitude smaller. If the time of passage of the thermal wave

through the bed is less than one half the cycle time, as is easy to achieve

with liquid-solid systems, the separation will be as good as if the heat trans-

fer had occurred through the walls. In fact, a slight improvement occurs.

Furthermore, the excellent heat transfer into and out of the solid particles

themselves provides an efficient energy transport mechanism. This, then, is

travelling-wave heating and cooling and is a second mode of operation of the

cycling zone adsorber.

There is a complication in the use of multiple zones with the travelling

wave mode because of the requirement that adjacent zones be out of phase in

their temperature cycles. If the thermal wave velocity is greater than the

wave velocity of fluid concentration changes, as with liquid-solid systems,

the thermal wave will emerge from one zone before it can properly be put into

the next zone downstream. The condition can be corrected by using interstage

heaters or coolers or by using insulated heat regenerators to delay the thermal

waves until they are needed for proper temperature-concentration phasing.
Such regenerators would be filled with solid particles having heat capacity
but no mass absorption capacity. In this way the process would provide for
efficient reuse of the heat supplied to the feed stream. Alternatively, inert
particles having thermal capacity but no absorptive ability can be mixed with
adsorbent particles in the bed itself to retard the progress of the changes
in solid temperature.

EXPERIMENTAL

Gas-Solid System

Single Zone - Standing-Wave Forcing. A 3 mole percent methane in
helium stream (160 cc/min) was fed to a 20-cm by 1.3-cm ID bed of 12 to 30
mesh Pittsburgh BPL activated carbon which was heated externally by an elec-
trical resistance heater and cooled by water in a jacketed column. The
temperature changes in the bed were represented by a sine wave of 12°C ampli-
tude and 0.34 cycles/min at a mean temperature of 51°C. The maximum separation
factor (maximum effluent concentration/minimum effluent concentration) = 2.8.
The maximum methane effluent concentration = 5.3 mole percent; the minimum
was 1.9 mole percent.

Liquid-Solid System

Single Zone - Standing-Wave Forcing (Fig. 5). A 0.0647-N aqueous
acetic acid stream (7.0 cc/min) was fed to a 26-cm by 1-cm ID bed of 50 to
140 mesh Pittsburgh CAL activated carbon which was heated and cooled by a
water jacket. The temperature changes in the bed were represented by a square

wave of 28°C amplitude and 0.03 cycles/min at a mean temperature of 32°C. The

maximum separation factor was 8.9. The maximum acetic acid effluent concen-

tration was 0.1599-N; the minimum was 0.0179-N.

Single Zone - Travelling Wave Forcing. The above column was insulated

and the water jacket was removed. The feed stream was heated and cooled at

the same conditions before being fed to the column. The maximum separation

factor was 10.5. The maximum concentration was 0.1680-N; the minimum was

0.0160-N.

Double Zone - Standing Wave Forcing (Fig. 5). The jacketed system

above was used except that a duplicate column was added in series which was

heated and cooled through the walls one half cycle out of phase with the

first. The maximum separation factor = 33.0. The maximum concentration was

0.1850-N; the minimum was 0.0056-N.

DISCUSSION

Because of the wave-like properties of the equations of transport

applicable to the cycling zone adsorber (Pigford, Baker, and Blum, 1969)

the most attractive interpretation of the data is in terms of the behavior

of concentration waves in the fluid as it passes through the adsorbent bed.

Consider the direct mode of operation in which a zone's temperature is changed

instantaneously throughout its length and sinusoidally in time. There will

be a standing wave of fluid concentration which is present throughout the bed.

In addition, because the fluid is moving, concentration waves travelling in

the fluid flow direction will also occur. If the entering fluid has a fixed

composition the two waves must just cancel at the entrance. Whether they

reinforce or cancel at the exit will depend on the ratio of the concentration wave velocity, u, to the product of impressed frequency and length, ωZ.

The fluid concentration leaving the first zone of length Z is given by the equation

$$\frac{y_1(Z,t) - y_f}{y_f} = \frac{a}{1 + m_o} \left[\sin \omega t - \sin(\omega t - \omega Z/u) \right] \tag{1}$$

where, as in our previous publication (1969), m_o is a solid-to-fluid distribution coefficient on a phase volume basis and a is the change in the distribution coefficient caused by the temperature sine wave. Reinforcement of the standing and travelling waves occurs when length or frequency are chosen such that $\omega Z/u$ is an odd-integer multiple of π. Then the right side of the equation becomes simply $2[a/(1 + m_o)] \sin \omega t$. The assumption is implied in the equation that the deviations in composition and temperature are small.

If the fluid having composition changes according to Eq. (1) is sent to a second adsorption zone in which the temperature changes are opposite to those in the first, the fluid leaving this zone will follow the equation

$$\frac{y_2(Z,t) - y_f}{y_f} = \frac{a}{1 + m_o} \left[-\sin \omega t + 3 \sin(\omega t - \omega Z/u) \right] \tag{2}$$

and if the same choice is made of $\omega Z/u$, the right side of the equation becomes $-4[a/(1 + m_0)] \sin \omega t$ or twice the amplitude obtained in the first zone. For n zones the right side is $(-1)^n 2n[a/(1 + m_o)]$. The amplification can be continued by the addition of more zones, but the linear theory is obviously defective when the concentrations become large. The highest cycle-averaged separation that can be accomplished is to reduce y to zero in

half the volume of fluid and to increase it to $2 y_f$ in the remaining half, just as in the batch operation of the parametric pump at the same frequency. However, the cycling zone adsorber accomplishes this separation, while maintaining a positive feed of fluid; it therefore produces a product.

The reason for the enhancement of the separation in the second and succeeding zones is that it is always possible to put a fluid through a bed of adsorbent without a change in the concentration profile which the fluid has upon entering, provided the solid temperature is not changed. The arrival of the concentration profile at the exit may be delayed because of the slowness of concentration waves passing through, but under the assumptions of the linear equilibrium theory which we are using, the waves are not distorted. However, if the temperature of the solid is increased suddenly while a wave is in transit solute which was in storage on the adsorbent will be added to the fluid, regardless of the concentration it may have had already. The converse is true for a sudden reduction in temperature. Obviously the temperature changes have to be timed and phased correctly so that composition changes will be in the right direction. The changes have to occur when the proper concentration waves have arrived in the particular zone.

A quantitative discussion of cycling zone adsorption, including a discussion of the effects of concentration-dependent equilibrium distribution coefficients, which cause wave distrotion, and of finite mass transfer rates, is planned for a later paper.

ACKNOWLEDGMENTS

NOMENCLATURE

a = equilibrium distribution coefficient change, dimensionless

m = equilibrium distribution coefficient, dimensionless

n = number of cycles

t = time, sec

T = temperature, °C

u = velocity of propagation of concentration wave, cm/sec

y = fluid concentration, moles solute/mole fluid

Z = column length, cm

ω = cycle frequency, rad/sec
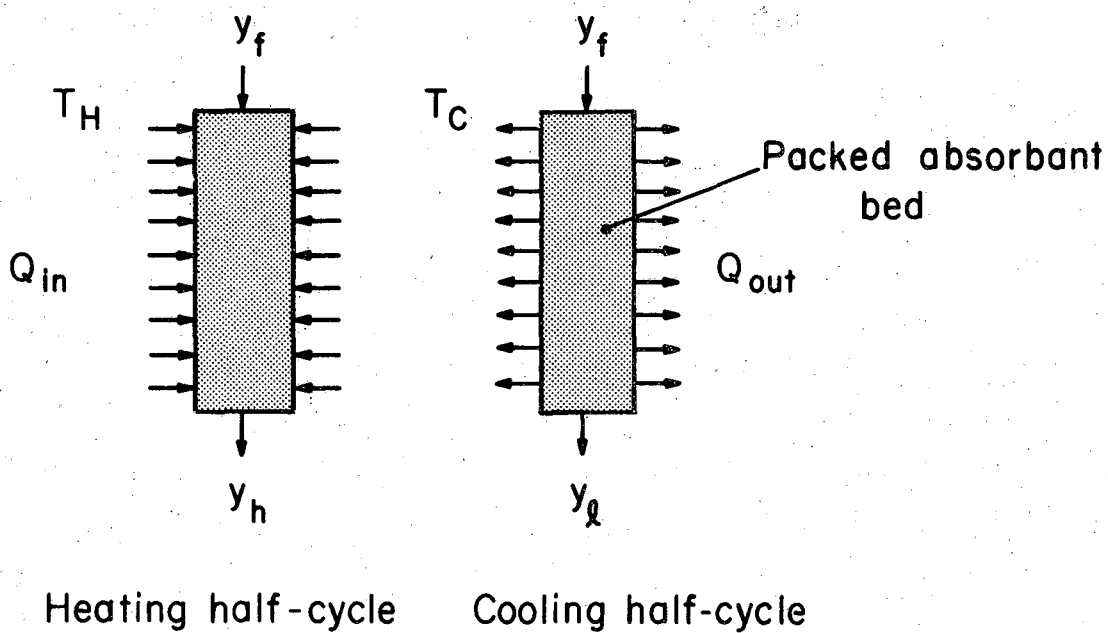
Subscripts

C = cold

f = feed

h = high

H = hot

ℓ = low

n = zone number

o = at mean temperature

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T_H

Q_{in}

y_f

y_h

T_C

y_f

Q_{out}

Packed absorbant bed

y_ℓ

Heating half-cycle   Cooling half-cycle

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Fig. 1. Single-zone, standing wave operation of cycling zone adsorber.
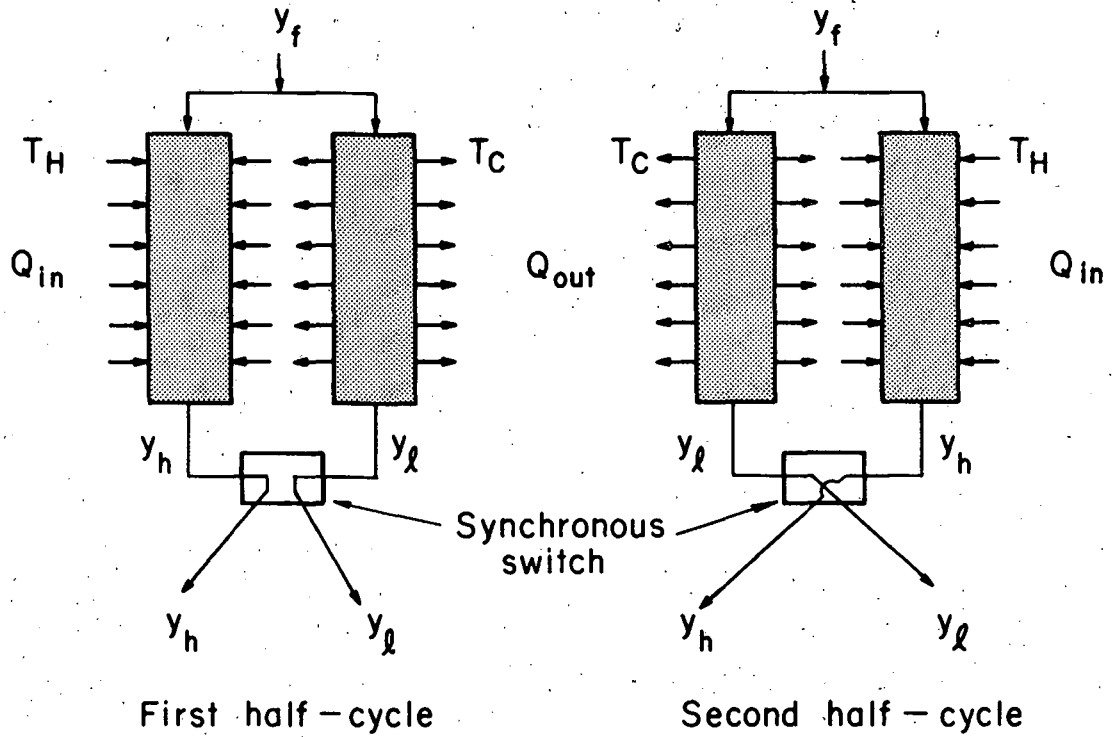
Fig. 2. Single-zone, standing wave operation of cycling zone adsorber for continuous production.
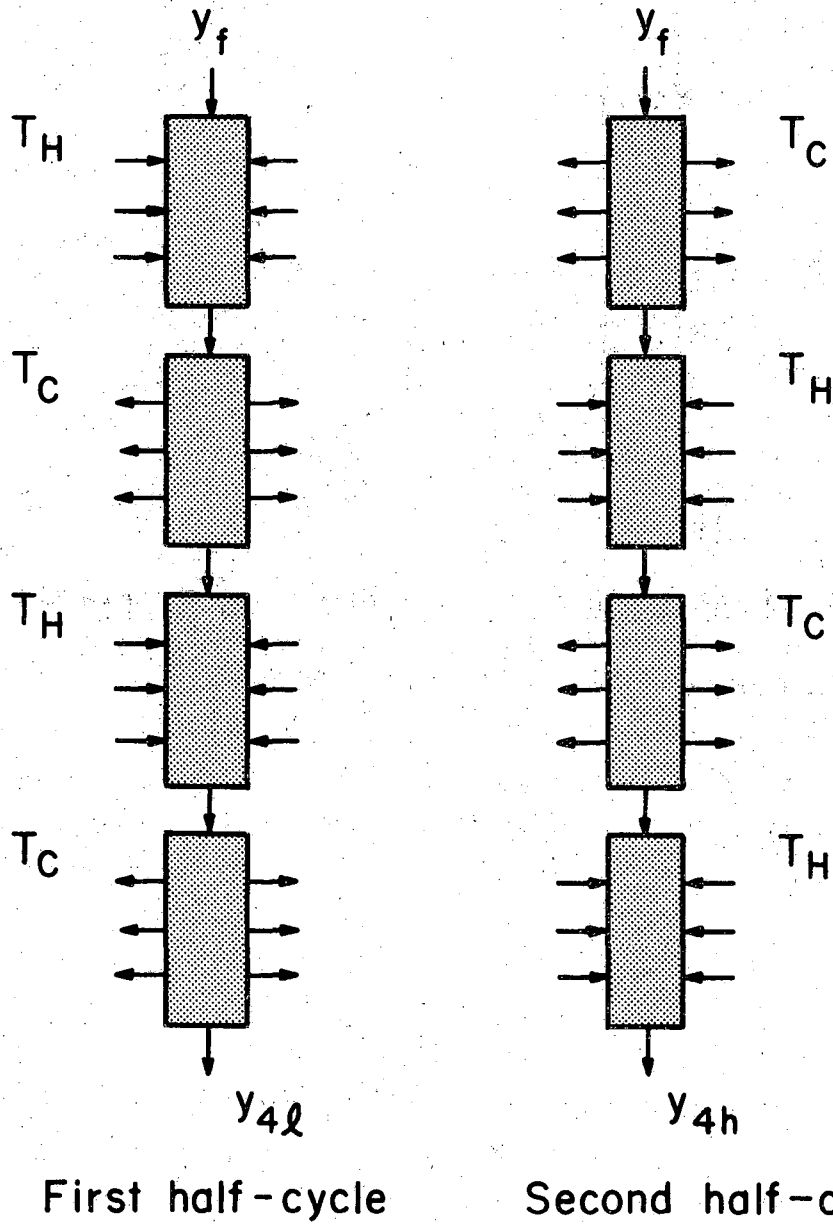
Fig. 3. Multiple-zone, standing wave operation of cycling zone adsorber.

First half-cycle   Second half-cycle
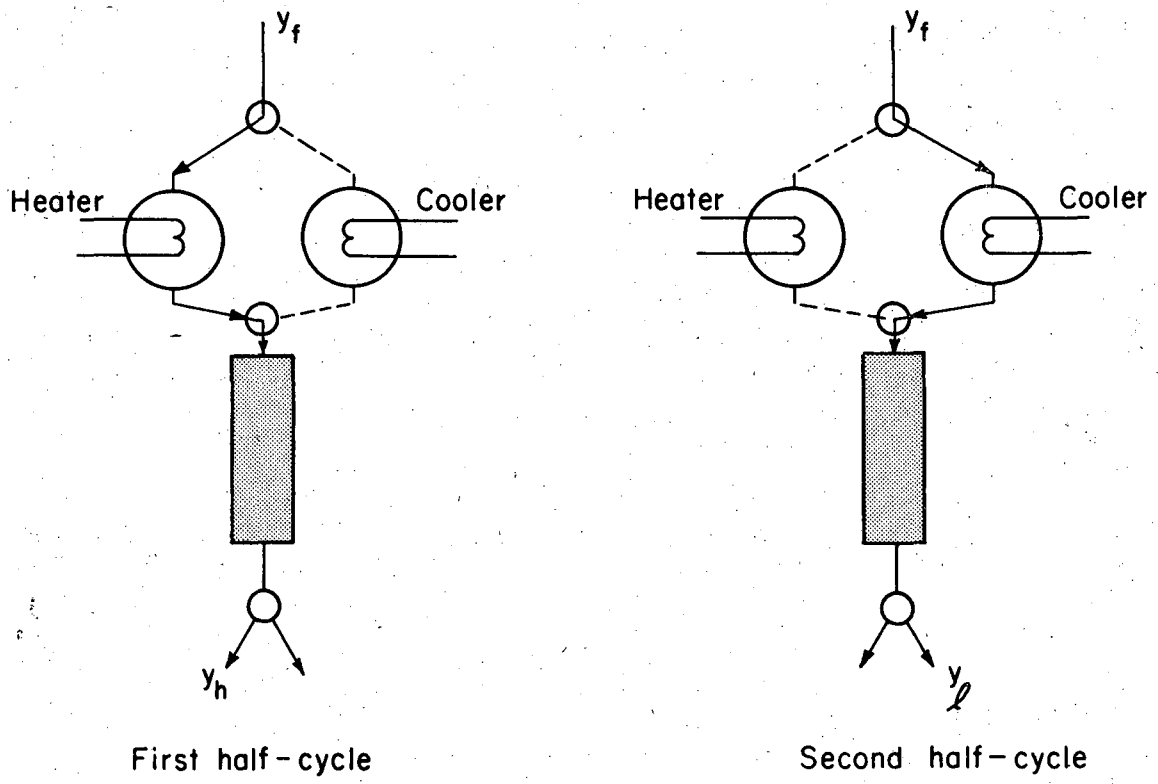
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Fig. 4. Single-zone, travelling wave operation of cycling zone adsorber.
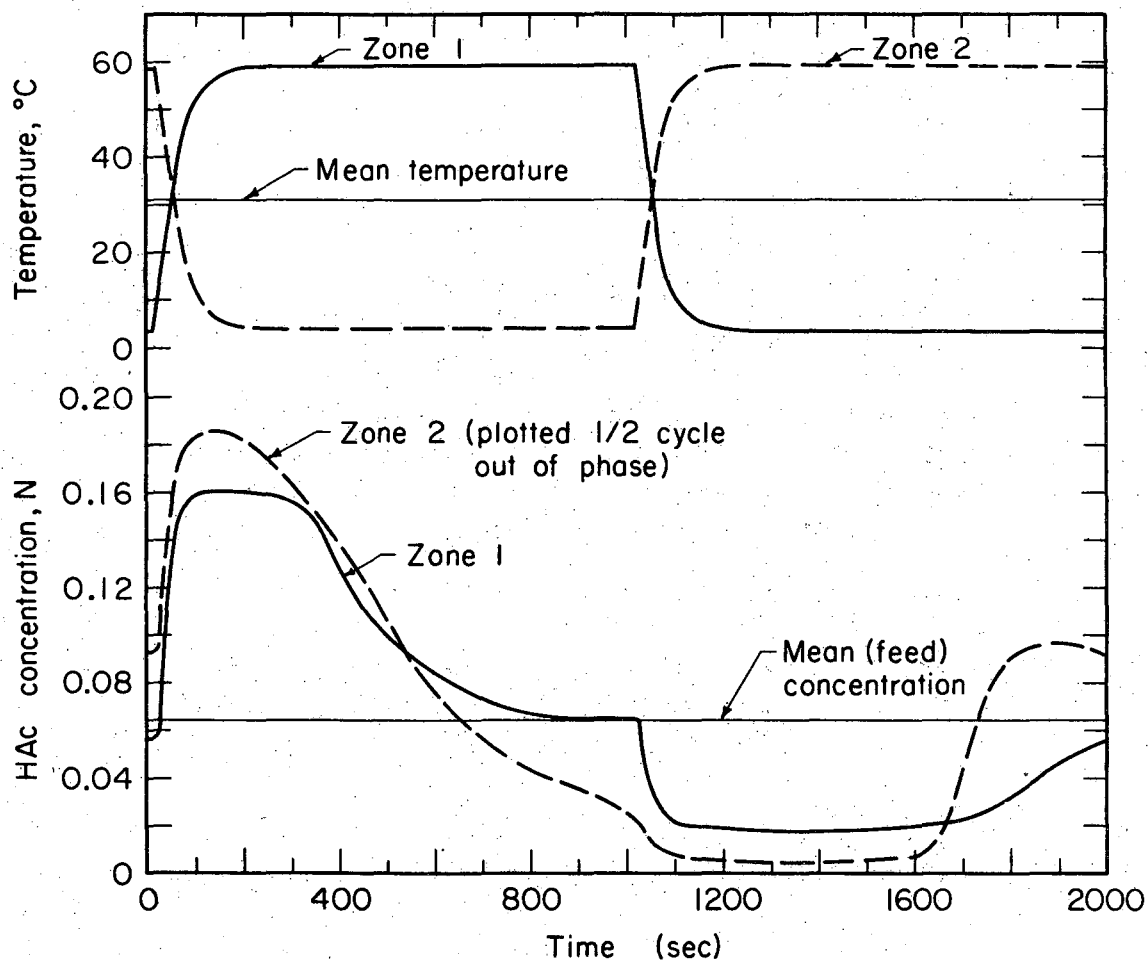
Fig. 5. Comparison of single and double-zone, standing wave operation for the separation of acetic acid-water with activated carbon.

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