Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Siegell, Jeffrey H. , Pirkle JR, J. Carl and Dupre, Gerald D.(1984) 'Crossflow Magnetically Stabilized Bed Chromatography', Separation Science and Technology, 19: 13, 977 — 993
To link to this Article: DOI: 10.1080/01496398408058342
URL: http://dx.doi.org/10.1080/01496398408058342

SEPARATION SCIENCE AND TECHNOLOGY, **19**(13-15), pp. 977-993, 1984-85

Crossflow Magnetically Stabilized Bed Chromatography

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Abstract

A device for continuous chromatographic separation of multicomponent feeds is described. It consists of a magnetically stabilized fluidized bed (MSB) in which bed solids move crossflow to the fluidizing fluid. Adsorbable components of the feed move in two directions; with the fluidizing carrier fluid to the bed surface, and with the solids across the bed to different positions depending on their sorption characteristics. The features that make the crossflow MSB chromatograph attractive are the ability to continuously separate feed mixtures into multiple products in a single vessel with no moving mechanical parts. The MSB is ideally suited for chromatographic operation. The fluid and solids move in plug flow, and the pressure drop is limited to the weight of solids per unit bed area, independent of the particle size and fluid throughput. Using tracer gases, the operation of a crossflow MSB chromatograph has been demonstrated. Increasing the height of the crossflow bed has been shown to improve the resolution of adjacent peaks. Mixtures of up to five gaseous hydrocarbons have been separated. Mathematical modeling indicates that the major mechanisms for peak spread are intraparticle diffusion, vertical and lateral dispersion, and external diffusion.

INTRODUCTION

The crossflow magnetically stabilized bed chromatograph is a device for continuous separation of multicomponent feeds by sorption. The device uses a Magnetically Stabilized Fluidized Bed (MSB) (*1*) with crossflow of solids in which the components are separated by the solids and carrier fluid

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moving in different directions. The crossflow MSB chromatograph is attractive for process separation applications due to its ability to continuously separate feeds into multiple products in a single vessel with no moving mechanical parts.

Chromatographic separation makes use of the difference in sorption equilibria of components in the feed when contacted with a suitable chromatographic packing material. This packing material is usually a porous or granular solid which in some cases may be coated with a liquid substrate.

The conventional chromatographic process consists of introducing a pulse feed into a packed column of adsorbent solid with a continuous flow of carrier fluid. The components of the feed are stratified in the column by selective adsorption and desorption on the solid. This process causes the different components to exit from the column with the carrier fluid at different times. The components that were the least adsorbed in the column will exit first and the components that were most strongly adsorbed will exit last. This process, however, is only suitable for batch operation.

There have been numerous attempts to operate chromatographic separators in a continuous fashion (*2–4*). In particular, the concept of crossflow chromatography has been previously attempted in at least three different operational modes. The initial disclosure of crossflow operations seems to be by Martin (*5*). He described an annular space between two concentric cylinders, packed with adsorbent solids, for continuous separations. Carrier fluid was fed axially while the bed was slowly rotated. He also suggested the use of a circular array of tubes rather than the continuous packed bed. This device, however, is mechanically complicated due to the difficulty of having large systems of tubes or beds rotated. In addition, the efficiency is limited because, as in other packed chromatographic systems, particle size cannot be substantially reduced due to pressure drop limitations.

Using two rotating disks placed closely together and coated with a thin layer of solvent, Sussman and Huang (*6, 7*) operated a radial flow continuous chromatograph. Carrier fluid was injected at the center of the disks while feed was introduced at a single point. The crossflow occurs between the angular motion of the disks and the radial flow of the carrier fluid. A limitation in this device is in the small capacity of a single disk system.

Another crossflow chromatography device, described by Tuthill (*8*), operates by continuously injecting a multicomponent feed into the corner of a rectangular slab, packed with adsorbent, and then the direction of carrier flow changes at right angles with a change in the temperature. The inability to use very fine particles, due to excessive pressure drop, limits the separation efficiency.

THE DEVICE

The crossflow MSB chromatograph consists of a magnetically stabilized bed with solids flowing horizontally as shown in Fig. 1. These solids tend to flow in plug fashion without a significant vertical or horizontal gradient. Carrier fluid is introduced to the stabilized bed as the fluidization medium and flows vertically in plug flow through the bed. A multicomponent feed is injected continuously in a zone at the bottom of the bed. The components in this feed have varying adsorption/desorption characteristics with the bed solids. These components have velocities in two directions. They move in the direction of the carrier fluid toward the top surface of the bed and also, due to adsorption on the solid, in the direction of the movement of solids. Weakly adsorbed components come to the surface of the bed close to the feed point, and strongly adsorbed components are transported downstream with the solids and reach the top of the bed at different positions. Collection of the different components may be achieved by removing them at the bed surface at these different positions. Figure 2 shows the trajectory of components in crossflow beds.

Properties of crossflow MSB chromatography which provide for its use as a separation tool are listed in Table 1. These include the nearly plug flow of both gas and solids, without which the device would not work. In addition, since the bed is fluidized, the pressure drop is limited to the weight of solids per unit bed area, independent of the particle size and fluid throughput. Thus, smaller particle sizes and higher carrier fluid rates may be used without suffering the higher pressure drops of the previous packed-bed devices.

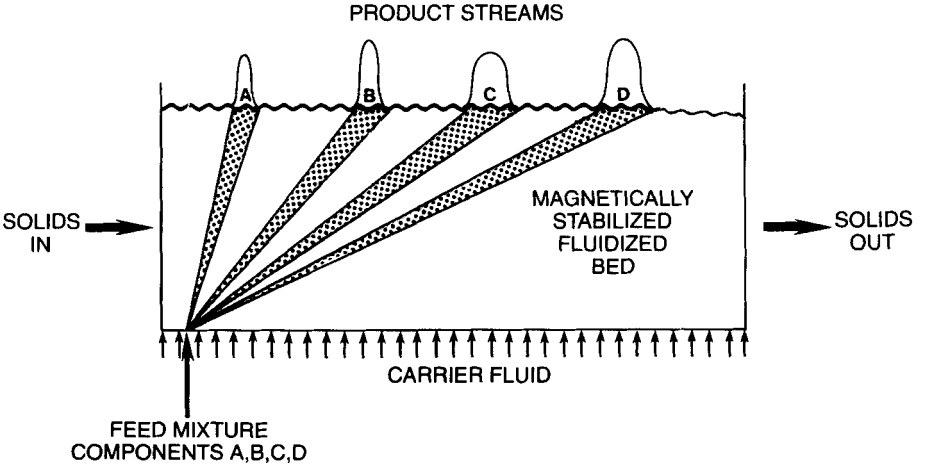


FIG. 1. Crossflow magnetically stabilized fluidized bed chromatography.

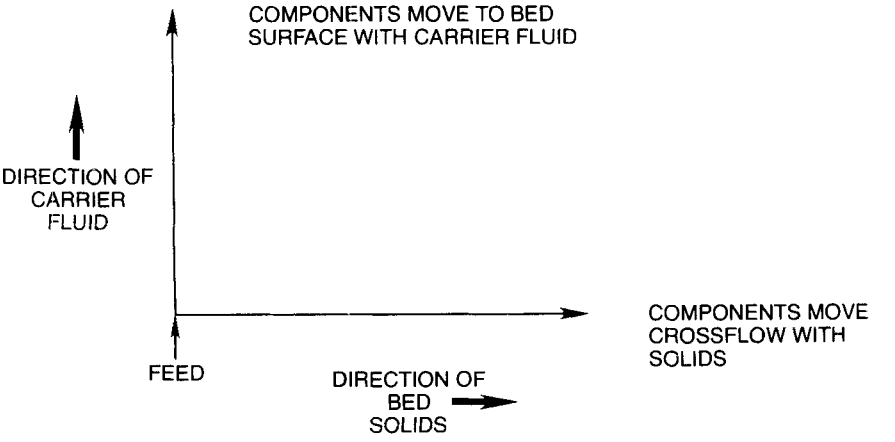


FIG. 2. Trajectory of components in crossflow MSB chromatography.

Since the bed consists of free-flowing fluidized solids, it is mechanically simple, with the solids being the only moving part. In addition, since it is stabilized, the attrition normally associated with fluidized beds is virtually eliminated.

The quiescent, fluidlike MSB is free of bubbles or pulsations, and results when a magnetic field is applied to a bed of magnetizable solids, preferably in a direction colinear with that of the fluidizing gas flow. This magnetic stabilization produces a nonbubbling fluid state with operating velocities ranging between the normal minimum fluidization velocity in the absence of the applied magnetic field, and an upper limit given by the superficial fluid velocity required to cause bubbling to occur in the bed.

The stably fluidized solids resemble a liquid and are easily transported. Similar to unmagnetized fluidized beds, the pressure drop is independent of

TABLE 1
Characteristics of MSB Crossflow Chromatography

Plug flow of gas
Plug flow of solids
Constant pressure drop vs flow rate
Constant pressure drop vs particle size
Mechanically simple (solids only moving part)
Free-flowing fluidized solids
Attrition prevented

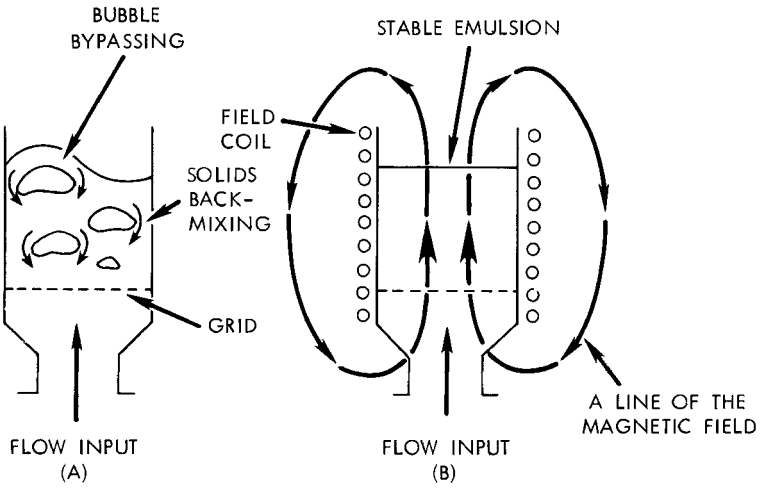


FIG. 3. Comparison of bubbling and stabilized fluidized states.

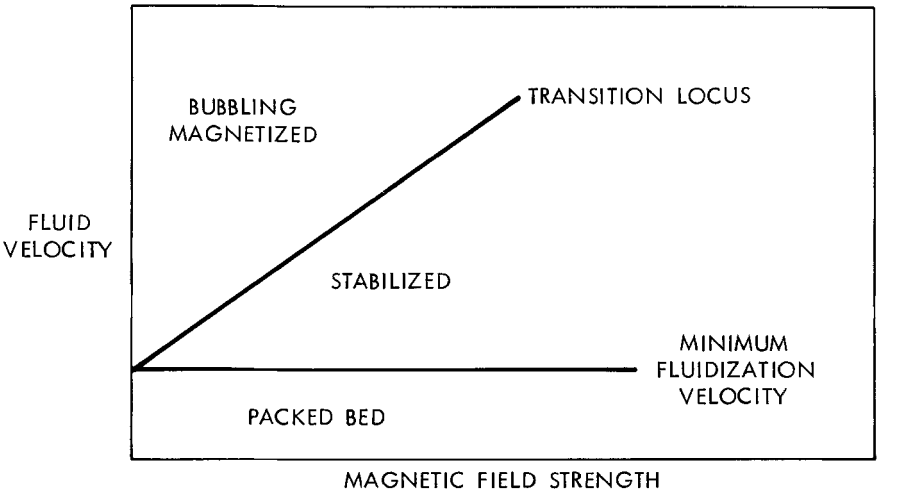


FIG. 4. Fluid/solids/magnetics phase diagram.

particle size or fluid throughput. The MSB exhibits the absence of gas or solids backmixing which normally occurs in bubbling fluidized beds. A graphical comparison of magnetically stabilized and bubbling fluidized beds is shown in Fig. 3.

Figure 4 shows that the fluid/solid/magnetic system exists in one of three regimes. Below the minimum fluidization velocity the pressure drop across the bed is less than the bed weight per unit area and the bed is "unfluidized." In the stabilized regime, the bed is free of mixing motions. In the regime denoted bubbling magnetized, the bed bubbles even though magnetized. The transition between these two regimes is rather sharp and reproducible. The MSB regime existing at velocities between the minimum fluidization velocity and transition velocity to bubbling is the one of interest in performing crossflow chromatographic separations.

When increasing the gas velocity in an MSB, as shown in Fig. 5, the breakpoint of the pressure drop curve corresponds to a minimum fluidization velocity U_{mf}. Thereafter, as in unmagnetized bubbling fluidized beds, the pressure drop through the MSB equals the weight of bed solids per unit bed area, independent of particle size or gas velocity.

EXPERIMENTAL

Experimental data for the crossflow MSB chromatograph were obtained with the equipment shown in Fig. 6. The crossflow MSB was approximately

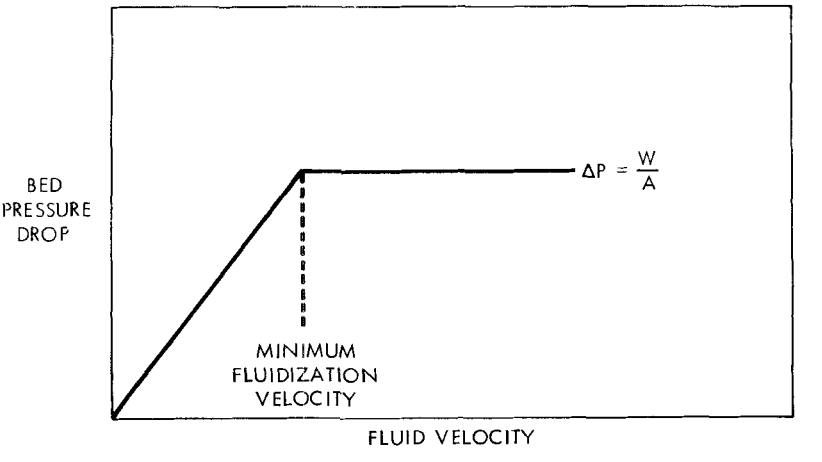
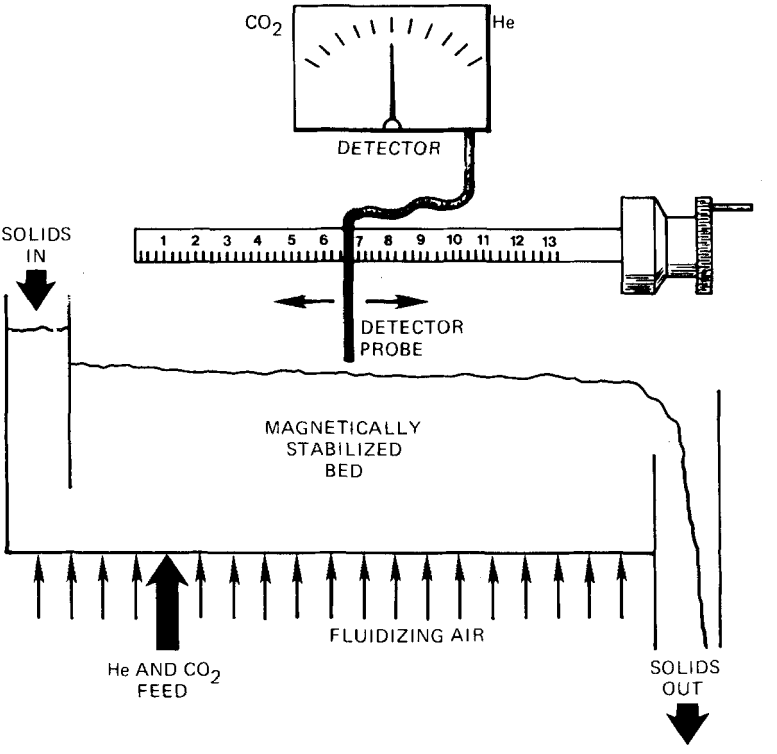


FIG. 5. Magnetically stabilized fluidized bed pressure drop behavior.



SOLIDS: NALCO COMPOSITE
70 WT.% SS/ALUMINA
-20 + 60 U.S. SIEVE

U_o = 30.3 CM/SEC

V_s = 0.56 CM/SEC

H_a = 191.7 OERSTED

BED HEIGHT = 14 CM

FIG. 6. Experimental crossflow unit for MSB chromatography.

69 cm long and 7.62 cm wide, with means to convey solids pneumatically from an overflow weir back to the other end of the bed. It was filled with −20 + 60 U.S. Sieve composite material of alumina and stainless steel (70 wt%) to a depth of about 14 cm. Air was used as the fluidizing carrier fluid and also as a means of conveying the solids. The density of the solids was 1.71 g/cc, the superficial air velocity was 30.3 cm/s, the crossflow velocity of solids was 0.56 cm/s, and the applied magnetic field was 192 Oersted.

To check that a separation could be achieved, a mixture of He and CO_2 was used as a tracer gas with a thermal conductivity detector (GOW MAC, leak detector, Model 21-150) used as a monitor. The detector probe could be moved along the top surface of the bed to determine the elution points of the tracers.

With continuous injection of the He and CO_2 at the bottom of the bed, Fig. 7 shows the profile on the top of the bed as a function of the position in the direction of solids flow. Since helium causes a negative deflection of the detector indicator due to its high thermal conductivity relative to air, and CO_2 causes a positive deflection due to its low value of thermal conductivity, it is clear that separation is taking place. By repeating this experiment with each of the pure tracer gases individually, the amount of overlap of the

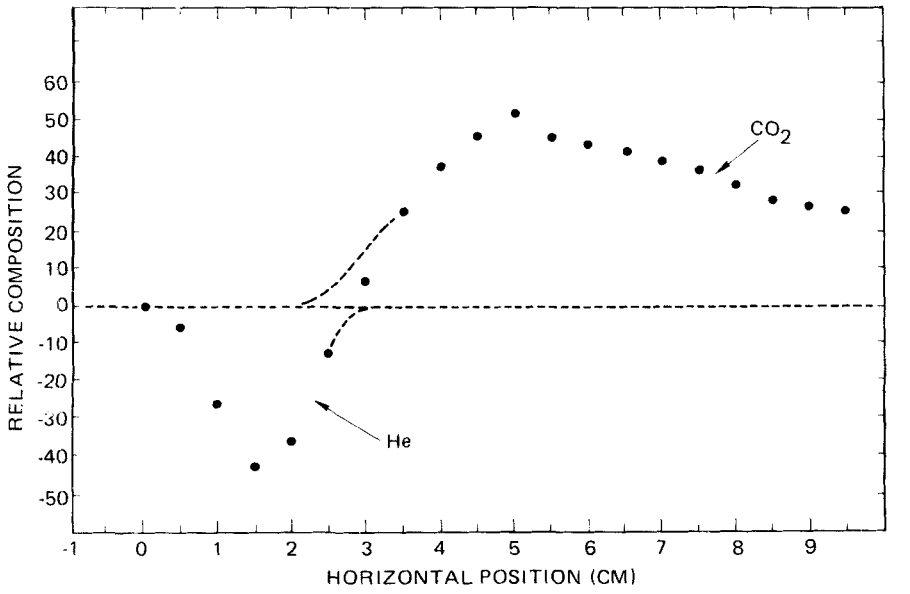


FIG. 7. Results of the continuous chromatographic separation of He and CO_2 in a crossflow magnetically stabilized fluidized bed.

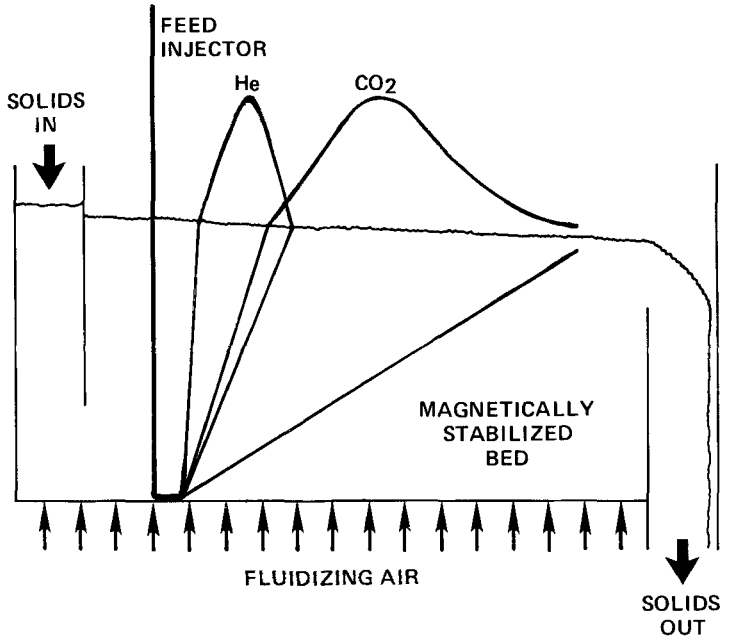


FIG. 8. Pictorial representation of separation of He and CO_2 in a crossflow magnetically stabilized bed chromatograph.

peaks was determined. This experimental separation is shown pictorially in Fig. 8.

A true test of the crossflow MSB chromatograph was the continuous separation of a multicomponent stream of five normal hydrocarbons. The results of this test are shown in Fig. 9. It should be noted that the elution positions for the components in the mixture are nearly the same as for the injections of the individual components. This experiment was performed in the 14-cm high crossflow MSB used for the He/CO_2 separation, at nearly the same operating conditions. In this experiment the detector was a flame ionization organic vapor analyzer (Century Systems, Model OVA-128).

It was expected that as the height of the bed was increased, the separation of individual components would improve. Figure 10 shows what happens to the separation of methane, *n*-butane, and *n*-pentane when the bed height was increased from 14 to 22 cm. Although the components that are strongly adsorbed tend to elute at a further distance from the feed point, the separation achieved has been improved and is what would be termed "baseline." Higher bed heights would certainly improve the separation even

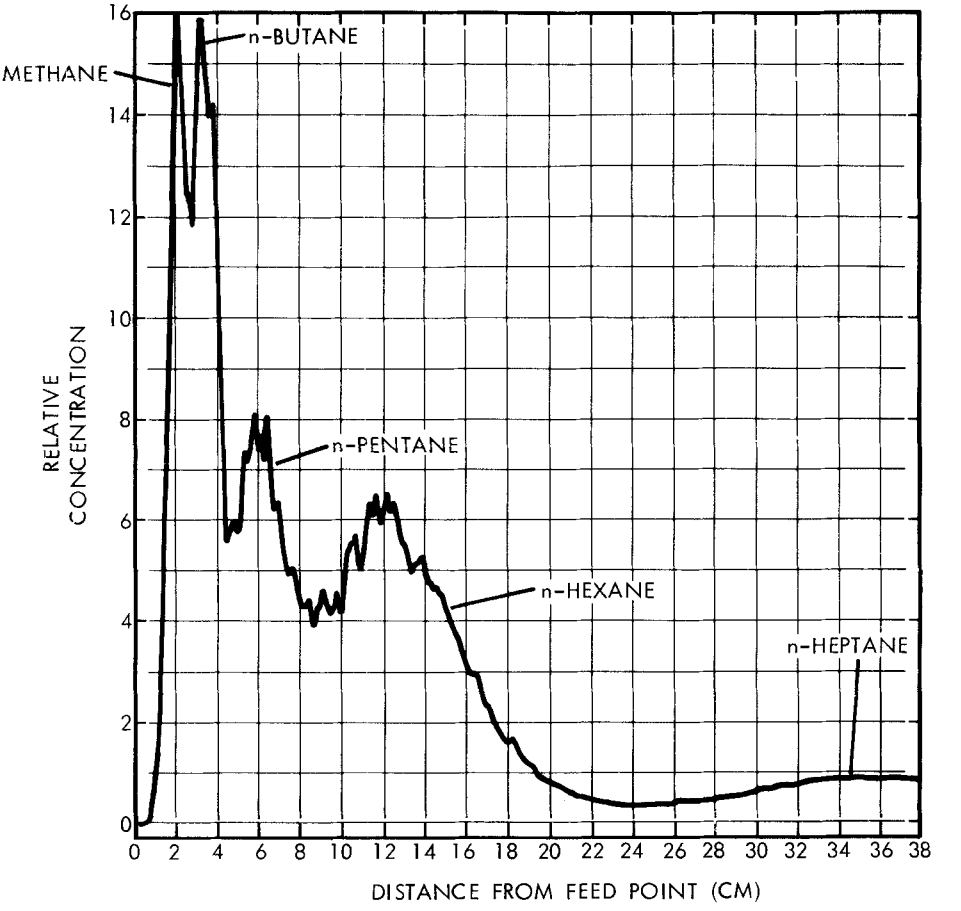


FIG. 9. Results of the continuous chromatographic separation of five normal paraffins in a crossflow magnetically stabilized fluidized bed.

further. Thus, high purity components can be recovered without contamination due to peak overlap.

MODELING

The governing differential equations for the crossflow MSB chromatograph can be derived from differential mass balances over infinitesimal elements of space. Figure 11 shows the physical basis of the model.

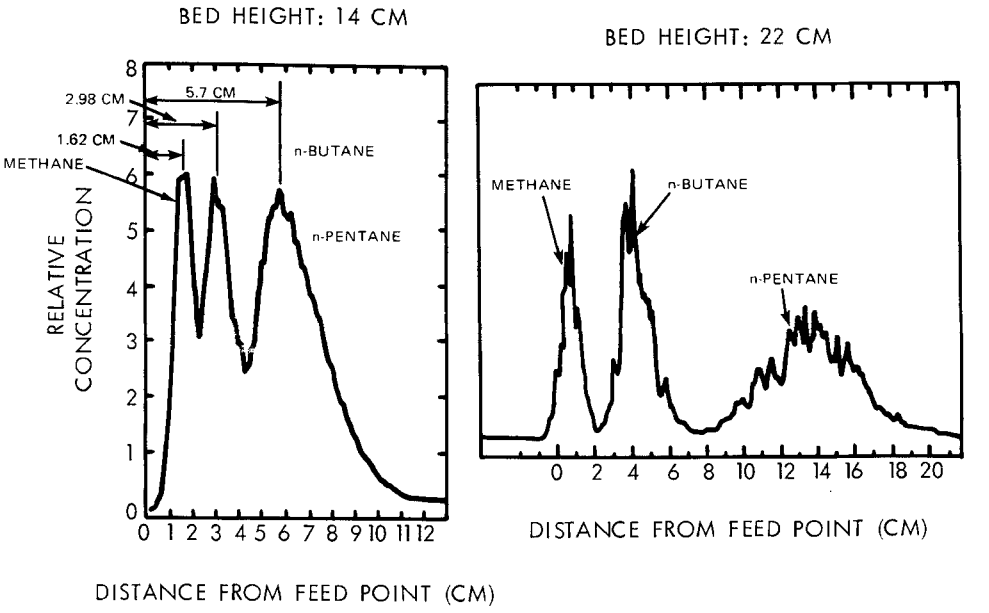


FIG. 10. The effects of bed depth on separation in a crossflow magnetically stabilized fluidized bed chromatograph.

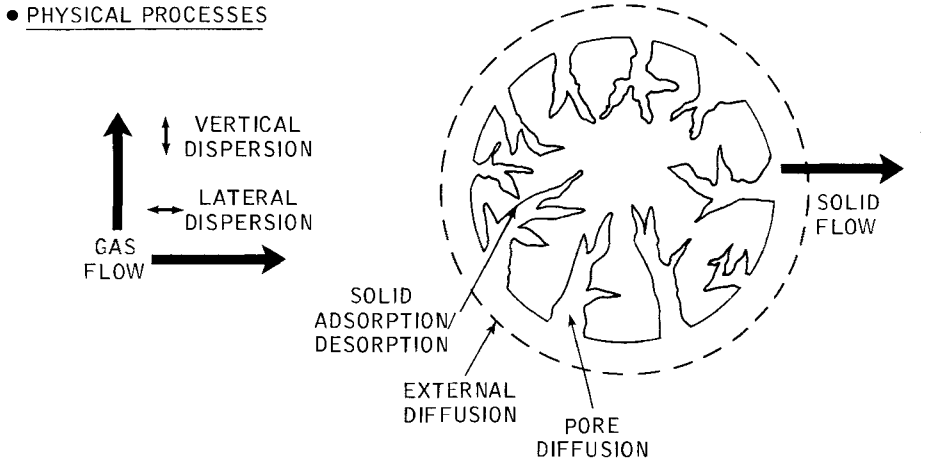


FIG. 11. Pictorial representation of the mathematical model of continuous crossflow magnetically stabilized fluidized bed chromatography.

Assumptions were steady-state and uniform temperature, pressure, bed voidage, particle size, intraparticle voidage, gas-phase velocity, and solid-phase velocity.

The external fluid phase mass balance equation states that the rate at which a species leaves the external fluid phase is equal to the rate at which it diffuses into the adsorbent:

$$D_X \frac{\partial^2 C}{\partial X^2} + D_Y \frac{\partial^2 C}{\partial Y^2} - V_X \frac{\partial C}{\partial X} - V_Y \frac{\partial C}{\partial Y} = \frac{3D_P(1-\varepsilon)\beta}{\varepsilon R_P} \left.\frac{\partial Q}{\partial R}\right|_{R=R_P}$$

The intraparticle fluid phase mass balance equation states that the rate at which a species diffuses through the particle equals the rate of local accumulation in the particle. Diffusion across the external stagnant film is equated to diffusion into the particle interior:

$$V_S\left[\frac{\partial Q}{\partial X} + \frac{\partial N}{\partial X}\right] = D_P\left[\frac{\partial^2 Q}{\partial R^2} + \frac{2}{R}\frac{\partial Q}{\partial R}\right]$$

In the above equation, N is the concentration of a species adsorbed on the intraparticle surfaces per unit of pore volume. The rate at which a species is adsorbed on the intraparticle surface as the particles move horizontally is given by the solid-phase mass balance equation:

$$V_S \frac{dN}{dX} = K_P(K_A Q - N)$$

Solution of these equations yields, in concise algebraic form, equations relating the quality of separation in an MSB to the system parameters and operating conditions.

A summary of the results of the crossflow MSB chromatography modeling for the experiments conducted is shown in Table 2. From fundamental physical properties and operating conditions, the peak location, peak width, and unit size can be calculated. The four controlling physical mechanisms for peak spread were found to be the intraparticle diffusion, vertical dispersion, lateral dispersion, and external diffusion. Finally, Table 2 lists several means which the model indicates could be used to improve the resolution of adjacent peaks.

Calculated values using the model for prediction are given in Tables 3 and 4 for the crossflow separation of argon and CO_2. Table 3 lists the fundamental properties and operating conditions for the bed. Table 4 gives the individual contributions of the physical mechanisms to the peak spread

TABLE 2
Crossflow Modeling Studies

Calculated results:
Peak location
Peak width
Unit size
Controlling physical mechanisms for peak spread identified:
Intraparticle diffusion
Vertical dispersion
Lateral dispersion
External diffusion
Improved resolution of peaks obtained by:
Decreasing particle size
Decreasing carrier velocity
Decreasing bed voidage
Increasing intraparticle voidage
Increasing intraparticle diffusivity
Increasing bed height

as well as a comparison of the calculated values of the peak variance to the experimentally determined values. For CO_2, which is the more strongly adsorbed component, the experimental value is within 15% of that calculated by the model.

DISCUSSION

Crossflow MSB chromatographs are most suitably applied where the components have very similar properties (i.e., boiling points) but differ substantially in adsorbtivity on a suitable solid support. Separations of hydrocarbon isomers such as ethylene/ethane and the butylenes are examples of such applications. In each of these cases, the separation could be achieved more easily by chromatography than by distillation.

Another possible reason for choosing chromatography over distillation would be to avoid the heat effects. Some compounds may tend to decompose even at the low temperatures of vacuum stills. Others may start to degrade due to a substantial temperature swing. The temperature and heat effects of chromatographic processes are usually very mild.

The separation of helium and carbon dioxide described here demonstrates the feasibility of MSB crossflow separations. Although other available separation techniques will provide efficient separation of these components, the present study has demonstrated that a mixture can be

TABLE 3
Parameters and Operating Conditions for Separation of CO_2 and Argon in Air at P = 1 atm, T = 298 K. Particles Used Were Stainless Steel/Alumina

Quantity	Value
W	0.159 cm
ε	0.5
β	0.693
V_S	0.54 cm/s
R_P	0.0152 cm
L	14 cm
V_{fY}	61 cm
V_{fX}	0.54 cm/s
ρ_f	1.19×10^{-3} g/cm^3
μ_f	1.7×10^{-4} g/cm · s
Re_P	12.97
Pe_X	2300
Pe_Y	64.5

Quantity	Value	
	Argon	CO_2
M, g/mol	33.9	44.0
D, cm^2/s	0.193	0.165
Sc	0.740	0.866
Sh	3.95	4.06
k_f, s^{-1}	4950	4350
D_K, cm^2/s	2.16×10^{-2}	2.05×10^{-2}
D_μ, cm^2/s	1.94×10^{-2}	1.82×10^{-2}
D_p, cm^2/s	0.00932	0.00874
X_{exptl}, cm	1.82	5.59
K_A	17.8	61.7

introduced continuously to a crossflow magnetically stabilized bed and can be effectively separated into individual components.

A comparison of theoretical and experimental separation parameters for argon and carbon dioxide (Table 3) has been made. The theoretical and experimental values are in very good agreement and indicate the validity of the model for calculating MSB separation parameters. These calculations demonstrate that, of the seven factors which contribute to the total peak spread, the two dispersion and the intraparticle diffusion terms predominate.

Separation of the five normal paraffins, as presented in Fig. 6,

TABLE 4
Comparison of Experimental and Theoretical Values of Standard Deviations of Elution Curves; Separation of CO_2 and Argon in Air at P = 1 atm, T = 298 K. Particles Used Were Stainless Steel/Alumina

Contribution to σ^2/L^2	Argon	CO_2
Adsorption, vertical dispersion	0.000412	0.004588
Adsorption, intraparticle diffusion	0.000276	0.003279
Adsorption, external film resistance	0.000023	0.000296
Horizontal dispersion	0.000870	0.000870
Width of feed band	0.000011	0.000011
Horizontal convection	0.000003	0.000003
Total σ^2/L^2	0.001595	0.009047
$\sigma_{theoret}$, cm	0.56	1.33
σ_{exptl}, cm	0.78	1.52

demonstrates the ability to separate a multicomponent hydrocarbon mixture in an MSB chromatographic system. The chromatogram shows incomplete resolution of the individual components and a somewhat "ragged" peak shape of the *n*-pentane and *n*-hexane peaks compared to conventional gas chromatograms. A 14-cm alumina conventional gas chromatographic column at room temperature, however, would not be expected to completely resolve these components (*9*).

The effect of an increase in bed height on resolution of a three-component mixture is shown in Fig. 10. The three components which were incompletely resolved in a 14-cm high bed were completely resolved in one 22 cm high. The baseline resolution of the three components indicates that individual pure components can be obtained from a mixture with appropriate design of the bed.

Other applications may include the recovery and separation of trace components in waste streams, and the general area of separation of organic from inorganic compounds.

Operation of the device is projected using either a liquid or gaseous carrier fluid. It may also be useful as an analytical tool for laboratory preparative chromatography or for continuous process monitoring. A broad literature base already exists on the analytical chromatographic separation of almost all known compounds. In many cases these data are directly applicable from batch analytical to continuous crossflow.

Various improvements such as temperature programming and recycle of partially separated peaks are under consideration. Development efforts on the fluid mechanics of crossflow MSBs are being reported separately (*10*).

SYMBOLS

C	external fluid-phase concentration of species i (mol/cm^3)
D	diffusion coefficient for species i in desorbent (cm^2/s)
D_K	Knudsen diffusivity (cm^2/s)
D_P	effective intraparticle diffusivity (cm^2/s)
D_X	horizontal dispersion coefficient (cm^2/s)
D_Y	vertical dispersion coefficient (cm^2/s)
K_A	equilibrium adsorption coefficient for species i
K_P	interphase mass transfer coefficient between intraparticle fluid and intraparticle surface (s^{-1})
L	depth of bed of adsorbent (cm)
M	molecular weight of species i (g/mol)
N	intraparticle adsorbed-phase concentration (mol/cm^3)
Pe_X	$V_Y L/D_X$ = horizontal Peclet number
Pe_Y	$V_Y L/D_Y$ = vertical Peclet number
Q	intraparticle fluid-phase concentration (mol/cm^3)
R	Radius of adsorbent particle (cm)
Re_P	$2V_Y R_P \rho/\mu_F$ = Reynolds number
V_S	solid velocity (cm/s)
V_X	interstitial gas-phase velocity in horizontal direction (cm/s)
V_Y	interstitial gas-phase velocity in vertical direction (cm/s)
W	feedband width (cm)
X	horizontal position variable in adsorbent bed (cm)
Y	vertical position variable in adsorbent bed (cm)
β	intraparticle porosity
σ^2	spatial variance of the product peak
μ	spatial location of the product peak
ρ	fluid density
μ_f	fluid viscosity

Acknowledgment

The authors wish to thank Mr Jerry E. Hankins for his assistance on the experimental aspects of the work, and Mr Nick Boris for his help with the computer modeling.

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Received by editor March 16, 1984
Revised April 2, 1984