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 Rutherford, W. M.(1981) 'A Generalized Computer Model of the Transient Behavior of Multicomponent Isotope Separation Cascades', Separation Science and Technology, 16: 10, 1321 — 1337
To link to this Article: DOI: 10.1080/01496398108058304
URL: http://dx.doi.org/10.1080/01496398108058304

SEPARATION SCIENCE AND TECHNOLOGY, 16(10), pp. 1321-1337, 1981

A Generalized Computer Model of the Transient Behavior of Multicomponent Isotope Separation Cascades

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ABSTRACT

The time dependent performance of large separation systems is a major consideration in the enrichment of the isotopes of elements that have a direct role in nuclear fuel cycles. The transient behavior of multicomponent separation cascades is described by a set of nonlinear partial differential equations that are similar in form for chemical exchange, distillation, gaseous diffusion, thermal diffusion, and other countercurrent processes. The Mound computer model is set up to solve the differential equations by a fast, implicit forward difference technique. Systems of up to 10 components can be handled with a wide variety of multiple input and output streams. With modifications, the program can be used to model systems of two or more cascades. It has been applied to the separation of the isotopes of uranium, the noble gases, carbon, oxygen, nitrogen, chlorine, sulfur and calcium. A neon isotope separation problem is given as an example of the precision with which performance can be predicted for multicomponent systems.

I. INTRODUCTION

The time dependent behavior of separation systems becomes a major concern when the ratio of system holdup to the design product rate is large. This is almost always the case for the separation of isotopes of the same element by conventional reversible and irreversible stage-wise countercurrent processes such as distillation, chemical exchange, gaseous diffusion, and thermal diffusion. Such separa-

tions play an important role in the various concepts for fission and fusion fuel cycles. Uranium-235 and heavy water enrichment, of course, are well known processes related to the production of nuclear energy. Other systems of importance include: lithium isotopes and deuterium-tritium for fusion reactors; noble gas isotopes for tracing fuel element leaks in fast breeder reactors, oxygen-16 separation for plutonium-238 fueled isotopic heat sources, and extraction of krypton-85 from fission product krypton. The production of elementary pure, isotopically tailored structural components for nuclear reactors is considered to be a future possibility.

II. THEORETICAL BACKGROUND

The transient behavior of close separation cascades is described by a set of nonlinear first order partial differential equations. There are n-1 independent equations in the set, where n is the number of components in the mixture.

The equation of continuity for component i is:

$$\frac{\partial w_i}{\partial t} = -\frac{1}{\mu}\frac{\partial \tau_i}{\partial z} \tag{1}$$

where w_i = the mass fraction of component i

t = time

μ = the mass holdup per unit of length

z = the length coordinate

τ_i = the net transport of component i along the z-direction

The transport, τ_i, is given by a phenomenological equation for the particular process in question. Thus, for thermal diffusion we have [1]

$$\tau_i = H_o w_i \sum_{j=1}^{n} m_{ij} w_{ij} - K \frac{dw_i}{dz} + \sigma w_i \tag{2}$$

where n is the number of compoents, H_o is the reduced initial transport coefficient, K is the remixing coefficient, and σ is the local net mass flow through the separation column. The quantity m_{ij} is defined by:

$$m_{ij} = \frac{M_i - M_j}{M_i + M_j} \simeq \frac{M_i - M_j}{2\bar{M}} \tag{3}$$

where M_i and M_j are the atomic or molecular weights of the two species and $\bar{M}$ is the average atomic or molecular weight.

For chemical exchange, distillation and barrier diffusion problems it is more appropriate to write equations (1) and (2) in terms of molar quantities and discrete stages; thus, if we consider the system to be a continuum in the number of stages, s, we have:

$$\frac{\partial x_i}{\partial t} = -\frac{1}{H_s}\frac{\partial J_i}{\partial s} \tag{4}$$

where x_i is the mole fraction of component i, and where the transport J_i is now in units of moles per unit time, and the specific holdup H_s is in units of moles per equilibrium stage. The transport J_i is given by

$$J_i = x_i L_s \sum_{j=1}^{n} (\psi_{ik} - \psi_{jk}) x_j - L_s \frac{dx_i}{ds} + P_s x_i \tag{5}$$

where $\psi_{ik} = \alpha_{ik} - 1$ and where α_{ik} is the elementary separation factor for component i relative to an arbitrarily selected key component. P_s is defined as the local net molar flow rate through the system, and L_s is the local upflow (or downflow). It should be noted that we are implicitly assuming high reflux ratios, so that $L_s >> P_s$. This condition is fulfilled for most isotope separation problems.

Although equations (1) and (2) differ in detail from (4) and (5), the two sets are mathematically equivalent, and they can be solved by the same procedures.

Exact solutions of the transient problem can be obtained for some relatively trivial cases involving binary mixtures [2]; however, modeling of complex systems for separating multicomponent mixtures requires the use of numerical techniques and high speed digital computers. The remainder of this report will be devoted to a description of a general purpose computer program for modeling such systems, and examples will be given of its application.

III. NUMERICAL SOLUTION OF THE TRANSIENT PROBLEM

A simple explicit approach to the numerical solution of Equation (1) involves estimation of new concentrations, w_i, at time step k + 1 based on values of the transport, τ_i, calculated at time step k. Thus, the local compositions in the separation system are advanced in time according to

$$w_{i,m,k+1} = w_{i,m,k} - \frac{(\tau_{i,m,k} - \tau_{i,m-1,k})(t_{k+1} - t_k)}{\mu_m (z_m - z_{m-1})} \qquad (6)$$

where the index k refers to the time step, and the index m refers to the distance step along the cascade. This system of equations, however, tends to be unstable except at very small values of the time increment.

According to Burris and Tunstall [3] the stability criterion for the barrier diffusion process requires that

$$t_{k+1} - t_k < \frac{\Delta s^2 H_s}{2L_s} \qquad (7)$$

and for the thermal diffusion problem,

$$t_{k+1} - t_k < \frac{\mu \Delta z^2}{2K} \qquad (8)$$

The stable time increment can be unrealistically small for some problems, rendering the simple explicit method relatively unsatisfactory for modeling on small computers.

An implicit forward difference approximation was developed in order to circumvent the stability problem of the explicit method[4]. In simple terms, the transport of component i during the k^{th} time interval is taken to be the average of the transport at the beginning of the interval, $\tau_{i,m,k}$ and the transport at the end of the interval, $\tau_{i,m,k+1}$. Thus,

$$w_{i,m,k+1} = w_{i,m,k} - \frac{\Delta t}{\mu_m \Delta z}\left[\frac{(\tau_{i,m,k} + \tau_{i,m,k+1}) - (\tau_{i,m-1,k} + \tau_{i,m-1,k+1})}{2}\right] \qquad (9)$$

where, for the thermal diffusion problem,

$$\tau_{i,m,k} = H_o \bar{w}_{i,m,k} \sum_{j=1}^{n} m_{ij} \bar{w}_{j,m,k} - K \frac{(w_{i,m,k} - w_{i,m-1,k})}{(z_m - z_{m-1})} + \sigma \bar{w}_{i,m,k} \quad (10)$$

with

$$\bar{w}_{i,m,k} = (w_{i,m,k} + w_{i,m-1,k})/2 \quad (11)$$

As indicated in Figure 1, the subscript m refers to the distance step along the separation device. At points where feed streams are added or product streams removed an additional term δ must be added to the right-hand side of (10) where

$$\delta = \frac{\Delta t}{\mu_m \Delta z} \left[F_m w_{i,m,F} - P_m (w_{i,m,k} + w_{i,m,k+1})/2 \right] \quad (12)$$

The quantities F_m and P_m are feed and product flow rates, respectively, and $w_{i,m,F}$ is the corresponding feed composition.

The system of equations given by (9) cannot be solved explicitly for the $w_{i,m,k+1}$, although the equations can be reduced to a set of tridiagonal equations for each of the components. Thus,

$$A_m w_{i,m-1,k+1} + B_m w_{i,m,k+1} + C_m w_{i,m+1,k+1} = D_{i,m} \quad (13)$$

The $D_{i,m}$ contain the new concentrations in the form of the nonlinear part of Equation (9); hence, the solution of (13) cannot be obtained directly. A first approximation to the $D_{i,m}$ can be calculated from the old set of concentrations. It can be used to calculate approximate values of the new concentrations, and new values of the $D_{i,m}$. This iterative procedure, if convergent, can be repeated until the desired accuracy is obtained.

The implicit method is inherently stable and relatively large time steps can be used; however, there is more computation required per step than for the explicit method. The net result is an approximate tenfold gain in speed over the explicit method.

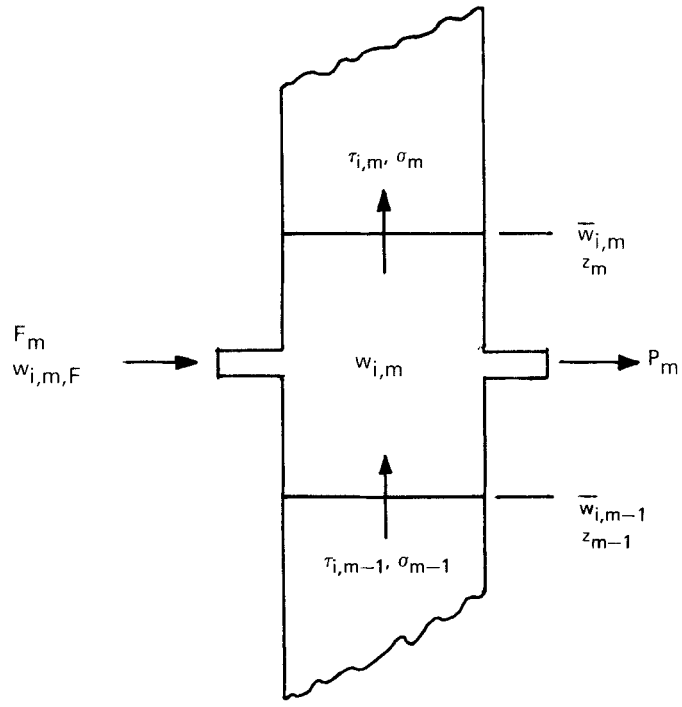

FIGURE 1. Finite difference scheme for the transient problem. The figure depicts one finite difference step, $z_m - z_{m-1}$, along a thermal diffusion column. $\tau_{i,m}$ and σ_m are the isotopic transport and the bulk flow, respectively, at the location z_m. $w_{i,m}$ is the composition within boundaries defined by z_m and z_{m-1}. $\bar{w}_{i,m}$ is the composition at the location z_m. F_m, $w_{i,m,F}$ and P_m define a feed stream and a product stream.

IV. A COMPUTER MODEL FOR MULTICOMPONENT SEPARATION CASCADES

A computer model based on the implicit finite difference scheme was developed for solving the transient problem for systems of up to 10 components. The associated computer program is designed to offer the user the greatest possible flexibility in choice of initial and boundary conditions for series combinations of up to 19 square cascade sections [5]. A simplified schematic of a typical separation system is shown in Figure 2. Feed streams and product streams can be specified at each interstage point and at the ends of the system. System parameters, mixture characteristics, initial conditions and boundary conditions are specified, as required, in the following categories:

System Parameters

The user specifies, for each of the cascade sections, total flow, total distributed holdup, and the number of equilibrium stages in the section. The details of these specifications depend upon the process being used. Holdup at the ends of the cascade and at the interstage points is specified separately.

Mixture Parameters

The user specifies the elementary single stage separation between each component and the n^{th} component, where the n^{th} component can be either the heaviest or lightest of the mixture. Again, the details of these specifications depend upon the process being used.

Initial Composition Profile

The user may choose a fill of uniform composition, or he may specify an arbitrary composition at each of the interstage points.

Feed Streams

Feed streams can be specified at as many as five points in the cascade, including the ends of the system. In the present version

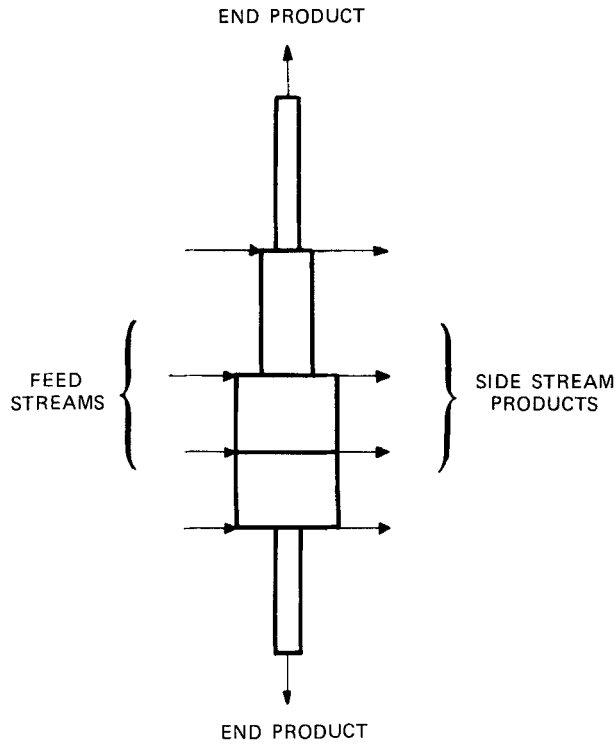

FIGURE 2. Simplified schematic of a separation cascade.

of the program the material balance is closed on the first feed stream specified. For all other feed streams the user specifies the flow rate, composition and the time at which to start. The user may specify a schedule for each feed stream wherein the feed location, flow rate and composition are varied in steps as functions of time. The quantity of feed available can also be given so that flow will stop after that amount has been fed.

Product Streams

Fixed rate product streams can be defined at as many as five points in the cascade, including the ends. A schedule can be specified for each stream so that withdrawal location and flow rate

change in steps at predetermined times. Another option permits the rate of the product stream to vary so as to maintain the mass fraction of one of the components at a specified level. A simple algorithm equivalent to single mode proportional control is used to calculate the required rate.

Parasitic Streams

A feature is provided to allow the user to model the effect of parasitic streams. A parasitic stream is a steady external flow of material from one point in a separation cascade to another point at a different composition. Such flows degrade cascade performance. They may take place as the result of incomplete reflux reactions in closed cycle chemical exchange processes wherein products of a reflux reaction at one end of the cascade are used as reactants at the other end.

Timing

The user specifies the time interval at which he desires to have results printed and the time at which the calculation is to be stopped. The program handles all other timing considerations. Each problem is started on the basis of a time step estimated as a multiple of that predicted from Equation 7 or Equation 8. The time step is adjusted upward or downward as the calculation proceeds in order to optimize accuracy and computational speed.

Problem Storage and Retrieval

All pertinent problem data can be stored on a tape or disk file at the specified end of a calculation. The data can be retrieved and the problem can be restarted at the point where it last stopped. New operating conditions can be specified for the new time segment.

V. APPLICATION OF THE MODEL

The transient model has been invaluable in solving experimental problems connected with the separation of noble gas isotopes by gas

phase thermal diffusion. It has been used to predict the performance of complex systems for such difficult isotopic separations as neon-21, krypton-82, argon-38 and xenon-124. It has been used for the quantitative prediction of the concentrations of the radioisotopes argon-37[6], krypton-81, argon-39 and krypton-85 in mixtures subjected to various enrichment or depletion processes.

The model has been useful for problems involving the separation of uranium isotopes by chemical exchange, including uranium-235 enrichment and the depletion of uranium-232 from thorium fuel cycle materials. It has been used to predict the behavior of liquid phase thermal diffusion systems for sulfur[7] and chlorine isotope separation, to calculate transient response of chemical exchange systems for calcium, carbon, and sulfur isotope separation, and to solve problems related to a single stage carbon monoxide distillation process.

The separation of the three-component neon isotopic system is a particularly good illustration of the use of the transient model[8]. A four-stage gas phase thermal diffusion cascade (Figure 3) comprises the first cascade of a two-cascade system for separating the rare intermediate isotope neon-21 at high enrichment. The side stream from the first cascade, which is the partially enriched feed to the second, must meet stringent requirements with respect to the ratio of neon-21 to neon-20 in order to assure that the desired product assay can be reached in the second cascade. Top and bottom assays in the first cascade must be carefully maintained to get the prescribed recovery of neon-21 from the feed and to prevent loss of accumulated neon-21 inventory out the ends of the system.

The four-column primary cascade was initially filled with neon of natural isotopic abundance (90.4% neon-20, 0.27% neon-21, 9.3% neon-22). Separation was allowed to proceed for a short time until first the top, and then the bottom, concentration reached the design value of 0.1% neon-21. Top and bottom withdrawal rates were adjusted to maintain the neon-21 at that level, which was equivalent to recovery and retention in the cascade of approximately 2/3 of the neon-21 fed to the system. The middle isotope was allowed

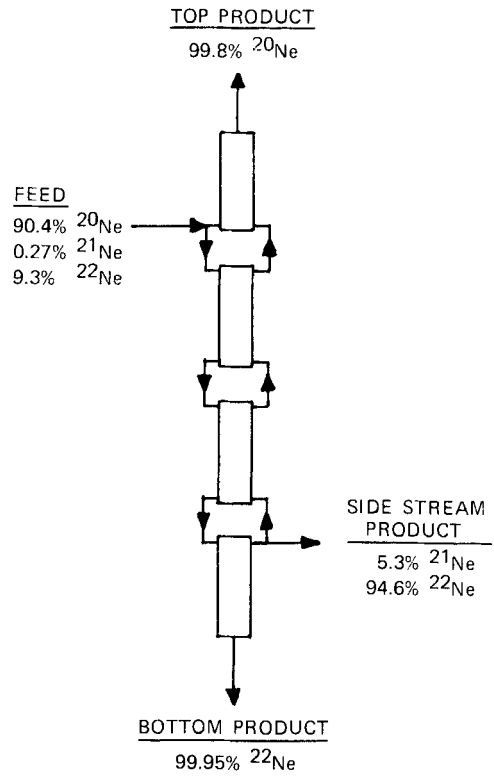

FIGURE 3. Neon isotope separation system.

to accumulate in the cascade for 90 days. At the end of that period a slight adjustment in the operation of the cascade dropped the bottom assay to 0.05% and shifted the composition profile of the system to a more favorable location for the onset of production of the sidestream.

Model calculations, which are plotted along with the experimental results in Figure 4, predicted the behavior of the system almost perfectly, including the sharp peak in neon-21 concentration at the bottom of the cascade just prior to the start of bottom product flow at day 7. The calculations were performed in segments with the aid of the storage and retrieval features of the computer program. Thus, it was possible to retrieve problem conditions in

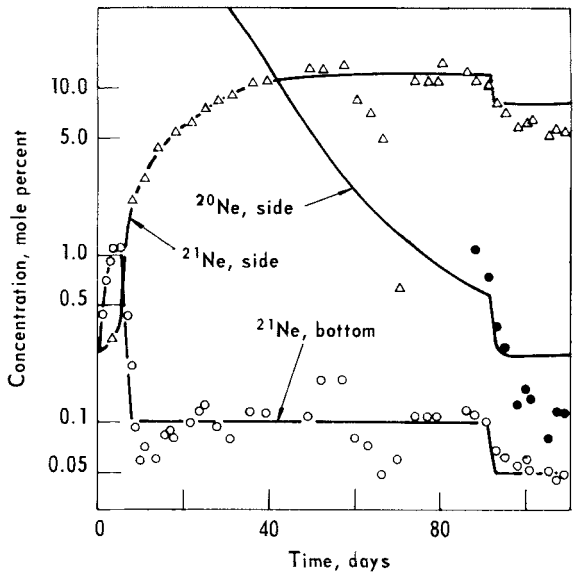

FIGURE 4. Transient behavior of the neon isotope separation system. The solid lines are calculated.

order to work out the adjustment to the bottom assay which was required at 90 days in order to position the composition profile to yield the optimum set of concentrations in the side stream.

Table 1 contains a comparison of predicted and observed flow rates and compositions of the several product streams after nearly steady state conditions had been reached. The side stream composition is especially sensitive to positioning of the system composition profile in relation to the point at which the side stream is removed; therefore, some variation between theory and experiment is to be expected.

VI. INTERCONNECTED CASCADES

The basic computer model has been adapted to handle cases involving two interconnected separation cascades, as illustrated in Figure 5. Problems of this nature have been solved for the separation of carbon-13 by low temperature distillation of carbon mon-

TABLE 1
Compositions and Flow Rates for a Neon Isotope Separation Cascade During Nearly Steady State Conditions

		Flow Rate, STD ml/hr	Composition, mole % Neon-21	Neon-22
Top stream	experimental	300	0.11	0.12
	theory	299	0.10	0.077
Side stream	experimental	8.3	5.3	94.6
	theory	9.0	7.9	91.9
Bottom stream	experimental	23.7	0.048	99.95
	theory	22.3	0.052	99.95

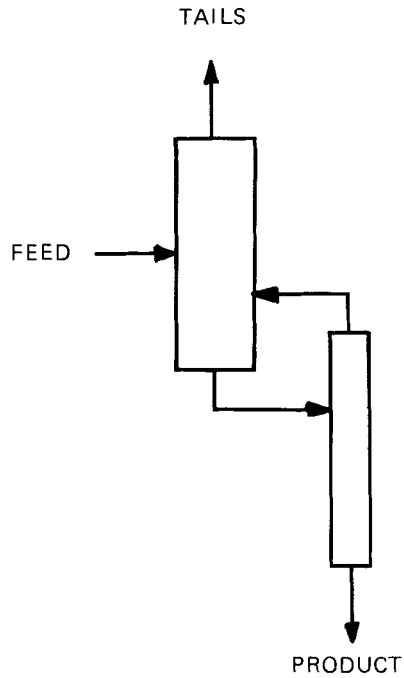

FIGURE 5. Interconnected separation systems.

oxide[9] and the separation of sulfur-34 by liquid phase thermal diffusion of carbon disulfide[6]. These particular processes are molecular separations rather than atomic; thus, in order to reach high enrichments it is necessary to pass the feed stream from cascade 1 to cascade 2 through a reactor to induce scrambling of the several species of isotopically substituted molecules in the mixture.

In the carbon-13 separation process the undesired molecule $^{12}C^{18}O$ is concentrated at the bottom of the distillation system along with the more abundant $^{13}C^{16}O$, thus restricting the attainable carbon-13 enrichment to slightly more than 90%. Higher enrichments of carbon-13 can be reached by passing the product through a catalytic reactor to re-establish an equilibrium mixture of carbon monoxide molecules:

$$^{12}C^{18}O + {}^{13}C^{16}O \rightleftarrows {}^{13}C^{18}O + {}^{12}C^{16}O \qquad (14)$$

The equilibrated mixture passes to a second cascade in which the products of the isotopic equilibration are processed to yield as product a mixture of $^{13}C^{16}O$ plus a small amount of $^{13}C^{18}O$.

In the case of the sulfur-34 separation, cascade 1 produced a high enrichment of the mixed molecule $C^{32}S^{34}S$. The mixed molecule was partially converted to the doubly substituted species $C^{34}S_2$ according to the following reversible reaction:

$$2C^{32}S^{34}S \rightleftarrows C^{32}S_2 + C^{34}S_2 \qquad (15)$$

The doubly substituted molecule was then separated as product from the bottom of the second cascade. Figure 6 is a simplified schematic diagram of the system used for sulfur isotope separation and Figure 7 is a comparison of the observed transient behavior with that calculated from the model.

Figure 7 depicts the late stages of the startup of the ^{34}S enrichment system during which time the second cascade was increased in length from four to five columns. Two separate calculations were thus required to model the process. A very similar sort of problem arises in fuel recycling schemes for fusion reactors. Recycled mixtures of protium, deuterium and tritium are to be separated by low temperature fractional distillation. The mixed hydrogen mole-

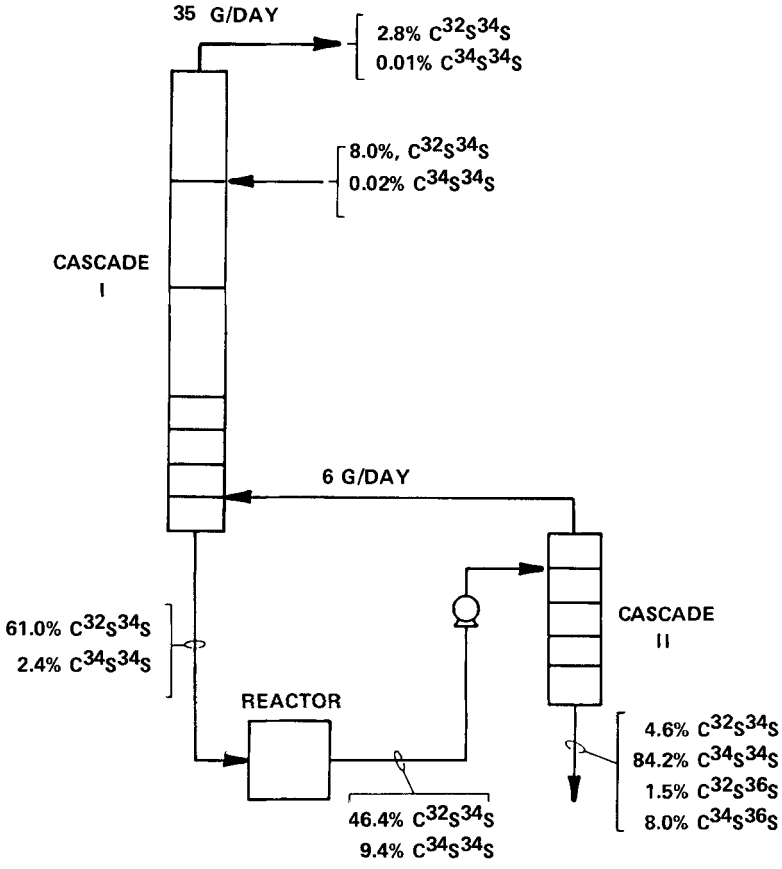

FIGURE 6. Sulfur isotope separation system.

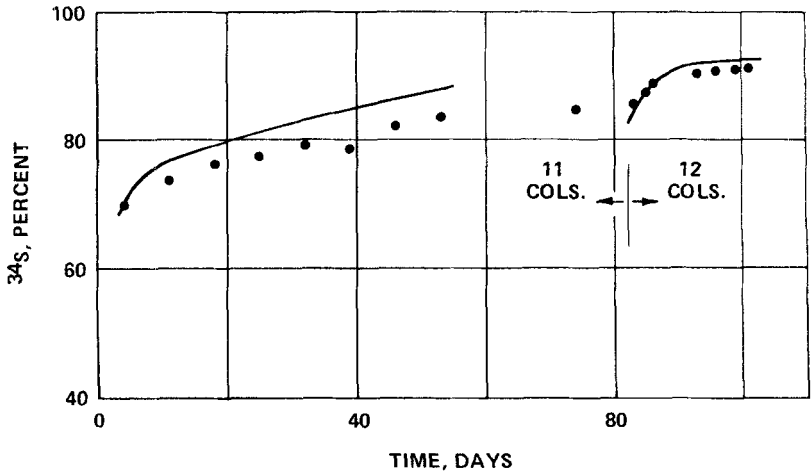

FIGURE 7. Transient behavior of the sulfur isotope separation system. The solid lines are calculated.

cules do not undergo isotopic exchange at cryogenic temperatures; hence, multiple stages of separation are required with intermediate high temperature isotopic equilibration of the interconnecting streams.

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