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A Differential Homotopy Continuation Method for Interlinked Solvent Extraction Cascades

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ABSTRACT.

A robust differential homotopy procedure is developed that is suitable for solving the bordered block tridiagonal systems of non-linear equations that result from liquid-liquid extraction models. The procedure is capable of readily utilizing newton, fixed-point, and custom homotopy mapping. It is shown to have an efficiency far superior to Kubicek's method and comparable to that of Rheinboldt. Application of the method to liquid-liquid extraction cascade models revealed that the newton homotopy would converge to a solution as rapidly as a simultaneous correction procedure and that use of a custom homotopy resulted in faster convergence.

INTRODUCTION

Modeling procedures for hydrometallurgical solvent extraction systems have received comparatively little

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attention in comparison to dual solvent systems eg. [1,2] and systems employing quasichemical equilibrium expressions [3,4]. The traditional approach has been to capitalize on the linear form of the material balances, and to include the equilibrium relations in them, thereby reducing the system of equations by a factor of two. The resulting set of equations (known as the sum-of-the-rates or SR form) is then solved. Usually the substitution has been for the organic phase species. Thus only the aqueous phase species are found by iteration. The techniques utilized to iterate the resulting equation set to a solution include relaxation followed by the newton method [5], the newton method with damped iterates [6], and quasi-newton procedures. This paper focuses on use of the full equation set (known as simultaneous convergence or the SC method) combined with an alternate method of iteration.

Any multispecies multicascade model results in a series of nonlinear equations that represent the component material balances, equilibrium relationships, and the energy balance. Grouping these balances by stage results in the well known block tridiagonal structure. If a global specification is included, the additional equation and single variable are appended to provide a bordered block tridiagonal structure. If the cascades of stages are interlinked, additional off diagonal matrices are included.

The method suggested by Stadtherr [7,8] is often used to create a bordered block structure that is simultaneously converged. A sequence of two interlinked solvent extraction cycles results in such a system. Without extensively elaborating, the results of others [9] have shown that it is distinctly advantageous to simultaneously converge cascade structures rather than sequentially converge them. This is particularly necessary for highly nonlinear systems. Ketchum [5] found that it was necessary to combine damped Newton or relaxation methods for the initial iterates with the newton method to obtain convergence. The extraction code, MATEX [10], is structured to allow the user to specify a fixed number of relaxation iterates followed by a quasi-newton hybrid method that combines the powell and newton methods. The use of these combined methods is to aid in solution of highly nonlinear problems. Specifically, they condition the initial estimate so that it lies within the region of convergence (domain of attraction) of the solution.

Table 1 includes representative simultaneous convergence procedures for solving solvent extraction cascade separation problems. The procedure discussed by Ricker et al.[12] is the most detailed model. In his

Table 1.
CHARACTERISTICS OF SIMULTANEOUS CONVERGENCE MODELS FOR EXTRACTION

o Single cascade models	
o McSwain & Durbin (1966) [4]	1 solute transfer, no solute interactions, 2 concentrations per stage.
o Chapman (1978) [11]	Multiple solute transport for a hypothetical hydrometallurical system with two competing reactions, 2 concentrations per stage.
o Ricker, Nakashio & King (1981) [12]	Multiple solute transfer with solute interactions, 4 concentrations per stage.

example 3, utilizing oxalic, succinic and malonic acids, multiple solutes that compete for the same extractant are included. However, the system has relatively minor nonlinearities in comparison with those in hydrometallurigical systems employing mass action equilibrium expressions. Imaginary concentrations are used to represent the base concentrations in the aqueous phase.

An alternative approach to converge these problems is to use a continuation method. Variously known as differential homotopy, continuation, or parameter imbedding, these procedures map from an initial solution to a final nonlinear solution. They utilize a prediction or prediction-correction method. They have been previously applied to diffusion and reaction problems and distillation. It is believed that this research represents the first application of these methods to a hydrometallurgical solvent extraction system.

HOMOTOPY CONTINUATION PROCEDURES

Mathematically steady, state hydrometallurgical solvent extraction systems are represented as a set of simultaneous nonlinear algebraic equations.

$$\begin{aligned} f_1(x_1,x_2,x_3, \ldots x_n) &= r_1 \\ f_2(x_1,x_2,x_3, \ldots x_n) &= r_2 \\ f_3(x_1,x_2,x_4, \ldots x_n) &= r_3 \\ &\vdots \\ f_n(x_1,x_2,x_3, \ldots x_n) &= r_n \end{aligned} \qquad (1)$$

These equations may be written in simplified form as $F(X) = R$. Solution of these models requires determination of the fixed points, or roots, of this system of equations. (i. e. the values of X for which $F(X) = 0$).

The classical and most widely used method for solving these types of problems is Newtons method. This procedure operates by repeated solution of a linear approximation to the problem. The basic formula for Newtons method can be found in any text on numerical analysis and is given by equation 2.

$$X^{k+1} = X^k - \left(\frac{\partial F}{\partial X}\right)^{-1} R \qquad k = 1,2,\ldots \qquad (2)$$

Where $\left(\frac{\partial F}{\partial X}\right)$ represents the jacobian.

$$\left(\frac{\partial F}{\partial X}\right) = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\ \vdots & \vdots & & \vdots \\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{bmatrix} \qquad (3)$$

An initial estimate of the solution, X^0, is made and equation 2 is repeated until the difference between X^{k+1} and X^k is less than a desired tolerance. Newtons method is intimately related to the topology of the

system of equations being solved. As such, local minima, saddle points, cusps and other topological phenomena will interfere with, and possibly prevent, convergence of the technique. Methods which are not as intimately related to the topology of the problem are necessary to solve patheological problems or problems which do not have good initial estimates of the solution. One such method is called homotopy continuation.

Homotopy continuation procedures employ a series of mapping functions labeled here as H_i. The mapping function H_i, maps from the function $F \in R^n$ to the function $G_i \in R^m$.

$$H_i : F \in R^n \longrightarrow G_i \in R^m \quad \text{where } m > n \qquad (4)$$

Examples of problems where m=3 and n=1 can be found in Seydell(1979) [13]. For the separation problems considered here, however, the homotopy path is considered to be a one dimensional connected component of $H^{-1}(0)$ from X^0 to X^* (the solution of F(X) = 0).

$$H_i : F \in R^n \longrightarrow G_i \in R^{n+1} \qquad (5)$$

The first mapping function of the sequence, H_0, is structured such that the solution to G_0 , $G_0^{-1}(0)$, is readily apparent or easily obtainable. The next map in the sequence, H_1, is then used to map F onto G_1. This map is structured such that $G_1^{-1}(0)$ is "close" to $G_0^{-1}(0)$. The proximity of $G_1^{-1}(0)$ to $G_0^{-1}(0)$ can be exploited in obtaining $G_1^{-1}(0)$. If $G_0^{-1}(0)$ is sufficiently close to $G_1^{-1}(0)$, $G_1^{-1}(0)$ can be expected ,with a high degree of certainty, to be within the domain of attraction of an iterative procedure such as Newtons method with $G_0^{-1}(0)$ as the initial estimate of the solution, X^0. Wyburn(1958) has proven that there exists a finite region about $G_0^{-1}(0)$ in which $G_1^{-1}(0)$ is within the domain of attraction of the Newton-Raphson iterative solution method. This procedure is repeated using a sequence of mapping functions, H_i. Solutions to $G_i^{-1}(0)$ are obtained using $G_{i-1}^{-1}(0)$ to initiate the solution procedure. The sequence, or homotopy, of mapping functions progress successively toward the mapping function H_n which maps the function F onto itself. The solution to the original problem X^* can be obtained using $G_{n-1}^{-1}(0)$ as the initial estimate of the solution. The path by which the deformation progresses from $G_0(X)$ to $G_n(X)$ is called the homotopy path. Homotopy continuation is the numerical procedure by which one traces the one dimensional homotopy from X^0 to X^*. Historical use of continuation methods for solution of distillation, absorption, and stripping problems is summarized in table 2.

Table 2.
USE OF CONTINUATION PROCEDURES FOR SOLUTION OF SEPARATION PROBLEMS

Reference	Problem Characteristics	Algorithm
Salgovic et al. (1981) [26]	Absorption & Distillation algorithm	Fixed stepsize, Euler predictor, Kubicek
Byrne and Baird (1983) [27]	Stripping & Distillation	Rheinboldt algorithm (1981)
Wayburn & Seader (1983, 1984) [9, 28]	Distillation	Euler predictor, Newton corrector (arclength)
Bhargava & Hlavacek (1984) [29,30]	Distillation	Fixed step algorithm (refined Kubicek algorithm)
Vickery & Taylor (1985) [24]	Distillation	Custom Imbedding
Holland & coworkers (1985)[31]	Distillation	Comparison of Euler predictor Newton corrector with Gears method, Michaelson method.

MAPPING FUNCTIONS

The degree or extent of deformation of the map, H, from the original function F(X) to G(X) is controlled by the value of a parameter called the continuation variable, t. The map is formed by incorporating the continuation variable into the original set of equations. It is incorporated in any convenient fashion such that at one value, t^0, the system of equations ($G_0(X)$) collapse to a set whose solution can be easily obtained and at another value, t^1, the system solved ($G_n(X)$) is identical to the original system of equations. Alternately the mapping function can be formed by using a generalized formula such as the one given by equation 6.

$$H(X,t) = a(t)*F(X) + b(t)*G(X) = 0 \qquad (6)$$

This generalized formula can represent most of the common homotopy forms used in separations (see table 2).

It should be noted that Eq. 6 is strictly a mathematical contrivance and is not related to any particular set of equations and hence cannot specifically address the nonlinear features of the problem under investigation.

There are three major types of homotopy equations currently used. These are the Newton homotopy, the fixed point homotopy and the affine homotopy. The homotopy formula of Boggs[17] has also been widely studied. The formula parameters for these equations are given as follows:

Newton homotopy

$$H(X,t) = 0 = F(X) - F(X^0)*t \qquad (7)$$

Fixed point homotopy

$$H(X,t) = 0 = (1-t)*F(X) + t*(X-X^0) \qquad (8)$$

Affine homotopy

$$H(X,t) = 0 = (1-t)*F(X) + t*\left(\frac{\partial F}{\partial X}\right)*(X-X^0) \qquad (9)$$

Boggs homotopy

$$H(X,t) = 0 = F(X) - e^{-\alpha}F(X^0) \qquad (10)$$

$$\alpha \in [0,\infty)$$

Kubicek, Holoniok, and Marek[14] have studied the use of other homotopy equations. At this time, however, no specific class of homotopy equation has been shown conclusively to be the most efficient.

All of the above homotopy equations begin the mapping sequence with the continuation variable, t, equal to one. At this point the equations collapse in such a fashion that the solution at t = 1 is simply the initial estimate of the solution. At a value of t = 0 the equations reduce to the original set of equations. Each of the homotopy equations has different characteristics and advantages. Because of its structure the fixed point homotopy is guaranteed a unique solution at t = 1. This feature is valuable in that it satisfies one of the conditions required to guarantee that a connected solution set from the initial estimate to the final solution exists [Rheinboldt(1983)15]. Unfortunately this form of the homotopy equation is very poorly scaled and may give calculational difficulties during the course of the mappings. The Newton homotopy, on the other hand, is very well scaled. It does not, however, guarantee the

existence of a unique solution at t = 1. The affine homotopy equation represents an attempt to combines the best aspects of both the Newton homotopy and the fixed point homotopy. Like the fixed point homotopy, it is structured such that a unique solution is guaranteed to exist at t = 1. The poor scaling characteristics of the fixed point homotopy are corrected by the inclusion of a scaling factor, here represented by the jacobian matrix. The choice of homotopy formula has a strong effect on the convergence characteristics of the problem.

THE ALGORITHM

The algorithm has two major sections these are the integration procedure and the correction procedure. To facilitate integration through bifurcation points, (degenerate points) the integration procedure is carried out with respect to the arc length of the solution set. To prevent the jacobian matrix from becoming ill-conditioned as bifurcations are encountered the variable chosen as the continuation variable changes continuously throughout the course of the integration. Approximations to the homotopy path are obtained using Eulers method. The stepsize was calculated using a modification of the method of Georg [16]. Improved control of the stepsize is obtained by linking it to the number of corrections required to converge on the path.

The correction procedure utilizes the standard Newton-Raphson procedure to close on the homotopy curve. If necessary the algorithm will converge the initial estimates to the homotopy path before starting the integration procedure. The corrections are made in the hyperplane orthogonal to the tangent vector of the homotopy path. Corrections for the first point (if necessary) and for the solution are made in the hyperplane of t = constant. In the event of failure of the correction procedure the step size of the predicted step is damped and another correction procedure attempted. Repeated failure of the correction procedure causes the integration to be reattempted from the original starting point with more stringent controls on the step length control parameters.

Numerous algorithms of this general type are available in the literature. The algorithm developed here has three distinguishing features. These are:

1. The ability to easily specify the type of homotopy equation used. Options include the Newton homotopy, the fixed point homotopy, Boggs homotopy [17], or a user designed custom homotopy. The custom homotopy is completely general and can be any homotopy formula or arbitrary imbedding of the continuation variable into all or some of the equations.

2. The ability to custom tune the correction procedure to the type of problem being solved. The control parameters of the correction procedure employed in the algorithm are user specified. As such the curve following procedure can be modified through experimentation to efficiently handle problems ranging from the most severe which require stringent control over the correction procedure to well behaved function where execution time can be greatly reduced by relaxing some or all of the correction parameters.
3. The ability to determine multiple solutions to systems of equations. A user specified option is available which upon successfully completing the integration of the homotopy path will search for other solutions to the problem by continuing the integration past the boundary of the continuation variable. While there is no guarantee that other solutions, if they exist, will be found with this procedure, it has been successfully demonstrated on a wide range of problems.

AN EXAMPLE

The problem of Kubicek [18] represents the dynamic behavior of a cascade of two continuous stirred tank reactors with recycle. First order reactions occur in both reactors (See figure 1). A set of four simultaneous ordinary differential equations is used to describe this system.

$$\frac{dy}{dt} = (1-\Lambda)y_2 - y_1 + Da_1(1-y_1)\exp\frac{\Phi_1}{(1+\Phi_1/\gamma)}$$

$$\frac{d\Phi_1}{dt} = (1-\Lambda)\Phi_2 - \Phi_1 + Da_1 B(1-y_1)\exp\frac{\Phi_1}{(1+\Phi_1/\gamma)} - \beta_1(\Phi_1 - \Phi_{c1})$$

$$\frac{Da_2}{Da_1}\frac{dy_2}{dt} = y_1 - y_2 + Da_2(1-y_2)\exp\frac{\Phi_1}{(1+\Phi_2/\gamma)} \qquad (11)$$

$$\frac{Da_2}{Da_1}\frac{d\Phi_2}{dt} = \Phi_1 - \Phi_2 + Da_2 B(1-y_2)\exp\frac{\Phi_2}{(1+\Phi_2/\gamma)} - \beta_2(\Phi_2 - \Phi_{c2})$$

Here y is the reactant conversion, Φ is the dimensionless temperature, and $\Lambda \in (0,1]$, $\gamma \in [10,\infty)$,

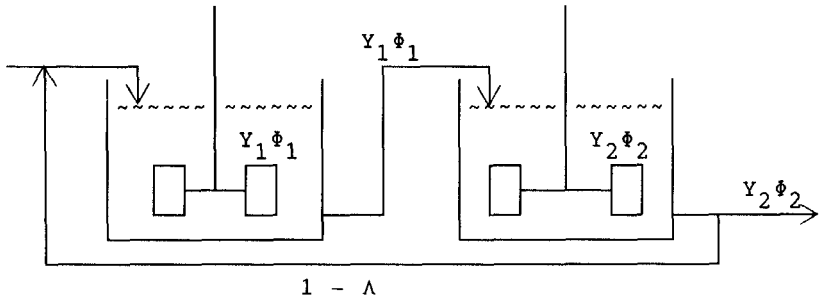

Figure 1. Linked CSTR's with recycle

$B\in[0,60]$, $Da\in[0,60]$, $\Phi_c\in[-5,2]$, and $\beta\in[0,3]$ are physical parameters. Indices 1 and 2 correspond to reactors 1 and 2 respectively. In this example $Da=Da_1=Da_2$, $\gamma=1000$, $B=22$, $\Phi_{c1}=\Phi_{c2}=0$, $\beta_1=\beta_2=2$, $\Lambda=1.0$. To determine the dependance of the steady state solution on a parameter, the equations are written as a set of simultaneous algebraic equations and are integrated using homotopy continuation. The continuation variable is assigned to the physical parameter that the solution set dependency is to be examined. For steady state dependency,

$$\frac{dy_1}{dt} = \frac{dy_2}{dt} = \frac{d\Phi_1}{dt} = \frac{d\Phi_2}{dt} = 0 \qquad (12)$$

and equations (11) reduce to the following set of algebraic equations ,

$$\begin{aligned}
0 &= (1-\Lambda)y_2 - y_1 + Da_1(1-y_1)\exp\frac{\Phi_1}{(1+\Phi_1/\gamma)} \\
0 &= (1-\Lambda)\Phi_2 - \Phi_1 + Da_1 B(1-y_1)\exp\frac{\Phi_1}{(1+\Phi_1/\gamma)} - \beta_1(\Phi_1-\Phi_{c1}) \\
0 &= y_1 - y_2 + Da_2(1-y_2)\exp\frac{\Phi_1}{(1+\Phi_2/\gamma)} \\
0 &= \Phi_1 - \Phi_2 + Da_2 B(1-y_2)\exp\frac{\Phi_2}{(1+\Phi_2/\gamma)} - \beta_2(\Phi_2-\Phi_{c2})
\end{aligned} \qquad (13)$$

The solution curve for the dependency of this set of equations on the recycle rate is given in figures 2,

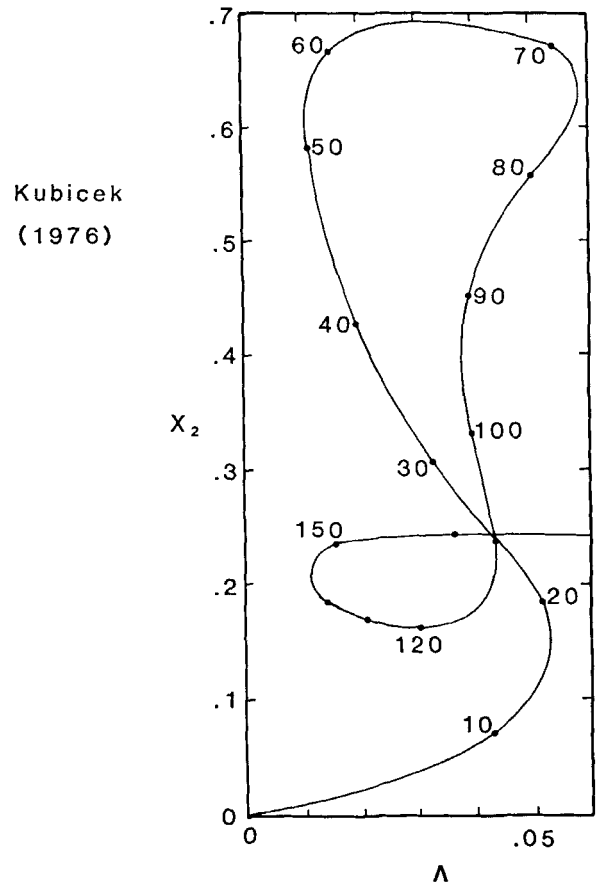

Figure 2. Homotopy Path Integration - Kubicek.

3, and 4. A comparison of the algorithm with two others is shown in table 3. The results include a measure of the CPU time for execution on a VAX 11/780 system.

APPLICATION TO CASCADED SYSTEMS

The algorithm and formulas developed so far have been applicable to general systems of equations. Engineering and scientific applications however, frequently deal with specialized systems of equations.

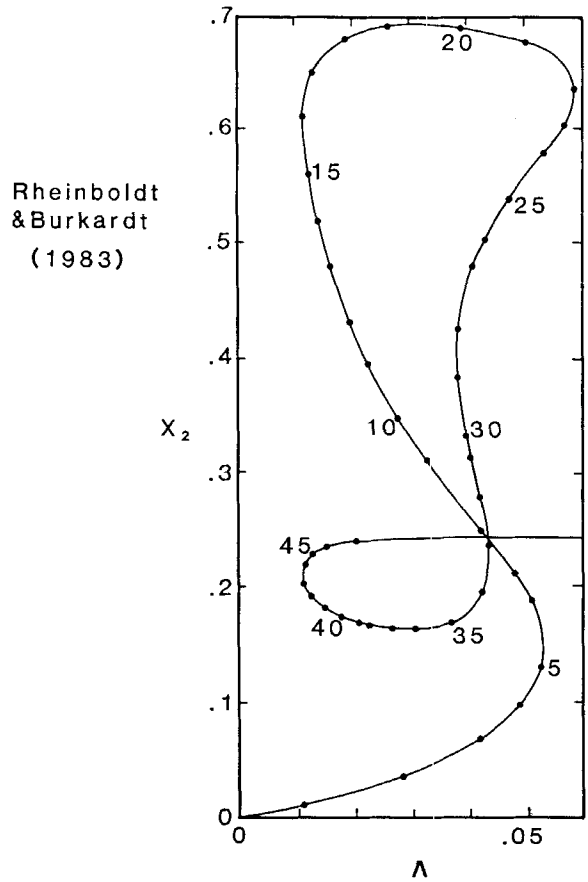

Figure 3. Homotopy Path Integration - Rheinboldt.

One such system commonly encountered is structured from models involving cascaded operations. Typical cascaded operations are distillation and liquid-liquid extraction. These operations form sets of equations which have tridiagonal or block-tridiagonal jacobians such as the one illustrated in figure 5. In an effort to efficiently accommodate these systems the matrix operations of the homotopy continuation method have been optimized to take advantage of the special properties of the system. Customization of the homotopy continuation method involves two modifications of the general homotopy procedure. These are,

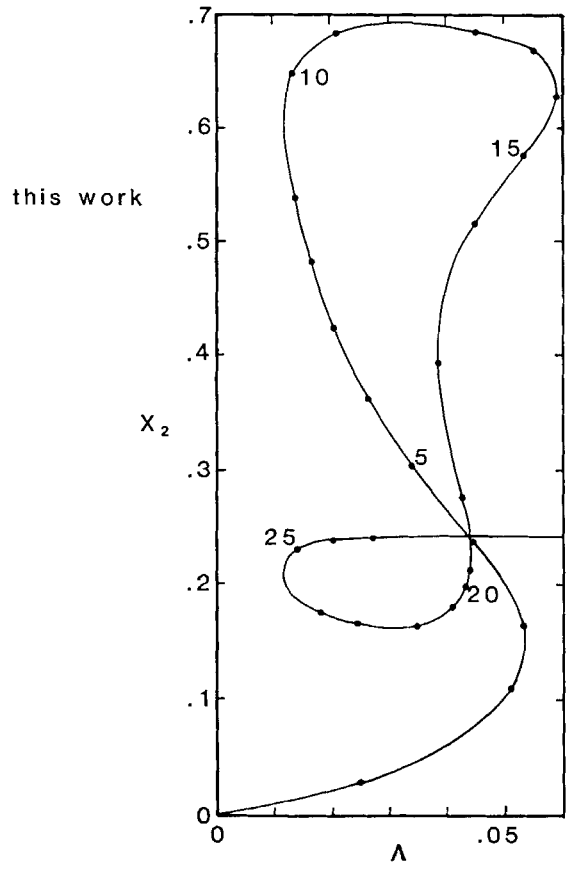

Figure 4. Homotopy Path Integration - This Work.

1. Exploitation of the sparcity of the jacobian. The sparcity of the matrix is utilized to reduce both the computational load of the program as well as its storage requirements. The reduction of the computational load is accomplished in two ways. The first involves eliminating the calculation of partial derivatives for elements which are known to be zero. The second involves utilizing a modified version of gaussian elimination developed by (Thomas[19], Newman[20]) to solve the system. Savings in storage requirements are achieved by not storing the off diagonal elements of the jacobian.

TABLE 3 Algorithm Performance Comparison

Algorithm	Steps Required	Function Evaluations	Total Jacobian Evaluations	CPU* time msec
Algorithm 502 Kubicek (1976)	209	2358	1572	2670
Algorithm 596 Rheinboldt (1983)	61	1410	201	5150
this work	37	1307	175	2890

* All calculations are performed in double precision on a VAX 11/780 computer.

The modified gaussian elimination procedure developed by Thomas is applicable to tridiagonal or block tridiagonal systems. Both the calculation of the Euler estimation of the homotopy curve and the calculation of the correction to the homotopy curve require that the original system be inflated to a higher dimension and an extra equation be supplemented to the system to make it determinant. This destroys the tridiagonal nature of the jacobian thereby preventing direct use of the Thomas algorithm. Investigation of the structure of the modified system of equations reveals that the jacobian is structured such that the system is bordered block tridiagonal. A generalized form of the jacobian matrix for homotopy continuation systems is given in figure 7. To exploit the sparcity of this structure, a modification of the standard Thomas algorithm was written. This modification extends the gaussian elimination procedure, developed by Thomas, to include the presence of the border elements in the matrix. Like the Thomas algorithm, it optimizes the elimination of this form of the jacobian by not storing elements known to be zero, not performing unnecessary elimination calculations, and not calculating the partial derivatives of elements whose elements are known to be zero. Combined, these modifications greatly reduce the computational load and the storage necessary to solve the bordered block tridiagonal systems found in homotopy continuation solution of separation problems.

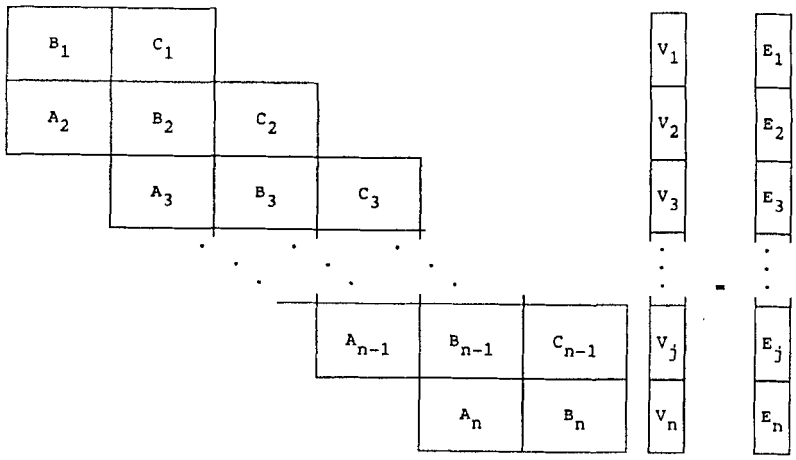

Figure 5.
Structure of Jacobian Matrix for Block Tridiagonal Systems j = n - 1

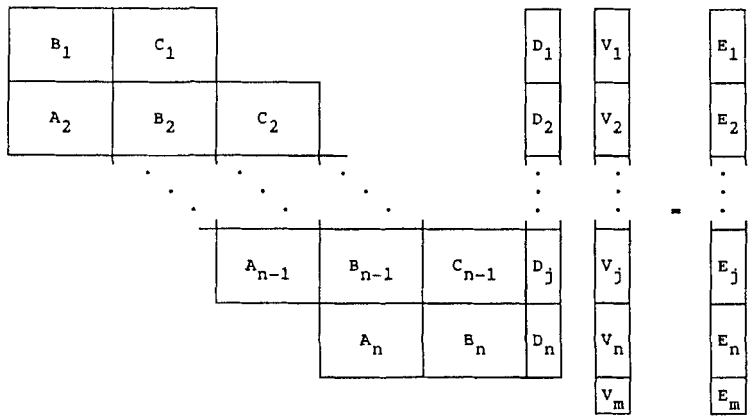

Figure 6. Structure of Jacobian for Cascaded Systems Including an Artificial Imbedding Parameter.
j = n - 1, m = n + 1

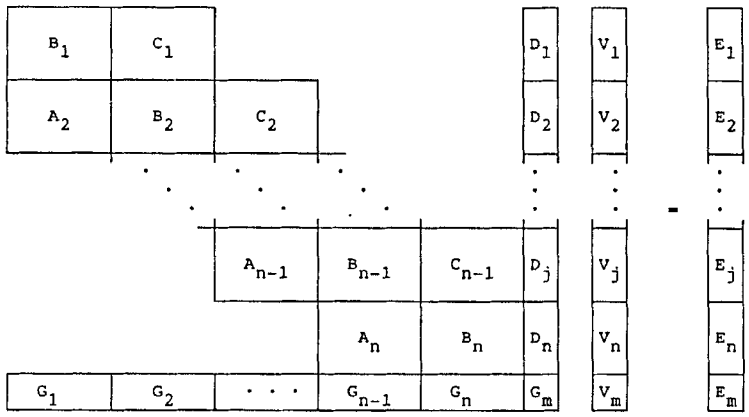

Figure 7. Bordered Block Tridiagonal System
$j = n - 1$, $m = n + 1$

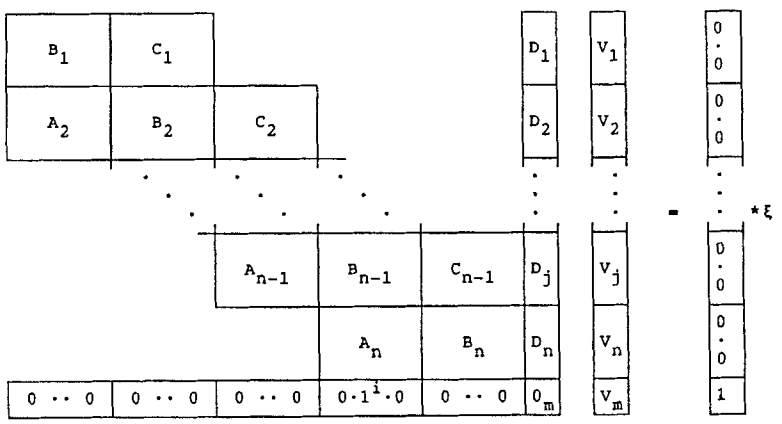

Figure 8. Bordered Block Tridiagonal System Utilizing The Natural Basis Vectors e^i and e^n for the G and E Vectors Respectively. $m = n + 1$, $j = n - 1$

2. Preservation of bordered Block tridiagonal form. The general homotopy procedure automatically changes the variable used as the continuation variable at each step along the homotopy path. This is done in an effort to avoid numerical instability brought about by the increasingly singular nature of the jacobian as bifurcation points are crossed. This is accomplished by supplementing the jacobian with e^{i} (i is the index of the local continuation variable) and choosing e^{n+1} as the residual vector. The structure of this matrix is given in figure 8. At this point most general algorithms simplify the matrix to an n by n system. This is accomplished by eliminating the column of the continuation variable and then switching the columns of the matrix to orient the local continuation variable such that it has the last index of the string. Figures 9 and 10 illustrate these forms of the matrix. The dependency of the system on the continuation is isolated and the system is treated as a standard n by n system. For general system of equations, with dense jacobians, this process poses no computational problems. For separation systems, however, this procedure destroys the tridiagonal nature of the jacobian. Elimination procedures for systems such as this are complicated because as the index of the continuation variable changes the structure of the resultant matrix also changes. This greatly complicates efficiently solving the system and prohibits usage of the modified Thomas algorithm. To allow the use of the modified Thomas algorithm, the bordered block tridiagonal structure of the system must be preserved. This is easily accomplished by not "simplifying" the problem by reducing it to an n by n system. Instead the full bordered block tridiagonal form given by figure 7 is used to calculate the tangent vector. As stated previously, efficient modifications of the Thomas algorithm have been developed in this work to solve bordered block tridiagonal systems. For the prediction jacobian, further simplifications are made by exploiting the known form of the residual vector. Realizing that the residual vector is known to be the natural basis vector of index n+1, the forward substitution of this system is not performed on the residual vector.

APPLICATION TO EXTRACTION CASCADES

The problem chosen for detailed analysis is found as an example in Nuclear Chemical Engineering by Benedict, Pigford and Levi [21]. The problem is the separation of zirconium from hafnium discussed by Huré and Saint James [22]. A zirconium fraction recovery of .98 and a decontamination factor of zirconium from hafnium of 200 are desired in the extract stream.

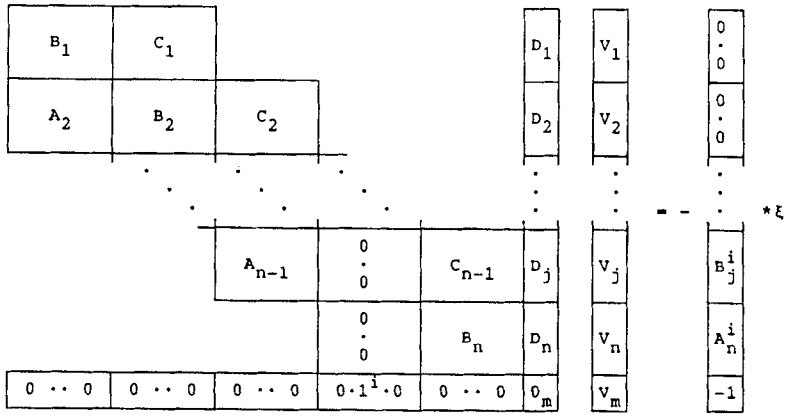

Figure 9. Elimination of the i^{th} Column of the Bordered Block System

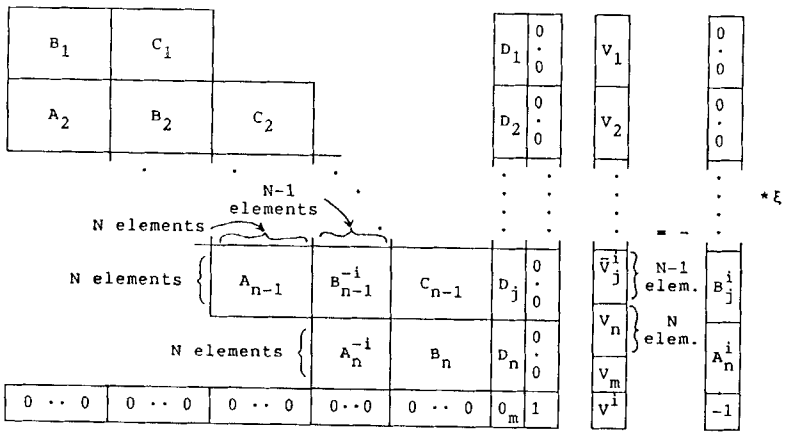

Figure 10. Switching Columns of the Block Tridiagonal System

Interlinked extraction and scrubbing cascades are used to accomplish this task. The solution proposed by Benedict, Pigford and Levi tears all the material balances in each cascade individually. The material balance condition around the feed stage is not met in their analysis.

The feed for the column consists of 3.5M $NaNO_3$, 3.0M HNO_3, .123M $Zr(NO_3)_4$, and .00246M $Hf(NO_3)_4$. The scrubbing section has an aqueous feed of 3.0M HNO_3 and 3.5M $NaNO_3$. The extraction section receives an organic feed containing 2.25M TBP and 1.6M HNO_3. The volume of organic feed is 100 liters and the aqueous feeds are both 48 liters. The problem is illustrated in figure 11.

The process chemistry of this problem is given in figure 12. Three highly nonlinear mass action equilibria are required to describe this system. Unlike most other solution procedures, a simultaneous convergence scheme without scaling, artificial parameters, and special treatment converges rapidly to a solution (O'Quinn & VanBrunt [23]). In this work, continuation methods are applied to the same problem.

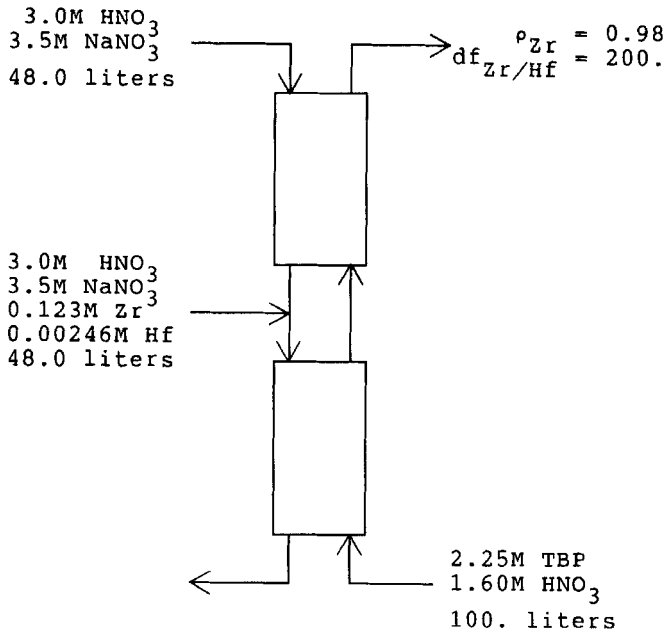

Figure 11. Zr/Hf Column

$$H^+_{(aq)} + NO^-_{3(aq)} + TBP_{(o)} \rightleftharpoons HNO_3 \cdot TBP_{(o)}$$
$$K_H = 0.145$$

$$Zr^{4+}_{(aq)} + 4NO^-_{3(aq)} + 2TBP_{(o)} \rightleftharpoons Zr(NO_3)_4 \cdot 2TBP_{(o)}$$
$$K_{Zr} = 0.0032$$

$$Hf^{4+}_{(aq)} + 4NO^-_{3(aq)} + 2TBP_{(o)} \rightleftharpoons Hf(NO_3)_4 \cdot 2TBP_{(o)}$$
$$K_{Hf} = 0.00032$$

Aqueous Phase	Organic Phase
H^+, Na^+	$HNO_3 \cdot TBP$
Zr^{4+}, Hf^{4+}	$Zr(NO_3)_4 \cdot 2TBP$
NO^-_3	$Hf(NO_3)_4 \cdot 2TBP$
	TBP

Figure 12.
Mass Action Equilibria for Zr/Hf Problem.

The results are shown in table 4. They indicate the efficiency of the continuation procedure over a simultaneous convergence method. The newton homotopy converged to the solution quicker and without scaling to prevent negative iterates. The fixed point homotopy diverged, even though the initial iterate was on a path, that path did not have a zero. Excellent results were obtained with custom imbedding procedures. It is believed that these results indicate the first time that a separation process has been converged with a continuation method at a rate comparable to a newton procedure.

Following Vickery and Taylor [24], the nonlinear term that represents the equilibrium can be gradually introduced exponentially(see equation 14). The physical reasoning for introducing the nonlinearity in this manner is that initially the solutes are introduced linearly into an organic phase that is equilibrated with the acid. The nonlinearity is gradually introduced.

$$y_{Zr} - K\, x_{Zr}(x^4_{NO_3} y^2_{TBP})^t = 0 \quad t \in [0,1] \qquad (14)$$

Table 4.
Zr - Hf SOLUTION COMPARISON

Method of Solution	Number of Steps	Newton Corrections
SC Linearization		5
SC linearization damped to prevent negative concentrations		11
Newton homotopy	1	4
Fixed point homotopy	failed to converge	
Custom homotopy # 1	1	4
Custom homotopy # 2	1	3

Specifically limiting the imbedding to the extractant solution concentration had the most profound effects. The resulting solution procedure is imbedded with the process chemistry. That is the imbedding is according to the extent to which the extractant is combined to form each metal complex.

$$y_{Zr} - K\, x_{Zr}\, x_{NO_3}^{4}\, y_{TBP}^{2t} = 0 \quad t \in [0,1] \qquad (15)$$

Not only did the procedure converge most rapidly; but also the physical chemistry was brought into the solution process. Solution from a wide range of starting points were examined. In each case, the procedure that represented the process chemistry appeared to be the most efficient.

In the specification problem described by O'Quinn and Van Brunt [23] a region of reduced convergence was obtained for a SC linearization. Using the continuation procedure, convergence to the solution was obtained from a point outside the domain of attraction of newton's method. In other words convergence was attained from a starting point from which other methods would diverge.

In summary, the method outlined here can be contrasted with an SC linearization. First, the procedure can obtain multiple solutions, if they exist.

Second, solution can be obtained from an area outside the domain of convergence of an SC method. Third, the procedure is capable of converging as rapidly or more rapidly than an SC method. And fourth, the procedure is able to include the process chemistry of metal complexation in the solution process. All of these advantages have been illustrated by the solution behavior given in table 4 and discussed above.

The Purex chemistry described by Jubin [25] suggests a similar custom homotopy mapping to the one outlined above. Particularly, if the distribution maps given for this system are examined in detail, the linearity of the nitric acid concentration is markedly different from the nonlinear metal chemistry. This effect is most noted at low metal concentrations.

$$\begin{aligned}
&UO_2^{2+} + 2NO_3^- + 2TBP \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP && K_U \\
&Pu^{4+} + 4NO_3^- + 2TBP \rightleftharpoons Pu(NO_3)_4 \cdot 2TBP && K_{Pu} \\
&H^+ + NO_3^- + TBP \rightleftharpoons HNO_3 \cdot TBP && K_{H1} \\
&H^+ + NO_3^- + 2TBP \rightleftharpoons HNO_3 \cdot 2TBP && K_{H2}
\end{aligned} \qquad (16)$$

The custom homotopy mapping suggested by Purex chemistry is

$$\begin{aligned}
&y_U - K_U x_U x_{NO_3}^2 y_{TBP}^{2(1-t)} = 0 \\
&y_{Pu4} - K_{Pu4}\, x_{Pu4} x_{NO_3}^4 y_{TBP}^{2(1-t)} = 0 \quad t \in [1,0] \\
&y_{H2} - K_{H2} x_H x_{NO_3} y_{TBP}^{2(1-t)} = 0
\end{aligned} \qquad (17)$$

CONCLUSION

This work developed a robust continuation method useful for separation problems. Successful application to the solution of hydrometallurgical separations revealed that the procedure is capable of converging more rapidly than a simultaneous convergence procedure. Customized procedures based on the solution chemistry were utilized in the most efficient calculation method.

NOMENCLATURE

a - arbitrary function
b - arbitrary function
Da - Damköhler number
e - the natural basis vector
E - arbitrary function vector
f - dependant variable
F - dependant variable vector
G - deformed function, F
h - homotopy function
H - homotopy function vector
r - residual
R - residual vector
t - continuation variable
x - independent variable
X - independent variable vector
y - reactant concentration

subscripts

0-9 - parameter number
n - number of equations
i,j,k - arbitrary parameter number

superscripts

k - iteration number
-1 - the inverse function
0 - initial value
f - final value
-i - denotes lack of column or element k
n - number of equations

greek

Φ - dimensionless temperature
$\partial()$ - partial differentiation

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