1968

Predictive control of an extraction column

William Erskine Jr.

Iowa State University

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PREDICTIVE CONTROL OF AN EXTRACTION COLUMN

by

William Erskine, Jr.

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NOMENCLATURE

**Latin**

A = coefficient matrix (21x21), Equation 2

\( a_{ij} \) = equilibrium regression constants representing the effect of the aqueous concentration of solute j on the organic concentration of solute i, Equation 1

b = constant vector (21x1), Equation 2

\( b_i \) = regression constant in the i\textsuperscript{th} solute equilibrium equation, Equation 1

C = coefficient matrix (21x21), Equation 4

D = coefficient matrix (21x21), Equation 4

E = tributyl phosphate (TBP) flow rate in liters per minute

F = feed flow rate in liters per minute

\( F \) = coefficient matrix (21x3), Equation 4

G = high gain factor in Equation 22

H = aqueous holdup of mixer-settler in liters, Equation 6

h = organic holdup of mixer-settler in liters, Equation 6

I = unity matrix

K_C = proportion gain in Equation 22

L = constant in exponential circuit, Figure 9

M = nitrate molarity

\( M \) = coefficient matrix (21x21), Equation 4

\( m_i \) = regression constants in Equation 13

N = coefficient matrix (21x21), Equation 4
\( n_i \) regression constants in Equation 14

\( P \) \((MA+N)\), Equation 5

\( Q \) \((C+DA)\), Equation 5

\( R \) reflux ratio

\( R_f \) reflux ratio from feedback control

\( R_p \) reflux ratio from predictive control

\( r \) regression correlation coefficient

\( S \) scrub stream flow rate in liters per minute

\( S^* \) \( S+F \), Equation 3

\( T \) \((Db+Fx^f)\), Equation 5

\( T_i \) reset time in minutes, Equation 22

\( t \) time in minutes

\( V \) total volume of mixer-settler in liters, Equation 6

\( x \) state variable vector \((21x1)\), Equation 2

\( \dot{x} \) \( \frac{d}{dt}(x) \), Equation 4

\( x^f \) feed concentration vector \((3x1)\), Equation 4

\( x_{R} \) raffinate purity, Equation 10

\( x_{f} \) feed concentration of solute \( i \), Equation 3

\( x_{in} \) aqueous nitrate molarity of solute \( i \) in stage \( n \), Equation 1

\( \dot{y} \) state variable vector \((21x1)\), Equation 2

\( y \) extract purity, Equation 9

\( \dot{y} \) \( \frac{d}{dt}(y) \), Equation 4

\( y_E \) extract purity, Equation 9

\( y_{E} \) predicted value of \( y_E \) from Equation 14

\( y_{E_{sp}} \) setpoint of \( y_E \), Equation 13 and 22
\( Y_{in} \) organic nitrate molarity of solute \( i \) in stage \( n \),
Equation 1

\( Z \) generalized output for exponential circuit, Figure 9

**Greek**

\( \alpha \) \( S/E \), scrub section flow ratio, Equation 11

\( \beta \) \( E/(S+F) \), extract section flow ratio, Equation 12

\( \Gamma \) initial value of generalized output for exponential circuit, Figure 9

\( \tau \) \( Y_E - Y_{E_{SP}} \), error signal in Equation 22

\( \xi \) constant in exponential circuit, Figure 9

**Subscripts of state variables**

\( i \) refers to solute, \( i = 1,2,3 \)

1 = La(NO_3)_3

2 = Pr(NO_3)_3

3 = HNO_3

\( n \) refers to stage number, \( n = 1,2,...7 \)
INTRODUCTION

Solvent Extraction

Solvent extraction is a separation process based on the distribution of liquid or solid solutes between two immiscible phases. A common example of a multicomponent extraction system is an organic solvent contacting an aqueous feed containing several solutes. Most solutes do not divide equally between the two phases, but tend to concentrate more in one phase or the other. The measure of this phase selectivity for a solute is called the distribution coefficient, which is defined as the ratio of the organic phase concentration to the aqueous phase concentration at equilibrium. The ease with which two solutes can be separated is indicated by the ratio of their distribution coefficients. This ratio is called the separation factor when both solutes are present. As this quantity departs from unity, the separation of two species becomes easier.

One area in which solvent extraction has been shown to have a potential advantage over other separation techniques is in the rare earth industry where fractional crystallization and ion exchange have long been used as means of separation and purification. Rare earths are not really rare, but are usually found together in nature and their chemical similarities make them difficult to isolate.

Initial work in rare earth extraction was directed toward
finding a solvent or a combination of solvents that produced the greatest separation factors. As more work was done in this area, several significant difficulties became apparent. A major problem not always encountered in other multicomponent systems was the strong interdependence of the solute equilibrium data. This interdependence rendered the presentation of equilibrium data difficult, and without a complete knowledge of the equilibrium, extraction columns could not be adequately designed to perform a given separation. Since the most commonly used ores contain at least four rare earths, this problem was of major significance.

Another difficulty was the slow rate of approach of the extractor to steady state caused by the large capacitance of the system, the relatively low flow rates, and the complex nature of the equilibria. Since these factors made the operation of rare earth extraction columns difficult, it seemed reasonable to develop a control scheme from a computer simulation of the extraction column.

Simulation

The equations describing the operation of an extraction column are ordinary differential equations, which can be solved on either an analog or digital computer. An analog simulation has an advantage in that all operations are performed simultaneously, and a continuous solution of the
equations is produced. A digital simulation has the advantages of accuracy, non-linear capability, and unlimited problem size. Many of the advantages of both techniques can often be combined by using a digital simulation program.

DIAN (3, 4, 15) is a digital simulation program which simulates an analog computer. It is programmed from an analog type flowsheet and the computations are done in such a way as to approach a simultaneous solution of the equations. The DIAN program was used to simulate an extraction column on the digital computer.

Control

The principle of feedback control is fundamental to most control schemes, the purpose being to maintain the system output at a preassigned setpoint. The difference between the system output and the setpoint, called the error, is fed to a controller which sends a signal to the final control element, such as a valve, thus producing a change in the value of the system output. The controller functions in such a way as to drive the system output to the setpoint value of the controlled variable. Since an extraction column has large time lags, feedback control was not thought to be sufficient since an error in the controlled variable must have actually occurred before any error can be sensed by a feedback control system. For this reason a more
sophisticated control technique was needed.

One recently developed control strategy which has proved beneficial to systems with large time lags is predictive control. In predictive control a mathematical model of the system is constructed and subjected to the same inputs as the real system. However, the model operates many times faster, effecting output changes before the real system does. When an upset occurs in an input, the model almost instantaneously predicts the eventual system output should this upset persist. It is this predicted signal that is compared with the setpoint, and sent to the controller. Hence, the controller acts before the upset can effect the system output. However, the mathematical model is blind to all outputs and to any unmeasured inputs; therefore, feedback control is usually added in the form of a "feedback trimmer" to correct the system and prevent offset.

Another type of predictive control is one in which the model is used to predict the value of the final control element necessary to maintain the system at the setpoint. Here again a feedback loop is needed to correct for inaccuracies in the model. Both types of predictive control in conjunction with feedback control appear to be effective in controlling processes which have long time lags or large time constants.
Purpose

The purpose of this work was to develop a control strategy for a seven stage center fed rare earth extraction column with extract reflux. Regression analyses on steady state data obtained from a mathematical model of the column were used to produce two types of predictive control models. The first predicted the extract purity; the second predicted the reflux ratio necessary to maintain a specified extract purity. Both were used in conjunction with feedback control to control the mathematical model of the extraction column.
LITERATURE REVIEW

Solvent Extraction

Most of the equilibrium data available for solvent extraction are for single solute systems. For multicomponent systems, equilibrium data are sparse and the representation of this data is difficult. However, for multicomponent rare earth systems, the equilibrium concentrations of one solute in each phase are dependent on the concentrations of every other rare earth present and also on the pH of the solution. A reliable method of predicting rare earth equilibrium concentrations was developed by Sharp and Smutz (13).

They prepared an organic solution of a rare earth and nitric acid, mixed it with water, and allowed the phases to separate. Many such equilibrium runs were made for different rare earths, after which, each phase was analyzed for total nitrate molality and the nitrate molality of the rare earth. Total distribution coefficients and nitric acid distribution coefficients for these runs were tabulated as a function of total nitrate molality and rare earth nitrate molality for each phase. The separation factors of the different rare earth combinations were computed as a function of total nitrate molality for each phase.

Prediction of the concentrations of the solutes for a multicomponent system required interpolation of the data in
these tables. Each rare earth, in turn, was assumed to be the only rare earth present in the organic phase at a concentration equal to the total rare earth nitrate molality. The total nitrate distribution coefficient and the nitric acid distribution coefficient were obtained as a weighted average of the coefficients in these tables. Individual aqueous rare earth molalities were then calculated from the total nitrate distribution coefficients, the nitric acid distribution coefficient, the organic phase molalities of the rare earths, and the separation factors between the rare earths.

Once an equilibrium calculation scheme was developed, steady state equilibrium concentrations of all solutes in an extraction column could be predicted as shown by Sebenik, Sharp, and Smutz (11). They contacted a feed containing four rare earths and nitric acid with tributyl phosphate (TBP) in a center fed extraction column. An initial estimate was made of the extract composition for given flow rates and feed composition. The raffinate composition was determined by an over-all mass balance. Successive equilibrium calculations and mass balances from both ends of the column determined all the stage compositions. The sequence of calculations stopped at the feed stage with two independent values of the feed stage composition. If the two values of feed stage composition were equal, then the initial estimate
of extract composition was correct. If these two values did not match then the solute that was most mismatched at the feed was adjusted in its extract composition. The calculations stopped when all compositions meshed at the feed stage within certain limits.

Other investigators of steady state calculations for rare earth extraction systems were Sharp and Smutz (13), and Bochinski et al. (1). All of these methods depended on a table of data for the equilibrium calculation.

Solvent Extraction Simulation

Halligan and Smutz (5) simulated the extraction of nitric acid with tributyl phosphate in a mixer-settler extractor. In constructing a mathematical model of the extractor they developed an analytical relationship for the equilibrium data. Four models were proposed to describe the behavior of a series of mixer-settlers in an extraction column. They were called the Perfectly Mixed Model, the Plug Flow Model, the Equilibrium Model, and the Hybrid Model.

All the models assumed perfect mixing and equilibrium contact in the mixer. The Perfectly Mixed Model assumed that each phase in the settler was perfectly mixed and that the exit composition of each phase was equal to the bulk composition of each phase. The Plug Flow Model assumed each phase moved in plug flow through the settler with no back-
mixing, and the Equilibrium Model assumed negligible holdup in the settler.

The fourth model proposed was based upon experimental observation. The organic phase in the settler appeared to be dispersed as droplets in the aqueous phase as it moved toward the interface where the drops coalesced. Hence, the Hybrid Model assumed that the aqueous phase in the settler was perfectly mixed while the organic phase moved in plug flow. For a single stage the Hybrid Model best fitted the experimental data.

However, for six stages or more all of the models gave approximately the same response. Therefore, in an extraction simulation involving more than six stages, the simplest model (Equilibrium Model) can be used with no loss of accuracy.

The authors used DIAN, a digital simulation program developed by Farris and Burkhart (3, 4), to simulate the extractor. DIAN combines many of the advantages of both a digital and an analog computer. The data flowsheet resembles and analog computer. The data flowsheet resembles and analog flowsheet rather than a FORTRAN program and DIAN has since been modified by Torrey et al. (15) to produce better accuracy and more versatility.

The work of Halligan and Smutz (5) can be considered as the first step toward the dynamic simulation of a rare earth extractor since the ternary system which was studied forms the basis of any rare earth extraction process. The work of
Sebenik, Sharp and Smutz (11) on the steady state behavior of a rare earth extraction column provided general knowledge of typical feed concentrations, flow rates, separation, etc., which would be found in rare earth extraction column. At higher concentrations some rare earths precipitate or form highly viscous solutions. For this reason preliminary tests of the model proposed in the present work involved feed concentrations and flow rates in the neighborhood of those reported by Sebenik, Sharp and Smutz so that the gel region was hopefully avoided.

Control Theory

The study of control of extraction columns used with rare earth systems is particularly appropriate because such processes are usually monitored rather than controlled. The monitoring consisted of keeping interface levels constant and flow rates constant. Any upset in the feed is allowed to propagate and is detected by a change in the color gradient in the mixer-settlers. In contrast to the lack of work done on control of extraction columns, distillation units have received much attention from control engineers. The analogy between distillation and extraction as explained by Woodle (17) is outlined in Table 1.
Table 1. Distillation-extraction analogy

<table>
<thead>
<tr>
<th>Distillation</th>
<th>Extraction</th>
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<tr>
<td>overhead condenser</td>
<td>extract stripper</td>
</tr>
<tr>
<td>bottoms cooler</td>
<td>raffinate stripper</td>
</tr>
<tr>
<td>overhead condenser heat out</td>
<td>extract stripper solvent out</td>
</tr>
<tr>
<td>distillate product</td>
<td>extract product</td>
</tr>
<tr>
<td>bottoms cooler heat out</td>
<td>raffinate stripper solvent out</td>
</tr>
<tr>
<td>bottoms product</td>
<td>raffinate product</td>
</tr>
<tr>
<td>heat in to reboiler</td>
<td>solvent fed to column</td>
</tr>
<tr>
<td>distillate enthalpy, BTU/lb.</td>
<td>extract solvent content</td>
</tr>
<tr>
<td></td>
<td>lb. solvent/lb. extract</td>
</tr>
<tr>
<td>bottoms enthalpy, BTU/lb.</td>
<td>raffinate solvent content</td>
</tr>
<tr>
<td></td>
<td>lb. solvent/lb. raffinate</td>
</tr>
<tr>
<td>feed enthalpy, BTU/lb.</td>
<td>feed solvent content</td>
</tr>
<tr>
<td></td>
<td>lb. solvent/lb. feed</td>
</tr>
<tr>
<td>enthalpy-concentration diagram</td>
<td>solvent-composition diagram</td>
</tr>
</tbody>
</table>

A typical distillation tower studied by Williams (16) consisted of an overhead condenser, many stages, and a reboiler. The most common procedure was to control the distillate composition by varying the reflux ratio. The basic type of control studied was feedback control. To envision how this control scheme works, suppose the feed suddenly becomes richer in the less volatile component. As this change propagates up the column the temperature on the top plate will increase and the product purity will decrease. The
temperature measurement on the top plate is directly correlated with the distillate composition and when compared with the setpoint temperature the error will be fed to the reflux controller which causes an increase in the reflux ratio. Increasing the reflux ratio corrects the overhead composition and prevents an inferior product from being collected. Also, the column is enriched with respect to the more volatile component. The temperature on the top plate decreases and the column returns to steady state.

More sophisticated types of control for distillation towers have been reported by Lupfer and Parsons (6), Luyben and Gerster (8), MacMullan and Shinskey (9), Zahradnik et al. (18) and Shinskey (14). Most of the work presented in these articles involves computing the feed enthalpy and deriving models of the system which can be used for predictive control.

Predictive control has several definitions in the literature. The two types of predictive control that appear to be most common are based upon output prediction and control variable prediction. In the former, a mathematical model continuously predicts the output of the system from the measured inputs. The inputs measured and fed to the model are those inputs which are expected to vary and which are uncontrolled. The predicted output is compared with the setpoint value. The difference forms an error signal which is
sent to the controller. This method compensates for upsets before they have a chance to appear at the output of the process.

In the latter predictive scheme, a mathematical model is used to predict the value of the control variable necessary to maintain the setpoint condition. The predicted value of the control variable is sent directly to the system rather than to a controller. Again, the measured inputs are those that are uncontrolled and are expected to vary.

Both predictive control models are ignorant of all outputs and of any unmeasured inputs. This type of control is open loop control. A feedback control system is usually used to correct the signal from the predictive model. This feedback system is called a feedback trimmer.

Predictive control was used in this work because the control action began immediately after an input change was detected. Feedback control alone would not have acted until an output change was sensed. For a system with long time delays or long time constants, predictive control preserves stability (7) in the system where feedback control might fail.
MATHEMATICAL DEVELOPMENT OF A RARE
EARTH EXTRACTION COLUMN

Description of Extraction Column

The equipment studied was a seven stage center fed
extraction column with extract reflux as shown in Figure 1.
A La(NO₃)₃-Pr(NO₃)₃-HNO₃-H₂O feed entered the fourth stage
and was extracted with tributyl phosphate (TBP) which
entered the seventh stage. An aqueous scrub stream entered
the first stage and flowed countercurrently to the TBP.

The fourth through seventh stages formed the extract
section of the column and the first through third stages
formed the scrub section. The organic phase flow rate was
the same in both sections of the column, and was equal to
the flow rate of TBP. The aqueous phase flow rate was
equal to the scrub stream flow rate in the scrub section
and was equal to the sum of the scrub stream flow rate and
the feed flow rate in the extract section of the column.

After the TBP and HNO₃ were removed from the organic
stream leaving the first stage, part of the rare earths
was mixed with the scrub stream and returned to the first
stage as reflux. The remaining fraction of the rare earths
was removed as product. The ratio formed by the rare earths
added to the scrub stream divided by the rare earths taken as
product was the reflux ratio. This reflux ratio was the
control variable and was manipulated to maintain the $\text{Pr(NO}_3\text{)}_3$ at its setpoint value. The prime function of the extraction column was to produce a high purity $\text{Pr(NO}_3\text{)}_3$ extract.

Qualitative sketches of the rare earth flow patterns are shown in Figure 1. Since the distribution coefficient for $\text{La(NO}_3\text{)}_3$ was much less than unity, most of the $\text{La(NO}_3\text{)}_3$ remained in the aqueous phase. Most of the $\text{La(NO}_3\text{)}_3$ that did go into the organic phase was back extracted into the scrub stream in the scrub section. Although the distribution coefficient for $\text{Pr(NO}_3\text{)}_3$ was also less than unity, it was much greater than the distribution coefficient for $\text{La(NO}_3\text{)}_3$. Therefore, there was much more $\text{Pr(NO}_3\text{)}_3$ than $\text{La(NO}_3\text{)}_3$ in the organic phase. This qualitative analysis is only valid for flow rates that are approximately equal.

Refluxing further enhanced the separation by mixing a portion of the $\text{Pr(NO}_3\text{)}_3$-rich extract product with the scrub stream entering the first stage. Since the distribution coefficient of $\text{Pr(NO}_3\text{)}_3$ was much greater than that of $\text{La(NO}_3\text{)}_3$, more $\text{Pr(NO}_3\text{)}_3$ than $\text{La(NO}_3\text{)}_3$ entered the already $\text{Pr(NO}_3\text{)}_3$-rich organic phase of the first stage. Most of the $\text{La(NO}_3\text{)}_3$, being less extractable, remained in the aqueous phase and eventually left the extractor in the raffinate. The purity of the extract product was measured by the mass fraction of $\text{Pr(NO}_3\text{)}_3$ on a nitric acid free basis.
Figure 1. Extraction column and rare earth flow patterns
Derivation of System Equations

Equilibrium calculations

Previous methods for steady state rare earth extraction calculations utilized several tables of data in carrying out equilibrium calculations. The concentrations of the solutes in each stage were calculated by an iterative procedure using these tables. Even though tabular data may be incorporated into a computer simulation, an analytical expression for the equilibrium relationships was more convenient in this work.

An expression for the organic phase concentration of a solute as a function of the aqueous phase concentrations of all solutes was obtained by a multiple linear regression analysis on the equilibrium data of Sharp and Smutz (13). These equations can be written as follows.

\[ y_{in} = a_{i1}x_{1n} + a_{i2}x_{2n} + a_{i3}x_{3n} + b_i \quad i=1,2,3 \quad n=1,2,\ldots,7 \]

Equation 1 is easily put into matrix form:

\[ y = Ax + b \]

\[ Y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} \quad \text{where: } \quad Y_i = \begin{bmatrix} y_{i1} \\ y_{i2} \\ y_{i3} \\ y_{i4} \\ y_{i5} \\ y_{i6} \\ y_{i7} \end{bmatrix}, \quad i=1,2,3 \]
\[ x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \quad \text{where: } x_i = \begin{bmatrix} x_{i1} \\ x_{i2} \\ x_{i3} \\ x_{i4} \\ x_{i5} \\ x_{i6} \\ x_{i7} \end{bmatrix}, \quad i = 1, 2, 3 \]

\[ b = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} \quad \text{where: } b_i = \begin{bmatrix} b_{i1} \\ b_{i2} \\ b_{i3} \end{bmatrix}, \quad i = 1, 2, 3 \]

\[ A = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \quad \text{where: } A_{ij} = a_{ij}; I = 7 \times 7 \text{ unity matrix} \]

i = 1, 2, 3

j = 1, 2, 3

The data in the regression analysis extended over a rather narrow range of concentrations. The nitric acid mass fractions of Pr(NO₃)₃ in the organic phase were between 0.400 and 0.845, and in the aqueous phase between 0.333 and 0.666. A qualitative relationship between the data and the regression analysis
is shown in Figure 2. Region I represented the range of the data used in the regression. Since the regression equation did not pass through the origin it was difficult to obtain a perfect separation. When the regression was extrapolated into region II, incorrect concentrations were calculated. However, when the equation was extrapolated into region III, negative concentrations were calculated. These had no physical significance, of course, and therefore were of no value in the simulation studies.

**Unsteady state equations**

Each stage of the extraction column was considered to be a mixer-settler. Halligan and Smutz (5) showed that for a six stage column, the transient responses of different models were identical. Since the column under investigation in this work had seven stages, the simplest model, the Equilibrium Model was used.

Material balances on the $i^{th}$ solute around each stage yielded the following set of equations.
Region

I  Good estimation of equilibrium concentrations
II  Poor estimation of equilibrium concentrations
III  Unacceptable region — negative concentrations

Figure 2. Limitations of equilibrium regression analysis
\[ \frac{d}{dt} \tilde{y}_{1i} + \frac{d}{dt} \tilde{x}_{1i} = S(x_{i0} - x_{i1}) + E(y_{i2} - y_{i1}) \]

\[ \frac{d}{dt} \tilde{y}_{12} + \frac{d}{dt} \tilde{x}_{12} = S(x_{i1} - x_{i2}) + E(y_{i3} - y_{i2}) \]

\[ \frac{d}{dt} \tilde{y}_{13} + \frac{d}{dt} \tilde{x}_{13} = S(x_{i2} - x_{i3}) + E(y_{i4} - y_{i3}) \]

\[ \frac{d}{dt} \tilde{y}_{14} + \frac{d}{dt} \tilde{x}_{14} = Sx_{14} - Sx_{i4} + E(y_{i5} - y_{i4}) + Fx_f \]

\[ \frac{d}{dt} \tilde{y}_{15} + \frac{d}{dt} \tilde{x}_{15} = S^*(x_{i4} - x_{i5}) + E(y_{i6} - y_{i5}) \]  \hspace{1cm} (3)

\[ \frac{d}{dt} \tilde{y}_{16} + \frac{d}{dt} \tilde{x}_{16} = S^*(x_{i5} - x_{i6}) + E(y_{i7} - y_{i6}) \]

\[ \frac{d}{dt} \tilde{y}_{17} + \frac{d}{dt} \tilde{x}_{17} = S^*(x_{i6} - x_{i7}) + E(y_{i8} - y_{i7}) \]

where: \( i=1,2,3 \)

\[ S^* = S + F \]

\[ y_{i8} = 0, \ i=1,2,3 \]

\[ x_{i0} = \begin{cases} \frac{E}{S} \left( \frac{R}{R+1} \right) y_{11} & , \ i=1,2 \\ 0 & , \ i=3 \end{cases} \]

The \( x_{i0} \) term was calculated by a mass balance on the extract stream after the TBP and HNO\(_3\) had been removed. The rare earths in this stream were divided into an extract product stream and an extract reflux. The total amount of solute
(i=1,2) leaving the first stage in the organic phase was $EY_{i1}$. The amount taken as product was $(\frac{1}{R+1})EY_{i1}$, and the amount refluxed was $(\frac{R}{R+1})EY_{i1}$. Therefore, the ratio of the amount refluxed to the amount taken as product was equal to $R$, the reflux ratio.

The material balance equations were written in matrix form:

$$ M\dot{X} + NX = CX + DX + FX^f $$

where:

$$ M = hI $$

$$ N = HI $$

where $I = 21 \times 21$ unity matrix

$$ C = \begin{bmatrix}
C_{11} & C_{12} & C_{13} \\
C_{21} & C_{22} & C_{23} \\
C_{31} & C_{32} & C_{33}
\end{bmatrix} $$

$$ C_{ij} = \begin{cases}
-S & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -S & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -S & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & S^* & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & S^*-S^* & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & S^*-S^* & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & S^*-S^*
\end{cases} $$

where; $C_{ij} = \begin{cases}
0 & , i=j \\
\end{cases}$
where, $D_{ij} = 0$, $i \neq j$

$$
\begin{array}{cccc}
D_{11} & D_{12} & D_{13} \\
D_{21} & D_{22} & D_{23} \\
D_{31} & D_{32} & D_{33}
\end{array}
$$
\[
\begin{bmatrix}
F_{11} & F_{12} & F_{13} \\
F_{21} & F_{22} & F_{23} \\
F_{31} & F_{32} & F_{33}
\end{bmatrix}
\]

where:
\[
F_{ij} = \begin{cases} 
0 & , i=j \\
F & , i\neq j
\end{cases}
\]

\[
\begin{bmatrix}
x_1^f \\
x_2^f \\
x_3^f
\end{bmatrix}, \dot{x} = \frac{d}{dt}(x), \dot{y} = \frac{d}{dt}(y)
\]

Equation 4 was written in terms of \(x\) only by the substitution of Equation 2.

\[
\begin{aligned}
M(A\dot{x}) + N\dot{x} &= Cx + D(A\dot{x} + b) + Fx^f \\
(MA + N)\dot{x} &= (C + DA)x + Db + Fx^f
\end{aligned}
\]
If one defines,

\[ (MA + N) = P \]
\[ (C + DA) = Q \]
\[ (Db + Fx^f) = T \]

then the resulting system of equations is

\[ \frac{P x}{x} = Q x + T \] \hspace{1cm} (5)

Equation 5 was deceivingly simple in matrix form but a detailed look at the coefficient matrices revealed some complex features. The \( P \) and \( Q \) coefficient matrices remained constant when only the feed concentrations changed. However, any other upset to the column, such as a flow rate change or reflux ratio change, would cause \( P \) and \( Q \) to be functions of time. One further complication was that the reflux ratio appeared in the coefficient matrix \( Q \) of the state variables in the form \( R/(R+1) \). Thus, the variable used to control the extraction column was not only inseparable from the state variables but also a non-linear term.

The complex nature of the \( C \) and \( D \) matrices was due to the strong interdependence of the solutes. Another complication was that the holdup of a phase was assumed to be proportional to the flow rate of that phase. The holdup terms were calculated as follows.
\[
H = \begin{cases} 
\frac{SV}{S+E}, & n=1,2,3 \\
\frac{(S+F)V}{S+F+E}, & n=4,5,6,7 
\end{cases} \tag{6}
\]

\[h = V - H, \quad n=1,2,...,7\]

Thus, each stage acted as two continuous stirred tanks with variable volume whenever any flow rate varied.

**Steady state equations**

When the extraction column is at steady state, none of the concentrations of the solutes in the stages change. Hence, at steady state, \( \dot{x} = 0 \) and Equation 5 reduces to Equation 7.

\[Qx = -T \tag{7}\]

or

\[x = -Q^{-1}T \tag{8}\]

There are seven degrees of freedom in Equation 7 - \( S, E, F, x_1^f, x_2^f, x_3^f, \) and \( R \). Combinations of these parameters were said to form a valid set of operating conditions if all the elements of \( x \) and \( y \) were non-negative. Negative concentrations were calculated whenever the extrapolation of Equation 2 went into region III. Another reason for the existence of region III was the strong interdependence of solutes.
Solution of System Equations

Steady state

The steady state behavior of the column was studied first in order to approximate the limits of the parameters that would produce valid operating conditions. Also, the results of the steady state equations were to be used to develop the predictive control models by performing a regression analysis on the data.

Equation 7 was solved by Gauss elimination to yield the aqueous concentrations of each solute in every stage. The organic phase concentrations were then calculated by Equation 2.

Initial estimates of the defining parameters of Equation 7 were obtained from the work of Sebenik, Sharp, and Smutz (11). These values were chosen to avoid any viscous region that might have existed and also to use as a starting point in searching for the valid operating region.

In order to search the seven dimensional space efficiently, preliminary runs were made according to a factorial design of the three flow rates, extract flow rate, scrub flow rate, and the feed flow rate. The feed composition was fixed in the neighborhood of the ones reported by Sebenik, Sharp, and Smutz (11) and a zero reflux condition was used. The measured outputs were extract purity ($Y_E$) and raffinate purity ($X_R$) as defined in Equations 9 and 10.
\[ Y_E = \frac{Y_{21}}{Y_{21} + Y_{11}}, \text{ mass fraction } \text{Pr(NO}_3\text{)}_3 \text{ on a nitric acid free basis} \tag{9} \]

\[ X_R = \frac{X_{17}}{X_{17} + X_{27}}, \text{ mass fraction of } \text{La(NO}_3\text{)}_3 \text{ on a nitric acid free basis} \tag{10} \]

It was convenient in the analysis of these runs to calculate flow ratios in each section of the column as defined in Equations 11 and 12.

\[ \alpha = S/E, \text{ scrub section flow ratio} \tag{11} \]
\[ \beta = E/(S+F), \text{ extract section flow ratio} \tag{12} \]

The results for one feed condition with extract purity contours and raffinate purity contours are shown in Figure 3. Similar plots were obtained for different feed conditions. Once \( \alpha \) was specified, the value of the extract purity was independent of the value of \( \beta \). In a similar manner, once the value of \( \beta \) was specified the raffinate purity was nearly independent of the value of \( \alpha \). Thus, for the range of parameters studied the extract purity depended only on the scrub section flow ratio, and the raffinate purity depended only on the extract section flow ratio.

On the basis of these preliminary results, the flow rates were replaced by the flow ratios as parameters in later runs. Since only two flow ratios replaced three flow rates, one of the flow rates still had to be specified in order to
Feed composition: La(NO₃)₃ = 0.8M, Pr(NO₃)₃ = 0.8M, HNO₃ = 3.0M.

Nitric acid free mass fraction of Pr(NO₃)₃ in feed = 0.5.

Nitric acid free mass fraction of Pr(NO₃)₃ in feed = 0.5.

Figure 3. Flow rate ratio plot with extract and raffinate purity contours.
completely determine the system. The feed rate was chosen since it was desired to vary the feed rate independently. However, the factorial design showed that once $\alpha$ and $\beta$ were specified, the value of the feed rate had no effect on either extract purity or raffinate purity for the range of parameters considered. Therefore, only one value of the feed rate was used in subsequent runs.

When $\alpha$-$\beta$ plots similar to Figure 3 were made with different values of the nitric acid concentration in the feed, the contours shifted only slightly. Therefore, only one value of the nitric acid feed concentration was used in later work.

On the basis of the preliminary results then, the feed rate and nitric acid feed concentration were fixed and the operating conditions were then specified by $\alpha, \beta, x_1^f, x_2^f,$ and $R$.

At first, it appeared that a simple factorial over all these factors would produce enough information to approximate the boundaries of the valid operating region. However, the preliminary results showed that the range of $\alpha$ and $\beta$ could be covered more efficiently than with a factorial design. These results showed that each output purity depended on the flow ratio in that section of the column. Therefore, $\alpha$ and $\beta$ were used in a latin square type of arrangement while $x_1^f, x_2^f,$
and R were combined factorially.

The manner in which these parameters were combined is shown in Figure 4. The range of reflux ratios covered was from 0 to 10 by increments of 2. Therefore, each combination of \( x_1^f - x_2^f \) was used for six different values of reflux ratios at four different flow ratio combinations. For example, feed composition b meant that \( x_1^f = 0.8 \), and \( x_2^f = 1.0 \) was used for \( R = 0, 2, 4, 6, 8, \) and 10 at \( \alpha = 0.09, \beta = 0.9, \) and \( \delta = 0.10, \beta = 1.0, \) and \( \alpha = 0.11, \beta = 1.1, \) and \( \alpha = 0.12, \beta = 1.2. \) Thus each feed combination produced 24 operating conditions. Higher values of reflux ratio were obtained by extending the range of R from 12 to 22. The results for one feed combination are shown in Figure 5.

The data generated by the procedure shown in Figure 4 was used to develop the predictive control models. Both models were constructed by performing multiple linear regressions on the data.

\[
\frac{dR}{dp} = m_1 d\alpha + m_2 d\beta + m_3 dx_1^f + m_4 dx_2^f + m_5 dy_{E_{sp}} \quad (13)
\]

\[
\frac{dy_E}{dp} = n_1 d\alpha + n_2 d\beta + n_3 dx_1^f + n_4 dx_2^f + n_5 dR \quad (14)
\]

Unsteady state - DIAN

The system of linear ordinary differential equations represented by Equation 4 was solved on a digital computer using the DIAN digital simulation program (3, 4, 15).
Figure 4. Parameter design used to generate steady state data
Figure 5. Effect of scrub section flow rate ratio on the extract purity
A problem written for DIAN uses differentials as in a digital computer, but is set up using an analog type flowsheet with analog type components. The connections between the components are coded on punch cards, which become data cards for the DIAN program. These data cards also contain the initial values of all state variables and parameters of the system which, in this case, defined a steady state operating condition.

The DIAN flowsheet was begun by considering Equation 3 with \( i = 1, 2, 3 \). These equations were written in differential form and the diagram was developed from them one stage at a time. For simplicity, consider the third stage for solute 1.

\[
\frac{d y_{13}}{d t} + \frac{H}{d x_{13}} = S(x_{12} - x_{13}) + E(y_{14} - y_{13})
\]  
(15)

The differential form of Equation 1 was substituted in place of the organic concentration term of the left hand of Equation 15 to give

\[
\frac{dx_{13}}{dt} = \frac{[S(x_{12} - x_{13}) + E(y_{14} - y_{13})] - [h_{12} dx_{23} + h_{13} dx_{33}]}{H + h_{11}}
\]  
(16)

Equation 1 was substituted only into the left hand side of the equation. The organic concentration on the right hand side was retained so that it could be generated continuously. Hence, the flowsheet was constructed to solve Equation 4 in the form of Equation 16.

Initially, all the flow rates were assumed constant and perturbations were only allowed in the parameters \( x^f_1, x^f_2, x^f_3 \),
and R. The DIAN diagram for Equation 16 is shown in Figure 6. The aqueous concentration of solute 1 in the third stage was accumulated in integrator 3 while integrator 4 held the organic concentration. These concentrations were multiplied by their respective flow rates and the products sent to summer 1.

The product $S_{x_{13}}$ was used in stage 4 and $E_{y_{13}}$ was used in stage 2. The inflow of solute 1 from stages 2 and 4 to stage 3 entered summer 2. Summer 6 added the contribution of the dependence of solute 1 on solutes 2 and 3. The output of summer 6 was multiplied by $-h$ and fed to summer 2. Thus, the output of summer 2 was the numerator of Equation 16. The left hand side of Equation 16 was obtained by multiplying the output of summer 6 by $1/(H+h_{a_{11}})$. The integral of this was the aqueous concentration of solute 1 in stage 3. The organic concentration was calculated by integrating the differential form of equation 1 which was generated in summer 5.

The next step in the development in the mathematical model of the extraction system was to provide a convenient method for changing the flow rates. Step changes in the flow rates could have been handled by the constant flow rate DIAN diagram but it would have necessitated changing the initial conditions of over eighty data cards. The initial concentrations would remain the same but all the constant multi-
Figure 6. DIAN flowsheet for constant flow rates

Equilibrium data input
pliers for flow rates and holdups would be changed. The generalized model could perform a step change when only one data card was changed.

With this modification the model could be used to find the response to a change in flow rate, solute feed concentration, or reflux ratio. To make this change, all the constant multipliers involving flow rates were changed to function multipliers. The resulting flowsheet is shown as the shaded portion of Figure 7.

The way in which Equation 16 was diagrammed for the variable flow case is outlined as follows. The value of the organic concentration of solute 1 in stage 3 was found from Equation 17.

\[ a_{11}(dx_{13}) + a_{12}(dx_{23}) + a_{13}(dx_{33}) = (dy_{13}) \]  

(17)

The organic and aqueous concentrations were multiplied by their respective flow rates and summed as in Equation 18.

\[ (dS)(dx_{12}) - (dS)(dx_{13}) + (dE)(dy_{14}) - (dE)(dy_{13}) \]

\[ \times d[S(x_{12} - x_{13}) + E(y_{14} - y_{13})] \]  

(18)

Equation 19 represents the divider that replaced constant multiplier 7 in Figure 6.

\[ \frac{d[S(x_{12} - x_{13}) + E(y_{14} - y_{13})]}{d(H + ha_{11})} \]

\[ + d\left[ \frac{S(x_{12} - x_{13}) + E(y_{14} - y_{13})}{H + ha_{11}} \right] \]  

(19)
Figure 7. DIAN flowsheet of the $n$th stage for variable flow rates.
Equation 20 replaced constant multipliers 7 and 8 in Figure 6 for the calculation of the dependence of solute 1 on solutes 2 and 3.

\[
\frac{dh}{dt} = \frac{d(H+ha_{11})}{H+ha_{11}} + d\left[\frac{h}{H+ha_{11}}\right]
\]  \hspace{1cm} (20)

The right hand side of Equation 20 was integrated with respect to \(x_{23}\) and also with respect to \(x_{33}\). These integrals were multiplied by the appropriate regression constant and added to the time integral of Equation 19 to give

\[
\frac{dx_{13}}{dt} = \int \left[ \frac{S(x_{12} - x_{13}) + E(y_{14} - y_{13})}{H + ha_{11}} \right] dt
- a_{12} \int \left[ d\left(\frac{h}{H+ha_{11}}\right) \right] dx_{23}
- a_{13} \int \left[ d\left(\frac{h}{H+ha_{11}}\right) \right] dx_{33}
\]  \hspace{1cm} (21)

Solving Equation 4 in the form of Equation 21 led to Figure 8. The holdup terms, \(H\) and \(h\), and the flow rates \(S, E, \) and \(F\) were calculated at the bottom of Figure 8. These calculations were done separately because they were used in each stage.

All of the step changes in the mathematical model of the extraction column were made by use of an exponential circuit as shown in Figure 9. Integrator 1 generated a
Figure 8. DIAN flowsheet for the control of a seven stage extraction column
\[ Zdt = \Gamma dt + L(1 - e^{-\xi t})dt \]

where: \( Z = E, S, F, x_1^f, x_2^f, x_3^f \), and \( Y_{Esp} \)

**Figure 9. Exponential circuit**
decreasing exponential decay with an initial condition of unity. The rate of decay was specified by the constant multiplier $\xi$. There is a constant multiplier of $-L$ and an integrator associated with each of the parameters $S$, $E$, $F$, $x^f_1$, $x^f_2$, $x^f_3$, and $Y_{Esp}$. All values of $L$ were zero except for the parameter that was changing. That parameter changed $L$ units in about two minutes of extraction time compared to a time constant of 20 minutes for the extractor. In this way a step change in a parameter, such as a flow rate, could be made by only changing the data card that had the value of $L$ for that parameter.

Control Equations of an Extraction Column

Once DIAN was successful in moving the system from one steady state to another, the control studies were initiated. The objective was to develop a predictive control strategy that would maintain the extract purity at a preassigned setpoint value by manipulating the reflux ratio. A diagram of the control strategy is shown in Figure 10.

The initial steady state condition of the extraction column that was used for the control studies was defined as follows.
Figure 10. Control strategy for extraction column
\[ \alpha = 0.12 \quad F = 3.0 \text{ liters/minute} \]
\[ \beta = 1.20 \quad x_1^f = 0.8M. \quad Y_E = 0.911 \]
\[ R = 4.00 \quad x_2^f = 1.0M. \quad Y_E^{sp} = 0.911 \]
\[ x_3^f = 3.0M. \quad X_R = 0.478 \]

The effectiveness of the different control schemes was judged by the column response to an upset in the feed concentration of \( Pr(NO_3)_3 \).

**Feedback control**

The first objective of the control studies was to develop a feedback control circuit for the column. This control circuit formed a basis of comparison for predictive control methods and also served as a feedback trimmer in conjunction with predictive control. A trimmer was needed because the predictive models were blind to all systems outputs and offset could occur if the model was not perfect.

The equation used for feedback control of the system was

\[ dR_f = G [-K_c \dot{\varepsilon} - \frac{K_c \varepsilon dt}{T_I}] \tag{22} \]

where  
\[ G = \text{a high gain factor} \]
\[ K_c = \text{proportional gain} \]
\[ \varepsilon = \text{error, } Y_E - Y_E^{sp} \]
\[ T_I = \text{reset time (minutes)} \]
\[ R_f = \text{reflux ratio from feedback control} \]
There was a negative sign associated with $K_c$ because a positive error required a negative change in the reflux ratio. The high gain factor was used as a weighting factor when the feedback control circuit was used as a feedback trimmer. The high gain factor was now set to unity during the studies of pure feedback control and values of $K_c$ and $T_i$ were chosen to produce a response curve with the customary one-quarter damping ratio.

**Predictive control**

Predictive control operates on the assumption that the inputs of a system that are expected to vary can be measured. The values of these inputs are fed to a model of the system that predicts the effect that these inputs will have on the system. This effect may be either the output of the system that must be controlled or the value of the manipulative variable that is required to maintain the output at the setpoint value. In either case, the predictive model cannot sense any outputs or any unmeasured inputs. The predicted effect is then used to control the system.

Predictive control operates in an open loop fashion between the measured inputs of the system and the system itself. It does not use any output information and therefore, cannot detect an offset. Feedback control is used to correct for any offset that may have occurred due to inaccuracies in the predictive model.
Reflux ratio prediction model  A multiple linear regression on the steady state data produced Equation 13 which was used to predict the value of the reflux ratio required to maintain the extract purity at the setpoint condition.

\[
\frac{dR_p}{\text{sp}} = m_1 d\alpha + m_2 d\beta + m_3 d\chi_{f} + m_4 d\chi_{22} + m_5 dY_E
\]

The predicted value of the reflux ratio changed immediately when any of the inputs changed and stopped changing when the inputs stopped changing. When a feedback trimmer was added, the value of the reflux ratio sent to the column was determined by Equation 23.

\[
dR = dR_f + dR_p
\]

The feedback signal was weighted by changing the value of the high gain factor G. Different values of this factor were tried until the response curve returned rapidly to the setpoint with no overshoot.

Extract purity prediction model  A multiple linear regression on the steady state data also produced Equation 14, which was used to predict the value of the extract purity that would exist for current values of all the inputs.

\[
dY_E = n_1 d\alpha + n_2 d\beta + n_3 d\chi_{f} + n_4 d\chi_{22} + n_5 dR
\]

The predicted value of the extract purity was compared to the setpoint and the error was sent to a controller. The output of this controller was a predicted value of the reflux ratio. When a feedback trimmer was added, the value of the reflux
ratio sent to the column was determined by Equation 23. Again, the effect of the trimmer was weighted by varying the value of the high gain factor.
RESULTS AND DISCUSSION

Static Equations

Equilibrium calculations

A multiple linear regression analysis was performed on the equilibrium data presented by Sharp and Smutz (13) for the \( \text{La(NO}_3\text{)}_3-\text{Pr(NO}_3\text{)}_3-\text{HNO}_3-\text{H}_2\text{O-TBP} \) system. The result was a response surface which defined the equilibrium behavior of the solutes and was described by Equation 1.

\[
y_{in} = a_{i1}x_{1n} + a_{i2}x_{2n} + a_{i3}x_{3n} + b_i \quad i=1,2,3 \quad n=1,2,\ldots,7
\]

The values of the regression coefficients are in Table 2.

Table 2. Equilibrium regression coefficients for rare earth data

<table>
<thead>
<tr>
<th>i</th>
<th>( a_{i1} )</th>
<th>( a_{i2} )</th>
<th>( a_{i3} )</th>
<th>( b_i )</th>
<th>( \sqrt{r^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.09066</td>
<td>-0.02369</td>
<td>-0.01031</td>
<td>0.07391</td>
<td>0.9431</td>
</tr>
<tr>
<td>2</td>
<td>0.01572</td>
<td>0.19735</td>
<td>-0.01606</td>
<td>0.07864</td>
<td>0.9701</td>
</tr>
<tr>
<td>3</td>
<td>0.19343</td>
<td>0.15132</td>
<td>0.28893</td>
<td>0.86448</td>
<td>0.9929</td>
</tr>
</tbody>
</table>

The nitric acid coefficients were negative in the two rare earth equations because nitric acid slightly suppressed extraction. The \( \text{Pr(NO}_3\text{)}_3 \) coefficient was negative in the \( \text{La(NO}_3\text{)}_3 \) equation because \( \text{La(NO}_3\text{)}_3 \) was less extractable than \( \text{Pr(NO}_3\text{)}_3 \), and also because \( \text{Pr(NO}_3\text{)}_3 \) suppressed the extraction of \( \text{La(NO}_3\text{)}_3 \). Obviously, \( a_{ii} \) was greater than \( a_{ij} \) (for
\( i, j = 1, 2, 3; i \neq j \) since each solute was mainly dependent upon itself.

**Steady state equations**

For the range of parameters considered, the extract purity depended only on the scrub flow ratio and the raffinate purity depended only on the extract flow ratio. This was shown in Figure 3. Plots of this type were also used in determining that the influence of both the feed rate and the nitric acid concentration in the feed on extract purity and raffinate purity was small. When the nitric acid concentration in the feed was increased from 2.0M to 4.0M, the extract purity contours shifted slightly to the left and the raffinate purity contours moved slightly upwards. Thus for a given set of flow ratios, when \( x_f^3 \) increased \( Y_E \) increased and \( X_R \) decreased but the change was not important over the range used in this work. Once the flow ratios \( \alpha \) and \( \beta \) were specified the value of the feed rate had a negligible effect on the position of either of the purity contours.

The valid range of operating conditions was found to be prescribed mainly by the two flow rate ratios and the reflux ratio. The inverse of Equations 11 and 12 can be written,

\[
S = \alpha \beta F/(1-\alpha \beta) \tag{24}
\]

\[
E = \beta F/(1-\alpha \beta) \tag{25}
\]

These equations hold only for \( 1-\alpha \beta > 0 \) and so combinations of \( \alpha \) and \( \beta \) had to lie beneath the hyperbola \( \beta = 1/\alpha \). Further, \( \alpha \)
α had to be less than about 0.15 and β less than 1.8 to avoid calculating negative concentrations of the solutes in the stages. The range of valid flow rate ratios is shown in Figure 11 and this corresponds to Regions I and II in Figure 2.

The reflux ratio was also restricted within this set of flow rate ratios. Graphs similar to Figure 5 showed that the reflux ratio was limited to low values for low values of the scrub section flow ratio and to high values for high values of the scrub section flow ratio. This is also shown in Figure 11.

Plots of equilibrium lines and operating lines were also made to check the values of the concentrations of the solutes with those reported by Sebenik, Sharp, and Smutz (11). An equilibrium line is a locus of points representing the equilibrium concentration of a solute in the phases in a stage. An operating line is a locus of points representing the concentration of a solute in the phases passing one another between stages. The scrub side operating line has a slope of α and the extract side operating line has a slope of 1/β. These two lines intersect at the feed concentration of the solute. Typical X-Y diagrams for one set of flow rate ratios and feed conditions are shown in Figures 12, 13, and 14. When the equilibrium line fell above the operating line, solute was extracted into the
Figure 11. Region of valid operating conditions
Figure 12. X-Y diagram for Pr(NO₃)₃ for reflux ratio = 0

Feed composition:
- La(NO₃)₃ = 0.8M
- Pr(NO₃)₃ = 1.0M
- HNO₃ = 3.0M
- F = 3.0 liters/min
- z = 0.1
- γ = 0.9
- R = 0
Feed composition: $\text{La(NO}_3\text{)}_3 = 0.8\text{M}$.
$\text{Pr(NO}_3\text{)}_3 = 1.0\text{M}$.
$\text{HNO}_3 = 3.0\text{M}$.

$F = 3.0$ liters/min.
$a = 0.1$
$b = 0.9$
$R = 2$

Figure 13. X-Y diagram for $\text{Pr(NO}_3\text{)}_3$ for reflux ratio = 2
Feed composition: $\text{La(NO}_3\text{)}_3 = 0.8\text{M}$.
$\text{Pr(NO}_3\text{)}_3 = 1.0\text{M}$.
$\text{HNO}_3 = 3.0\text{M}$.

$F = 3.0$ liters/min.
$\tau = 0.1$
$\theta = 0.9$
$R = 10$

Figure 14. X-Y diagram for La(NO$_3$)$_3$ for reflux ratio = 10
organic phase. When the equilibrium line was located below the operating line, the solute was scrubbed back into the aqueous phase. At zero reflux all the solutes were extracted in the extract section and were scrubbed back into the aqueous phase in the scrub section.

When the reflux ratio was increased, La(NO$_3$)$_3$ and HNO$_3$ still behaved in this manner but Pr(NO$_3$)$_3$ was extracted in both sections of the column and the separation was significantly improved. This phenomenon of one solute extracting in both sections is shown in Figure 13 and it has been observed in the laboratory (1). At high reflux ratios the equilibrium curve for La(NO$_3$)$_3$ had an unusual shape as shown in Figure 14. Curves similar in shape were also reported by Sebenik (10).

The range of concentrations obtained for La(NO$_3$)$_3$ compared very well with those reported by Sebenik, Sharp, and Smutz (11) in their sample problem. The concentration range of Pr(NO$_3$)$_3$ obtained was narrower but was located in the upper region of the concentration in this sample problem. Thus, the mathematical model did indeed display the characteristics particular to an actual rare earth extraction column.
Dynamic Equations

DIAN

The unsteady state equation, Equation 5, was solved for a variety of conditions.

\[
\frac{d\phi}{dt} = \phi x + T
\]  

(5)

Several runs, in which different parameters were changed were made to verify that the DIAN program was successful in moving the extraction column from one steady state condition to another. A steady state condition was assumed when the dynamic solution gave solute concentrations which differed by less than \(1 \times 10^{-5}\)M. from the steady state concentrations. This showed that the mathematical model of the extraction column was capable of handling upsets in flow rates, feed composition, and reflux ratio.

Control studies

The effectiveness of the different control schemes was judged by the response of the column to a change in the \(\text{Pr(NO}_3\text{)}_3\) feed concentration. An extract purity of 0.911 was used as the setpoint condition. A proportional-integral controller was developed as a basis of comparison for predictive control and the control parameters, \(K_c\) and \(T_I\), were chosen such that they produced a one-quarter damping ratio in the response curve (2).
Under the influence of feedback control, the extract purity returned to the setpoint slowly. About 2-1/2 hours was required after a 40% change in $x^f_2$ was introduced. An upset in the feed produced a maximum undershoot of 4% in the extract purity, $Y_g$. An uncontrolled response would have resulted in an 8-1/2% offset.

**Reflux ratio predictor** The first predictive control model used was the reflux ratio predictor described by Equation 13.

$$
\frac{dR_p}{dt} = m_1 d\alpha + m_2 d\beta + m_3 dx^f_1 + m_4 dx^f_2 + m_5 dy^E_{sp} \quad (13)
$$

The values determined for the regression coefficients, $m_k$, are in Table 3.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$m_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-6.72298</td>
</tr>
<tr>
<td>2</td>
<td>0.44409</td>
</tr>
<tr>
<td>3</td>
<td>12.52123</td>
</tr>
<tr>
<td>4</td>
<td>-20.48387</td>
</tr>
<tr>
<td>5</td>
<td>44.0060</td>
</tr>
<tr>
<td>$\sqrt{r^2}$</td>
<td>0.9851</td>
</tr>
</tbody>
</table>

The value of reflux ratio to the column was the sum of the output from the reflux ratio predictor and the contribution from the feedback control circuit. At the beginning of an
input change, the feedback signal was zero and had no effect on the system. However, the predicted value of the reflux ratio changed as soon as the input disturbance occurred, and it acted before the upset could produce an effect on the output. Once the inputs stopped changing, the predicted value of the reflux ratio remained constant and feedback control alone returned the column to steady state.

The speed and overshoot of the response was controlled by the high gain factor, $G$. For $G=1$ the response was too slow and for $G=10$ the response cycled with a damping ratio close to unity. A value of $G=2.5$ produced the best response and returned the extract purity to the setpoint in about 30 minutes with a maximum overshoot of 1.04%. This response is compared to feedback control in Figures 15 and 16.

When the setpoint was changed to 0.950, both feedback control and predictive control brought the column to steady state in about the same time. However, predictive control had a faster initial response to the setpoint change.

**Extract purity predictor** The predictive control model based on extract purity was described by equation 14. The values of the regression coefficients are given in Table 4.
Figure 15. System response to an upset in the feed composition
Figure 16. Response of control variable to an upset in the feed composition.
\[ dy_E = n_1 d\alpha + n_2 d\beta + n_3^f dx_1 + n_4^f dx_2 + n_5 dR \] (14)

Table 4. Regression coefficients for extract purity predictor

<table>
<thead>
<tr>
<th>i</th>
<th>( n_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03084</td>
</tr>
<tr>
<td>2</td>
<td>0.01426</td>
</tr>
<tr>
<td>3</td>
<td>-0.04166</td>
</tr>
<tr>
<td>4</td>
<td>0.20988</td>
</tr>
<tr>
<td>5</td>
<td>0.01986</td>
</tr>
<tr>
<td>( \sqrt{r^2} )</td>
<td>0.9901</td>
</tr>
</tbody>
</table>

The predicted value of extract purity from this model was sent to a controller which, in turn, generated a value for the reflux ratio. In this way the reflux ratio was changed before the upset had propagated down the column.

The value of the reflux ratio sent to the extraction column was the sum of the outputs from feedback control circuit and the extract purity predictive control model. When an input changed, the predicted value of the extract purity changed immediately and continued to change as the reflux ratio moved to correct for the disturbance. The problem that arose was that for small values of the high gain factor there was a time when the predictive control reflux signal and the feedback control reflux signal were equal in magnitude but opposite in sign. If this occurred
when the extract purity was fairly constant there would be no change in the reflux ratio in the column. Hence, there would be no further change in either predictive control or feedback control and offset would occur. As the high gain factor was increased, the amount of offset decreased and the feedback trimmer approached bang-bang control.

Results of this model were compared to the other predictive control model and feedback control in Figures 15 and 16. The oscillations in the reflux ratio versus time curve indicated the presence of bang-bang control. For G=500 the maximum undershoot was about 0.066% and the extract purity was essentially at the setpoint after 15 minutes.

When the setpoint was changed to 0.950 the extract purity predictor could not control the column because the reflux ratio could not be confined within limits. Presently, work is being done by Torrey\(^1\) to develop a limiter for the DIAN simulation program that would permit one to set maximum and minimum limits on any variable. Once this is done the reflux ratio can be maintained between predetermined upper and lower limits.

The proposed predictive control models returned the

simulated extraction column to the specified setpoint between 5 and 10 times faster than conventional feedback control. The importance of this improvement is magnified when considered in the light of recent advances in the utilization of rare earths. As the need for the separation and purification of rare earths increases, so does the need for better control. The large scale production of rare earths will demand control strategies that can handle start-up procedures efficiently, as well as unexpected upsets in the normal operation of an extractor. The basic groundwork of such a control strategy is presented in this work and the next step is its implementation.

When this control technique is used on an extractor, the predictive model needs an accurate measure of the solute concentrations in the feed. This may be done by an on-line spectrophotometric analysis which is presently being developed for different rare earth salts. The solvent removal, which was not studied in this work may be accomplished by either evaporation or distillation.

Even though a limited range of equilibrium data was used in this work, the equilibrium equation obtained could be used in the implementation or perhaps more data could be taken over a wider range of solute concentrations. Better equilibrium equations could be obtained by dividing the equilibrium data into sections and using a linear regression
over each section. Also, a non-linear regression over the whole range of concentrations will yield an equilibrium equation. A better extract purity predictor can be obtained by considering the reflux ratio in the form of \( \frac{R}{R+a_0} \). The best value of \( a_0 \) can be determined by a one dimensional search technique using the residual sum of squares as an objective function.

Even though some slight difficulties presently exist, they are not insolvable and predictive control appears to have a use in the future of the rare earth industry. The underlying theory of such control and its effect have been presented in this work.
CONCLUSIONS

1. Even though the equilibrium regression model was a linear regression, it reflected many characteristics of the \( \text{La(NO}_3\text{)}_3-\text{Pr(NO}_3\text{)}_3-\text{HNO}_3-\text{H}_2\text{O-TBP} \) system. The signs of the regression coefficients were consistent with the extraction behavior of the solutes.

2. The concentration and range of concentrations of the rare earths produced by the steady state equations compared very favorably with those reported by Sebenik, Sharp and Smutz.

3. The DIAN digital simulation program was successful in handling a problem with over 360 components. DIAN moved the simulated extraction column from one steady state condition to another with errors of only \( 1 \times 10^{-5} \) M. between the calculated steady state concentrations and those reached by letting the dynamic equations approach steady state.

4. Both predictive control models easily surpassed feedback control in effectiveness. Of the two predictive models proposed, the extract purity predictor gave a better response but a bang-bang trimmer had to be used to prevent offset. However, only the reflux ratio predictor was capable of handling a setpoint change with the present
DIAN program. Once DIAN can be used to set upper and lower limits on a variable, setpoint changes with the extract purity predictor model can be studied.
RECOMMENDATIONS

1. There are several ways to obtain a more accurate expression for equilibrium relationships between the solutes. More equilibrium data are needed over a wider range of rare earth concentrations.
   A. A segmented linear model can be used to obtain an analytical expression of the equilibrium relationships of the solutes. This would divide the concentration range into sections and a linear regression analysis would be performed in each section.
   B. A non-linear representation of the equilibrium data can be developed over a wide range of experimental data.

2. Once the equilibrium equations have been refined, the model of the system could be expanded and made more versatile.
   A. More stages should be incorporated to obtain a more realistic separation.
   B. Startup procedures using different control schemes should be investigated.

3. The extract purity predictor model would be more accurate if it were not linear with respect to the reflux ratio. One possible alternative would be in the form of $R/(R+a_o)$.  


The best value of $a_0$ could be determined by a one
dimensional search technique using the residual sum of
squares as an objective function.

4. The bang-bang trimmer could be replaced in two ways.
   A. A bias function might be developed that would
      select either feedback control or predictive control
      depending on the input conditions. If the inputs
      are changing this bias function would choose
      predictive control. When the predictive response
      begins to level out the bias function would cause a
      transfer to feedback control and no offset would
      occur. The optimal switching point could also be
      investigated using present optimal control theories.
   B. An adaptive control system should be developed that
      would continuously update the extract purity model
      by changing the regression constants.
LITERATURE CITED


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