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THE MONITORING AND CONTROL OF TRUEX PROCESSES

VOLUME ONE - THE USE OF SENSITIVITY ANALYSIS TO DETERMINE KEY PROCESS VARIABLES AND THEIR CONTROL BOUNDS

by

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ABSTRACT

The Generic TRUEX Model (GTM) was used to design a flowsheet for the TRUEX solvent extraction process that would be used to determine its instrumentation and control requirements. Sensitivity analyses of the key process variables, namely, the aqueous and organic flow rates, feed compositions, and the number of contactor stages, were carried out to assess their impact on the operation of the TRUEX process. The results of these analyses provide a basis for the selection of an instrument and control system and the eventual implementation of a control algorithm. Volume Two of this report is an evaluation of the instruments available for measuring many of the physical parameters.

Equations that model the dynamic behavior of the TRUEX process have been generated. These equations can be used to describe the transient or dynamic behavior of the process for a given flowsheet in accordance with the TRUEX model. Further work will be done with the dynamic model to determine how and how quickly the system responds to various perturbations. The use of perturbation analysis early in the design stage will lead to a robust flowsheet, namely, one that will meet all process goals and allow for wide control bounds. The process time delay, that is, the speed with which the system reaches a new steady state, is an important parameter in monitoring and controlling a process. In the future, instrument selection and point-of-variable measurement, now done using the steady-state results reported here, will be reviewed and modified as necessary based on this dynamic method of analysis.

SUMMARY

Sensitivity analyses were carried out to assess how the loss of one or more stages and variations in flow rates and feed compositions would affect TRUEX process goals. With these analyses, an operating range for every case study was obtained. Operating within this range guarantees that the process still maintains its performance. Based upon these analyses, control bounds are made on the process variables requiring them. Although this study related specifically to given process goals in a specific TRUEX flowsheet, these guidelines can be

applied for controlling any TRUEX process. Instruments to monitor and control every variable studied are recommended in Volume Two. Flow rates and pH levels can be monitored and controlled by present technologies. However, the existing technology is inadequate for monitoring actinide and nitrate concentrations, especially on-line. Analytical techniques are being developed at other DOE laboratories in these areas. It should be noted that the sensitivity analyses presented herein are confined to the perturbation of one or more variables at steady state. Future efforts should include perturbation analyses of multiple variables for either a steady-state or a dynamic system.

In general, the success of a specific TRUEX process will be achieved by properly maintaining the organic and aqueous flow rates and the feed composition and by monitoring and controlling the plutonium and americium concentrations. While we expect to develop a monitoring and control system for the various flow streams and their compositions based on existing technology, the measurement and control of transuranic elements, especially at low concentrations, present a formidable task. Volume Two is devoted to establishing the control of a TRUEX process flowsheet based on a set of typical operating conditions. By examining the status of the process variables (e.g., mass flow rates, concentrations, and radioactivities at critical locations), we can determine operating limits, the sensitivity requirements for various instruments, the need for duplicate instrumentation (redundancy), and the appropriate control functions.

I. INTRODUCTION

As a part of developing the instrumental control and monitoring requirements of the TRUEX process, we have focused on its control needs, which include feed and product flow rates and concentrations of the transuranic (TRU) elements from TRU-containing waste and high-level waste (HLW). For this study we chose a waste composition typical of that generated during plutonium scrap recovery operations at the Westinghouse Hanford Plutonium Finishing Plant (PFP). We did that for two reasons: (1) it is typical of many such TRU wastes found throughout the DOE complex from the recycling, purification, and recovery of plutonium, and (2) its relatively simple composition makes the sensitivity analysis easier and quicker.

This report is divided into three parts. In the first section we describe the TRUEX process and the goals associated with implementing it. In the second, we present a brief review of the wide field of process control for readers unfamiliar with this field. Those who are familiar with process control may wish to go directly to Sec. III, where we describe how control system analysis is applied to the TRUEX process. In Sec. III, we first introduce the Generic TRUEX Model (GTM). Next, we consider the equations that govern it; and finally, we use the GTM to perform a sensitivity analysis. In Sec. III.C, perturbations to key process parameters such as flow rates, feed compositions, and number of stages are presented. As a result of this sensitivity analysis, an operating range in which the process maintains its goals is derived and is presented in a graphical and tabular form. Recommendations of instruments to monitor and control the process using this operating range are made in Volume Two.

A. The TRUEX Process

When the TRU content of a waste stream can be lowered to below 100 nCi/g of solid, the waste can be classified as nonTRU, and, if ^{137}Cs and ^{90}Sr levels are acceptable or can be reduced to an acceptable level, it will be eligible for near-surface or greater-confinement disposal. In the case of PUREX high-level waste (HLW), this would mean that only the TRU-concentrate product (≤ 1 wt % of the initial mass) may need to be placed in deep geologic disposal. In addition, plutonium recovery is often highly desirable because plutonium can be separated from americium and uranium during stripping of the loaded TRUEX solvent.

The key ingredient in the TRUEX solvent extraction process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated OϕD[iB]CMPO, but is generally called simply CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent, typically a normal paraffinic hydrocarbon (NPH), to formulate the TRUEX solvent.

The potential for successfully implementing TRUEX processes at the various DOE nuclear production and processing facilities is substantially enhanced by carrying out the processes in centrifugal contactors. The small size, high efficiency, and easy maintenance of centrifugal contactors allow retrofitting of a TRUEX process into an on-line facility in existing space. Also, the short contact times in the centrifugal contactor enhance the separation of TRU elements from iron and ruthenium.

Figure 1 is a flowsheet for a typical TRUEX process. As shown in this figure, the organic solvent passes from left to right and the aqueous solute from right to left. In this example, there are nineteen stages* divided into four sections.** The first section, the extraction section, contains four stages. The extraction feed entering at stage 4 is the TRU-containing waste stream. The TRUEX solvent enters the process at stage 1. As the TRU-containing waste solution travels from stage 4 to stage 1, it becomes decreasingly lower in TRU content in each subsequent stage. Concurrently, the concentration of TRU elements in the TRUEX solvent increases as the solvent progresses from stage 1 to stage 4.

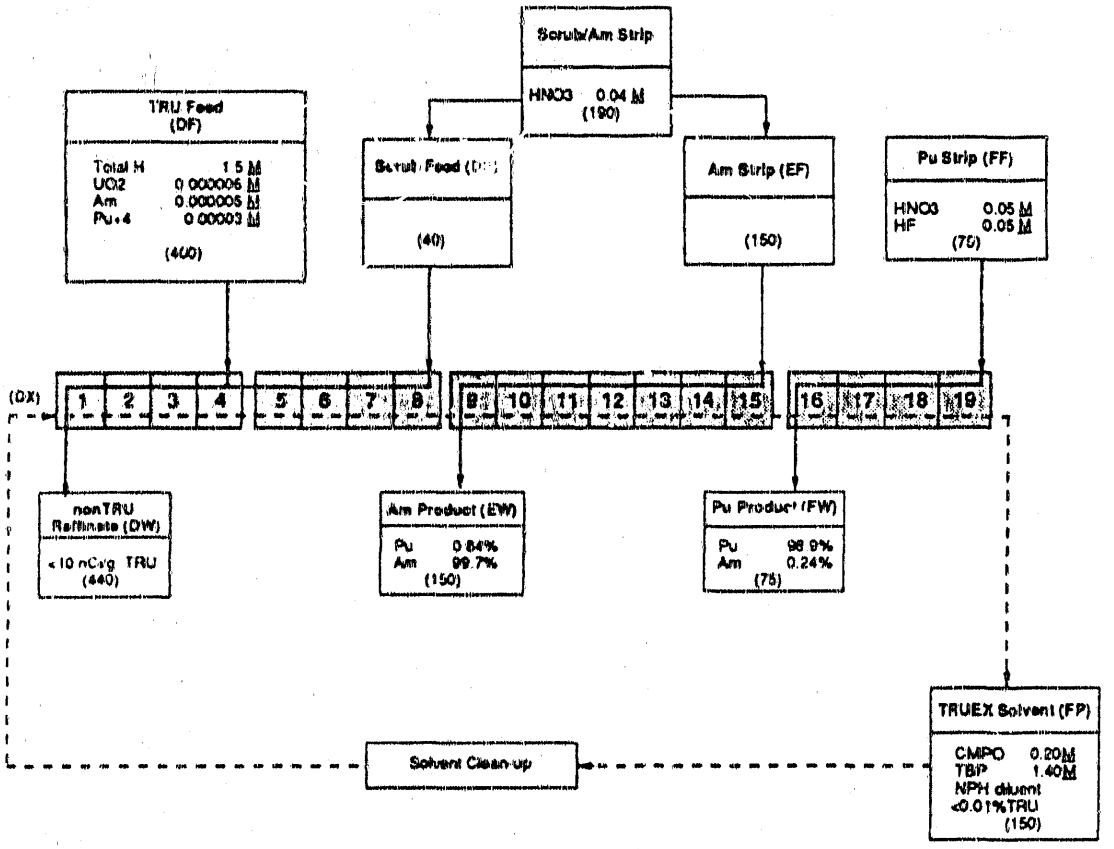

Fig. 1. Flowsheet for Base Case Tests with Synthetic PFP Waste. Numbers in parentheses are flow rates and may be expressed in any units of volume per unit time. All other flow rates are relative to the TRU feed (DF).

The solvent next enters the scrub section. The objective of this section (stages 5 through 8) is to wash back impurities, which are either entrained or dissolved in the solvent, and to lower the concentration of nitric acid in the solvent so that americium will be effectively stripped in the

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*A stage in a countercurrent solvent-extraction process performed in a centrifugal contactor is a physical unit where a single equilibration between two phases takes place.

**A section is identified by the incoming aqueous phase that enters it at its last stage and either exits at the first stage or continues on to the next section. In the example presented in Fig. 1 there are four sections, identified in terms of four incoming aqueous-feed streams.

first strip section. Note that no effluent stream leaves the process at stage 5; the aqueous stream from the scrub section mixes with the extraction feed in stage 4. The scrub feed enters the process at stage 8.

Stages 9 through 15 make up the first (or americium) strip section. In this section, americium, curium, and rare earth elements are removed from the solvent and exit in the americium product stream. As the solvent moves from stage 9 to stage 15, its concentration of these elements decreases from stage to stage. As the aqueous phase moves from stage 15 to stage 9, its concentration of these elements increases. The aqueous product stream exits the process at stage 9.

Stages 16 through 19 make up the second (or plutonium) strip section. In this section, plutonium and any residual americium left from the preceding section are removed from the solvent into the aqueous strip solution. The plutonium product stream exits at stage 16 and the depleted organic solvent at stage 19. In an actual process, the solvent would be further processed through a series of solvent cleanup sections before being recycled to stage 1. These sections are denoted by the box on the organic recycle line (Fig. 1).

The TRUEX process was invented in the Chemistry (CHM) Division of Argonne National Laboratory and is being developed in the Chemical Technology (CMT) Division. Westinghouse Hanford Company (formerly, Rockwell Hanford Operations) used the TRUEX process to treat the PFP waste and is considering it for use with stored high-level waste (HLW), neutralized cladding removal waste (NCRW), and complexant concentrate waste (CCW). The process has been demonstrated at Hanford in Argonne-designed 4-cm centrifugal contactors using actual PFP waste. Construction of a plant-scale facility using an Argonne-designed 10-cm contactor to treat wastes in PFP is planned.

Development of an optimized TRUEX process for a specific application will depend on the flowsheet designed for that application. An important factor is the selection of appropriate monitoring instruments for the critical process variables and the implementation of control strategies based on the inherent characteristics of multistage centrifugal contactors. The selection and placement of sensors will depend on both the static and dynamic behavior of the multicomponent separation process. Successful development of a control system will require on-line monitoring of such key variables as flow rate, solution composition, and α activity levels. Since the concentration of TRU elements in the TRUEX feed solution is low and will be reduced in the raffinate by 10^2 to 10^6, on-line monitoring of their concentrations in the effluent streams may be, in many cases, beyond the capability of existing instruments.

Currently, we are evaluating the instruments required to monitor and control the TRUEX processes and assessing via mathematical modeling the interrelationship among the various components and process variables. One of our eventual goals is to develop a knowledge-based computer (expert) system that will be used to (1) analyze potential and hypothetical failure modes, (2) study propagation of failure modes and their consequences, (3) select instruments for detecting fault-initiating events, and (4) control the operations of an optimized, feed-specific TRUEX process.

B. Goals of the TRUEX Process

An important consideration in designing a system to monitor and control the TRUEX process is to look at what the process is supposed to do: which functions are priorities, which are useful but not essential to have, and which are unimportant to the facility needs. The possible functions and goals of the TRUEX process are listed below in a generally accepted order of priority:

1. Reducing the TRU concentration in the extraction raffinate to less than 100 nCi/g of solid, enabling the solidified form to be classified as a nonTRU low-level waste. (A concentration of <10 nCi/g to make it less than class C low-level waste has also been stated as a process goal.)

2. Recovering ≥99% of the plutonium in a separate product stream for recycling in a plutonium purification process.

3. Recovering the remaining plutonium and other TRU elements in a waste stream suitable for producing a waste form certifiable for the Waste Isolation Pilot Plant (WIPP).

4. Recovering >99.99% of the TRU-element mass in the strip product streams, thus allowing the solvent cleanup sections to act as a sink for solvent degradation products and any uranium extracted into the solvent.

5. Concentrating the plutonium and other TRU elements in their respective product streams to greater than their initial feed concentrations.

6. Purifying plutonium in the plutonium product stream.

Item 1 is certainly the primary function of the process. TRUEX processes are designed with this goal in mind, and the monitoring and control of the system are intended primarily to meet this function. Because of the high salt and acid concentrations in potential feeds to the TRUEX process, the final volume of solid TRU waste will be typically reduced by 20 to 200 times due to TRUEX processing. If immediate disposal is not intended, converting the bulk of the waste to nonTRU is also an important consideration if storage space for TRU waste is in short supply.

Item 2, recovery of plutonium, was once the highest priority, but it is less important currently. However, if plutonium inventories need to be replenished, there are large quantities in stored wastes. Even at the low concentrations found in most waste streams, their large volumes contain significant quantities of plutonium.

Items 3 and 5 are also important considerations in designing a TRUEX process. Item 3 is designed into the process flowsheet and maintained during processing by monitoring feed, interstage, and effluent concentrations and by controlling feed flow rates and, perhaps, strip- and

scrub-feed compositions. Item 5 is designed into the process by setting flow rates and the number of strip stages appropriately.

Item 4, highly efficient stripping of the TRUEX solvent, is designed into the process and is an important concern for monitoring and control of the process. It is important for (1) keeping the TRU elements out of the solvent wash, thus allowing that section to function as a strip for solvent degradation products and uranium, and (2) maintaining a low TRU content in the solvent before its recycle to the extraction section, which is critical to producing a nonTRU raffinate.

Item 6 is a secondary consequence of specific TRUEX processing and is not a design criteria to be monitored or controlled.

Figure 1 was designed to meet items 1 to 4 above for a typical composition of waste generated from the Plutonium Reclamation Facility at Hanford. (See Sec. III.C.) By using a split scrub/strip section, the TRU waste stream (the americium product stream) could have been further concentrated by pinching americium in that section. Americium can build up in the strip section by having a very low americium D value where the solvent leaves the section and a very high americium D value where the aqueous phase leaves the section. In other words, the americium organic and aqueous concentrations exiting the section are low, leaving americium trapped in this section. The trade-off for such a modification is the need for more contactor stages in the scrub/strip and extraction sections. Generating a purified plutonium stream was not considered important. Effects of perturbations in flow rates and feed compositions were analyzed in regard to meeting specific process specifications. The needs and the means for monitoring and control of TRUEX processes in general were evaluated by analyzing this specific case. The means and equipment available to monitor and control solvent extraction processes are discussed in Volume Two.

II. CONTROL SYSTEM ANALYSIS

During the past few years, process control has evolved from an art to a science. No longer do control engineers rely only on rules of thumb to calculate and control equipment. Instead, steady-state and dynamic analyses are used to help select equipment. These tools enable engineers to improve the performance of equipment, to optimize productivity or product quality, and to reduce the investment in control instruments.

In spite of the complexity of a chemical process such as TRUEX solvent extraction, it is fairly easy to achieve reasonably good control. The weakest part of designing a control system is usually the interpretation of the dynamic data being generated by the process. The responses of the controllers, valves, and measuring devices may be known to within 5 to 10 percent; however, the errors in predicting dynamic behavior for the process are usually two or three times greater [HARRIOTT]. Fortunately, computers can be used to construct fairly accurate models for dynamic systems. These models simulate a large number of cases at significantly lower costs. The information obtained can then be used to analyze the potential operating conditions at which a failure can occur and to select process equipment and measuring and control instruments.

Process control is a wide field. A few important concepts will be explained in detail to facilitate the understanding of this report by the uninitiated reader. Further information can be obtained in any of several well-known process control textbooks [BALCHEN, HARRIOTT, and JOHNSON].

A. The Process Model

Many physicochemical processes are extremely complicated, and considerable effort is required to construct mathematical models that will adequately simulate the dynamics of the actual system. It is a fairly simple task to formulate mathematical equations that govern the physicochemical and thermodynamic laws of a particular process. What is not simple is obtaining a solution to these equations. Engineers analyze the complex system and propose simplified versions that can be used to describe a real process with minimum error. Errors in modeling are usually accounted for in the design and control of a process.

With the recent development of computer aided design (CAD), engineers can test several different models and select the one that best describes the process. Testing different control strategies on the same process to find the best one can also be done using CAD.

1. Steady-State and Dynamic Models

Over the years, the design of most chemical processing equipment has been based on steady-state models. From the standpoint of process control, both steady-state and dynamic characteristics are important. However, because they are difficult to calculate, dynamic considerations have been relegated to very minor design considerations. Dynamic characteristics have been seen as those that come with the system instead of as a result of a particular design requirement.

It is helpful to visualize the steady-state characteristics as a special case of the dynamic model. Study of a nonlinear dynamic chemical process often requires extensive calculations, and the representation of the results becomes complicated and confusing. It is then customary to combine the description of both steady-state and dynamic behavior. The steady-state characteristics are based on constant operating conditions, and the dynamic characteristics are based on small perturbations around a fixed operation point.

Continuous chemical processes typically operate with a constant set point for hours or days at a time. Changes in set points are usually minor adjustments. Perturbations in the system usually cause larger errors than changes in set points. These perturbations can be presented in forms such as uncontrollable flows, temperatures, pressures, and concentrations. The dynamic model is traditionally associated with the response of the control system to a perturbation. A step change is usually used to represent the disturbance. Because a step change is the most severe type of disturbance, it shows the maximum error that can occur to a given perturbation. If several control systems or control settings are being compared, the system with the best response to a step-change disturbance generally will have the best response to random fluctuations of that variable.

2. Process Time Delay

An important parameter that is sought in a dynamic model of a process is the process time delay. The process time delay is defined as the time required for output variables to respond to a given change, either a process perturbation or a set-point change. Instrument selection, as well as the actual point of measurement, depends on this parameter.

3. Process Variables

The number of variables in a chemical process such as TRUEX is by its nature significantly large. It is unreasonable as well as costly to try to control every variable in a given process. A sensitivity analysis is usually performed to identify which variables are more susceptible to perturbations in the system. Once the principal process variables are identified, the direct observation and control of these variables need to be studied. If a given variable is not observable or controllable, other methods of indirectly measuring and influencing this variable need to be examined.

B. Instrumentation

The performance of the control system is directly proportional to the quality of the measurement of the control variables. The choice of instruments involves compromises among important factors such as accuracy, sensitivity, precision, cost, ruggedness, and maintainability.

A large amount of the information is available in the technical literature from instrument manufacturers. This literature is very useful in learning the capabilities and limitations of various sensors and transducers, and it is analyzed in Volume Two.

C. Lag in Process Control Systems

No physical system responds instantaneously to a change due to the inherent lag, which may be classified as: process lag, measurement lag, and transmission lag. They dictate the dynamic characteristics of a process variable and must be taken into account when selecting instruments.

D. Expert Systems

In recent years, special emphasis has been placed on the development of expert systems. The expert systems use combinations of many sophisticated techniques now available to provide algorithms that can control the process under abnormal operating conditions. They must be able to diagnose troubled conditions and prescribe corrective actions.

III. CONTROL SYSTEM ANALYSIS APPLIED TO THE TRUEX PROCESS

Three major steps are necessary in selecting a control system for any given process. The first step involves the identification of the process variables needed to be monitored and the range to which they need to be controlled. The second step, instrument selection, can be done once step 1 is completed. This step involves the selection of the instrumentation candidates that might monitor and control the process variables in the range found in the first step. In the third step, the instruments selected in step 2 are tested to see which ones do a better job at monitoring and controlling the process variables.

To accomplish these steps, the following work was done. The steady-state model of the process was used to determine the variables that need to be monitored and the range to which they need to be controlled. This was accomplished by using the Generic TRUEX Model (GTM), which is briefly described in the next section. A base case was selected and perturbations to some of the system variables were examined. After an analysis of the perturbations, monitor and control bounds were established. This type of analysis is commonly known as a "sensitivity analysis."

After the bounds on the monitor and control variables were established, a literature review was done to determine which of the commercially available instruments could perform the given task. In this selection, the bounds obtained for the given variable were taken into consideration as well as the environment in which this instrument needs to be used. They are presented in Volume Two.

The last step involves testing the instruments selected and will be accomplished in the future by using the dynamic model of the GTM. With this model, several control system algorithms and instrument choices will be tested before being actually implemented.

A brief description of the GTM model is presented below to familiarize the reader with the model used in the sensitivity analysis. Then, the dynamic response of the GTM is discussed. Although this will be the last step (step 3) needed in the selection of a control system, we have included it before the sensitivity analysis (step 1), since the steady-state model used in the sensitivity analysis is just a special case of the more general dynamic model.

A. Introduction to the Generic TRUEX Model

The Generic TRUEX Model was used in this study to develop criteria for monitoring and controlling a TRUEX process. It was developed to generate site-specific flowsheets to (1) establish a TRUEX process for specific waste streams, (2) assess the economic and facility requirements for installing the process, and (3) improve, monitor, and control on-line the TRUEX process. The second-generation GTM is now available to the DOE processing and production community as a tool for the design and assessment of TRUEX processes for specific waste streams. This model is under continual improvement.

The GTM is composed of three sections that are linked together and executed by Excel software. The heart of the model is the SASSE (Spreadsheet Algorithm for Stagewise Solvent

Extraction) code, which calculates multistaged, countercurrent flowsheets based on distribution ratios calculated in the SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section. The third section of the GTM, the SPACE (Size of Plant and Cost Estimation) section, estimates the space and cost requirements for installing a specific TRUEX process in a glovebox, shielded-cell, or canyon facility.

The SASSE section was developed to allow the design and detailed evaluation of proposed flowsheets in conjunction with distribution ratios generated in SASPE. In addition to establishing that each feed component reaches its design composition in the extraction raffinate and product streams and providing the compositions of the organic and aqueous solutions in each stage of the flowsheet at steady state, SASSE can be used to identify key points for process monitoring and control. An early version of SASSE [LEONARD-1987] was used to assist Westinghouse Hanford in countercurrent testing of the TRUEX flowsheet for PFP waste [LEONARD-1985] using actual PFP waste.

The SASPE section of the GTM will calculate distribution ratio (D) values for each aqueous-phase composition from user-specified feeds (feed menu) or from stage compositions generated in SASSE. Many modules in the SASPE section are necessary for calculating D values for all conceivable aqueous-phase and TRUEX-solvent combinations.

B. Dynamic Response of GTM

To develop a control algorithm that will enable the selection of monitor and control instruments, we constructed a dynamic model using the new (2.1) version of the GTM. This version employs a new model for the mass and flow balances in the SASSE section, which calculates an analytical steady-state solution in a single step [LEONARD-1990]. This SASSE section can be used independently when the appropriate distribution ratios or equations for calculating these ratios are specified by the user, or, if the worksheet is used within the GTM, the distribution ratios are calculated by SASPE. Our problem was to analyze the new SASSE model for the dynamic response of the organic- and aqueous-phase compositions to changes in the inlet compositions or the flow rates of the TRUEX process.

Because of the complexity of the GTM model, we will first introduce the concept of process dynamics for a much simpler system. The most elementary of the simple systems is the first-order transfer stage [JOHNSON]. An example of a first-order transfer stage is the continuous stirred-tank reactor (CSTR), in which mixing occurs, and in which a simple first-order chemical reaction can take place (see Fig. 2).

Fig. 2. CSTR Performing as Perfect Mixer

For the case of a perfect mixer, the volumetric in-flow and out-flow rates are equal to q, and the respective stream compositions are x and y, expressed in moles of solute per unit volume. A material balance on the solute yields

$$\frac{Vdy}{dt} = qx - qy \tag{1}$$

or, simply, accumulation equals in-flow minus out-flow. V is the volume of liquid in the reactor. Perfect mixing is assumed, namely, effluent concentration is taken to be the same as the average in the tank.

For most problems in process dynamics, it will be advantageous to write the dynamical equations in terms of a deviation variable rather than the absolute values of the variable. This can be accomplished as follows: for steady-state conditions, Eq. 1 can be written as

$$q\, x_{ss} - q\, y_{ss} = 0 \tag{2}$$

where the subscript ss denotes steady state.

We can divide Eq. 1 by q and set T equal to V/q. For this system, the time constant T is the average holdup time in the reactor, or the time required for a volume equal to the liquid volume in the reactor to flow through the reactor. Then, subtracting Eq. 2 from Eq. 1, we obtain

$$T\, \frac{d\left[y - y_{ss}\right]}{dt} + \left[y - y_{ss}\right] = \left[x - x_{ss}\right] \tag{3}$$

By defining the deviation variable Y as $y - y_{ss}$ and X as $x - x_{ss}$, we obtain

$$T\, \frac{dY}{dt} + Y = X \tag{4}$$

The form of Eq. 4 is known as a first-order transfer stage, in which Y is the response variable to the forcing function X. If we abruptly change the concentration in the feed to the tank to some new steady-state value A units different from the initial condition, the forcing function X will be a step function of magnitude A. Therefore, Eq. 4 becomes

$$T\, \frac{dY}{dt} + Y = A \tag{5}$$

whose solution is

$$Y = A\left[1 - e^{-t/T}\right] \tag{6}$$

This solution can be verified by direct substitution of Eq. 6 into Eq. 5 and using the boundary condition Y = O at t = 0.

The response to the forcing function A is shown in Fig. 3 for time intervals equal to the time constant T. The recovery that occurs can be expressed as a fraction of the forcing function at the start of the interval, that is, as $1 - e^{-1}$ or 0.632. In other words, the response in any time interval T, after the initial step change, covers 63.2 percent of the amount left to be covered at the start of the time interval.

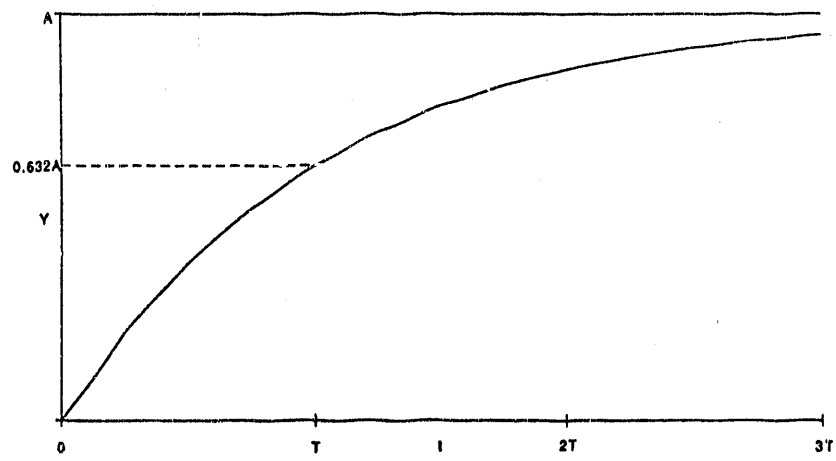

Fig. 3. First-Order Step Response of Y to a Change in Forcing Function A. (Time intervals = T)

The quantity accompanying the time variable, in this case -1/T, is known as the eigenvalue of the system and is defined as λ. Using this λ, Eq. 6 becomes

$$Y = A\left[1 - e^{\lambda t}\right] \tag{7}$$

The relationship between the eigenvalues and the stability of the system can be seen in Eq. 7. For this system the values of λ (-1/T) are negative; therefore, the system is guaranteed to reach the new steady state. If the time constant is small (so that λ is large), the system will respond faster; conversely, if the time constant is large, the system will respond slower.

In complex systems, multivariable interaction and nonlinearity often complicate the solution of the differential equations that describe the dynamic behavior of the process. In many

cases, computational algorithms can be used to aid in the solution, especially to calculate the eigenvalues or time constants of the system, which in the majority of cases are not as obvious as in the CSTR mixers.

In the following sections we will show how a similar dynamic analysis was done on the much more complex system that describes a TRUEX process. In this analysis, all the equations needed to calculate the eigenvalues, as well as the response of the system to a step-forcing function, were derived. Numerical calculations can easily be performed once a flowsheet is specified. As a result of this analysis, the process time delays can be identified, helping in the selection and placement of monitoring and control instruments. Also, several control systems or control settings can be compared by evaluating which one responded more rapidly to a perturbation.

1. Analysis for Changes in Feed Composition with No Change in the Input Flows

The GTM model has been analyzed for a dynamic behavior only for changes in feed-stream compositions with constant flow rates. Flow rates are considered environmental variables, i.e., totally observable and controllable. Therefore, a perturbation in the flow can easily be detected and corrected by on-line mechanisms. If the TRUEX process directly threatens the raffinate of another process, changes in composition of the aqueous feed to the extraction section, in particular, would be beyond immediate control and therefore represent a perturbation to the system.

The new GTM model analyzes the solvent extraction in both continuous and differential contacting equipment as if they were stagewise processes [LEONARD-1990], where the back mixing or other-phase carryover for either phase can be large.

To obtain equations for the component concentrations for high amounts of back mixing, the input data indicated on the schematic of a column stage (Fig. 4) must be specified. The variable $f_{o,i}$ is the fraction of aqueous phase in the organic phase leaving the stage, and $f_{a,i}$ is the fraction of organic phase in the aqueous phase leaving the stage. We also need to specify the volumetric flow rates for the organic and aqueous feeds to stage i, $q_{f,o,i}$ and $q_{f,a,i}$, respectively, and the fraction of the organic and aqueous streams from stage i that are taken as effluents, $f_{e,o,i}$ and $f_{e,a,i}$, respectively. Finally, the molar concentration of component j given for any aqueous or organic feed at stage i, $x_{f,i}$ and $y_{f,i}$, respectively, needs to be known.

Based on the known (input) data shown in Fig. 4, the unknown flows, $q_{o,i}$ (the organic flow rate out of stage i) and $q_{a,i}$ (the aqueous flow rate out of stage i) can be calculated. Since we are interested in changes in feed composition with no changes in the input flows, $q_{o,i}$ and $q_{a,i}$ can be obtained from the steady-state solution given in [LEONARD-1990].

With $q_{o,i}$ and $q_{a,i}$ calculated for all m stages and the molar concentration of component j given for any aqueous or organic feed to each stage i ($x_{f,i}$ and $y_{f,i}$, respectively), the unknown concentrations for the aqueous and organic phases in stage i (x_i and y_i, respectively, i = 1,...,m) can now be determined. Note that while this derivation is done for component j, it

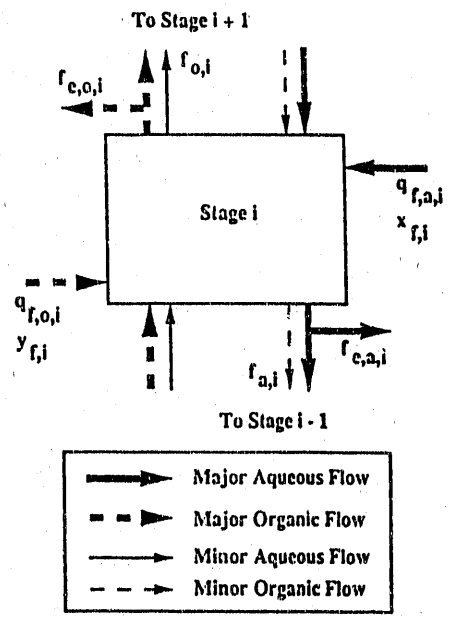

Fig. 4. Schematic for Stage i with User-Specified Quantities Shown

applies to each of the n components with j = 1,...,n. The subscript j is not shown here as a matter of convenience.

First, it is assumed that the distribution ratio (D_i) for each stage i is known or can be determined for a system with m stages. Then, since these are assumed to be equilibrium stages,

$$D_i = y_i/x_i \tag{8}$$

Thus, all y_i values for component j can be replaced by $D_i x_i$ in the material balance equations for component j. The final unsteady-state material balance equation for stage i is

$$a_i x_{i-1} + b_i x_i + c_i x_{i-1} - d_i = -\left[V_{a,i} + D_i V_{o,i}\right] \frac{dx_i}{dt} \tag{9}$$

where

$$a_1 = 0 \tag{10}$$

$$a_i = -\left[1 - f_{e,o,i-1}\right]\left[D_{i-1} + R_{o,i-1}\right] q_{o,i-1} \qquad 2 \le i \le m \tag{11}$$

$$b_i = \left[D_i + R_{o,i}\left[1 - f_{e,o,i}\right]\right]q_{o,i}$$

$$+ \left[1 + R_{a,i}\left[1 - f_{e,a,i}\right]D_i\right]q_{a,i} \qquad 1 \le i \le m \qquad (12)$$

$$c_i = -\left[1 - f_{e,a,i+1}\right]\left[1 + R_{a,i+1}D_{i+1}\right]q_{a,i+1} \qquad 1 \le i \le m-1 \qquad (13)$$

$$c_m = 0 \qquad (14)$$

$$d_i = x_{f,i}q_{f,a,i} + y_{f,i}q_{f,o,i} \qquad 1 \le i \le m \qquad (15)$$

and $V_{o,i}$ and $V_{a,i}$ are the stage volumes in the organic and aqueous phases, respectively. In addition, since all of the aqueous phase is taken as effluent at stage 1 and all of the organic phase is taken as effluent at stage m,

$$f_{e,a,1} = 1 \qquad (16)$$

and

$$f_{e,o,m} = 1 \qquad (17)$$

Equations 9 to 17 apply to all m stages and form a set of m equations for component j.

In these equations, the quantities $R_{o,i}$ and $R_{a,i}$ are the ratios of the other phase to the main phase. These ratios, which are related to the amount of back mixing, are given by

$$R_{o,i} = f_{o,i}/\left[1 - f_{o,i}\right] \qquad (18)$$

and

$$R_{a,i} = f_{a,i}/\left[1 - f_{a,i}\right] \qquad (19)$$

At steady state, Eq. 9 can be written as

$$a_i\, x_{i-1,ss} + b_i\, x_{i,ss} + c_i\, x_{i+1,ss} - d_{i,ss} = 0 \qquad (20)$$

Subtracting Eq. 20 from Eq. 9 and introducing the deviation variables $X_i = x_i - x_{i,ss}$ and $U_i = d_i - d_{i,ss}$ give

$$a_i X_{i-1} + b_i X_i + c_i X_{i+1} - U_i = \frac{-\left[V_{m,i} + D_{j,i}\, V_{o,i}\right] dX_i}{dt} \tag{21}$$

The introduction of a deviation variable results in a more general solution that is free of initial conditions, because the initial value of X is zero. In control theory the primary concern is the deviations of system variables (in this case, concentration) from their steady-state values. Therefore, the use of deviation variables is natural as well as convenient.

Equation 21 can be written for every component at every single stage. Solving Eq. 21 will provide the means to obtain the transient response of the given component at stage i to any forcing function. These forcing functions will be reflected in the variable U_i and will correspond to changes in the feed compositions only.

The system of equations generated by writing Eq. 21 for i=1, ...m, where m is the total number of stages, can be solved in several different ways. Some of these ways are Root-Locus Methods (Laplace transforms), Frequency-Response Methods (Bode and Nyquist diagrams), and phase space analysis [RAVEN]. Analysis indicates that phase-space solutions are suitable because they do not introduce many mathematical concepts.

2. <u>Solution</u>

Writing Eq. 21 for a given component and for all m stages results in a system of m linear differential equations with constant coefficients. A matrix representation of this system of equations is as follows:

$$\begin{array}{llll}
b_1' X_1 + c_1' X_2 & & +U_1' & = \dfrac{dX_1}{dt} \\
a_2' X_1 + b_2' X_2 + c_2' X_3 & & +U_2' & = \dfrac{dX_2}{dt} \\
\quad a_3' X_2 + b_3' X_3 + c_3' X_4 & & +U_3' & = \dfrac{dX_3}{dt} \\
\qquad a_4' X_3 + b_4' X_4 + c_4' X_5 & & +U_4' & = \dfrac{dX_4}{dt} \\
\qquad\quad \cdots\cdots\cdots\cdots & & & \\
\qquad\quad a_i' X_{i-1} + b_i' X_i + c_i' X_{i+1} & & +U_i' & = \dfrac{dX_i}{dt} \\
\qquad\quad \cdots\cdots\cdots\cdots & & & \\
\qquad\quad a_{m-1}' X_{m-2} + b_{m-1}' X_{m-1} + c_{m-1}' X_m & & +U_{m-1}' & = \dfrac{dX_{m-1}}{dt} \\
\qquad\qquad\qquad a_m' X_{m-1} + b_m' X_m & & +U_m' & = \dfrac{dX_m}{dt}
\end{array} \tag{22}$$

where

$$a_i' = - a_i/\left[V_{a,i} + D_i V_{o,i}\right]$$

$$b_i' = - b_i/\left[V_{a,i} + D_i V_{o,i}\right]$$

$$c_i' = - c_i/\left[V_{a,i} + D_i V_{o,i}\right]$$

$$U_i' = \quad U_i/\left[V_{a,i} + D_i V_{o,i}\right]$$

Note that the subscript j, which represents the component number, has been omitted for clarity. Nevertheless, these m equations are for the single component j. The solution of this system of equations can be given in terms of the eigenvalues of the matrix of coefficients defined as $\underline{\underline{S}}$. Equation 22 can then be written in terms of $\underline{\underline{S}}$ as

$$\underline{\underline{S}}\ \underline{X} + \underline{U}' = \frac{d\underline{X}}{dt} \tag{23}$$

whose solution is

$$\underline{X} = \sum_{i=1}^{m} \frac{\underline{w}_i^T\ \underline{\underline{S}}^{-1}\ \underline{U}'}{\underline{w}_i^T\ \underline{Z}_i}\ \underline{z}_i\ e^{\lambda_i t} - \underline{\underline{S}}^{-1}\ \underline{U}' \tag{24}$$

where $\underline{w}$, $\underline{z}$, and $\underline{\lambda}$ are the eigenrows, eigenvectors, and eigenvalues, respectively, of the system matrix $\underline{\underline{S}}$. The eigenvalues are given by

$$|\underline{\underline{S}} - \lambda_i\ \underline{\underline{I}}| = 0 \qquad i=1,\ldots m \tag{25}$$

the eigenvectors by

$$(\underline{\underline{S}} - \lambda_i\ \underline{\underline{I}})\underline{z} = 0 \qquad i=1,\ldots m \tag{26}$$

and the eigenrows by

$$(\underline{\underline{S}}^T - \lambda_i \underline{\underline{I}})\underline{w} = 0 \qquad i=1,\ldots m \qquad (27)$$

where $\underline{\underline{I}}$ is the identity matrix.

Equation 24 can be verified by substituting directly in Eq. 23 and using the boundary condition $\underline{X} = \underline{0}$ at t = 0. Note the similarity between the analysis of the process dynamics of the GTM and that of the CSTR performing as a perfect mixer, as shown in Eqs. 1 through 7.

This study examines the effect of deviations from steady state due to perturbations in the feeds. In the next stage of this project, we will numerically solve this eigenvalue problem for specific TRUEX flowsheets. By focusing on the time response of a system to a perturbation, we can observe which stages and which components respond faster to a perturbation and which variables change by orders of magnitude with respect to their steady-state values. From this analysis, those variables that respond quickly in time to perturbations with large changes (orders of magnitude) are good candidates for monitoring.

For dynamic control to have any quantitative meaning, some measure or criterion must be available to specify how good the control is, namely, how far the process is from the desired conditions. Once the process is defined, the needed quantities in Eq. 24 (eigenvalues, vectors, and rows) can be computed. Equation 24 can be a guide in selecting monitoring instruments and the control algorithm by giving a measurement of how the system responds to a given perturbation. The instruments and algorithms selected can be tested by adding a constraint in the dynamic system and solving the new controlled system. The best instruments and algorithms will be those in which the system response to a perturbation is damped in the least amount of time within the process acceptable bounds.

Future work on the dynamic response of the system to perturbation on either or both feed composition and flow rate will be done in the next phase of this study. Perturbations in the feed flow rates represent a much more complicated analysis than the one presented in this report and will be done in the future. One of the key steps is to obtain a dynamic model that expresses the stage volumes as functions of the flows. This step must be done before the flow rates can be determined at every stage. Once stage flows and volumes are determined, concentrations can be obtained. Once the dynamic model is fully developed, the development of control algorithms will follow. With these algorithms, the instrumentation selected can be tested by model calculations before being physically implemented.

C. Sensitivity Analysis

To establish which process variables need to be monitored and the ranges to which they need to be controlled, a sensitivity analysis using the GTM was done. First, the steady-state concentrations of all components present in both phases in all stages for a specific flowsheet with a given number of sections and stages, feed flow rates and compositions, and back mixing coefficients were obtained. Second, by altering the value of one or several of the feed variables

(composition or flow rate) and re-evaluating the flowsheet, one can numerically perform a sensitivity analysis that will identify an appropriate strategy for process monitoring and control.

A sensitivity analysis using the GTM version 2.1 was done on a TRUEX process flowsheet designed to treat PFP waste. The base case, given in Fig. 1, meets the following process goals for treatment of this waste: the raffinate should be nonTRU ([TRU] ≤ 10 nCi-α/g solid); 99.7% or more of the americium in the feed should be removed by strip 1; 98.9% or more of the plutonium in the feed should be removed by strip 2; and less than 0.01% of the TRU elements in the feed should be in the organic solvent as it leaves the second strip section with the solvent. The flow rates and compositions of the feeds and the effluent streams for the base case are shown in Table 1.

Table 1. Concentration Results Determined for Base Case with NPH as Diluent

Stream Identity[a]	Flow Rate[b]	Component Concentration, M					
		H	Fe	Ni	Al	Na	Ca
DX	150	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15
DF	400	1.50E+00	3.00E-02	4.00E-04	4.30E-01	4.00E-02	6.00E-02
DS	40	4.00E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	150	4.00E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
FF	75	1.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
DW	440	1.26E+00	2.73E-02	3.64E-04	3.92E-01	3.64E-02	5.46E-02
EW	150	3.66E-01	9.74E-08	5.62E-13	5.11E-10	5.62E-11	8.43E-11
FW	75	5.37E-02	2.22E-14	3.29E-28	1.51E-25	3.29E-26	4.93E-26
FP	150	2.53E-02	1.33E-17	5.61E-37	3.54E-39	5.61E-35	8.42E-35

Stream Identity[a]	Flow Rate[b]	Component Concentration, M						
		Cu	Mg	UO_2	Am	Pu(IV)	F	HSO_4
DX	150	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15	1.00E-15
DF	400	3.00E-04	6.00E-02	3.00E-06	6.00E-06	3.00E-05	9.00E-02	1.00E-02
DS	40	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	150	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
FF	75	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.00E-02	0.00E+00
DW	440	2.73E-04	5.46E-02	2.15E-14	4.65E-11[c]	1.25E-13[c]	8.19E-02	9.11E-03
EW	150	4.22E-13	8.43E-11	3.54E-08	1.60E-05	6.69E-07	1.55E-04	1.08E-11
FW	75	2.46E-28	4.93E-26	6.86E-06	7.43E-08	1.57E-04	2.51E-03	3.28E-27
FP	150	4.21E-37	8.42E-35	4.50E-06	4.91E-11[d]	2.63E-08[d]	2.37E-02	1.62E-36

[a]See Fig. 1 for identity of each stream.
[b]Flow rates can be in any unit of volumetric flow rate. The important criterion is that flow rate is relative to the extraction feed (DF).
[c]This is equal to 3.86×10^{-2} nCi/g of α activity from TRU.
[d]Corresponds to only 0.003% of TRU in this stream.

Figures 5 and 6 show the concentration profile for americium and plutonium. The TRUEX process can be briefly described as follows. The TRU-containing waste is fed into the contactor at stage 4, and the aqueous raffinate, containing the bulk of the waste, exits the process at stage 1 as a nonTRU waste. Note how the concentrations of americium and plutonium decrease from stages 4 to 1, attaining their minimum values at stage 1 (raffinate). Also, observe how their organic concentrations in these 4 stages increase as the solvent passes from stages 1 to 4.

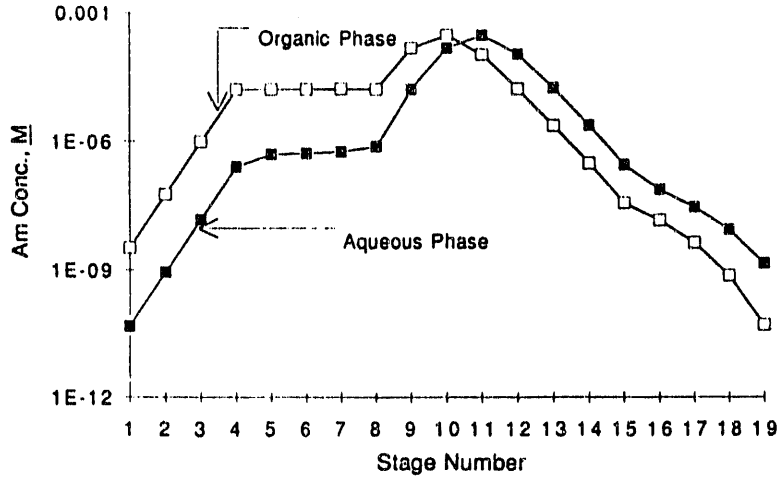

Fig. 5. Molar Concentration of Americium in the Aqueous and Organic Phases for Each Stage

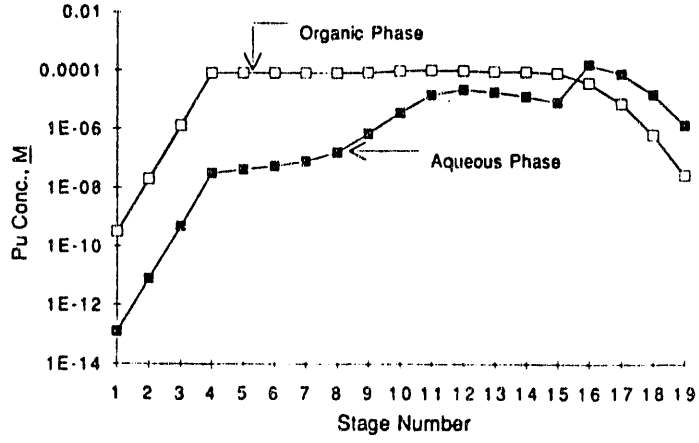

Fig. 6. Molar Concentration of Plutonium in the Aqueous and Organic Phases for Each Stage

The loaded solvent is then scrubbed in stages 5 to 8 for a cleaner separation. This section has almost no effect on the americium and plutonium concentrations in the solvent. The solvent is then stripped with dilute acid to recover the TRU elements that are tripositive cations, (e.g., americium). Figure 5 shows how much the americium concentration in the organic phase decreases from stages 9 to 15, and how much it increases the aqueous concentration from stages 15 to 9. Note in Fig. 6 that the plutonium concentration remains relatively constant in the organic phase for this section. In the second strip, plutonium may be stripped from the solvent

by adding a complexant or reductant in the aqueous feed (e.g., HF). Figure 6 shows that the concentration of plutonium in the organic phase decreases between stages 16 and 19. In the aqueous phase, the concentration of plutonium increases from stages 19 to 16. Residual americium and plutonium left in the solvent will be removed in a solvent cleanup step.

Some of the plutonium is being stripped in the first strip (stages 9 to 15 in Fig. 6) and some of the americium is always stripped in the second strip (stages 15 to 19 in Fig. 5). Thus, it is particularly important to minimize these amounts (second and third items of the process goals).

Figure 7 shows the concentration profile for the total H^+ present in the process. In the extraction section (stages 1 to 4), both organic and aqueous concentrations remain constant. In the scrub section, the aqueous-phase concentration increases in stage 5 due to a high organic-to-aqueous (O/A) flow ratio and a large decrease in the D value for HNO_3 (due to large decrease in the nitrate concentration), then it decreases in stages 6 through 8. In the first strip (stages 8 to 15), the concentrations in both phases continue to decrease, since HNO_3 is stripped from the organic to the aqueous. By the end of the first strip, this process is almost complete, as indicated by a constant H^+ in the aqueous phase by the end of the first strip. In strip 2, stages 15 to 19, $[H^+]$ increases in both phases due to the HF in the second strip feed.

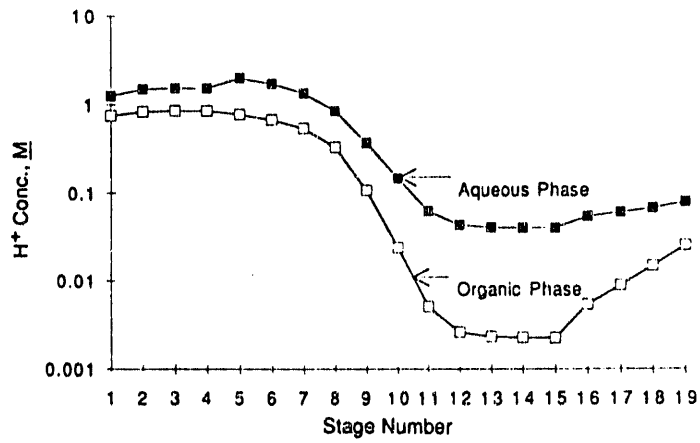

Fig. 7. Molar Concentration of H^+ in the Aqueous and Organic Phases for Each Stage

Figure 8 shows the concentration profile of fluoride ion in the process. The fluoride concentration in the aqueous phase remains constant in the extraction section; this is due to Al^{3+} complexes that limit partitioning to the organic phase and keep it in the aqueous phase leaving in the raffinate. In the scrub and the first and second strip sections, where there is no Al to complex F^-, the distribution ratio of fluoride is much higher (~0.9).

Once the base case was defined, some the of system variables were perturbed. After changing the base value of a given variable, the model was rerun, and the results were analyzed to see if they met the process goals. Obviously, not every perturbation will lead to a flowsheet within process bounds. These are the cases for which monitoring and control become important.

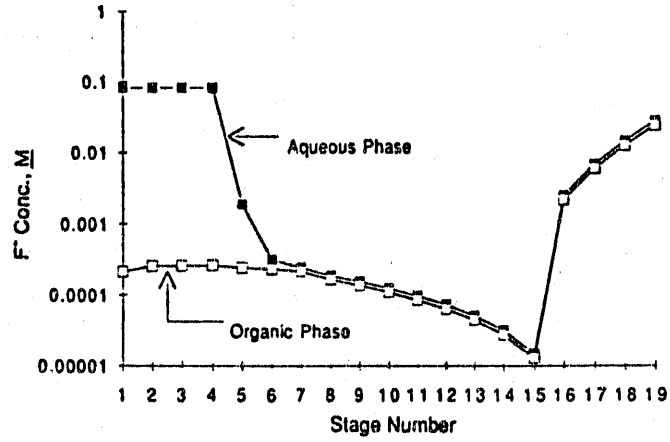

Fig. 8. Molar Concentration of F^- in the Aqueous and Organic Phases for Each Stage

By analyzing the cases in which the process criteria do not hold anymore, it is possible to obtain the bounds for the observable process variables. Using these bounds, one can establish the specifications for monitoring and control.

The effect of varying important variables such as flow rate, concentration, and number of stages is analyzed in the following sections for treatment of PFP waste. In each case, the four process goals were examined and plotted versus the fractional change with respect to the base value of the variable perturbed. The first criterion, that the aqueous raffinate contain only nonTRU elements, is observed in terms of the total nCi/mL that exits in this stream, which should be less than 10 nCi/mL. The second criterion, the high percent of americium (with respect to the total americium present in the feed) that comes out of the first strip, is translated to make the percent of americium in the second strip less than 0.3%. The third criterion, the high percent of plutonium (with respect to the total plutonium present in the feed) that comes out of the second strip, is translated to make the percent of plutonium in the first strip less than 1.1%. The fourth and last criterion, the total TRU lost in the organic stream exiting strip 2, is observed in terms of an activity basis (nCi-α) being less than 0.01% of the total in the feed.

1. Flow Rates

A TRUEX process, like any solvent extraction process, is designed with specific flow rates set for the various influent streams. Equipment is chosen to reliably deliver those flow rates within a prescribed range. A study was initiated to estimate the allowable variations in the five feed flow rates for the TRUEX process flowsheet in Fig. 1. Independent perturbations to the flow rates of the feed streams were analyzed. These streams include the organic and aqueous feeds in the extraction section (DX, DF) and aqueous feeds in the scrub, strip 1, and strip 2 (DS, EF, FF).

For each case, the flow rate was varied by some fraction above and below the base case. This is shown in terms of a fractional change with respect to the base value of flow perturbed. For each given flow rate, the GTM was run, and organic and aqueous compositions in

every stage and for every effluent stream at steady state were obtained. Using the new compositions, we analyzed the quantities of the TRU elements in the extraction raffinate to see if they met the nonTRU criterion when plotted versus the fractional changes in the flow rates. Also plotted against changes in the flow rates were the percentages for americium in strip 2 and plutonium in strip 1 and the TRU exiting the organic stream in strip 2. The results are shown in Figs. 9 to 13 and are discussed below.

a. Organic-Feed Flow Rate

Variations in the organic-feed flow rate are generally the most drastic flow-rate-related perturbation of a solvent extraction flowsheet. In the TRUEX process, increases in organic-feed flow tend to make the extraction section more effective in removing TRU elements from the aqueous feed. This is accomplished by increasing the extraction factor, the product of distribution ratio (D) and organic-to-aqueous phase ratio (Q). The method is to increase Q or to increase D values by decreasing solvent loading.* By the same means, the scrub and strip sections decrease in effectiveness in stripping nitric acid and actinides, respectively, from the solvent as the organic-feed flow is increased. Conversely, decreases in the organic-feed flow rate decrease the effectiveness of the extraction section and increase the effectiveness of the scrub and strip sections.

Over a ±20% range in organic-feed flow rate, the extraction raffinate was nonTRU, that is, the TRU concentration was less than 10 nCi/mL (Fig. 9a), but the amount of TRU exiting strip 2 exceeded the maximum value of 0.01% (Fig. 9d). Figures 9b and 9c show the effect of a perturbation in the organic extraction feed flow rate on the amount of americium and plutonium being stripped. Also shown in Figs. 9b and 9c are horizontal lines that represent the PFP process criteria (0.3% of americium present in strip 2 and 1.1% of plutonium present in strip 1, respectively). Therefore, all points which lie below these lines are cases in which the perturbation in the organic-feed flow rate still meets process goals. Increasing the organic feed increases the limiting amount of americium lost in the second strip, but decreases the plutonium lost in the first strip, whereas decreasing the organic feed decreases the americium lost in the second strip but increases the plutonium lost in the first strip. This counter-balancing effect enables us to obtain upper and lower bounds for this variable. Figures 9b, 9c, and 9d all have intersection points for which the process goals stop being accomplished, giving upper and lower bonds to the allowed variability of the organic-feed flow rate. These bounds provide input to the selection of monitoring and controlling instruments. This is discussed in detail in Volume Two. Based on the results shown in Figs. 9b and 9c, the extractant organic feed needs to be controlled in the 0.935-1.01 range to meet process goals.

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*Solvent loading is defined as extracting enough of a metal salt into the organic phase that its presence significantly decreases the concentration of CMPO available for extracting additional metal salts ($CMPO_{free}$). It is assumed that the extraction of one mole of $Am(NO_3)_3$ requires three moles of CMPO (n=3), and that the extraction of one mole of $UO_2(NO_3)_2$ and $Pu(NO_3)_4$ requires two moles of CMPO (n=2); $[CMPO_{free}]_{org} = [CMPO_{total}]_{org} - \Sigma\, n[M]_{org}$.

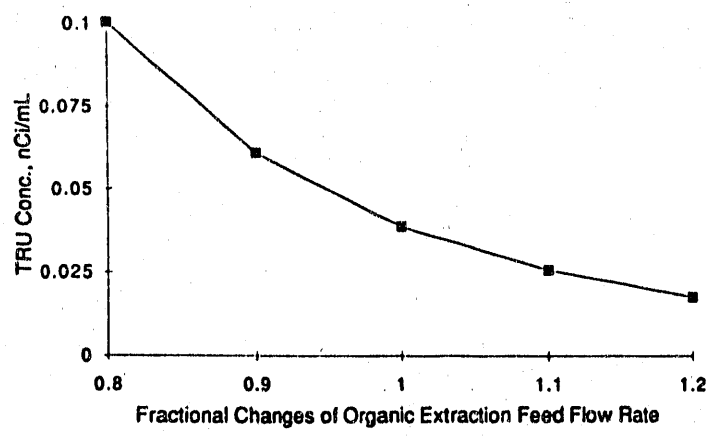

Fig. 9a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

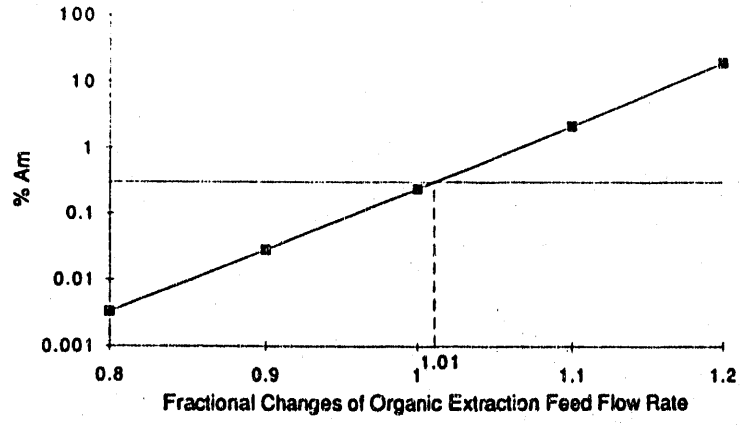

Fig. 9b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

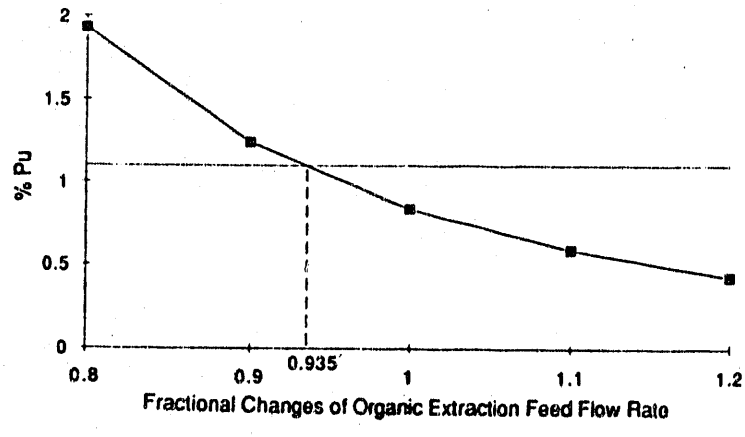

Fig. 9c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

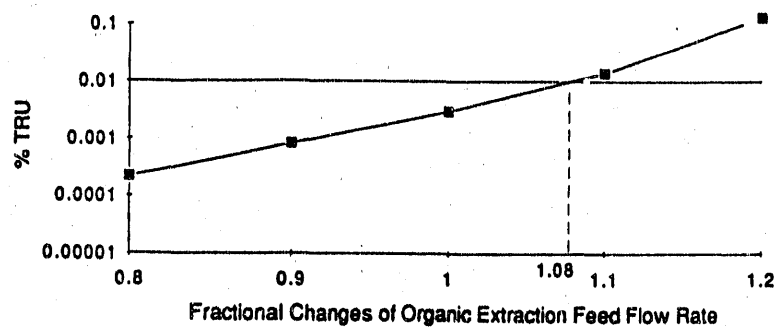

Fig. 9d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

An expert system should be able to use this type of analysis. For example, the data shown in Figs. 9a to 9d can be represented in a mathematical form along with the intersection points for the bounds that set the operating range. These analyses can then be done automatically once a detailed data base is generated.

b. Aqueous-Feed Flow Rate

Increasing or decreasing the aqueous-feed flow rate to the extraction section has the opposite effect to varying the organic feed rate. Increasing this flow rate decreases the effectiveness of the extraction section to remove TRU elements from the feed, and vice versa. Effects in the other sections are minimal unless solvent loading occurs or the extraction of nitric and/or hydrofluoric acid is significantly altered.

An increase in the aqueous feed flow can result in a significant increase in solvent loading by the actinides. This will lower their distribution ratios in the scrub and strip sections; a decrease in the aqueous-feed flow rate will have the opposite effect.

The extraction of nitric acid by the TRUEX solvent in the extraction section can be significantly increased by increasing the aqueous-feed flow rate. This will reduce the ability of the scrub section to remove enough nitric acid from the solvent. The concentration of nitric acid in the first-strip stages will be higher, thus decreasing the effectiveness of the first-strip section to recover americium from the solvent. Of equal consequence, less plutonium will be removed by the first strip; therefore, the second-strip effluent stream will have a higher yield of plutonium, but it will be less free of americium.

A decreased concentration of nitric acid in the solvent exiting the extraction section will increase the effectiveness of the first-strip section in recovering americium from the solvent. Further, more plutonium will be removed by the first-strip effluent; plutonium yield from the second strip will decrease, but its purity will increase.

Because fluoride complexes of plutonium are much more stable than those of americium, changes in the HF concentration in the solvent entering the first-strip section will have a much greater impact on the stripping of plutonium than americium. Increases in HF concentrations in the first strip will increase the plutonium loss to the first-strip effluent and, therefore, lower its yield in the plutonium product stream. Conversely, decreases in the concentration of HF will increase the plutonium yield in the second-strip effluent.

Perturbations above and below the base case for the aqueous extraction feed flow rate can be seen in Figs. 10a through 10d. For fractional changes above 4.03, the raffinate becomes nonTRU (Fig. 10a). Perturbations to the base-case flow rate affect the stripping process by increasing the americium concentration as the fractional change increases and by decreasing the plutonium concentration as the fractional change increases. For all cases studied, the amount of americium exiting in strip 2 and the TRU percent exiting in the organic flow from strip 2 are within process goals (Figs. 10b and 10d). For cases below 0.1, the amount of plutonium exiting in the first strip exceeds the process goal of 1.1%. An operating range between 0.1-4.03 will meet all process goals.

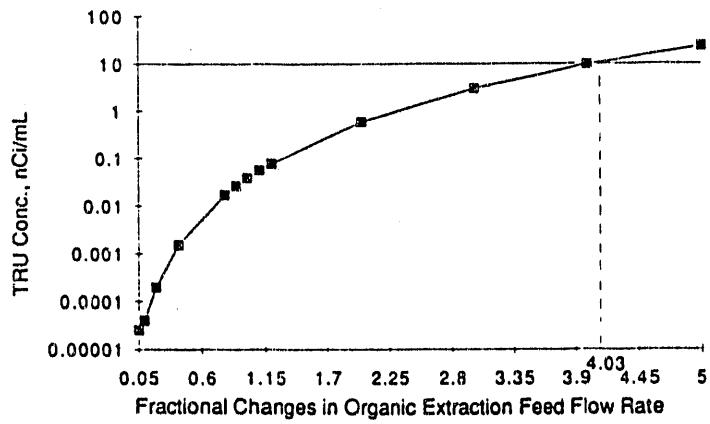

Fig. 10a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Aqueous Extraction Flow Rate. Flow rates are relative to the base case, shown in Fig. 1.

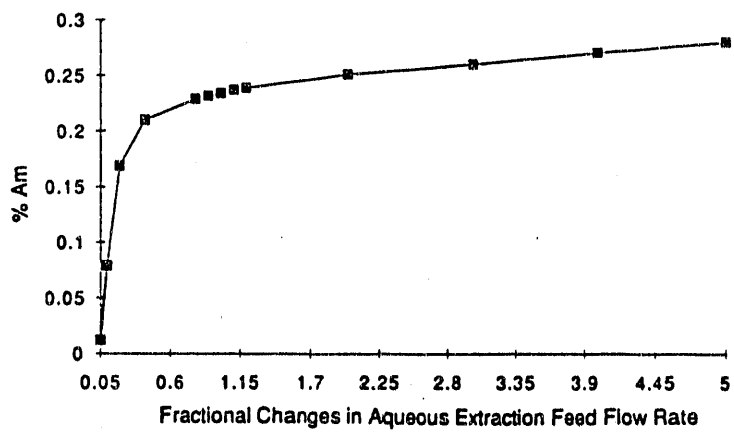

Fig. 10b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Aqueous Extraction Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

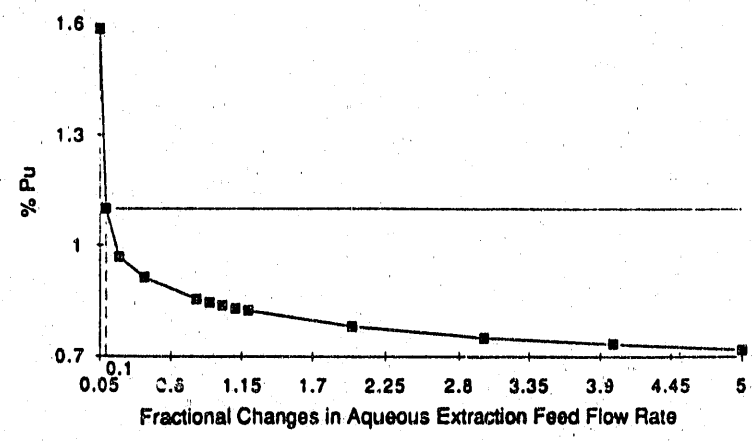

Fig. 10c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Aqueous Extraction Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

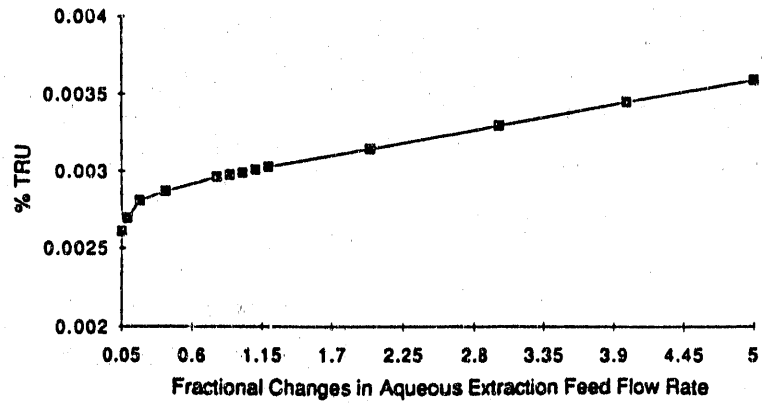

Fig. 10d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Aqueous Extraction Feed Flow Rate. Flow rates are relative to the base case, shown in Fig. 1.

c. <u>Scrub-Feed Flow Rate</u>

The scrub-feed flow rate directly affects the effectiveness of the scrub section in removing nitric acid from the solvent before the solvent enters the first-strip section. In general, increases in the scrub-feed flow rate will increase the effectiveness of the first-strip section in removing americium from the solvent, decreasing the amount of americium in the plutonium product of the second strip. It will also increase the plutonium removed in the first-strip section, increasing the concentration of plutonium in the first-strip effluent and decreasing the yield of the plutonium in the second-strip effluent. Decreases in the scrub-feed flow rate will decrease the effectiveness of the first strip, increasing the amount of americium and plutonium present in the plutonium product.

Variations in the scrub-feed flow rate also affect the composition and the volumetric flow rate of the raffinate exiting from the extraction section, but effects of those

changes on the nonTRU raffinate are specific to each process. Increases in the scrub-feed flow rate will scrub nitric acid from the solvent more effectively. If the rate becomes very large, it will also act to scrub actinides (especially americium) from the solvent, returning them to the extraction-feed stage. The increased mass of actinides in the extraction section and the increased aqueous-phase volumetric flow rate will have a compensating effect in the concentration of TRU elements in the raffinate. The decreased nitric acid concentration in the extraction section caused by a high scrub feed rate will also influence distribution ratios for all components, either decreasing or increasing them depending on the extraction feed composition. Conversely, a decreased scrub flow rate will affect the nonTRU raffinate.

Increasing the flow rate of the scrub feed increases the concentration of TRU elements exiting in the raffinate (Fig. 11a), but the over-design in this section stops this from being a problem. Figures 11b and 11c, however, do show important effects of perturbations in the aqueous scrub feed. A counter effect is observed due to changes in the effectiveness of the scrub section. As the flow rate in the scrub feed increases, the americium mol % in strip 2 decreases while the plutonium mol % in strip 1 increases. The opposite effect is seen in the americium and plutonium mol % as the flow rate decreases. An operating range between 0.959 and 1.17 will guarantee that process goals are achieved. The amount of plutonium lost in the organic stream exiting strip 2 was above 0.01% for changes below 0.477 only (Fig. 11d). But since 0.959 obtained from the first optimization criterion is a higher lower bound, 0.959 should be used as the lower bound for the operating range.

d. First-Strip Feed

Variations in the first-strip feed flow rate can affect only the strip sections. Increasing this flow rate will make the first strip more effective at recovering both americium and plutonium from the solvent, thus increasing the purity and decreasing the yield of plutonium in the second-strip product. Decreasing this flow rate will decrease the purity and increase the yield of plutonium in the second-strip effluent.

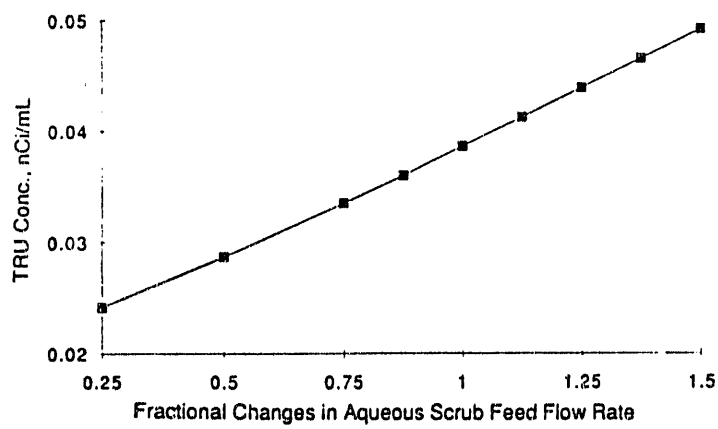

Fig. 11a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Aqueous Scrub Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

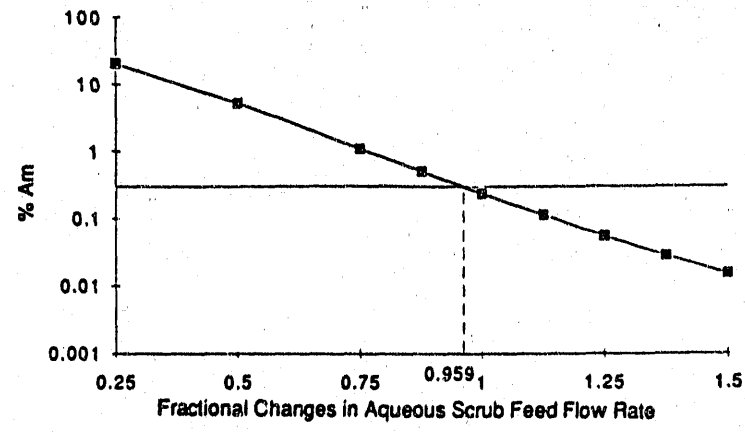

Fig. 11b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Aqueous Scrub Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

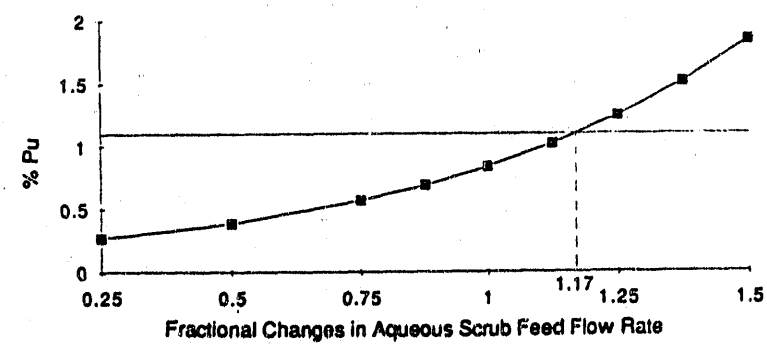

Fig. 11c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Aqueous Scrub Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

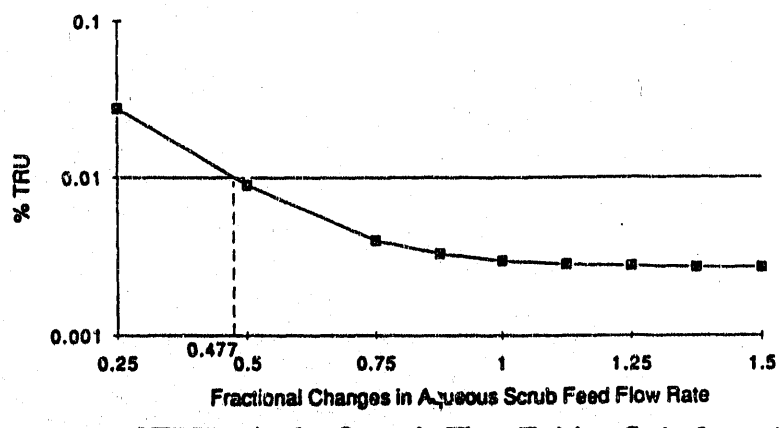

Fig. 11d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Aqueous Scrub Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

Variations on the first-strip feed flow can be observed in Figs. 12a through 12d. A range of operation between 0.986 and 1.13 will assure that process goals are met. Note that the Fig. 12a plot is horizontal, which is expected because the strip section acts independently of the extraction section. Figures 12b and 12c show counter effects; by increasing the flow rate, the first strip becomes more effective at recovering both americium and plutonium and the plutonium yield decreases in strip 2.

e. Second-Strip Feed

Variations in the second-strip feed flow rate will only affect the second-strip section. Increasing this flow rate will increase the effectiveness of this strip, increasing the yield of plutonium and allowing less to leave the section still in the organic solvent; conversely, decreasing it will decrease the plutonium yield and cause more plutonium to be lost to the solvent and eventually to the solvent wash solutions.

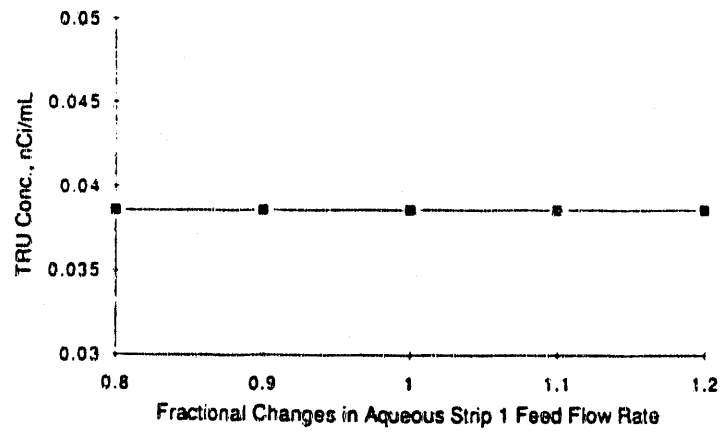

Fig. 12a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Aqueous Strip 1 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

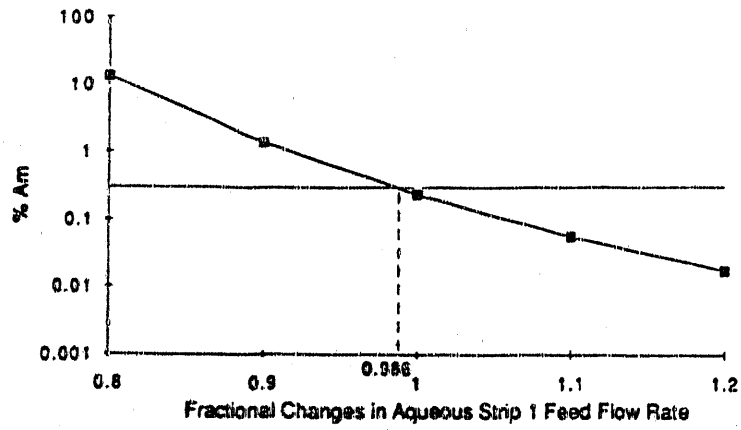

Fig. 12b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Aqueous Strip 1 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

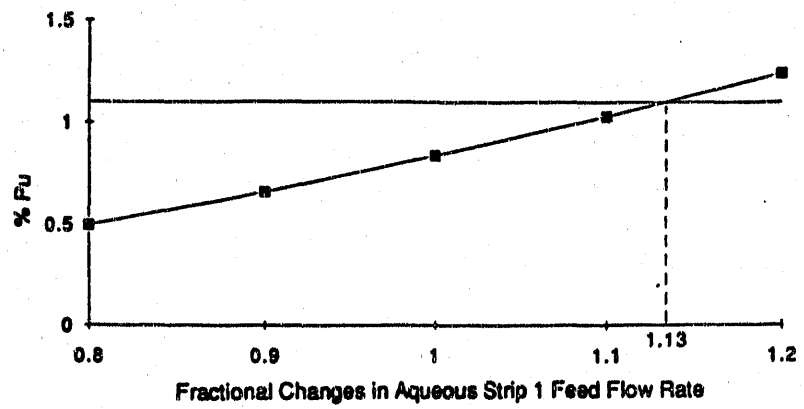

Fig. 12c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Aqueous Strip 1 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

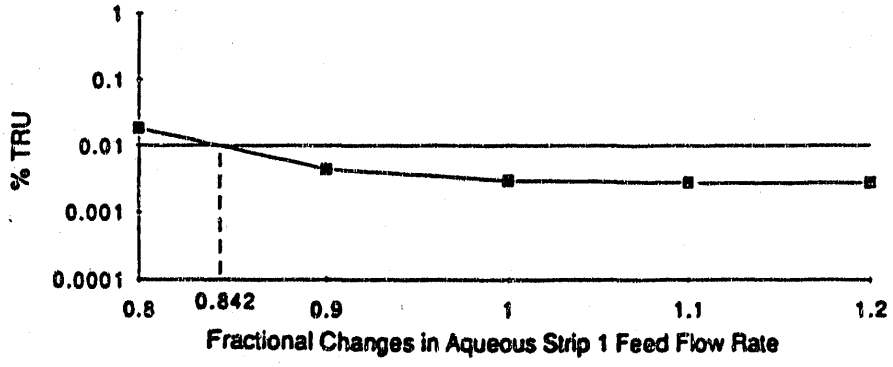

Fig. 12d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Aqueous Strip 1 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

As expected, changes in the feed to the second strip do not affect the TRU-concentration of the raffinate or the amount of americium or plutonium covered in the first strip (Figs. 13a, 13b, and 13c). However, the amount of TRU lost in the solvent exiting the second strip increases as the flow rate to the second strip decreases. (See Fig. 13d.) Hence, operating conditions greater than 0.902 will permit process goals to be obtained. Higher flow rates will be limited by equipment size.

2. Number of Stages

Loss of a stage in a centrifugal contactor can occur if a rotor fails to turn; loss of a stage in other solvent extraction equipment is usually due to a drop in stage efficiency. The GTM was used to measure the effects of stage loss in each section of the flowsheet. The obvious consequence of the loss of a stage in a specific section is a drop of the effectiveness of that section to perform its function. For example, loss of an extraction stage compromises the ability of the extraction section to generate a nonTRU waste stream; loss of a scrub or first-strip stage will decrease the recovery of americium in the first-strip section and increase the concentration

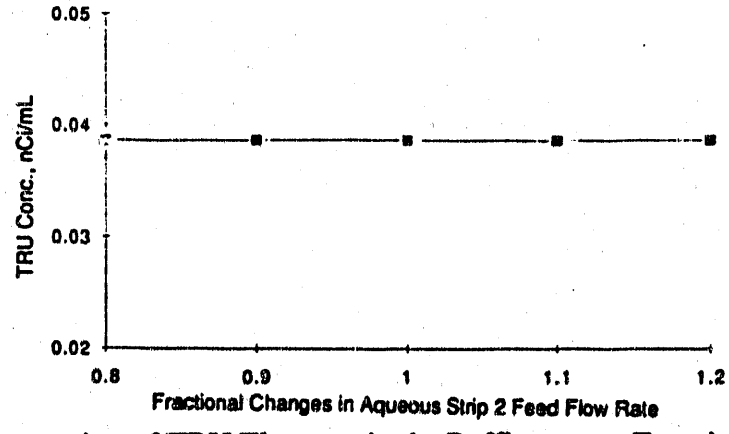

Fig. 13a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Aqueous Strip 2 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

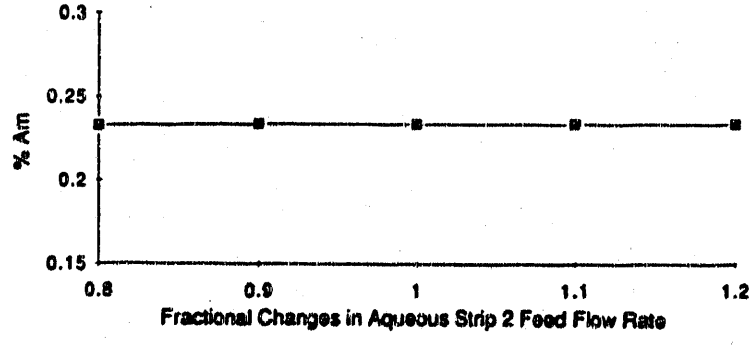

Fig. 13b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Aqueous Strip 2 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

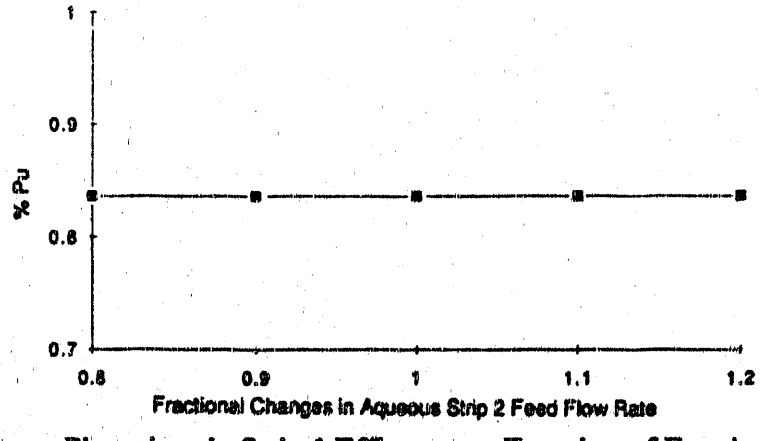

Fig. 13c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Aqueous Strip 2 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

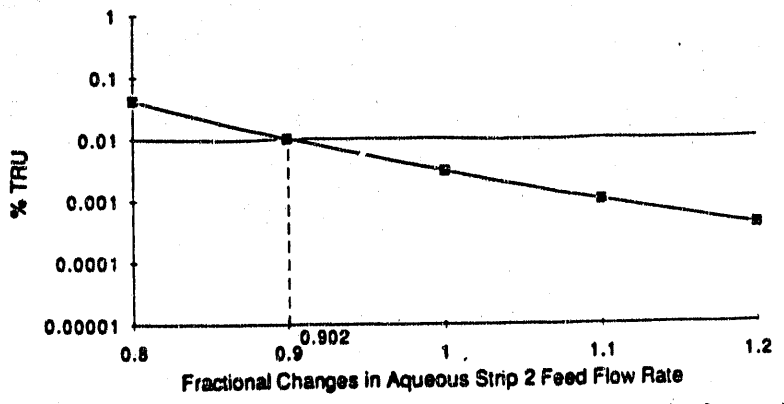

Fig. 13d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Aqueous Strip 2 Feed Flow Rate. Flow rates are relative to the base case shown in Fig. 1.

of americium in the plutonium product. Loss of a second-strip stage decreases the plutonium yield and increases loss of TRU elements to the solvent leaving the second-strip section.

The effect of losing one and two stages in the extraction section with respect to the total TRU going out in the raffinate is shown in Fig. 14a. Note that the extraction section is over-designed so that loss of one stage will still allow a nonTRU raffinate. Loss of a stage in the other sections also will not affect the TRU content of the raffinate. Losing a stage in the scrub and first strip increases the amount of americium in the second strip. The effect is more severe in the case of the first strip. The effect of losing a stage in a given section is shown in Figs. 14a to 14d. Losing one stage in any given section does not adversely affect the percentage of plutonium in the first strip effluent. Also, losing a stage in the second strip causes a higher-than-permissible amount of TRU material to leave with the organic stream from the second strip-section. This information can be used as an aid in process control. For example, several problems can cause the amount of americium stripped to drop to an undesirable level. Then, the expert system will instruct the user to check various conditions (e.g., amount of plutonium being stripped, other component concentrations, and flow rates) and will try to develop a logical solution path. One particular problem might result from the loss of a stage in a given section. With the use of more information, this hypothesis can either be eliminated or proven.

3. Concentrations of Feed Components

The feed to the TRUEX process is a waste stream generated during the production, recovery, or purification of plutonium. Its composition is therefore fixed by one or more upstream processes, and experience at Hanford and elsewhere has shown that composition can vary significantly depending on the feed to, and/or the operation of, the upstream process. Concentrations of nonradioactive components (e.g., nitric acid, aluminum nitrate, and sodium nitrate) can vary by an order of magnitude. Concentrations of actinide components of more than three orders of magnitude are possible. Variations in other feed streams to the TRUEX process would be the result of operator error or breakdown of solution make-up equipment. Both scenarios have been analyzed.

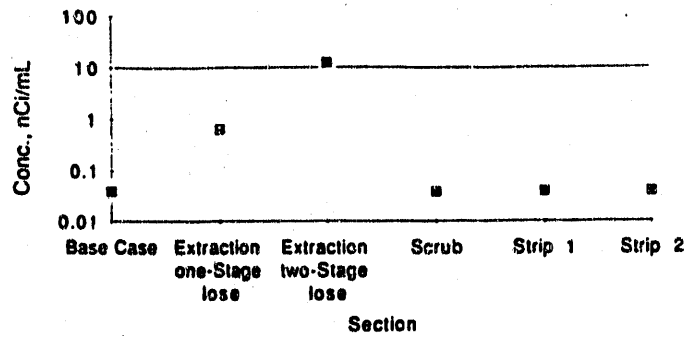

Fig. 14a. Concentration of TRU Elements in the Raffinate as a Function of Losing a Stage in Given Section

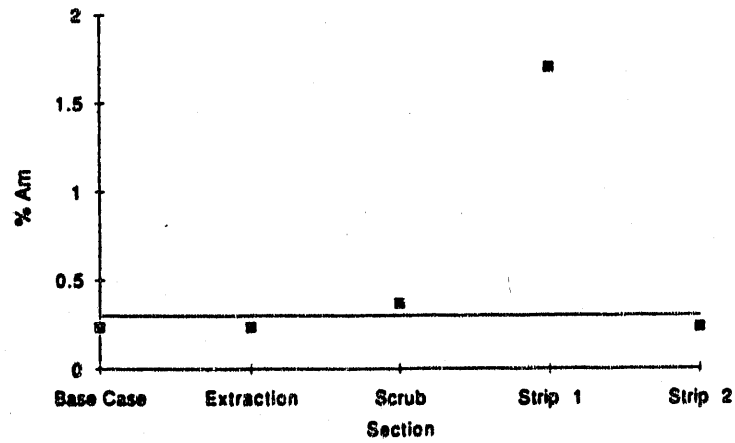

Fig. 14b. Percent Americium in Strip 2 as a Function of Losing a Stage in Given Section

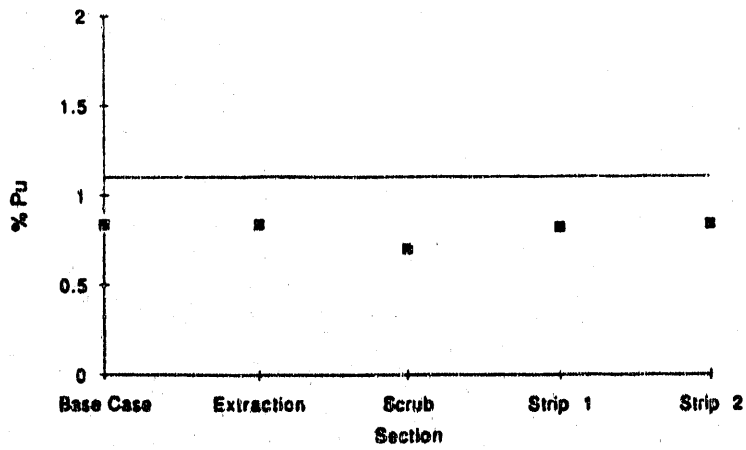

Fig. 14c. Percent Plutonium Concentration in Strip 1 as a Function of Losing a Stage in Given Section

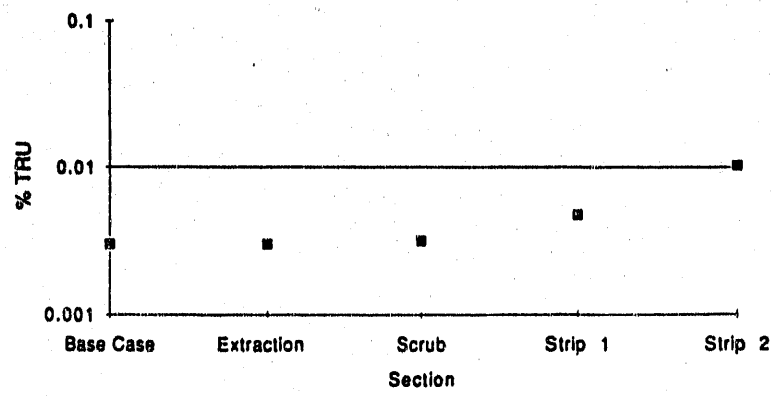

Fig. 14d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Losing a Stage in Given Section

As in the flow-rate analysis, the concentration of certain components in the feeds was increased or decreased from its base value. The component concentrations were perturbed either independently of other variables or in combination with them. Also, the perturbation was done in either one or two streams at a time. After a feed composition was modified, the GTM was run and steady-state concentrations in every stage were obtained. Using this concentration profile, calculations were performed to see if the process goals still held. Recall that the goals for the PFP waste were a nonTRU raffinate (<10 nCi/g); the percent of americium and plutonium (with respect to the total present in the feed) greater or equal to 99.7 and 98.9, respectively, in the first and second strip; and 0.01% (with respect to the total present in the feed) or less of TRU exiting the organic stream in strip 2.

Because the concentrations of Am(III), Pu(IV), and U(VI) are all below 10^{-4}M in the base case, they have essentially no effect on the distribution ratios of any component in the process; therefore, lowering their concentrations will only help meet the first process goals. Increasing their concentrations (especially that of americium, which is typically the most difficult to extract from aqueous solutions) makes attaining a nonTRU raffinate more difficult. As their concentrations increase above 0.001M, they act to decrease the D values of extractable metal species in the feed stage by loading the solvent; as they increase above 0.01M, solvent loading becomes a very important factor in decreasing D values of metal species in the feed stage and other stages in the extraction section. Also, nitric acid extraction can be enhanced in the feed stage due to the influence of these metal ions on the nitrate ion activity. Significantly increasing the nitric acid concentration in the solvent exiting the extraction section puts an additional burden on the scrub section and will reduce the effectiveness of the strip sections.

The distribution ratios of Pu(IV) and U(VI) are about 2000 in the extraction section when solvent loading is not a factor. Under the same conditions, D_{Am} is about 60; therefore, solvent loading affects the removal of americium from the waste stream feed to a much larger extent than that of the other actinides. Additionally, the third-order dependence on $[CMPO]_{free}$ of D_{Am}, as opposed to a second-order dependence for D_{Pu} and D_U, makes solvent loading even more deleterious to americium extractability.

By lowering distribution ratios of all components, solvent loading increases the effectiveness of the first-strip section for removing americium from the solvent. It may also cause increased stripping of plutonium. Because distribution ratios of metal cations are proportional to the nitrate activity in the aqueous solution to the second to fourth power, and because stripping of a nitrate salt from the organic phase can substantially increase the nitrate activity of the aqueous phase, the effect of solvent loading on the first-strip section must be examined on a case-by-case basis. Effects of high solvent loading on individual-component distribution ratios depend on the species in the organic phase and their concentrations.

The influence of solvent loading on the effectiveness of the second strip is complicated by the fact that all three actinides have low distribution ratios in this section. Although solvent loading will continue to lower distribution ratios of all actinides, stripping of a concentrated component (1) adds nitrate ion to the aqueous phase and (2) reduces the free fluoride concentration by its complexation; both actions increase the distribution ratios for all actinides.

a. Americium Concentration in the Extraction Feed

The result of a perturbation in the americium concentration in the extraction feed is shown in Figs. 15a through 15d. For all the cases analyzed, the raffinate was nonTRU if the increase in americium concentration was less than 203 times higher than its base-case concentration (Fig. 15a). Increasing the amount of americium in the extractant feed increases the americium lost in the second strip and the plutonium lost in the first strip. This effect is first seen in the americium lost to strip 2 at about 12.7 times its base-case concentration (Fig. 15b). The plutonium lost to strip 1 becomes too high at a factor of 90.2 (Fig. 15c). Also, the amount of plutonium lost in the organic stream exiting strip 2 was always below 0.01% (Fig. 15d). Therefore, to guarantee process goals, the americium concentration should be between 0 and 12.7 times its base-case concentration. If the concentration of americium lies out of this range, the flowsheet must be modified.

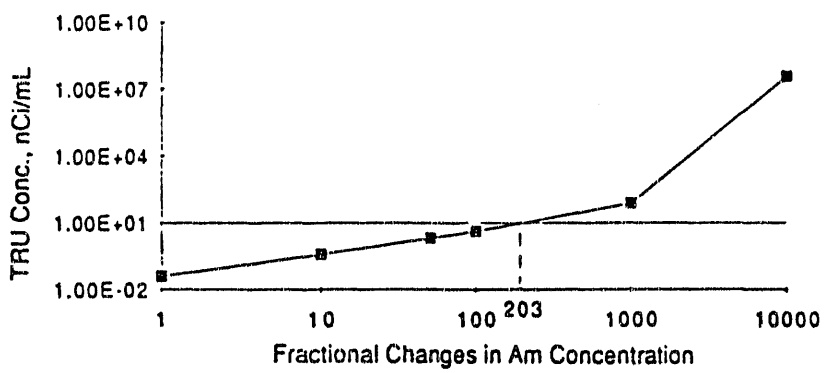

Fig. 15a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Americium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

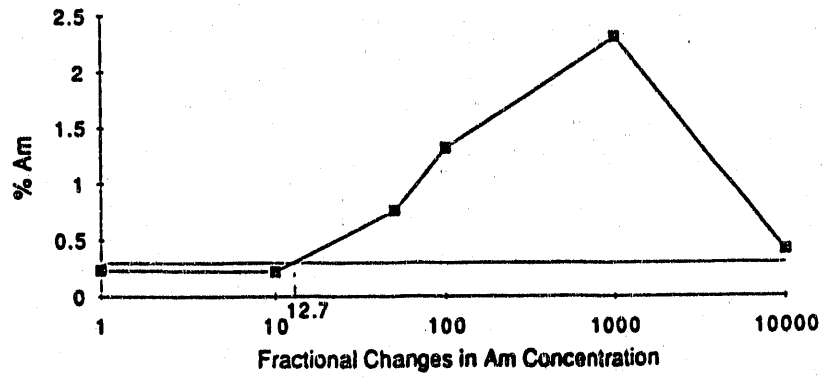

Fig. 15b. Percent Americium in Strip 2 as a Function of Fractional Changes in the Americium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

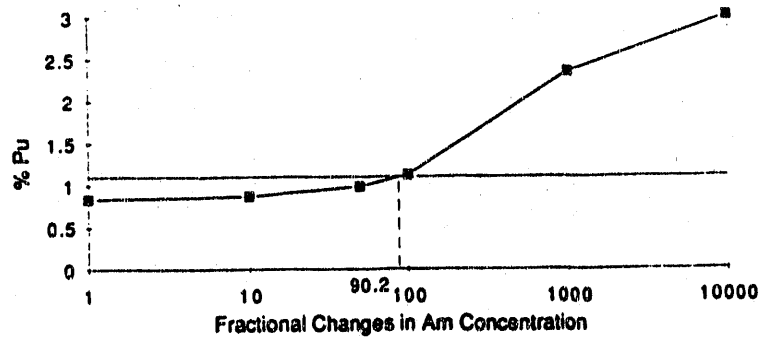

Fig. 15c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the Americium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

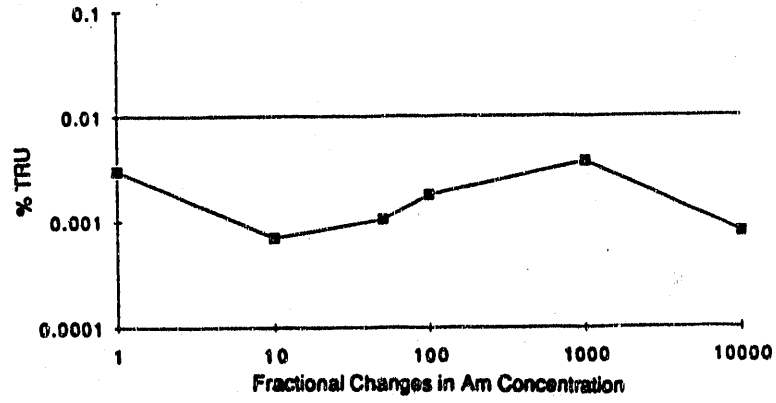

Fig. 15d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Americium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

b. Plutonium Concentration in the Extraction Feed

Figures 16a to 16d show the effect of a perturbation in the plutonium concentration in the feed. Decreasing its base value has no effect on the process goals. A nonTRU raffinate can still be achieved in the designed process if the plutonium concentration in the feed is not increased above 689 times its base-case concentration (Fig. 16a). An increase in plutonium concentration in the feed will never negatively affect the americium loss to the second strip (Fig. 16b). However, increasing the concentration of plutonium beyond a certain value sharply increases the amount of plutonium recovered in strip 1. At a concentration increase of 103 times, the amount of plutonium lost to the first strip lies above the goals (Fig. 16c). Also, the TRU concentration in the organic stream exiting strip 2 increases beyond its process limit at a plutonium feed concentration of only 4.14 times that of the base case (Fig. 16d). Therefore, the concentration of plutonium in the aqueous extraction feed may not exceed 4.14; above this limit, some change in the flowsheet design is necessary.

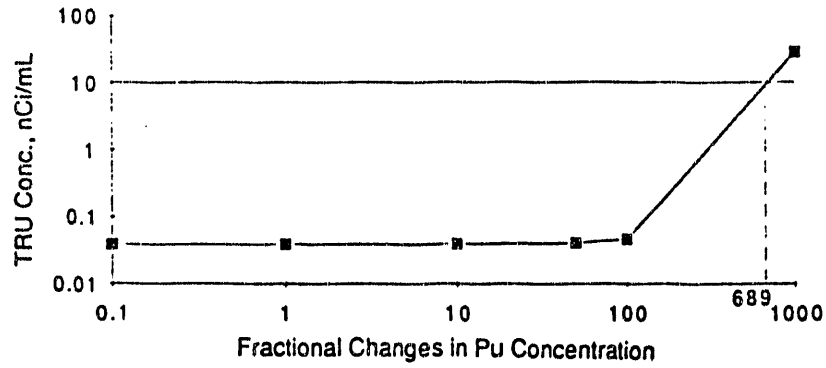

Fig. 16a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Plutonium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

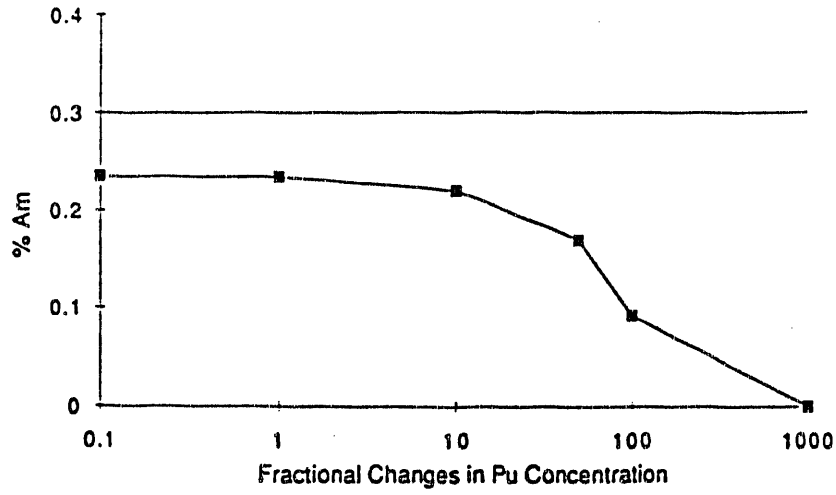

Fig. 16b. Percent Americium in Strip 2 as a Function of Fractional Changes in the Plutonium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

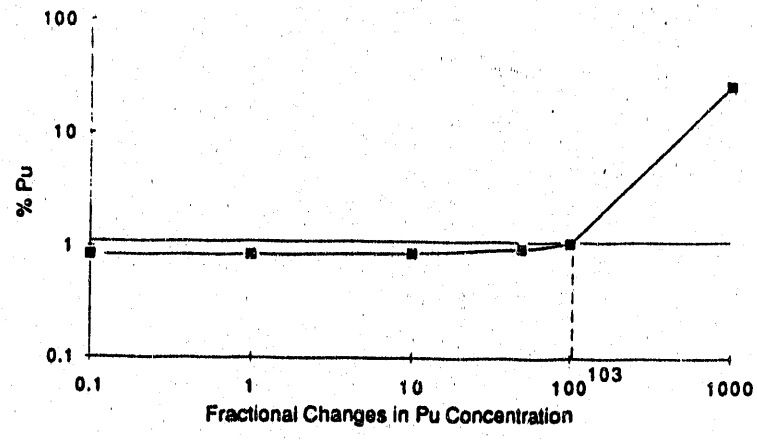

Fig. 16c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the Plutonium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

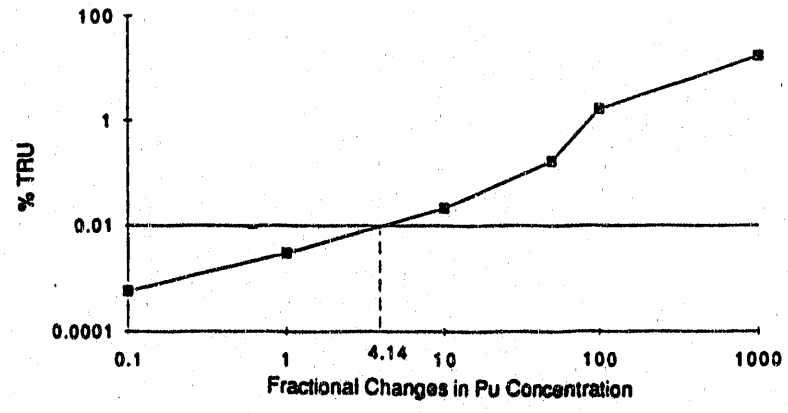

Fig. 16d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Plutonium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

c. <u>Uranium Concentration in the Extraction Feed</u>

For uranium concentrations $\leq$1000 times the base case ($\leq 3 \times 10^{-3}$M), the negative effect in the amount of americium or plutonium lost to extraction raffinate was small; the waste remained nonTRU over this range (Fig. 17a). The amount of americium in strip 2 or plutonium in strip 1 will not exceed the process goals when the uranium feed concentration increases by a factor of 1000 (Figs. 17b and 17c). However, the amount of TRU lost in strip 2 exceeds the process goals for increases of $[UO_2^{2+}] \geq 620$ of the base case (Fig. 17d). Therefore, process conditions are guaranteed as long as feed concentrations of uranium do not exceed 620 times the base case.

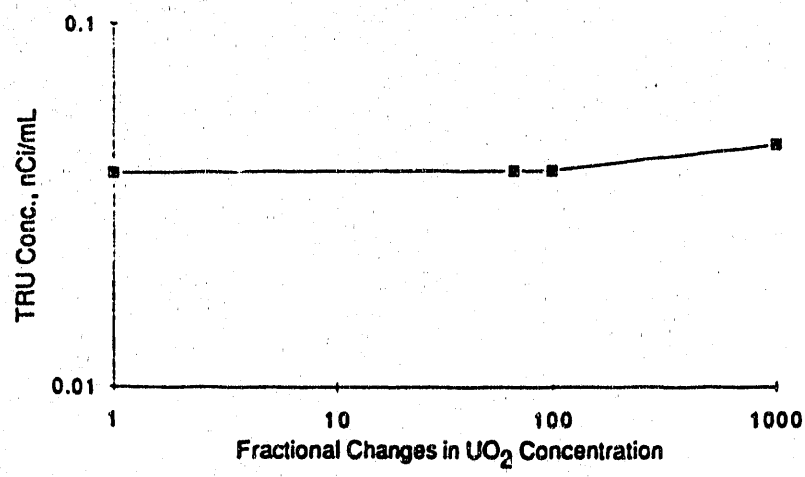

Fig. 17a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in Uranium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

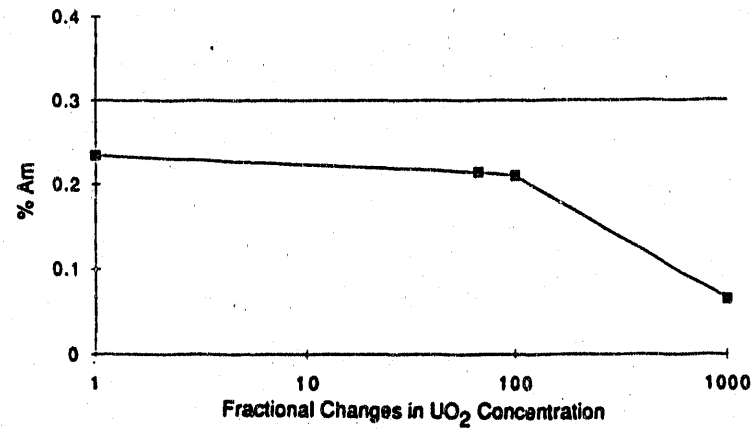

Fig. 17b. Percent Americium in Strip 2 as a Function of Fractional Changes in the Uranium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

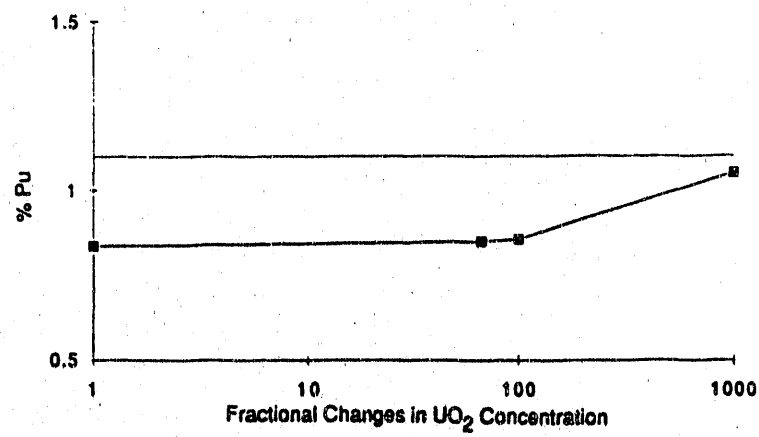

Fig. 17c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the Uranium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

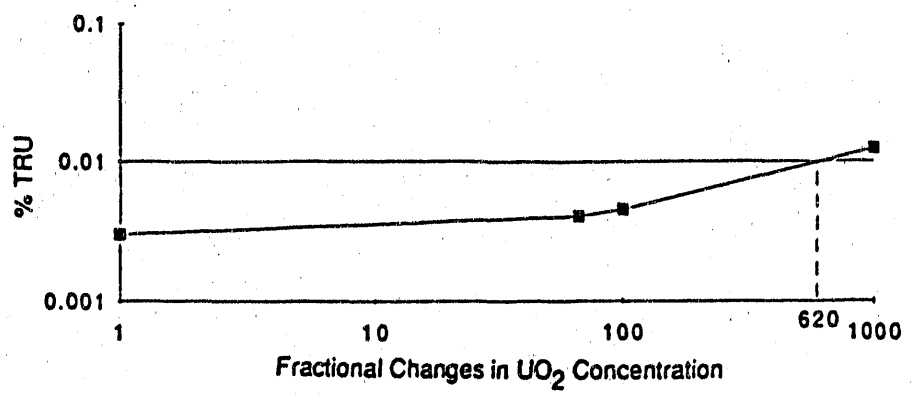

Fig. 17d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Uranium Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

d. Aluminum Nitrate in the Extraction Feed

The presence of aluminum nitrate in the feed increases distribution ratios in the extraction section for all metal species and nitric acid, while those for hydrofluoric acid are reduced. It does this by increasing the nitrate activity, decreasing the water activity, and complexing fluoride ion. Therefore, if the aluminum nitrate concentration is increased above the base case, the concentrations of TRU elements in the extraction raffinate decrease; decreasing the concentration of aluminum nitrate increases the TRU concentration of the raffinate.

If the feed concentration of aluminum nitrate is decreased, less nitric acid will be extracted into the solvent, making the scrub and first-strip sections more effective; more americium will be recovered in the first-strip effluent and less will be found in the plutonium product. Also, less fluoride will be complexed in the extraction section, allowing an increase in the extraction of HF by the solvent. Therefore, plutonium will be lost to the first-strip effluent due to the lower nitric acid and higher hydrofluoric acid concentrations in this section. Increasing the aluminum nitrate concentration in the feed will decrease the effectiveness of the scrub and strip sections. More americium will be found in the plutonium product; less plutonium will be lost to the first-strip effluent; and more TRU will exit the second-strip section in the organic solvent.

For all cases studied, the raffinate was always nonTRU (Fig. 18a) and the amount of TRU lost in the second strip was below 0.01% (Fig. 18d). Changes in the $Al(NO_3)_3$ concentration from the base case in the aqueous extraction feed are bound by its effect on the strip sections. This effect can be seen in Figs. 18b and 18c. Decreasing the base concentration of aluminum nitrate decreases the amount of americium in the second strip and increases the plutonium in strip 1. This behavior reduces the range in which process goals are met to controlling the concentration of $Al(NO_3)_3$ in the bounds of 0.904 to 1.15 the base-case concentration.

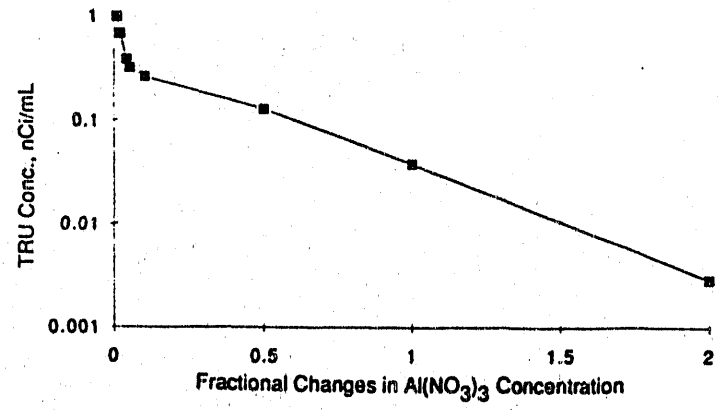

Fig. 18a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the $Al(NO_3)_3$ Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

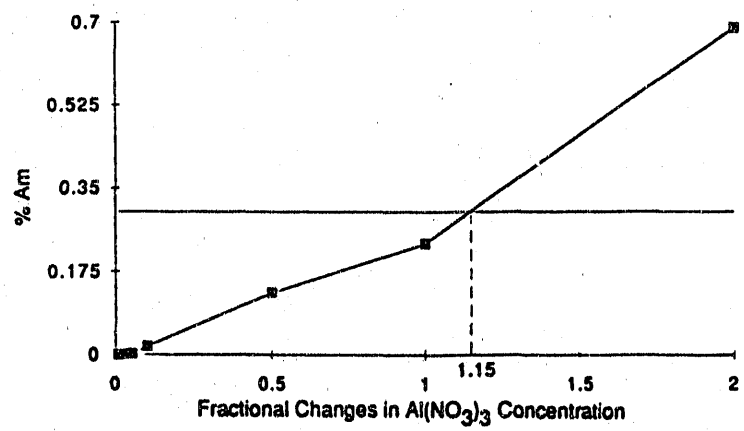

Fig. 18b. Percent Americium in Strip 2 as a Function of Fractional Changes in the $Al(NO_3)_3$ Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

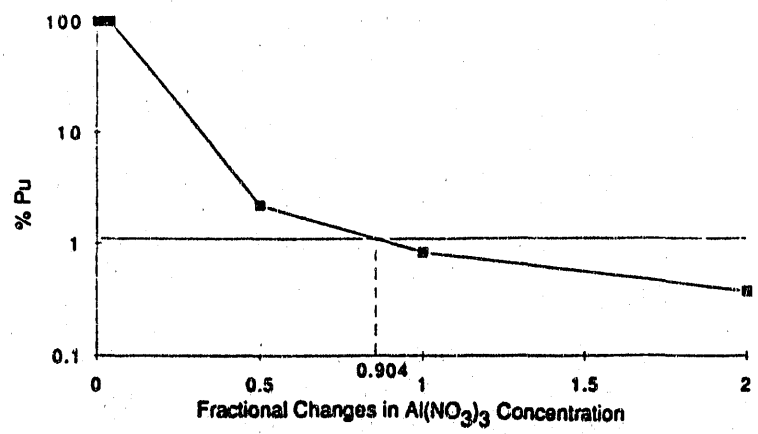

Fig. 18c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the $Al(NO_3)_3$ Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

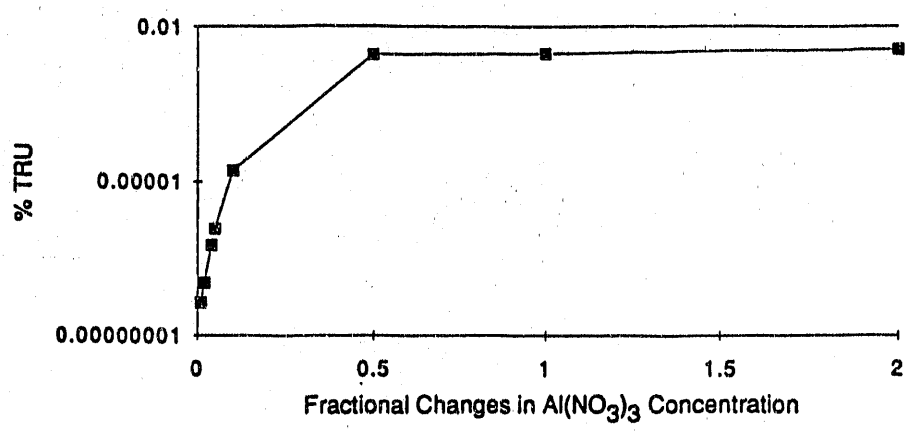

Fig. 18d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Changes in the $Al(NO_3)_3$ Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

When both aluminum nitrate and fluoride ion concentrations are varied in the feed proportionately, the effects of aluminum ion complexation of fluoride ion are far less important. The distribution ratio of HF is nearly independent of the Al/F concentrations in the feed. Therefore, the loss of plutonium to the first-strip effluent is only slightly increased as the concentration of aluminum ion decreases and only slightly decreased when this concentration increases. Because americium ion is not that strongly complexed by fluoride ion, the changes in its behavior between these two perturbations will be minimal.

When the amount of $Al(NO_3)_3$ and F^- in the aqueous extraction feed is increased, the amount of americium in strip 2 increases. This behavior can be seen in Fig. 19b. A range of operation at less than 1.17 times the base case concentrations for $Al(NO_3)_3$ and F^- is required to achieve process goals. For all cases the other process goals were always met. (See Figs. 19a, 19c, and 19d.) Note that when aluminum alone was perturbed independently (Figs. 18a through 18d), the range of operation for $Al(NO_3)_3$ was between 0.904 and 1.15. This indicates that the effects due to perturbations of a combination of variables may differ if the variables are perturbed separately. Different types of perturbations occurring at the same time often produce favorable results. One of our future goals is to study this interaction between perturbations in more detail.

e. Nitric Acid in the Extraction Feed

Because of the fairly high concentrations of nitrate salts in the feed (~1.5M), nitric acid additions above this concentration decrease the effectiveness of the extraction section by tying up CMPO as nitric acid species, lowering the extractability of metal salts. Likewise, lowering it to 0.3M increases the effectiveness of the extraction section. An increase in the concentration of nitric acid in the TRUEX solvent also places a burden on the scrub section. As the ability of the scrub to remove sufficient nitric acid is lost, the stripping of americium and plutonium in the first-strip section is degraded. As the concentration of nitric acid is increased even higher, the effectiveness of the second scrub is also diminished.

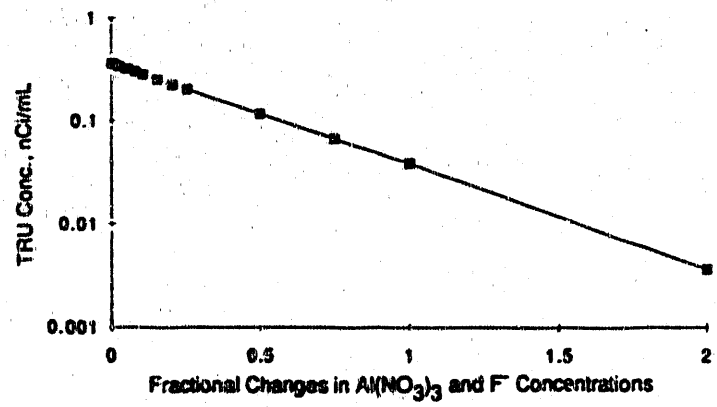

Fig. 19a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the $Al(NO_3)_3$ and F^- Concentrations in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

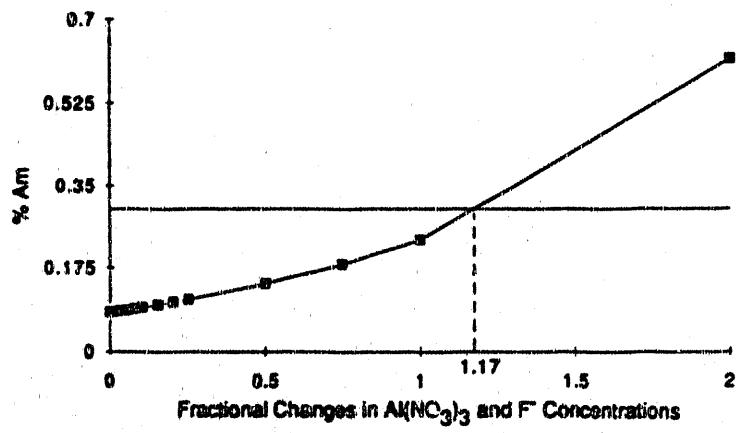

Fig. 19b. Percent Americium in Strip 2 as a Function of Fractional Changes in the $Al(NO_3)_3$ and F^- Concentrations in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

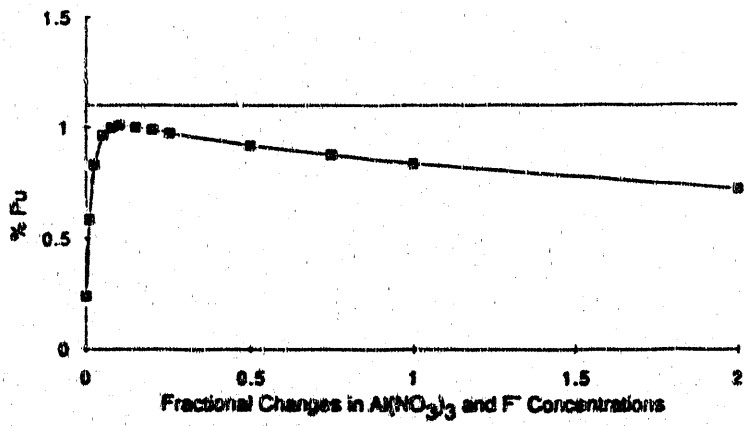

Fig. 19c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the $Al(NO_3)_3$ and F^- Concentrations in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

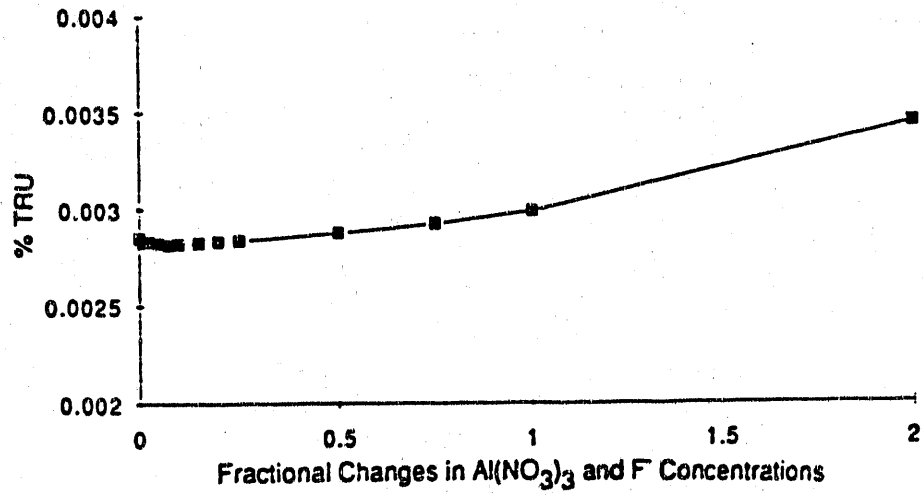

Fig. 19d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the $Al(NO_3)_3$ and F^- Concentrations in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Table 1.

For this feed, variations of nitric acid in the feed always produce a raffinate that is nonTRU (see Fig. 20a). Perturbations of the concentration of HNO_3 in the aqueous extraction feed have a counter effect on the amount of americium in the plutonium strip and plutonium in the americium strip products (Figs. 20b and 20c). The amount of americium entering the second strip increases as HNO_3 concentration increases; beyond 1.11 the process goal is not met. The plutonium coming out in the second strip decreases as HNO_3 increases, but below 0.435 the process goal does not hold. The amount of TRU lost in the second strip always meets the process criteria over the range identified (see Fig. 20d).

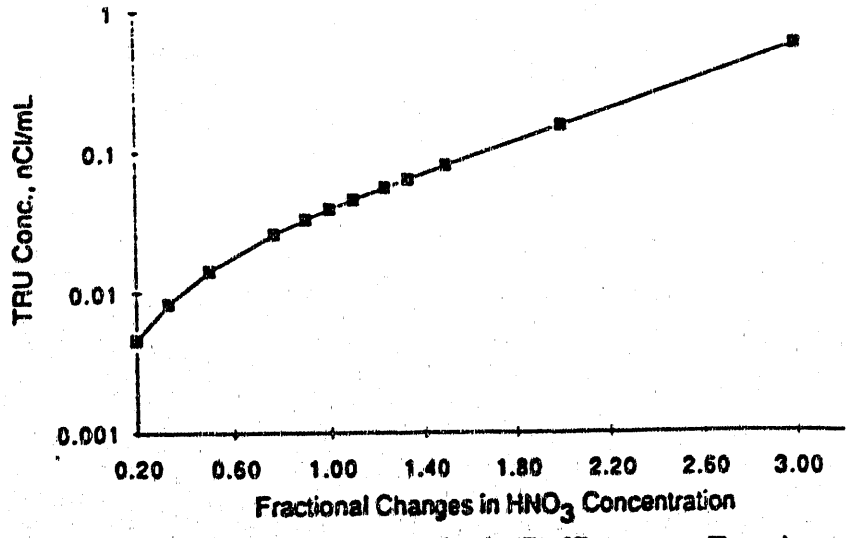

Fig. 20a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the HNO_3 Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

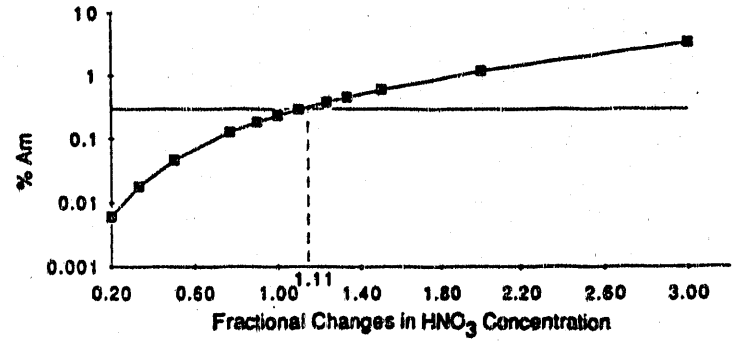

Fig. 20b. Percent Americium in Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

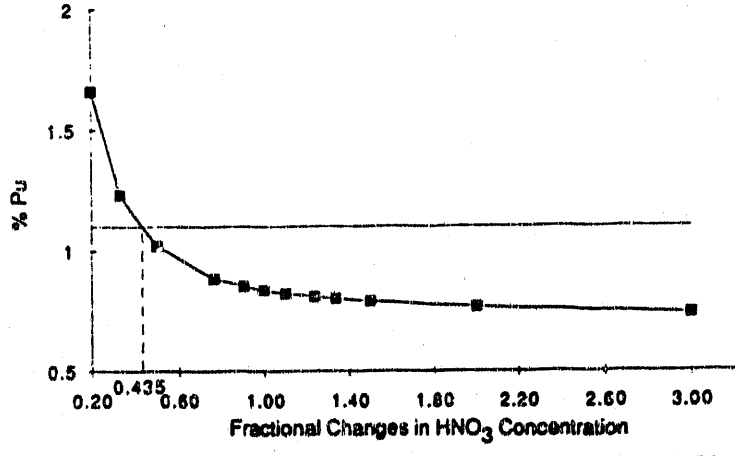

Fig. 20c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the HNO_3 Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

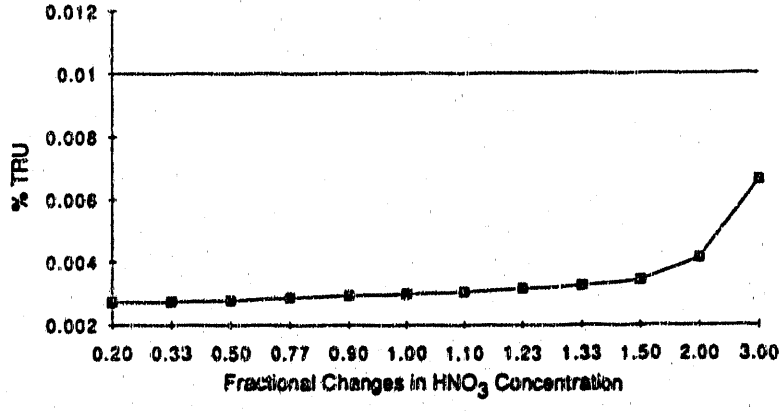

Fig. 20d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in Aqueous Extraction Feed. Concentrations are relative to the base case shown in Fig. 1.

f. Nitric Acid in the Scrub and First-Strip Feeds

In the base case, the aqueous feeds to the scrub and the first strip have a concentration of 0.04M nitric acid. By using the same nitric acid concentration for both feeds, scrub and first strip, the same storage tank can be used. This would decrease the storage area, creating a more compact process that still meets the process goals. The composition of these feeds and their volumetric flow rates were chosen so that the concentration of nitric acid in the stages of the first-strip section was such that nearly all the americium and nearly none of the plutonium in the solvent would exit in the aqueous effluent from the first strip. Increasing or decreasing these nitric acid concentrations had only a minor effect on the TRU concentration of the extraction raffinate (Fig. 21a). Ignoring the possible effects of acidic impurities or degradation products in the TRUEX solvent, the general rule is as follows: the lower the concentration of nitric acid, the more effective the strip. Therefore, less americium and plutonium are stripped from the solvent as the concentration of nitric acid is increased. As the first strip loses its effectiveness due to an increased concentration of nitric acid to the scrub and first-strip section, more americium appears in the plutonium product and more TRU elements are lost to the solvent exiting the second strip.

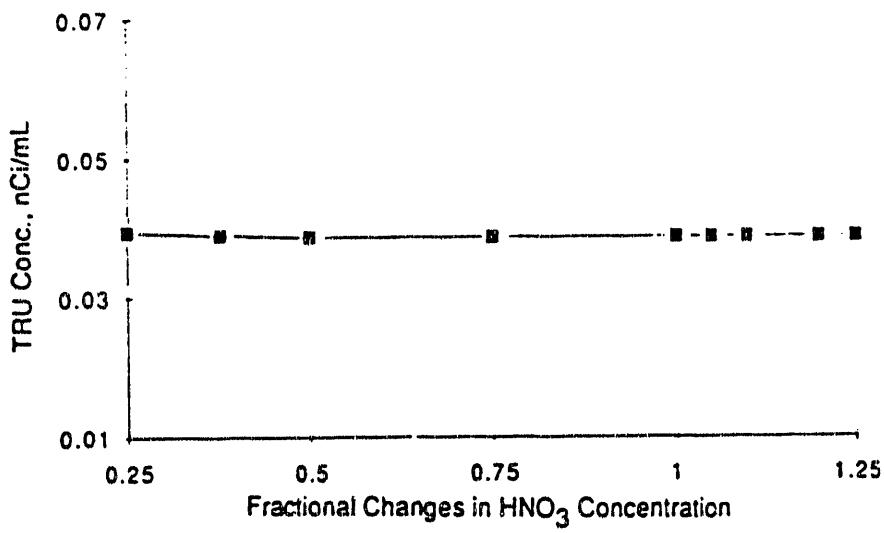

Fig. 21a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the HNO_3 Concentration in Scrub and Strip 1 Feed. Concentrations are relative to the base case shown in Fig. 1.

Figures 21b and 21c show the effect of changes in the HNO_3 concentration in the scrub and first strip. The amount of plutonium coming out in the first strip decreases, whereas the amount of americium coming out in the second strip increases as the HNO_3 concentration increases. A tight upper bound of 1.02 is required to keep the americium present in the second strip below the process goal of 0.3%. Lowering the nitric acid below 0.43 will cause a greater-than-acceptable loss of plutonium to the first strip. Extrapolating the line in Fig. 21d indicated that higher nitric acid concentrations will cause the process specifications to be exceeded for the TRU lost in the organic stream in the second strip (see Fig. 21d).

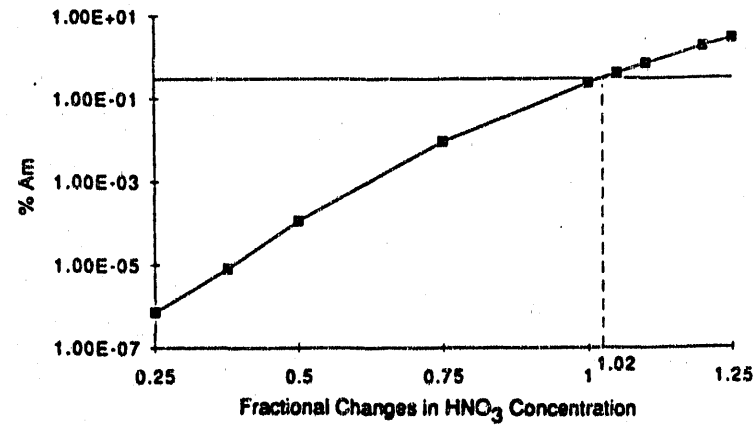

Fig. 21b. Percent Americium in Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in Scrub and Strip 1 Feed. Concentrations are relative to the base case shown in Fig. 1.

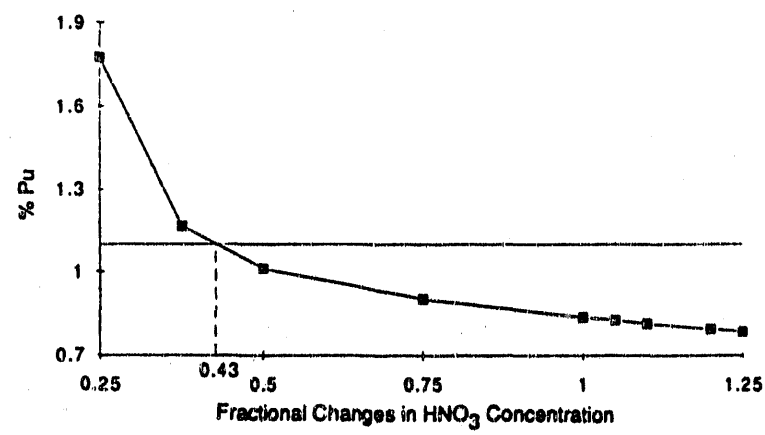

Fig. 21c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the HNO_3 Concentration in Scrub and Strip 1 Feed. Concentrations are relative to the base case shown in Fig. 1.

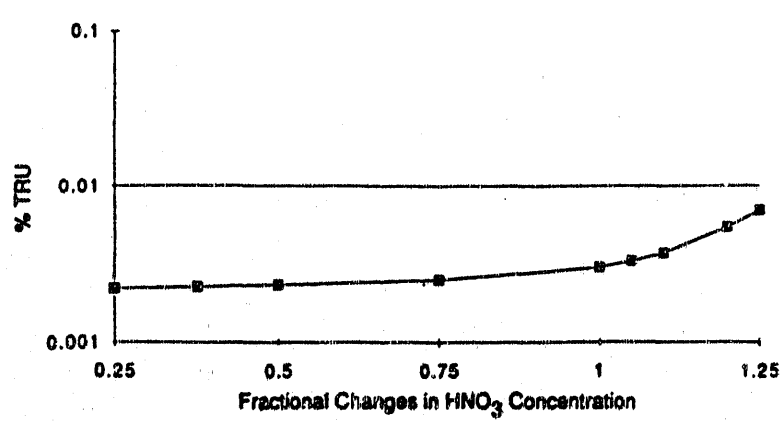

Fig. 21d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in Scrub and Strip 1 Feed. Concentrations are relative to the base case shown in Fig. 1.

g. Nitric and Hydrofluoric Acids in the Second-Strip Feed

The composition of the second-strip feed (0.05M HNO_3/0.05M HF) has been formulated so that plutonium will be essentially completely removed from the solvent while most of the uranium will remain in the solvent, from which it will be eventually removed in the solvent-wash sections. Typically, D_U and D_{Pu} are between 1 and 0.1 in this section. Changes in the composition of the feed to the second strip will affect only the organic and aqueous effluents from this section; therefore, they can have no effect on the amount of plutonium lost to the first strip or the TRU concentration of the extraction raffinate. Increasing the fluoride concentration will increase the effectiveness of stripping all actinides from the solvent; the effect will be strongest when nitrate concentration drops as fluoride concentration is increased. Decreasing the fluoride concentration will cause the second strip to be less effective, especially if fluoride is replaced by nitrate.

The effect of a perturbation in the F^- concentration at constant H^+ concentration in the feed in strip 2 can be seen in Figs. 22a through 22d. In this case, no negative effect was observed for the first three process criteria (Figs. 22a, 22b, and 22c). Decreasing the F^- concentration below 0.886 of its base-case concentration increases the TRU lost in strip 2 beyond process bounds. Figures 23a through 23d show the effects of a variation in the amount of HF present in strip 2 at a constant HNO_3 concentration. No effect is seen for the first three process goals (Figs. 23a, 23b, and 23c). In the case of the amount of TRU lost in the second strip, when nitric acid concentration is held constant at 0.05M, it can be seen that, at a fluoride concentration below 0.745 of its base-case concentration, the fourth criterion will not hold (Fig. 23d). Note the allowance of lower fluoride in the case when nitrate ion does not increase as fluoride decreases.

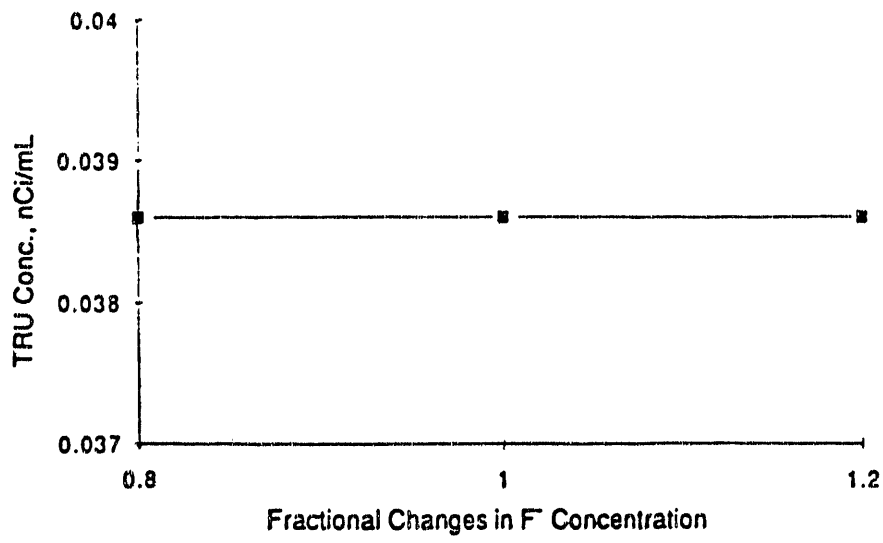

Fig. 22a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the F^- Concentration at Constant H^+ in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

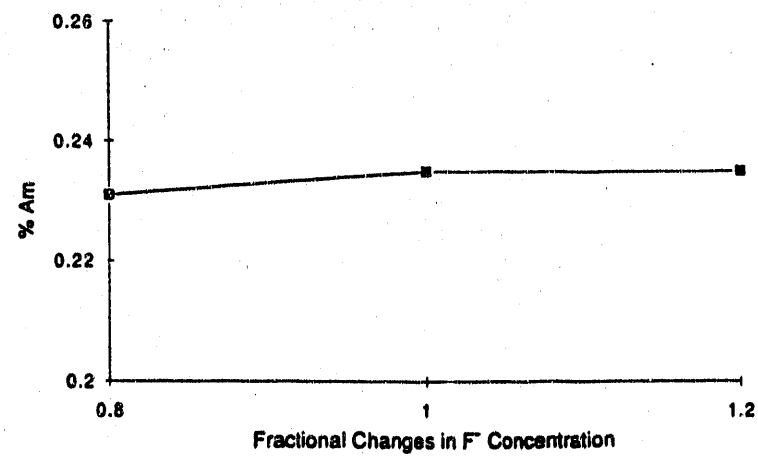

Fig. 22b. Percent Americium in Strip 2 as a Function of Fractional Changes in the F^- Concentration at Constant H^+ in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

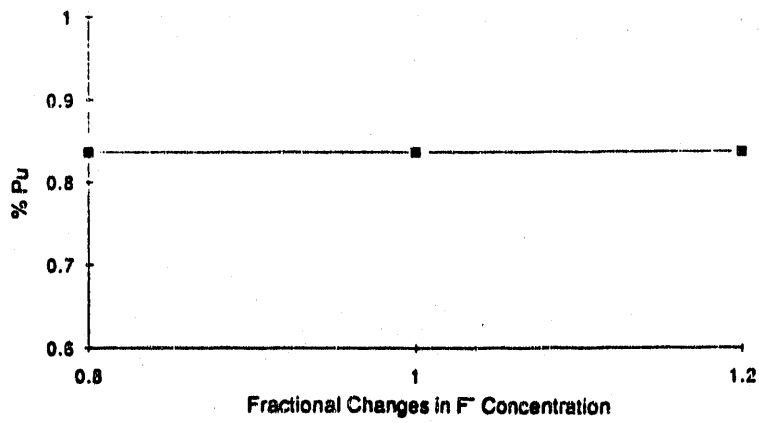

Fig. 22c. Percent Plutonium in Strip 2 as a Function of Fractional Changes in the F^- Concentration at Constant H^+ in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

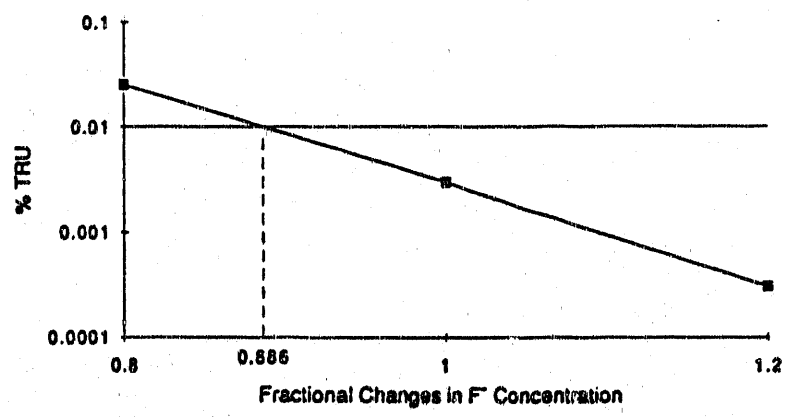

Fig. 22d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the F^- Concentration at Constant H^+ in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

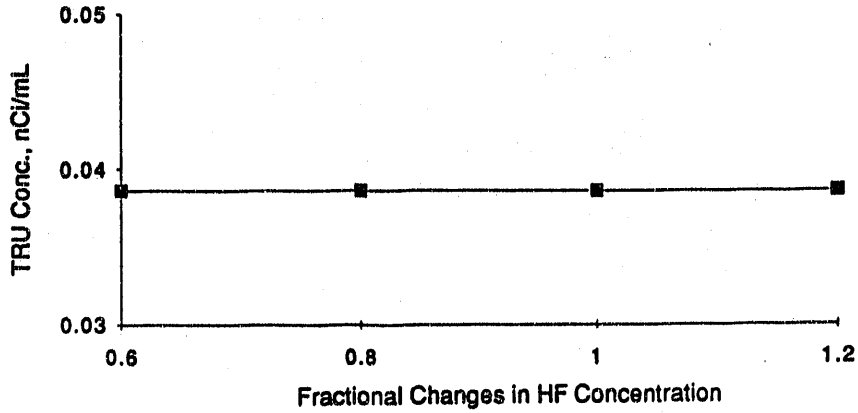

Fig. 23a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the HF Concentration at Constant HNO_3 in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

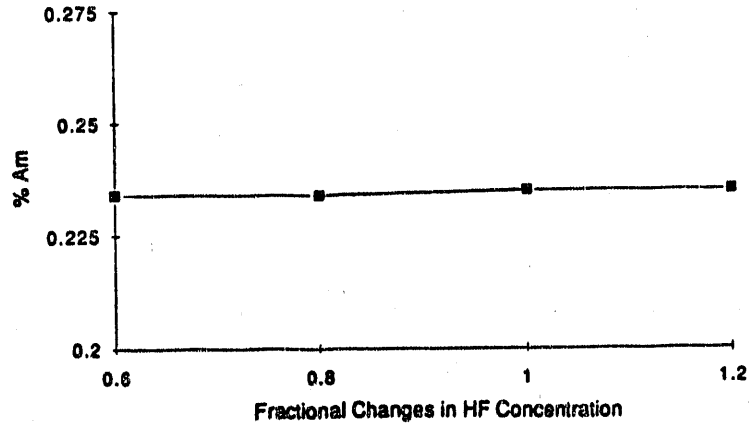

Fig. 23b. Percent Americium in Strip 2 as a Function of Fractional Changes in the HF Concentration at Constant HNO_3 in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

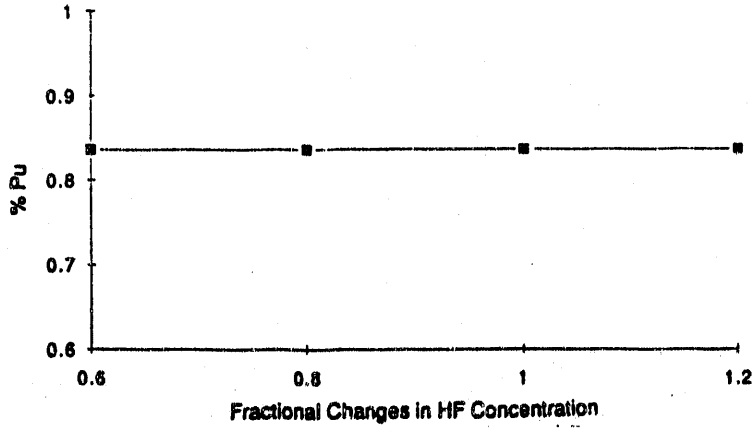

Fig. 23c. Percent Plutonium in Strip 1 as a Function of Fractional Changes in the HF Concentration at Constant HNO_3 in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

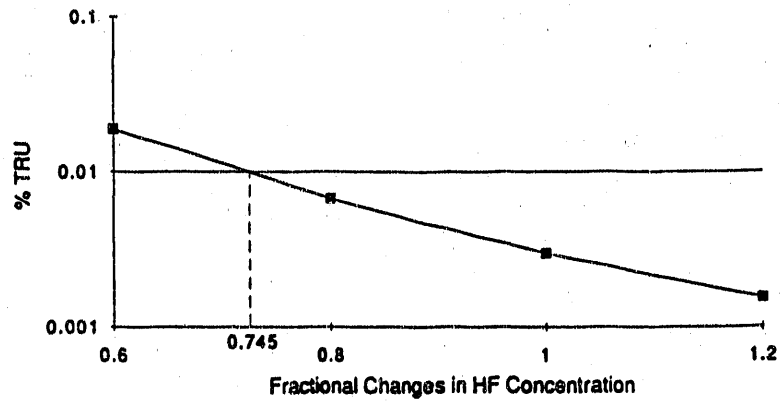

Fig. 23d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the HF Concentration at Constant HNO_3 in Strip 2 Feed. Concentrations are relative to the base case shown in Fig. 1.

D. Conclusions

In Volume Two, we will discuss how sensors for the monitoring and control of the parameters analyzed in this section (e.g., flow rate and feed compositions) can be selected based on this perturbation analysis. Tables 2 through 4 give a summary of the bounds obtained for every case studied. Also given in these tables are the four process goals used in the sensitivity analysis. For each of these goals we give a range in which the given goal is satisfied. For every perturbation study we give the base value. Note that these perturbation values are relative, with the bounds being given in a fractional form.

Of all the perturbations analyzed, only one of them, the perturbation to the aqueous feed in the extraction section, was limited by the most important process goal, a TRU concentration in the raffinate of less than 10 nCi/mL. But even in this case, the flow rate can be up to four times greater than its base value of 400 mL/min without exceeding the process goals.

The tightest bounds obtained were in the cases of (1) the flow rate of the organic feed and (2) the concentration of HNO_3 in the aqueous feed in the scrub and in the first strip. For these cases, the upper value could not exceed 1% and 2%, respectively, of the base value before the americium percentage in the second strip exceeds 0.3%. In these circumstances, the basic flowsheet (base case) should be redesigned to increase the operating range of these two parameters. This can be accomplished by adding more stages to the first strip so that less americium is lost in the second strip. However, these additional stages will also cause more plutonium to be lost in the first strip. To avoid this loss, the acid concentration in the organic solvent that enters the first-strip stage must be increased, which can be done in the scrub feed. Increasing the acid concentration in the organic solvent increases the distribution ratios for plutonium. A D_{Pu} of about 200 can be obtained by using 0.5M HNO_3 in the scrub feed. A D_{Pu} of 200 will permit a loss of plutonium in the americium strip of only about 0.53%. Since the maximum loss of plutonium in the americium strip is 1.1%, an HNO_3 concentration of 0.5M in the scrub will permit changes in the scrub acid concentration that will not be too sensitive to the amount of plutonium lost in the first strip.

Table 2. Control Bounds for Flow Rates

Variable (Base-Case Value)	Allowable Fractional Change[a]	Criterion 1: Range in Which the TRU Concentration in the Raffinate Is Less Than 10 nCi/mL	Criterion 2: Range in Which the Am % in Strip 2 Effluent Is Less Than 0.3%	Criterion 3: Range in Which the Pu % in Strip 1 Effluent Is Less Than 1.1%	Criterion 4: Range in Which the TRU Lost in the Organic Flow Exiting Strip 2 Is Less Than 0.01%
Organic Extraction Feed (150)	0.935-1.01	Not Limiting	<1.01	>0.935	<1.08
Aqueous Extraction Feed (400)	0.1-4.03	<4.03	Not Limiting	>0.1	Not Limiting
Aqueous Scrub Feed (40)	0.959-1.17	Not Limiting	>0.959	<1.17	>0.477
Aqueous Strip 1 Feed (150)	0.986-1.13	Not Limiting	>0.986	<1.13	>0.842
Aqueous Strip 2 Feed (75)	>0.902[b]	Not Limiting	Not Limiting	Not Limiting	>0.902

[a]Fractional change with respect to the base case for which the process goals still hold.
[b]Higher flow rates will be limited by equipment size.

Table 3. Effects of Losing Stages in Different Sections

Section	No. of Stages Lost	Process Goals Met	Comments
Extraction	1	yes	TRU Conc. in Raffinate <10 nCi/mL % Am in Strip 2 Effluent <0.3 % Pu in Strip 1 Effluent <1.1 % TRU in Strip 2 <0.01
Extraction	2	no	TRU Conc. in Raffinate >10 nCi/mL
Scrub	1	no	% Am in Strip 2 Effluent >0.3
First Strip	1	no	% Am in Strip 2 Effluent >0.3
Second Strip	1	no	%TRU in Strip 2 >0.01

Since the acid concentration in the organic solvent coming into the first strip increased, the distribution ratios for americium also increased for the first two stages. As a result, two stages in the first strip are lost. It is then necessary to add two more stages in the first strip to compensate for the lost stages. Since the scrub and americium feeds now have different HNO_3 concentrations, the same storage tank cannot be used for both feeds. This trade-off is necessary to obtain a more robust flowsheet.

Figure 24 shows the new, redesigned flowsheet with a 0.5M acid concentration for the scrub feed and two more stages in the first strip. Note that the scrub and the americium strip are now independent. Figures 25 through 27 show how the limiting bounds for the original base have been improved. Figure 25 shows the four process goals plotted against the changes in the organic-feed flow rate for both the new and old flowsheets. Since the extraction section has not been changed, the TRU concentration in the extractant is not affected (Fig. 25a). Perturbations to the organic-feed flow rate in the new base case have the same effect as in the old base case, as discussed in detail in Sec. C.1.a; however, by increasing the acid in the scrub and adding two more stages, we have made the flowsheet less sensitive to this perturbation. The old range (from 0.935 to 1.01) in which process goals hold has been increased (from 0.764 to 1.105). The organic flow rate can now be increased by 10%, as shown in Figs. 25b and 25d, or decreased by 24%, as shown in Fig. 25c, without losing the process goals. Also the TRU lost to the organic

Table 4. Control Bounds for Feed Concentrations

Variable (Base Case Value)	Allowable Fractional Change[a]	Criterion 1: Range in Which the TRU Concentration in the Raffinate Is Less Than 10 nCi/mL	Criterion 2: Range in Which the Am % in Strip 2 Effluent Is Less Than 0.3%	Criterion 3: Range in Which the Pu % in Strip 1 Effluent Is Less Than 1.1%	Criterion 4: Range in Which the TRU Lost in the Organic Flow Exiting Strip 2 Is Less Than 0.01%
Am in Aqueous Extraction Feed (6×10^{-6}M)	<12.7	<203	<12.7	<90.2	Not Limiting
Pu in Aqueous Extraction Feed (3×10^{-5}M)	<4.14	<689	Not Limiting	<103	<4.14
UO_2 in Aqueous Extraction Feed (3×10^{-6}M)	<620	Not Limiting	Not Limiting	Not Limiting	<620
$Al(NO_3)_3$ in Aqueous Extraction Feed (0.43M)	0.904-1.15	Not Limiting	<1.15	>0.904	Not Limiting
$Al(NO_3)_3$ and F^- in Aqueous Extraction Feed (0.43M and 0.09M)	<1.17	Not Limiting	<1.17	Not Limiting	Not Limiting
HNO_3 in Aqueous Extraction Feed (1.5M)	0.435-1.11	Not Limiting	<1.11	>0.435	Not Limiting
HNO_3 in Aqueous Scrub and Strip 1 Feed (0.04M)	0.43-1.02	Not Limiting	<1.02	>0.43	Not Limiting
F^- at Constant H^+ in Aqueous Strip 2 Feed (0.05M)	>0.886	Not Limiting	Not Limiting	Not Limiting	>0.886
HF at Constant HNO_3 in Aqueous Strip 2 Feed (0.05M)	>0.745	Not Limiting	Not Limiting	Not Limiting	>0.745

[a]Fractional change with respect to the base case for which the process goals still hold.

flow in the second strip becomes less sensitive (Fig. 25d) due to an increase in the amount of americium that is being stripped in the first strip. Although more plutonium is coming out in the organic flow exiting the second strip, it is not enough to increase the percentage of TRU lost in this stream because more americium is lost to the first strip.

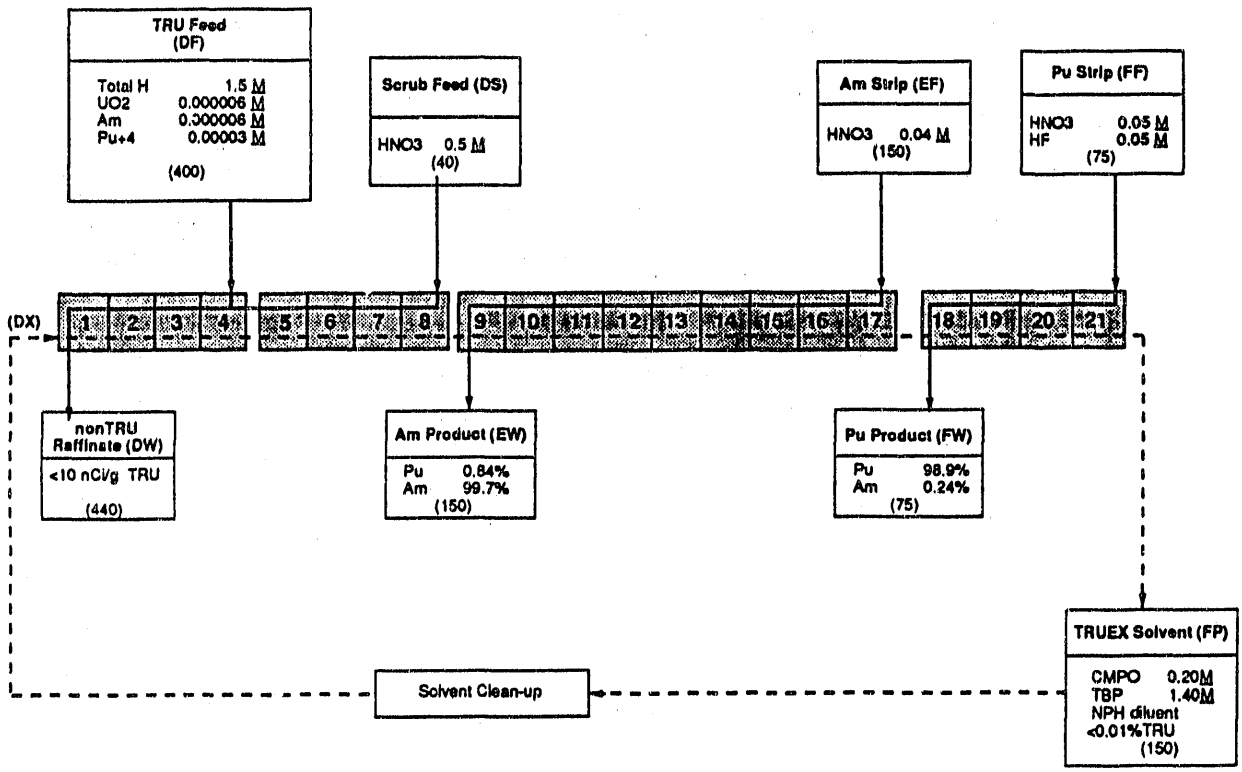

Fig. 24. Redesigned Flowsheet for Test with Synthetic PFP Waste. Numbers in parentheses are flow rates and may be expressed in any units of volume per unit time. All other flow rates are relative to the TRU feed (DF).

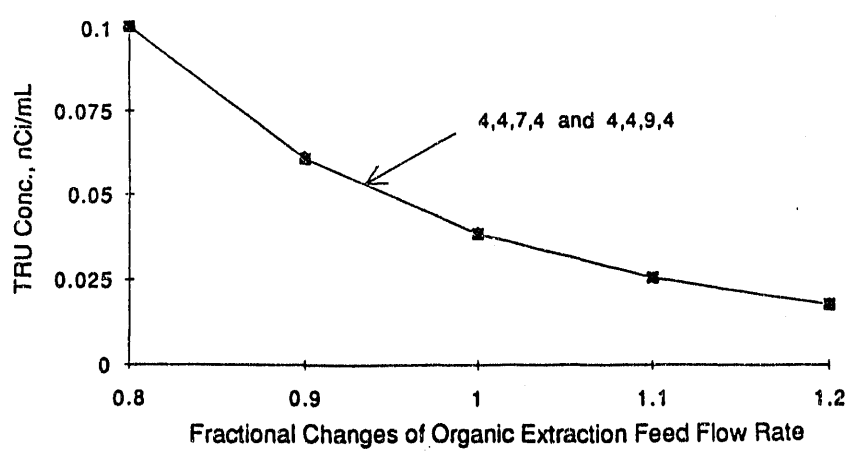

Fig. 25a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the redesigned base case shown in Fig. 24.

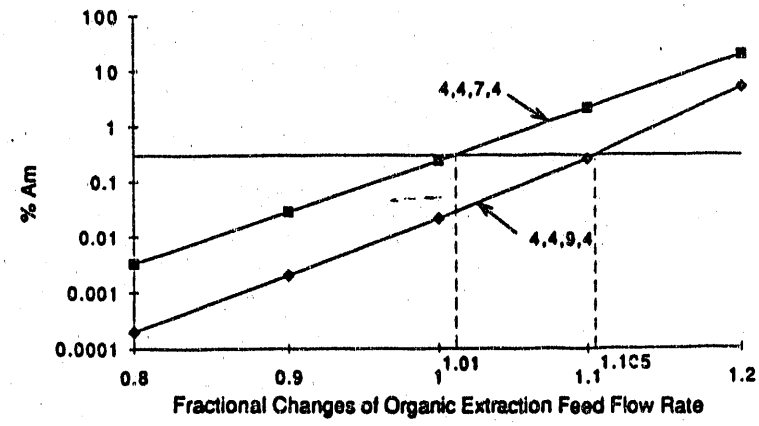

Fig. 25b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the redesigned base case shown in Fig. 24.

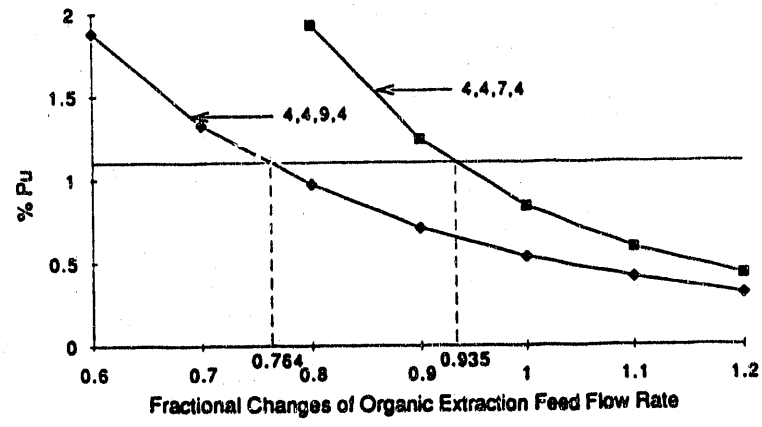

Fig. 25c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the redesigned base case shown in Fig. 24.

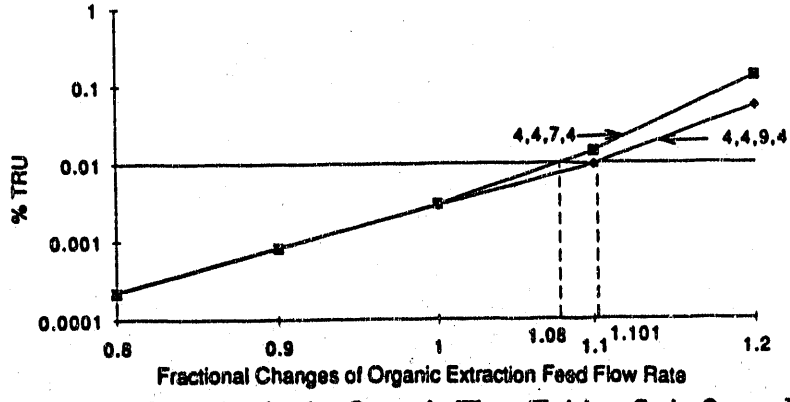

Fig. 25d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the Organic Extraction Feed Flow Rate. Flow rates are relative to the redesigned base case shown in Fig. 24.

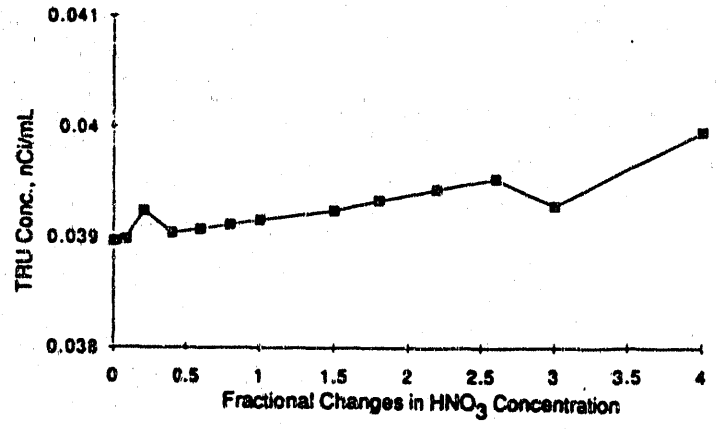

Fig. 26a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the HNO_3 Concentration in the Scrub Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

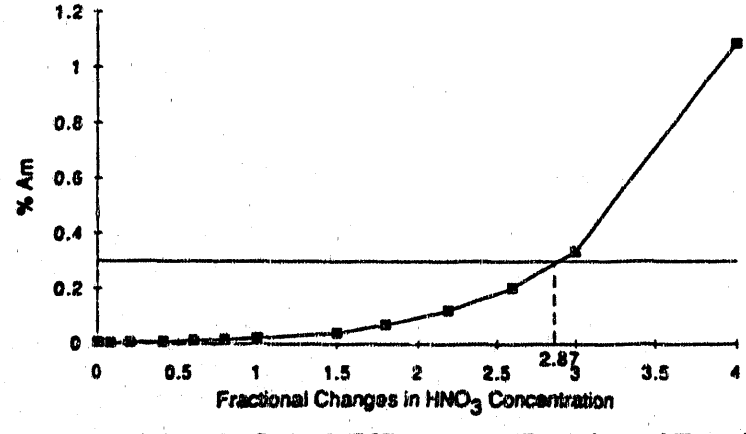

Fig. 26b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the HNO_3 Concentration in the Scrub Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

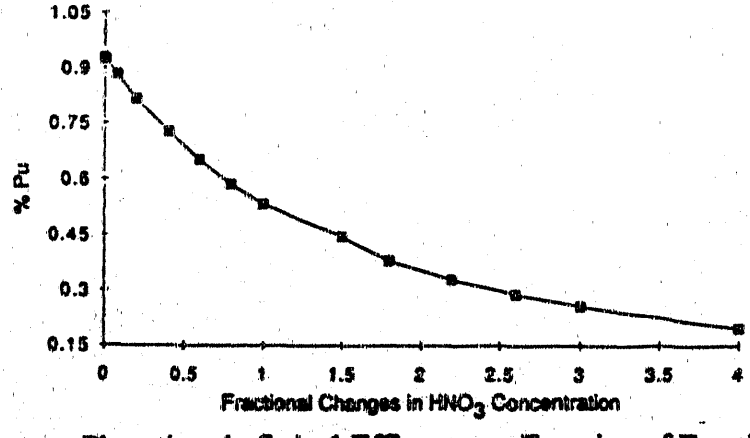

Fig. 26c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the HNO_3 Concentration in the Scrub Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

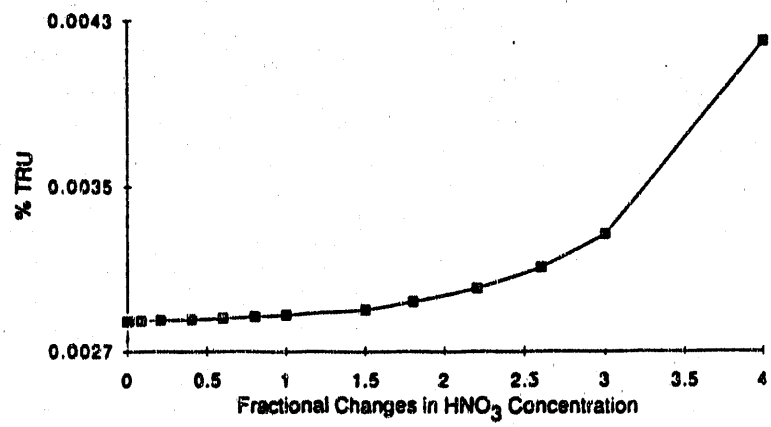

Fig. 26d. Percentage of TRU-α in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in the Scrub Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

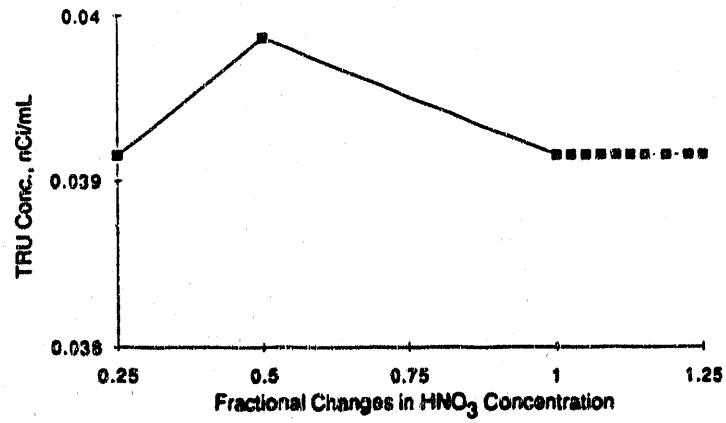

Fig. 27a. Concentration of TRU Elements in the Raffinate as a Function of Fractional Changes in the HNO_3 Concentration in the Strip 1 Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

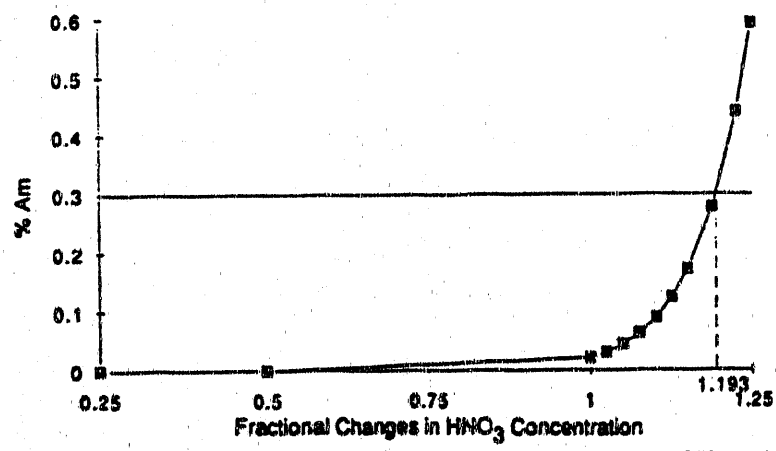

Fig. 27b. Percent Americium in Strip 2 Effluent as a Function of Fractional Changes in the HNO_3 Concentration in the Strip 1 Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

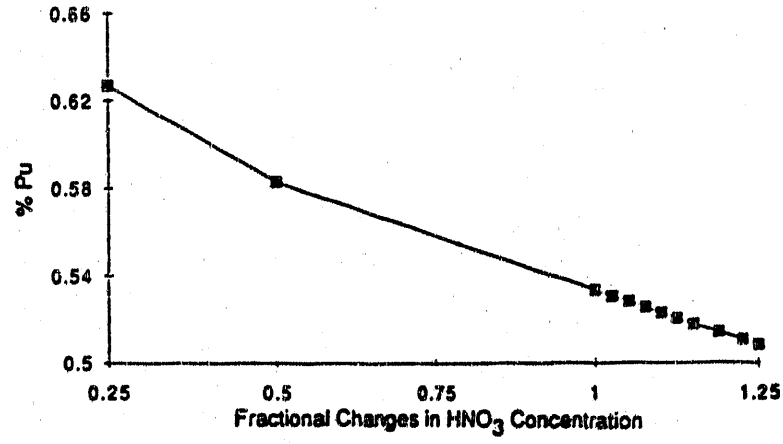

Fig. 27c. Percent Plutonium in Strip 1 Effluent as a Function of Fractional Changes in the HNO_3 Concentration in the Strip 1 Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

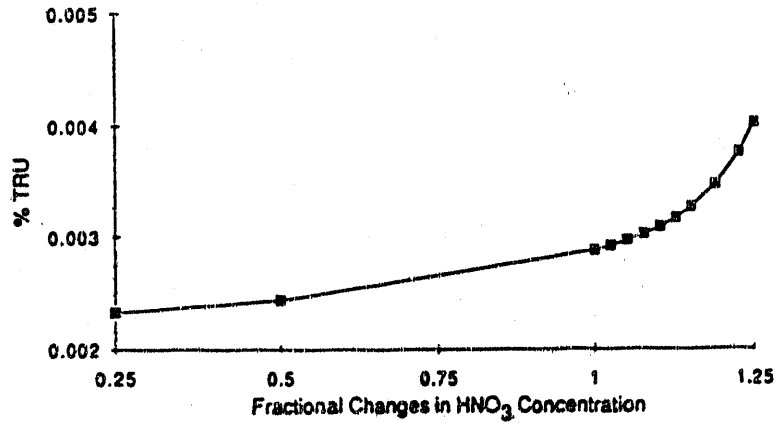

Fig. 27d. Percentage of TRU in the Organic Flow Exiting Strip 2 as a Function of Fractional Changes in the HNO_3 Concentration in the Strip 1 Feed. Flow rates are relative to the redesigned base case shown in Fig. 24.

In Figs. 26 and 27, we can see how independent changes in the nitric acid concentration in the scrub and first strip affect the process goals. Because the scrub and the first strip no longer have the same HNO_3 concentration in their feed, they do not need to be perturbed simultaneously, as they were in the case discussed in Sec. C.3.f. In the original base case, when the nitric acid was perturbed for both the scrub and the first strip, the fractional change of the HNO_3 concentration needed to be within the range of 0.43 to 1.02. Thus, it could be decreased by 57% but could only be increased by 2%. By increasing the scrub HNO_3 concentration to 0.5M and adding two more stages in the first strip, the HNO_3 concentration can be increased by 187% in the scrub section and by 19.3% in the first-strip section. The HNO_3 concentration for the new base case, shown in Fig. 24, can now be in the range of 0.002 to 2.87 for the scrub feed and 0.25 to 1.193 in the first-strip feed. However, a higher nitric acid concentration in the scrub

feed is necessary to assure that the amount of plutonium lost in the first strip, as the organic flow rate decreases, stays within the desired bounds.

The rate at which the process goals decrease or increase, with respect to the changes in the perturbed variable, is of great importance. The slopes in Figs. 8 through 24 should be as horizontal as possible. Nearly horizontal slopes appear when large changes from the base values can be made with a minimal effect on the process goals, as in Fig. 13b. Cases with steep slopes, minimal changes to the base values produce large changes in the process goals, as in Fig. 10c. These cases should be avoided as much as possible when designing a flowsheet.

Perturbation, or sensitivity, analysis is often tied up with flowsheet design. The use of this analysis early in the design stage will lead to a robust flowsheet, i.e., a flowsheet that will meet all process goals and allow for wide control bounds. Also important for designing a process is the instrumentation available to monitor and control it, which will be addressed in Volume Two.

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