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Use of the SEPHIS-MOD4 Program for Modeling the Purex and Thorex Solvent Extraction Processes*

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ABSTRACT

The SEPHIS-MOD4 computer program simulates solvent extraction in the Purex and Thorex processes. The program employs simple mass balance equations to describe the movement of solutes through the idealized mixer-settler stages which are used in the model. These differential mass-balance equations are integrated by an iterative scheme that allows the user to observe transient changes and the resulting steady state profile in the mixer-settler system. Correlations describe the equilibrium concentrations in the aqueous and organic phases. Kinetic rate equations are used to simulate the reduction of plutonium by hydroxylamine nitrate and uranium(IV).

The value of the SEPHIS-MOD4 program lies primarily in its application to the design and testing of solvent extraction flowsheets. Given a set of operating conditions, the program can predict the solute concentration profile at steady state and during the approach to steady state. Changes in the operating conditions can be used to determine the influence of important system variables or to simulate the effects of a process upset.

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This type of information has been used to evalute the flowsheets in solvent extraction experiments and to aid in understanding the results of the experiments. Comparisons between experimental results and the calculated results of the program are generally good and demonstrate the accuracy of the program. The program should become a useful tool in planning for the processing of spent nuclear fuel.

INTRODUCTION

The SEPHIS-MOD4 program is a computer simulation of solvent extraction processes (1-3). In particular, the program works with the Purex and Thorex processes for recycling spent nuclear fuel. The solutes that the program considers for the Purex process are uranium, plutonium, nitric acid, a plutonium reductant, and inextractable nitrates. The solutes in the Thorex process are uranium, thorium, nitric acid, and inextractable nitrates. The program can easily be modified to handle other solutes in these processes or other solvent extraction processes.

The mathematics of the SEPHIS-MOD4 program are tailored to resemble mixer-settler equipment. The idealized stage model and the equations used to describe the model were designed specifically for countercurrent mixer-settler operation. However, other types of equipment can be simulated to the extent that they can be characterized by an equilibrium stage model. The CONSEPT program, another model of solvent extraction, has stages that are tailored to resemble stages in centrifugal contactors (4). This program is currently being tested, and its features will be mentioned later.

The SEPHIS-MOD4 program has three basic uses. The primary use is in designing and testing flowsheets for spent fuel processing. Given a set of operating conditions, the SEPHIS-MOD4 program can predict the solute concentrations that would be found in the processing equipment and in the product streams. By varying the operating conditions, the user of the program can determine which operating conditions fulfill the criteria for his particular flowsheet. In many flowsheets conflicting priorities must be balanced, and this calculational approach is a fast and inexpensive way to examine the trade-offs that must be made. Although the calculated results are reasonably accurate, the proposed flowsheet must still be tested experimentally. The results of the experiment can then be compared with the results from the SEPHIS program, and frequently this comparison will show where further experimental development is needed.

The second use of the SEPHIS-MOD4 program is in simulating the performance of fuel processing plants. The effects of process upsets and the general performance of the plant can be gauged by using the program. This information is helpful in assessing the safety of the plant and in preventing the occurrence of criticality accidents.

The third major use of the program is in developing safeguards strategies to prevent the diversion of fissile material. The program is being used to devise flowsheets that either do not produce pure plutonium streams or that cannot produce such streams without major flowsheet changes. The program is also being used to estimate the time that could elapse between the start of a diversion and its detection. The elapsed time can then be used to estimate the amount of fissile material that might be lost before detection.

MODEL DESCRIPTION AND GENERAL MATHEMATICS

The mathematical foundation of the SEPHIS-MOD4 program is based on the idealized mixer-settler stage (Fig. 1). Each stage is composed of a mixer, an aqueous settler, and an organic settler. The streams entering a stage are (1) the aqueous stream from the preceding stage, (2) the organic stream from the succeeding stage, (3) an aqueous feed stream, and (4) an organic feed stream. These four streams enter the stage and are combined with the contents of the mixer. In the mixer, the solutes are assumed to be at an equilibrium distribution between the phases. In this

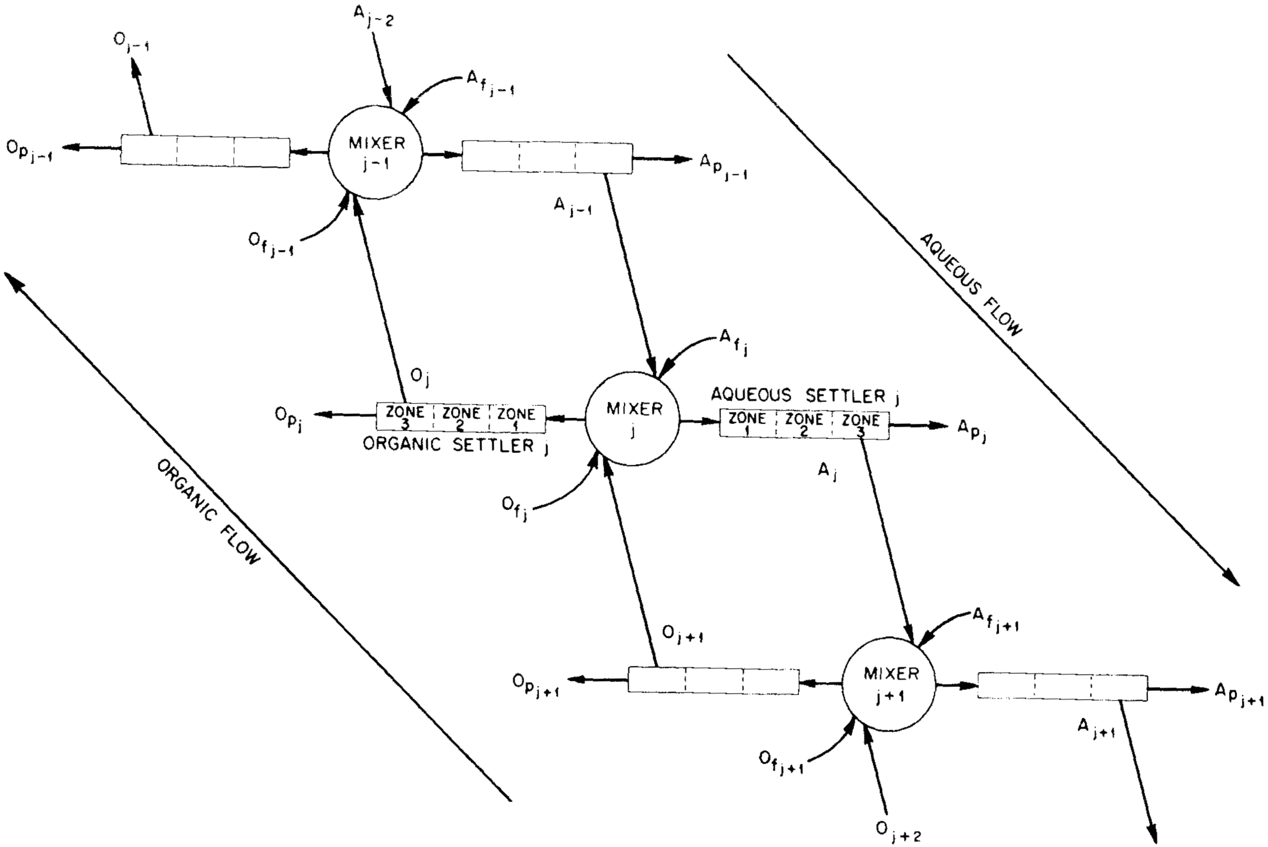

Fig. 1. Idealized model used by SEPHIS-MOD4 for mixer-settlers.

way, the aqueous and organic concentrations can be related by a distribution coefficient.

The overflow from the mixer enters the settlers. In actual equipment, the phases disengage at this point. In the model, the settlers provide a time delay between when a solute leaves one mixer and when it enters the next one. The settlers are subdivided into three zones; these zones are considered to be three consecutive stirred tanks. The use of three zones provides a compromise between plug flow and well-mixed flow through the settlers. Well-mixed flow would be described by one zone, whereas plug flow would require an infinite number of these zones. After passing through the settlers, the streams either leave the system as a product stream or go to the next stage.

The flow of solutes through this idealized stage is described by unsteady state mass balance equations. For the mixer, these mass balances state that the change in the amount of a particular solute in the mixer is equal to the difference between the amount that flows in and the amount that flows out:

$$V_{aj}\frac{\partial x_j}{\partial t} + V_{oj}\frac{\partial y_j}{\partial t} = A_{j-1}x_{j-1} + A_{fj}x_{fj} + O_{j+1}y_{j+1} + O_{fj}y_{fj} - (A_j + A_{pj})x_j - (O_j + O_{pj})y_j \ , \qquad (1)$$

where

V = volume,
x = aqueous-phase solute concentration,
y = organic-phase solute concentration,
t = time,
A = aqueous-phase flow rate,
O = organic-phase flow rate,
subscript a = aqueous phase,
subscript o = organic phase,
subscript j = stage number,

subscript f = feed stream,

subscript p = product stream.

In the mixer the phases are in equilibrium, so the aqueous concentration x_j and the organic concentration y_j are related by a distribution coefficient D ($D = y/x$). Using the distribution coefficient, the mass balance simplifies to a form that is easily evaluated:

$$\frac{\partial x_j}{\partial t} = \frac{A_{j-1}x_{j-1} + A_{fj}x_{fj} + O_{j+1}y_{j+1} + O_{fj}y_{fj} - [A_j + A_{pj} + D(O_j + O_{pj})]x_j}{V_{aj} + DV_{oj}} \quad (2)$$

This equation relates change in the aqueous concentration to the other variables. Thus to calculate the solute concentrations in the mixer, the program integrates this differential equation.

CHEMICAL DESCRIPTION OF THE EXTRACTION SYSTEM

The distribution coefficients in Eq. (2) are determined by correlations written in terms of the aqueous concentrations. The correlations for the Purex process describe the distribution of uranium, plutonium, and nitric acid; those for the Thorex process are for uranium, thorium, and nitric acid.

The correlations for the Purex process were originally developed by Horner (5) and were revised by Richardson (6,7) and then by Watson and Rainey (8). The SEPHIS-MOD4 program currently uses the Watson-Rainey version of these correlations with a correction factor recently found by Jubin (9). Watson and Rainey were the developers of the correlations for the Thorex process (10,11).

The correlations for both processes are based on fitting equations to literature data. The data-fitting procedure used mass action expressions to describe the distribution of a particular solute and its interdependence on the other solutes in the system. For example, the mass action expression for uranium is

$$K_u = \frac{[UO_2(NO_3)_2 \cdot 2TBP]}{[UO_2{}^{2+}][NO_3{}^-]^2[TBP]^2} , \tag{3}$$

where K_u is the mass action constant, brackets indicate "concentration of" the enclosed compound(s), and TBP is tributyl phosphate.

The uranium distribution coefficient is the ratio of the complexed organic form over the ionic aqueous form. The mass action constant K_u was fit to a polynomial function of the ionic strength of the aqueous solution. The interrelationship with the other solutes is through the nitrate ion concentration, the TBP concentration, and the ionic strength of the aqueous solution.

The SEPHIS-MOD4 program is also able to consider the kinetics of reactions in the system. Currently, the only reaction considered is the reduction of plutonium. The program can handle instantaneous reduction, reduction by uranium(IV), and reduction by hydroxylamine nitrate (HAN). The rate equation for reduction by uranium(IV) is adapted from the stoichiometry and kinetics proposed by Baxter and Naylor(12); reduction by HAN uses the stoichiometry and kinetics proposed by Barney (13). Additional reactions can be added by the user of the program.

USES OF THE PROGRAM

The values calculated by the SEPHIS-MOD4 program are based on an idealized mixer-settler stage, correlations for distribution coefficients, and published kinetics for reduction reactions; but the value of the program can be measured only by its ability to produce useful results. Examples of the results produced by the program clearly demonstrate its applications and abilities.

As stated previously, the primary use of the program is in the design and testing of flowsheets for use in processing spent nuclear fuel. To design a flowsheet, a set of criteria must be established with which the flowsheet must conform. These criteria might include the number of stages, the desired product stream concentrations, or the ambient temperature. The example shown in Fig. 2 is a coprocessing flowsheet, or at least the initial criteria that must be met. The feed stream (HAF) is the product of the dissolver for LWR fuel. It contains uranium with about 1% plutonium. The feed stream enters the extraction bank where all of the uranium and plutonium are transferred to the organic stream (HAX). The purpose of the scrub stream (HAS) is to remove fission products from the organic phase and to adjust the acidity of the organic product (HAP).

After leaving the extraction bank, the organic phase enters the partial partitioning bank. In this bank all of the plutonium is stripped from the organics by use of a reductant in the aqueous strip (1AS). Some uranium will also be stripped, but the goal of this flowsheet and of this bank in particular is to produce a stream with a plutonium content equal to 20% of the total heavy metal content. Consequently, this flowsheet requires a method to control the amount of uranium leaving in the aqueous product stream (1AP).

To complete the flowsheet design, an approximate flowsheet was found and parametric calculations were performed to determine the effects of the variables. Figure 3 shows the influence of the strip flow rate for two values of strip acidity. Increasing the 1AS flow rate will decrease the plutonium/heavy metal fraction of the product because more uranium will strip into the aqueous phase. Increasing the 1AS acidity will increase the plutonium/heavy metal fraction of the product because more of the uranium will be left in the organic phase.

To test the operation of the tentative flowsheet for the partial partitioning bank, an experiment was performed in which the 1AS flow rate was decreased and the acidity was increased. The experiment contained no plutonium, so the only goal was to determine if the uranium concentration in the aqueous product stream could be limited to a given level. The uranium concentration profile of the aqueous phase in the partial partitioning bank is shown in Fig. 4. The experimental data points are very close to the calculated line. The low uranium concentration in stage 16 indicates that the uranium concentration in the aqueous product stream can indeed be limited.

The experiment also demonstrated that further development is needed to modify the nitric acid profile which resulted. The nitric acid concentration profile for the aqueous phase is shown in Fig. 5. Although the experimental data points are close to the calculated line, the high acidity (>~1.0 mol/L) in stages 12 through 16 must be reduced for this flowsheet to work properly. If the acidity of the aqueous product stream is too high, the plutonium may not be quantitatively reduced and some of it may contaminate the uranium product stream (1AU). Figure 6 shows the influence of the HAS scrub stream acidity on the 1AP acidity for two strip flow rates. Decreasing the scrub acidity will decrease the product acidity, whereas decreasing the strip flow rate will increase the product acidity.

Figure 7 shows the interrelationships between uranium level and acidity in the product stream. Actions taken to decrease the product acidity also decrease the plutonium/heavy metal fraction of the product. Conversely, actions taken to enrich the product with plutonium also increase the acidity with the concomitant result that all the plutonium might not leave in the product stream. Using this information, the flowsheet designer can balance the conflicting priorities and limit the amount of experimental testing required to develop the flowsheet. The calculations will show which set of conditions will most nearly meet the criteria for the flowsheet.

In the case of this coprocessing flowsheet, a new set of operating conditions was chosen and an experiment was performed. The results of the experiment generally confirm what had been calculated. No plutonium was used in this experiment, but based on the uranium concentration in the 1AP, the plutonium would have

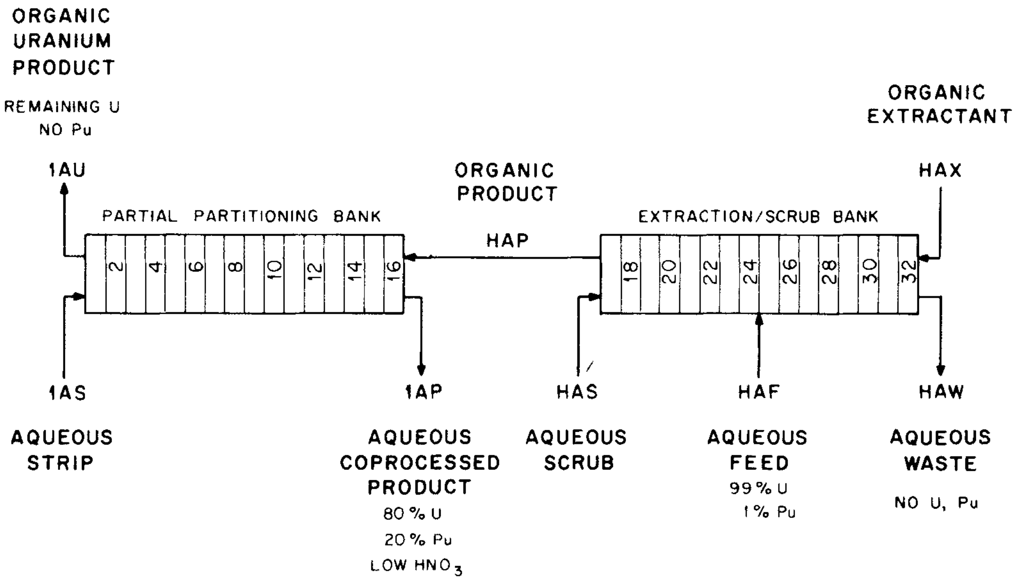

Fig. 2. Initial criteria to be met by a proposed coprocessing flowsheet.

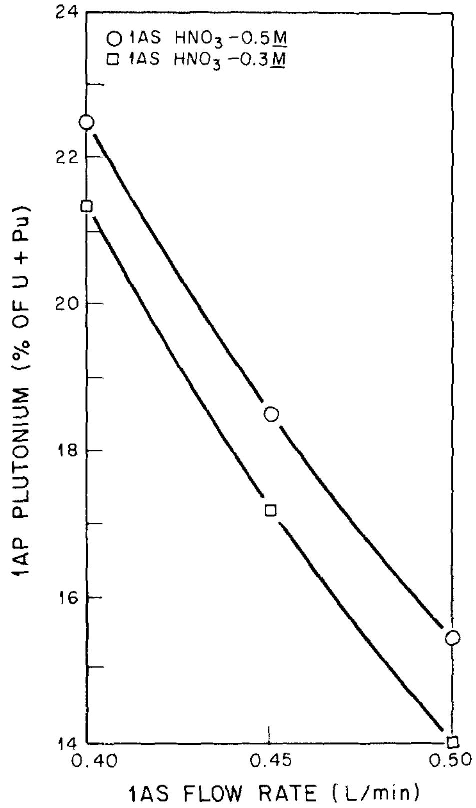

Fig. 3. Influence of the 1AS flow rate on the plutonium content of the aqueous product stream.

comprised about 16% of the heavy metal in the aqueous product (assuming complete stripping). The uranium concentration profile for the aqueous phase is shown in Fig. 8. The experimental data points are very close to the calculated line until stage 25, the point at which the feed stream enters the system. The differences between the data points and the calculated line in the dilute end of the system are probably due to stage inefficiences; however, the SEPHIS-MOD4 program assumes ideal stages. Figure 9 shows the same information on a linear scale. The data points indicate that the uranium is refluxing in the partial partitioning bank to a

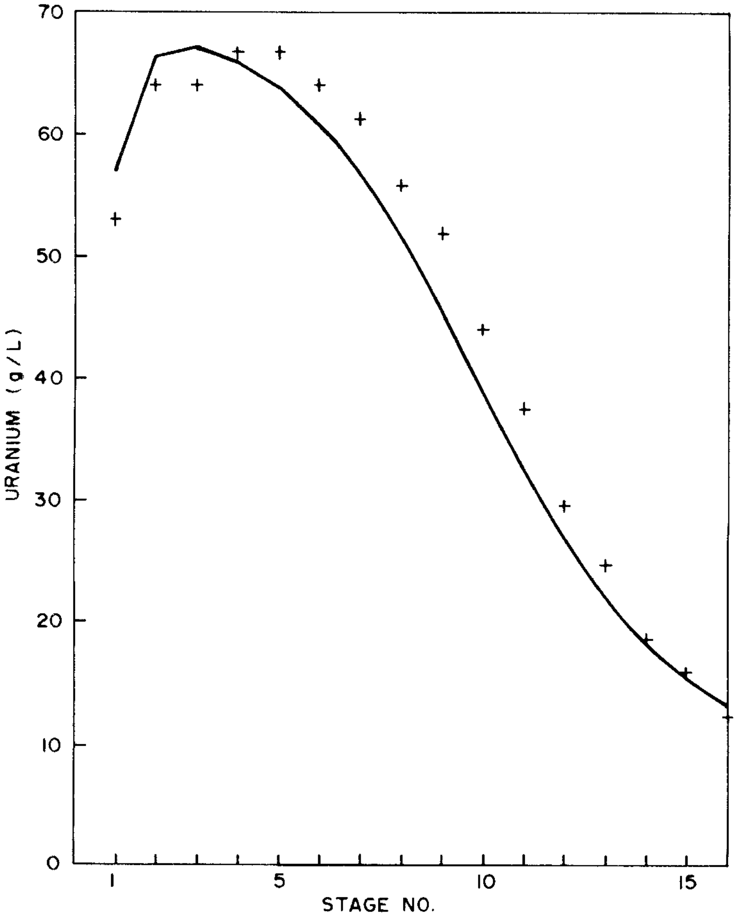

Fig. 4. Profile of the aqueous uranium concentration for the partial partitioning bank.

greater extent than expected. This can be due to slight experimental inaccuracies (e.g., flow rates, measured concentrations, and temperatures), or to small errors in the calculated distribution coefficients. Figure 10 shows the nitric acid concentration profile in the aqueous phase. The experimental data points are very close to the calculated line. The concentration in stage 16 was reduced from about 2.3 mol/L to about 1.9 mol/L HNO_3 as a

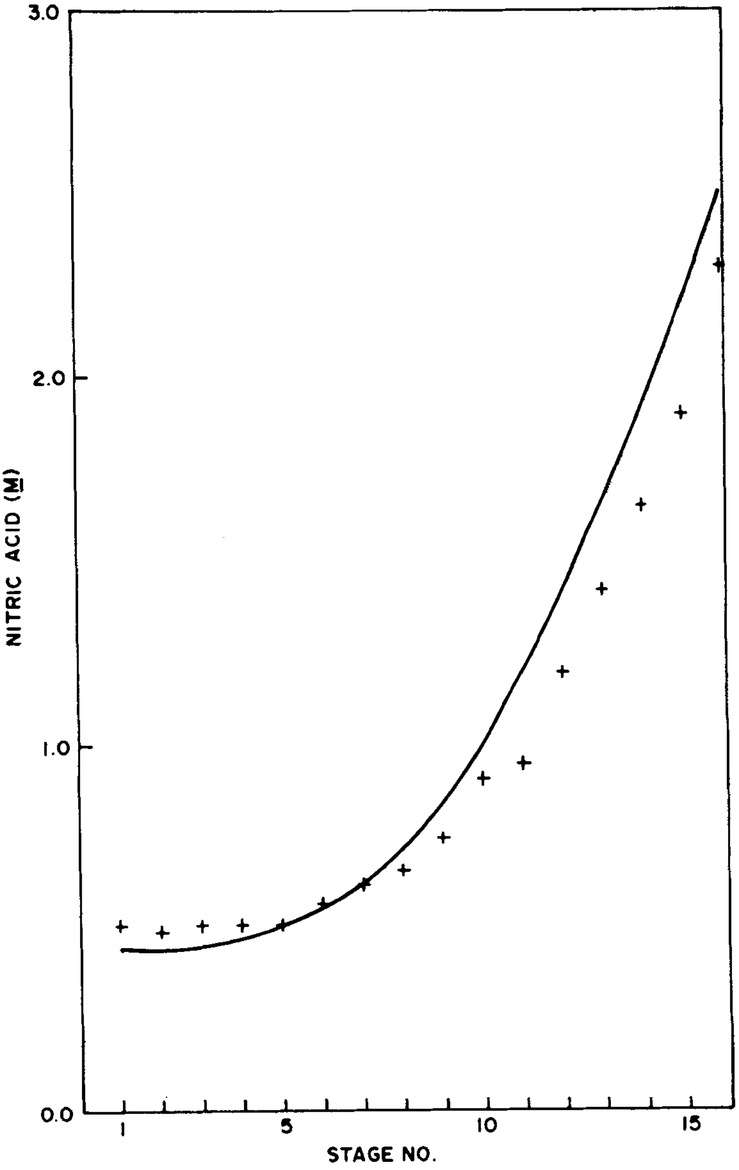

Fig. 5. Profile of the aqueous nitric acid concentration for the partial partitioning bank.

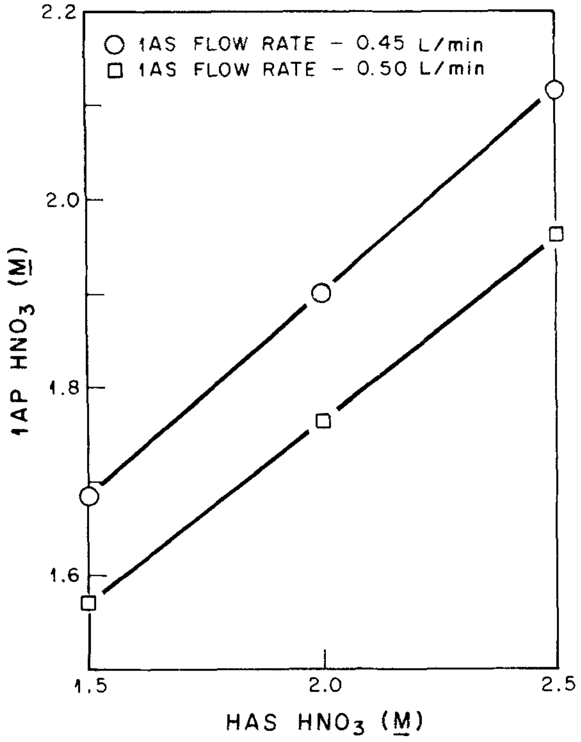

Fig. 6. Influence of scrub stream acidity on the acidity of the aqueous product stream.

result of the changed operating conditions, and only three stages have a concentration over 1.0 mol/L HNO_3. This is a significant improvement over the previous flowsheet, but even lower acid concentrations would be helpful.

The degree of correspondence between the experimental results and the results produced by the SEPHIS-MOD4 program varies from one experiment to the next. However, these samples demonstrate that the SEPHIS-MOD4 program can be used with confidence when designing solvent extraction flowsheets.

Although the discussion thus far has been limited to steady-state results, the SEPHIS-MOD4 program is also designed to produce

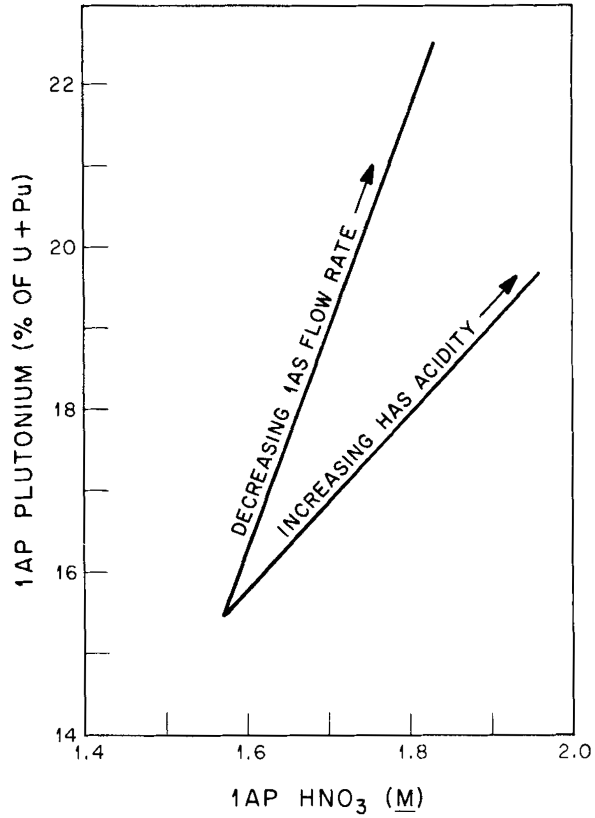

Fig. 7. An example of the conflicting requirements of this coprocessing flowsheet.

transient results during periods when operating conditions or concentrations are changing. Figure 11 shows the transient density response during the start-up of an experiment with a different flowsheet. After an initial rapid increase, the calculated results are slightly higher than the experimental results; this is probably due to inaccuracies in the density correlations used by the program. However, the main conclusion is that the program accurately indicates the time and speed at which changes occur in the product stream density.

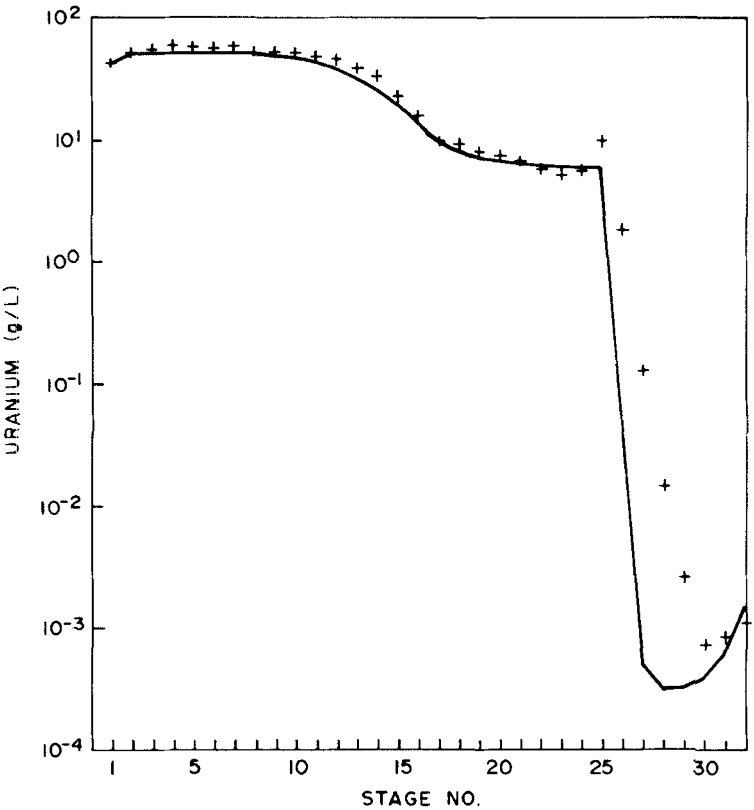

Fig. 8. Profile of the aqueous uranium concentration using revised operating conditions (log scale).

SUMMARY AND NEW DEVELOPMENTS

The SEPHIS-MOD4 program is able to predict steady-state and transient concentrations with reasonable accuracy. The program can easily be adapted to work with many contactor arrangements or with other solvent extraction processes. The program can save the flowsheet designer great amounts of experimental time and effort by allowing the designer to scout the operating conditions prior to conducting experiments. The program can also be used in safety analyses for fuel processing plants and in testing safeguards strategies.

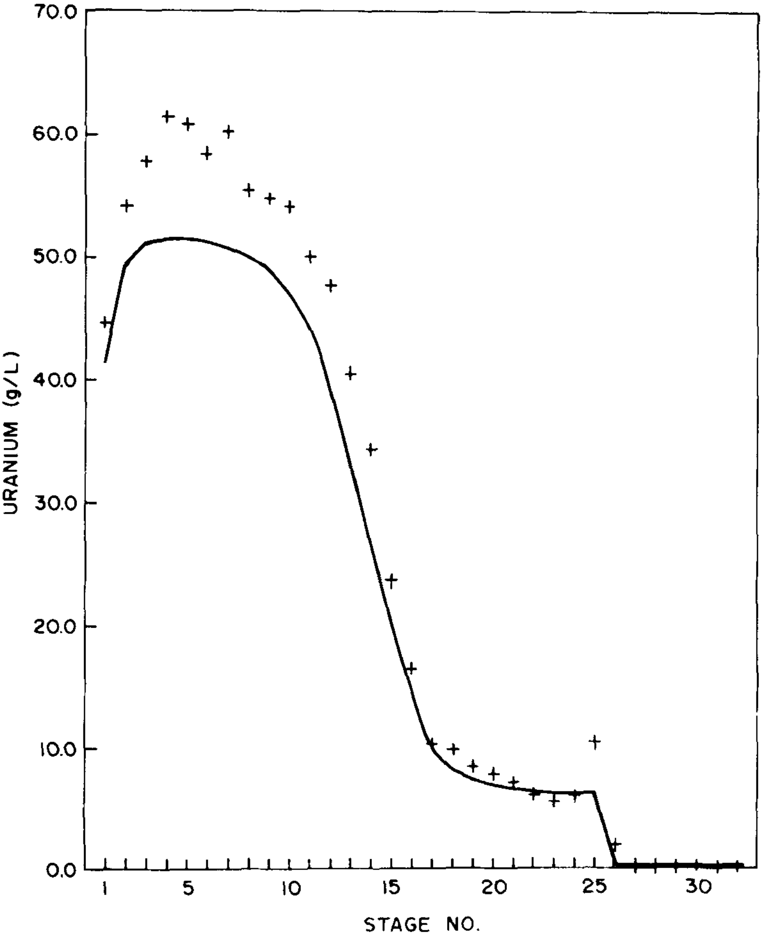

Fig. 9. Profile of the aqueous uranium concentration using revised operating conditions (linear scale).

Similar information can be obtained through use of the newly developed CONSEPT (controller-run solvent extraction process testing) program.' In contrast with the mixer-settlers of the SEPHIS-MOD4 program, the CONSEPT program was tailored to model centrifugal contactors. The feed stream flow rates and concentrations can be adjusted automatically by process controllers. The volumes and flow rates in the system vary with time as the

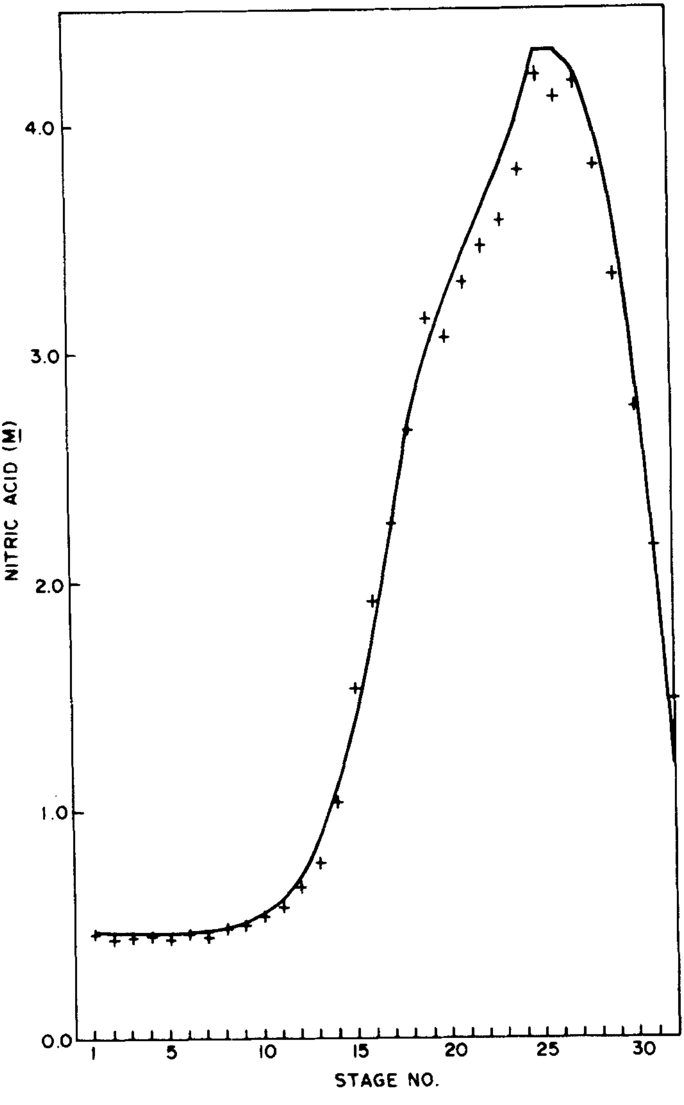

Fig. 10. Profile of the aqueous nitric acid concentration using revised operating conditions.

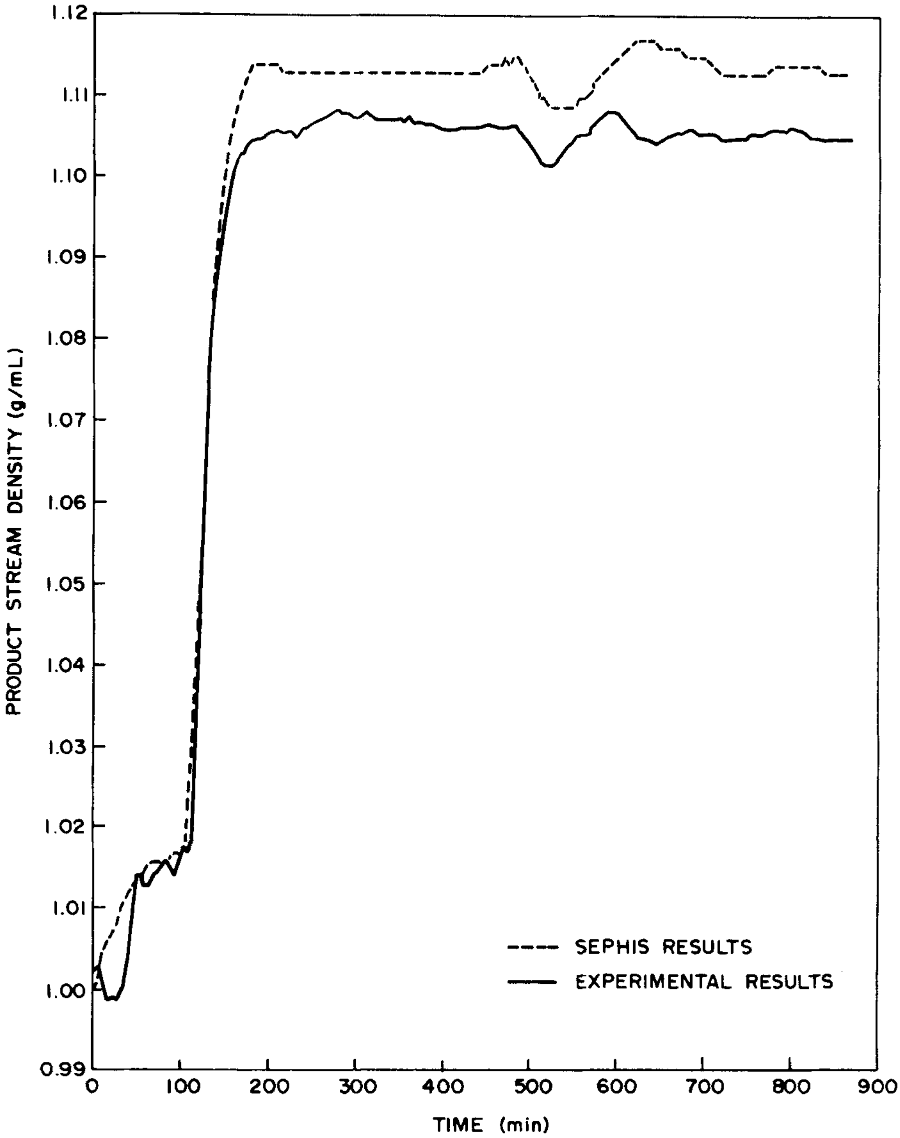

Fig. 11. A comparison of the transient density response predicted by SEPHIS-MOD4 with that measured experimentally.

feed streams change. In addition, various forms of errors can be imposed on the feed streams. The mechanics of the CONSEPT program make it particularly applicable in the areas of flowsheet design and reprocessing plant simulation. In conjunction with experimental testing, both of these computer programs should become useful aids in processing irradiated nuclear fuel.

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