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# EXPERIMENTAL VALIDATION OF PULSED COLUMN INVENTORY ESTIMATORS

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## ABSTRACT

Near-real-time accounting (NRTA) for reprocessing plants relies on the timely measurement of all transfers through the process area and all inventory in the process. It is difficult to measure the inventory of the solvent contactors; therefore, estimation techniques are considered. We have used experimental data obtained at the TEKO facility in Karlsruhe and have applied computer codes developed at Clemson University to analyze this data. For uranium extraction, the computer predictions agree to within 15% of the measured inventories. We believe this study is significant in demonstrating that using theoretical models with a minimum amount of process data may be an acceptable approach to column inventory estimation for NRTA.

## INTRODUCTION

Near-real-time accounting (NRTA) for reprocessing plants relies on the timely measurement of all transfers through the process area and all inventory in the process. Inventory in the process may be divided into two categories. The first includes inventory in tanks that can be measured by dip tubes or in-line instruments. The second includes that portion of the inventory that is difficult to measure, such as contactors and concentrators.

One major problem in applying NRTA at reprocessing facilities arises from the requirement to measure and verify the material in process. A particular problem arises in estimating the inventory of solvent extraction contactors, whether they be mixer settlers or pulsed columns. Several studies have considered the possibility of estimating the inventory of solvent extraction contactors from process data and the impact of the uncertainty of this estimate on the overall

material accounting uncertainty.<sup>1-4</sup> For example, modeling the contribution of throughput, measurable process inventory (in tanks), and inventory in solvent extraction contactors showed that for facilities of high throughput (50 kg Pu/day) contactor inventory uncertainties of 100% contributed an insignificant amount to the overall accounting uncertainty.<sup>4</sup> Even for low throughputs (5 kg Pu/day) and measurable inventories greater than 40 kg of plutonium, only contactor uncertainties greater than 50% contributed significantly to the overall uncertainty.

The present study was directed to study how well the inventory of pulsed columns could be estimated compared to actual measured values.

## **TEKO EXPERIMENTAL DATA**

The TEKO facility was developed by DWK in Karlsruhe to develop process equipment, including solvent extraction contactors, for the proposed Wackersdorf reprocessing plant.<sup>5</sup> The uranium-extraction-cycle facility was used to test equipment and to assess possible processes for the first extraction cycle of a commercial reprocessing plant with a daily capacity of 4 tons of heavy metal. This full scale (1:1) plant was one of the test facilities for large-size components operated for the Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen by the Research Department of the Wiederaufarbeitungsanlage Karlsruhe Betriebsgesellschaft mbH (WAK).

This uranium extraction plant was built in the TEKO (Teststand für Grosskomponenten) testing facility for full-scale components within the Nuclear Research Centre at Karlsruhe and was put into operation in autumn 1981. Between 1982 and 1989, the plant was operated with depleted uranium. A simplified diagram of the facility is shown in Fig. 1.

## **INVENTORY ESTIMATION METHODS**

Two methods will be used to estimate the uranium contactor inventory for the TEKO facility. One of these is a first principles computer code CUSEP (Clemson University Solvent Extraction Program),<sup>6</sup> which simulates the operation of each solvent extraction column. This computer code not only estimates the nuclear material inventories of each contactor but it also calculates the concentration profiles of each species and the contactor flow rates. The second method is the Simplified Inventory Estimation Model (SIEM),<sup>7</sup> which estimates steady-state nuclear-material-contactor inventories from the measured nuclear material concentrations in the tanks feeding each

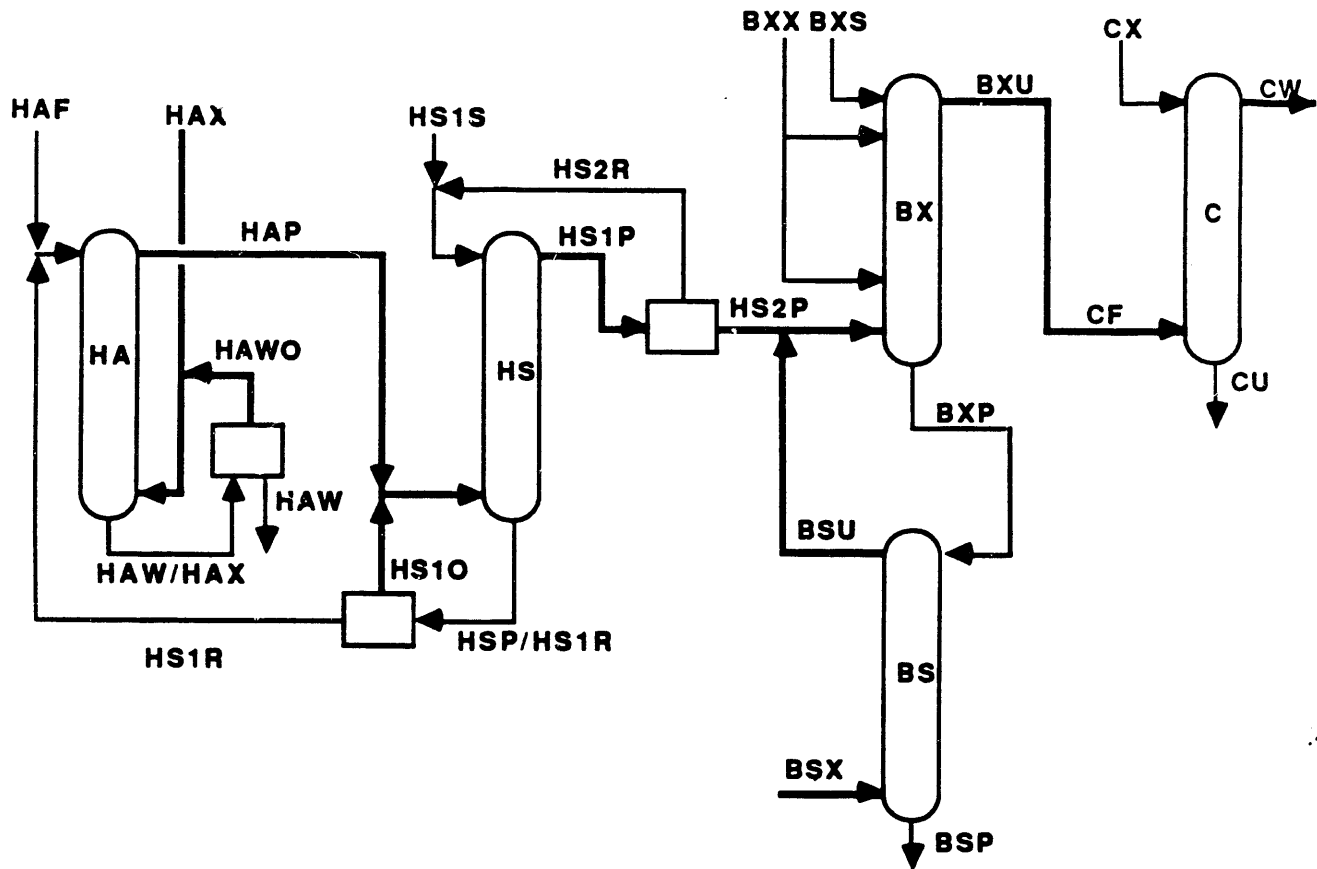


Fig. 1. Simplified diagram of the FRG-TEKO facility.

purification cycle. Remaining factors affecting the inventory such as flow rates and acid concentrations are accounted for parametrically. SIEM was developed to provide an accurate estimate of nuclear material inventories with minimal computational equipment (desk calculator or small computer) and a minimal knowledge of the plant flowsheet (only nominal flowsheet data are needed).

The details of CUSEP have already been presented<sup>6</sup> and only a brief description is given here. The CUSEP code generates both the time-dependent and steady-state concentration profiles by integrating the mass balance equations for each chemical species in the contactor by a fourth order Runge Kutta integration method. The coefficients for the equilibrium distribution of U(VI) and Pu(IV) between the aqueous and organic phases are calculated from Richardson's correlations<sup>8</sup> as modified by Geldard, Phillips, and Beyerlein.<sup>9</sup> The distribution coefficients for U(IV) and Pu(III) are calculated from correlations in the latter reference. Except for C-type stripping contactors (organic to aqueous extraction) that operate at a low acid concentration (less than 0.1M), mass transfer equilibrium between phases is assumed. This is justified by comparisons<sup>6</sup> of

CUSEP calculations with measured data<sup>10</sup> obtained from the pilot scale facility at Allied General Nuclear Services at Barnwell, South Carolina in 1983. The mass-transfer rate constants that account for deviations from equilibrium in C-type stripping contactors optimize the agreement between CUSEP calculations and the measured data of Ref. 10. The rate equations for the rate of reduction of Pu(IV) to Pu(III) are given in Refs. 11–14 for U(IV) reductant and hydroxylamine nitrate. The aqueous-to-organic-phase volume ratio needed to calculate the inventory from the concentration profile is calculated from empirical correlations<sup>15</sup> that reproduce the measured data in Ref. 10. One of the major differences between CUSEP and previous codes is that CUSEP explicitly accounts for pulsed flow and its longitudinal mixing effect on the concentration profile.<sup>6</sup> The effects of pulsed flow are significant. This can be readily understood after realizing that the pulsed flow, calculated as the product of the pulsing frequency and pulsing amplitude, is a factor of 10 larger than the steady flow.

The working equations for the Simplified Inventory Estimation Model (SIEM) for estimating the steady state pulsed column inventory are<sup>6</sup>

$$H_{\alpha} = C_{\alpha}^a \left\{ \Gamma_{\alpha} + \frac{\lambda_{\alpha}}{[1 - 2r'(C_U^a \delta_U + C_{Pu}^a \delta_{Pu}) / (8.71B)]^2} \right\}, \quad (1)$$

$$H_{\alpha} = C_{\alpha}^a \Lambda_{\alpha}^{\eta}, \quad (2)$$

where  $H_{\alpha}$  is the inventory of the nuclear material labeled  $\alpha$  ( $\alpha \equiv U$  or  $Pu$ ),  $C_{\alpha}^a$  are the measured nuclear material concentrations for the tanks feeding the purification cycle that contains the pulsed column of interest,  $r'$  is the ratio of the flow rate of the aqueous feed stream feeding nuclear materials to the cycle containing the contactor of interest to the flow rate of the organic stream within the contactor of interest, and  $B$  is the tri-n-butyl phosphate (TBP) volume fraction. Equation (1) is applied to A-type aqueous-to-organic extraction contactors, and Eq. (2) is for stripping or partitioning contactors ( $\eta \equiv s$  or  $p$  represents stripping or partitioning, respectively). Other factors affecting the inventory, such as absolute flow rates and acid concentrations, are accounted for by the parameters ( $\Gamma_{\alpha}$ ,  $\Lambda_{\alpha}^{\eta}$ ,  $\delta_{\alpha}$ ,  $\lambda_{\alpha}$ ) which may be calculated from formulae<sup>7,15</sup> that require only nominal flowsheet data. The parameters would need to be evaluated when the contactor is put into service and at such times when the flowsheet is substantially modified. Once the parameters are evaluated for a particular reprocessing facility, the nuclear material inventories for either uranium or plutonium are easily evaluated from measured feed tank concentrations using Eq. (1) or (2).

## RESULTS OF ANALYSIS

In Table 1 the contactor uranium inventories, calculated using the computer program CUSEP<sup>6</sup> and the process flowsheet, are compared for each contactor with inventories based on measured concentration profiles. We see in general that the agreement between the measured inventories and those obtained by computer simulation is excellent.

**TABLE I**

Comparison of measured uranium inventories with values obtained by computer simulation using the CUSEP pulsed column computer model and values estimated from the simplified inventory estimation model

Contactor	C <sub>U</sub> <sup>a</sup> (g/L)	C <sub>R</sub> <sup>a</sup> (g/L)	U Inventory (g)		
			Measured	CUSEP	Simplified Model
HA	289	0.0	11690	11320	10101
HS	289	0.0	40198	41830	42930
BX	289	109.0	82064	68740	59492
BS	289	109.0	564	427	1205
C	289	0.0	<u>10860</u>	<u>13000</u>	<u>10486</u>
<b>TOTAL</b>			145376	135317	124214

The inventories estimated using the simplified inventory estimation model (SIEM)<sup>7</sup> are about 15% lower than the results obtained by measurement or CUSEP simulation, which is still good agreement. The equations used to estimate the SIEM inventories by contactor are

HA Contactor

$$H_U = C_U^a \left[ 34.15 + \frac{0.0104}{[1 - 0.0764(1.21C_U^a + 1.61C_{Pu}^a)/B]^2} \right], \quad (3)$$

HS Contactor

$$H_U = C_U^a \left[ 144.9 + \frac{0.288}{[1 - 0.0728(1.027C_U^a + 1.062C_{Pu}^a)/B]^2} \right], \quad (4)$$

**BX Contactor**

$$H_U = \langle C_U \rangle 200 , \quad (5)$$

**BS Contactor**

$$H_U = \langle C_U \rangle 4.06 , \text{ and} \quad (6)$$

**C Contactor**

$$H_U = \langle C_U \rangle 35 . \quad (7)$$

In the above equations,

$$\langle C_U \rangle = C_U^a + r_a C_R^a , \quad (8)$$

$C_R^a$  is the U(IV) reductant concentration,  $r_a$  is the ratio of the total flow rate of aqueous streams carrying U(IV) reductant to the BX contactor to the flow rate of the feed stream carrying nuclear materials to the facility. The numerical constants in Eqs. (3) to (7) represent the values of the parameters  $(\Gamma_\alpha, \Lambda_\alpha^\eta, \delta_\alpha, \lambda_\alpha)$  of Eqs. (1) and (2). These parameters are calculated from the flowsheet data for the TEKO facility and formulae given in Ref. 6.

The first principles computer model, CUSEP, calculated not only the column inventory but also all details of the column operation. The availability of measured-concentration uranium profiles from the TEKO facility provides a rare opportunity to check the accuracy of CUSEP in describing the entire column behavior. The measured and CUSEP-calculated concentration profiles are compared in Figs. 2-7. Only the calculated concentrations that correspond to column positions where the measurements were obtained are given in the figures.

The simulated uranium concentration profiles are also in good agreement with the measured results. In making this evaluation, we have taken into account the differences observed in Figs. 5 and 7 for the BX and C contactors, respectively. For the latter case (C contactor) the measured uranium concentration profiles are lower than the simulated values in the C contactor (see Fig. 7). In examining this data, one should bear in mind that the C contactor contains only a small

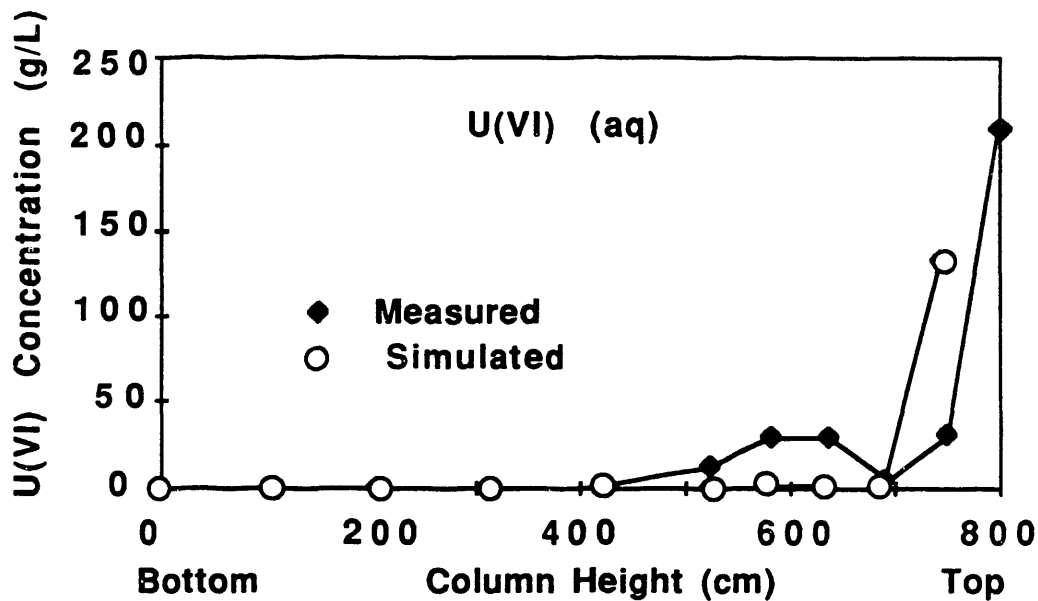


Fig. 2. Comparison of the measured concentration profiles with the CUSEP simulated concentration profiles for the HA contactor.

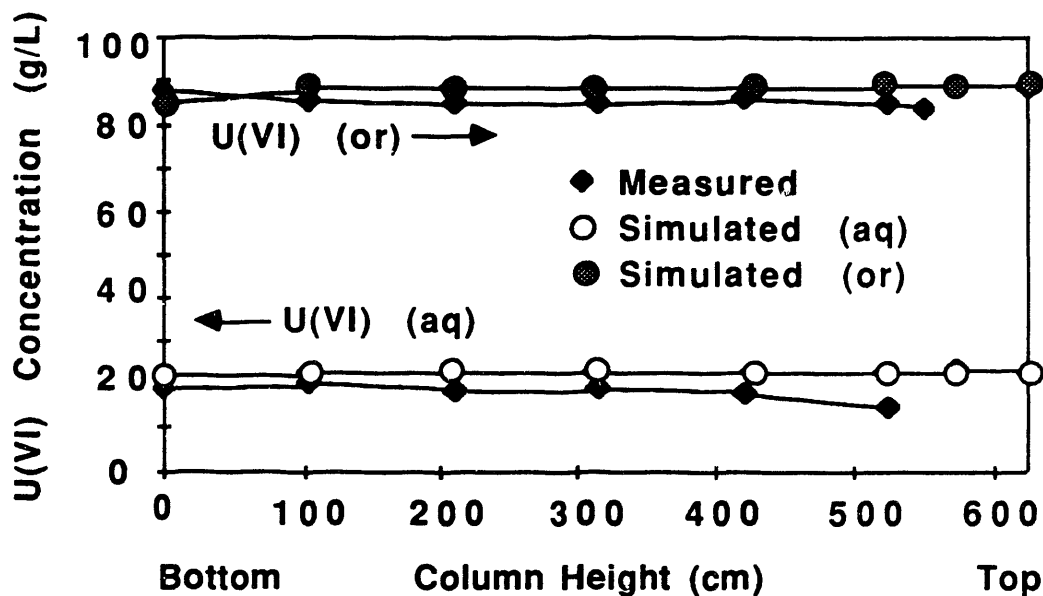


Fig. 3. Comparison of the measured concentration profiles with the CUSEP simulated concentration profiles for the HS contactor.



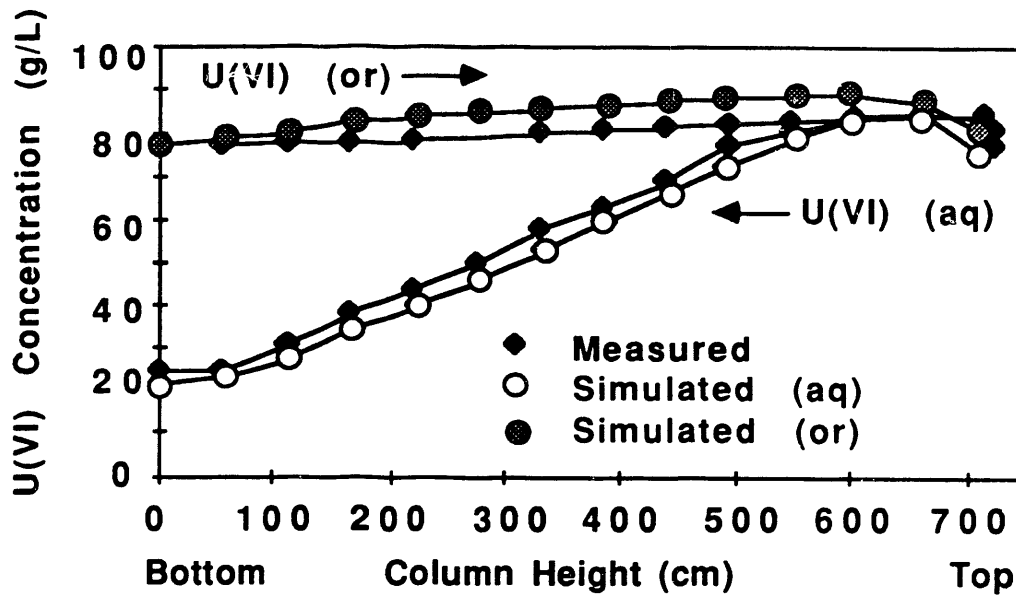


Fig. 4. Comparison of the measured U(VI) profiles with the CUSEP simulated concentration profiles for the BX contactor.

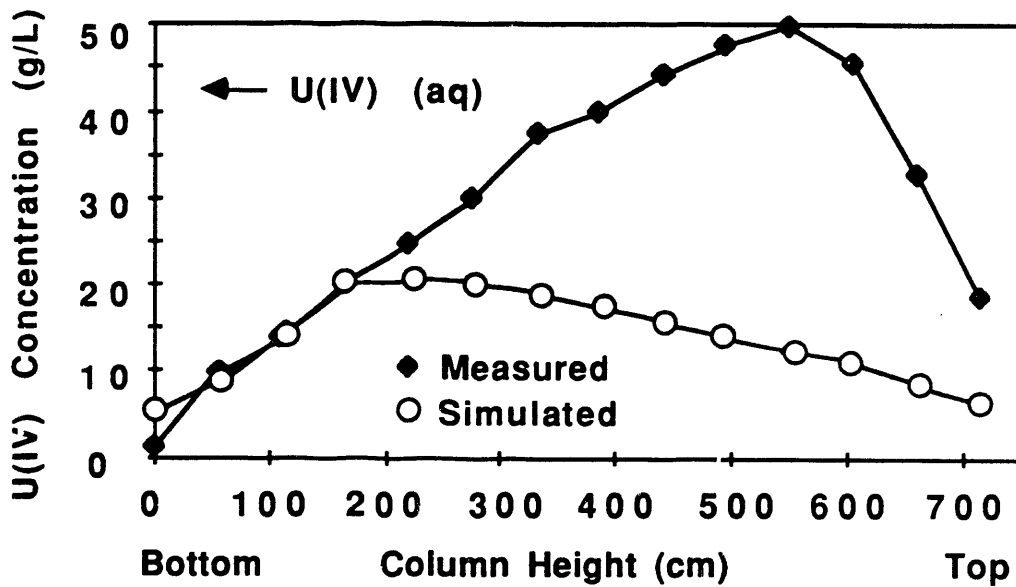


Fig. 5. Comparison of the measured aqueous U(IV) reductant profiles with the CUSEP simulated concentration profiles for the BX contactor.

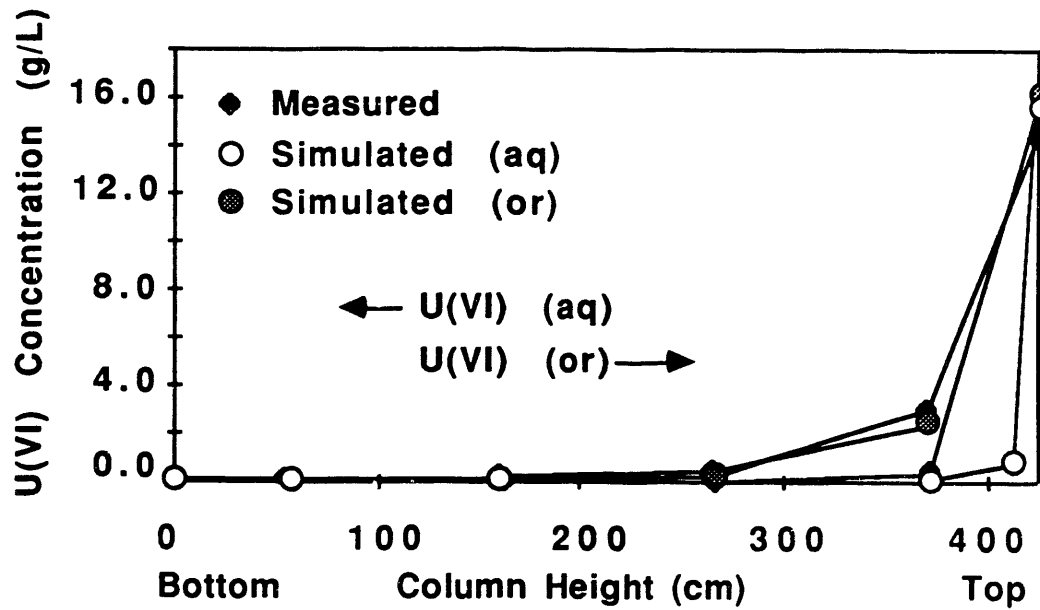


Fig. 6. Comparison of the measured concentration profiles with the CUSEP simulated concentration profiles for the BS contactor.

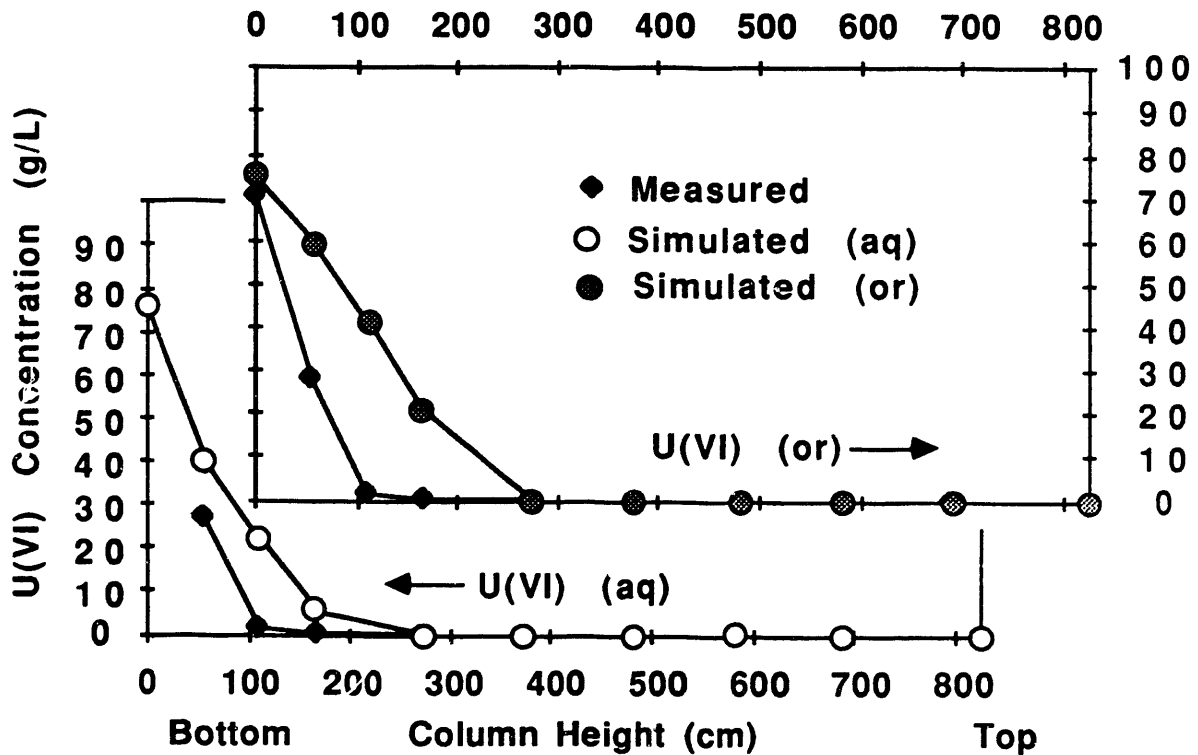


Fig. 7. Comparison of the measured concentration profiles with the CUSEP simulated concentration profiles for the C contactor.

amount of uranium and the differences one observes in Fig. 7 for this contactor do not produce large overall differences. In fact, the measurements show that the uranium is stripped efficiently from the organic phase and this behavior is predicted by the CUSEP simulations. Most of the uranium in the C contactor is in the lower part (which includes the disengaging chamber) where the calculated concentrations agree with the measured concentrations. Thus for the C contactor the overall agreement between the measured data and the computer simulations is good, as one can see from a comparison of the measured and simulated inventories in Table 1.

The only differences between the computer-simulated concentration profiles and the measured values, which are perhaps inexplicable, occur for the U(IV) reductant in the BX contactor (see Fig. 5). The measured concentration profiles peak at 50 g/L in the upper portion of the contactor, whereas the simulated values are never larger than 20 g/L. However one should couple this difference with the almost exact agreement between the predicted and measured U(VI) concentration profiles for this same contactor (see Fig. 4). This means that for the overall uranium concentration and uranium inventory (see Table 1) the measured and calculated values are in good agreement for the BX contactor. The experimental data on U(IV) suggest that it is difficult to extract U(IV) to the organic phase. In view of this, if we assume a limiting case in which U(IV) is not extracted to the organic phase, we would predict that the aqueous phase cannot contain more 20 g/L of U(IV) with the given flow sheet. We therefore believe that the measured values peaking at 50 g/L may be high. One could argue that the high measured values can result from a small extraction coefficient combined with a backflow effect from a loaded organic phase. However, we believe that it is unlikely that backflow can explain a value (50 g/L) so far above the value (20 g/L) one would obtain from the limiting case where there is no U(IV) extraction to the organic phase.

For the sake of brevity we have not presented figure presentations of the acid concentration profiles. However the calculated aqueous and organic acid concentration profiles are almost in exact agreement with the measured concentration profiles for almost all contactors. The single exception is the BX contactor in which differences (the simulated values are about 25% lower) occur between the measured and simulated acid concentration. However when one considers the complex processes involving acid in the BX contactor [both extraction and oxidation of U(IV) to U(VI)], the agreement is very good.

## SUMMARY AND CONCLUSIONS

Experimental data taken at the TEKO facility were compared to results calculated with the CUSEP and SIEM models. The data show that by using only the concentration of uranium in the process feed tank, the agreement between the TEKO measured inventory and the inventory estimated using the SIEM equations is within 15% for the total inventory of 145 kg of uranium in the five columns. Most of the discrepancy occurs in the BX column where uranium reduction using added U(IV) occurs.

In general, the concentration profiles and uranium inventories obtained by CUSEP computer simulation are in very good agreement with profiles and inventories from the TEKO facility. This represents the most rigorous check of the CUSEP code obtained thus far and the results indicate that very reliable predictions of pulsed column behavior can be obtained by computer simulation. Because all of the computer simulations reported herein were obtained for the case of mass-transfer equilibrium between the aqueous and organic phases, the comparisons support our earlier conclusions that pulsed columns operate very near mass-transfer equilibrium. Exceptions to this may be pulsed columns operating at very low acid concentrations such as the stripping contactors (extraction from organic to aqueous phases).

We believe that this study is significant in indicating that theoretical models with a minimum amount of process data (concentration in process feed tanks) can be used to estimate column inventories for NRTA.

## REFERENCES

1. M. CANTY, "The Influence of Contactor and Evaporator Holdup on Detection Sensitivity," *Nucl. Mater. Manage.* XV(2), 17-23 (1987).
2. F. WALFORD, A. L. MILLS, M. J. WATERMAN, and S. A. BOLER, "Variations in the Plutonium Inventory of Solvent Extraction Contactors," in *Proceedings Fifth Annual Symposium on Safeguards and Nuclear Materials Management*, ESARDA 16 (1983), pp. 57-62.
3. E. A. HAKKILA, J. W. BARNES, and J. F. HAFER, "The Use of Process Information for Verification of Inventory in Solvent Extraction Contactors in Near-Real-Time Accounting for Reprocessing Plants," *Nucl. Mater. Manage.* XVII (Proceedings Issue), 866-870 (1988).

4. E. A. HAKKILA, J. W. BARNES, R. G. GUTMACHER, and R. R. PICARD, "Near-Real-Time Verification Approaches for the Process Area of Reprocessing Plants," *LA-11615-MS*, Los Alamos National Laboratory (June 1989).
5. J. F. GELDARD and A. L. BEYERLEIN, "CUSEP-A New Mathematical Model of Pulsed Column Contactors Using the Purex Process," *Nucl. Technol.* 85, 172-186 (1989).
6. S. K. EIBEN and H. ZIMMERMANN, "Uranium Extraction Cycle in the TEKO Facility," *Atomenergie Kerntechnik* 47(2), 83-86 (1985).
7. A. L. BEYERLEIN and J. F. GELDARD, "Contactor Inventory Variations and Nuclear Material Accounting for Reprocessing Systems," *Nucl. Mater. Manage.* XVIII, 985-991 (1989).
8. G. L. RICHARDSON, "Effect of High Solvent Irradiation Exposures on TBP Processing of Spent LMFBR Fuels," *HEDL-TME-73-51*, Hanford Engineering Development Laboratory (June 1973).
9. J. F. GELDARD, L. PHILLIPS, and A. L. BEYERLEIN, "Correlation Functions for the Distribution Coefficients of U(IV) and Pu(III) Ions between Aqueous Nitric Acid and 30% TBP in an Aliphatic Diluent," *Nucl. Technol.* 70, 394 (1985).
10. R. H. HAAS, "Development and Verification of a Mathematical Model for a Pulsed Extraction Column," M.S. Thesis, Iowa State University (1983).
11. A. L. BEYERLEIN and J. F. GELDARD, "Nuclear Material Inventory Estimation in Solvent Extraction Contactors," Final Report on IAEA Contract 4441/TC (September 1987).
12. K. GONDA and S. FUKUDA, "Calculation Code Revised MIXSET for Purex Process," *PNCT 841-77-60*, Power Reactor and Nuclear Fuel Development Corporation, Tokai, Japan (1977).
13. K. GONDA, K. OKA, and S. FUKUDA, "Calculation Code MIXSET for Purex Process," *PNCT 841-79-26*, Power Reactor and Nuclear Fuel Development Corporation, Tokai, Japan (1979).

14. G. L. RICHARDSON and J. L. SWANSON, "Plutonium Partitioning in the Purex Process with Hydrazine Stabilized Hydroxyl Amine Nitrate," *HEDL-TME-75-31*, Hanford Engineering Development Laboratory (June 1975).
  
15. A. L. BEYERLEIN and J. F. GELDARD, "Nuclear Material Inventory Estimation in Solvent Extraction Contactors," Final Report on IAEA Contract 4942/TC (March 1989).

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