SIMULATION AND CONTROL SYNTHESIS FOR A PULSE COLUMN
SEPARATION SYSTEM FOR PLUTONIUM-URANIUM RECOVERY

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Simulation and control synthesis for a pulse column
separation system for plutonium-uranium recovery

by

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NOMENCLATURE

Aq	Aqueous phase flow rate
Aq'	Pseudo aqueous phase flow rate used to determine holdup derivatives
c	Molar concentration
C	Free TBP concentration used for the Pu(III), Pu(IV) and U(VI) distribution coefficients
C'	Nominal TBP concentration
C''	Free TBP concentration used for the nitrous acid distribution coefficient
Δt	Time step for digital simulation calculations
E	Distribution coefficient
h	Organic phase holdup
H	Aqueous phase holdup
i	Equilibrium stage subscript or ionization subscript
j	Chemical specie subscript
k	Reaction rate constant or regression model constant
k_i	Ionization constant
K	Equilibrium constant related to an empirical function of the ionic strength or one of the coefficients of the feedforward regression equation
K_d	Dissociation constant for PuNO_3^{+3}
m	Molar concentration
<u>M</u>	Solute molecular weight
μ	Aqueous solution ionic strength
Or	Organic phase flow rate
Or _f	Organic feed flow rate

Or'	Pseudo organic phase flow rate used to determine holdup derivatives
P	Fraction of nitrous acid in nitric acid solution
ρ	Solution density
ρ_o	Solvent density
t	Time
τ	Interstage time constant used in calculating the pseudo flow rates between stages
x	One of the eight chemical species of interest
X	Molar concentration of one of the eight chemical species of interest
z	Charge of the solute ion

Simulation and control synthesis for a pulse column
separation system for plutonium-uranium recovery

Edward Barrett McCutcheon

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Control of a plutonium-uranium partitioning column was studied using a mathematical model developed to simulate the dynamic response and to test postulated separation mechanisms.

The column is part of a plutonium recycle flowsheet developed for the recovery of plutonium and uranium from metallurgical scrap. In the first step of the process, decontamination from impurities is achieved by coextracting plutonium and uranium in their higher oxidation states. In the second step, reduction of the plutonium to a lower oxidation state allows partitioning of the plutonium and uranium. The use of hydroxylamine for the plutonium reduction in this partitioning column is a unique feature of the process. The extraction operations are carried out in pulse columns.

The process is now operational but under manual control. Apparent instabilities in the partitioning column

have caused loss of control and have forced the plant to be shutdown periodically. Analysis of the process revealed that failure is caused by shifts in the balance between plutonium oxidation and reduction reactions resulting in movement of the steep bottom edge of the plutonium profile within the column. Small changes in the feedstream variables or the aqueous flow rate can force this profile edge downward increasing the contamination of the uranium product by orders of magnitude.

Five key reactions were used to simulate the complex chemical reaction system in the column. The plutonium-hydroxylamine reduction reaction is opposed by the oxidation of plutonium by nitric acid, an autocatalytic reaction in which nitrous acid is both a product and a catalyst. Hydrazine is added to destroy the nitrous acid. It also reduces small quantities of plutonium. Hydroxylamine also destroys some of the nitrous acid.

After verifying the simulation by comparison with experimental plant data, feedforward and feedback control systems were designed to maintain a variety of process requirements by manipulating the aqueous strip stream flow rate. Because the controlling constraint, the plutonium contamination of the uranium product stream, responds quickly to small changes in the control variable, a feedback algorithm proved to be superior in terms of both control and

implementation. However, a simple predictive scheme considering all feed stream variables and implemented manually offered significant improvement with only small changes in the present operating procedure and instrumentation.

INTRODUCTION

With the rising pressure for more energy and less dependence on fossil fuels for this energy, the demand for high-grade nuclear fuels is rapidly increasing. But increases in nuclear fuel production are subject to several constraints. The Nuclear Regulatory Commission has very high standards for not only the fuel's purity but also its physical properties and containment. Economics, of course, play an important part in the selection of production and processing techniques. Just as important in evaluating all phases of the nuclear program are safety and environmental considerations. Any viable production flowsheet must combine the requirements of high product quality, economic return and minimum danger and damage to the environment.

While several fissionable materials have been investigated during the short span of the nuclear age, only plutonium and uranium have found commercial application in the nuclear generation of electric power. Separating these metals from waste materials and from each other is a significant part of fuel element processing. While many methods have been proposed, only countercurrent liquid-liquid extraction systems have shown commercial promise. Such separation depends on differences in the distribution coefficients of the materials to be separated. The distribution

coefficient of a solute between two immiscible phases is a basic system property and may depend on the oxidation state of the solute ions, the presence of complexing agents or other elements of the chemical environment in each phase. Several successful extraction processes have been developed for the reprocessing of nuclear fuels and wastes. One particularly interesting flowsheet being developed at the Atlantic Richfield Hanford Company is the subject of this research.

The basic three-unit process was developed to recover plutonium and uranium from fuel elements scrapped for a variety of reasons during manufacture. This nonirradiated material poses a problem in the overall economics of fuel production not only because of the cost of the plutonium and uranium but also because such reject material cannot easily be discarded. Figure 1 shows the scrap recovery flowsheet developed at Atlantic Richfield.

The system consists of three liquid-liquid extraction columns. The first, a decontamination column, uses tributylphosphate (TBP) to form complexes with plutonium, uranium and nitrate ions (as $\text{Pu}(\text{NO}_3)_2 \cdot 2\text{TBP}$, $\text{PuO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$). This complexing causes plutonium and uranium mass transfer to the carbon tetrachloride organic phase while the various impurity ions remain in aqueous solution. The second unit is a partitioning column. The

UNIT I: EXTRACTION UNIT II: Pu PURIFICATION UNIT III: FINAL Pu REMOVAL
 Figure 1. Uranium-plutonium partitioning flowsheet developed by ARHCO

plutonium is chemically reduced so that it transfers to the aqueous phase while the uranium remains preferentially in the organic. In the third column the remaining plutonium is stripped from the organic phase by a strong acid solution and returned to Unit I for rework.

Several features distinguish this flowsheet from others which have been developed for plutonium-uranium partitioning.

In Unit II the use of hydroxylamine as the reducing agent for the key plutonium reduction reaction is one of the important features of the process. While there are other reagents that will selectively reduce plutonium but not uranium in the Unit II chemical environment, the use of hydroxylamine has the advantage that no impurity ions remain after the reduction and that any hydroxylamine left unreacted in the plutonium product stream can be destroyed. Other reducing agents leave impurity ions that must be removed by additional extraction equipment.

Extremely important to the overall economics of the ARHCO flowsheet is the plutonium reflux from Unit II to Unit I. By allowing a high concentration of plutonium to be established in the organic stream common to the two columns, the extraction efficiency of the first column is improved so much over older technologies that additional extraction cycles are not required. In addition to minimizing the separation equipment needed, refluxing eliminates much

of the equipment necessary to concentrate the plutonium product solution after it leaves Unit II and before it is returned to the manufacturing process.

Another feature of the ARHCO flowsheet is the use of hydrofluoric acid in Unit III to complete the partitioning. This last unit is required because of the radiation degradation of TBP to dibutylphosphoric acid (DBP). Plutonium complexed with DBP is almost completely insoluble in the aqueous phase and thus cannot be reduced by the hydroxylamine. Concentrated nitric and hydrofluoric acids strip out the small amounts of plutonium remaining in the uranium product stream. This is an essential step in the recovery of all the plutonium.

In general the flowsheet is designed to operate by controlling phase preferences through manipulation of oxidation states and by controlling the nitrate ion concentration in the aqueous phases of the three columns. While both plutonium and uranium can exist in several oxidation states, only four of these are significant to the present research: U(VI), Pu(III), Pu(IV) and Pu(VI) where the Roman numerals indicate the positive oxidation states. Of these Pu(III) strongly favors the aqueous phase under all conditions encountered in the process. The equilibrium ratio of ion concentrations, organic to aqueous, for the other three species depends on several factors but is

largely a function of the nitrate ion concentration in the aqueous phase.

Presently the flowsheet is operational but is manually controlled. Complete automation would require control system designs for all three columns as well as the auxiliary equipment groups. Such an integrated control scheme might also govern such mechanical parameters as the pulsing frequency and amplitude and the interface location for each pulse column. To insure safe operating conditions and, if necessary, an orderly shutdown, the same control system might maintain safeguards on the process integrity despite mechanical or instrumentation malfunctions or human errors. The primary control system function would be the adjustment of flow rates, concentrations and other chemical system variables to achieve the desired process outputs despite changing feed conditions and disturbance inputs.

The control scheme synthesized in this research deals with the chemical process control of the partitioning column. In the years of development, chemistry related problems have been the major hindrance to successful operation. The control system proposed here considers only flow rate and concentration variables. The mechanical pulse column parameters are not considered. While difficulties with the pulse column operation do occur, these problems are largely separate from the chemical stability problems discussed here.

Many authors have studied extraction column control but little work has been done with combined chemical reactor-extractor separation columns.

The partitioning column is especially difficult to control because of the variety of competing chemical reactions. The important Pu(IV) reduction reaction by hydroxylamine is opposed by the nitrous acid catalyzed oxidation of Pu(III) by nitrate ions. This latter reaction is autocatalytic and can predominate under certain operating conditions. The result is poor separation and serious problems for the equipment further downstream. In the present flowsheet design hydrazine is added to the aqueous phase in Unit II to control the nitrous acid catalyst. However, significant control and operating problems still occur.

The control system design had several objectives. Success in maintaining operation for extended periods of time has been marginal. The primary research objective was to develop techniques for monitoring system performance and controlling the separation within design specifications. Despite 17 years of effort, many of the basic process mechanisms have remained clouded by seemingly conflicting data. A second objective, closely linked to the realization of the first, was identification of those factors which have the greatest effect on the performance of the column. Though

not specifically a part of the work here, the process understanding obtained could also lead to proposed design and operating changes for improved separation at reduced cost.

The research problem defined by these objectives involved several areas. With only a minimum of qualitative and quantitative information available, the initial efforts were directed at identifying the system chemistry and quantifying the stoichiometries and reaction rates of the principal material interactions. These combined with hydrodynamic and mass transfer equations yielded a mathematical simulation for the column. After verifying the model with the limited data available, control algorithms were designed and tuned to maintain stable, continuous operation with maximum performance despite wide ranging input conditions.

Parameters from the Atlantic Richfield Hanford facility were used throughout the research. However, the results should be readily adaptable to other systems using the flowsheet for scrap recovery. While the reprocessing of irradiated wastes is a far more difficult task, the present work should provide a basis for control studies of reclamation operations employing concepts from the ARHCO flowsheet design for irradiated fuels.

Separation processes are found in almost all areas of chemical engineering practice. Many of these processes rely on equilibrium mass transfer to effect the separation. The

plutonium-uranium partitioning in the Atlantic Richfield Hanford Company flowsheet relies on chemical reaction kinetics as well. This same type of combined reactor-extractor system could conceivably find application in other kinetically controlled chemical processes such as pharmaceutical manufacture or the biological production of chemicals. The modeling and control techniques used in this research might be as significant in the control system design for these processes as they were for the plutonium-uranium partitioning column.

LITERATURE REVIEW

The literature available for this research can be divided into four groups: the separation process, pulse column simulation, chemical reaction simulation and control system design techniques.

The Separation Process

Commercially feasible processes for separating plutonium and uranium from impurity ions are almost as old as the atomic age. In concept the present ARHCO flowsheet is similar to the Redox and Purex processes developed during the early 1950's. All three processes are alike in that the separation is based on an initial extraction of plutonium and uranium in higher oxidation states from impurities and a second step in which plutonium in a reduced oxidation state is separated from uranium. Each process also includes additional steps as needed to achieve the desired purities of plutonium and uranium and for secondary material recovery. While differences in specific equipment and solvents are found in the three processes, two major differences stand out between the older flowsheets and the ARHCO system. Plutonium reflux is a major technical advance that greatly improves extraction efficiency and reduces the amount of plutonium concentrating equipment needed beyond the

separation stage. Although the same hydroxylamine reducing agent used in the ARHCO flowsheet has been proposed as a choice for both the older technologies, iron(II) sulfamate is usually mentioned in the literature of Redox and Purex systems. The use of iron(II) sulfamate, while avoiding the chemical instabilities due to the destruction of the nitrous acid by sulfamate, as described in Biddle and Miles (6) and Cleveland (11), has the problem of introducing impurity iron into the plutonium product stream. Additional processing is then necessary to achieve the required plutonium purity. One of the many references exploring these older flowsheets is the Benedict and Pigford text (5).

The advantages of plutonium reflux in the extraction process were first noted by Judson (28). Although his flowsheet was for plutonium "scrap recovery" implying a very minimum of uranium in the feed materials, it was the basis for the present ARHCO partitioning flowsheet. A primary benefit of plutonium reflux in such a process was the concentration of the plutonium product. Judson also discussed the major problem with plutonium reflux, the radiation degradation of the TBP complexing agent.

About 10 years later, in the late 1960's, the Atlantic Richfield Hanford Company proposed scrap recovery and partitioning flowsheets based on the plutonium reflux with hydroxylamine as the reducing agent. These flowsheets had much

to offer in terms of high extraction efficiency and reduced equipment costs. However, the operational problems in obtaining satisfactory control of the second unit, the partitioning column, in the face of wide ranging input changes were formidable. The cause of these problems was the oxidation of the desired Pu(III) and the ability of the oxidation reactions to dominate the system at some operating conditions. Bruns (10) described the flowsheet and its operational problems in some detail.

Operational control was not feasible with the Bruns (10) flowsheet. To destroy the nitrous acid, hydrazine was included in the aqueous strip stream. At this time the hydrazine flowsheet has not been thoroughly documented. Specific details came from Pease (35) and discussions with ARHCO personnel. While control of the destabilizing oxidation reactions improved, no well-defined control principles were delineated to insure continuous operation through the expected transients.

A variety of additional materials were available outlining the work at Atlantic Richfield Hanford Company on both the hydrazine flowsheet^{1,2} and the similar hydroxylamine-

¹Klem, M. J. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. June 6, 1974.

²Klem, M. J. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to C. J. Francis. March 5, 1973, with addendum dated May 9, 1973.

only separation system^{1,2}. Included in these internal documents were outlines for design test programs, operating guidelines, product specifications, control recommendations, qualitative discussion of system performance and theories on the separation mechanisms.

Pulse Column Simulation

Most of the early pulse column research was concerned with relationship of such variables as pulsing frequency and amplitude, physical dimensions of the column, perforated plate open areas and process flow rates to the extraction parameters describing mass transfer between the phases. Two such references were Troutman and Consiglio (40) and Cohen and Beyer (12). In the first a computer model was proposed for steady state correlation of the H.T.U., height of a transfer unit, in terms of the amplitude-frequency product of the pulse generator. The results could only be checked to $\pm 20\%$. In the second reference the relationship of column efficiency and the limits of pulsing amplitude and frequency

¹Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to L. M. Knights. May 27, 1971.

²Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to A. J. Low. December 13, 1971.

to the physical properties of the fluids was developed. Again these results had little direct application to the problem of designing a control system.

The development of a simulation model for any chemical process depends on the information required from the model. For control modeling the pulse column can be viewed as either a staged extractor with well-mixed stages approaching a series of mixer-settlers or as a continuous separator approaching a packed column.

In practice the actual column operation is somewhere between these extremes. During the pulsing cycle there is insufficient time for complete phase separation and coalescence in each stage. An ideal mixer-settler allows complete coalescence at each stage while the continuous packed column has phase separation only at the column ends. An analogy to the lumped and distributed parameter modeling techniques could be made in the comparison of the two types of liquid-liquid extractors.

Although conceptually the continuous column model could have been developed for either design or control purposes, the authors who worked with this approach were concerned with design. Wilburn and Nicholson (42) analyzed the pulse column extraction system for steady state performance with differential equations in terms of the space coordinate. A fundamental part of this work was the inclusion of

longitudinal dispersion terms. The model included such parameters as column length and diameter; sieve plate spacing, open area and hole size; pulsing frequency and amplitude; density, viscosity and interfacial surface tension; solute diffusivity and distribution coefficient; and phase flow rates. While a generalized reaction term was included, the use of this model for Unit II would require considerable expansion for dynamic simulation. It was significant that for computational purposes the differential equations were linearized and written for discrete column segments in a form similar to a staged model.

For solution by digital or analog techniques the continuous model must usually be broken up into discrete elements or stages. Biery and Boylan (7) started with a continuous dynamic model written in terms of partial differential equations that described the diffusion and hydrodynamic effects with assumptions that the pulsing behavior could be ignored, that longitudinal turbulent diffusion was negligible and that the column was operated in the emulsion region. For actual simulation the end-fed column model was divided into staged segments using a variety of assumptions on the ideality of the mixing and the approach of each stage to equilibrium stage performance. In comparing their results with experimental data, the authors found that an equilibrium stage model provided good correlation particularly for

a large number of equilibrium stages.

Kelly (30) used an equilibrium stage approach to develop a control system for a pulse column. His simulation of the data of Biery and Boylan (7) failed to reproduce the system dynamics without the use of additional time lags in the interstage flow rates.

Another approach to stage-wise dynamic modeling of a pulse column for control purposes was developed by Watjen and Hubbard (41). Starting from a general differential equation for the mass transfer and fluid mechanics, the authors linearized the resulting model and used stages based on the physical stages created by the perforated plates in the column. Stage efficiencies accounted for the nonequilibrium performance of the physical stages. Attempts to fit the response data from actual column to the results predicted by the model were not entirely satisfactory, however.

An equilibrium stage analysis has been applied to Unit II by ARHCO. The SEPHIS (Solvent Extraction Processes Having Interacting Solutes) program developed at Oak Ridge by Groenier (22) was used as a starting point. Although highly detailed in some areas such as the calculation of volume flow rate corrections and distribution coefficients, the program accounted for only the very basic reaction chemistry. With only a model for the Pu(IV) reduction reaction, it was not possible to use the SEPHIS program to predict

unacceptable performance due to oxidation reaction dominance. Thus the program was not applicable to studies in control system design.

Because of the similarity of pulse column performance to conventional liquid-liquid extractors, the work of authors dealing with these systems was of interest. Halligan and Smutz (23) developed four different dynamic stage models for a conventional extraction system for separating rare earths. These models varied in their complexity but it was found that the simple equilibrium stage model reproduced the dynamic test data particularly when the number of stages was greater than seven.

Several authors have investigated the performance characteristics of series of mixer-settlers. In dynamic response the mixer-settlers behave much like a pulse column separation system. Of particular interest were the results of Seeman and Burkhart (37) with the simulation of a series countercurrent mixer-settler separation process for rare earths. Because the mixer-settlers were a series of open vessels, significant time lags in flow rate disturbance propagation were noted between stages. Additional time lags in the equilibrium stage model provided the needed dynamics to simulate the experimental response characteristics.

Development of a typical stage model with chemical

reactions for the pulse column was considered to parallel the derivation of equations for a continuously stirred tank reactor, one of the favorite dynamic models in chemical engineering. The CSTR model has been formulated in Douglas (17) and in many other references.

The majority of the research in multistage separation operations has been in the area of distillation. While the methods of stagewise dynamic analysis have proven quite useful for simulation purposes, the control system design techniques developed simultaneously were the most important results for the present research. Although few distillation systems involve simultaneous chemical reactions, their sluggish response due to long time constants and deadtimes dictated control system requirements much like those of the partitioning column.

Chemical Reaction Simulation

One of the most important and difficult portions of the research effort was defining the chemical reaction environment. In addition to the extensive chemistry of plutonium, the presence of reducing agents, multiple phases and radiation degradation effects make the process a complex reaction system. While many chemical reactions have been known to occur in the partitioning column, five were found to be sufficient to define the dynamic response of the system.

The specific literature used to quantify kinetic models for these five reactions are listed below. In each case several sources of data were found and each source was carefully evaluated. Those listed represent the most current and complete information available.

Most important in terms of column design is the plutonium-hydroxylamine reduction reaction because the plutonium entering in the feed as Pu(IV) must be reduced to Pu(III) before it will transfer into the aqueous phase. The most recent studies of this reaction were carried out by Barney (2) at the Atlantic Richfield Hanford Company. This work, along with later modifications¹ in the stoichiometry of the reaction, was used to develop the appropriate kinetic model used in the process simulation.

The reaction that causes the operational problems in Unit II is the nitric acid oxidation of Pu(III). In nitric acid solutions of the strength found in the column, Pu(III) is relatively stable unless small amounts of nitrous acid are present. Since nitrous acid is one of the products of the nitric acid oxidation of Pu(III) and also acts as a catalyst, the reaction is autocatalytic. Therefore, it proceeds at an increasing rate unless the nitrous acid is

¹Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Letter to G. L. Richardson, Westinghouse Hanford Company, Richland, Washington. May 29, 1974.

destroyed. The stoichiometry for this important nitric acid reaction came from research¹ at Atlantic Richfield. The rate model was proposed by Dukes and is described in Cleveland (11).

In addition to catalyzing the Pu(III) oxidation reaction nitrous acid also destroys some of the hydroxylamine. In the Bruns flowsheet design (10) this reaction alone was intended to control the nitrous acid. However, it was found that the oxidation reaction predominated at certain operating conditions. Barney (3) formulated both the stoichiometry and the rate expressions for the nitrous acid-hydroxylamine reaction, which is more significant for the nitrous acid destroyed than for the hydroxylamine consumed.

Hydrazine is added to the column to destroy the nitrous acid. The reaction proceeds rapidly at rates and stoichiometries which have been determined by Biddle and Miles (6). Although the actual quantities of materials involved are quite small, the reaction provides an important stabilizing influence on the column.

Hydrazine is also capable of reducing the Pu(IV) to Pu(III). Although the amount of plutonium reduced by the hydrazine is small compared to that reduced by hydroxylamine,

¹Klem, M. J. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. June 6, 1974.

the reaction is important because it removes hydrazine from the system. The rate model for this reaction was developed from analytical chemistry data obtained by Moore and Hudgens and reported in the monograph compiled by Cleveland (11). The stoichiometry used in the process simulation came from an assumed reaction suggested in Audrieth and Ogg (1).

In addition to these five chemical reactions many others occur but are not significant in control studies. They are summarized in the monograph by Cleveland (11) which deals with the entire spectrum of plutonium chemistry. Various oxidation-reduction reactions between plutonium species of different oxidation states are possible but these disproportionation reactions are of little importance compared to the hydroxylamine, hydrazine and nitric acid reactions. Plutonium species can also be involved in hydrolysis reactions, complexed with nitrate ions in the aqueous phase and polymerized into colloidal particles. The nitrogen oxide gaseous by-products of several of the five important reactions can also be involved in other reactions, particularly dissolution into the aqueous phase to form nitrous and nitric acids. Details of these reactions are given in Denbigh and Prince (15) but due to the slow rates of dissolution and the apparent absence of important oxide species from the reaction environment found in the column, the effects on the important nitrate and nitrite concentrations

were assumed negligible.

Personnel at Atlantic Richfield have suggested possible hydroxylamine instabilities in the aqueous phase in the column. With the low acid concentrations and with the simulation results indicating other reasons for the apparent hydroxylamine loss, these instabilities did not appear important.

As discussed in Judson's first work with the reflux flowsheet (28), radiation effects are quite important to the overall process operation. These effects can be broken into two parts: reduction of Pu(IV) to Pu(III) and the degradation of TBP to dibutylphosphoric acid (DBP). The reduction reaction by alpha radiation is desirable but is so slow as to have little effect. Connick (13), Cleveland (11) and Keller (29) all examined this reduction reaction. Cleveland, Keller and Bruns (10) each looked at the organic phase degradation problem. Plutonium and uranium complexed with TBP in the organic become almost completely insoluble in the aqueous phase. Since the plutonium complexed with DBP cannot be extracted into the aqueous phase, it is lost to the organic uranium product stream. This problem is the reason for the third unit in the flowsheet where the plutonium complexed with dibutylphosphoric acid is stripped from the organic feed by the strong acids present.

To reduce the number of variables to a computational level, relationships between the organic and aqueous concentrations for each specie were required. Solubility in the carbon tetrachloride organic phase depends on the ability of the solute to complex with TBP. According to Durrant and Durrant (18) hydroxylamine and hydrazine are essentially insoluble in CCl_4 and do not complex with TBP. Cleveland (11), Bruns (10) and Keller (29) all discuss the very low solubility of plutonium in the +3 oxidation state due to its inability to complex with TBP. Operation of the partitioning column depends on this insolubility and on the ability to control the plutonium oxidation state. The hydrogen ion is only soluble in the organic phase with nitrate as an $\text{HNO}_3 \cdot \text{TBP}$ complex. Plutonium in the +4 oxidation state and uranium and plutonium in the +6 oxidation state all form nitrate-TBP complexes. Cleveland (11) defines these complexed species as $\text{Pu}(\text{NO}_3)_2 \cdot 2\text{TBP}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, and $\text{PuO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ respectively. Nitrous acid is soluble in the organic phase due to the formation of complexes with TBP. Although Biddle and Miles (6) found the complexing stoichiometry to be identical to that of nitric acid (i.e., $\text{HNO}_3 \cdot \text{TBP}$), the nitrous acid complex is significantly stronger according to Fletcher, Scargill and Woodhead (20).

The distribution coefficients for the organic soluble

species are strong functions of the competition between species for the TBP. Distribution coefficients for Pu(IV), U(VI) and nitric acid have been determined for a TBP organic system with dodecane diluent and nitric acid aqueous phase. Their relationships developed by Baumgaertal, Ochsenfeld and Schieder (4) and expanded by Horner (25), relate the coefficients to the nominal TBP concentration, the aqueous nitrate concentration and the aqueous solution ionic strength. Horner's work was done as a part of the SEPHIS simulation program development. Equations for the nitrous acid distribution coefficient in plutonium, uranium, nitric acid and TBP-dodecane systems have been developed by Marin, Sellier and Gourisse (32). Although the data for the distribution coefficients are for TBP diluted with dodecane rather than the carbon tetrachloride used in the present study, Taube (39) pointed out that extraction is very similar for a variety of nonpolar diluents.

Because of the dependence of the distribution coefficients on the ionic strength in the aqueous phase, characterizing the degrees of ionization of each specie was essential. Durrant and Durrant (18) showed that nitric acid ionizes completely while nitrous acid dissociates little in the Unit II aqueous environments. Both the plutonium reducing agents are dissociated almost completely. Data for verifying this conclusion for hydroxylamine comes from

Barney (2) and Jolly (26). A similar conclusion for hydrazine results from the data in Audrieth and Ogg (1). Cleveland (11) examined in some detail the ionization of Pu(IV) and Pu(VI) nitrate complexes in the aqueous phase and the uranium nitrate ionization needed to complete the description of the aqueous phase came from Day and Powers (14).

The general availability of data for describing the chemical reactions and chemical environment varied widely with the topic. Because the Purex process emerged as the established technology for plutonium and uranium recovery, research efforts concentrated on its operating problems. As a result much data were available for the Pu(IV) distribution coefficient because of its importance in the first separation unit of the Purex process. Because the second unit was relatively problem-free, data on the Pu(III) distribution coefficient, the Pu(III)-nitric acid reaction and the entire area of nitrous acid including its sources and effects on the Pu(III) oxidation reactions were difficult to find and often far from complete. Much of the data were for operating conditions typically found in the Purex process. In particular the acidities in the second Purex column were much higher than those found in the column studied in this research. Since hydroxylamine was never effectively used in partitioning and hydrazine used for

little more than analytical tests for plutonium, work on the reactions of these reducing agents with Pu(IV) has been very limited. Certainly the inherent economic potential of the plutonium recycle flowsheet provides sufficient justification for further studies of the reactions described here.

Control System Design

The general area of chemical process control is a particularly fertile one for research at the present time. Sophisticated control systems are under development in many chemical process industries but are still in relative infancy in comparison to the control technology found in the aerospace industry. There are several obvious reasons for this delay in development. The primary thrust of control technology came during and following World War II in weapons systems. The trickle of control technology came to the chemical industries with mathematic analysis techniques and control instrumentation during the 1950's. Application was slowed by the complexity and nonlinearity of the myriad of equipment types used. Instrumentation development also lagged somewhat because of the severe technological problems offered by the corrosive environments found in chemical plants.

In the 1960's some major breakthroughs occurred

including the application of feedforward control concepts and the use of electronic instrumentation with the resulting move toward integrated control centers suitable for digital computer control systems. Many of the first digital control applications met with failure because processes were not well enough understood to realize the benefits of more sophisticated control systems. However, the roots were formed and during the 1970's, with steady development in process instrumentation and computers, digital control with its ability to handle the complex continuous and sequential processes found in the chemical industries is now firmly established.

The control of multistage separation systems has been a particularly interesting area of research because of the wide application and the typically slow responses of these systems. Focusing on liquid-liquid extraction systems, three types have similar performance characteristics: packed columns, mixer-settlers in series and pulse columns. Propagation of disturbances at the input to the column ends shows marked transport delays and transient time lags. Because of such slow response to input disturbances control based on the output variables can result in poor performance. By the time a disturbance has propagated to the output, the internal column variables have shifted such that significant off-specification output can be produced until changes in

the manipulated variables propagate back into the column to compensate for the disturbance.

The same problems in distillation columns prompted research work in the development of new control algorithms to overcome the deficiencies of conventional feedback control. By monitoring the system input variables and compensating for upsets according to a predictive model, the manipulation of the control variables could be made before the disturbance propagated through the entire system. This type of feedforward controller was studied for distillation columns by Bollinger and Lamb (8). Their work was with a linearized system model using s-domain design techniques. It was noted that for some cases it was possible to exactly compensate for disturbances both statistically and dynamically.

Several authors developed the feedforward control concept for additional separation and reactor systems described by linear and nonlinear models. The text by Luyben (31) provides an excellent summary of conventional control and modeling techniques and also contains the results of several of his published papers in the area of feedforward control. With much the same thoroughness but with a more practical, problem oriented approach, Shinskey (38) discusses in depth feedforward design techniques as applied to several separation systems.

At Iowa State University there has been a long term development program for the control of liquid-liquid separation systems. Some of the important results from this work were the design of feedforward control schemes for a rare-earth extraction column by Erskine, Seeman and Burkhart (19). Using a simple equilibrium stage model they synthesized two control algorithms. In one the predictive model generated actual values for the manipulated control variables based on the inputs. In the second the model outputs were predicted system outputs. A conventional feedback controller was then designed to work with these predicted outputs. Seeman and Burkhart (37) developed a feedforward control system for a series of mixer-settlers for rare-earth separation. The feedforward algorithm consisted of a steady state regression model that predicted the value of the manipulated variable as a function of the inputs. To apportion changes in the manipulated variable out in time to minimize upsets in the system outputs during the transient between steady states, a dynamic compensation term was added to the control algorithm. To adjust for model inaccuracies and for disturbances not measured in the input stream, a conventional proportional-plus-integral feedback controller complemented the predictive scheme. An interesting result of this work was the ability to control two product streams with only one manipulated variable

because of the particular system configuration and the manner in which the specifications on the product streams were written. Working with data obtained by Biery and Boylan (7) for an end-fed pulse column, Kelly (30) designed a feedforward-feedback controller that showed significant performance improvement over feedback-only control.

Doto (16) has documented operating procedures used for the partitioning column. While these did not give accurate definition to the control problems experienced during operation, they do provide a qualitative appreciation for the control techniques attempted during manual column operation.

Additional data of interest concerning instrumentation came from a meeting with Atlantic Richfield personnel and from the paper by Jones and Lyon (27) which gave a background on the types of instrumentation that were used in the Purex plant at Hanford. This paper was of particular interest since it defined the state of the art for measurement systems required for computer control of the partitioning column.

THE OPERATING COLUMN

The Unit II pulse column is a part of the scrap recovery equipment group located in the Plutonium Reclamation Facility shown in Figure 2. The system is maintained not only for processing metallurgical scrap but also as a part of continuing research program in nuclear fuel reprocessing.

The majority of the process equipment is suspended from racks in an operating canyon that can only be reached through gloveboxes during normal operation. The equipment is subjected to an extremely corrosive atmosphere due to the strong acids present. Stainless steel, glass and special plastics are used extensively to survive this environment.

The partitioning column is 51 feet tall and four inches in diameter. It is constructed entirely of stainless steel and is divided into three sections. The top end-section is three feet long to allow for phase disengagement. The middle section is 45 feet in length and contains perforated stainless steel plates with approximately 23% open area at two-inch spacing. The bottom three-foot end-section is for phase disengagement and is where the interface is maintained during normal operation of the column. Gases produced by the chemical reactions are vented through a scrubber system to prevent release of contamination to the atmosphere. The column has a minimum of external connections because of the

Figure 2. Plutonium Reclamation Facility: The two tall columns in the area labeled "1" extending from the process cell area are Units I and II

problems of corrosion and potential leaks. There are no intermediate taps along the column for data sampling.

Immediately adjacent to the partitioning column is the decontamination column which is quite similar in physical description. The stripping column is also located in close proximity but is much shorter than the other two columns. Providing storage capacity between the columns and for mixing streams, numerous small diameter cylindrical tanks proportioned for nuclear criticality protection are also mounted in the equipment canyon.

In addition to the three basic columns there are several additional equipment groups. The aqueous waste stream from the first unit (the CAX stream) is sent to a three-column waste handling system which uses di-n-butyl-n-butylphosphonate (DBBP) to extract the last traces of plutonium and also any traces of americium present. Other waste materials are discarded to long term storage.

To recycle the TBP-CCl_4 organic phase the uranium product stream from the stripping column is routed to a series of scrubbers which first remove the uranium, then destroy the DBP by washing the organic with carbonate and finally reacidify the organic for introduction as scrub streams in the Unit I and Unit II columns.

At the "head end" of the process a dissolver contacts

the scrap fuel elements with concentrated nitric acid to prepare the aqueous feedstock for Unit I. At the end of the process is an evaporator that concentrates the product plutonium to approximately 200 grams/liter for reintroduction into the fuel element manufacturing process. One last area of interest is the chemical preparation section where make-up quantities of the various reagent solutions are prepared. While a rather typical arrangement for reagent preparation, the batch system has important implications in the control system design. With the hydroxylamine, hydrazine and nitric acid concentrations fixed (at least for individual batches) the only strip stream parameter that is easily varied in the partitioning column is the aqueous flow rate.

Figure 3 is a schematic of the instrumentation systems presently found on Unit II. The flow rates of the three input streams are monitored with flow meters and recorders. To maintain proper control of the pulse generator, static and differential pressures are measured at intermediate points along the column. These pressures are recorded along with the pulsing parameters. At the bottom of the column in the disengagement section is a conductivity probe to sense the interface location. The uranium product stream flow rate is automatically adjusted according to this interface location. Three neutron monitors continuously sense

Figure 3. Schematic of Unit II's existing instrumentation systems

radiation levels from the nuclear materials to insure that nuclear criticality conditions are not approached. A gamma monitor on the uranium product stream completes the radiation instrumentation. For an indication of the reducing agents remaining in the plutonium product stream an oxidation-reduction-potential sensor monitors the reflux stream on its way to the oxidation tank. The input and output streams are periodically sampled and chemically analyzed in the chemistry laboratory. Except for the uranium product stream flow rate, all control is done manually from a central control room.

The operation of the partitioning column is governed by general procedures described in Doto (16) and Pease (35) which cover start-up, steady state, upset conditions and shut-down. With only a minimum of process data available, control is largely a matter of conservative operation. Depending on the problems that arise during operation, the aqueous flow rate is varied up or down in 5% increments. Problems are indicated in the control room by three parameters: the uranium concentration in the plutonium product stream, the plutonium concentration in the uranium product stream and the color of the plutonium product stream. Plutonium in aqueous solution has distinctive colors dependent on the oxidation state. Pu(III) has a deep blue color while Pu(IV) is a dark brown or black in solution. To maintain

proper operation the plutonium product stream is periodically examined for the blue tint.

With concentrated acids, powerful reducing agents and nuclear materials present, the assurance of worker safety has a strong influence on operating procedures. There is also economic incentive to maintain equipment integrity since the unusual and harsh environment makes maintenance and repair difficult. In addition to the specified procedures there are several interlock systems that coordinate operation of key valves to prevent any potentially hazardous situation.

In the operating procedures the problems of pulse column control and separation control are distinguished. It is assumed that with proper pulsing, chemical problems are separate from mechanical operation.

The hydrazine flowsheet represents the latest refinements in a long development program. Many of the mechanical problems have been resolved although with the harsh environment and maintenance difficulties both mechanical and instrument malfunctions are still part of the operating experience as are problems in maintaining the mechanical operation of the pulse column. Prevention of flooding and entrainment is somewhat hampered by the quantities of nitrogen oxide gases released by the chemical reactions effecting the partitioning.

Several factors affect chemical stability. With the large column volume and relatively low flow rates, time lags and dead times are long. Coupled with this are the infrequent measurement schedule and the possibility of large process upsets due to the variety of feed materials entering the scrap recovery process. In addition, a lack of process understanding has led to attempts to cure problems in other parts of the process by inadvertently forcing the partitioning column toward instability. In particular the reaction vessel located in the recycle stream between Units I and II, where Pu(III) is oxidized to Pu(IV) for reintroduction into the decontamination column, represents a problem area with direct bearing on the performance of the partitioning column. To effect the oxidation, all of the hydroxylamine and hydrazine entering the vessel must be destroyed. If large quantities of the reducing agents remain in the aqueous stream entering the reaction vessel, gassing and incomplete oxidation can occur. The flow rate of the aqueous stream might be reduced to consume more of the hydrazine and hydroxylamine before it leaves the column. However, as observed in actual practice and as predicted by the simulation model, such efforts are not particularly effective in aiding the reflux problem and can quickly lead to serious operating problems in the partitioning column.

Because there are no intermediate sampling points along

the column, the only way that plutonium and uranium profile data could be taken was with radiation detection instruments. Gamma counters¹ were used to obtain a plutonium profile during operation of the hydroxylamine-only flowsheet developed by Bruns (10). Unfortunately input and output conditions for the plutonium profile scan were not listed. Bruns (9) also provided valuable insight into the shapes of the plutonium profiles by physically simulating the partitioning column with mixer-settlers in series. Although the results were not for the hydrazine flowsheet, the operation on the two flowsheets was quite similar during stable operation. The profiles were by far the most complete steady state data available and along with qualitative considerations provided important simulation verification. No profiles have been produced from the hydrazine flowsheet.

Profiles of the other materials of interest in the partitioning column were not available.

No dynamic test data were available.

To complete the discussion of Unit II's operation, input and output specifications are listed in Appendix A.

¹Hawkins, A. R. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to A. J. Low. December 9, 1971.

MODEL DEVELOPMENT

Because of the difficulty in obtaining data from the actual operating column due to its lack of instrumentation, the infrequency of flowsheet operation and the administrative controls over its operation, the development of an accurate dynamic model facilitated control system design over a wide range of process conditions in a much shorter time than would have been possible using the actual column.

Process Chemistry

In a qualitative sense the paths of plutonium and uranium can be traced through the pulse column. The two nuclear materials enter the column in the organic feed stream near the top of the column. Also present in the feed stream are nitric and nitrous acids. In the turbulent mixing area near the feed stage all four materials diffuse into the aqueous phase in quantities determined by their relative affinity for the TBP in the organic phase and by the composition of the aqueous phase. In the aqueous phase the plutonium reacts with the reducing agents, hydroxylamine and hydrazine. The resulting change in oxidation state dramatically decreases the solubility of the plutonium in the organic phase because plutonium in the reduced oxidation state does not complex with TBP. The plutonium and uranium in the aqueous phase tend to rise toward the top of the

column. Here uranium is scrubbed back into the organic phase. With essentially no competition from the Pu(III) for the fresh solvent at the top of the column, the scrubbing operation is quite effective.

Below the feed stage the mass transfer of plutonium and uranium into the aqueous phase continues until essentially all of the plutonium has been transferred. The continued reflux of uranium within the column reaches equilibrium and uranium is carried out of the bottom of the column in the organic waste stream. Ideally there would be no plutonium reflux. The chemical reduction of Pu(IV) is not stable, however. Depending on the operating conditions, varying amounts of the Pu(III) are oxidized. Over a large operating range, especially when the output plutonium concentration is low, the oxidation reaction reactions have little effect. However, at other conditions these reactions can dominate the system and cause the plutonium concentrations throughout the column to rise. Unacceptable separation occurs when the plutonium reflux increases until the reduction reaction can no longer maintain all of the plutonium in the reduced oxidation state. Some Pu(IV) then remains in the organic stream as it leaves the bottom of the column.

The various reactions possible in the column can be separated into six groups: Pu(IV) reduction, Pu(III)

oxidation, oxidation control, other plutonium reactions, reactions directly affecting the separation process and reactions with little effect on the system.

Plutonium reduction is the driving force in the operation of the partitioning column. There are only a few reducing agents that selectively react with Pu(IV) while leaving the uranium unaffected. The Purex process uses iron (II) sulfamate. The scrap recovery flowsheet studied in this work uses hydroxylamine, which has the advantage of not introducing impurity ions into the system. When hydroxylamine reacts with plutonium the only products are the reduced Pu(III), hydrogen ions, gaseous nitrogen products and water.

Although not the primary purpose for adding hydrazine to the column, small amounts of Pu(IV) are also reduced by hydrazine in a reaction similar to the hydroxylamine-Pu(IV) reaction. This reaction is far more important for its removal of hydrazine from the column than for the small amounts of Pu(IV) reduced.

There are several other reactions which can potentially reduce Pu(IV) to the desired +3 oxidation state. Pu(IV) can undergo disproportionation to produce Pu(III) and Pu(VI). The rate and the equilibrium yield of this reaction are highly dependent on the hydrogen ion concentration in the system. The net reaction is (11):

Although there has been some speculation on the importance of this reaction, particularly in light of tests conducted at very low acid strengths by Bruns (10) in which it was possible to maintain the desired Pu(III) by disproportionation alone, the data indicate that the reaction is not significant in terms of column performance.

One of two radiation effects of interest is the reduction of Pu(IV) by alpha, gamma and X-radiation. In these reactions the mechanism appears to be the radiolysis of water which produces small quantities of reducing agents. Hydrogen peroxide is produced in the case of alpha radiation and the very slow reduction rate, only a few percent of the plutonium per day, is characteristic of the weak reductant. For gamma and X-radiation the reduction, as described in Cleveland (11), proceeds because of the production of hydrogen peroxide and atomic hydrogen. However, hydroxide radicals are also generated which tend to oxidize Pu(III). The net effect is a very slow reduction. Because the sources of gamma radiation are not intense within or around the column and because the reaction rates are very slow for the low radiation levels encountered, the reduction effect is not important in the development of the dynamic model.

A potentially more important influence on oxidation of the desired Pu(III) is the radiolysis of nitrates to the nitrous acid catalyst by gamma radiation. However, again since there is no significant gamma radiation source, this reaction is not essential to the control simulation.

In some of the feedstocks as much as 10% of the plutonium may enter the column in the +6 oxidation state. Pu(VI) is not as reactive as Pu(IV) because the oxygen bonds (Pu(VI) exists in solution as PuO_2^{+2}) must be broken as part of the chemical reduction. In general because of the small amounts of Pu(VI) found in the system in comparison to the total quantity of plutonium and because of the similarity of the reduction reactions of the plutonium in the two oxidation states with hydroxylamine, the system can be adequately described for control purposes by the Pu(IV) reactions alone.

If the reduction reactions dominated within the entire range of operating conditions, there would be little problem controlling the partitioning column. However, the oxidation of Pu(III) by nitric acid can easily overshadow the plutonium reduction reactions at some operating conditions. Oxidation of Pu(III) by nitric acid is an extremely slow reaction without the presence of a catalyst, but since nitrous acid is introduced in the feed stream and also produced in the Pu(III)-nitric acid reaction, this oxidation

stands out as the dominate source of operational problems. Once triggered by the external catalyst, the autocatalytic oxidation reaction can sustain itself and its effects can spread rapidly throughout the column.

Because the Pu(III)-nitric acid oxidation reaction is so dramatically influenced by the nitrous acid catalyst, control of the reaction depends on control of the catalyst. An upper limit for nitrous acid strength is set by its own instability in acid solution. This limit is only a few percent of the nitric acid concentration. There is no evidence that it is ever reached in the partitioning column. The only reactions that actually remove nitrous acid from the chemical environment are the hydroxylamine- HNO_2 and hydrazine- HNO_2 reactions. In Bruns' hydroxylamine flowsheet (10) it was hoped that the reducing agent could perform the double function of reducing the Pu(IV) and controlling the nitrous acid catalyst. While a great deal of test work was undertaken to develop the flowsheet, the hydroxylamine-only approach to partitioning was abandoned in favor of the Pease flowsheet (35) in which hydrazine is added to the aqueous strip stream to control the nitrous acid. The lack of total process control indicated that, although hydrazine did significantly improve operational stability, the oxidation reaction still strongly influenced column performance.

The inability of hydrazine or hydroxylamine to

completely stabilize the partitioning column is due to the peculiar complexing of nitrous acid with the tributylphosphate in the organic stream. Nitrous acid forms a very stable complex with TBP because of the hydrogen bonding between the phosphate group and the hydrogen in the acid group. This bonding not only holds the complex together but also stabilizes the nitrous acid by equilibrating the two nitrogen-oxygen bonds. Also adding to the behavior is the very low ionization of HNO_2 in aqueous solution, making it readily available for organic complexing. Fletcher, Scargill and Woodhead (20) used these concepts to explain why the distribution coefficient of nitrous acid can be as much as two orders of magnitude greater than that for nitric acid. The implications of this unusual behavior are that most of the nitrous acid remains in the organic phase and thus out of contact with the hydroxylamine and hydrazine. With only a very small amount of catalyst needed to accelerate the nitric acid-plutonium oxidation reaction, the large "storage" of nitrous acid represents a severe limitation to column control.

Plutonium can also be involved in several other reactions. In weakly acidic solutions it forms a colloidal polymer that, once formed, is extremely difficult to dissolve. Table 1 shows the maximum acidities for Pu(IV) polymerization. Although inhibited somewhat by nitrate

Table 1. Approximate acidity of incipient polymerization of Pu(IV) solutions at 25°C^a

[Pu(IV)], gm/l	Maximum [H ⁺] for polymerization, M
1	0.12
2	0.16
5	0.20
10	0.26
15	0.32

^aThe source for the data is Cleveland (11), Table 4.3.

ions. The rate of polymer formation is rapid enough to have some potential effect, but several factors indicate that this effect is minimal. The simulation model shows acidities higher than the maximum for polymerization everywhere in the column except at the very bottom where the plutonium concentrations are at a minimum. Unless the polymer begins to precipitate its formation would actually be beneficial since more plutonium would be held in the aqueous phase. However, there is no evidence from operating experience to indicate significant polymerization.

Two plutonium complexes are of interest. Hydrolysis or complexation with the hydroxyl ion could be important for two reasons. Some effect on the ionic strength of the aqueous solution with the resulting effects on reaction

rates and distribution coefficients would be noted if hydrolysis were extensive. Formation of organic insoluble complexes in the aqueous phase would be beneficial to overall column operation since there would be less reliance on the plutonium reduction reactions to effect separation. However, in the acid environment found in the column it is doubtful that there are enough hydroxyl ions to produce significant complexing.

The other complexes, the plutonium-nitrate species, are very important. The plutonium in the organic phase exists as the Pu(IV)-nitrate complex. This specie diffuses across the organic-aqueous interface and breaks down into other compounds. Pu(III) also forms complexes with nitrate. Because of the stability of the complexes, as shown in Table 2, significant quantities of plutonium are complexed at equilibrium. However, the distribution coefficient and reaction kinetics expressions which depend on plutonium and nitrate concentrations are based on the nominal concentrations rather than the exact species present.

Two other groups of reactions possible in the chemical environments found in the partitioning column do not directly involve the plutonium. The first group includes those reactions which might have an effect on overall column performance while the other reactions apparently have no noticeable effects.

Table 2. Stability constants for nitrate complexes^a

Reaction	Equilibrium Constant
$\text{Pu}^{+3} + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)^{+2}$	5.9 ± 0.5
$\text{Pu}(\text{NO}_3)^{+2} + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_2^+$	14.3 ± 0.8
$\text{Pu}(\text{NO}_3)_2^+ + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_3$	14.4 ± 0.8
$\text{Pu}^{+4} + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)^{+3}$	5.5 ± 0.2
$\text{Pu}(\text{NO}_3)^{+3} + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_2^{+2}$	23.5 ± 0.1
$\text{Pu}(\text{NO}_3)_2^{+2} + \text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_3^+$	15 ± 10

^aThe source for the data is Cleveland (11), Table 5.1 and p. 110.

U(VI), as the UO_2^{+2} specie, complexes with nitrate ions. From Day and Powers (14) the stabilities of the U(VI)-nitrate complexes are much lower than those of the plutonium nitrates. The first equilibrium constant is 0.24, indicating a predominance of the dissociated species. Again, however, since the rates and distribution coefficients are based on nominal uranium and nitrate ion concentrations, the uranium complexing was neglected.

At the Atlantic Richfield Hanford Company the stability of hydroxylamine in the relatively low acidity found in this column, has been questioned. Despite the fact that hydroxylamine can be stored for long periods of time in acid solutions of the strength found in Unit II, reagent instability has been advanced to explain losses above those needed for Pu(IV) reduction. Simulation results indicate that the unexplained losses are due to the additional plutonium reductions required because of the nitric acid oxidation reaction. With these results, the comments in Partington (34) and Holleman (24) on hydroxylamine stability and ARHCO's own experience¹, it is assumed that the phenomenon is negligible.

Another column reaction is the radiation degradation of tributylphosphate to dibutylphosphoric acid. Both uranium and plutonium complexed with DBP exhibit very large distribution coefficients, as shown in Table 3. With such preference for the organic phase there is little diffusion to the aqueous phase where Pu(IV) can be reduced. The quantities of plutonium complexed with DBP cannot be separated from the uranium in the partitioning column and

¹Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Letter to G. L. Richardson, Westinghouse Hanford Company, Richland, Washington. May 29, 1974.

Table 3. Pu(IV) and U(VI) distribution coefficients between nitric acid and 0.5 molar dibutylphosphoric acid (DBP)^a

$[\text{HNO}_3]_a$, molar	$E_{\text{Pu(IV)}}$	$E_{\text{U(VI)}}$
0.1	5300	575
1.0	1200	293
3.0	1050	250

^aThe source for the data is Cleveland (11), Table 7.18.

must be stripped from the organic phase by hydrofluoric acid in the stripping column labeled as Unit III in Figure 1.

There has been some work¹ on methods to minimize the rate of organic degradation. Two concepts suggested are the addition of iron(III) nitrate to the Unit I feed stream and the addition of diazomethane to the organic diluent which reacts with DBP to form a compound very similar to TBP in its extraction characteristics. While the problem has not been too difficult to control in regular operation, two factors will increase the importance of the degradation reaction. With newer fuel cycles the distribution of plutonium isotopes in the spent fuel will change resulting in

¹Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. August 30, 1972.

higher radiation levels which will increase the rate of solvent degradation. Second, an improved control system will allow higher plutonium concentrations to be maintained in the column and further increase the amount of radiation present. Process changes may minimize the problems but such work is beyond the scope of the present research.

A problem with DBP complexing that is important to the present work is the difficulty of distinguishing between plutonium complexed with the two phosphate compounds. While the DBP-complexed material is lost, the TBP-complexed material indicates a control problem. Though important to the overall flowsheet operation, the radiation degradation problem involves extremely small quantities of plutonium and is not significant to the simulation of the column.

There is some indication that the nitrous acid present in the system is responsible for some of the organic breakdown. ARHCO has found that the quantities of DBP generated in the system correspond to unrealistically high radiation levels.

Ionization of various chemical species in the column determines the ionic strength on which several reaction rates and distribution coefficients depend. The degrees of ionization of hydroxylamine nitrate, hydrazine, nitric acid and nitrous acid are of interest. In the relatively low acid solutions encountered, nitric acid is essentially

completely ionized. Because of its weak ionization, nitrous acid dissociates very little as shown by the ionization constant given in Durrant and Durrant (18):

$$K_1 = 4.5 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]} .$$

Since the hydrogen ion concentration is due principally to the nitric acid, equilibrium shifts away from the ionized species. Hydrazine dissociation is essentially complete. Audrieth and Ogg (1) give the following equilibrium constant:

$$K_1 = 8.5 \times 10^{-7} = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} .$$

In the acid environment the hydroxyl ion concentration is negligible and equilibrium is shifted toward the ionized species. Jolly (26) has found that hydroxylamine dissociates readily and Barney (2) has shown that the nitrate salt also dissociates completely in the partitioning column.

Reactions of both hydrazine and hydroxylamine produce gaseous nitrogen oxide by-products. The gases can be vented from the column avoiding contamination of the liquid phases with impurity--a major reason for the use of the two reagents in the process. There has been speculation by Bruns (10) that these nitrogen gas products are the source of the small

quantities of nitrous acid needed to trigger the Pu(III)-nitric acid oxidation reaction. Some preliminary simulation work was done using this mechanism. However, after additional literature review and process study, it became apparent that there were other far more important sources of nitrous acid. According to Denbigh and Prince (15) the rate of nitrogen gas absorption into the aqueous phase is far too slow to be significant and without nitrogen oxide (NO) the absorption does not produce nitrous acid. There is no indication in the reaction stoichiometries or test results from vent gas analyses¹ from the column to indicate NO production.

Nitrous acid entering from external sources increases the catalyst level in the column. There appear to be three external sources. A small quantity is in equilibrium with the nitrate in the aqueous strip stream. This source is probably rather insignificant since the nitrous acid tends to extract into the organic immediately upon entering the column. Much more important are the quantities of nitrous acid entering in the feed stream. In the first step of the process, where scrapped fuel materials are dissolved in nitric acid, nitrous acid is produced which then enters the

¹Wheelwright, E. J. Battelle Memorial Institute Pacific Northwest Laboratories, Richland, Washington. Letter report to L. E. Bruns, Atlantic Richfield Hanford Company, Richland, Washington. February 4, 1970.

system as feed to the decontamination column. The organic phase in this first column rapidly picks up large quantities of the catalyst along with the uranium and plutonium which are subsequently fed to the partitioning column. Also, when the Pu(III) is taken-off the top of the second column, some of it is oxidized to Pu(IV) by concentrated nitric acid for recycle to the decontamination column. Additional quantities are produced by this oxidation and are picked up by the organic phase in the first column as before. While it is difficult to quantify these sources of nitrous acid, it is assumed that with the rather low equilibrium values of nitrous acid and the additional reactions taking place at each source, its production is largely independent of the plutonium concentrations.

In their work with a partitioning flowsheet similar to the Atlantic Richfield scrap recovery process, Schulz, Bouse and Kupfer (36) theorized that the source of nitrous acid was the radiolysis of nitric acid in Unit I. With radioactive wastes in high concentrations this might be the case, but for scrap recovery where radiation levels are much lower, it does not seem feasible that the large quantities of nitrous acid introduced into Unit II can be caused by radiation alone.

Some work has been done on methods of nitrous acid destruction before it can enter Unit II. In the flowsheet

proposed by Schulz, Bouse and Kupfer (36) urea was added to the Unit I strip stream (their first column used a secondary amine rather than TBP as the plutonium and uranium extractant) to destroy nitrous acid in the column. While this is not really important in the first column, destruction of the nitrous acid before it reaches the partitioning column appears to be critical for the next evolutionary development in process control beyond the system designed here.

Up to this point there has been little mention of uranium. Despite the rather active chemical environment uranium does not take part in any reactions, probably due to its generally lower reactivity in comparison to plutonium and to the diminished reactivity of the +6 oxidation specie due to the oxygen bonding. There is a feeling at Atlantic Richfield that uranium has a greater affinity for DBP than Pu(IV) and thus aids in preventing plutonium extraction by DBP. Also, when the process is operated with high uranium input concentrations, it has been found necessary to increase the plutonium input to the decontamination column either by selectively scheduling scrap inputs to the dissolver or by increasing the reflux from the second column. The plutonium acts as a salting agent and forces the uranium into the organic phase, increasing the extraction efficiency for uranium in the first column. These

effects and the influence on distribution coefficients and the ionic strength within Unit II are the only effects produced by the uranium.

Chemical Reaction Simulation

Despite the chemical complexity of the partitioning column, five reactions have been found to describe the process adequately. The Pu(IV)-hydroxylamine reaction is responsible for the partitioning. It is aided to some extent by the Pu(IV)-hydrazine reaction. Stable operation depends on the relative importance of the Pu(III)-nitric acid reaction. This autocatalytic oxidation is controlled primarily by the hydrazine-nitrous acid reaction and secondarily by the hydroxylamine-nitrous acid reaction. Kinetic models and stoichiometries for each of these reactions are detailed in the next paragraphs.

Reaction 1: Pu(IV)-hydroxylamine

The rate and stoichiometric equations used for this research for this reaction were developed by Barney (2) with refinements¹ and are:

¹Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Letter to G. L. Richardson, Westinghouse Hanford Company, Richland, Washington. May 29, 1974.

Rate:

$$-\frac{d}{dt}[\text{Pu(IV)}] = k \frac{[\text{Pu(IV)}]^2 [\text{NH}_3\text{OH}^+]^2}{[\text{Pu(III)}]^2 [\text{H}^+]^4 (K_d + [\text{NO}_3^-])^2}$$

$$k = 0.0235 \pm 0.00617 \text{ (mole/l)}^5 \text{sec}^{-1}$$

$$K_d = 0.19$$

Stoichiometry:

The exact stoichiometry is a function of acid strength although the nature of the relationship between the stoichiometry and acidity is not yet fully understood. A net reaction was assumed with 1.45 moles of Pu(IV) reduced for each mole of hydroxylamine consumed and 1.75 moles of H^+ produced for each mole of Pu(IV) reduced. The rate expression does take into account the Pu(IV)-nitrate complex as shown in the last term in the denominator.

Reaction 2: Pu(III)-nitric acid

The destabilizing nitric acid-Pu(III) oxidation reaction is reported in Cleveland (11) from which the rate

expression was taken although further work¹ has been done to define the stoichiometry. The equations used in the simulation are:

Rate:

$$-\frac{d}{dt}[\text{Pu(III)}] = k[\text{Pu(IV)}][\text{HNO}_2][\text{H}^+][\text{NO}_3^-]$$

$$k = 1.5 \text{ (mole/l)}^{-3} \text{sec}^{-1}$$

Stoichiometry:

With the nitrous catalyst as one of the products, the autocatalytic nature of the reaction is evident.

Reaction 3: Pu(IV)-hydrazine

Little information is available on the Pu(IV)-hydrazine reduction reaction. Although hydrazine has been used in analytical chemistry studies for plutonium identification, it has not been used in a partitioning flowsheet. Because the reaction has largely been ignored, both the rate expression developed from data given by Cleveland (11) and the stoichiometry of the reaction are estimates. The assumed

¹Klem, M. J. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. June 6, 1974.

stoichiometry is analogous to the Pu(IV)-hydroxylamine reaction and is suggested by the oxidation-reduction half reactions in Audrieth and Ogg (1) and by their comments on the similarity of hydrazine and hydroxylamine as reducing agents. The hydrazine reduction reaction is much slower than the Pu(IV)-hydroxylamine reaction². The chemical models used here are:

Rate:

$$-\frac{d}{dt}[\text{Pu(IV)}] = k[\text{Pu(IV)}][\text{N}_2\text{H}_5^+]$$

$$k = 0.0693 \text{ (mole/l)}^{-1}\text{sec}^{-1}$$

Stoichiometry:

Reaction 4: Nitrous acid-hydrazine

Although the nitrous acid-hydrazine reaction is the essential controlling reaction in the separation process, it has received little attention in the literature. The following rate data were taken from Biddle and Miles (6) and the stoichiometry used was developed from work done at

¹Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. October 23, 1974.

Atlantic Richfield¹. The following chemical models were used:

Rate:

$$-\frac{d}{dt}[\text{HNO}_2] = k[\text{N}_2\text{H}_5^+][\text{HNO}_2][\text{H}^+]^2$$

$$k = 0.234$$

Stoichiometry:

Reaction 5: Nitrous acid-hydroxylamine

Of importance for nitrous acid control is the hydroxylamine-nitrous acid reaction. The data were taken from the work of Barney (3) and provided the following models:

Rate:

$$-\frac{d}{dt}[\text{NH}_2\text{OH}^+] = f(\mu)[\text{HNO}_2]$$

$$f(\mu) = 0.91 \mu^{1/2} - 1.521$$

Stoichiometry:

¹Klem, M. J. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to R. E. Felt. June 6, 1974.

The quantity μ is the ionic strength of the aqueous phase. Its calculation is discussed in detail later.

To define the chemical reaction system aqueous concentrations are necessary for the following seven species: Pu(III), Pu(IV), H^+ , NO_3^- , HNO_2 , hydroxylamine and hydrazine. The uranium concentration, though not included in the reaction models, is required to define the purity of the plutonium product stream and to account for uranium salting effects. This makes a total of eight variables that must be defined in the aqueous phase.

Distribution coefficients

Because there are two phases present in the column, 16 concentration variables are theoretically necessary to completely define the system. However, some of the eight species are found only in the aqueous phase. For those which exist in both phases, distribution coefficients can be used to obtain the additional equations needed.

Neither hydroxylamine nor hydrazine is soluble in the organic phase and the hydrogen ion is only found in combination with the nitrate ion as part of the nitric acid-TBP complex. Also, since nitrous acid dissociates so little, it need not be considered as a source of hydrogen ions.

Pu(III) is almost completely insoluble in the organic

Table 4. Pu(III) extraction coefficients into 19% TBP^a

$[\text{HNO}_2]_a$, molar	$E_{\text{Pu(III)}}$
0.2	0.0027
0.65	0.0089
1.20	0.0157
2.0	0.0167
3.0	0.0161

^aThe source for the data is Cleveland (11), Table 7.2.

phase. It is this property of the reduced plutonium ion which is used as the basis for the plutonium and uranium separation. The small degree of organic phase solubility of Pu(III) as a function of the nitric acid concentration is shown in Table 4. Graphically the differences of the solubilities of the plutonium and uranium ions can be seen by the representative curves in Figure 4. The insolubility of Pu(III), hydroxylamine, hydrazine and hydrogen ion in the organic phase reduces the number of variables necessary from 16 to 12. This number is reduced to eight by the four distribution coefficients developed in the following paragraphs.

Baumgaertal, Ochsenfeld and Schieder (4) developed analytical expressions for the distribution coefficients of Pu(IV) and U(VI). To correlate their experimental data

Figure 4. Representative distribution coefficients for Pu(III), Pu(IV) and U(VI) as functions of the nitric acid concentration (from Keller (29), Figure 2.6)

taken in a system with tributylphosphate diluted with dodecane, they formulated explicit equations for distribution coefficients in terms of empirically determined equilibrium constants related to the ionic strength of the aqueous solution. As a part of the SEPHIS program development, Horner (25) expanded their work to include a similar expression for the nitric acid distribution coefficient.

Nominal values of the concentration variables were used for the ionic strength in these correlations neglecting the dissociation of the plutonium and uranium nitrate species. The presence of the hydrazine and hydroxylamine are accounted for in the relationship used in this research. In general, ionic strength is defined as the summation of one half the molality of each charged specie times the square of its charge. From Moore (33) this can be written as:

$$\mu = \sum \frac{1}{2} m_j z_j^2 \quad .$$

For the concentration variables used in the model development the following correction is required to convert the concentrations to approximate molality:

$$m = \frac{c}{\rho - \frac{M c}{1000}} \quad .$$

For the dilute solutions in Unit II this reduces to

approximately $m = c/\rho_0$. The aqueous solvent density, to a first approximation, is the same as water. This reduces the correction to unity. Noting that the U(VI) specie is actually UO_2^{+2} , the resulting ionic strength expression is:

$$\mu = \frac{1}{2}[\text{NO}_3^-] + \frac{1}{2}[\text{H}^+] + \frac{1}{2}[\text{NH}_3\text{OH}^+] + \frac{1}{2}[\text{N}_2\text{H}_5^+] + 2[\text{U(VI)}] \\ + 8[\text{Pu(IV)}] + 4.5[\text{Pu(III)}] \quad .$$

This same definition is used for the ionic strength variable in the rate expression for the hydroxylamine-nitrous acid reaction.

The distribution coefficient expressions for Pu(IV), U(VI) and nitric acid used in the simulation model are:

Pu(IV)

$$\sqrt{E_{\text{Pu(IV)}}} = - \frac{1 + K_H [\text{H}^+][\text{NO}_3^-]}{4\sqrt{K_{\text{Pu}}} [\text{NO}_3^-]^2 \left([\text{Pu(IV)}] + \frac{K_U[\text{U(VI)}]}{K_{\text{Pu}}[\text{NO}_3^-]^2} \right)} \\ \times \left(1 - \sqrt{1 + \frac{8C K_{\text{Pu}} \left([\text{Pu(IV)}] + \frac{K_U[\text{U(VI)}]}{K_{\text{Pu}}[\text{NO}_3^-]^2} \right)}{\left(\frac{1 + K_H[\text{H}^+][\text{NO}_3^-]}{[\text{NO}_3^-]^2} \right)^2}} \right)$$

U(VI)

$$\sqrt{E_{U(VI)}} = - \frac{1 + K_H[H^+][NO_3^-]}{4\sqrt{K_U}[NO_3^-] \left([U(VI)] + \frac{K_{Pu}[Pu(IV)][NO_3^-]^2}{K_H} \right)}$$

$$\times \left(1 - \sqrt{1 + \frac{8C K_U \left([U(VI)] + \frac{K_{Pu}[Pu(IV)][NO_3^-]^2}{K_U} \right)}{\left(\frac{1 + K_H[H^+][NO_3^-]}{[NO_3^-]} \right)^2}} \right)$$

NO₃⁻

$$E_{NO_3^-} = - \frac{K_H (K_H[H^+][NO_3^-] + 1)}{4 (K_U[NO_3^-][U(VI)] + K_{Pu}[NO_3^-]^3[Pu(IV)])}$$

$$\times \left(1 - \sqrt{1 + \frac{8C (K_U[NO_3^-]^2[U(VI)] + K_{Pu}[NO_3^-]^4[Pu(IV)])}{(K_H [H^+][NO_3^-] + 1)^2}} \right)$$

where all concentrations are for the aqueous phase and
 $C = C' - E_{HNO_2} [HNO_2]$ where C' is the nominal organic
 TBP concentration ($C' = 0.731$ for 20% TBP).

In the calculations it was assumed that nitrous acid takes

preference over the other materials competing for the TBP due to its unusual complex with the phosphate group. The three empirically determined ionic strength functions taken from Baumgaertel, Ochsenfeld and Schieder (4) are:

$$K_{Pu} = 12.163 - 9.033\mu + 2.230\mu^2 - 0.163\mu^3$$

$$K_U = 8.791 + 6.071\mu - 6.176\mu^2 + 1.579\mu^3$$

$$K_H = 0.385 - 0.155\mu + 0.024\mu^2 \quad .$$

The nitrous acid distribution coefficient is large because of the very stable complex between the acid and TBP in the organic phase and because so little of the nitrous acid dissociates in the acid aqueous phase. In a system similar to the Unit II chemical environments Marin, Sellier and Gourisse (32) found a linear relationship between the uncomplexed TBP and the nitrous acid distribution coefficient:

$$E_{HNO_2} = 18.5 C''$$

where

$$C'' = C' - E_{Pu(IV)}[Pu(IV)] - E_{U(VI)}[U(VI)] - E_{NO_3^-}[NO_3^-] \quad .$$

Calculation by this method results in distribution coefficients for nitrous acid significantly larger than those for nitric acid. Data in Biddle and Miles (6) confirm this

behavior.

Before proceeding to the development of the material balances some discussion on the effects of temperature changes is in order. The rates of the five principal chemical reactions are all temperature dependent. However, the separation process does not depend explicitly on thermal effects and can be studied without using temperature as a variable. With the relatively large volume of the extractor, the small quantities of reacting materials and the large surface area for heat transfer with the surroundings, there has been little evidence that the temperature at any point within the column differs from the ambient temperature.

The Column Model

The most straightforward approach to dynamic modeling of the pulse column is the use of the equilibrium stage concept. The form of the material balances for each stage is as follows:

$$\text{Input} - \text{Output} + (\text{Lost to Reaction}) + (\text{Gained from Reaction}) = \text{Accumulation} \quad .$$

For a typical stage (using the convention that stages are numbered from the top of the column) the material balance equation is:

$$\begin{aligned}
& Aq(X_{a,i+1} - X_{a,i}) + Or(X_{o,i-1} - X_{o,i}) \\
& + (\text{Material } x \text{ from reactions}) \\
& - (\text{Material } x \text{ lost to reactions}) \\
& = \frac{d}{dt}(HX_{a,i} + hX_{o,i}) \quad .
\end{aligned}$$

If it is possible to assume that the holdup derivatives are small in comparison to the concentration derivatives, the accumulation term can be simplified considerably. In the absence of experimental data it can be assumed that the ratio of the holdups is equal to the ratio of the flow rates. Further assuming that the distribution coefficients change slowly with time, the general accumulation term takes the following form:

$$\text{Accumulation} = H(1 + \frac{Or}{Aq} E_x) \frac{d}{dt} X_{a,i} \quad .$$

For those materials not soluble in the organic phase (i.e., $E_x \rightarrow 0$) there are obvious additional simplifications.

This model, because of its simplicity, was particularly useful for steady state analysis. With the complex forms of the chemical reaction models and the general mathematical complexity, determination of steady state conditions by setting the time derivatives equal to zero and iterating the material balances offered no obvious simplifications.

Generating steady state data by allowing the system to damp out its own response also had the advantage of providing insight into the dynamic column response.

Hydrodynamically the pulse column is quite complex. Even if it is assumed that the pulsing character can be neglected, the description of output responses to input flow rate changes is difficult. Qualitatively if a sudden increase in the aqueous strip stream flow rate is introduced with the other inputs held constant, the immediate response is a rise in the liquid level in the column which rapidly increases the aqueous flow out the top. The organic flow rate tends to increase slightly due to the increased head but the effect is small. In order to establish equilibrium for the new operating conditions the holdup ratio must change to realize the original head to maintain the same organic flow rate. Since the height of the liquid head has increased due to the increased aqueous flow rate, the average density must decrease to create the same pressure at the bottom of the column. Thus the aqueous holdup increases slightly. The organic flow from the column is slightly higher while the holdup ratio is changed to the new equilibrium values.

Due to the relatively large column volume in relation to the holdups and the small gravitational forces that drive the system to its new steady state, the flow rate changes

for holdup adjustment are small in magnitude and spread over a relatively long period of time. Many investigators have neglected these holdup and hydrodynamic transients because of their small effect on mass transfer. The presence of chemical reactions and the effects of the change in aqueous volume, which is essentially the "reactor" volume, on the reaction rates is of importance in the present work.

It should be mentioned that the flow rate changes are not due exclusively to gravitational forces. Because the two phases have different viscosities, the perforated plates represent different resistances to flow for each liquid. The pulsing character of the column tends to pump one phase through the column at a higher rate than the other. This effect depends on the operating regime within the column and is offset by deviations from the proportionality between holdups and flow rates. The pumping effect is neglected here.

A change in the feed flow rate has entirely different transient effects on the column. At the time of the upset the liquid volume in the column again increases for an increase in the feed flow rate. The aqueous phase flow rate increases almost immediately while the organic flow from the bottom of the column increases more gradually. The two output flow streams also experience transients due to the holdup adjustments that must be made to again realize

pressure equilibrium.

From qualitative considerations based on pulse column operating experience and a general qualitative analysis of the pulse column dynamic properties in the context of the Unit II separation process, the following assertions are postulated:

1. Flow rate disturbances propagate rapidly through the column.
2. Holdup changes are propagated slowly through the column.
3. The holdup adjustments are significant to the separation dynamics because of the effects on the stage "reactor" volumes.

With these assertions a set of relationships between the holdup dynamics and flow rate disturbances were developed using the propagation of pseudo flow rate changes through the column. Although the actual phase flow rates into and out of the column are assumed identical at all times, the pseudo flow rates vary between column stages much as the flow rates vary between mixer-settler stages during transient periods as discussed in Seeman and Burkhardt (37). Assuming proportionality between flow rates and holdup ratios, the holdup time derivatives were calculated in terms of the pseudo flow rates and used in defining a new accumulation term.

Before proceeding into the accumulation term development, one further assumption should be considered. Considerable quantities of nitrogen oxide gases are evolved when the nitrous acid levels are high and the plutonium concentration is low. While some problems have been noted with the top phase disengagement section due to gassing¹, the gas is assumed to have little effect on the column hydrodynamics and holdups.

The pseudo flow rate time derivatives are defined below in terms of empirical interstage time constants. To avoid any confusion between actual and pseudo flow rates the latter are distinguished by primes.

$$\frac{d}{dt} Aq_i' = \frac{1}{\tau_{a,i}} (Aq_{i+1}' - Aq_i')$$

$$\frac{d}{dt} Or_i' = \frac{1}{\tau_{o,i}} (Or_{i-1}' - Or_i') \quad i \neq \text{feed stage}$$

$$\frac{d}{dt} Or_i' = \frac{1}{\tau_{o,i}} (Or_{i-1}' - Or_i' + Or_f) \quad i = \text{feed stage} .$$

The basic accumulation expression can be expanded as follows:

¹Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to G. L. Richardson, Westinghouse Hanford Company, Richland Washington. May 29, 1974.

$$\begin{aligned}\text{Accumulation} &= \frac{d}{dt}(HX_a + hX_o) \\ &= H \frac{d}{dt} X_a + X_a \frac{d}{dt} H + h \frac{d}{dt} X_o + X_o \frac{d}{dt} h .\end{aligned}$$

If the total stage volume is assumed constant, the time derivative of the organic holdup is the negative of the aqueous holdup derivative. With the assumptions of negligible time derivatives of the distribution coefficients and of proportionality between the ratio of holdups and the ratio of flow rates, the accumulation term becomes:

$$\text{Accumulation} = (1 - E_x)X_a \frac{d}{dt} H + H(1 + \frac{Or'}{Aq'} E_x) \frac{d}{dt} X_a .$$

The second term on the right hand side is the previously derived accumulation term. The first term takes into account the additional time lags between stages. Beginning with the general definition of holdup, an expression relating the flow rate derivatives defined above and the holdup time derivative can be generated:

$$H + h = V$$

$$H(1 + \frac{Or'}{Aq'}) = V$$

$$H = \frac{Aq'}{Aq' + Or'} V .$$

Using the stage numbering conventions established:

$$H_i = \frac{Aq'_{i+1} V}{Aq'_{i+1} + Or'_{i-1}} \quad i \neq \text{feed stage}$$

$$H_i = \frac{Aq'_{i+1} V}{Aq'_{i+1} + Or'_{i-1} + Or_f} \quad i = \text{feed stage} .$$

After taking the appropriate derivatives and inserting the flow rate derivatives, the holdup derivatives can be written as:

$$\frac{dH_{a,i}}{dt} = \frac{V (Or'_{i-1}) \frac{dAq'_{i+1}}{dt} - V (Aq'_{i+1}) \frac{dOr'_{i-1}}{dt}}{(Aq'_{i+1} + Or'_{i-1})^2} \quad i \neq \text{feed stage}$$

$$\frac{dH_{a,i}}{dt} = \frac{V (Or'_{i-1} + Or'_i) \frac{dAq'_{i+1}}{dt} - V (Aq'_{i+1}) [\frac{dOr'_{i-1}}{dt} + \frac{dOr_f}{dt}]}{(Aq'_{i+1} + Or'_{i-1} + Or_f)^2} \quad i = \text{feed stage} .$$

With this result the complete accumulation term can be constructed by substitution. The only undefined quantities are the interstage time constants. While it is anticipated that these vary with location along the column, average time constants are assumed sufficiently accurate for the control system design.

In terms of the column model in which the pseudo flow rates were neglected, the eight material balances for a

typical stage can be written as:

Pu(IV)

$$\begin{aligned} & \text{Aq}([\text{Pu(IV)}]_{a,i+1} - [\text{Pu(IV)}]_{a,i}) + \text{Or}(E_{\text{Pu},i-1} [\text{Pu(IV)}]_{a,i-1} \\ & - E_{\text{Pu},i} [\text{Pu(IV)}]_{a,i}) - H(\text{Rxn 1} - \text{Rxn 2} + \text{Rxn 3}) \\ & = (1 + E_{\text{Pu},i})H \frac{d}{dt} [\text{Pu(IV)}]_{a,i} \quad . \end{aligned}$$

Pu(III)

$$\begin{aligned} & \text{Aq}([\text{Pu(III)}]_{a,i+1} - [\text{Pu(III)}]_{a,i}) + H(\text{Rxn 1} - \text{Rxn 2} + \text{Rxn 3}) \\ & = H \frac{d}{dt} [\text{Pu(III)}]_{a,i} \quad . \end{aligned}$$

U(VI)

$$\begin{aligned} & \text{Aq}([\text{U(VI)}]_{a,i+1} - [\text{U(VI)}]_{a,i}) + \text{Or}(E_{\text{U},i-1} [\text{U(VI)}]_{a,i-1} \\ & - E_{\text{U},i} [\text{U(VI)}]_{a,i}) = (1 + E_{\text{U},i})H \frac{d}{dt} [\text{U(VI)}]_{a,i} \quad . \end{aligned}$$

HNO₂

$$\begin{aligned} & \text{Aq}([\text{HNO}_2]_{a,i+1} - [\text{HNO}_2]_{a,i}) + \text{Or}(E_{\text{HNO}_2,i-1} [\text{HNO}_2]_{a,i-1} \\ & - E_{\text{HNO}_2,i} [\text{HNO}_2]_{a,i} + \frac{1}{2}H(\text{Rxn 2}) - H(\text{Rxn 4}) \\ & = (1 + E_{\text{HNO}_2,i})H \frac{d}{dt} [\text{HNO}_2]_{a,i} \quad . \end{aligned}$$

Hydroxylamine

$$\begin{aligned} & \text{Aq}([\text{NH}_3\text{OH}^+]_{a,i+1} - [\text{NH}_3\text{OH}^+]_{a,i}) - 0.89 \text{ H(Rxn 1)} - \text{H(Rxn 5)} \\ & = \text{H} \frac{d}{dt} [\text{NH}_3\text{OH}^+]_{a,i} \quad . \end{aligned}$$

Hydrazine

$$\begin{aligned} & \text{Aq}([\text{N}_2\text{H}_5^+]_{a,i+1} - [\text{N}_2\text{H}_5^+]_{a,i}) - 0.25 \text{ H(Rxn 3)} - \text{H(Rxn 4)} \\ & = \text{H} \frac{d}{dt} [\text{N}_2\text{H}_5^+]_{a,i} \quad . \end{aligned}$$

H⁺

$$\begin{aligned} & \text{Aq}([\text{H}^+]_{a,i+1} - [\text{H}^+]_{a,i}) + \text{Or}(E_{\text{HNO}_3,i-1}[\text{NO}_3^-]_{a,i-1} \\ & - E_{\text{HNO}_3,i}[\text{NO}_3^-]_{a,i}) + \text{H}(1.25 \text{ Rxn 1} - 1.5 \text{ Rxn 2} \\ & + 1.75 \text{ Rxn 3} + \text{Rxn 4} + \text{Rxn 5}) \\ & = \text{H}(\frac{d}{dt}[\text{H}^+]_{a,i} + E_{\text{HNO}_3,i} \frac{d}{dt}[\text{NO}_3^-]_{a,i}) \quad . \end{aligned}$$

The only hydrogen ions in the organic phase that are of interest are those complexed with TBP and NO_3^- since they can be carried back and forth across the liquid-liquid interface. Also, only the organic $[\text{NO}_3^-]$ derivative is needed in the accumulation term because aqueous $[\text{NO}_3^-]$ changes with time do not involve H^+ ions.

$$\begin{aligned}
& \frac{\text{NO}_3^-}{\text{Aq}} ([\text{NO}_3^-]_{a,i+1} - [\text{NO}_3^-]_{a,i}) + 0r(E_{\text{HNO}_3,i-1} [\text{NO}_3^-]_{a,i-1} \\
& + {}^4E_{\text{Pu},i-1} [\text{Pu(IV)}]_{a,i-1} + 2E_{\text{U},i-1} [\text{U(VI)}]_{a,i-1} \\
& - E_{\text{HNO}_3,i} [\text{NO}_3^-]_{a,i} - {}^4E_{\text{Pu},i} [\text{Pu(IV)}]_{a,i} - 2E_{\text{U},i} [\text{U(VI)}]_{a,i}) \\
& - \frac{1}{2}H(\text{Rxn } 2) = (1 + E_{\text{HNO}_3,i})H \frac{d}{dt} [\text{NO}_3^-]_{a,i} \\
& + {}^4HE_{\text{Pu},i} \frac{d}{dt} [\text{Pu(IV)}]_{a,i} + 2HE_{\text{U},i} \frac{d}{dt} [\text{U(VI)}]_{a,i} \quad .
\end{aligned}$$

Nitrate ions can complex in the organic phase with TBP alone or with Pu(IV) or U(VI) and TBP.

Two additional subjects needed to complete the simulation model are the number of equilibrium stages required and the type of calculation routine used.

The number of equilibrium stages would logically be determined by the separation performance. Insufficient data were available for such a determination, however. Bruns' work (10) with the hydroxylamine-only flowsheet assumed 24 equilibrium stages for Unit II. Discussions with ARHCO personnel indicated that the column probably exhibited more stages than were actually necessary to achieve the desired separation. The work with the SEPHIS program (21) used 12 equilibrium stages. In physically simulating the pulse

column with mixer-settlers in series, Bruns (9) used 20 stages with the feed stream entering at stage four. This configuration was assumed for the mathematical model.

In order to use a digital computer for generation of the response data from the simulation model, the continuous derivatives must be approximated. A backward finite difference technique was assumed in this work. The approximation has the form:

$$\frac{d}{dt}X_i = \frac{(X_{i,t+\Delta t} - X_{i,t})}{\Delta t} \quad .$$

Determining the approximate size of the time step was a part of the preliminary work with the simulation model. The results include a discussion of the time step size evaluation.

RESULTS OF THE SIMULATION MODEL

Comparison of results from the simulation model with the test data from the operating column and also with the qualitative system characteristics obtained from discussions with personnel involved in the development and operation of the process demonstrated the suitability of the model for control system design and also its usefulness in understanding the mechanisms of the separation process. The simulation model predicted steady state output values, the influence of process variable changes on the plutonium profile, the apparent suddenness of partitioning failure, the logic of manual control procedures and the positive effect of uranium on flowsheet operation. Although dynamic test data are not yet available, the general response character of the simulated column also corresponded to that observed by operating personnel and reported in the published literature on pulse column dynamics.

One of the single most important results was the confirmation of the importance of the nitrous acid catalyst and its effect on the performance of the column. During the development of the simulation model, it became apparent that the assumptions regarding the interaction of nitrous acid with the chemical system could provide a unifying concept to the various problems experienced with the column. However,

the quantities of the catalyst generated by either the absorption of nitrogen oxide or the radiation degradation of nitrates were insufficient to account for the observed system characteristics. Examination of the flowsheet revealed potential sources for the catalyst. These were later confirmed by tests of the actual process.

For direct comparison of the simulation results one set of steady state data was available from the work of Pease (35). The set was incomplete because of the omission on nitrous acid concentrations but the data for the model and the actual column compared quite well using assumed catalyst levels in the input streams. These results are shown in Table 5.

Several differences between the model results and the Pease data (35) can be seen in Table 5. In general mass flow rates agreed better than concentrations because of the volume changes which take place in the column. While plutonium values in the aqueous product stream compared closely, the uranium levels were somewhat different. In addition to possible experimental error, two factors may be responsible for this difference. The column may not have been in equilibrium when the experimental data were taken since the material inputs and outputs are not in balance. This may also affect other comparisons as well. Second, the higher uranium contamination may be due to poor phase

Table 5. Comparison of model results and hydrazine flowsheet data

Variable	Model	Actual Column ^a	
Plutonium Product Stream			
Aqueous flow rate	44.0 l/hr	46.0 l/hr	
Plutonium conc.	37.1 gm/l	35.2 gm/l	
Mass flow rate	1634.2 gm/hr	1619.2 gm/hr	
Uranium conc.	0.05 gm/l	0.15 gm/l	
Mass flow rate	2.2 gm/hr	6.9 gm/hr	
Hydroxylamine conc.	0.259 M	0.31 M	
Molar flow rate	11.4 mole/hr	14.26 mole/hr	
Hydrazine conc.	0.039 M	< 0.05 M	
Molar flow rate	1.72 mole/hr	< 2.3 mole/hr	
Nitrate conc.	1.41 M	1.13 M	
Molar flow rate	62.0 mole/hr	52.0 mole/hr	
Hydrogen ion conc.	0.60 M	0.77 M	
Molar flow rate	26.4 mole/hr	35.4 mole/hr	
Nitrous acid conc.	~ 0.0	- ^b	
Molar flow rate	~ 0.0	- ^b	
Uranium Product Stream			
Organic flow rate	114.8 l/hr	113.0 l/hr	
Plutonium conc.	~ 0.0	< 0.01 gm/l	
Mass flow rate	~ 0.0	< 1.13 gm/hr	
Uranium conc.	9.17 gm/l	9.3 gm/l	
Mas flow rate	1052.3 gm/hr	1050.9 gm/hr	
Nitric acid conc.	0.076 M	0.012 M	
Molar flow rate	8.67 mole/hr	1.36 mole/hr	
Nitrous acid conc.	0.021 M	- ^b	
Molar flow rate	2.42 mole/hr	- ^b	
Input Conditions			
Feed stream		Strip stream	
Plutonium conc.	17.6 gm/l	Hydroxylamine	
Uranium conc.	11.5 gm/l	nitrate	0.40 M
Nitrous acid conc.	0.02 M ^b	Hydrazine	0.05 M
Nitric acid conc.	0.14 M	Nitric acid	0.01 M ^b
Organic flow rate	91.8 l/hr	Nitrous acid	0.20 M
		Aqueous f.r.	44.0 l/hr
Strip stream			
Nitric acid conc.	0.2 M		
Organic flow rate	23.0 l/hr		

^a The source for these data is Pease (35).

^b These are assumed values since data were omitted in Pease.

disengagement in the top end-section aggravated by gassing within the column. The phase disengagement problem has been investigated¹ and found to be mechanical rather than chemical in nature.

The nitrate, hydrogen ion and hydroxylamine discrepancies are more difficult to explain. The experimental data fail to confirm the assumed Pu(IV)-hydroxylamine reaction stoichiometry² even assuming negligible oxidation and secondary reduction of the plutonium. According to personnel at Atlantic Richfield the analytical techniques on which the data are based are difficult to perform and subject to large experimental errors. Therefore either the assumed stoichiometry or the experimental data may be at fault and the differences cannot be resolved without further information. In the organic output stream the differences in nitrate concentrations are again difficult to interpret. The plutonium found in the uranium product stream is assumed to be almost entirely due to DBP complexing. Despite these differences between the simulation and actual

¹Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to A. J. Low. January 20, 1972.

²Barney, G. S. Atlantic Richfield Hanford Company, Richland, Washington. Letter to G. L. Richardson, Westinghouse Hanford Company, Richland, Washington. May 29, 1974.

results, the overall prediction accuracy is considered remarkable.

Additional simulation results using the hydrazine flow-sheet conditions (35) are presented in Figures 5, 6, 7, 8 and 9. The concentration profiles and distribution coefficients shown are typical of the magnitudes and profile shapes found during extensive model testing although significant differences, discussed later, can occur with changes in operating conditions.

Plutonium profiles from the simulation model were compared qualitatively with data gathered at the Plutonium Reclamation Facility by radiation scans^{1,2} of the operating column and also with experimental data gathered from pilot plant work using mixer-settlers to carry out the separation (9). Direct comparison was not possible because process conditions were not given for the experimental data. The effects of reducing the aqueous to organic flow rate ratio in the model produced the same plutonium profile broadening that was noted by Bruns in the mixer-settler experiments.

¹Hawkins, A. R. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to A. J. Low. December 9, 1971.

²Campbell, M. H. GE Hanford Atomic Products, Richland Washington. Internal office reported entitled "Plutonium Profile of the Recuplex H-3 Column." October, 1961.

Figure 5. Nitrous acid, hydrazine and hydroxylamine profiles from simulation of hydrazine flowsheet data (35)

Figure 6. Hydrogen ion and nitrate profiles from simulation of hydrazine flowsheet data (35)

Figure 7. Plutonium(III), plutonium(IV) and uranium(VI) profiles from simulation of hydrazine flowsheet data (35)

Figure 8. Plutonium(IV) and uranium(VI) distribution coefficients from simulation of hydrazine flowsheet data (35)

Figure 9. Nitric and nitrous acid distribution coefficients from simulation of hydrazine flowsheet data (35)

This effect, which is important in determining the maximum amount of separation possible, can be seen in the simulation results in Figures 10 and 11.

Sources of qualitative process information were the plant operating manual (16), the hydrazine flowsheet process test description (35) and guidelines for operating the hydroxylamine-only flowsheet^{1,2}. These documents outlined manual control procedures for the partitioning column as well as other parts of the flowsheet and provided a useful method for correlating actual column experience with the results of the simulation model. Although such comparisons were of a general nature, several specific examples can be cited. To control the uranium concentration in the plutonium product stream, the aqueous flow rate was decreased in 5% increments resulting in increased plutonium concentration at the top of the column. Since plutonium salts the uranium into the organic phase, as shown by the simulation, increased plutonium concentrations can reduce the uranium contamination. Another example of interpreting manual

¹Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to L. M. Knights. May 27, 1971.

²Bruns, L. E. Atlantic Richfield Hanford Company, Richland, Washington. Internal office communication to A. J. Low. December 13, 1971.

Figure 10. Broadening of the aqueous [Pu(IV)] profile with decreasing aqueous flow rate

Figure 11. Broadening of the aqueous [Pu(III)] profile with decreasing aqueous flow rate

control procedures, discussed earlier, was provided by the problems with oxidizing Pu(III) to Pu(IV) for reflux between the first two columns in the flowsheet. Again, the comparison of experimental and simulation results gave validity to the model while allowing insight to process mechanisms. As a third example, several references were made in the process documents to column control based on plutonium inventory because large quantities of plutonium seemed to aggravate the stability problems. The inventory was maintained by sensing the plutonium concentration profile edge with neutron counters along the column as shown in Figure 3. However, the simulation showed that the large inventories were a result of the plutonium reflux within the column rather than a cause for instability. The techniques suggested for inventory control are very similar to the methods developed later in this report for far different concepts of process control.

Since dynamic test data were not yet available for the partitioning column, the transient performance of the model was evaluated in light of the results reported in the literature on other pulse column separation systems. Considerable work in designing, testing and simulating pulse columns has been done at Iowa State University since the

1950's. This background¹ was valuable in establishing the "reasonableness" of the assumptions used in the mathematical development and in the analysis of the results.

The two forms of the dynamic model showed significant differences in their response characteristics. Figure 12 shows the response of the plutonium concentration in the aqueous stream leaving the column to a step decrease in the aqueous flow rate. In the first model, which neglected the holdup time derivatives, the immediate decrease in the aqueous holdup reduced the reaction volume slowing the plutonium reduction reaction and tending to oppose the rise in plutonium concentration. In the pseudo flow rate model the aqueous holdups at the top of the column initially remained constant. The plutonium reduction continued at the same rate while the decrease in the flow rate produced higher output concentrations. The plutonium level reached a maximum in excess of its final value until holdup changes propagated to the top of the column. The effect of different interstage time constants was small for the values tested; 500, 750 and 1500 seconds. For the control study a value of 750 seconds was used.

The success of the simulation model permitted substantial

¹Burkhart, Lawrence E. Iowa State University, Ames, Iowa. Much of the background came from conversations with Dr. Burkhart.

Figure 12. Comparison of the dynamic response characteristics of the two simulation models

verification of the assumed process mechanism. Partitioning depends on the balance between the plutonium oxidation and reduction reactions. The oxidation reaction, which causes plutonium to recycle from the one phase to the other within the column, results in high nuclear material concentrations below the feed stage, excessive consumption of hydroxylamine and the possibility of sudden increases in the uranium product stream contamination.

Control of the partitioning process can be defined in two ways. In a broad sense, control implies identifying the process variables that contribute to undesirable performance and adjusting the chemical system to maximize the process goals. In a more narrow sense, control is limited to the adjustment of a few manipulated variables to make the performance insensitive to disturbances. The control techniques developed for the partitioning column, which are reported in the next sections, were defined for this narrower objective. However, during the course of the research several process design changes were tested in an effort to improve partitioning. These results are discussed in the following paragraphs.

The plutonium oxidation reaction is difficult to control in part because the large quantities of catalyst in the feed stream are protected from the hydrazine. With nitrous acid distribution coefficients at least an order

of magnitude higher than those of other organic soluble species, the rate of the hydrazine-nitrous acid reaction is low due to the small quantities of catalyst in the aqueous phase. The organic phase thus provides a reservoir of nitrous acid along the entire length of the column.

Several design changes were attempted to improve column performance. In the development of the partitioning flow-sheet a value of 0.05 molar was specified for the hydrazine concentration. An increase to 0.10 molar is helpful in controlling the nitrous acid problem because more hydrazine reaches the upper portions of the column to slow the oxidation of Pu(III) and slow the internal reflux of plutonium.

Increases in the hydroxylamine concentration were complicated by the simultaneous addition of nitrate since the reducing agent is added as the nitrate salt. The higher nitrate level increases the Pu(IV) distribution coefficient, as shown in Figure 4, causing the plutonium to travel further down the column before transferring into the aqueous phase for reaction with hydroxylamine. Since the first Pu(IV) reduction occurs lower in the column the residence time for the oxidation reaction increases with the resulting increase in plutonium reflux and poorer partitioning performance. If only the hydroxylamine concentration is increased, which may be easier to simulate than to accomplish in actual practice, column performance is improved because

of the increased rate of Pu(IV) reduction and nitrous acid destruction higher in the column.

Increasing the hydrazine and hydroxylamine concentrations to higher and higher levels is not the answer to system control, however. Since the reactions involving these materials evolve gaseous by-products, there is a limit to the quantities that can be introduced before the effect on holdup and phase disengagement reduce the separation efficiency. Such gassing also influences the pulse column internal mixing. Within a small range, the gas promotes phase interaction and increases separation performance. However, if the third phase becomes too prominent, channeling of the liquid phases decreases the mixing resulting in lower mass transfer rates and poorer partitioning.

In an attempt to destroy the nitrous acid near its point of introduction, a side stream of hydrazine added two stages below the feed stage was simulated. This is the same type of control proposed by Bruns (10) although his side stream introduced additional hydroxylamine. The relative insolubility of the nitrous acid coupled with its low reaction rate with hydrazine combine to make this method of control totally ineffective.

In only one sense is the increased plutonium reflux within the column beneficial. By adjusting the aqueous flow rate for best partitioning with the highest output

plutonium concentration, the hydrazine and hydroxylamine are essentially totally consumed in the column. With the low residuals of these reducing agents, the oxidation step required in the recycle stream between Units I and II requires less nitric acid for complete oxidation and has fewer gassing problems.

One of the goals of the control system was to obtain maximum concentration of the plutonium product. If the output can be maintained at 80 gm/l, then its subsequent concentration to 200 gm/l in the product evaporators can be accomplished in one step. Within the range of inputs surveyed using a hydrazine level of 0.10 molar and with the present design conditions, this goal is not feasible. None of the design tests discussed above, except for the hydrazine concentration increase, offered any obvious ways to raise the level of performance.

As a part of the control system design discussed in the next sections, 17 sets of input conditions were optimized for maximum plutonium output concentration subject to several constraints. The data summarized in Appendix B provide significant insight into the influence of each input variable on column performance. Using the operating condition at which all variables are at their midpoint values as a reference, the effects of changes in each input variable can be seen in terms of the maximum plutonium

output concentration that can be obtained or in terms of the corresponding aqueous flow rates.

As the plutonium input level rises (data sets 9, 10 and 11), the output concentration can be increased. The limits of partitioning performance are defined by the internal reflux of plutonium caused by the oxidation of Pu(III) to Pu(IV). With these test conditions the nitrous acid catalyst input is held constant. Although the aqueous flow rate cannot be held constant allowing a direct increase in output plutonium levels with the increased input, the additional hydrazine required to control the nitrous acid can be supplied with only small increases in aqueous flow rate.

The salting effect of uranium on the process can be seen in data sets 9, 12 and 13. In the organic phase, uranium competes with the plutonium for the tributylphosphate and forces the plutonium into the aqueous phase at a higher location in the column where there is less opportunity for oxidation by nitric acid to occur. The effect is small, however.

Despite its importance on column performance, the results indicate a relative insensitivity to the nitrous acid feed stream level with other variables held constant (data sets 9, 14 and 15). While there was a general improvement in performance with decreasing nitrous acid level, a trend

that additional data showed to continue with even lower catalyst inputs, the effect appears quite small in comparison to the large changes in nitrous acid feed concentration surveyed. The reason for this is the very small changes in nitrous acid concentration in the aqueous phase of the partitioning column. While the size of the nitrous acid reservoir tends to increase with increased feed stream input, the changes in catalyst level in the aqueous phase are minimized by the increased reaction rate with hydrazine and hydroxylamine and by the large distribution coefficient for the nitrous acid. In the aqueous phase only a small amount of catalyst is needed to trigger the oxidation reaction. Once the oxidation is initiated its autocatalytic behavior assures that it will continue at a rate determined more by other process conditions than by the feed stream concentration of nitrous acid.

The effect of organic flow rate variations is minimal and the output concentration that can be achieved at different feed flow rates is nearly constant (data sets 9, 16 and 17).

While the system is not very sensitive to feed stream variables, small changes in the aqueous flow rate can have large effects on performance. As can be seen in Figures 10 and 11, decreasing the aqueous flow rate not only increases the output plutonium concentration but also

increases internal reflux, causing the sharp edge of the plutonium concentration profile to move further down the column. Although this movement is reasonably predictable with changes in the aqueous flow rate, the plutonium contamination in the uranium product stream can change orders of magnitude with aqueous flow rates only differing by a few percent when lower edge of the profile reaches the bottom of the column. It is this steep shape of the lower edge of the profile that causes the apparent suddenness in column failure and not catastrophic changes in the separation mechanisms.

To conclude some remarks should be made about the solution of the equations used for the model. The size of the time increment must be carefully chosen. The smaller the step size the closer the model will approach equilibrium. Because of the relatively fast rates of some of the chemical reactions, the time step must be reduced greatly to avoid numerical inaccuracies in the steady state solution. For a time step of 7.5 seconds the material balances for the nuclear materials are resolved to within one percent. If the step size is increased, the material balances show greater discrepancies. At a step size of 30 seconds, some of the reactions can go essentially to completion in one time step and an erroneous numerical solution is obtained.

With small time steps many iterations are needed to

march out in time the 300 minutes that are required for the system transients to die out after an upset. Using the IBM System 370/155 digital computer at the Iowa State University Computation Center, the run time for the 2400 iterations of the simulation program required between 400 and 500 seconds of CPU time depending on the particular model form and the input and output requirements.

CONTROL SYSTEM DESIGN

The design of an effective control system for a chemical process can only be achieved if the process is understood well enough to define the correct output variables to be controlled and to select those input variables that can be manipulated to effect the desired control. The types of disturbances must be considered both as a part of the process analysis and as a part of the instrumentation system design. The latter problem in defining variable ranges, required accuracy and operating environment is often more challenging than the application of control theory. In weighing benefits against costs, the designer must choose and detail not only the control algorithms but also the hardware systems for realizing the desired process performance. The resulting "control system" may be anything from simple guidelines for manual control to extensive automated monitoring and computer control facilities.

Appendix A lists the product stream specifications for the partitioning column. These are:

1. Minimum plutonium in the organic effluent.
2. Uranium concentration below 50 ppm in the aqueous product stream.
3. Minimum concentrations of the reducing agents in the aqueous product stream.

4. Maximum concentration of the plutonium product in the aqueous product stream.

In general the number of controlled output variables must be complemented by a like number of manipulated or control variables. However, if the product specifications are written in terms of ranges rather than set points and if a change in a control variable simultaneously improves more than one output, the number of control variables can often be reduced. Seeman and Burkhart (37) used this characteristic to control two product qualities with one manipulated flow rate in a rare earth mixer-settler separation system.

The process goals for the partitioning column show this effect. Increasing the plutonium output concentration reduces the hydrazine and hydroxylamine leaving in the aqueous stream because the increased plutonium reflux within the column consumes more of the reagents. By salting the uranium back into the organic at the top of the column, the higher plutonium levels also reduce the uranium contamination in the plutonium product stream. Decreasing the strip stream flow rate has little effect on the plutonium in the organic stream leaving the column until the bottom edge of the profile moves too far down the column. With three of the four process variables driven toward better performance with decreasing aqueous

flow rate, the operating constraint becomes the contamination of the uranium product stream and control can be achieved by manipulating only the aqueous flow rate.

Because of the unusual response to aqueous flow rate changes, the control problem is reduced substantially. If the process specifications had been written in terms of set points, additional control variables such as the hydrazine, hydroxylamine and nitrate concentrations in the strip stream would have been required.

The partitioning column experiences a variety of upsets during its operation. The very nature of scrap recovery causes a wide range in the feed stream concentrations of plutonium and uranium. However, these fluctuations are damped by the decontamination column which acts as a dynamic filter between the sharp upsets in nuclear material levels leaving the dissolvers and the concentration in the feed stream entering the partitioning column. Although in some manner related to the operation of the dissolvers, the decontamination column and the oxidizing tank between Units I and II, it is assumed that the nitrous acid concentration in the feed stream to the partitioning column changes slowly with time considering the mechanisms for nitrous acid production and transfer to Unit I discussed earlier. Other input concentrations in the feed stream and all concentrations in the scrub stream and the strip stream are constant.

The feed flow rate varies slowly within a small range.

In addition to these changes in the inputs several more subtle disturbances occur during column operation. The organic solvent degradation causes some variation in the dibutylphosphoric acid concentration while changes in the ambient temperatures in the equipment canyon affect the column slightly. Due to a variety of problems ranging from radiation effects to corrosion, foreign materials build-up slowly in the column and affect mixing and flow characteristics. However, this is more of a maintenance problem than a process control difficulty.

To maintain the desired system performance some method relating the manipulation of the control variable to the upsets must be developed.

Feedback is the conventional form of process control. One or more of the output variables are monitored and corrective action taken according to the magnitudes, the time integrals or the time derivatives of the errors between the monitored variables and their set points. Enough process understanding is required to select the manipulated and measured variables and to specify the controller modes whether proportional, integral, derivative or a combination of these. The disturbances and the system transient response need not be known although such knowledge will generally reduce the amount of tuning required to achieve the

best performance. A variety of tuning guidelines are available, the most widely used being the technique originally proposed by Zeigler and Nichols (43). The equipment needed for a typical feedback control application is readily available from a variety of manufacturers although specialized instrumentation systems may require more design work.

Because of the propagation delays and larger time constants which occur in some chemical processes, feedback control may allow significant changes to occur within the system before the controller senses the upset and takes corrective action. Feedforward control, in which the manipulated variables are adjusted in response to changes in monitored inputs, may give better process regulation in these cases. While simple in concept, feedforward control requires more process understanding to implement. Not only must each possible disturbance be identified if corrective action is to be taken to minimize its effects but the necessary corrective action must be defined for each disturbance. Feedforward control is open loop in the sense that the outputs are not checked to verify that the predicted changes in the manipulated variables maintain the proper outputs or to detect unmonitored disturbances. Generally far more process analysis is required for feedforward design but increased cost can often be recovered

from a well-designed system by the achievement of near perfect control.

Control equipment includes instrumentation to detect the input disturbances as well as the programmed hardware for adjusting the manipulated variable. While not necessarily any more complex than feedback controllers the feedforward system is typically designed for a particular application.

To draw on the strengths of each system and to minimize their weaknesses, feedforward and feedback are often used together. The feedforward controller responds quickly to upsets and minimizes the output variable errors while a feedback trimmer drives these errors toward zero and compensates for unmeasured disturbances, long term variations in the process and inaccuracies in the predictive model.

The partitioning column exhibited the delay times and slow response typical of separation systems indicating the possible application of feedforward control. A predictive control scheme was developed by analyzing the aqueous flow rate requirements necessary to maintain the best partitioning performance over the range of possible input conditions. With the background from preliminary simulation results, a statistical experiment¹ was designed to reduce the number of

¹Mensing, R. W., H. A. David and O. Kempthorne. Iowa State University, Ames, Iowa. Private communication, Statistical Department. 1974.

computer runs needed to develop a regression analysis relating the aqueous strip stream flow rate to the feed stream inputs. To test all possible combinations of the four inputs each at three levels, 81 aqueous flow rates would have to be determined. However, because the system response surface was expected to show a smooth contour, this number was reduced to 17 with more extensive testing about the condition with all inputs at their median values. At each of the 17 operating conditions the aqueous flow rate was reduced until the plutonium level in the organic stream at the bottom of the column began to rise. Simultaneously the other product specifications were checked to insure that they were within acceptable limits.

When a disturbance is detected, the feedforward regression equation generates a control response to drive the system to a new steady state meeting the criteria established for good performance. The regression equation disregards the system dynamics, however, providing no information on how the new steady state is to be approached. If the change in aqueous flow rate is applied immediately the initial effect will be an overcompensation near the bottom of the column. For example, if the predicted response is a decrease in the aqueous flow rate, the sudden change will tend to increase the plutonium contamination of the uranium product stream as the plutonium profile drops lower in the

column. When the disturbance has propagated through the column, a new steady state will be approached and the organic stream contamination will again be minimal. Conversely, a sudden increase in the control variable will push the plutonium upward in the column. While this effect is not undesirable, the needless dilution of the plutonium product stream and the excess use of hydrazine and hydroxylamine are cost penalties. To avoid these transient conditions, the feedforward control model may be dynamically compensated.

Dynamic compensation was added by determining the transfer function between the aqueous flow rate and the input disturbances for a constant plutonium concentration in the organic phase of the simulation model. Because both the feed stream variables and the aqueous flow rate are independent variables until control is imposed on the system, the desired transfer function was evaluated by dividing the percentage output response to a feed stream variable upset by the percentage output response to a step change in aqueous flow rate.

A feedback control algorithm was also designed. Results from testing the simulation model showed that the rapid drop-off in the Pu(IV) profiles near the bottom of the column remained distinct in shape over the range of operating conditions expected. This fact was used as the

basis for selecting the plutonium concentration at an intermediate location within the column as the set point for the feedback controller. The organic Pu(IV) concentration at the bottom of the column was not used at the set point for two reasons. First, it is difficult to control from a zero set point. If the output variable goes above zero, off-specification material has already been produced. With negative values being physically impossible the controller cannot sense when the error has the opposite sign. Second, the small amounts of Pu(IV) complexed with di-butylphosphoric acid might cause control instabilities since changes on the aqueous flow rate have no effect on these plutonium levels.

Radiation sensors to determine plutonium concentrations have been used extensively in nuclear material processing and have been discussed by Jones and Lyon (27) and in documents¹ dealing with the scrap recovery flowsheet development. Measurement of the overall plutonium concentration near the bottom of the column could be easily accomplished. However, it was found that the Pu(III) levels at that location are greater than the Pu(IV) levels and vary with operating condition. Since the overall plutonium level

¹Campbell, M. H. GE Hanford Atomic Products, Richland, Washington. Internal memorandum entitled "Plutonium profile of the recuplex H-3 column." October, 1961.

does not directly correspond to the Pu(IV) in the organic phase, its concentration cannot be used as the set point. Although a more complex instrumentation system is required to measure the organic Pu(IV) level alone, two techniques for the measurement are conceivable. For continuous measurement a small amount of the organic might be withdrawn through a specially designed sampling tube or membrane using differences in the physical properties of the two phases to sample only the organic phase. This material could then be transferred to a shielded radiation sensor for the plutonium concentration measurement. A periodic sampling method might involve several steps. The sequence would begin with the withdrawal of fluid from the sample point followed by a dead time to allow phase coalescence. Finally the radiation could be measured from the organic phase alone.

Tests of these control system designs were conducted using the simulation model both to obtain design data and to analyze the effectiveness of the control algorithms.

RESULTS OF THE CONTROL ANALYSIS

In the control analysis both feedforward and feedback control systems were tested alone and in combination to determine their effectiveness as well as their potential application problems.

The data from the regression analysis for the feedforward model are shown in Appendix B. For each of the 17 operating conditions established for the experimental design, the aqueous flow rate was adjusted to achieve an organic Pu(IV) concentration of 0.001 molar at stage 18. Because of the sharp drop-off in the plutonium profile, this level insured essentially no contamination of the uranium product stream while also maximizing the aqueous plutonium concentration at the top of the column. Because of the lengthy computer runs required for each operating condition, the flow rates were obtained to approximately $\pm 2.0\%$ accuracy.

Using a standard statistical analysis program¹ for multivariable linear regression, several possible predictive equations of the following general form were tested to determine the regression constants and their statistical

¹Statistical Analysis System, Computation Center, Iowa State University, Ames, Iowa.

properties:

$$\begin{aligned}
 A_q = & k_0 + k_1x_1 + k_2x_2 + k_3x_3 + k_4x_4 + k_5x_1x_1 + k_6x_2x_2 \\
 & + k_7x_3x_3 + k_8x_4x_4 + k_9x_1x_2 + k_{10}x_1x_3 + k_{11}x_1x_4 \\
 & + k_{12}x_2x_3 + k_{13}x_2x_4 + k_{14}x_3x_4
 \end{aligned}$$

where

A_q = the aqueous flow rate predicted for the feed conditions

x_1 = Pu(IV) feed concentration

x_2 = U(IV) feed concentration

x_3 = HNO_2 feed concentration

x_4 = organic feed flow rate

k = regression model constant.

To test the steady state feedforward algorithm, the predicted aqueous flow rates from the regression equations were compared to the flow rates required for plus and minus 10% changes in the plutonium feed concentration from the median value operating condition (data set 9, Appendix B). Although the predicted values were within 1.5% of each other, considerable steady state error would have resulted using most of the values because of the sensitivity of the partitioning process to small differences in the aqueous

flow rate.

With additional data from the results of the 10% changes in the Pu(IV) feed concentrations the regression model parameters shown in Appendix C were obtained. By selecting models with terms whose coefficients are statistically significant, the analysis can often be useful in developing process mechanisms. However, since four of the six models tested (designated 2, 3, 4 and 6 in Appendix C) had highly significant terms, such was not the case in this research. Of importance for control purposes are the regression coefficient and the sum of the squared errors shown in the appendix. The first is a measure of the prediction accuracy numerically given by the second. Of the models with significant terms, the number two model has the best accuracy in predicting the 19 aqueous flow rates in the data set. Although errors in the predicted flow rate within only a few percent are expected at other operating conditions, the sensitivity of the separation system to flow rate changes magnifies any inaccuracy. Without additional data to improve the prediction accuracy, feedforward control has inherent limitations for this application.

Through the rest of the testing program, only plus and minus 10% feed concentration upsets from the median operating condition were considered for several reasons. Since dynamic data to verify the simulation model were not

available, it is the control concepts that are of interest here. Fine tuning the controllers for the simulation model would have little value if the transient response of the actual column differed significantly. Second, tests of the response to step changes in the feed stream inputs showed that the uranium and nitrous acid upsets had far less effect than plutonium or flow rate upsets. Considering the flowsheet design, the plutonium concentration disturbances are more severe than the gradual flow rate adjustments. Third, because of the similarity and predictability of the different disturbances on the column operation as shown throughout the model development program, it is assumed that a control system designed for plutonium upsets is adequate for all other disturbance conditions.

To assess the transient response to steady state feedforward control, the system at the median operating conditions was subjected to plutonium upsets with and without simultaneous aqueous flow rate corrections. The response of the organic Pu(IV) concentration at stage 18 can be seen in Figures 13 and 14. In reviewing these figures the differences in plutonium scale factors should be considered as well as the fact that the system was not quite in equilibrium at time zero resulting in the initial drift in the plutonium level.

The sudden application of feedforward control resulted

Figure 13. System response to a 10% $[Pu]_f$ step increase; uncontrolled, feed-back, steady state feedforward and dynamically compensated feed-forward

Figure 14. System response to a 10% $[Pu]_f$ step decrease; uncontrolled, feedback, steady state feedforward and dynamically compensated feedforward

in overcompensation at the bottom of the column until the disturbance and control effects "merged" in the new steady state. While the transient upset was more pronounced for the plutonium input decrease, in neither case did the controlled system show unacceptable plutonium contamination of the organic stream leaving the column.

A dynamic compensation curve for feedforward application was developed by dividing the percentage output response to the uncontrolled plutonium feed concentration increase shown in Figure 13 by the percentage response to a step decrease in the aqueous strip stream flow rates shown in Figure 15. The resulting transfer function between the upset and the control action for constant Pu(IV) organic concentration at stage 18 was approximated by the two discrete forms shown in Figure 16 and tabulated in Appendix C. One discrete curve closely approximated the continuous dynamic compensation curve although the other compensation sequence proved to be better for control purposes as shown in Figure 14. Each corrective action experiences propagation delays through the system. Accounting for these delays shifts the entire incremental dynamic compensation curve to the left. Such behavior has been noted by others including Kelly (30) and Seeman and Burkhart (37).

From the results shown in Figure 14, dynamic

Figure 15. System response to a 10% decrease in the aqueous flow rate, the control variable

Figure 16. Feedforward dynamic compensation curve, with the two-incremental approximations tested

compensation for the positive upset was not as effective in maintaining a zero transient error as in the negative upset case. More tuning of the dynamic compensation curves and using individual compensation curves for increases and decreases in aqueous flow rate changes may result in further improvements.

A conventional proportional plus integral feedback controller, tuned for the partitioning column simulation, was also studied. A set point of 0.001 molar organic Pu(IV) concentration measured at stage 18 was selected. Not only does this level yield high performance but it is also insensitive to the DBP complex problem. Using the hydrazine flowsheet data (35) the Pu(IV) complexed with the radiation degradation product is approximately 0.00004 molar or only 4% of the total plutonium in the organic phase at that location.

The feedback results were very good. As anticipated the Ziegler-Nichols guidelines (43) were too severe for the sampled data system with initiation of a control cycle every five minutes. These control settings of 12.5 gain and 1140 seconds for the integral time constant were "softened" to 5.0 and 10,000, respectively, resulting in the curves shown in Figures 13 and 14 and, on a greatly expanded scale, in Figure 17. Even with these control settings which could be improved by a lower integral time

Figure 17. System response to + 10% $[Pu]_f$ step changes; uncontrolled, feedback only and combined feedforward feedback

constant to allow a faster approach to zero steady state error, the feedback controller out performed either form of feedforward control. While the system as a whole does exhibit the dead times and slow response usually associated with feedforward applications, the fast response of the organic plutonium level at stage 18 to aqueous flow rate changes as shown in Figure 15 is the critical factor in the feedback performance.

To get a feel for the sampling intervals required for the feedback control system, the same controller was tested with 10 and 12 minute sampling times. With sampling at 10 minute intervals the organic Pu(IV) concentration limit cycled between 0.0002 and 0.0017 molar. Detuning the control slightly would eliminate the cycling at a small penalty in performance. With 20 minute sampling the Pu(IV) level cycled slowly between 0.0 and 0.03 molar, very unacceptable performance. Such a sampling frequency would require considerable detuning of the controller to achieve a stable output with the possibility of severely degraded performance.

To complete the control system evaluation a combined dynamically compensated feedforward and feedback algorithm was tested. The results in Figure 17 show improvement over the feedback control but such gains are exaggerated by the expanded scale.

CONCLUSIONS AND RECOMMENDATIONS

With the end of this study of the plutonium-uranium partitioning column a variety of conclusions can be drawn regarding both the process design and the application of control.

The most fundamental conclusion concerns the simulation model itself. Its ability to simulate the complex chemical reaction-extraction system gives credibility to the modeling techniques and assumptions used throughout the development. Not only was such an analysis useful for control system design but it also focused attention on basic process mechanisms and fundamental design problems which must be addressed to realize even better partitioning performance.

In particular three conclusions are possible about the system in its present form. The nitrous acid input is the limiting factor to performance. The only way to approach the desired 80 gm/l output plutonium concentration is to minimize the nitrous acid input, raise the plutonium feed concentration to its maximum and use a hydrazine concentration of 0.1 molar. The first requirement is the most difficult to achieve since increasing the plutonium recycle will increase the production of nitrous acid. The hydrazine level can be set arbitrarily.

The control analysis indicated that improved regulation and stability could be achieved with all systems tested. However, in light of the relative performance of each and the practical problems of implementing each strategy, the following conclusions were reached.

Significant improvement in manual control of the partitioning column can be realized by application of the steady state feedforward control algorithm. Unlike present procedures which relate the aqueous flow rate primarily to the feed flow rate with secondary adjustment for operating problems, use of a predictive scheme even in a very simple form such as the linear equation of model 6 in Appendix C will provide more stable operation. Because the calculations are elementary for a simple regression equation, the only change in present operating procedures would be the periodic measurement of the nitrous acid level with the other feed stream variables. To insure product quality the flow rates calculated from the simulation should be increased by a few percent to compensate for the longer sampling interval. Even with the slight increase in flow rate, considerable performance improvement can be realized in comparison to present operating standards.

For automatic control of the partitioning column the feedback control system stands out with superior performance and relatively simple installation. Measurement of the

organic plutonium near the bottom of the column will require the design of an effective sampling and measuring system. However, the necessary instrumentation concepts are well established. The controller itself may be either analog or digital though some problem may be encountered with standard electronic analog controllers in obtaining the relatively long integral time constants required.

Since the total plutonium profile at the bottom of the column displays a steep edge similar to the organic Pu(IV) profile, measurement of its location, accomplished by simply relocating one of the existing neutron monitors, could be used as the basis for feedback control. Partitioning performance would suffer, however. Because the total plutonium at any point is a function of the Pu(III) and Pu(IV) concentrations in the aqueous phase and the holdup ratio as well as the organic Pu(IV) concentration, the set point for the aqueous flow rate must be selected conservatively to insure minimum contamination of the uranium product stream. As a result the aqueous product stream will tend to have a lower plutonium concentration with higher residual concentrations of the reducing agents.

An automated feedforward control system whether alone or in combination with a feedback algorithm would require considerably more instrumentation to monitor the feed stream variables assuming that on-line instruments replace

the analytical chemistry lab measurements presently used. It is doubtful that the cost of such instrumentation and the hardware necessary to implement the feedforward algorithm could be justified by improved performance when compared to the feedback controller alone.

It is hoped that the work here will serve as a catalyst (at least as tenacious as the nitrous acid) for additional work with the partitioning column as well as with the recycle flowsheet which offers much in the difficult economics of nuclear fuels reprocessing. A few recommendations are mentioned in the next paragraphs.

More data from the operating column are needed. Such data gathering need not be very extensive. Periodic sampling of all input and output streams might provide steady state data and enough transient response characteristics to verify the simulation model and the assumptions concerning the input disturbances. Additional radiation scans to determine the plutonium profiles at different (and known) operating conditions and a few dynamic tests are also important. The work here provides an outline for the types of data needed for process design and control studies.

Refinement of the rate and stoichiometry models for the hydrazine reactions with nitrous acid and Pu(IV) is needed. While the models used seemed adequate, the level

of sophistication was far higher for the other reactions.

Another area that should receive more study is the development of distribution coefficients for a system containing all the chemical species found in the partitioning column. Such work might also produce techniques for forcing both Pu(IV) and nitrous acid into the aqueous phase where they can undergo reaction more readily.

A variety of work might also be done with the simulation model. A flowsheet designed to operate with only one reducing agent, either hydroxylamine or hydrazine, would offer simplicity as well as cost savings. Bruns (10) was never able to successfully operate the hydroxylamine-only flowsheet. With minor modifications the simulation model could be used to analyze the feasibility of his design. A search of nitrogen compounds similar to hydrazine and hydroxylamine might find one that reacts at a high rate with both Pu(IV) and nitrous acid. Its effects on column performance could be determined in a very short time using the simulation model.

One design change appears to offer improvement. Reducing the overall nitrate level in the column, particularly near the feed stage if that is possible, would decrease the Pu(IV) distribution coefficient allowing the primary reduction to occur higher in the column. Conceptually, such a design change has merit although other problems such

as plutonium polymerization may appear.

While a variety of calculations could be added to improve the hydrodynamic modeling, to include the Pu(VI) and to account for changes in solution volume, there is real need for work in the opposite direction--streamlining the model for faster computation.

There is considerable interaction between the first two units of the flowsheet due to the plutonium recycle. Consideration of both separation units together could result in mutual operating benefits for each such as lower nitrous acid production and higher plutonium concentrations in the partitioning column feed, both contributing to increased plutonium-uranium separation. The application of the simulation and control techniques used in this work with the second column can provide the foundation for the successful realization of the scrap recovery flowsheet.

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Through all of my life the inspiration and challenge to succeed were largely due to the rivalry of my twin brother, Frank Stanton McCutcheon, III. Together we helped each other through the public schools and college. After college I was able to go on to graduate school and an engineering career while the fortunes of life led my brother to a gun post at Landing Zone Cindy in South Vietnam where on February 2, 1971, he was killed in action. Since that time it has been the memory of the 56,000 Americans who met a similar fate in service to a nation that would prefer to forget that inspires me to accept the more difficult challenges that life offers.

APPENDIX A: INPUT-OUTPUT SPECIFICATIONS
FOR THE PARTITIONING COLUMN

Table A1. Input specifications for the partitioning column

Material	Specification
Feed stream	
Phase	20% tributylphosphate in carbon tetra- chloride
Pu	$10 \leq [\text{Pu}] \leq 30 \text{ gm/l}$
U	$0 \leq [\text{U}] \leq 30 \text{ gm/l}$
HNO ₂	$0 < [\text{HNO}_2] < 0.3 \text{ molar}^a$
HNO ₃	0.14 molar
Flow rate	91.8 l/hr $\pm$ 10%
Scrub stream	
Phase	20% tributylphosphate in carbon tetra- chloride
HNO ₃	0.20 molar
Flow rate	23.0 l/hr
Strip stream	
Phase	Aqueous nitric acid
HNO ₃	0.20 molar
HNO ₂	0.01 molar ^a
Hydroxylamine nitrate	0.40 molar
Hydrazine	$0.05 \leq [\text{HZ}] \leq 0.10$

^aThese are estimated values. The discussion section below details their calculation.

Table A2. Output specifications for the partitioning column

Material	Specification
Plutonium product stream	
Pu	$40 \leq [\text{Pu}] \leq 80 \text{ gm/l}^a$
U	$[\text{U}] \leq 500 \text{ ppm}$, preferably $[\text{U}] \leq 50 \text{ ppm}^b$
Hydroxylamine	Minimum concentration ^c
Hydrazine	Minimum concentration ^c
Uranium product stream	
Pu	$[\text{Pu}] \approx 0.0^d$

^aLevels higher than 80 gm/l result in excessive TBP degradation. Levels much below 80 gm/l require two concentration steps for return to the fuel element manufacturing process.

^bThe higher limit can be tolerated but the lower limit is preferred.

^cThe lower the concentrations of these reducing agents, the easier the oxidation step for plutonium recycle can be controlled.

^dSome Pu(IV) will be complexed with DBP. Essentially no Pu(IV) complexed with TBP should remain in this stream.

Nitrous Acid Concentration Calculations

Only a small amount of data were available on the nitrous acid levels in the two partitioning column input streams. A concentration of approximately 0.2 molar was found in the feed stream although this level is expected to increase to 0.3 molar when new dissolvers are added to the

process upstream of the decontamination column.

These levels were consistent with predictions based on the sources and stability of nitrous acid. Both the initial dissolving process and the oxidation of Pu(III) to the +4 specie for recycle from the partitioning column to the decontamination column generate significant quantities of the catalyst. The amounts of nitrous acid supplied to the partitioning column as a function of the equilibrium between nitric and nitrous acids in solution can be calculated as follows using the Pease flowsheet data (35):

From the reflux reaction vessel:

$[\text{HNO}_3] = 3.3$ molar leaving the vessel

$[\text{HNO}_2] = 3.3$ P

Flow rate = 38 l/hr.

If the organic phase in the decontamination column extracts 95% of the nitrous acid, the rate of nitrous acid input to the second column from this source is:

$(0.95) (38 \text{ l/hr}) (3.3 \text{ P mole/l}) = 119 \text{ P mole/hr.}$

From the dissolver:

$[\text{HNO}_3] = 2.0$ molar in the feed stream to the decontamination column

$[\text{HNO}_2] = 2.0$ P

Flow rate = 150 l/hr.

With the same assumptions as above, the nitrous acid input to the partitioning column from the dissolvers is:

$$(0.95) (150 \text{ l/hr}) (2.0 \text{ mole/l}) = 285 \text{ P mole/hr.}$$

The estimate of the nitrous acid concentration in the partitioning column feed stream is 0.3 molar. The required value of P is:

$$P = \frac{0.3 (91.8)}{119 + 285} = 0.068 \quad .$$

While Denbigh and Prince (15) suggest that nitrous acid levels only reach a few percent of the nitric acid concentrations, the 7% figure may be reasonable for two reasons. The breakdown of the nitrous acid may not reach equilibrium before the acid is picked up by the organic in the decontamination column. Also the equilibrium (26) is related to the square of the pressure since one of the decay products is NO gas. Although the pressures in the system are greater than atmospheric only because of liquid heads, the effects on the equilibrium are significant.

The nitrous acid concentration in the aqueous strip stream to the partitioning column was not available. Because of the storage of this liquid before its use, the

catalyst level is expected to be only 5% of the nitric acid level. The assumed nitrous acid level is:

$$[\text{HNO}_2]_{\text{strip}} = (0.05) (0.2 \text{ molar}) = 0.01 \text{ molar} \quad .$$

APPENDIX B: FEEDFORWARD CONTROL DESIGN DATA

Table B1. Steady state regression models

Data Set	Symbol ^a	[Pu] _f ^b	[U] _f	[HNO ₂] _f	Q _{feed}	Q _{strip} ^c	[Pu] _{a,1} ^c
1	CCCC	0.0558	0.0211	0.05	0.0238	0.00824	38.5
2	CCAA	0.0558	0.0211	0.25	0.0272	0.01022	35.5
3	ACAC	0.1116	0.0211	0.25	0.0238	0.01094	58.0
4	ACCA	0.1116	0.0211	0.05	0.0272	0.01143	63.5
5	CAAC	0.0558	0.1055	0.25	0.0238	0.00756	42.0
6	CACA	0.0558	0.1055	0.05	0.0272	0.00764	47.5
7	AACC	0.1116	0.1055	0.05	0.0238	0.00870	73.0
8	AAAA	0.1116	0.1055	0.25	0.0272	0.01099	66.0
9	BBBB	0.0837	0.0633	0.15	0.0255	0.00962	53.0
10	ABBB	0.1116	0.0633	0.15	0.0255	0.01015	67.0
11	CBBB	0.0558	0.0633	0.15	0.0255	0.00850	40.0
12	BABB	0.0837	0.1055	0.15	0.0255	0.00887	57.5
13	BCBB	0.0837	0.0211	0.15	0.0255	0.1052	48.5
14	BBAB	0.0837	0.0633	0.25	0.0255	0.00991	51.5
15	BBCB	0.0837	0.0633	0.05	0.0255	0.00903	56.5
16	BBBA	0.0837	0.0633	0.25	0.0272	0.01017	53.5
17	BBBC	0.0837	0.0633	0.25	0.0255	0.00898	53.0
18	-BBB ^d	0.09207	0.0633	0.25	0.0255	0.01014	55.54
19	-BBB ^e	0.07533	0.0633	0.25	0.0255	0.00938	48.94

^aThe range of each variable was divided in sixths with the low value indicated by C at the one-sixth point, the B value at the one-half point and the A value at the five-sixth point.

^bThe feed concentrations are molar while the flow rates are in units of liters/second. The aqueous Pu concentration is in units of grams/liter.

^cIn the first 17 data sets the aqueous Pu concentrations were determined to approximately 0.5 grams/liter to give organic Pu(IV) concentrations of 0.001 molar. These data sets were used in the original regression analysis. The last two data sets were obtained as part of the feedforward control testing.

^dThe aqueous flow rate was determined for a Pu feed concentration 10% above the median value.

^eThe aqueous flow rate was determined for a Pu feed concentration 10% below the median value.

APPENDIX C: FEEDFORWARD CONTROL PARAMETERS

Model 3	Model 4	Model 5	Model 6
0.00658	0.00672	0.00482	-0.00210
	-0.01799	-0.03292	0.03619
	0.00458	0.00458	-0.01799
			0.00458
		-0.40376	0.35471
		0.080907	
		0.05607	
1.53264	1.42692	3.93526	
-0.66580			
0.19637			
0.90252	0.91084	0.98580	0.97721
21.8	20.0	3.2	5.1

Table C2. Dynamic compensation constants^a

Time, min	12 Step	14 Step	Time, min	12 Step	14 Step
0.0	0.1	0.0	140.0	0.7	0.525
20.0	0.2	0.05	160.0	0.7	0.625
40.0	0.2	0.10	180.0	0.8	0.70
60.0	0.3	0.15	200.0	0.9	0.775
80.0	0.4	0.25	220.0	1.0	0.85
100.0	0.5	0.325	240.0	1.0	0.925
120.0	0.6	0.425	260.0	1.0	1.00

^aGraphical representations of the dynamic compensation approximations can be seen in Figure 16.