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A SURVEY OF SIMULATION METHODS FOR MODELING
PULSED SIEVE-PLATE EXTRACTION COLUMNS

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FOREWORD

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1. INTRODUCTION

Pulsed extraction columns have been used in the nuclear fuel reprocessing industry for many years. They were employed in the original Redox and Purex processes and are still looked upon with favor for reprocessing operations because they are relatively trouble-free, have a reasonably small residence time, and good extraction efficiency. Despite many years of research on the theory and operation of such columns, prediction of their performance is still difficult.

Recently the need for an accurate model of the pulse column has arisen because of increased interest in nuclear safeguards and nuclear materials accountability. This report presents a thorough review of the published literature on pulse columns with particular emphasis on the current state of information needed for developing an effective model of the column for materials accountability in nuclear fuel reprocessing plants.

The report first considers briefly the use of liquid-liquid extraction in nuclear fuel reprocessing and then describes the operation of the pulse column. After this ground work has been laid, currently available simulation models of the column are reviewed and this is followed by an analysis of the information presently available from which the necessary parameters can be obtained for use in a model of the column. Finally, overall conclusions are given regarding the information still needed to develop an accurate model.

2. LIQUID EXTRACTION

The Purex process for the reprocessing of irradiated nuclear fuels

discharged from power reactors utilizes liquid-liquid extraction as a means of separating uranium and plutonium from the fission products generated by the fission reaction that occurs in the reactor. The spent fuel is dissolved in acid to form an aqueous solution which is then contacted with tributyl phosphate (TBP), an organic solvent immiscible with water. The acid feed and the TBP solvent flow countercurrent to each other in a cascade arrangement that may consist of a series of mixing and settling tanks (called stages) to provide intimate contact between the two liquids or may be a column containing packing or sieve plates to disperse one liquid in the other. It is also common in column-type extractors to supply additional agitation from rotating discs or paddles or to pulse the liquids as they flow through the column.

In the initial or co-extraction step of the process, solvent enters one end of the extractor and preferentially co-extracts the uranium and the plutonium (which are kept in their higher oxidation states of U^{+6} and Pu^{+4} by the oxidizing action of the acid) as it flows countercurrent to the aqueous feed stream, which enters at an intermediate point in the column or cascade. The feed stream in turn becomes increasingly depleted in uranium and plutonium. If the extraction end of the cascade is sufficiently long almost all of the uranium and plutonium can be removed from the aqueous phase which then contains only fission products plus traces of uranium and plutonium.

As the solvent phase passes the feed point it contains practically all of the uranium and plutonium but also contains an excessive amount of fission products. Most of these remaining fission products are removed from the uranium and plutonium rich solvent in those stages of the cascade

beyond the feed point or, in column-type units, by the additional length of column beyond the feed point. One thus has a cascade or a column in which the feed enters at an intermediate point, solvent enters at one end (the extraction end) and a stream of the same phase as the feed enters at the other end (the scrub end). In the scrub of the cascade the fission products are "scrubbed" or back extracted out of the solvent by the entering scrub stream. The uranium and plutonium rich solvent then leaves the extractor containing only traces of fission products. In this fashion the extractor serves to separate the feed into a solvent product stream containing essentially pure uranium and plutonium and an aqueous waste stream containing fission products and only traces of uranium and plutonium.

The uranium and plutonium rich solvent is then sent to a second extractor where the plutonium is separated from the uranium and, from this second extractor, the uranium stream and the plutonium stream are subjected to still further extraction to achieve the desired degree of purification and fission product removal. These additional steps will be discussed later in the report as necessary. A useful introductory discussion of aqueous fuel reprocessing occurs in Scientific American in an article by Bebbington (7).

The ease of separation depends upon the differences in the distribution coefficients of the different species in the column. The distribution coefficient is defined as the ratio of the concentration of a solute in the two phases under equilibrium conditions. The distribution coefficient is a basic system property and may depend on temperature, oxidation state, the presence of complexing agents, or other elements of the chemical environment in each phase.

When the extraction cascade consists of mixer-settler units the number of stages required to perform a given separation is reasonably straightforward since each stage can be designed to be very nearly an equilibrium contact (i.e., the stage efficiency is nearly 100%) and the concept of the number of theoretical (or equilibrium) stages is useful in describing the separation which can be achieved by the extractor. However, for column-type extractors the two phases are in continuous contact and there are no physically separate stages. Still, the stage concept is often employed in design procedures by defining a term called the HETS or the "height equivalent to a theoretical stage" as that length of column which would produce the same separation as one equilibrium contact between the two phases. Other concepts such as the mass transfer coefficient or the height of a transfer unit are more applicable to column extractors and these terms will be discussed later. At this point a sufficient conclusion is that the efficiency or the degree of separation attainable in a column extractor is considerably more difficult to predict than it is for a mixer-settler cascade.

In spite of this and other difficulties, column extractors are attractive for fuel reprocessing operations because of their fewer moving parts and their short residence times. Their mechanical simplicity contributes to easier maintenance and their short residence time minimizes solvent degradation due to the intense radioactivity of the irradiated fuel. Pulse columns, the subject of this report, have been the most widely used extractors in fuel reprocessing plants and are likely to remain in widespread use in the future.

3. DESCRIPTION AND OPERATION OF THE PULSE COLUMN

Credit for the invention of the pulse column is usually given to Willhem Van Dijck. The equipment described in his 1935 patent (74) is for a countercurrent extraction column which contains sieve plates spaced at intervals along a central shaft. The two liquids are dispersed by a motor which moves the plate assembly up and down. Although such a column is now marketed commercially by the Chem-Pro Equipment Company, this is not the basic operating principle of what has come to be known over the last 30 years as a "pulse column." Van Dijck is properly cited as the inventor of the pulse column, however, because his patent also mentions the possibility of pulsing the liquid in a column with stationary plates.

Carl Groot, who worked on the early development of liquid-liquid contactors for use in nuclear fuel reprocessing, first suggested that a perforated-plate column in which the two liquid phases were dispersed by pulsing the contents of the column up and down be used in fuel reprocessing operations. Although this required a greater power input than the moving plate technique, it permitted the pulsing equipment to be placed some distance from the column. For processing highly radioactive materials, this meant that the pulse generator could be remotely located in a shielded area away from the column and attached to the column by a pulse leg which served to isolate the radioactive material in the column and thus permit easier maintenance of the pulse generator since it could be placed in an area of low level radioactivity.

The pulse column as we know it today uses the idea of pulsing the liquids in the column. It has been used widely in the nuclear industry

over the past 35 years and its service record in such applications has been very good.

A functional diagram of a pulse column is shown in Figure 1. Perforated plates are spaced at intervals up the column. Heavy liquid enters from the top of the column and light liquid enters from the bottom. Ordinarily the size of the holes in the perforated plates is small enough that no countercurrent flow occurs due to gravity alone. The pulse generator disperses the two liquid phases and also pumps them through the column.

In Figure 1 the light phase is the dispersed or discontinuous phase and the heavy phase is the continuous phase. The light phase is present in the smaller quantity, as is customary for the discontinuous phase, and the principal interface is located in the top phase-disengaging section of the column. If the heavy phase were the discontinuous phase the principal interface would be at the bottom of the column.

Figure 2 shows the operating characteristics of a pulse column. The curve was presented by Sege and Woodfield (6) to illustrate the various types of dispersion obtained as a function of the flow rates and the pulse frequency. The curve only shows general trends and has no numerical values along its axes.

Choose an arbitrary total flow rate and follow a horizontal line across the figure. Region A is a flooding region in which the column will not operate because the amount of pulsation is too small to pump liquid through the column as fast as it is fed at each end. At a point on the line marked "pulse volume velocity," the pulsation applied to the column is just sufficient to maintain a new flow equal to the superficial flow

Figure 1. Diagram of perforated plate pulse column.

Figure 2. Operating characteristics of pulse column at constant amplitude.

rates, or the rates at which the two liquids are being fed to the column. This point is called the lower flooding limit of the point of incipient flooding due to insufficient pulsation. Quantitative relationships for predicting this flooding point as a function of column operating variables have been developed by Edwards and Beyer (17).

When the pulse frequency is increased so that the column operates in area B, the two phases settle out completely between pulses. There is an alternating sequence of mixing and settling in each portion of the column between two adjacent perforated plates and this area is called the "mixer-settler" region. When a pulse column is operated in region C, the two phases in the column give the appearance of an homogeneous emulsion at all times and so this area is called the "emulsion region."

Increasing the pulse frequency still further causes the dispersion to become irregular and nonuniform. Large globules of the liquid begin to appear and local flooding, or reversal of the dispersion, may occur. This unstable region is indicated by area D in Figure 2. The transitions between regions B and C, and between regions C and D are gradual and not well-defined.

The flooding curve which separates regions D and E represents the locus of points at which the net flow of liquids through the column is again just equal to the superficial flow rates. This time the cause of flooding is not too little pulsation but too much pulsation. Hindered rising has reduced the net flow of liquid through the column. A point on this line is referred to as the upper flooding point or the point of incipient flooding due to excessive pulsation. Prediction of this flooding point is more difficult since complex hydrodynamic phenomena are involved.

The most extensive work on predicting this condition has been done by Groenier, et al. (28) who surveyed the work of many authors, presented a critical analysis of correlation methods, and developed new correlations.

The pulse column thus has two flooding points. Both are sharply defined and the permissible operating range of the column is sandwiched between them. Extraction efficiency varies throughout this range and the resulting degree of separation which can be obtained depends on the net effect of two opposing phenomena. Ideally, increasing the pulsation applied to the extractor produces better dispersion of the phases and creates more interfacial area for mass transfer. Turbulence within the column is increased, tending to improve the rate of extraction. On the other hand, backmixing or axial dispersion becomes increasingly important as the amount of pulsation increases. This decreases the local concentration gradient and reduces the extraction efficiency.

3.1. Dispersed phase holdup

The amount of dispersed phase present in the column is an important parameter affecting column operation and is called the "holdup." The residence time distribution, interphase mass transfer rates and degree of backmixing are all a function of the holdup. Holdup in the pulse column is defined as the percent of total volume occupied by the dispersed phase between all the sieve plates.

In the mixer-settler region the holdup decreases as the amplitude or frequency of pulsation increases and reaches a minimum value at the transition point between mixer-settler and emulsion operation. As pulsation is increased further the droplets become smaller and rise more slowly. The holdup in the column increases and reaches a maximum at the upper

flooding point.

The dispersed phase holdup in a pulse column is a function of the geometry of column, the pulse amplitude, the pulse frequency, the dispersed phase flow rate, the surface properties of the plate materials, and the physical properties of the liquids involved. It increases with the dispersed phase flow rate but the continuous phase flow rate, unless it is large, has little effect.

3.2. Backmixing

Backmixing in a pulse column is a nonideal flow pattern that is intermediate between the two ideal cases of plug flow and perfect mixing. For pulse column operation in the mixer-settler region, the rising droplets of light phase collect and coalesce under the plates at the end of each stroke of the pulse generator. The heavy phase is backmixed principally during the upstroke. The coalesced light phase is first forced through the plate and the remaining volume of liquid displaced during an upstroke then consists of heavy phase as a backmix stream.

As the pulse frequency is increased through the mixer-settler region all of the rising droplets do not have sufficient time between pulsation cycles to collect under the plates. Hence, the thickness of the coalesced layer under each plate decreases and the amount of heavy phase recycled increases. As the pulsation becomes still greater, the effect of the distribution of droplet velocities becomes more important and light phase droplets are pulled back through the plates. In the emulsion region axial mixing of the dispersed phase becomes truly diffusive owing to increased droplet interactions and it can be treated as a second continuous phase.

Backmixing reduces the local concentration gradients and decreases

the extraction efficiency. In some production sized extraction columns, it has been reported that 60 to 75% of the necessary effective height of the column may be accounted for by the effects of backmixing.

3.3. Mass transfer efficiency

The rate of mass transfer of a solute from one phase to the other in a pulse column is a function of three parameters--the interfacial area between the two phases, the difference in the solute concentration in the two phases, and a coefficient, called the "mass transfer coefficient" which incorporates into a single number the combined effects of many variables relating to column geometry, to column operating conditions, and to the physical properties of the solutions being processed. Precise measurement and evaluation of these three parameters is quite difficult and for many years simplified approaches have been used to compute the efficiency of the column.

The HETS, discussed earlier, has been used but for a multicomponent system this number tends to be different for each transferring species in the column. The HTU or "height of a transfer unit" is often used. It is defined as the flow rate divided by the mass transfer coefficient times the interfacial area and is more likely to remain constant along the length of the column. It is also more likely to be more nearly the same for the various solutes in the column. Because of the difficulty in measuring the mass transfer coefficient and the interfacial area independently, they are almost always measured and correlated together as the product " ka ."

4. PULSE COLUMN SIMULATION

4.1. Comprehensive sources of information

There are a significant number of survey and review articles concerning pulse column simulation, operation, and design that contain potentially useful information either because they discuss simulation methods, present data that are helpful in computing parameters for simulation models, or present a summary of the present state of our knowledge of pulse columns.

A book by Hanson (31) provides a comprehensive treatment of nearly all phases of liquid-liquid extraction with especially good chapters on the chemistry of extraction processes, response characteristics and control, and longitudinal mixing. It is not a textbook but rather a collection of contributed chapters by invited authors. The book can be best described as a sourcebook and a guide to the literature up to about 1971. The information is well organized and presented but it is not reviewed critically. The most notable feature of the work is its broad coverage and its large numbers of literature citations. Some of the key chapters contain from 100 to 700 references per chapter. In all, there are 1423 references given.

On August 5-6, 1976 a workshop was held at the Battelle Seattle Research Center in Seattle, Washington to collect, evaluate, and document data on solvent extraction process equipment, control, and operation as applied to the nuclear industry. The results of the workshop were presented in a report (26) consisting of three volumes. Part I is a non-critical review of the literature and contains 697 references. Of these 697 references, 129 were selected as being of significant interest and

from them a summary was prepared describing the information available on pulse columns, mixer-settlers, and centrifugal extractors. Sixty-seven pages are devoted to pulse columns. Part II is a report of the proceedings of the workshop and contains the general consensus of the participants about the present state of knowledge of solvent extraction equipment for the nuclear industry. Part III is a condensed summary of Parts I and II.

A final important source of information on pulse columns is the Purex Technical Manual (59). Although it first appeared in 1955, this manual still contains some of the most useful data available on pulse column parameters, particularly column efficiencies and capacities, and describes in great detail the construction of plant-sized pulse columns. It is currently being revised and updated.

Although these three general survey references do not bear directly on the problem of pulse column simulation they represent collectively a very compact source of much of the available information on pulse columns and they contain a large fraction of the literature references which exist on the pulse column. Such information assumes great importance when one begins searching for actual numerical values for the constants and parameters in any mathematical model of the pulse column.

To date, the only truly critical survey of the dynamics of liquid-liquid extractors is a review article by Pollock and Johnson (60) published in 1974. Working from a list of seventy-eight references they chose thirty-three for critical review, the most recent one having been published in 1971. They concluded that:

- (1) Essentially all of the theoretical and numerical work in extraction dynamics has used one of the following four models:
 - (a) Two phase differential contact with plug flow
 - (b) Two phase differential contact with axial mixing
 - (c) Two phase stagewise contact with ideal mixing
 - (d) Two phase stagewise contact with backmixing
- (2) Pulsed, packed, and Scheibel-type columns have been studied most.
- (3) The use of distributed parameter models tend to give results that compare unfavorably with experimental data unless they are differentiated and solved numerically.
- (4) The use of pulse testing and frequency response analysis is becoming increasingly important in the study of extraction dynamics.
- (5) Except for the work of Erskine, Seemann, and Burkhart (21), no control studies of center fed columns have been published.
- (6) Accurate guides to control methods are still lacking and there is a wide range of behavior where feedforward control is applied.
- (7) Steady-state values of the model parameter: can be used to develop good predictions for one phase. When backmixing terms are included, fairly good agreement can be obtained for both phases.
- (8) The most realistic and useful model is the stagewise model with backmixing. This approach offers the most hope for realistic studies involving both control and simulation.

Since 1971, little activity has occurred to modify these conclusions except to add that much of the work in this area since 1971 has been done on RDC (rotating disc) contactors.

4.2. Review of simulation methods and dynamic studies

The literature abounds with a wide variety of simulation studies of the pulse column. However, some of the work has only limited potential for application to modeling real columns. Very simplified theoretical equations were used, linear equilibrium lines assumed, and only a single solute considered. The results give qualitative but not quantitative information. While such efforts are of scientific value, they are often not definitive because the effect of the omissions and assumptions on the results and conclusions are difficult to assess. Other work, experimental in nature, was carried out on laboratory columns of only one or two stages or on extremely small columns of about one inch diameter. The extrapolation of such data to larger columns must be made cautiously. These papers are included in an exhaustive bibliography at the end of the report. Although they were reviewed, they are not discussed unless they contained specific information of value in the simulation of plant sized columns.

4.2.1. Deterministic models

For simulation in the time domain, the basic material balance equations for continuous countercurrent contact as shown in Figure 3 are, for each solute in the system

(1) for the aqueous phase

$$E_a \frac{\partial^2 X_a}{\partial z^2} - F_a \frac{\partial X_a}{\partial z} - k_o a V (X_o - X_o^*) = \frac{\partial}{\partial t} (H X_a) \quad (4.1)$$

(2) for the organic phase,

$$E_o \frac{\partial^2 X_o}{\partial z^2} + F_o \frac{\partial X_o}{\partial z} + k_o a V (X_o - X_o^*) = \frac{\partial}{\partial t} (h X_o) \quad (4.2)$$

The first term in each equation represents longitudinal dispersion or transport in the direction of decreasing concentration, the second term accounts for convective transport, the third term accounts for mass transfer between the two phases. The accumulation term on the right represents the rate of change of the mass of solute at a point in the column.

For stagewise countercurrent contact, shown in Figure 4, the equations for each phase are given by the following relations for each solute

(1) for the aqueous phase

$$F_a [(1 + \alpha_{a,i-1})X_{a,i-1} + \alpha_{a,i+1}X_{a,i+1} - (1 + 2\alpha_{a,i})X_{a,i}] - k_o aV(X_{o,i} - X_{o,i}^*) = \frac{d}{dt} (H_i X_{a,i}) \quad (4.3)$$

(2) for the organic phase

$$F_o [(1 + \alpha_{o,i+1})X_{o,i+1} + \alpha_{o,i-1}X_{o,i-1} - (1 + 2\alpha_{o,i})X_{o,i}] + k_o aV(X_{o,i} - X_{o,i}^*) = \frac{d}{dt} (h_i X_{o,i}) \quad (4.4)$$

In these equations α is the backflow coefficient or the ratio of backflow to main flow for each phase. It is analogous to, but not equal to, the longitudinal dispersion coefficient in Equations 4.1 and 4.2.

There has been much discussion in the literature about which of these two approaches should be used to model the pulse column. For practical purposes, Equation 4.1 and 4.2 cannot be used for most real systems because the necessary equations for the distribution coefficients of the solutes used are complex and nonlinear empirical relations. Equations 4.1 and 4.2 must therefore be converted to a finite difference form and solved numerically. As a difference equation, for example, Equation 4.1 is

$$E_o \frac{\partial^2 X_o}{\partial z^2} - F_o \frac{\partial X_o}{\partial z} - k_o a (X_o - X_o^*) = \frac{\partial}{\partial t} (HX_o)$$

$$E_o \frac{\partial^2 X_o}{\partial z^2} - F_o \frac{\partial X_o}{\partial z} - k_o a (X_o - X_o^*) = \frac{\partial}{\partial t} (hX_o)$$

Figure 3. Diagram and equations for continuous differential model of the pulse column.

$$F_0 [(1+a_{0,i-1})X_{0,i-1} + a_{0,i+1}X_{0,i+1} - (1+2a_{0,i})X_{0,i}]$$

$$-k_0 a (X_{0,i} - X_{0,i}^*) = \frac{d}{dt} (H_i X_{0,i})$$

$$F_0 [(1+a_{0,i+1})X_{0,i+1} + a_{0,i-1}X_{0,i-1} - (1+2a_{0,i})X_{0,i}]$$

$$+k_0 a (X_{0,i} - X_{0,i}^*) = \frac{d}{dt} (h_i X_{0,i})$$

Figure 4. Diagram and equations for stagewise model of the pulse column.

$$E_a (X_{a,i+1} - 2X_{a,i} + X_{a,i-1}) / (\Delta Z^2) - F_a (X_{a,i+1} - X_{a,i-1}) / (2\Delta Z) \\ - k_{0a} V (X_{0,i} - X_{0,i}^*) = \frac{\partial}{\partial t} (H X_a) \quad (4.5)$$

in which form it closely resembles its stagewise counterpart, Equation 4.3. Thus, for almost all real extraction systems, the actual solution techniques become the same. The similarity between Equations 4.3 and 4.5 permits an expression to be derived from which the backmixing coefficient, which cannot be measured experimentally, may be computed from values of the longitudinal dispersion coefficient, which can be measured experimentally.

If column efficiency is assumed to be 100% then the terms containing the mass transfer coefficient disappear and Equations 4.3 and 4.4 can be added together to give a single equation,

$$F_a [(1 + \alpha_{a,i-1})X_{a,i-1} + \alpha_{a,i+1}X_{a,i+1} - (1 + 2\alpha_{a,i})X_{a,i}] \\ + F_o [(1 + \alpha_{o,i+1})X_{o,i+1} + \alpha_{o,i-1}X_{o,i-1} - (1 + 2\alpha_{o,i})X_{o,i}] \\ = \frac{d}{dt} (H_i X_{a,i} + h_i X_{o,i}) \quad (4.6)$$

If in addition the effect of backmixing is also neglected then Equation 4.6 can be simplified still further to give

$$F_a (X_{a,i-1} - X_{a,i}) + F_o (X_{o,i+1} - X_{o,i}) = \frac{d}{dt} (H_i X_{a,i} + h_i X_{o,i}) \quad (4.7)$$

All deterministic models of the pulse column use some form of Equations 4.1-4.7.

The first study of the control of extraction columns was published by DiLiddo and Walsh (16) in 1961. They did a theoretical analysis of the behavior of a pulse column during start-up and of the response of the

extract concentration to step changes in pulse frequency, solvent flow rate, and solvent input concentration. The uncontrolled extract response was found to be affected most by the solvent flow rate. However, changes in the pulse frequency gave the most rapid extract response. The closed loop control strategy used was to apply a combination of proportional plus integral feedback control to the aqueous phase flow rate. Their model, written for the uranium-nitric acid-TBP system used experimental equilibrium data but was based on equations which described mixer-settler type operation of the pulse column, a mode which is seldom employed in production columns. It also used a Murphree efficiency to account for incomplete mass transfer. The use of a Murphree efficiency was shown by later investigators to be an invalid approach for extraction columns, although it has been widely used in distillation column design (58).

In 1961 Biery and Boylan (70) studied both theoretically and experimentally the operation of a pulse column 20 ft. high and 3 in. in diameter using the water-nitric acid-TBP system. Their model equations were similar to Equation 4.6 except that the mass transfer term was retained. The initial estimate of the mass transfer coefficient was obtained from transfer unit (NTU) calculations based on terminal concentrations. The work was carefully documented, used values of the operating variables in the same range as those encountered in a fuel reprocessing plant, used a similar physical system, and recorded valuable measurements of dispersed phase holdup and mass transfer coefficients. The transient response curves were similar to those of DiLiddo and Walsh.

Watjen and Hubbard (74) investigated the dynamic behavior of a small 3/4-in. dia. pulse column with 2 and 3 plates. For their simulation they

used equations of the form of Equation 4.5, i.e., differenced forms of the equation for continuous countercurrent contact but concluded that their model was too simple and that more sophisticated models were required.

4.2.2. The SEPHIS code

The most widely used pulse column model in the nuclear industry is the SEPHIS (Solvent Extraction Processes Having Interacting Solutes) program developed for studying flowsheet modifications needed to adapt the Purex process to LMFBR fuels. Although written by Gronier of ORNL, its roots can be traced back to the work of Lowe (44) at the Savannah River Laboratory.

Lowe's model consisted of discrete stages, each with a settling section and a high intensity mixing zone. All interphase mass transfer was assumed to occur in the mixing zone, the settling section providing only a holdup time between mixers in the countercurrent cascade. The model had provision for feed or take-off at any arbitrary stage. Thus, center-fed extractors could be simulated. The time unit for the computations was that required for one volumetric displacement of the fastest flowing stream in an ideal mixer-settler stage. Because the distribution coefficient was a function of concentration, the material balances on each stage were iterated to some prescribed tolerance. The resulting equilibrium output streams were then corrected for failure to achieve equilibrium contact by use of a relation similar to a Murphree efficiency supplied as a program input. The model was applied to problems in the Tramex process for separating curium from irradiated plutonium and to the SRP enriched uranium process. Incentive for development of the program came from the fact that fissile material concentrations are greater at points inside a

center-fed extractor than in the inlet and outlet streams and that during transient periods these peaks change in magnitude and location, thus making knowledge of concentration profiles important in nuclear criticality safety analyses.

The comparatively high plutonium levels of LMFBR fuels present potential criticality problems during reprocessing. In searching for a mathematical model to study the development of extraction flowsheets for LMFBR fuels, Groenier (30) found the basic approach of Lowe to be an attractive one (29) and modified the program to permit its use for U-Pu processing. In so doing he added internal recycle streams so that the code could also be used for contractors other than mixer-settlers. Use of these internal recycle streams permits the specification of phase ratios (holdup) in the stages that are different from the ratio of the flow rates in the extractor. The program also incorporated a simple expression for the effect of temperature on the distribution coefficients. Since only U, Pu, and nitric acid mass transfer is considered, the code applies to extraction and stripping contactors but does not include the effects of chemical reactions for valence control in U-Pu partitioning so it cannot be used for simulating U-Pu separations.

In 1971 Richardson and Nance (60) revised the SEPHIS program by substituting improved equilibrium relationships and convergence criteria. They mentioned that the major limitations to SEPHIS are (1) that it is a stagewise model and that pulse columns are continuous, (2) in regions of low concentration and steep concentration profiles such as at the waste end of an extraction section backmixing is very important but is not included in SEPHIS, (3) the HETS (height equivalent to a theoretical stage)

is different for different components, and (4) that transfer governed by chemical reaction cannot be represented.

A further change in Richardson's SEPHIS program was made by Watson and Rainey (61). They changed the program structure, modified it for use in the Acid Thorex Process for reprocessing thorium fuels, added the ability to include the common-ion or salting effect of nonextractable nitrate salts, added provisions for estimating the partitioning of plutonium from uranium by entering the reductant normality as a negative plutonium concentration but did not include the effect of reaction kinetics (an important consideration in actual processing facilities), provided for calculations on a solute-free basis, and added the capability of computing the change in profile temperature with time.

In 1975 Richardson and Swanson (62), in an important and elegant study of plutonium partitioning in the Purex process with hydrazine-stabilized hydroxylamine nitrate, compared their experimental results with a further modified version of SEPHIS and obtained, in their words, fair to good agreement. The new code provided for simultaneous mass transfer of U, Pu(IV), Pu(III), and nitric acid. They thus added the effect of chemical reaction to the SEPHIS capability to the extent that the kinetics of the reaction of hydroxylamine nitrate to reduce Pu(IV) to Pu(III) was included. However, they also stated that caution should be exercised in using the program for U-Pu partitioning because (1) the effects of plutonium re-oxidation and loss of the hydrazine holding reductant are not included, (2) it is based on stagewise calculations that are not truly applicable to continuous contactors, and (3) no backmixing effects are included (a factor they felt to be of considerable importance in column contactors

like the pulse column). They felt that the greatest limitation to the use of this latest version of SEPHIS in partitioning calculations was the lack of a means of accounting for the re-oxidation of plutonium and for the reaction of hydrazine with Pu(IV) and nitrous acid. This last version of SEPHIS by Richardson and Swanson represents, so far as can be determined, the current state of the SEPHIS code. It is known that a number of simulation codes for solvent extraction processes exist in private organizations but these programs are proprietary and could not be reviewed. It is believed that most are versions of SEPHIS. It is doubtful that any of them represent a more sophisticated version than that of Richardson and Swanson. In all probability, they are less advanced since the Richardson version is based on the most current laboratory results of U-Pu partitioning chemistry.

4.2.3. The McCutcheon-Burkhart partitioning model

In 1975, McCutcheon, Burkhart, and Felt (47) published the results of a simulation study of the U-Pu partitioning column in the Plutonium Reclamation Facility at Richland, Washington in which the re-oxidation of Pu(III) by nitric acid was found to contribute significantly to the development of chemical instability and loss of partitioning. Their model, which was based on equations of the form of Equation 4.6 included terms to account for the kinetics of the following chemical reactions which occur in columns for the partitioning of uranium and plutonium,

- (1) plutonium reduction by hydroxylamine
- (2) plutonium re-oxidation by nitric acid
- (3) plutonium reduction by hydrazine
- (4) destruction of nitrous acid by hydrazine
- (5) destruction of nitrous acid by hydroxylamine

The concept of the model differs from that of the SEPHIS code in several respects. The time increment could be chosen arbitrarily and was not fixed by the residence time of the phases in each stage. This eliminated the need to iterate on each stage during the calculation but, in general, increased the number of time steps required because smaller time increments were used. The model did not account for the effect of temperature on the distribution coefficients, for the extraction of water by TBP, or for backmixing. As with most other models developed to date, the holdup in each stage was assumed to be proportional to the flow rates. This is the most detailed model of U-Pu partitioning that has yet been developed. In addition to the publication cited above, more complete details of the model are available in the doctoral dissertation of McCutcheon (48).

4.3. Analysis of available pulse column simulation models

The previous review has concentrated on the most important simulation models of the pulse column, particularly as they apply to nuclear fuel reprocessing. The overall subject of pulse column simulation as a practical technique must go beyond the writing of unsteady-state material balances around the extractor. While the ongoing argument of whether or not a stagewise model can be used effectively to represent a continuous contactor like the pulse column the need, cited earlier, for differencing the equations describing continuous countercurrent contact in order to use actual distribution coefficient data precludes the employment of the continuous differential equations, in their differential form, to describe a real column unless the distribution relations can be reduced to a sufficiently accurate linear form. The work of McCutcheon, Burkhart, and Felt (47) is a reasonable compromise between using the differential equations

and using the SEPHIS approach which, by virtue of the constraints on the time increment, leads to rather large time steps.

The detail which can be incorporated into a model depends upon the use for which it is intended. In past work the complexity of the models used have, to a large measure, been a function of the availability of accurate parameters and also the computer time involved in the solution. For a "state-of-the-art" model without major regard for the time and computing facilities required, the availability of good data and correlations from which to obtain distribution coefficients, mass transfer coefficients, backmixing coefficients, and dispersed phase holdup determine whether or not these terms can be included. In effect, one can write equations containing these terms but often cannot find numbers to put into them. The same comments hold true for the inclusion of chemical reaction terms to handle U-Pu partitioning. The stoichiometry of the reactions and their kinetic rate equations must be known.

If the simulation model is to be used for on-line control or information purposes the problem is different. One then requires simpler models. But simpler models must of necessity leave out certain terms representing physical phenomena that occur in the real system. A decision must then be made as to which information from the model must be accurate and where accuracy can be sacrificed in the interest of model reduction. In this area nondeterministic models can play a major role.

The following paragraphs are devoted to a literature review and summary of the present information on the key parameters needed for an accurate deterministic model of the pulse column.

5. PREDICTION OF EQUILIBRIA

5.1. Methods and data for predicting equilibria

In metal extraction systems such as those used in nuclear fuel re-processing the solutes interact with each other at macro-concentrations and the use of single component data is not possible unless the concentrations are very dilute. This increases the amount and precision of the data required and also makes the correlations more complex. A generalized reaction equation can be used to describe the simultaneous extraction of the various metal nitrates and nitric acid by TBP as follows (6,56):

The thermodynamic equilibrium constant for the reaction is,

$$K_M = \frac{a_{M(NO_3)_n \cdot b TBP}}{a_M \times a_{NO_3^-}^n \times a_{TBP}^b} = \frac{\alpha_{M(NO_3)_n \cdot b TBP}}{\alpha_M \times \alpha_{NO_3^-}^n \times \alpha_{TBP}^b} \times \frac{[M(NO_3)_n \cdot b TBP]_{or}}{[M]_{aq} [NO_3^-]_{aq}^n [TBP]_{or}^b}$$

where the α 's are activity coefficients, the a 's are activities, and the quantities in brackets are concentrations.

Calculation and use of the thermodynamic equilibrium constants, although preferable, is not yet feasible for all the species involved so an apparent equilibrium constant, sometimes called a pseudo-mass-action equilibrium constant, has been used by all investigators who have developed correlations for the distribution coefficients which have been used in actual extraction calculations. The two most widely used apparent equilibrium constants are of the form,

$$K_M' = \frac{[M(NO_3)_n \cdot b \text{ TBP}]_{or}}{[M]_{aq} [NO_3^-]_{aq}^n [TBP]_{or}^b} = K_M \times \frac{\alpha_M^n \times \alpha_{NO_3^-}^n \times \alpha_{TBP}^b}{\alpha_{M(NO_3)_n} \cdot b \text{ TBP}} \quad (5.2)$$

and,

$$K_M'' = \frac{[M(NO_3)_n \cdot b \text{ TBP}]_{or}}{[M]_{aq} [TBP]_{or}^b} = K_M [NO_3^-]_{aq}^n \times \frac{\alpha_M^n \times \alpha_{NO_3^-}^n \times \alpha_{TBP}^b}{\alpha_{M(NO_3)_n} \cdot b \text{ TBP}} \quad (5.3)$$

The relationship between the two pseudo-equilibrium constants is,

$$K_M'' = K_M' [NO_3^-]_{aq}^n \quad (5.4)$$

and, defining the distribution coefficient E_M as the ratio of the concentration in the organic phase to that in the aqueous phase gives,

$$E_M = \frac{[M(NO_3)_n \cdot b \text{ TBP}]_{or}}{[M]_{aq}} = K_M' [NO_3^-]_{aq}^n [TBP]_{or}^b = K_M'' [TBP]_{or}^b \quad (5.5)$$

The reactions usually assumed to apply to Purex extractions are

Until recently, the most widely used equilibrium relations have been those presented by Groenier (30) in his documentation of the original SEPHIS program. The K_M' pseudo-mass-action equilibrium constant was employed and, following traditional physical chemistry procedures, the K_M' values were correlated with the total ionic strength, μ , of the system using experimental

data to fit a polynomial expression for K_M' as a function of μ ,

$$K_M' = a + b\mu + c\mu^2 + d\mu^3 + \dots \quad (5.9)$$

In correlating values of K_M' with ionic strength using existing data, Horner (33) noted that it was possible to develop more than one set of polynomial coefficients by optimizing for the best fit for each individual solute separately. In the original SEPHIS program 36 regression coefficients for the ionic strength correlations were obtained by fitting the data for Pu^{4+} , UO_2^{2+} , and HNO_3 separately as shown in Table 1. The correlation was obtained from only a single set of experimental data which did not include the very dilute or the heavily saturated regions. Moreover, it was restricted to a constant temperature of 25°C and a specific TBP concentration of 15 volume percent. Richardson (60) extended the code to higher temperatures and TBP concentrations by deriving new equilibrium correlations using K_M'' as described in Equation 5.5. He also assumed that nitric acid forms both the mono- and di-solvates with TBP and obtained a better fit for the nitric acid data. Empirical equilibrium expressions for K_U'' , K_{Pu}'' , K_{H1}'' , and K_{H2}'' were derived for 100% TBP as a function of total nitrate salting strength in the aqueous phase because this avoided uncertainties in defining ionic strength at high solute concentrations. Extension to other temperatures and TBP concentrations were made by multiplying the K_M'' values (developed at 25°C and 100% TBP) by different correction factors. Richardson's correlations were derived from a large amount of published data (13,15,33,54,56,57) and covered TBP concentrations from 2.5 to 100%, temperatures from 0 to 70°C, uranium concentrations to 2.0 M, aqueous nitric acid concentrations to about 6.0 M, and plutonium concentrations to 0.2 M.

Table I. Experimental Correlations of Equilibrium Coefficients

System	$\text{Pu}(\text{NO}_3)_4\text{-HNO}_3/\text{TBP - dodecane (17)}$	$\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3/\text{TBP - dodecane (17)}$	$\text{Pu}(\text{NO}_3)_4\text{-UO}_2(\text{NO}_3)_2\text{-HNO}_3/\text{TBP - dodecane (1)}$	$\text{Pu}(\text{NO}_3)_4\text{-UO}_2(\text{NO}_3)_2\text{-HNO}_3/\text{TBP - dodecane (11)}$
μ	$10[\text{Pu}^{4+}] + [\text{H}^+]$	$3[\text{UO}_2^{2+}] + [\text{H}^+]$	$[\text{H}^+] + 2[\text{UO}_2^{2+}] + 10[\text{Pu}^{4+}]$	$[\text{H}^+] + 3[\text{UO}_2^{2+}] + 10[\text{Pu}^{4+}]$
K'_{Pu}	$-0.43 + 3.11\mu^{-1} + 1.79\mu^{-2}$		$12.163 - 9.033\mu + 2.230\mu^2 - 0.163\mu^3$	$2.415 - 0.701\mu + 0.05271\mu^2 + 0.0333\mu^3 *$ $3.882 - 0.4838\mu + 0.05814\mu^2 + 0.006005\mu^3 **$
K'_{U}		$28.392 - 14.225\mu - 2.057\mu^2 + 2.035\mu^3$	$8.791 + 6.071\mu - 6.176\mu^2 + 1.579\mu^3$	$12.22 + 381\mu - 4.798\mu^2 + 2.477\mu^3 *$ $18.39 + 5.114\mu - 4.174\mu^2 + 1.892\mu^3 **$
K'_{H}	$0.385 - 0.155\mu + 0.024\mu^2$	$0.385 - 0.155\mu + 0.024\mu^2$	$0.385 - 0.151\mu + 0.024\mu^2$	$0.4076 - 0.166\mu + 0.03319\mu^2 *$ $0.4841 - 0.1445\mu + 0.02216\mu^2 **$
Experimental Conditions	$\mu = 0.3 \sim 6.0$ [TBP] = 20% ~ 30%	$\mu = 0.3 \sim 6.0$ [TBP] = 20% ~ 30%	$[\text{UO}_2^{2+}] = 0.1 \sim 0.6 \text{ M.}$ $[\text{Pu}^{4+}] = 0.01 \sim 0.2 \text{ M.}$ $[\text{HNO}_3] = 0.6 \sim 3.0 \text{ M.}$ [TBP] = 20% in n-dodecane $= 0.6 \sim 5.5$	$[\text{UO}_2^{2+}] = 0.1 \sim 0.6 \text{ M.}$ $[\text{Pu}^{4+}] = 0.01 \sim 0.2 \text{ M.}$ $[\text{HNO}_3] = 2 \sim 4 \text{ M.}$ [TBP] = 15% in n-dodecane $= 2.0 \sim 5.0$
Data Source	(56) (12)	(56) (12)	(6) (12)	(33) (12) * based on Pu distribution ** based on U distribution

Table 1. (continued...)

System	Pu(NO ₃) ₄ - UO ₂ (NO ₃) ₂ - HNO ₃ /TBP in n-dodecane	Pu(NO ₃) ₄ - UO ₂ (NO ₃) ₂ - HNO ₃ /TBP in n-dodecane (20,22)
μ	$[H^+] + 3[UO_2^{2+}] + 10[Pu^{4+}]$	$TNM = [H^+]_a + 2[UO_2^{2+}]_a + 4[Pu^{4+}]_a + [\text{nonextractable nitrates}]$
K_{Pu}^*	$2.7832937 - 0.51696092\mu + 0.04649217\mu^2 + 0.029783378\mu^3 *$ $5.4904842 - 0.39458656\mu + 0.04383080\mu^2 + 0.00558217\mu^3 **$	$K_{Pu}^{II} = K_{Pu}^{II}(0.20 + 0.55F^{1.25} + 0.0074[TNM]^2 *) (a)$ $K_{Pu}^{III} = K_{Pu}^{III}(4F^{-0.17} - 3) \exp(200\tau) ** (b)$
K_U^*	$7.6288233 + 8.71385480\mu - 2.9776511\mu^2 + 2.14147280\mu^3 *$ $22.75242 + 7.2565203\mu - 2.7138472\mu^2 + 2.1633701\mu^3 **$	$K_U^{II} = 3.7[TNM]^{1.57} + 1.4[TNM]^{3.9} + 0.011[TNM]^{7.3}$ $K_U^{III} = K_U^{III}(4F^{-0.17} - 3) \exp(2500\tau)$
K_H^*	$0.4926728 - 0.16650909\mu + 0.0294042\mu^2 *$ $0.56466365 - 0.12194633\mu + 0.01474504\mu^2 **$	$K_{H1}^{II} = K_{H2}^{II} = 0.135[TNM]^{0.82} + 0.0052[TNM]^{3.44}$ $K_{H1}^{III} = K_{H2}^{III} = K_{H1}^{III}(1 - 0.54 \exp(-15F)) \exp(340\tau)$
Experimental Conditions	$[Pu^{4+}] = 4.43 \sim 19.2 \text{ gm/l}$ $[UO_2^{2+}] = 67.7 \text{ gm/l} ***$ $[HNO_3] = 3.2 \sim 4.1 \text{ M.}$ $[TBP] = 15.3 \sim 86.7\% \text{ in n-dodecane}$ 23°C	$[Pu^{4+}] = 0 \sim 2 \text{ M.} (a) K_{H1}^{II} \text{ based pm } 25^\circ\text{C and } 100\% \text{ TBP}$ $[UO_2^{2+}] = 0 \sim 2 \text{ M.}$ $[HNO_3] = 0 \sim 6 \text{ M.} (b) K_{H1}^{III} \text{ corrected for other temp. and TBP conc.}$ $[TBP] = 2.5 \sim 100\% \text{ in n-dodecane}$
Data Source	(30) (20)	(13, 15, 33, 54, 57, 70) (5, 7, 11, 16, 18, 21)
	* based on Pu distribution ** based on U and HNO ₃ distribution *** only estimate. Conc. used was not specified	* F = fraction of TBP in dry, solute free solvent (TBP+diluent) ** $\tau = 1/T - 1/298$ T = equilibration temperature

Table 1. (continued...)

System	$\text{Pu}(\text{NO}_3)_4 - \text{Pu}(\text{NO}_3)_3 - \text{HNO}_3/\text{TBP} - \text{CCl}_4$	(8,9)	20% TBP
μ	$[\text{HNO}_3] + [\text{HN}] + \frac{1}{2}\{[(4-m)^2 + (4-m)\text{Pu}^{4+}] + \frac{1}{2}\{[(3-p)^2 + (3-p)\text{Pu}^{3+}] + \sum \frac{1}{2} m_i z_i^2 (\text{inert salts})$ where: m, n, p are the extent of complexing of metal nitrate complexes as a function of TNM		
[TNM]	$m[\text{Pu}^{4+}] + n[\text{UO}_2^{2+}] + p[\text{Pu}^{3+}] + [\text{H}^+] + [\text{HN}] + [\text{inert salt nitrates}]$	HN = hydroxylamine	
$K_{\text{Pu}^{4+}}^1$	$\exp\{0.1135 + 0.8516 \ln[\text{SS}] - 0.1719(\ln[\text{SS}])^2 + 0.171(\ln[\text{SS}])^3\}$	$[\text{SS}] = ([\text{TNM}] \times \mu)^{1/2}$	
$K_{\text{Pu}^{3+}}^1$	$0.04 [\text{TNM}]^{-1.2} + 3(10)^{-5} [\text{TNM}]^4$		
K_{U}^1	$\exp\{1.8586 + 1.4209 \ln[\text{SS}]\}$		
K_{H1}^1	$\exp\{-2.135 - 0.1808 \ln[\text{SS}] + 0.2358(\ln[\text{SS}])^2 - 0.0379(\ln[\text{SS}])^3\}$	for Pu effect	
K_{H2}^1	$\exp\{-2.394 - 0.2622 \ln[\text{SS}] + 0.2817(\ln[\text{SS}])^2 + 0.0276(\ln[\text{SS}])^3\}$	for U effect	
K_{Pu}	$\exp\{-2.867 - 1.08 \ln[\text{TNM}] - 0.722 \ln[\text{UO}_2^{2+}]_a\}$	plutonium correction for uranium extraction	
Data Source	(43) (28)		

The plutonium Reclamation Facility at Richland, Washington has plutonium feeds of higher concentration than those of either an LWR feed or an LMFBR feed and thus they are concerned with the upper end of the equilibrium concentration range where saturation effects become important. Klem (38) proposed two empirical equations for K'_{Pu} and K'_H as a function of total aqueous nitrate salting strength. They were developed from new data taken recently at Atlantic Richfield and used by Fort and Klem (22,23) in studying a proposed revision of the scrap recovery flowsheet from new laboratory work at concentrations up to about 95% solvent saturation. However the equations are for Pu-HNO₃, U-HNO₃, and HNO₃ systems and the correlation for the U-Pu-HNO₃ system have not yet been completed.

To date, improved equilibrium distribution correlations have been obtained by collecting data from additional sources as it becomes available. However, there is a lack of consistency, particularly at low acidities and low plutonium concentrations.

In U-Pu partitioning, particularly at high Pu concentrations, nitrous acid (HNO₂) is an important specie in the extraction system. Biddle and Miles (9) have shown that the nitrous acid distribution coefficient is larger by an order of magnitude than that for nitric acid because a very stable complex is formed between nitrous acid and TBP. It is generated as a product of the oxidation of plutonium by nitric acid, a reaction which it also catalyzes and so its presence even in low concentrations is important. Marin, et al. (46) determined an empirical linear relationship between the nitrous acid distribution coefficient and the free TBP as,

$$E_{HNO_2} = 18.5[TBP] \text{ for } 20\% \text{ TBP} \quad (5.10)$$

5.2. Discussion with other authors

To complete the survey of available distribution coefficient calculation procedures, direct contact was made with a number of the more important authors referred to in this report and also others who were considered knowledgeable. In general they (collectively) felt that much of the existing data at low plutonium concentrations are suspect because of possible errors in analytical procedures such as insufficient purification of the TBP, errors in alpha counting (perhaps lack of correction for americium), etc. Similarly, the data clearly show strong inconsistencies at high solvent loadings.

There appears to be a real need for a definitive study of the equilibrium distribution in plutonium-uranium-nitric acid/TBP-diluent systems. The word diluent rather than dodecane was used intentionally in the previous sentence since there is a tendency to move toward more radiation-resistant solvents (chlorinated, aromatic, etc.). Also, there is now an accepted effect of the diluent on the distribution coefficients. This has been observed at Richland and has been reported quantitatively in the Russian literature. It was also the subject of several papers presented at the 1977 International Solvent Extraction Conference in Toronto, Canada (proceedings are not yet available).

New data have been taken at Richland, especially in the regions of high solvent saturation. They have completed work for the plutonium-nitric acid system and the uranium-acid system and have scheduled work aimed at obtaining a correlation for the plutonium-uranium-acid system. Some of these data points, especially at high solvent loadings could improve existing equations for distribution coefficients in this region.

5.3. Conclusions and recommendations

All of the correlations so far have employed the same basic approach. The major centers of work in this area have been at ORNL where the SEPHIS program was initially written, at Richland, Washington where modification to SEPHIS has been made, and at Karlsruhe in Germany.

Recommendations for further work in this area are:

- (1) The new data at Atlantic Richfield should be included in the correlations since they have, or soon will have, more data at high solvent loadings and also at low plutonium concentrations.
- (2) Ultimately, a new project should be carried out to obtain a carefully done, consistent set of laboratory data for the Pu-U-HNO₃ system.
- (3) The effect of different diluents should be quantitatively determined.
- (4) The possibility of a different correlation method based on thermodynamic equilibrium constants should be explored before new data are taken to see if a new correlation approach would be more effective.

It is especially important to realize that the accuracy of any model of the pulse column for nuclear fuel reprocessing is ultimately limited by the accuracy of the equilibrium correlations available. With the limited current activity in the science of reprocessing it could be some time before better equilibrium data are available.

6. CALCULATION OF DISPERSED PHASE HOLDUP

In general, holdup of the dispersed phase in the emulsion region is a

complex function of many variables. First are those which are essentially geometric and are usually fixed during column design. These are plate spacing, hole diameter, percent free area of the plates, plate thickness, plate material, column diameter, and column height. Second, are those associated with the system--density, viscosity, interfacial tension, and the effect of changes in solute concentration on these physical property variables. Finally, there are the operating variables--flow rates, pulse amplitude, pulse frequency and pulse amplitude. Experience has shown that in practice the range of most of these variables is quite limited. Further, for a specific class of physical systems such as those normally encountered in nuclear fuel reprocessing the range is even smaller.

6.1. Review of the literature

Cohen and Beyer (14) reported some of the earliest data on dispersed phase holdup in pulse columns. They measured the ratio of the volumes of dispersed phase to continuous phase in a one inch diameter column by stopping the flow into the column after it had reached steady state operation and then draining its contents into a graduated cylinder. Since the volume drained also contained the liquid in both disengagement sections there was some error inherent in their data. The measured holdup ranged from 10 to 26%.

Li and Newton (42) found that the holdup increased with increasing flow rate of the discontinuous phase but was essentially independent of the flow rate of the continuous phase, conclusions later confirmed by other investigators. No attempt was made to obtain any type of correlation in these two early papers.

In a series of fourteen papers beginning in 1951, Thornton and

co-workers reported on a lengthy series of investigations covering holdup, flooding, and extraction efficiency for a variety of different types of extraction columns.

The work on pulse columns is described by Logsdail and Thornton (43), and the basic approach which they used for their holdup correlation is contained in the paper by Gayler, Roberts, and Pratt (25). They expressed the velocity of the droplets of the dispersed phase relative to the moving continuous phase in terms of a modified form of the Stoke's Law expression in which the buoyancy force was assumed to be proportional to the difference between the densities of the mixed phases and the dispersed phase. This resulted in a simple expression containing only the superficial velocities of the two phases and the dispersed phase holdup,

$$V_d + (\epsilon_d / (1 - \epsilon_d)) V_c = \bar{V}_0 \epsilon_d (1 - \epsilon_d) \quad (6.1)$$

A plot of $V_d + (\epsilon_d / (1 - \epsilon_d)) V_c$ against $\epsilon_d (1 - \epsilon_d)$ yielded, for each system tested, a straight line of slope $\bar{V}_0$. Since Equation 6.1 held for all velocities up to flooding it was thus valid at zero continuous phase velocity and very low dispersed phase velocity. Under these conditions $V_c = 0$ and $(1 - \epsilon_d)$ approaches 1.0 as V_d approaches zero so equation 6.1 reduces to,

$$\bar{V}_0 = \frac{V_d}{\epsilon_d} \quad (6.2)$$

which is simply the mean droplet velocity of the dispersed phase. This was called the "characteristic velocity" since it had a unique value for each system. Once this characteristic velocity had been determined for the

system the holdup could be found as a function of the superficial velocities of the two phases in the column by using Equation 6.1.

From previous experience with rotary annular columns and rotating disc columns, Logsdail and Thornton assumed that the characteristic velocity was a function of column geometry, energy input, and system physical properties but independent of phase flow rates. Their correlation was,

$$\frac{\bar{v}_0 \mu_c}{\gamma} = 0.60 \left(\frac{\Gamma \mu_c^5 q_c}{\rho_c \gamma^4} \right)^{-0.24} \left(\frac{d_o \rho_c \gamma}{\mu_c^2} \right)^{0.90} \left(\frac{\mu_c q}{\Delta \gamma^3} \right)^{1.01} \left(\frac{\Delta \rho}{\rho_c} \right)^{1.80} \left(\frac{\mu_d}{\mu_c} \right)^{0.30} \quad (6.3)$$

which was reported to have an accuracy of $\pm 15\%$ for columns of 3, 6, 9, and 12 inches in diameter. The characteristic velocity was found to be independent of column diameter over this range.

The correlation in Equation 6.3 was obtained for systems without mass transfer. When solute transfer takes place, however, interfacial effects tend to promote droplet coalescence and the $\bar{v}_0$ calculated from Equation 6.3 is no longer valid. For the water-acetone-toluene system, for example, the value of $\bar{v}_0$ computed from Equation 6.3 was enhanced by a factor of 2.6 when mass transfer took place from the solvent to the water phase. Thus, for use in calculating holdup, an experimental run is required to find $\bar{v}_0$ directly in the presence of mass transfer, or else an enhancement factor must be estimated for the value calculated from Equation 6.3.

Two important conclusions can be drawn from their work. First, the holdup was relatively insensitive to continuous phase flow rate, as was reported earlier by Li and Newton. Second, the general theory seems applicable to a variety of mechanically agitated columns.

Thornton's approach assumes some importance because it has been used

by several other investigators in correlating holdup data for pulse columns. Actually, the correlations were originally developed as an aid in design calculations in order to predict the upper flooding point for a pulse column. To do this one differentiates Equation 6.1 with respect to ϵ_d first considering V_d as the dependent variable and then considering V_c as the dependent variable. The resulting derivatives are then set equal to zero to obtain,

$$V_{df} = 2 \bar{V}_0 \epsilon_{df}^2 (1 - \epsilon_{df}) \quad (6.4)$$

$$V_{cf} = \bar{V}_0 (1 - \epsilon_{df}^2) (1 - 2\epsilon_{df}) \quad (6.5)$$

The f subscript indicates flooding since at the upper flooding point $dV_d/d\epsilon_d = 0$ and $dV_c/d\epsilon_d = 0$. Combining Equation 6.4 and 6.5 gives the holdup at flooding,

$$\epsilon_{df} = 2 / (3 + (1 + 8V_{cf}/V_{df})^{1/2}) \quad (6.6)$$

which shows that the holdup at the flooding point is a function only of the flow rate ratio and is independent of physical properties of the system, the column geometry, and the pulsing conditions.

Nicholson (54) used Equation 6.6 together with a large compilation of flooding point data assembled by Groenier et al. (28) to estimate the holdup in a pulse column. He chose, from the tables of Groenier, et al., an experimental point which gave the flooding conditions for a column and a system similar to the one he was considering. Then, using the values of V_{cf} and V_{df} so obtained, he computed ϵ_{df} from Equation 6.6. This value of ϵ_{df} , along with the values of V_{cf} and V_{df} , was then substituted into

Equation 6.1 to find $\bar{v}_0$, the characteristic velocity. According to the theory, $\bar{v}_0$ should be the same for less-than-flooding rates and so with $\bar{v}_0$ known he estimated ϵ_d for the conditions under which he was operating. This approach depends upon access to valid experimental flooding data or else an accurate flooding correlation. Although acceptable in principle, the method seems a very indirect way of obtaining holdup data unless no better way can be found. It would probably be most accurate if actual flooding data were available on a similar column.

The best generalized flooding correlation to use if this technique were to be employed in the absence of experimental flooding data on the column would be that of Groenier, et al. (28) who analyzed about 2200 data points representing over 20 different chemical systems having a wide range of physical properties and included mass transfer in both directions. Their correlation was, on the average, 8.6% higher than the experimental values.

The work of Thornton and his associates represents the first extended study of holdup in pulse columns. The second major effort was carried out by Babb and his students at the University of Washington (Seattle). In the first of a series of papers, Sehmel and Babb (67) reported on their holdup studies using a 2 inch diameter pulse column with hexane, benzene, and methyl isobutyl ketone as solvents. They studied the effects of pulse amplitude, phase flow rates, and pulse frequency. Their experimental method did not permit determination of the axial variation in holdup but they observed visually that in a column with 43 plates spaced 2 inches apart that the dispersed phase, which entered at the bottom of the column, continued to break up into smaller droplets with a corresponding increase

in local holdup for about seven to eleven plates above the inlet distributor. Above that point the local holdup appeared to remain reasonably constant.

They observed, as did Li and Newton and also Thornton and his associates, that the holdup was practically independent of the continuous phase flow rate. Further, they found that as the pulsation was increased the total holdup first decreased and then went through a minimum at the transition point between mixer-settler and emulsion operation, after which it continued to increase up to the flooding point. The transition frequency could be predicted by the equation

$$f_H = 40(0.3 + 9 \times 10^{-8} \mu_d \gamma \Delta \rho - \ln a) \quad (6.7)$$

where the empirical constants are functions of the column geometry.

In a later paper, Bell and Babb (8) measured both the total holdup and the axial distribution of the holdup in a pulse column. For a 2 inch diameter column with a 2.2 inch plate spacing they found that the local holdup passed through a maximum near the middle of a column containing less than 24 plates but that it was uniformly distributed in the axial direction for longer columns. Their data also showed that the average holdup increased as the number of plates increased (at fixed plate spacing) for columns with less than about 20 plates and remained constant for longer columns. Their holdup correlation was based upon their observations that:

1. The effects of amplitude and frequency were accounted for by the amplitude-frequency product.
2. The effect of dispersed phase flow rate can be accounted for by an organic flow rate ratio,

The final correlation presented was

$$\epsilon_d = \frac{V_d}{28.2} (K_1 + (1.25 \times 10^{-5} + 2.42 \times 10^{-7} V_c)(af - K_2)^2) \quad (6.8)$$

where the ratio $V_d/28.2$ is the organic flow rate ratio based upon a reference flow rate of 28.2 ft/hr, and the constants are functions of the column geometry and the physical properties of the system.

In a final paper from Babb's group, Foster, et al. (24) published the first study of the transient holdup behavior in a pulse column operating in the emulsion region. They wrote unsteady state material balances for the change in holdup in each stage following a hydrodynamic upset. During an upset, the superficial velocity of the dispersed phase is not known but the slip velocity, defined as the average velocity of the dispersed phase droplets relative to the continuous phase, can be determined as a function of the pulse volume velocity and the holdup by the relation

$$v_s = V_d/\epsilon_d + V_c/(1 - \epsilon_d) \quad (6.9)$$

Thus, from a correlation of slip velocities they wrote a material balance for $d\epsilon_d/dt$ in terms of quantities which could be measured. A simultaneous solution of these equations for each stage then gave the transient holdup response. The initial solution of these equations produced a curve which led the experimentally determined curve and so a first order lag was introduced into the equations to allow for the coalescence time of the droplets. Using a coalescence time constant of 0.1 minute gave a theoretical curve which matched the experimental one much more closely. Use of the equations requires that the steady state holdup characteristics be known in the form of a slip velocity correlation at the pulse volume velocities to be used.

The third major effort in the study of holdup in pulse columns is represented by the work of Miyauchi and Oya (51) who correlated their own data as well as that of Cohen and Beyer (14), Li and Newton (42), Sehmel and Babb (67), and Shirotuka, et al. (68). They first attempted the use of the "characteristic velocity" concept introduced by Thornton, but found that at high pulsation the correlation so obtained diverged significantly from their experimental data. Their final approach to holdup correlation, carried out as part of an extensive backmixing study, was to measure drop sized photographically and to correlate them by a semi-theoretical relationship first introduced by Endoh and Oyama (19) in which Kolmogoroff's local isotropy concept was applied to drop dispersion in a mixing vessel. Their equation for the mean drop size in dilute liquid suspension was

$$\bar{d}_p = 1.73 \times 10^{-2} \lambda_0 (\gamma \lambda_0 \rho / \mu_c^2)^{0.6} \quad (6.10)$$

where

$$\lambda_0 = (\nu_c^3 / \rho_c^3 \phi)^{1/4} \quad (6.11)$$

The variable ϕ is the mean rate of energy dissipation per unit mass of column fluid and, for the pulse column, has been determined by Jealous and Johnson (35) to be

$$\phi = 9.5 (af)^3 / (\delta_c \times L_0) \quad (6.12)$$

where δ_c is a function of s , the fraction of free hole area of the plate and is computed from,

$$\delta_c = s^2 / (1 - s)(1 - s^2) \quad (6.13)$$

The droplets of dispersed phase of mean diameter $\bar{d}_p$ were considered to move at a terminal velocity relative to the continuous phase of

$$V_s = V_d/\epsilon_d + V_c/(1 - \epsilon_d) \quad (6.14)$$

where the terminal velocity was represented by spheres travelling freely through a continuous medium, given by the equation

$$V_s = (4 g \bar{d}_p \Delta \rho / 3 c \rho_c)^{1/2} \quad (6.15)$$

Equations 6.10 through 6.15 were then combined to form a holdup correlation of the form

$$\epsilon_d = 0.66 V_d^{2/3} \psi^{0.84} \quad \psi < 0.21 \quad (6.16)$$

$$\epsilon_d = 6.32 V_d^{2/3} \psi^{2.4} \quad \psi > 0.21 \quad (6.17)$$

$$\psi = (af)/(E_c S_p)^{1/3} (u_d^2/\gamma \Delta \rho)^{1/4} \quad (6.18)$$

The semi-theoretical derivation shows that ϵ_d should be a function of V_d , but the data were fit best by using $V_d^{2/3}$. The authors postulated that the $2/3$ power dependence arose either from unsteady drop dispersion or from coalescence as the dispersed phase traveled through the column.

Eguchi and Nagata (18) used a 2.28 inch diameter column with the methyl isobutyl ketone-water system to study holdup in a pulse column and gave as their correlation the equation

$$\epsilon_d = 0.23 \left(\frac{af}{V_d} \right)^{-0.8} \left(1 + \frac{V_d}{V_c} \right)^{-0.8} \quad (6.19)$$

with a reported error of 20%. If V_c is large this equation reduces to the form

$$\epsilon_d = 0.23 (V_d/af)^{0.8} \quad (6.20)$$

and if V_d is very small, ϵ_d approaches zero. According to this equation the holdup is a function of the dispersed phase flow rate and the pulsing conditions. The holdup would decrease with increasing pulsation, in agreement with mixer-settler type operation. It thus appears that the work was done at low pulse amplitude and frequency.

Sato, et al. (8) used the methyl isobutyl ketone-acetic acid-water system in a 1.38 inch diameter column to measure the holdup in all operating regions. Three correlations were presented, one for each of the three different regions. The pulse volume velocity range for each region was also given. For the mixer-settler region, the pulse volume velocity range and the holdup correlation were

$$(af)_M < 1.3V_d^{0.22}L_o^{-0.32}d_h^{-0.37} \quad (6.21)$$

$$\epsilon_d = 0.52(af/V_d)^{-0.7}(1 + V_d/V_c)^{-0.7}L_o^{-1.2}d_h^{-0.26}$$

This equation is very similar to that of Eguchi and Nagata. It shows that the holdup will decrease with an increase in pulse volume velocity (af), but it also includes a functional dependence on plate spacing and hole diameter. In the mixer-settler region the equation predicts that holdup varies inversely with plate spacing and hole diameter.

For operation in the transition region, the pulse volume velocity range and holdup correlation were given as

$$1.3v_d^{0.22}L_o^{-0.32}d_h^{-0.37} \leq (af)_T \leq 0.8v_d^{0.22}L_o^{0.35}d_h^{-0.37} \quad (6.22)$$

$$\epsilon_d = 0.42 af v_d^{0.33} (1 + v_d/v_c)^{-0.7} L_o^{-0.68} d_h^{0.37}$$

From their experimental data plot there is a minimum point of holdup at the transition region.

For emulsion operation region, the corresponding pulse volume velocity and holdup correlation were

$$(af)_E \geq 0.8v_d^{0.22}L_o^{0.35}d_h^{0.37} \quad (6.23)$$

$$\epsilon_d = 0.54(af)^{2.4} (1 + v_d/v_c)^{-0.7} L_o^{-1.2} d_h^{0.89}$$

This equation shows that the holdup in the emulsion region will increase monotonically with an increase in pulse velocity. The larger exponent on the pulse volume velocity term (2.4) indicates that holdup is very sensitive to the energy input into the column.

Biery (10) studied the performance of a 3 inch diameter pulse column using the system (50% TBP-kerosene)-nitric acid-water and, although no holdup correlation was attempted, the data obtained are especially useful because the column used was about 30 feet long and thus represents one of the longer experimental columns for which information is available.

Rouyer, et al. (64) collected data on larger diameter columns using 30% TBP in dodecane as the organic phase. They studied holdup, mass transfer, and longitudinal dispersion in thirty 4 inch diameter columns having a variety of different geometries, in several 12 inch diameter columns, and in one 24 inch diameter column. Unfortunately, the specific details of each column were not given. However, of the details that were

provided, the amplitude-frequency products and the flow rates were typical of many commercial installations. Their approach, which is a modified combination of the work of Thornton (71), Nicholson (55) and Groenier, et al. (28) is worth examining in some detail since they reported very excellent agreement between their data and their correlation; however the data in the paper are too incomplete to permit a critical analysis of their results.

They observed that, at a fixed value of the amplitude-frequency product, the dispersed phase holdup was a linear function of the relative drop velocity with respect to the continuous phase (the "slip" velocity, v_s) according to the relation,

$$v_s = v_{sf} - A (\epsilon_d - \epsilon_{df}) \quad (6.24)$$

where

$$v_s = \frac{v_d}{\epsilon_d} + \frac{v_c}{1 - \epsilon_d} \quad (6.25)$$

They further noted that the flooding velocities could be related to the amplitude-frequency product by the equation,

$$v_{df} + v_{cf} = \frac{F}{af + C} \quad (6.26)$$

The constants A, B, and C in Equations 6.24 and 6.26 were then evaluated to provide the best fit of the experimental data. They found that when the continuous phase wet the plates that the constant A was positive and the slip velocity decreased with increasing dispersed phase holdup. On the other hand, if the dispersed phase wet the plates, the constant A was

negative, the slip velocity increased with increasing holdup, and Equations 6.19 and 6.21 were not suitable for correlation. The approach is interesting but, as mentioned earlier, very limited data were presented in their paper. It would be most useful if more of their work could be examined in greater detail.

6.2. Analysis of holdup data and correlations

Of the three major studies of dispersed phase holdup in pulse columns, the most promising approaches in the literature appear to be those of Thornton and of Miyauchi. The success of Thornton's "characteristic velocity" approach is somewhat controversial. Groenier, et al (28) report that the approach is valid. Rouyer, et al (64) also report that their modified correlation technique gave a very good correlation, but insufficient data are available to reach a definite conclusion. On the other hand, Miyauchi and Oya (51) found that, in attempting to obtain a correlation using the characteristic velocity approach of Thornton that their data showed significant scatter in the region of high pulsation, or at values of the parameter ψ greater than about 0.2. They therefore worked in terms of a "slip velocity". Actually, although Rouyer, et al claim to have used Thornton's approach, they in fact also used a slip velocity.

Godfrey, et al (27) feel that, for agitated columns, a better relation between slip velocity, characteristic velocity, and dispersed phase holdup is,

$$v_s = \bar{v}_0 (1 - \epsilon_d)^n$$

where both $\bar{v}_0$ and n must be determined experimentally. Similarly, Misek, in work cited by Landau and Houlihan (41), has proposed the relation,

$$v_s = \bar{v}_0 (1 - \epsilon_d) \exp [\epsilon_d (\frac{K}{k} - 4.1)]$$

to account for the coalescence effect of droplets in the column. The parameter, K , is called a coalescence coefficient and k is a velocity exponent which relates the mean drop diameter and the terminal settling velocity of the drops.

It appears that in many cases an effect probably related to drop coalescence becomes important at higher holdups. Both Landau and Houlihan (41) and Korchinsky (40) have found instances where the use of Thornton's basic approach gives results quite different from reported experimental data. Thus, based on information available in the literature, the use of Thornton's characteristic velocity concept has met with varying degrees of success. Much more recent data by Engler (20) shows that Thornton's characteristic velocity is not constant for their work. The basic idea is attractive but more work needs to be done to resolve the cause of the varying results obtained by different investigators.

Although the work of Miyauchi and Oya has been used by others less frequently than that of Thornton, it has an equally sound basis and may well be useful. However, a close examination of the correlation presented in their paper (51) showed that not all the results reported by the investigators whose data were cited were used in obtaining their correlation. When all the data from the papers cited are plotted, as shown in Figure 5, the apparent scatter is greater. Their correlation, given earlier as Equations 6.16 and 6.17, is shown by the dotted line on Figure 5. Although the data are quite scattered, the additional points in the range $\psi = 0.01$ to 0.05 show that the holdup increases at low values of the amplitude-frequency

Figure 5. Comparison of the proposed holdup equation with Miyauchi's equation and experimental data.

product. This is known from both theoretical and experimental work and represents pulse column in the mixer-settler region. These points were not plotted in the paper by Miyauchi and Oya, hence their equation continues to decrease with decreasing values of ψ .

A least squares fit of the data gave the following equations

$$\epsilon_d = 0.0073 V_d^{2/3} \psi^{-0.9485} \quad \psi < 0.09 \quad (6.27)$$

$$\epsilon_d = 1.4703 V_d^{2/3} \psi^{1.1515} \quad 0.09 < \psi < 0.3 \quad (6.28)$$

$$\epsilon_d = 1.058 V_d^{2/3} \psi^{0.856} \quad \psi > 0.3 \quad (6.29)$$

The curve was broken into three segments for a particular reason. If one is evaluating the usefulness of the correlation for application to pulse column models for nuclear fuel reprocessing studies then only a limited range of the variable ψ is of interest. This can be seen from an examination of the design and operating variables for pulse columns used at Richland, Washington and also those used in other parts of the world since many of the other plants were designed from the same data. The information shown in Table 2 was obtained from the Purex Technical Manual (59) and from telephone conversations with personnel at Richland. Considering that the basic Purex process still closely resembles the most probable process for the foreseeable future, this information should still contain the key elements of current pulse column design and Purex flowsheet conditions. It should also remain a reasonable estimation for possible flowsheet modifications for co-extraction where U and Pu are never separated in pure form, modifications for isolation of the actinides in future waste handling flowsheets,

Table 4. Design and operating parameters of purex pulse columns at the Hanford plant^a

Column type	Active height (ft)	Inside diameter (in)	Amplitude (in)	Frequency (cyc/min)	Disp. phase flow (gal/hr-ft ²)	Cont. phase flow (gal/hr-ft ²)	Direction of transfer	Flow rate ratio ^b	Volume velocity (gal/hr-ft ²)	Cartridge type
1A, 1A, 2P	13.5 (Extr.)	24 (Extr.)	1.1 (Extr.)	40-50	375 (O)	155 (A)	A O	2.42	530	Standard ^c
	13.2 (Scrub)	32 (Scrub)	0.6 (Scrub)		210 (O)	30 (A)	O A	0.14	240	
HC, 2E	18.0	34	0.53	40-50	330 (A)	180 (O)	O A	1.93	510	Fluorothene ^d
IC	18.0	34	0.53	40-50	330 (A)	220 (O)	O A	1.50	550	Fluorothene
IOX	28.0	27	0.84	40-50	355 (O)	25 (A)	O A	0.07	380	Standard
1B5	13.3	8	0.84	40-50	550 (O)	275 (A)	A O	2.00	820	Standard
2d	21	7	1.1	40-50	160 (O)	90 (A)	O A	0.56	250	Standard

^aFrom information contained in HW-31020 (Del.), "Purex Technical Manual" (41).

^bBased on direction of transfer.

^cTwo inch plate spacing, one-eighth inch holes, 23 percent free area, stainless steel.

^dFour inch plate spacing, three-sixteenths inch holes, 23 percent free area, fluorothene.

and the possible use of Th-U cycles.

The column diameters shown in Table 2 range from 7 to 34 inches and have processing capacities of about 10 tons of U processed per day. The columns built at the Nuclear Fuel Services plant at West Valley, New York range from 4 to 10 inches in diameter and will handle about one ton of U per day. At the Eurochemic plant in Belgium (29) the columns are 4 to 6 inches in diameter (one column, the IBS scrub column, is only 2 inches). Thus, in a plant, column diameters over the ten-fold range of about 3-30 inches are to be expected.

Using the data from Table 2, values of ψ and of holdup were calculated using Miyauchi's correlation. The results show that, for actual plant columns, the values of ψ fall within the range of 0.1 to 0.30 which according to the literature data analyzed for this survey is the range of greatest accuracy for the correlation, especially for physical systems most closely resembling those used in nuclear fuel reprocessing. With this in mind, one can see that, for constant physical properties and constant column geometry, the equation of Miyauchi and Oya reduces to,

$$\epsilon_d = K (af) v_d^{2/3} \quad (6.27)$$

whereas, the equation of Bell and Babb becomes,

$$\epsilon_d = K (af - K_1)^2 v_d \quad (6.28)$$

Similar analyses of the equations of Thornton and of Rouyer, et al yield cubic equations in ϵ_d . The solutions are straightforward but tedious and give three roots whose properties are functions of pulse amplitude, pulse

frequency, and flow rates. These are being analyzed to find those real solutions that are consistent with typical ranges of the operating variables in order to compare the results with Equations 6.27 and 6.28.

6.3. Conclusions and recommendations

The published correlations to date yield somewhat questionable results as a means of predicting dispersed phase holdup in extraction columns used for nuclear fuel reprocessing. There appears to be three principal reasons for this. First, much of the data were obtained from experiments with very small columns. Second, most of the physical systems used do not have physical properties similar to those liquids used in nuclear fuel reprocessing operations. Third, the correlations obtained give quite different results when applied to the same data, probably because the cause and effect relations have not yet been properly accounted for.

The most efficient method of developing a holdup correlation for use in a pulse column simulation model for fuel reprocessing would appear to be to use pulse amplitude, pulse frequency, dispersed phase flow rate (and probably continuous phase flow rate) to obtain the basic correlation and then correct for physical property changes through the use of operating temperature as the correlating variable. New holdup data being obtained by personnel at General Atomics Corporation and at Allied-General Nuclear Services will provide independent sets of data from which such a correlation can be obtained. Meanwhile, the corrected equations of Miyauchi and Oya (Equations 6.27, 6.28, and 6.29) are the most useful.

7. CALCULATION OF BACKMIXING COEFFICIENTS

Backmixing, like holdup fraction, is dependent on column geometry,

operating conditions, and system properties. It increases as the agitation in the column increases. Since pulse column usually operate in the highly agitated emulsion region, backmixing plays an important role.

A rather thorough review of backmixing in pulse columns has been given by Ingham (34) and will not be repeated here. Instead, the most important experimental data and correlations will be discussed and a probable method for including backmixing in the pulse column model will be presented.

7.1. Review of the literature

Burger and Swift (11), in 1953, found that backmixing was quite insensitive to pulse frequency, plate spacing, flow rate ratio, and total column throughput. The most important variables were found to be continuous phase flow rate and pulse amplitude. Mar and Babb (45) first proposed a dimensionless correlation for the continuous phase longitudinal dispersion coefficient. The correlation gave a reported average deviation of 17% from experimental measurements. Contrary to the findings of Burger and Swift, their equation and their experimental results show a fairly strong effect of pulse frequency and only a small effect of pulse amplitude on the dispersion coefficient. The only system property found to be important was the interfacial tension. Kagan, et al (36,37) presented data to show that the dependency of the dispersion coefficient on pulse frequency and pulse amplitude was too small in the correlation of Mar and Babb.

In subsequent work, Smoot and Babb (70) used the work of Mar and Babb to estimate the longitudinal dispersion coefficients for inclusion in a mathematical simulation of the concentration profile in a pulse column. They felt, after using the correlation, that it tended to give values that

were 20% to 30% low. In still later work Sehmel and Babb (67) remeasured and recorrelated the longitudinal dispersion coefficient data. This second correlation, however, was later questioned by Bell and Babb (8) who found that it did not agree with their results obtained during a study of dispersed phase holdup in the pulse column. The use of dimensionless groups as a means of obtaining correlations for longitudinal dispersion coefficients thus appears to be filled with uncertainties, probably because of the complex hydrodynamic phenomena involved.

The most satisfying work on backmixing in the pulse column was reported in a series of papers by Miyauchi (49,50,51,52,72). Miyauchi (49) and Miyauchi and Vermeulen (50) compared a differential model in difference form (Equation 4.5) for longitudinal dispersion in extraction columns with a stagewise model with backmixing (Equation 4.3) for a wide range of conditions and established a relation between the two models. By equating the theoretical extent of mass transfer at an infinite number of transfer units for their diffusion model with the limiting extent of mass transfer using the stagewise model they obtained the relation,

$$E_j = \frac{V_j}{\beta} \left(\alpha_j + \frac{1}{2} \right) \quad (7.1)$$

which relates the longitudinal dispersion coefficient E_j in the dispersion model to the backmixing coefficient in the stagewise model as function of flow rate V_j and a term β defined as the number of perfectly mixed stages in each real stage of the column, a real stage being defined as the region between two consecutive perforated plates. Further, they defined the backmixing coefficient, α_j , in Equation (7.1) by the equation,

$$\alpha_j = \frac{a f \epsilon_j}{V_j} \quad (7.2)$$

relating the backmixing coefficient to the flow rates, the amplitude-frequency product, and the holdup, ϵ_j . Equation (7.2) is the ratio of a specific phase backflow caused by pulsing to the main flow of that phase. The important result of their work is that, if longitudinal dispersion coefficients are measured for the continuous phase and if they fit a plot of Equation (7.1) using Equation (7.2) to calculate α_j , then one has a means of computing values of α_j (for a stagewise model) from values of E_j obtained by standard tracer injection techniques in the laboratory. Further, as long as relation (7.1) holds, then α_j can be found from Equation (7.2) which involves only pulse amplitude, pulse frequency, holdup fraction, and superficial flow rate.

Miyauchi and Oya (51) showed that Equation (7.1) did in fact represent their experimental data, but upon critical analysis it is seen that the experimental longitudinal dispersion data were taken on one and two inch diameter columns. It is important, therefore, to search for work done on larger diameter columns to see if the longitudinal dispersion data obtained on them would be consistent with the work of Miyauchi and Oya. Support comes from the work of Kagan, et al (36) in Russia and from Rouyer, et al (64) in France. Kagan studied longitudinal mixing in 2-inch and 12-inch diameter pulse columns having plate spacings of 2, 4, and 6 inches. He found that, for single phase flow in the absence of pulsation, the longitudinal dispersion coefficient was a linear function of the flow rate and as the column diameter and the plate spacing increased the value of the dispersion coefficient also increased. However, when pulsation was applied to the

column at a constant plate spacing the longitudinal dispersion varied linearly with the expression $(af + V_c)$, which is the effective velocity of the continuous phase under pulsation.

For two phase flow, such as occurs in an operating pulse column, Kagan found that above an effective velocity $(af + V_c)$ of 1.8 cm/sec the presence of the second phase had little effect upon longitudinal dispersion in the continuous phase since at higher pulsation intensities the dispersed phase droplets become smaller and their velocity approaches the pulsation velocity. Experimental data for E_c was fitted to the equation,

$$E_c = 0.49 L_0^{0.76} (af + V_c) \quad (7.3)$$

which held for single phase flow over the entire range of their experimental data, and for $(af + V_c) > 1.8$ cm/sec, it also fit their data for the continuous phase in two-phase flow. Now, Miyauchi's equation for the longitudinal dispersion coefficient can be written as,

$$E_c = \frac{L_0}{B} (afE_c + 0.5 V_c) \quad (7.4)$$

which is similar to Kagan's correlation. Further, in the variable ranges of interest for reprocessing plants the pulse velocity (af) is 1.0-2.0 cm/sec while the range of V_c is 0.1-0.2 cm/sec. In other words, (af) is about 10 times as large as V_c . Thus to a good approximation Kagan's equation is,

$$E_c = 0.41 af L_0^{0.76} \quad (7.5)$$

And Miyauchi's equation is,

$$E_c = \left(\frac{\epsilon_c}{\beta}\right) \text{ af } L_0 \quad (7.6)$$

So the basic structure of the two correlations is consistent. Further, ϵ_c has a value of 0.8 to 0.9 while β , according to Miyauchi, should be between 1 and 2. Therefore, ϵ_c/β should be approximately $0.85/\beta$ so for a 2-inch plate spacing the two approximate equations would be,

$$E_c = 1.69 \text{ af } \quad (\text{Kagan}) \quad (7.7)$$

$$E_c = \frac{4.32}{\beta} \text{ af } \quad (\text{Miyauchi}) \quad (7.8)$$

and the value of the parameter β in Miyauchi's correlation should be examined closely to see how it fits into Equation (7.8). His equation for β is:

$$\beta = \frac{0.57 \, m (D_T^2 L_0)^{1/3}}{d_h} \quad (7.9)$$

where m is percent free area of the plates, D_T is column diameter, L_0 is plate spacing, and d_h is the diameter of the holes in the plates.

Miyauchi and Oya (51) found that β ranged from 1 to 2 in their work, but they used only 1-inch and 2-inch diameter columns, and as can be seen from Equation (7.9), a rather strong column diameter dependence exists in their correlation. If a value of β is calculated from Equation (7.9) for the "standard cartridge" geometry used in most pulse columns a 2-inch diameter column yields a β value of 2.095. This is consistent with the work of Miyauchi and Oya since a 2-inch diameter column was the largest one used in obtaining their data. If a β of about 2.56 is used, the correlations of Kagan and of Miyauchi become essentially the same for pulse

columns greater than 3-inches in diameter. This result is further supported by the French work of Rouyer, et al (64) who reported experimentally measured values of E_c in two phase flow with a 24-inch diameter column having very nearly the same plate geometry.

Miyauchi and Oya (51) also measured longitudinal dispersion coefficients for the dispersed phase and found that, at low values of pulsation, longitudinal mixing was significantly affected by Taylor's velocity distribution mechanism but that, as the amount of pulsation applied to the column increased, the measured dispersion coefficients approached the behavior predicted by their equation for the continuous phase. Although much less experimental data are available for dispersed phase backmixing it appears reasonable that for column operation in the emulsion region the correlation of Miyauchi and Oya, as modified to correct the β values, can also be used for predicting longitudinal dispersion in the dispersed phase.

7.2. Conclusions and recommendations

Correlation of backmixing coefficients by dimensional analysis appears to give inconsistent results. The approach of Miyauchi and Oya holds the greatest promise of providing an accurate correlation. Use of the simple relation,

$$\alpha_i = \frac{a f L_i}{V_i}$$

was verified by Miyauchi for small columns but additional work should be carried out on plant sized units. The equation requires an accurate value of the holdup, ϵ_i , in the column. This makes accurate holdup data even more important.

8. CALCULATION OF COLUMN EFFICIENCY

8.1. Review of the literature

The extraction efficiency has usually been expressed in terms of the HTU-NTU concept which is based on the assumption of plug flow in both phases. Although the HETS has sometimes been used in the older literature, it is not a useful quantity for data correlation or analysis and so will not be considered here. With backmixing present, the concepts of HTU and stage efficiencies are somewhat clouded because HTU becomes a function of the contactor length and the backmixing coefficients. Hartland and Mecklenburgh (31) showed theoretically that only when there is low backmixing and the length of the contactor is relatively large can one think in terms of a constant HTU. Therefore, it is necessary to use separate mass transfer coefficients and backmixing coefficients in the simulation model. The true mass transfer and backmixing coefficients must be determined from experiments by measuring the actual concentration profile in the pulse column. In order to evaluate the true overall mass transfer coefficient from experimental concentration profile measurements, Miyauchi and Vermeulen (53) have defined three different NTU's:

- (1) The true NTU as originally proposed by Chilton and Colburn:

$$NTU_{ox} = \frac{k_{ox} a L}{V_x} \quad (8.1)$$

where k_{ox} is the overall mass transfer coefficient, a is the interfacial area, L the column length and V_x the superficial velocity.

- (2) The apparent or plug flow NTU defined in terms of the end concentration of the x-phase with a straight operating line.

$$(NTU_{ox})_p = \int_{X_{in}}^{X_{out}} \frac{dX}{X - X^*} \quad (8.2)$$

- (3) The measured NTU which is based on the true operating line, i.e., the actual concentration profile measured in the column which includes the backmixing effect.

$$(NTU_{ox})_m = \int_{X_o}^{X_{out}} \frac{dX}{X - X^*} \quad (8.3)$$

where X_o is the "concentration jump" from X_{in} at the inlet.

To compute the true NTU for a pulse column from experimental concentration values, the data are commonly interpreted in terms of a differential backmixing model:

$$E_x \frac{d^2 X}{dz^2} - F_x \frac{dX}{dz} - k_{ox} a (X - X^*) = 0 \quad (8.4)$$

and integration of this equation yields the true NTU,

$$NTU_{ox} = \int_{X_o}^{X_{out}} \frac{d\left(\frac{E_x}{F_x} \frac{dX}{dz}\right)}{(X^* - X)} - (NTU_{ox})_m \quad (8.5)$$

Graphical integration of this expression is difficult because of the second derivative. The best method of finding NTU_{ox} is to assume values of it and solve Equation (8.4) for the concentration profile. E_x is found by steady-state tracer injection without interfacial mass transfer. The calculated profiles are then graphically integrated to find $(NTU_{ox})_m$ which are compared and matched with the experimentally determined $(NTU_{ox})_m$. The true NTU_{ox} which corresponds to the measured $(NTU_{ox})_m$ can thus be determined.

In order to obtain the true NTU or the overall mass transfer coefficient for Purex plant columns, apparently the only possible method at present is to determine the NTU_{ox} from experimental measurements on small size pulse columns and then scale them up to large size columns. Unfortunately, such measurements even on small size columns are very few and can be found only in a limited amount of work by Smoot and Babb (69), Kagan, et al (36), Miyauchi, et al (52), Angelino and Molinier (1), Thornton (70), and Loqsdaill and Thornton (43). On the other hand, the plug flow NTU's are much easier to measure and calculate because they only require that the end concentrations in the column be known. Useful $(NTU_{ox})_p$ values obtained from cold tests on Purex plant prototypes and from hot pilot plant tests are contained in the Purex Technical Manual.

To obtain mass transfer coefficients for use in the simulation from presently available literature, one needs a relation between $(NTU_{ox})_p$ and NTU_{ox} . In most of the work concerning these three types of expressions for NTU, correlations have been given relating NTU_{ox} to $(NTU_{ox})_m$. Although this is preferable from a theoretical viewpoint, there is little data available on $(NTU_{ox})_m$ and none on systems related to fuel reprocessing.

Five different approaches to the problem of obtaining true values for the HTU have been presented in the literature and these are summarized below. It should be stressed that these correlations for estimating the extraction efficiency and the true number of transfer units require that the following assumptions be satisfied.

1. Constant, uniform operating conditions, including the flow rates, holdup of both phases and the backmixing coefficients.
2. Constant, uniform physical properties, including the distribution coefficient.

3. Solute only transferred from the raffinate (y phase) to the solvent (x phase).

Smoot and Babb (71) used the techniques of dimensional analysis to obtain the relation,

$$\begin{aligned} \frac{(NTU_{ox})_T}{L_o} = 502 \left(\frac{a f d_h r_y}{v_y} \right)^{-0.4} \left(\frac{v_x}{a f} \right)^{0.43} \left(\frac{v_x}{v_y} \right)^{0.56} \left(\frac{d_h}{L_o} \right)^{0.67} \left(\frac{r_y}{v_y} \right)^{b_5} \\ + \left(\frac{r_x}{r_y} \right)^{b_6} \left(\frac{v_y}{r_y D} \right)^{b_7} \left(\frac{v_x}{m v_y} \right)^{b_8} \end{aligned} \quad (8.6)$$

The constants apply only to the methyl isobutyl ketone-acetic acid-water system. The exponents b_5 through b_8 were not evaluated because of insufficient data. For the specific physical system used, an average deviation of 27% was reported.

Sleicher (69) presented an algebraic expression, based on theoretical work, which contained several functions of the extraction factor λ and the Peclet number for each phase:

$$\frac{(NTU_{ox})_P}{(NTU_{ox})_T} = \frac{P_x P_y}{P_x P_y + (NTU_{ox})_T \theta} \quad (8.7)$$

where $\theta = a P_x + b P_y + c (P_x P_y)^{-5} - d (P_x + P_y)^{-5} + e (P_x - P_y) \exp(-f (NTU_{ox})_T)$ in which a , b , c , d , e , and f are constants tabulated as functions of λ . The number of transfer units in plug flow are evaluated from Equation 8.2 using concentrations in the inlet and outlet streams, and the classic Colburn equation,

$$(NTU_{ox})_P = \frac{\ln \frac{x}{x_f + 1 - x}}{\lambda - 1} \quad (8.8)$$

where

$$\lambda = (x_{out} - y_{in}/m) / (x_{in} - y_{in}/m)$$

is used to find the number of plug flow transfer units. Miyauchi and Vermeulen (52), in another theoretical analysis, assumed that the behavior of $(NTU_{ox})_p$ in the two limiting cases of mass transfer controlling and of backmixing controlling is consistent with the addition of the reciprocals,

$$\frac{1}{(NTU_{ox})_p} = \frac{1}{(NTU_{ox})_T} + \frac{1}{(NTU_{ox})_D} \quad (8.9)$$

where $(NTU_{ox})_D$ is a term called the "number of overall dispersion units", with reference to the x phase. It is a function of λ , P_x , P_y , and probably also $(NTU_{ox})_T$. It was represented by the general form

$$(NTU_{ox})_D = \frac{\ln \lambda}{\lambda - 1} \Phi + (PB)_y \quad (8.10)$$

in which $(PB)_y$ is the overall Peclet group and is defined by the equation

$$(PB)_y = \left(\frac{F}{f_x P_x} + \frac{1}{f_y P_y} \right)^{-1} \quad (8.11)$$

where f_x and f_y are weighting factors and are functions of $(NTU_{ox})_T$ and λ . The values of f_x and f_y , to a reasonable degree of approximation, are given by

$$f_x = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} \lambda^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} \lambda^{-1.5-\alpha}} \quad (8.12)$$

$$f_y = \frac{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} \lambda^{-.5-\alpha}}{(NTU_{ox})_T + k'(NTU_{ox})_T^{2\alpha} \lambda^{+.5-\alpha}} \quad (8.13)$$

where the constants $\alpha = 0$ and $k' = 6.8$ provide the best results.

The coefficient ϕ has been determined from Equations 8.10 and 8.11 and a knowledge of the "exact" $(NTU_{ox})_D$. The expression is

$$\phi = 1 - \frac{.050}{(t(NTU_{ox})_T)^{.5} (PB)_y^{.25}} \quad (8.14)$$

Results of sufficient accuracy, however, may often be obtained by simply setting $\phi = 1$, according to the authors.

In a fourth method proposed by Stemerding and Zuiderweg (72) one uses Equation 8.9 and the definition of HTU can be used to obtain,

$$(HTU_{ox})_D = (HTU_{ox})_T + (HTU_{ox})_D \quad (8.15)$$

where $(HTU_{ox})_D$ is the overall height of a dispersion unit. $(HTU_{ox})_D$ can be determined from the following equations:

$$(HTU_{ox})_D = \frac{1}{p_0 + \frac{.8 \ln f}{L(f-1)}} \quad (8.16)$$

where

$$p_0 = \frac{\frac{0.1L}{(HTU_{ox})_T} + 1}{\frac{0.1L}{(HTU_{ox})_T} + \frac{p_1}{p_2}} p_1 \quad (8.17)$$

and

$$\frac{1}{p_1} = \frac{1}{p_x} + \frac{1}{p_y} \quad (8.18)$$

$$\frac{1}{P_2} = \frac{1}{P_x} + \frac{f}{P_y} \quad (8.19)$$

and, with this information one can find $(HTU_{ox})_p$ from Equation 8.15. In all previous methods the Peclet number used is based upon the column length. This can make design of a proposed column a trial and error procedure since the column length would not be known and the correlations cannot be solved explicitly for the efficiency.

Watson and Cochran (77) developed simple empirical equations for both single and double phase backmixing. This method of estimating η is useful in design studies since it uses only design parameters or directly measurable quantities.

For backmixing in a single phase $x(E_y = 0 \text{ or } P_y = \infty)$ the expression is

$$\eta = 1 - \frac{1}{NP_x + 1 - A + \frac{1}{(NTU_{ox})_p}} \quad (8.20)$$

The equation for backmixing in both phases is given approximately by the following equation:

$$\eta = 1 - \frac{1}{NP_x + 1 - A + \frac{1}{(NTU_{ox})_p}} \quad (8.21)$$

$$- \frac{A}{NP_y - 1 + A + \frac{1}{(NTU_{ox})_p}} \quad (8.22)$$

where $NP_x = (HTU_{ox})_p V_x/E_x$, $NP_y = (HTU_{ox})_p V_y/E_y$, $F = V_x/mv_y$, and $(NTU_{ox})_p$ can be calculated from Equation 8.8.

It was reported that the efficiencies estimated by this method do not

deviate from the exact calculated values by more than .06 to .07 when

$$(\text{NTU}_{\text{ox}})'_T \geq 2 \quad (8.23)$$

$$n \geq .2$$

Therefore column efficiency can be solved for explicitly by this method because the design parameters are not based upon the column length. The required column length can be predicted from the following expression:

$$L = \frac{(\text{NTU}_{\text{ox}})'_D (\text{NTU}_{\text{ox}})'_T}{n} \quad (8.24)$$

8.2. Conclusions and recommendations

The methods of Miyauchi and Vermeulen (53) and of Watson and Cochran (77) appear to be the most useful. All five reported methods were tested against experimental data for the methyl isobutyl ketone-acetic acid-water system as presented by Smoot and Babb (71) since theirs is the only substantial amount of experimental data available. Data from forty experimental runs were used. The results from the two methods given above were very close to each other, the values of $n = (\text{NTU}_{\text{ox}})'_D / (\text{NTU}_{\text{ox}})'_T$ differing from each other by only 0.06-0.07. The method of Miyauchi and Vermeulen is quite complex in use while that of Watson and Cochran is much easier to use and has the advantage that it is not a function of column length. The average deviation between the $(\text{NTU}_{\text{ox}})'_T$ calculated from experimental data and that estimated by these two approximation methods was ± 0.13 for typical values of $(\text{NTU}_{\text{ox}})'_T$ in the range of 1.00 to 6.00. These results would seem to indicate that the approach of Watson and Cochran could indeed be a very useful way of computing $(\text{NTU}_{\text{ox}})'_T$. A note of caution is necessary, however, since

Korchinsky (40) attempted to use the formulas of Watson and Cochran and obtained a negative column height for some combinations of variables. If the work were tested against the limited range of variables encountered in nuclear fuel reprocessing, however, it should prove useful.

9. PROCESS CHEMISTRY

In the partitioning of U from Pu by solvent extraction the Pu must be selectively reduced from Pu(IV) to Pu(III). Since the reduction is carried out in an oxidizing environment the reduction reaction chemistry is quite important in assuring stable chemical conditions in the column. Of the many reactions which take place, the five listed in Section 4.2.3 were considered to be the most important. The Pu(IV)-hydroxylamine reaction is responsible for the partitioning. It is aided to some extent by the Pu(IV)-hydrazine reaction. At higher plutonium concentrations stable column operation may depend on the relative importance of the Pu(III)-nitric acid reaction. This autocatalytic oxidation is controlled primarily by the addition of hydrazine to the column. Hydrazine destroys nitrous acid which is both a product of and a catalyst for the Pu(III)-nitric acid reaction. Some nitrous acid control can also be achieved by the reaction of hydroxylamine with nitrous acid, but experiments have demonstrated that hydroxylamine alone cannot effectively control the nitrous acid, hence the hydrazine is added. The autocatalytic oxidation is most important at high plutonium concentrations. The following reactions and rates represent the best estimates of some of the reactions. Much work remains to be done to verify some of them not only according to rate but also stoichiometry.

9.1. Rates and stoichiometry of key reactions

Reaction 1: Pu(IV)-hydroxylamine

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

where

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

$$K_d = 0.19$$

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 (3). 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

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

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

Stoichiometry:

This destabilizing nitric acid-Pu(III) oxidation reaction is reported in Cleveland (12) from which the rate expression was taken although further

work was done by Klem (38) to define the stoichiometry. With nitrous acid as one of the products, the autocatalytic nature of the reaction is evident.

Reaction 3: Pu(IV)-hydrazine

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

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

Stoichiometry:

Little information is available on the Pu(IV)-hydrazine reduction reaction.

Because the reaction has largely been ignored, both the rate expression shown above and developed from data given by Cleveland (12) and the stoichiometry of the reaction are estimates. The assumed 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 reaction (5).

Reaction 4: Nitrous acid-hydrazine

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

$$k = 0.234$$

Stoichiometry:

Although the nitrous acid-hydrazine reaction is the essential controlling reaction in the separation process, it has received little attention in the literature. The rate data shown above were taken from Biddle and Miles (9) and the stoichiometry shown was developed from work done at Atlantic Richfield (38).

Reaction 5: Nitrous acid-hydroxylamine

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

where

$$f(\mu) = 10^{(0.91\mu^{1/2} - 1.521)}$$

μ = aqueous solution ionic strength

Stoichiometry:

Of importance for nitrous acid control is the hydroxylamine-nitrous acid reaction. The data shown were taken from the work of Barney (4).

The quantity μ is the ionic strength of the aqueous phase.

9.2. Conclusions and recommendations

The chemistry of the partitioning and stabilizing reactions are not well understood and more work is required to produce accurate knowledge of them. While those given are probably reasonable, they should not be regarded as definitive, particularly the Pu(IV)-hydrazine, HNO_2 -hydrazine, and HNO_2 -hydroxylamine reactions. Additional work in this area must surely be done, not only to define the chemistry but also to study the quantitative effects of this complex reaction system as it affects chemical stability in the column and also the rate of interphase transfer of the species involved.

10. TABLE OF NOMENCLATURE

- a = pulse amplitude, peak-to-peak (length/cycle); interfacial area per unit volume in Equations 4.1 and 4.2.
- c = drag coefficient for spheres (dimensionless).
- D = molecular diffusivity (length²/time).
- d_h = diameter of holes in sieve plates (length).
- E = superficial longitudinal dispersion coefficient, (length²/time).
- F = volume flowrate of a given phase in the column (volume/time).
- $\bar{F}$ = volume rate of backflow of a given phase in the column (volume/time).
- f = pulse frequency (cycles/time); constant in Equation 8.7.
- g = acceleration due to gravity (length/time²).
- g_c = gravitational conversion factor (mass x length/force x time²).
- H = aqueous phase holdup per stage or volume fraction of aqueous phase between two consecutive sieve plates (volume).
- h = organic phase holdup per stage or volume fraction of organic phase between two consecutive sieve plates (volume).
- k_o = overall mass transfer coefficient (length/time).
- L = total active height of the column (length).
- L_o = distance between two consecutive sieve plates (length).
- m = distribution coefficient; organic phase concentration/aqueous phase concentration (dimensionless).
- NP = Peclet number using (HTU_{ou})_p for characteristic length (dimensionless).
- P = Peclet number, V_iL/E_i (dimensionless).
- s = fraction of free area of sieve plate (dimensionless).
- t = time.
- V = superficial linear velocity through the column for a given phase (length/time); total volume of liquid in a stage or between two consecutive sieve plates.

- $X_{a,i}$ = aqueous phase concentration in stage i (moles/volume).
- $X_{o,i}$ = organic phase concentration in stage i (moles/volume).
- Z = axial distance along the column measured from the top end (length).

Greek letters

- β = ratio of backflow to main flow in stagewise model (dimensionless); empirical constant in Equations 8.12 and 8.13.
- β = number of perfectly mixed stages in each real stage of the column and defined by Equation 7.9.
- β = maximum frictional power adsorbed per unit mass of fluid in the perforations in the sieve plates.
- γ = interfacial tension (force/time²).
- γ = holdup fraction of a given phase in active length of the column (dimensionless).
- γ = extraction factor, F_a/mF_o or V_a/mV_o (dimensionless).
- ρ = density of a given phase (mass/volume).
- η = viscosity (force/length $\times$ time); ionic strength in equilibrium distribution correlations.

Subscripts

- c = continuous phase.
- d = dispersed phase.
- i = phase i (stage i if i is the second subscript in a double subscripted variable).
- m = measured value.
- p = ~~plus~~-flow value.
- T = true value.
- x = phase x .
- y = phase y .

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