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REMOVAL OF ACTINIDES FROM ICPP FUEL REPROCESSING WASTES ENGINEERING STUDIES TERMINAL REPORT

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ABSTRACT

This report describes the engineering development work for a process to remove actinides from ICPP nuclear fuel reprocessing wastes. These wastes contain small amounts of actinides, primarily plutonium and americium. Removal of these actinides is one option being evaluated as a long-term disposal alternative. A solvent extraction process has been developed which successfully separates these actinides. Four major areas of development were examined in detail, namely the process chemistry, simulated column studies, miniature mixer-settler experiments, and pilot plant tests. Actual radioactive wastes containing actinides were used in several of these tests, though an actinide simulant (cerium) was used in the pilot plant experiments. Therefore, the relationship between actinide extraction and cerium extraction was also examined. As a result of these studies, a process was developed that will extract actinides from ICPP wastes using pulsed, sieve plate extraction columns. The resulting actinide free waste (after solidification) will be below ten nanocuries of actinides per gram, a Federal limit for transuranic waste. In addition, the Height of a Transfer Unit (HTU) was selected as being the better measure of pulse column separation efficiency than the Height Equivalent to a Theoretical Stage (HETS). Determination of column flooding, solvent cleanup and recycle considerations, and HTU/HETS calculations are also discussed.

SUMMARY

Engineering development work relating to the removal of actinides from nuclear fuel reprocessing wastes at the ICPP is described in this report. The objective of this work was to (1) develop a process to remove actinides from ICPP waste so that the final calcine contained less than 10 nCi actinides per gram of waste, (2) test the feasibility of the process in engineering equipment, and (3) obtain the engineering data necessary to establish the feasibility of building a full-scale actinide removal process. To accomplish this, the initial work concentrated on finding an extractant that preferentially extracted trivalent actinides from the nuclear wastes generated at the Idaho Chemical Processing Plant (ICPP). After many tests, the extractant, dihexyl-N, N-diethylcarbamylmethylenephosphonate (DHDECMP) diluted to 20% by volume with a 2:1 mixture of decalin and diisopropylbenzene, was found to extract these actinides. Information on solvent solubilities, toxicity, degradation, and cleanup was also collected.

Since the extractant proved favorable, simulated column experiments were conducted to collect distribution coefficients in the extraction, scrub, and strip operations. From tests using plutonium and americium, it was concluded that: (1) the extractable species behave as ideal solutes, as evidenced by the straight equilibrium lines; (2) the extraction and scrub sections operate efficiently, because of pinches for actinides in the scrub section and for HNO_3 and Zr in the extraction section; (3) two stages of scrubbing remove the coextracted Zr; and, (4) an actinide free raffinate can be produced. The pregnant organic was effectively stripped in a five stage simulated column.

In another test using miniature mixer-settlers in a small hot cell, extraction of actinides from actual radioactive coprocessing solution was demonstrated. This test proved that the concentration of actinides remaining in solution will produce a calcine below the federal transuranic waste limit of ten nanocuries of actinide activity per gram (10 nCi/g).

The last step in the development program was to demonstrate the process in pilot scale equipment. Due to their use in the nuclear industry, pulsed, sieve plate extraction columns were chosen as the contacting equipment for this process. Because of the location of the pilot plant, a nonradioactive simulant for the actinides, cerium, was used in these experiments. Further tests were run on the extraction efficiencies of pulse columns for the additional actinide simulants thorium and uranium. Additional pilot plant tests included flooding experiments, extraction, scrub and strip tests using cerium, and the effect of pulse column operating conditions on column efficiency.

The conceptual flowsheet shown in Figure 1 is the result of this development work. In this figure, there are three basic operations which are described in detail in this report. These three operations are 1) extraction of the actinides, 2) back extraction or stripping, and 3) solvent cleanup and recycle. In addition, the Height of a Transfer Unit (HTU) was determined to be a better indicator of column performance than the Height Equivalent to a Theoretical Stage (HETS). Consequently, the extraction column height was designed on an HTU basis. The extraction column height, including scaleup, is 4.0 metres. The scrub column should be 2.5 metres and the first strip column height is 3.0 metres. Further development is required to size the remaining unit operations and to fully establish process chemistry.

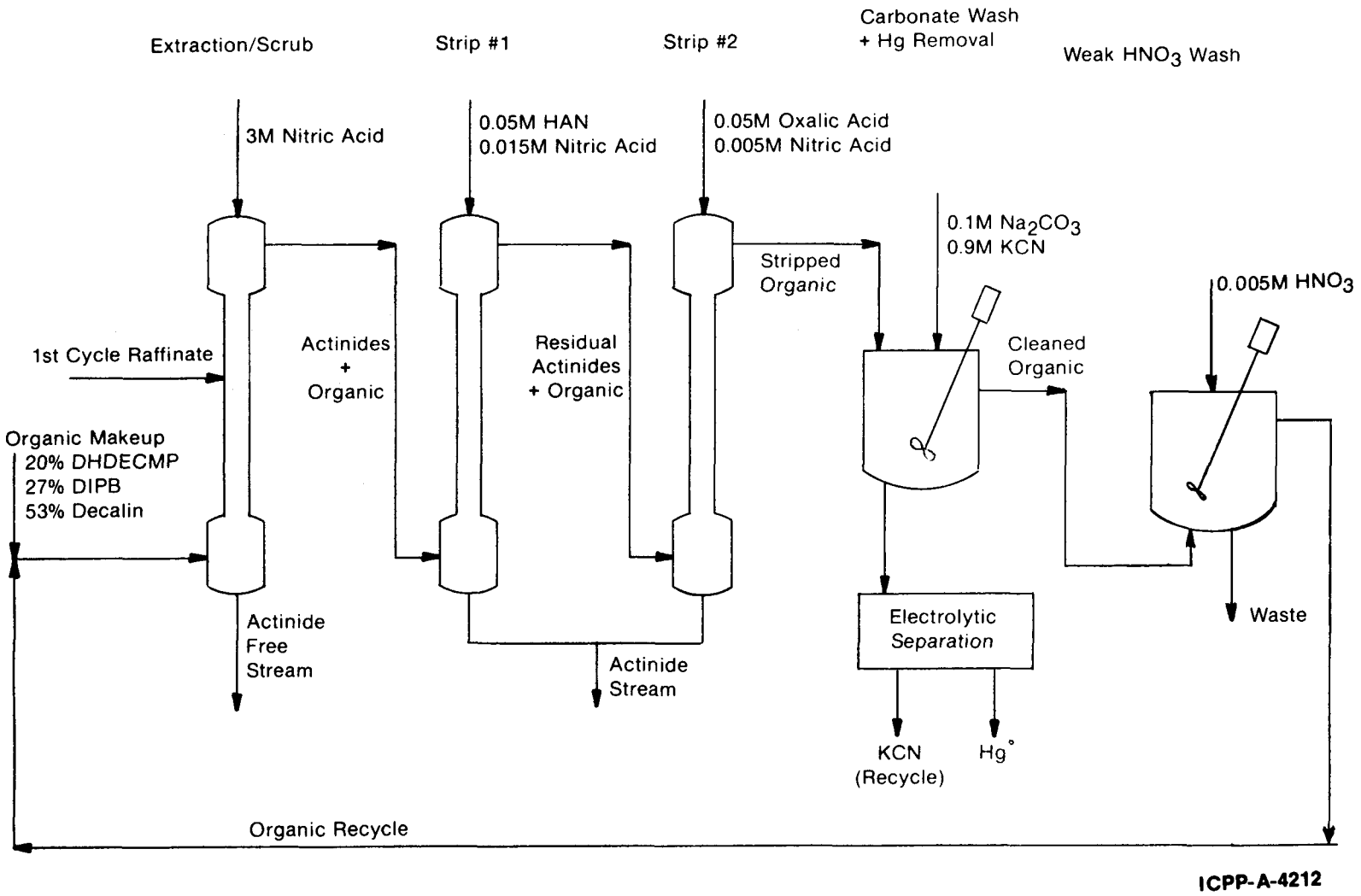

Figure 1. Conceptual Actinide Removal Process

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I. INTRODUCTION

1. Characterization of ICPP Actinide Waste

The Idaho Chemical Processing Plant (ICPP) is one of many facilities located at the Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho. The purpose of the ICPP is to safely process irradiated nuclear fuel from test, research, and naval reactors for the recovery of fissionable uranium (U). During reprocessing, nuclear fuel is dissolved into acidic solutions that are separated by extraction into one stream containing the fissionable U and a second containing the radioactive fission products, cladding components, chemical additives, and actinides.[1,2] The latter is referred to as high-level liquid waste (HLLW). The composition of one type of HLLW, called coprocessing raffinate is shown in Table I. The acidic HLLW is stored in stainless steel tanks until it can be converted to a free-flowing granular solid, called calcine, in a fluidized-bed. The volume and mobility of the waste are reduced significantly by its conversion to calcine. The calcine has been stored in stainless steel bins located in reinforced concrete vaults built on bedrock and extending to the surface. These bins have a projected service life of greater than 500 years.[3]

TABLE I

TYPICAL COMPOSITION OF ICPP COPROCESSING RAFFINATE

Macroconstituents		Actinides, g/ℓ	
H^{+}, M	1.62	Total U	2.0×10^{-4}
Al^{+3}, M	0.67	^{237}Np	1.24×10^{-5}
Zr^{+4}, M	0.45	^{238}Pu	3.70×10^{-4}
F^{-}, M	3.21	^{239}Pu	1.09×10^{-3}
B^{+3}, M	0.20	^{240}Pu	2.92×10^{-4}
NO_3^{-}, M	2.36	^{241}Pu	1.29×10^{-4}
Lanthanides, g/ℓ	0.20	^{242}Pu	4.33×10^{-5}
Hg^{+2}, M	0.002	^{241}Am	3.53×10^{-5}
		^{243}Am	9.77×10^{-7}
		^{244}Cm	5.87×10^{-7}

Calcine, despite its volume and mobility advantages compared to HLLW, may be only an interim solution to the waste management problem. Several total disposal methods are being investigated, including vitrification of the calcine as well as the removal of actinides from the waste. The reason for actinide removal can be seen from the decay curve for actinides as shown in Figure 2. According to federal guidelines,[4] nuclear waste is classified as a transuranic waste if the actinide activity is greater than ten nCi/g. Figure 2 illustrates that, without the removal of the actinides, the actinide activity in the calcine is greater than

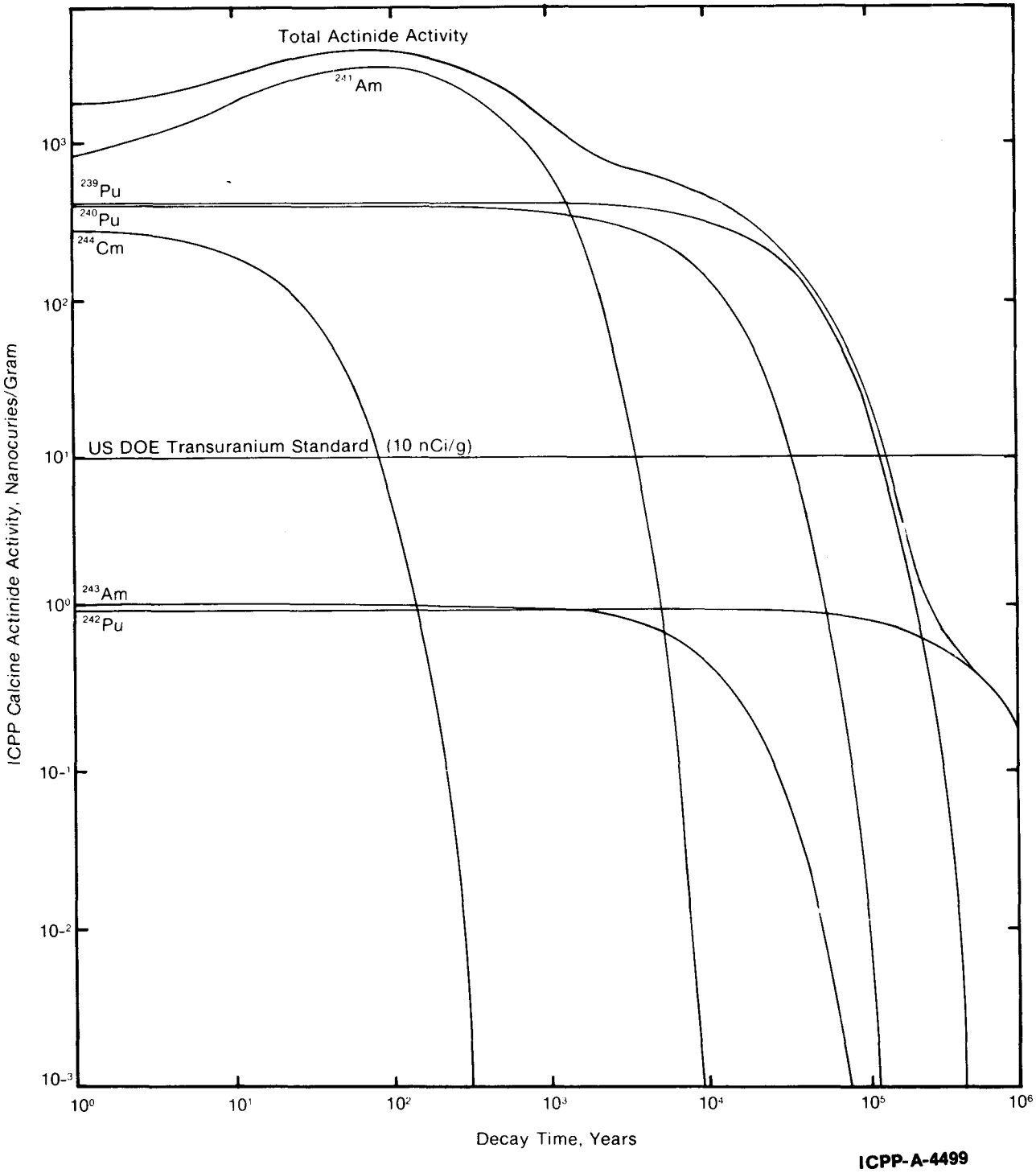

Figure 2. Actinide Decay in ICPP Calcine

10 nCi/g for over 100,000 years. If the actinides were removed from the calcine so that it could be classified as being "actinide free" or non-transuranic, the fission products could be stored in the existing storage facilities until they decay to acceptable levels. The decay time for the actinide depleted fraction is within the same time frame as the service life of the bin sets. The actinides would be sent to a geologic repository for disposal, or they would be fissioned as fuel in fast reactors. The reduced volume of waste requiring shipment to geologic storage would result in a significant decrease in transporation and storage cost for that site.

The "hazard index" is another method of classifying dangerous substances. The hazard index is defined as the number of dilutions of a material required to achieve safe drinking water. Figure 3 shows the actinide hazard index of ICPP calcine compared to natural ore deposits, including thorium deposits in the Lemhi Mountains of Southeastern Idaho. The removal of actinides from ICPP calcine reduces the hazard index of the calcine, when compared to the actinide-bearing calcine, principally after 1000 years, at which time most of the fission products have decayed. Figure 3 shows that: (1) ICPP calcine is hazardous for a long time, even with the actinides removed, (2) natural mineral deposits can be more hazardous than the calcine, and (3) there is some residual hazard in the calcine. This residual hazard is due to the chemical content of the calcine.

2. Actinide Removal - A Waste Management Strategy

In a separations process where actinides are removed from HLLW, two separate streams are produced, one with and one without actinides. The actinide fraction in liquid form, which would be approximately five to ten percent of the initial waste volume, could be disposed of in several different ways. These include solidification and burial in a repository, recycle to a fast fission reactor, or some type of special disposal such as space or seabed disposal.[5] Using either the hazard index or the 10 nCi/g limit as a waste management guide, the actinide-free fraction could be stored in existing surface facilities as mentioned above. One basic assumption in this scenario is that actinide-free waste can be stored onsite at the ICPP. If this is not allowed, then all waste will have to be transported to a federal repository, and the removal of actinides would not be advantageous.

There are several potential advantages in implementing the actinide removal process at the ICPP. First, it removes actinides from the proximity of the Snake River Plain Aquifer and eliminates potential releases to the environment. Second, the smaller volume of waste being shipped to a federal repository would result in lower shipping costs, including fewer and lighter shipping casks being used. Third, less repository space will be taken up by the actinide fraction then would be taken up by the short-lived beta-gamma waste, decreasing disposal costs to a small percentage of the cost of disposing of the bulk of the waste geologically. (Both shipping and storage costs are significant.) Fourth, fission product wastes could be stored in the existing calcine bins. Thus, waste storage costs would be reduced since geologic repository storage costs are greater. These advantages assume actinide storage at a Federal Repository. If however, the actinides were recycled to a reactor, there is the additional advantage that actinides would be converted into fission products which decay in approximately 500 years.

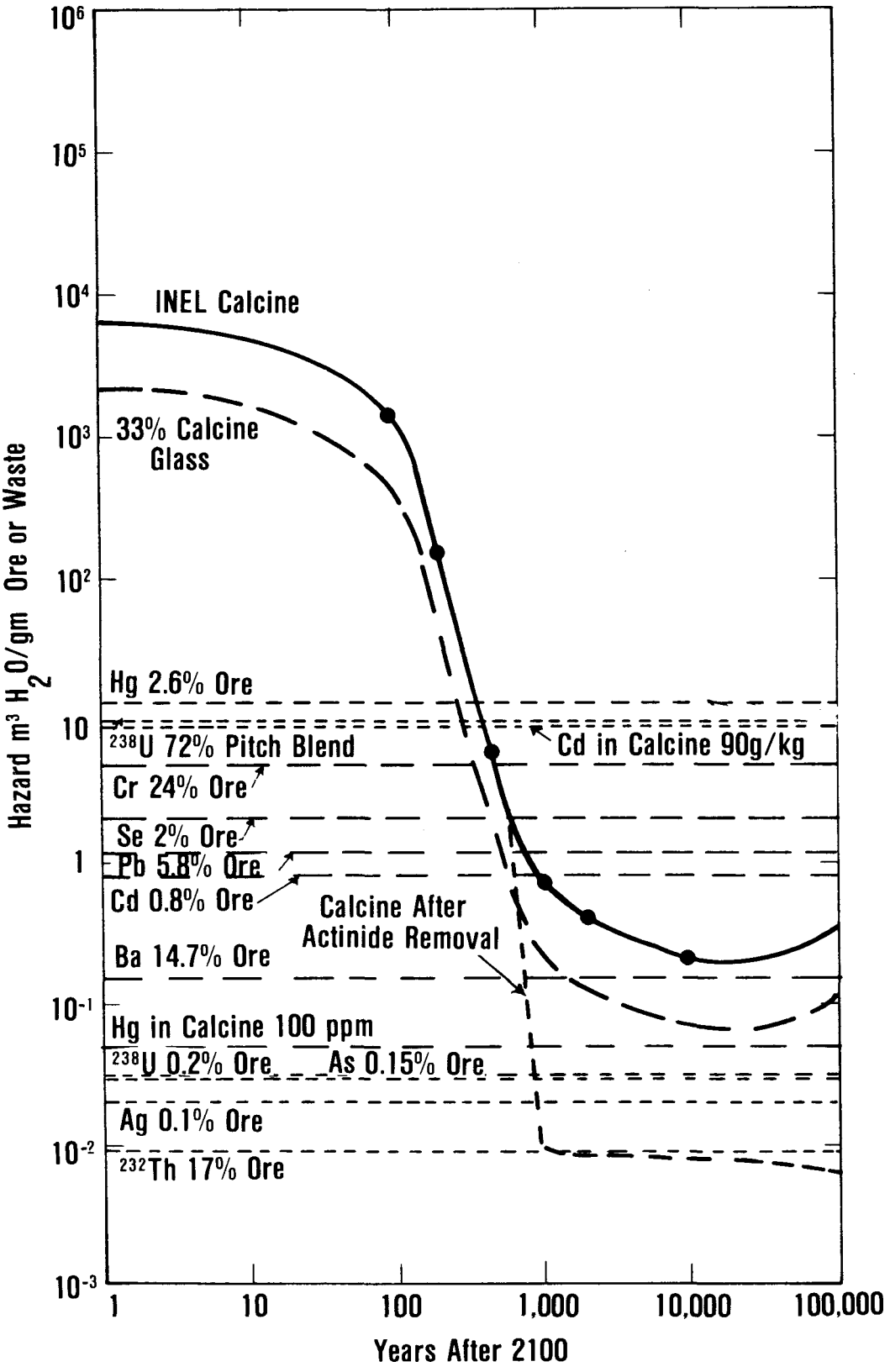

Figure 3. Hazard Comparisons for Various Waste Forms and Average Ores

There are also several potential disadvantages to implementing the actinide removal option. First, the bulk of the radioactive materials remain stored in Idaho. This issue has not been formally addressed, but it may be politically unacceptable. Second, increased handling and processing results in more routine releases of radioactivity to the environment, plus increased operating and equipment costs in reference to the present stratagy of bin storage of calcine. A third disadvantage is concerned with the dispositon of the present calcine, produced since 1963, that already has actinides present. This stored calcine may have to be dissolved, the actinides removed, and the waste recalcined. This lengthens the time needed for actinide disposal, increases the amount of waste generated, and complicates the management of nuclear waste. If not dissolved, then storage of the actinide bearing calcine would have to be acceptable, or the entire mass would have to be shipped offsite.

A comparison of the expected doses, risks, and costs of several ICPP waste management strategies, including actinide removal, are presented elsewhere.[6] Actinide removal could be implemented with other waste management options including calcine vitrification or pelletization.[7,8,9] In fact, both the actinide stream and the "actinide free" waste would benefit if they were made into these leach resistant forms. A summary of the costs of two options are presented in Table II. The first option is to ship all the calcine off-site. The second option is to remove the actinides, ship these offsite as a solid, and to store the actinide-free calcine onsite. These costs are only relative costs based on limited data and design. Future waste storage requirements may change their values.

TABLE II

COMPARISON BETWEEN ACTINIDE REMOVAL AND REPOSITORY DISPOSAL COSTS (COSTS IN MILLIONS OF DOLLARS)

	Option 1 Ship all calcine (as glass)	Option 2 Ship Only Actinide Fraction
Facility Cost		
Retrieval	5	5
Processing	30	150
Storage at ICPP	—	100
Operating Costs (manpower)	55	85
Materials	176	83
Utilities	1	3
Decontamination	3	10
Canisters	173	2
Casks	60	2
Transportation	140	3
Repository Costs	293	1
Total	936	444

3. Research and Development Program

The object of the pilot plant development described in this paper was to obtain the engineering scale-up information necessary to establish the feasibility of building a full-scale actinide removal process. The result of this development is the flowsheet, shown in Figure 1. The three basic operations shown include actinide extraction, stripping, and solvent cleanup. Each of these will be discussed in detail, including the work that was necessary to develop the flowsheet. Other aspects of the actinide removal scheme, such as their recycle to a reactor, are described in detail elsewhere.[10]

II. CHEMISTRY OF THE ACTINIDE REMOVAL PROCESS

1. Extractant Selection, Known Sources, and Purification

Development of a process to remove actinides from ICPP fuel reprocessing wastes was started in 1973. A literature survey disclosed a class of compounds first synthesized by T. H. Siddall in the 1960's.[11] From these compounds the bidentate organophosphorus compounds Dihexyl-N, N-diethylcarbamylmethylenephosphonate (DHDECMP) and its dibutyl homologue (DBDECMP) were chosen as the potential extractants. The chemistries of these extractants are similar to tributylphosphate (TBP) which has been used as an extractant in nuclear fuel reprocessing for many years. Unlike TBP, DHDECMP and DBDECMP are selective for the trivalent actinides as well as the higher valent plutonium (Pu) present in ICPP wastes.

The molecular structure of DHDECMP is:

$$(C_6H_{13}O)_2 - \overset{O}{\overset{\|}{P}} - CH_2 - \overset{O}{\overset{\|}{C}} - N(C_2H_5)_2.$$

Much of the early chemical development for this program was concerned with selecting an extractant. DBDECMP was used extensively because it was easier to purify by distillation than was DHDECMP. However, DBDECMP proved to be impractical because of its high solubility in aqueous HNO_3 solutions, 60 g/ℓ.[12] Therefore, DHDECMP whose solubility was measured to be 0.13 g/ℓ in 0.005 M HNO_3,[13] was eventually chosen as the extractant for this process. Much of the early work by McIsaac[14] was done using DBDECMP. The two extractants are similar enough in their extraction properties that conclusions about certain properties using DBDECMP may be safely applied to DHDECMP. In addition, the DHDECMP was investigated by Microbiological Associates, Bethesda, Maryland, to determine it's mutagenic potential. These results, which proved negative, are described elsewhere.[15]

Initially, all of the DHDECMP was purchased on a custom-synthesis basis from Wateree Chemical Co., Inc.* Lugoff, South Carolina. Multilitre amounts of technical grade DHDECMP were purchased from Wateree in 1977 for $100 per litre. The technical grade DHDECMP obtained from Wateree contained many impurities, i.e., unreacted starting materials and competitive reaction products.[16] This grade of DHDECMP is unsuitable for use as an extractant because some of the impurities form unstrippable actinide complexes. Large-scale production of adequately pure DHDECMP was not available from Wateree. Such a purification required a vacuum distillation of the DHDECMP to a purity of 86%.[17] In 1978 the Bray Oil Co,* Los Angeles, California was contracted to supply 200 litres of DHDECMP at 86% purity for a cost of $150 per litre. This was then used in the pilot plant without further treatment.

In addition to vacuum distillation several other methods of purifying DHDECMP were tried.[18] Although all the methods worked with some success, a procedure involving precipitation of DHDECMP with mercuric nitrate[19] was found to be easily performed in the laboratory. The procedure is fast, has a high recovery factor (~85%), results in a product of high purity (>95%), and is inexpensive to perform.

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* Purchase of the reagent DHDECMP from Wateree and Bray Oil Companies is not intended to be an endorsement of these companies. Purification by Bray Oil of the Wateree product was done simply because Wateree did not have the vacuum distillation facilities.

2. Extraction Mechanism, Acid and Diluent Effects

Much of the development work for this process was concerned with the effects of acid, percentage extractant, and diluent type upon the flowsheet. By varying the aqueous phase HNO_3 concentration, the direction of actinide mass transfer can be controlled. For example, a high aqueous phase HNO_3 concentration promotes extraction, while stripping of the actinides from the pregnant organic is achieved by a low aqueous phase concentration. This dependency is illustrated in Figure 4. These data were collected using a 30% mixture of DHDECMP in diisopropyl benzene (DIPB). Data for the 20% DHDECMP in the mixed-solvent diluent are similar in form, though slightly lower in value. From Figure 4, it can be seen that, as the HNO_3 concentration is lowered, the distribution coefficient for all of the actinides eventually drops below one. This relation allows the use of a weak HNO_3-hydroxylaminenitrate (HAN) solution to strip the actinides from the pregnant organic. HAN is used as a reductant to facilitate the stripping of plutonium.

McIsaac and Schulz have also reported the dependency of actinide extraction upon the DHDECMP concentration.[20] For Am, three DHDECMP molecules are thought to be associated with each Am molecule. This dependency was observed by Siddall in extractions of Ce(III) from HNO_3 by dihexyl-N, N-dibutylcarbamylmethylenephosphonate.[21] These studies suggest that Am is extracted as a neutral species by three DHDECMP molecules and by HNO_3 according to equation (1):

$$Am^{+3}_{(aq)} + 3NO_3^-{}_{(aq)} + 3DHDECMP_{(org.)} \rightleftarrows Am(NO_3)_3 \cdot 3DHDECMP_{(org.)} \qquad (1)$$

While the extraction of the other actinides may differ in detail, they all proceed by the formation of a neutral species and are dependent upon the nitrate and extractant concentrations. McIsaac[22] has also shown that the kinetics of actinide mass transfer are fast, usually within 30 seconds for a single contact.

The 86% pure DHDECMP as received from Bray Oil Co. has a viscosity of 32.9 centipoise and a specific gravity of 1.0 at 20°C. For the sake of simplicity in making volume percent dilutions, the 86% DHDECMP was considered to be pure. From equation (1), it would seem desirable to have as high a concentration of the extractant in the solvent as possible. For two major reasons, however, the extractant concentration must be limited. First, strip distribution coefficients favor the organic phase if the extractant concentration is too high, necessitating a taller strip column. Second, DHDECMP is too viscous and dense for use in process equipment. This DHDECMP is mixed with other organics, called diluents, to produce the organic solvent used in this process. McIsaac[23] has found that aliphatic diluents generally give high distributions for actinides but form a second organic phase, even at low ($\sim$3M) acidity. (Solvent extraction equipment could not be operated efficiently with a second organic phase present.) Aromatic solvents, when used as diluents, are free of the second organic phase, but result in lower actinide distribution coefficients. Of the many diluents tested, a mixture of decalin and diisopropyl benzene (DIPB) was found to give the most favorable distribution coefficients without the formation of a second organic phase.

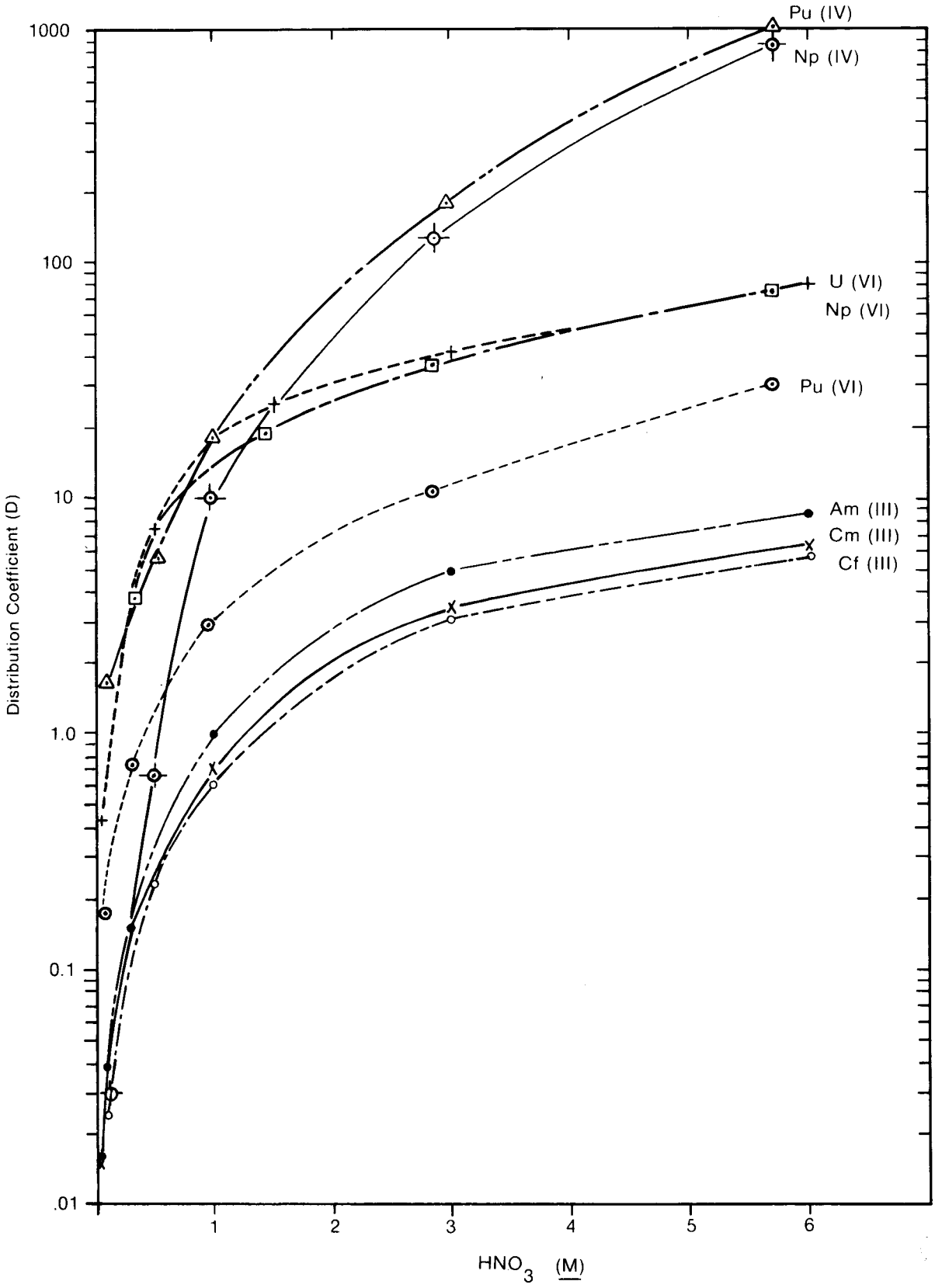

Figure 4. Extraction of +3, +4, and +6 Actinides From HNO_3 Solutions by 30% DHDECMP-DIPB Solvent

ICPP-A-3112

A 20% by volume DHDECMP solution in a 2:1 mixture of decalin-DIPB has a density of 0.9 and a viscosity of 3.0 centipoise at 20°C. The hydraulic properties of the system have proven to be acceptable in pilot plant operations. In addition, these diluents are inexpensive, and their flash points are in excess of 60°C. The DHDECMP, decalin/DIPB mixture will be referred to as the solvent.

Batch distribution data are reported in Table III for the extraction, scrubbing, and stripping of actinides and key elements between synthetic coprocessing raffinate and 20% DHDECMP in a solvent composed of 2 parts decalin and 1 part DIPB. All contacts were for five minutes at 24°C. Tracer techniques are used for the determination of distribution coefficients. Each feed component was investigated separately. Gamma-ray emitters were analyzed by NaI(Tl) and Ge(Li) spectrometry and alpha emitters by liquid scintillation counting. With the exception of Tc, which was carrier-free, macroscopic amounts of elements studied were present in the synthetic waste before each set of measurements. Actinides were present in the μg/mℓ range, others at approximately 0.1 μg/mℓ. Tracers plus carriers, where appropriate, were taken to near dryness several times with concentrated HNO_3 at least one hour before extraction contact. All measurements were made in duplicate.

TABLE III

DHDECMP EXTRACTION-SCRUB-STRIP STUDIES WITH SYNTHETIC Zr-Al COPROCESSING WASTE

	DISTRIBUTION COEFFICIENTS					
Feed	Extraction	Scrub	Strip Contacts[c,d]			
Component	Contact[a]	Contact[b]	1	2	3	4
Am(III)	7.6	3.7	0.21	0.015	0.013	—*
Pu(IV)	7.6	3.9	0.20	0.004	<0.05	—*
Np(V)	0.55	0.16	0.010	—*	—*	—*
U(VI)	55.0	34.0	2.7	0.22	0.25	0.010
Hg(II)	16.0	10.0	84.0	130.0	>200.0	>200.0
Ce(III)	4.8	4.1	0.28	0.017	0.023	—*
Ba(II)	0.015	0.011	—*	—*	—*	—*
Cs(I)	0.0004	—*	—*	—*	—*	—*
Cd(II)	0.014	<0.01	—*	—*	—*	—*
Pd(II)	1.9	0.62	0.80	1.4	7.2	17.0
Ru(III,IV)	1.2	0.81	7.4	8.2	14.0	8.4
Tc(VII)	1.4	0.93	2.7	1.0	0.68	0.84
Mo(VI)	0.26	0.20	—*	—*	—*	—*
Nb(V)	0.079	0.055	—*	—*	—*	—*
Zr(IV)	0.0095	0.016	—*	—*	—*	—*
Y(III)	0.36	0.41	0.015	—*	—*	—*
Sr(II)	0.018	0.015	—*	—*	—*	—*
H^+	0.23	—*	—*	—*	—*	—*

a Equal volume organic/aqueous (o/a=1) contact with 20% DHDECMP in 2:1 Decalin-DIPB.

b Scrub: 3 M HNO_3, o/a =5

c Strips 1-3: 0.015 M HNO_3-0.05 M HAN, o/a=1.

d Strip 4 : 0.005 M HNO_3-0.05 M $H_2C_2O_4$, o/a=1.

*Not measured.

3. Solvent Recycle Considerations

Repeated use in process equipment and in laboratory experiments has established the stability of the solvent. However, because of the effects of acid and radiation plus the coextraction of Hg (see next section), special treatment of the solvent is necessary. Radiation from fission products and the high acid concentrations found in the scrub section cause organic degradation products to form. These organic degradation products then combine with Pu to form complexes that cannot be removed from the organic in the first strip operation. To remove these residual actinides, a second strip operation, using oxalic acid, is needed. The organic degradation products have been successfully removed by subsequent sodium carbonate contacts. The formation of these degradation products is a function of the time that the organic is left in contact with acid. The use of high purity (>95%) DHDECMP significantly reduces the formation of these degradation products. In Table IV, Pu stripping data are presented for 86% and 95% pure DHDECMP as a function of acid contact time. The use of the higher purity extractant has obvious processing advantages with respect to stripping.

TABLE IV

STRIPPING OF Pu FROM DHDECMP AS A FUNCTION OF ACID CONTACT TIME

Time (hrs)	0	2	8	24
% Pu not stripped from 86% Pure DHDECMP	0.083	0.085	0.12	0.25
% Pu not stripped from 95% Pure DHDECMP	0.013	0.012	0.024	0.026

1. DHDECMP was diluted to 20% volume in 2:1 Decalin DIPB.
2. Pregnant DHDECMP prepared by one equilibrium contact with coprocessing solution and 2 scrub contacts with 3 M HNO_3.
3. Organic stripped with 0.05 M HAN three times (O/A = 1.0)
4. Stock DHDECMP (~86% pure) prepared by distillation.
5. Stock DHDECMP (>95% pure) prepared by Hg precipitation

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4. Mercury Removal

Mercury, which is present in some ICPP wastes because of its use as a catalyst during aluminum (Al) fuel dissolution, is extracted by the DHDECMP but is not readily removed in either of the two strip operations. Because of this, a separate method for removing the Hg is necessary. Several different methods to remove the extracted Hg from the DHDECMP have been investigated.[24] Among those methods that have been evaluated are direct electrolysis, electrolytic replacement by metals, and stripping with aqueous media containing complexants or reductants.

The most promising method for removing the Hg is complexing with potassium cyanide (KCN) in the sodium carbonate (Na_2CO_3) wash operation. The mercury-cyanide complex is then removed with the aqueous raffinate, and the Hg could be electrolytically recovered for recycle to the Al fuel dissolution process.

5. Resulting Flowsheet

The results of the chemistry work that have been completed on the actinide removal process indicate that the following unit operations are necessary: (1) an extraction, where the actinides, lanthanides, mercury, some HNO_3 and a small amount of zirconium are extracted from the actinide-bearing aqueous stream; (2) a scrub, where the Zr is back extracted by 3M HNO_3; (3) a strip, which removes the HNO_3 and the majority of the actinides and lanthanides from the pregnant organic with a weak HNO_3-HAN stream; (4) a second strip, which removes the residual U and Pu from the solvent with a weak oxalic acid stream; (5) a carbonate wash-mercury removal operation that removes residual acid, degradation products, and mercury from the solvent with a dilute Na_2CO_3 - KCN mixture; (6) a weak acid wash that neutralizes any residual Na_2CO_3 left in the organic.

III. FLOWSHEET VERIFICATION OF THE ACTINIDE REMOVAL PROCESS

1. Simulated Column Studies

The "batch pseudo countercurrent extraction," or "simulated column" can be used for solvent extraction flowsheet verification in the laboratory.[25] For the actinide removal process, the extraction, scrub, and strip operations were thus investigated. Solvent cleanup steps, though not studied on a countercurrent basis, were verified because the same solvent was used repeatedly in the simulated column experiments. An advantage of the simulated column is the accurate collection of equilibrium data over a wide concentration range. The major advantage of this experiment, though, is the information developed about the process on a countercurrent basis, e.g., flow ratios, equilibrium contacts, and feed concentration changes.

The lanthanide Ce was used as an actinide simulant for the majority of the pilot plant experiments because the pilot plant could not be used for radioactive service. The extraction and scrubbing of Ce (III) were studied in two simulated column experiments. In these experiments, the number of extraction and scrub stages, flow ratios, and feed concentrations were varied. Results of the first simulated column are presented as Ce and HNO_3 operating diagrams in Figures 5 and 6, respectively. These solute profiles represent the mass transfer that occurs in the actinide removal process. The first experiment had four extraction stages, two scrub stages, and a feed-to-solvent (A/O) ratio of 2:1. Five extraction stages, three scrub stages, and an A/O feed ratio of 1:1 were used in the second simulated column. For the first experiment, a feed of 0.2g Ce/ℓ was used; for the second, 0.3g Ce/ℓ was used. The second experiment was performed to establish the Zr profile in the process and to determine the effect of flow ratio upon the process. For both experiments, the A/O for the scrub section was 1:5.

From the experiments, it was concluded that: (1) pinches for Ce in the scrub section and for HNO_3 and Zr in the extraction section showed that the flow ratios were reasonable; (2) co-extracted Zr can be successfully removed from the pregnant organic in two scrub contacts; (3) distribution coefficients (D) were constant for Ce, HNO_3, and Zr for each experiment for the extraction and for the scrub sections; and, (4) the pregnant organic exiting the scrub section was about 0.4M in HNO_3. One anomaly, which has not been resolved, is that the D for Ce was reduced from 5.0 to 4.4 when the feed A/O ratio was reduced from 2.0 to 1.0.

Stripping of Ce and HNO_3 from the pregnant DHDECMP was studied in a five stage strip simulated column. As in the flowsheet, the A/O for the strip simulated column was 1:1. These results are presented in Figure 7 as an operating diagram for Ce. The D for the first strip stage is high because of the large amount of HNO_3 present in both phases. After the bulk of the HNO_3 is removed from the organic in the first strip contact, the Ce is quickly stripped to the detection limit.

For the simulated columns, ^{144}Ce tracer was used for the analysis of Ce, because the analysis was fast and efficient. Samples from the pilot plant experiments were analyzed for Ce using a spectrochemical method because tracer isotopes could not be used in the pilot plant. Using the ^{144}Ce analyses and

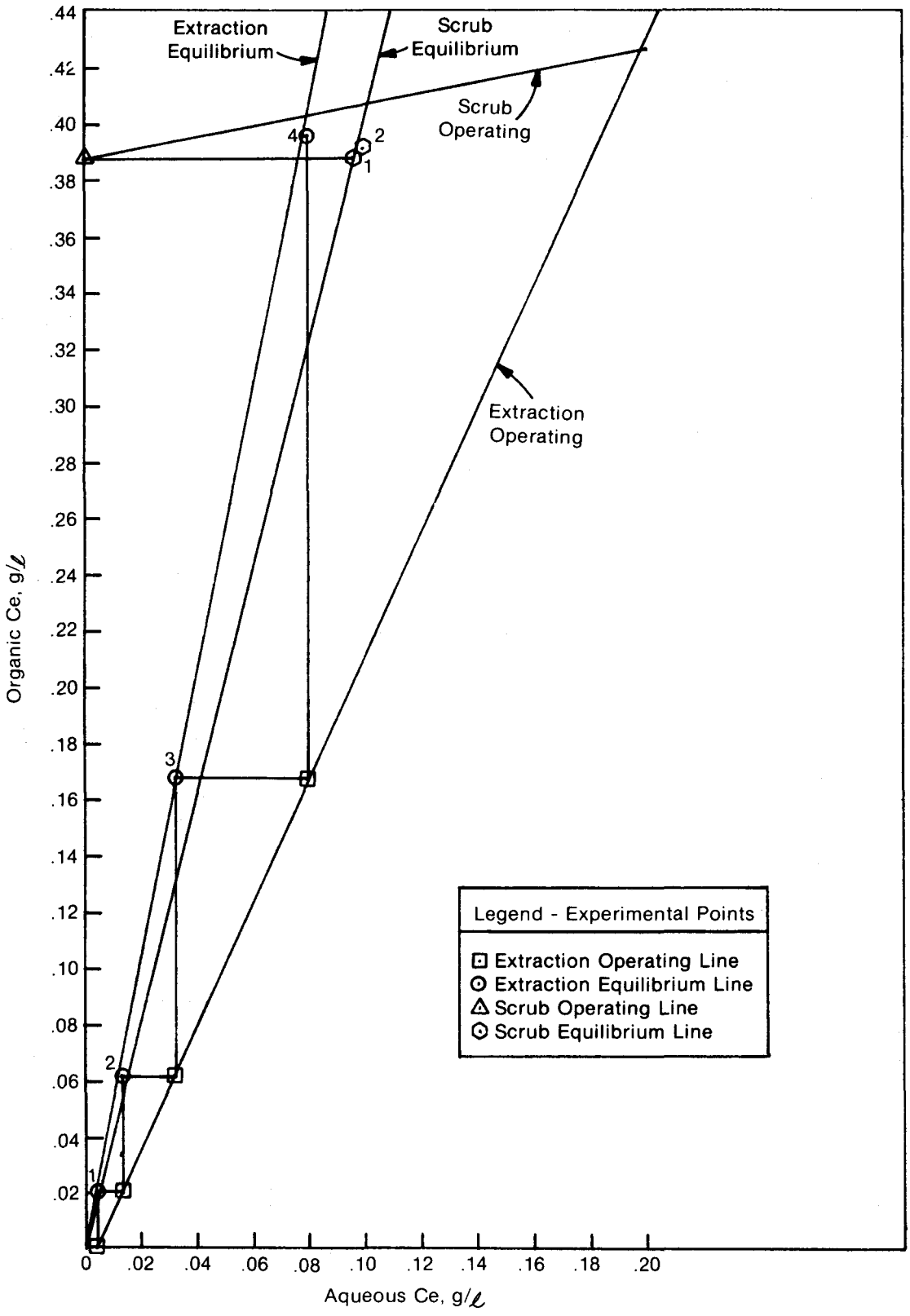

Figure 5. Ce Operating Diagram: Batch Simulated Compound Column

ACC-A-4036

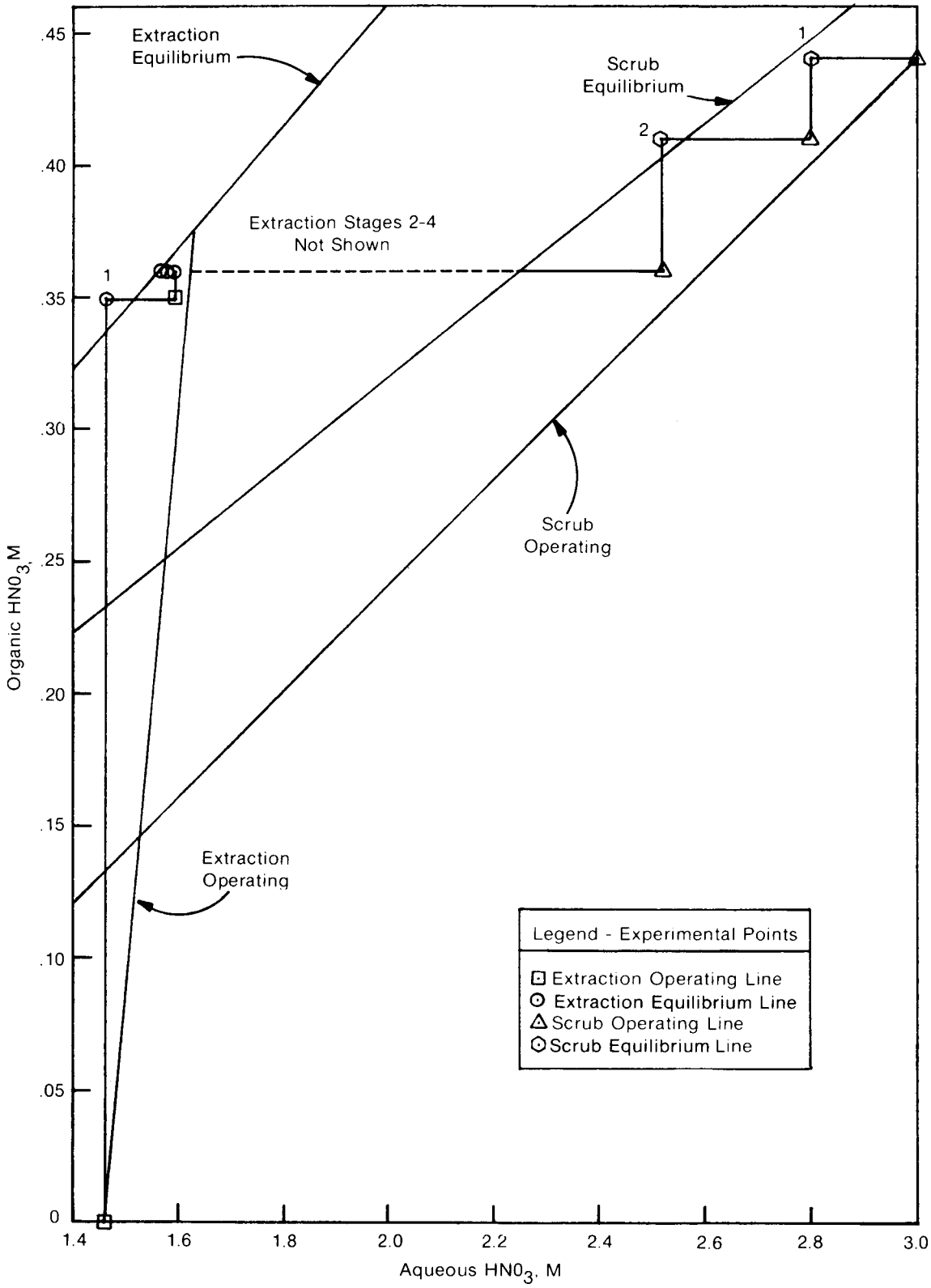

Figure 6. HNO_3 Operating Diagram: Batch Simulated Compound Column

ICPP-A-4035

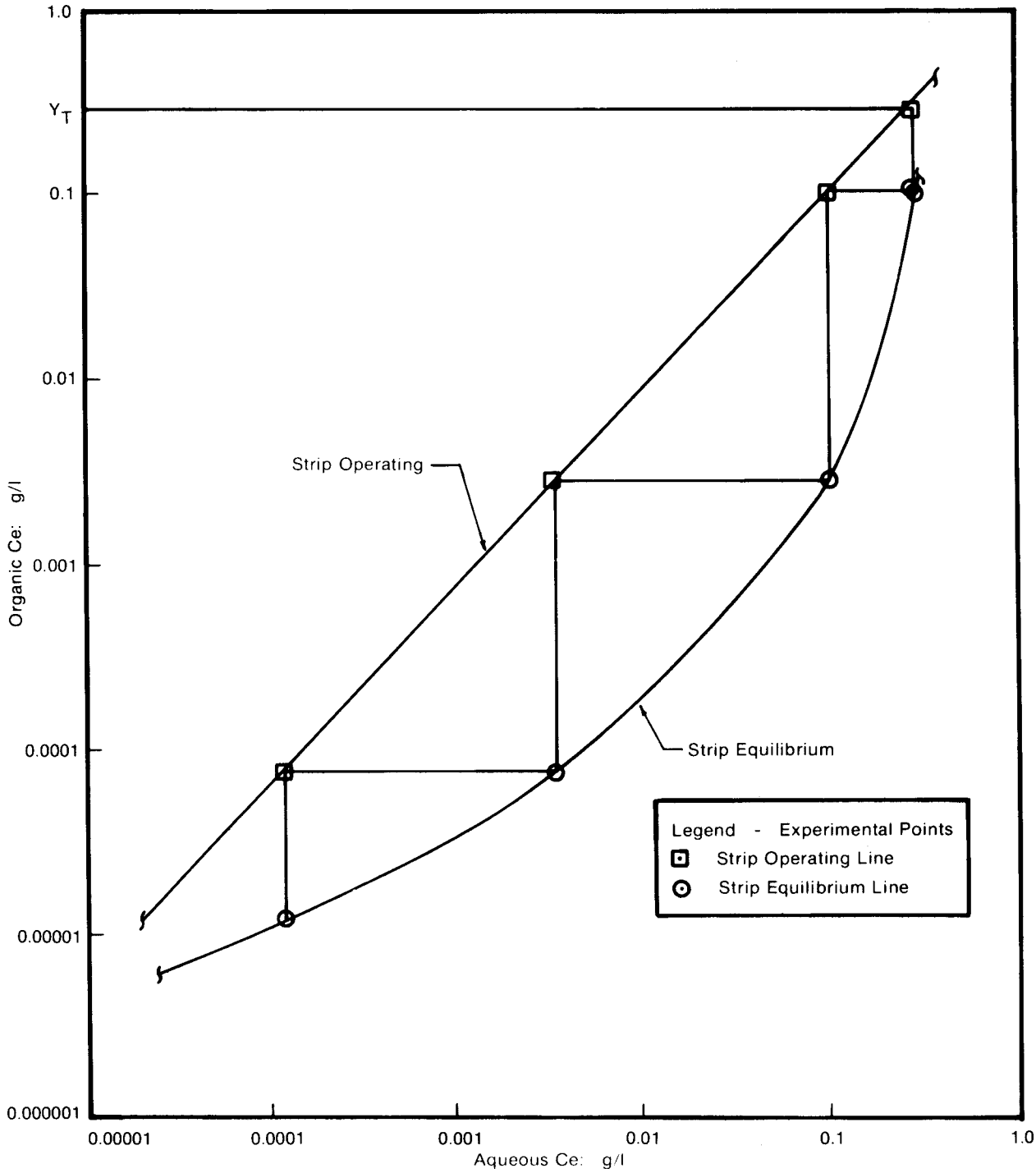

Figure 7. Ce Operating Diagram: Batch Simulated Strip Column

ICPP-A-4201

making overall and stagewise material balances as comparators, the accuracy of the Ce spectrochemical method was established. While not as accurate as the tracer method, the spectrochemical method was sufficiently exact for the concentration range studied. Acid and nitrate material balances were made for the overall simulated columns and for the individual stages. These analyses were also found to be accurate. By using material balances for three solutes, it was possible to confirm the experimental flow ratios and to judge which samples may have been analyzed incorrectly. Treybal[26] recommends that pilot plant material balances that do not close to within five percent should be discarded. For our experiments, a ten percent limit was set as a result of the simulated column work. In these respects, the simulated column was used as a precursor to the pilot plant work. By using limited amounts of chemicals, the actinide removal flowsheet was studied on a small scale prior to the pilot plant experiments. Some flowsheet variables could be studied in less time in a simulated column than in the pilot plant. Use of the simulated column technique is described in detail in Appendix C.

Americium (Am) and Plutonium (Pu) are the major contributors to the actinide fraction of ICPP wastes. Using the concentrations of Am and Pu actually present in ICPP fuel reprocessing raffinates, the extractability of these solutes by DHDECMP down to the lowest concentration levels was verified in simulated column experiments. These results are presented as Am and Pu operating diagrams for the extraction/scrub operations in Figures 8 and 9, respectively. The extraction and scrub equilibria are each constant for the extraction and scrub sections. Because such a low raffinate concentration is a requirement for this process, the foregoing information was an important flowsheet verification. The HNO_3 extraction/scrub operating diagrams for Am and Pu simulated columns are similar to Figure 6. The Pu and Am strip operating diagrams are similar to the Ce diagram, Figure 7. The solvent from the simulated columns was treated batchwise according to the flowsheet and reused in subsequent experiments. Thus, the actinide removal flowsheet has been proved in simulated columns using the actinides Am and Pu. Detailed information from all of the simulated column experiments is presented in Appendix C.

2. Miniature Mixer-Settler Studies

While the simulated column experiments showed that the actinides can be removed from ICPP wastes such that they are no longer classified as transuranic wastes, there are certain aspects of the flowsheet that were not established by use of this technique. For example, the degradation of the extractant in the presence of acid and radiation and the effect of this degradation were not demonstrated by the simulated column experiments. Another effect upon the solvent is that complexes of Pu which are not removed by the HAN strip, form in the presence of radiation. These complexes are removed by an oxalic acid strip. The miniature mixer-settler tests were performed in equipment that has been described by Alter.[27] The feeds to these mixer-settlers were actual radioactive ICPP coprocessing raffinates. Some of these experiments used the dibutyl homologue of DHDECMP, DBDECMP. These tests and the resulting flowsheet changes have been described by Baker.[28]

The terminal experiment of these tests used a mixer-settler with six extraction and two scrub stages. DHDECMP, 86% pure, was used in the mixed solvent diluent. Over a ten hour period, this solvent countercurrently contacted

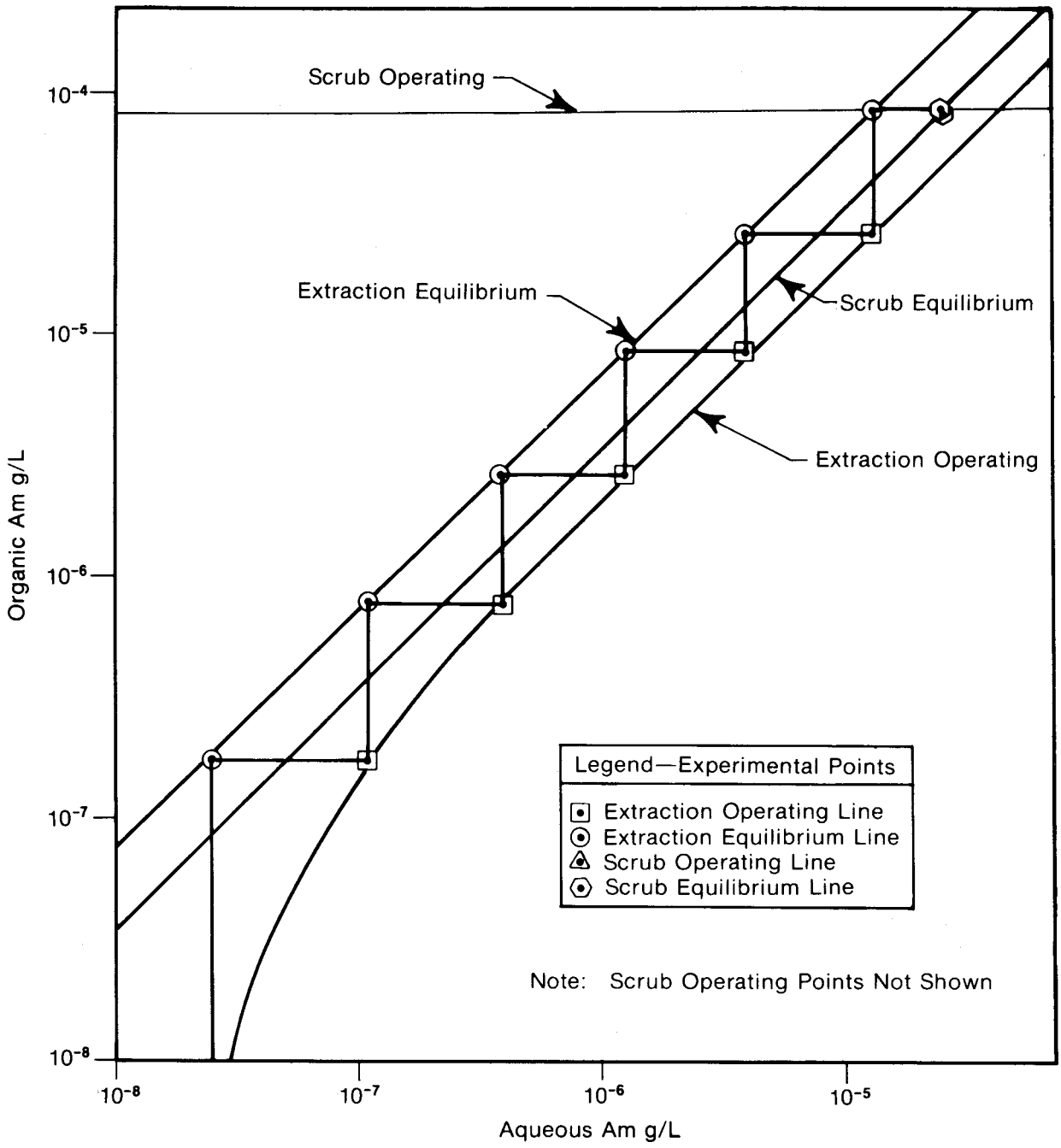

Figure 8. Am Operating Diagram: Batch Simulated Compound Column

ICPP-A-5085

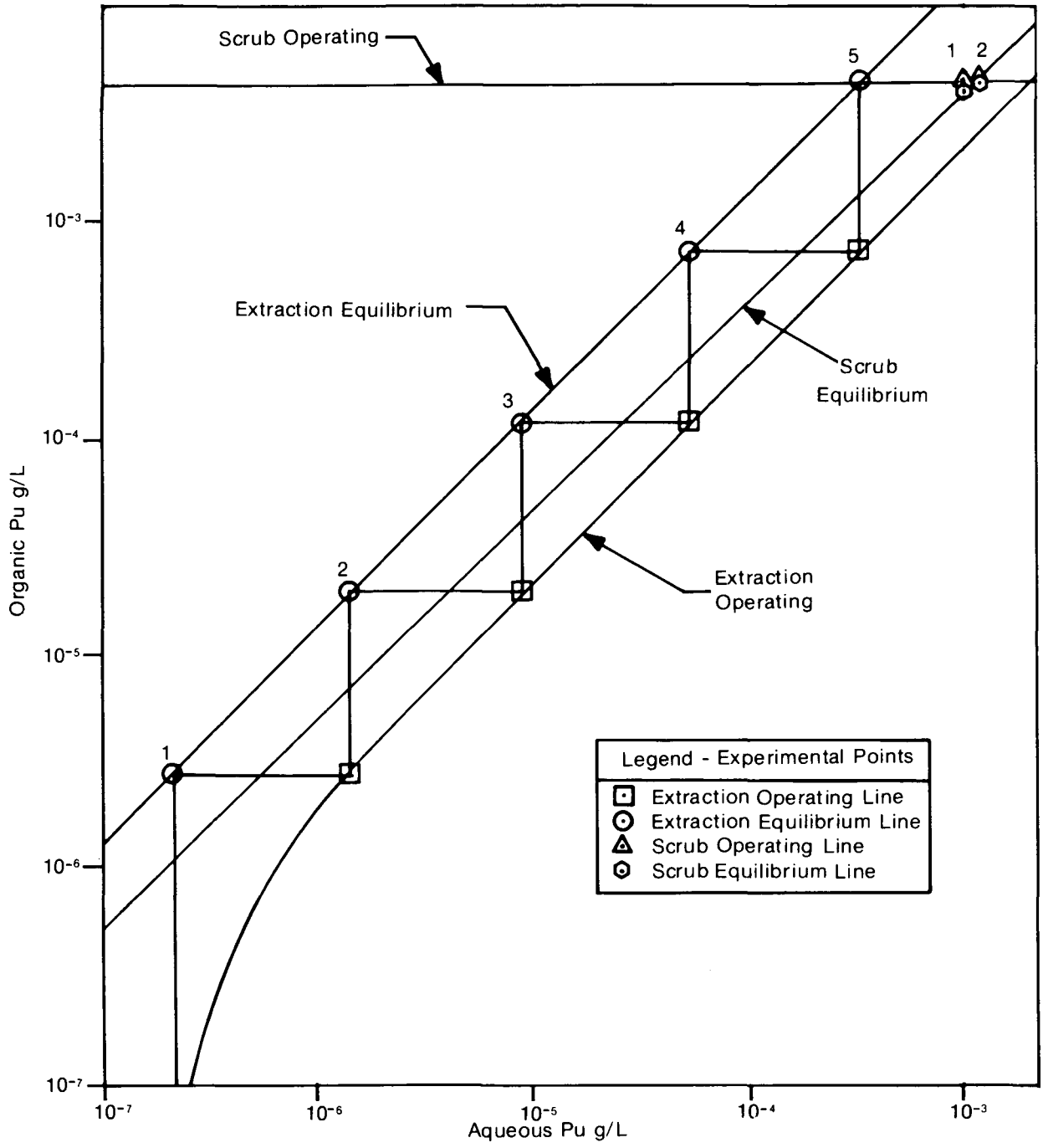

Figure 9. Pu Operating Diagram: Batch Simulated Compound Column

ICPP-A-4534

one litre of ICPP coprocessing raffinate until chemical steady-state was reached. The results of these tests are presented in Table V. Clearly, an actinide free raffinate has been produced. A six stage strip mixer-settler was used to remove the actinides from the pregnant organic. Oxalic acid, present in the aqueous strip feed, caused the lanthanides to precipitate. Consequently, provision was made in the flowsheet for two strips, the first of which used hydroxylamine nitrate as a stripping agent.

TABLE V

RESULTS OF MINIATURE MIXER-SETTLER EXPERIMENT

	Am		Pu	
	Concentration (g/ℓ)	Calcine Equivalent[a] (nCi/g)	Concentration (g/ℓ)	Calcine Equivalent[a] (nCi/g)
Feed	1.67×10^{-5}	∿200	1.08×10^{-3}	∿310
Mixer-Settler Raffinate	1.7×10^{-8}	∿0.2	3.45×10^{-7}	∿0.10

[a] 1 ℓ coprocessing raffinate calcines to ∿ 250 g.

3. Pilot Plant Studies

3.1 Introduction

Pulse sieve-plate extraction columns have been used for many years at the ICPP for the recovery of uranium from spent nuclear fuel. Pulse columns are simple, efficient, and easy to operate. For these reasons, pulse columns were chosen as the contacting equipment for this pilot plant development. Two pulse columns were used for these tests. Each is constructed of 5.1 cm (two inch) pyrex pipe and has stainless steel plates spaced 5.1 cm apart. The plates have 0.3 cm diameter holes and a free area of approximately 25 percent; they are wetted by the aqueous phase. The extraction/scrub column was center fed; its plate section height was 6.60 m. The plate section height of the strip column was 2.86 m. A more detailed description of the pilot plant is presented in Appendix D. The extraction feed used in these test was essentially the same as that described in Table I, except that there were no radioactive solutes present. The organic was the mixed (DHDECMP) solvent. Scrub and strip solutions were 3M HNO_3 and 0.05 M HAN/0.015 M HNO_3, respectively.

3.2 Flooding Tests

Flooding tests were made to establish the volumetric capacity of the pulse columns. The technique used in determining the flooding point is described in Appendix B. Sege[29] and Nicholson[30] have established the format in which these data are presented. Similar results were obtained and are presented in

Figure 10 and 11 for the extraction/scrub and the first strip, respectively. Flow ratios of 2:1 and 1:5 were used in the extraction and scrub sections, respectively. A simple (end-fed) column was used for the strip, where a flow ratio of 1:1 was used. For low frequencies, the pulse volume velocity (see Figures 10 and 11) describes the maximum flow to a column for a given pulsing condition. Greater flows would flood the column, i.e., the phase would short circuit the column and exit at the end to which it was fed. The pulse volume velocity was calculated by the method of Nicholson.[31] For the higher pulsing frequencies, the flooding line had to be determined experimentally. The following polynomials were fitted to the data:

$$Y = 6.5 - .053X + 1.2\ (10^{-4})\ X^2 \qquad \text{extraction/scrub} \qquad (2)$$

$$Y = 19.9 - .189X + 4.63\ (10^{-4})\ X^2 \qquad \text{strip} \qquad (3)$$

$$Y = \ell/hr \cdot cm^2 \qquad X = \text{cm/min (2.5 cm pulse)} \qquad (4)$$

For the mass transfer tests, the flowrates were set at a percentage of flooding. The flooding lines in Figures 10 and 11 were used to set this percentage.

It is possible to overdesign the strip column. If the column is made too tall so that a large separative capacity is assured, then there could be a portion of the column where essentially no mass transfer is occurring. For this process, the mass transfer bears significantly on the flooding. Using the same feedstreams, but two different column heights, the taller column was found to flood. From this observation, it was concluded that the dilute section of the taller column, where no mass transfer occurred, was prone to flooding.

3.3 Mass Transfer Tests

The pilot plant could not be used for radioactive tests because it is located in a cold area. So, the use of actinide—or fission product—bearing streams was not possible. Instead, Ce(III) was chosen as the extractable species because it is a nonradioactive rare earth chemically similar to Am(III). Mass transfer tests were made to establish the pulse column parameters — frequency, amplitude, percentage flooding, feed point location — at which this process could be operated. The results of the Ce extraction and strip tests are presented in Tables VI and VII, respectively. Column efficiency is measured by the Height of a Transfer Unit (HTU) and the Height Equivalent to a Theoretical Stage (HETS) for Ce. Percentage flooding was determined by the fitted curve of the experimental flooding data. From these tests, it was found that the Ce extraction HTU is reasonable, usually no greater than 0.55 meters. This is in the range of HTU's reported for diffusional processes. The variation of HTU with pulse amplitude and frequency is similar to that of PUREX processing.[32] The number of scrub stages was found to be relatively insensitive to feed location. There are usually two theoretical stages of scrubbing for Ce, and there is little Zr in the extract, indicating satisfactory column performance.

Using Ce as an actinide simulant, the hydraulics and simple mass transfer of the extraction and strip operations have been established. These characteristics are similar to those reported by Sege[33] for the extraction of uranyl nitrate by

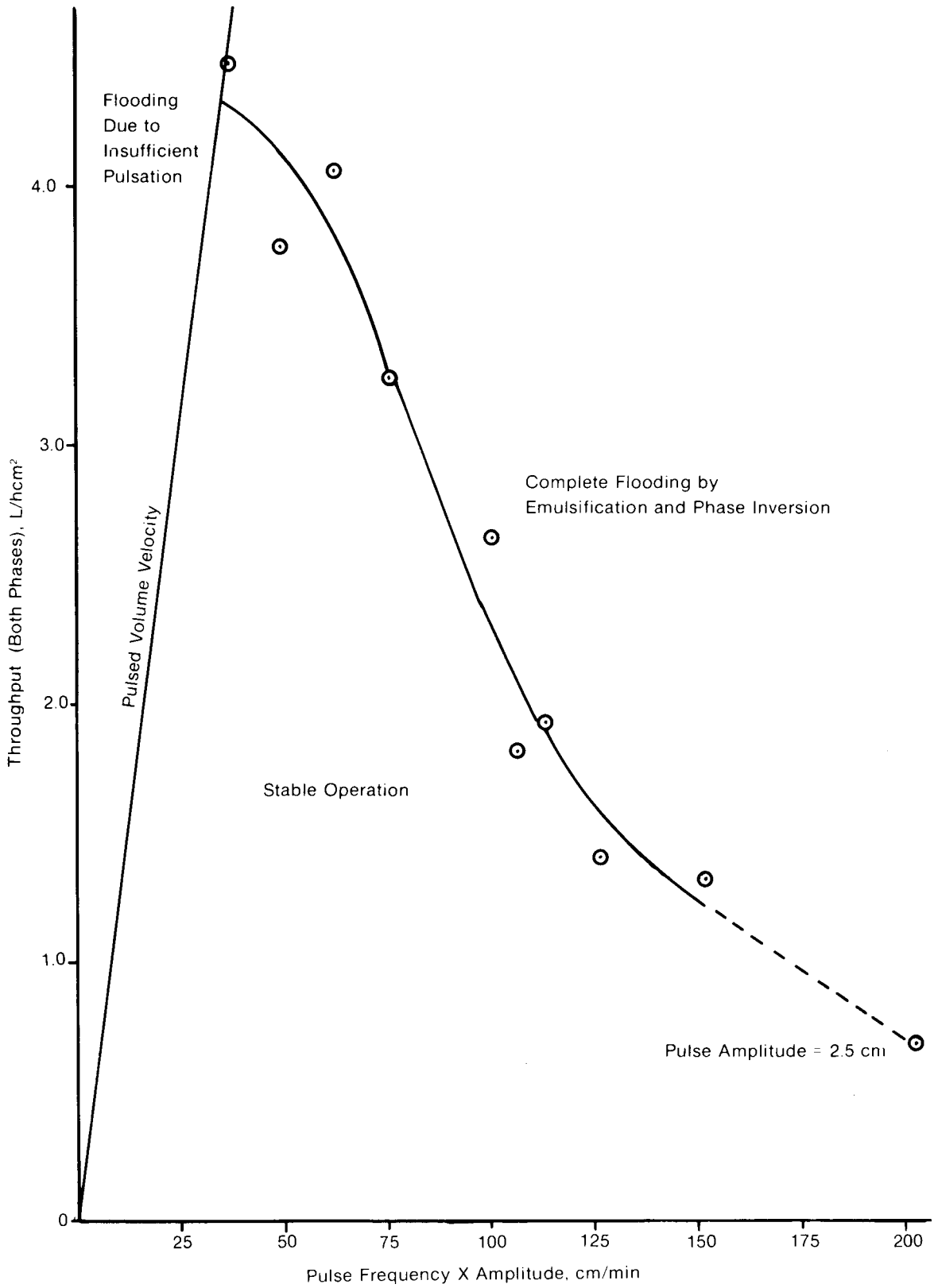

Figure 10. Flooding Curve - Compound Extraction/Scrub Column DHDECMP System

ICPP-A-4123

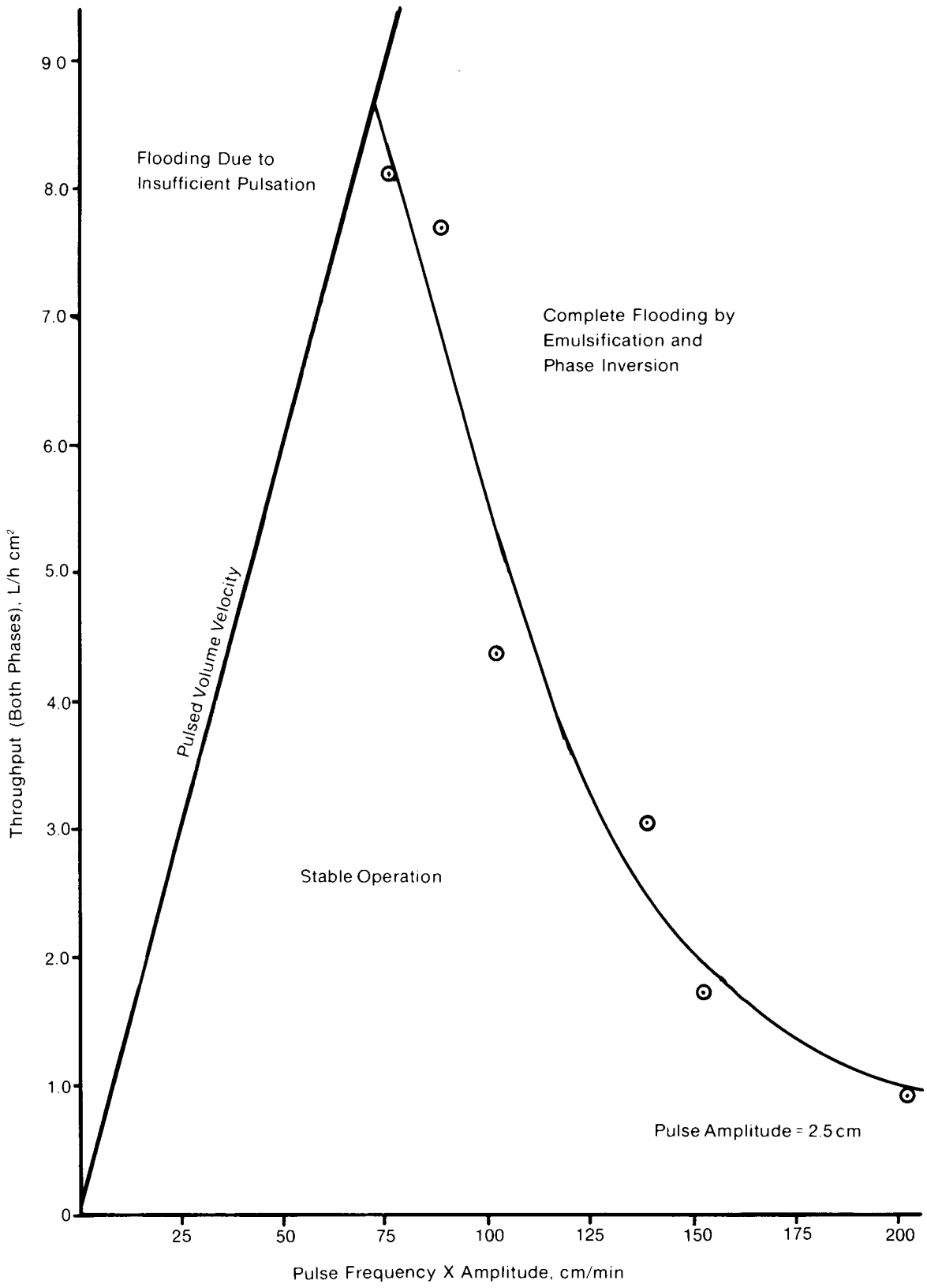

Figure 11. Flooding Curve - Strip Column DHDECMP System

ICPP-A-4124

TABLE VI

OPERATING AND SEPARATION DATA FOR DHDECMP EXTRACTION OF CERIUM

Run No.	Pulse Frequency (CPM)	Pulse Amplitude (Cm)	Percent of Flooding (%)	Section Phase Ratio (A/O) Ext.	Scrub	Stream Compositions Feed (g/l)	Raffinate (g/l)	Extract (g/l)	Extraction Section HTU (m)	HETS (m)	Scrub Section HTU (m)	HETS (m)
1	40	1.1	NM[c]	2.18	0.23	0.23	0.0054	0.41	0.92	1.36	4.6	0.80
2[b]	40	1.1	NM	2.28	0.24	0.23	0.0127	0.45	0.90	1.29	7.9	1.43
3[b]	40	1.1	NM	2.12	0.22	0.40	0.01	0.81	0.68	1.02	7.3	1.43
4	15	2.5	80	2.20	0.20	0.20	0.003	0.39	0.48	0.71	4.9	0.77
5	20	2.5	80	2.20	0.20	0.21	0.001	0.43	0.59	0.86	4.9	0.77
6	21.4	2.5	80	2.20	0.20	0.21	0.0003	0.45	0.47	0.70	4.9	0.77
7	30	2.5	50	2.20	0.20	0.24	0.0006	0.51	0.51	0.75	4.9	0.77
8	30	2.5	70	2.20	0.20	0.24	0.001	0.47	0.58	0.85	4.9	0.77
9	30	2.5	80	2.20	0.20	0.21	0.001	0.45	0.58	0.86	4.9	0.77
10	30	2.5	90	2.20	0.20	0.24	0.001	0.51	0.57	0.84	4.9	0.77
11	40	2.5	80	2.20	0.20	0.20	0.0004	0.43	0.50	0.73	4.9	0.77
12	20	2.5	80	2.44	0.19	0.19	<0.0003	0.46	0.36	0.51	5.1	0.78
13	30	2.5	80	2.64	0.14	0.20	<0.0003	0.48	0.37	0.50	6.6	0.78
14	40	2.5	80	2.72	0.11	0.22	<0.0003	0.52	0.41	0.55	7.9	0.78
15	20	2.5	80	2.44	0.19	0.044	<0.0003	0.11	0.45	0.64	5.1	0.78
16	30	2.5	80	2.64	0.14	0.051	<0.0003	0.12	0.39	0.53	6.6	0.78
17	40	2.5	80	2.72	0.11	0.050	<0.0003	0.14	0.41	0.54	7.9	0.78
18	20	2.5	80	2.44	0.19	2.10	0.072	4.73	0.89	2.54	5.1	0.78
19	30	2.5	80	2.64	0.14	1.92	0.021	4.75	0.60	1.45	6.6	0.78
20	40	2.5	80	2.72	0.11	2.21	0.066	4.92	0.80	2.32	7.9	0.78

a Extraction and Scrub Operated in a Compound Column.
b Column section heights of 3.78 meters for extraction and 2.85 meters for scrub. All other heights are 5.06 m and 1.56 m respectively.
c NM-Not measured.

TABLE VII

OPERATING AND SEPARATION DATA FOR STRIPPING OF CERIUM FROM DHDECMP

Run No.	Pulse Frequency (CPM)	Pulse Amplitude (Cm)	Percent of Flooding	Phase Ratio (A/O)	Stream Compositions			Strip Section	
					Feed[a] (g/l)	Raffinate (g/l)	Extract (g/l)	HTU (m)	HETS (m)
1[b]	40	1.1	NM[c]	1.71	0.39	0.22	0.0003	0.93	3.33
2	35	2.5	80	1.00	0.35	0.37	0.02	0.98	1.83
3	40	2.5	80	1.00	0.45	0.42	0.02	0.90	1.50
4	60	2.5	80	1.00	0.45	0.44	0.001	0.46	0.98
5	40	2.5	80	1.00	0.46	0.47	0.015	0.79	1.46
6	45	2.5	80	1.00	0.48	0.53	0.004	0.56	1.02
7	50	2.5	80	1.00	0.52	0.58	0.001	0.42	0.74
8	45	2.5	80	1.00	0.12	0.17	0.0007	0.53	1.49
9	50	2.5	80	1.00	0.14	0.12	0.0003	0.45	1.44
10	45	2.5	80	1.00	4.77	4.35	0.011	0.43	0.87
11	50	2.5	80	1.00	5.08	4.52	0.003	0.34	0.72

a Feed composition represents organic feed to the strip column

b Strip section height of 6.63 meters. All other runs had heights of 2.86 meters.

c NM- Not Measured.

TBP. The flowsheet for this process, Figure 1, shows that virtually all of the actinides and lanthanides are partitioned from the ICPP waste. Because the actinides and lanthanides are so low in concentration in the feed to the actinide removal process, a greater number of moles of HNO_3 are extracted than of these metals. Consequently, the pilot plant tests described so far have proved the larger chemical aspects of the process, i.e., the extraction of HNO_3 and the rare earths from the ICPP waste and have not demonstrated the removal of actinides from these wastes.

To prove that this process would separate the actinides in pulse columns, some inferences had to be made about the separative capacities of pulse columns with respect to concentration and solute. Concentration effects were studied by varying the Ce feed concentration and by sampling the profile of the pulse column. The profile was obtained by using samplers capable of separating pure organic and aqueous samples. Accurate intracolumn samples should fall on the material balance operating line, determined by the column endstream compositions. Column efficiency as a function of height (and concentration) should then be obtained. (N.B. Backmixing may be responsible for a sample pair which does not fall on the operating line.)

Solute effects were established by using the additional simulants, uranium (U) and thorium (Th). The hypothesis was that if the pulse column mass transfer of Ce, Th and U were all similar, then this information could be extended to the actinide system. Hafnium and zirconium are also chemically similar, yet their separation can be made by TBP.[34] Thus, chemical similarity does not ensure similar extraction behavior.

One further consideration for these tests was the standard with which to measure the performance of the pulse columns. Treybal[35] emphasizes that the use of equilibrium stage contacts to describe a contactor, such as a pulse column, is theoretically unsound since the mass transfer is differential rather than stagewise in character. Thus, the Height of a Transfer Unit (HTU) should be used to describe the pulse column, rather than the Height Equivalent to a Theoretical Stage (HETS).

Because Th formed a precipitate when added to the coprocessing feed, a 1.5 M HNO_3 solution containing 1.4×10^{-3} g moles/ℓ of Ce, Th, or U was used as the aqueous feed stream for these tests. The DHDECMP solvent contacted this stream in simple countercurrent extractions and strips. The character of these operations was established in simulated column experiments. In each case the HNO_3 profile was identical for the extraction and strip operations. The metal solute mass transfer behavior was identical except for the first stage of stripping for U. Here, an extraction occurred even though the HNO_3 concentration in the aqueous phase was 0.35M. The extraction was open in each case, i.e., no pinches occurred. Extraction distribution coefficients of 2, 41, and 64 were observed for Ce, Th, and U, respectively.

These extractions and strippings were next performed in the pulse columns. Four pulse frequencies were used for both the extraction and the stripping tests. By using the different pulsing conditions, experimental bias, which might be associated with any particular condition, was avoided and operational data over a wide operating range was collected. Pulse column HTU data for the DHDECMP

extraction of Ce, Th and U from 1.5M HNO_3 are presented in Table VIII and in Figure 12 for the "Feed Point Through Section 1" column of Table VIII. The corresponding HETS data are presented in Table IX and in Figure 13.

Sources of error in these calculations were: (1) Th and U values were below their detection limits in much of the column, (2) solute was sometimes present in the feed organic, and (3) mass transfer occurred not only in the plate section but also in the upper disengaging head of the columns. (Item (3) has an effect on scaleup.) In addition, the data were screened using material balances. Overall column analyses had to meet a ten percent material balance. The interstage analyses were rejected if they did not fall within a 25 percent material balance. Nevertheless, these data were grouped by solute for each operating condition. ANOVA[36] tables were constructed to test the following null hypothesis: for each frequency, the HTU (or HETS) is different for the sample population for each of the solutes, Ce, Th and U. In other words, if the null hypothesis is not satisfied, then the HTU (or HETS) is the same for all three solutes at a particular frequency. By this test, the HTU was found to be the same for the three solutes at 20, 30, and 50 CPM. The HETS was found to be the same for 40 CPM. In these tests, the F values chosen were for the 95% level of significance. Since much of the data are invalid at the higher frequencies, the conclusions made for these frequencies are not as certain. While the data are not overly forceful, it seems that the extraction HTU's are better than HETS's as indicators of column efficiency. This was true for a wide range of concentrations and for several solutes. Similar comparisons for the strip column are presented in Table X. No conclusions can be made for this operation because: (1) Th strip equilibrium data were not accurate enough to use; and, (2) the first stage of U stripping, as determined in the simulated column, was actually an extraction stage. Apparently, even a HNO_3 concentration of 0.35 M in the aqueous phase was sufficient to allow extraction, rather than stripping, to occur. A distribution coefficient of 4.7 was measured for the stage.

3.4. Pulse Column Emulsification Problems and Their Resolution

During these pilot plant tests, it was discovered that the maximum throughput for the columns changed with time. As Long suggests,[37] this is probably due to the buildup of organic impurities on the stainless steel plates. Therefore, periodic cleaning of the columns with Turco-4324* was necessary. (Turco is an ammonium carbonate salt.) The columns, when not in operation, were kept full of water and not allowed to dry in order to keep this buildup to a minimum. Impurities were also suspected as the cause of severe emulsification that occurred twice during the pilot plant tests.

To eliminate this emulsification, not only was Turco used to clean the column, but the solvent was cleaned using the flowsheet cleanup steps shown in Figure 1. The solvent was analyzed after each of the steps to determine the effect of the contacts. These solvents were also compared with a 99% pure DHDECMP. The analyses were performed using a Waters liquid chromatograph and Perkin-Elmer and Varian Superscan spectrophotometers, capable of resolution in the infrared, and visible and ultraviolet regions, respectively. For the

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* Turco Products, Division of Purex Corp., Carson, California.

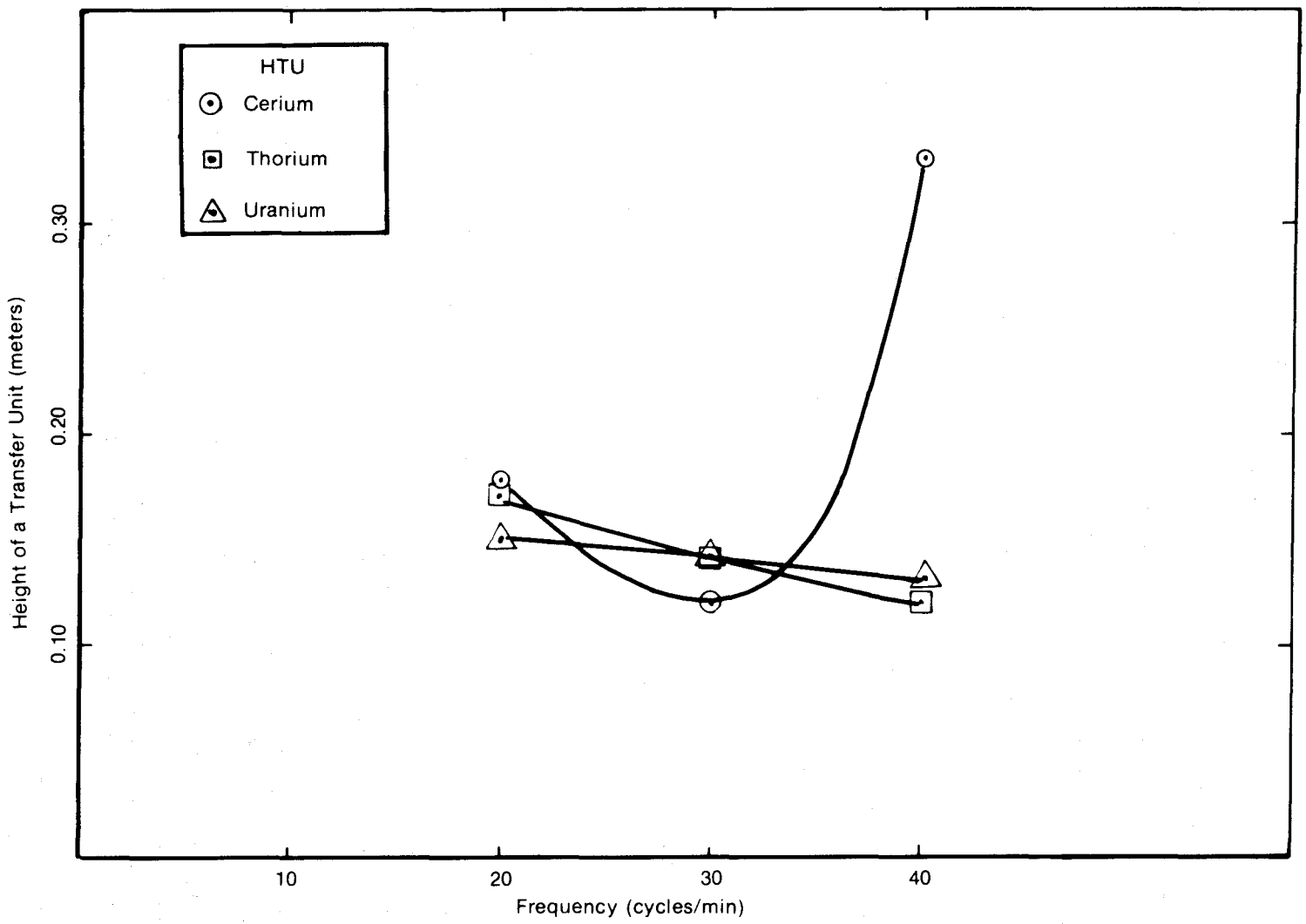

Figure 12. Pulse Column Separation Efficiencies for Extraction Using Ce, Th, & U, By HTU

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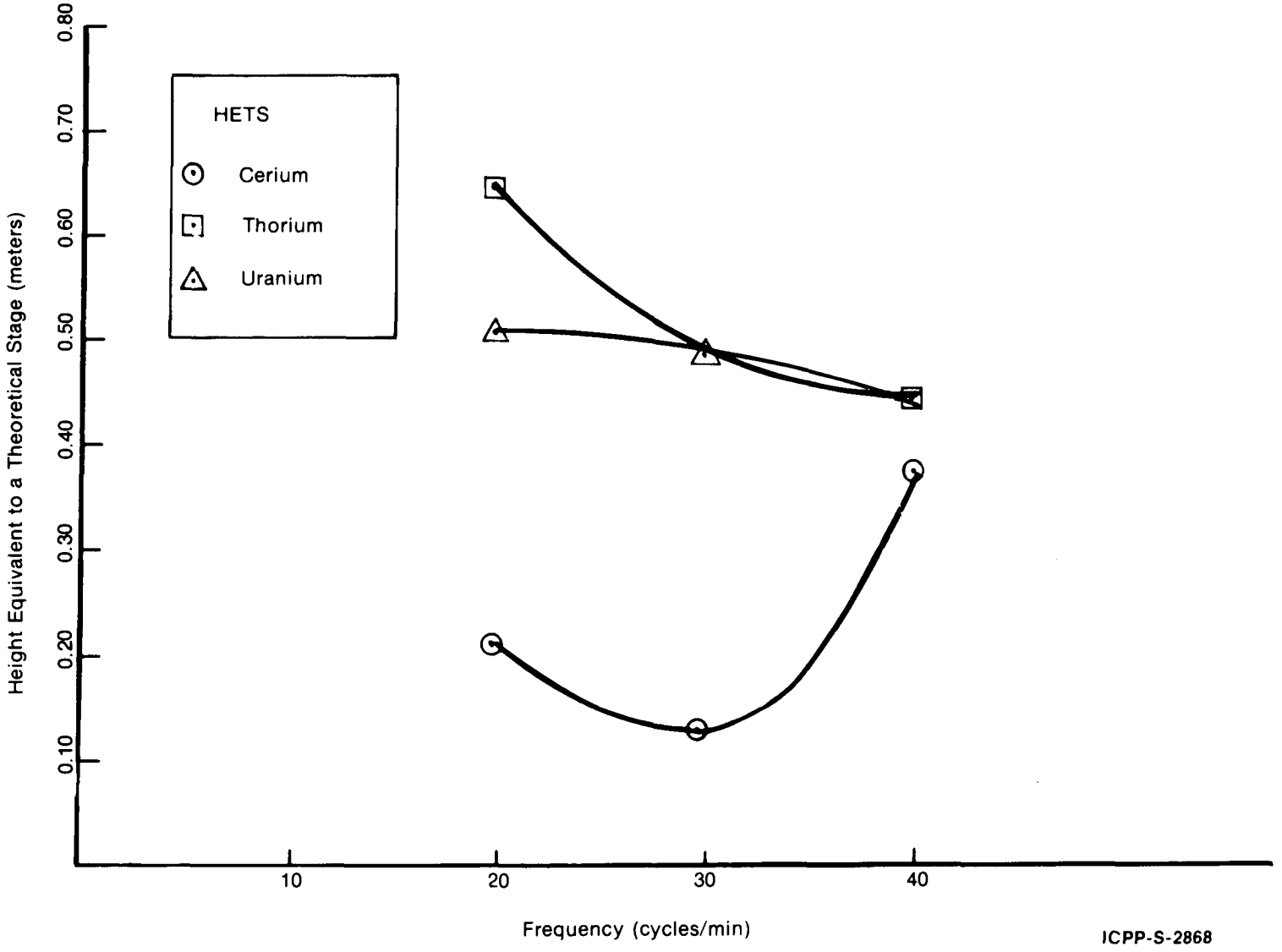

Figure 13. Pulse Column Separation Efficiencies for Extraction Using Ce, Th, & U, By HETS

TABLE VIII

PULSE COLUMN SEPARATION EFFICIENCES FOR EXTRACTION USING Ce, Th, & U, BY HTU

Operating Conditions 2.5 Cm Pulse (cycles/min)	Solute	Height of a Transfer Unit, m						
		Overall Column	Section 1, 0.64 m	Section 2, 0.64 m	Section 1-2, 1.28 m	Section 3, 0.94 m	Feed Point Through Section 1	Feed Point Through Section 2
20	Ce	0.25	0.23	0.24	0.23	0.32	0.18	0.20
	Th	0.35	0.22	0.29	0.21	NM	0.17	0.21
	U	0.68	*	0.22	*	NM	0.15	0.18
30	Ce	0.23	0.15	0.17	0.18	0.16	0.12	0.16
	Th	0.32	0.17	0.35	0.23	NM	0.14	0.20
	U	0.42	0.18	*	*	NM	0.14	0.18
40	Ce	0.51	0.47	0.48	0.47	0.66	0.33	0.39
	Th	#	*	*	*	NM	0.12#	0.20#
	U	0.40	*	*	*	*	0.13	0.18
50	Ce	#	0.11	0.11	0.13	*	*	*
	Th	#	0.17	*	*	NM	*	*
	U	#	0.21	NM	*	NM	0.13#	0.15#

Column material balance did not close to within 10%
* Section material balance did not close to within 25%
NM Not measurable due to solute value below detection limit.

TABLE IX

PULSE COLUMN SEPARATION EFFICIENCES FOR EXTRACTION USING Ce, Th, & U, BY HETS

Operating Conditions 2.5 Cm Pulse (cycles/min)	Solute	Height Equivalent To A Theroretical Stage, m						
		Overall Column	Section 1, 0.64 m	Section 2, 0.64 m	Section 1-2, 1.28 m	Section 3, 0.94 m	Feed Point Through Section 1	Feed Point Through Section 2
20	Ce	0.27	0.27	0.27	0.27	0.37	0.21	0.23
	Th	1.33	0.83	1.11	0.82	NM	0.65	0.82
	U	2.36	*	0.76	*	NM	0.51	0.61
30	Ce	0.26	0.17	0.20	0.20	0.18	0.13	0.18
	Th	1.15	0.65	1.36	0.82	NM	0.49	0.77
	U	1.44	0.63	*	*	NM	0.49	0.63
40	Ce	0.58	0.54	0.55	0.54	0.76	0.38	0.45
	Th	#	*	*	*	NM	0.45#	0.76#
	U	1.38	*	*	*	*	0.44	0.62
50	Ce	#	0.13	0.13	0.15	*	*	*
	Th	#	0.66	*	*	NM	*	*
	U	#	0.72	NM	*	NM	0.44#	0.53#

\# Column material balance did not close to within 10%
* Section material balance did not close to within 25%
NM Not measurable due to solute value below detection limit.

TABLE X

PULSE COLUMN SEPARATION EFFICIENCES FOR STRIPPING USING Ce, & U, BY HTU & HETS

Operating Conditions 2.5 Cm Pulse (cycles/Min)	Solute	Height Of A Transfer Unit, m			Height Equivalent To A Theroretical Stage, m		
		Overall Column	Dilute Section 1.56 m	Concentrated Section 1.33 m	Overall Column	Dilute Section 1.56 m	Concentrated Section 1.33 m
40	Ce U	0.59 0.44	0.44 0.62	0.59 0.76	1.50 0.62	0.88 0.94	1.74 1.16
45	Ce U	0.41 0.44	0.30 0.49	0.30 0.23	1.01 0.73	0.55 0.87	0.82 0.47
50	Ce U	0.46 #	* 0.41	* 0.48	1.467 #	* 0.80	* 0.86
55	Ce U	0.42 0.32	* *	* 0.30	1.45 0.69	* *	* 0.85

Column material balance did not close to within 10%
* Section material balance did not close to within 25%

chromatographic analyses, none of the organic samples contained a peak readily identifiable as an impurity. Infrared spectra of the various organics suspected to contain impurities revealed no major differences between any sample and pure DHDECMP. Thus, it is apparent that the impurity, if any, is present in less than parts per million concentration. The source of the impurities may have been a material present in unpurified DHDECMP and not subsequently removed, or a degradation product that is formed when the DHDECMP is pregnant with HNO_3. An ion exchange resin, A-26 resin,* OH^- form, has been used successfully to purify the solvent. DHDECMP undoubtedly forms a series of acid degradation products similar to the TBP degradation products.[38] Acid organics are known to cause foaming because of their tendency to emulsify. Several times the DHDECMP solvent has been exposed to acid for long periods which leads to the formation of organic acids. The A-26 resin has removed these acids. Under normal operating conditions, the solvent cleanup steps shown in Figure 1 adequately clean the solvent for recycle.

4. Associated Engineering Studies

4.1 Solvent Extraction Computer Program Development

The computer program, SEPHIS,[39] was modified for the actinide removal process. SEPHIS determines ideal stage profiles of a solvent extraction process. An important variable in the TBP extraction of U from acidic solutions is the HNO_3 profile. This profile affects the total solute loading in the TBP phase as well as the distribution coefficients for U. This computer program can greatly simplify extraction calculations.

SEPHIS was adapted to the actinide removal process for use on the INEL CYBER system. The simulated column results were compared with the solute profiles generated by SEPHIS. Solute profiles from SEPHIS were in excellent agreement with the simulated columns. Nevertheless, since the extraction/scrub distribution coefficients were constant, hand calculations were used to assess the pulse column performance. (See Appendix E for a typical set of calculations.) SEPHIS could have been used in two ways: (1) a scoping study could have been made of operating variables to select pilot-plant operating conditions; and, (2) pilot plant pulse column data could have been analyzed.

4.2 Materials of Construction Requirements

DHDECMP pregnant with HNO_3 has caused two types of problems in pilot plant operation. First, emulsifications were formed that probably were due to degradation of the solvent when loaded with HNO_3. Second, mild steel fittings in the pilot plant have been corroded by acid-loaded organic. For these reasons, a scoping study was performed to assess the corrosive properties of the DHDECMP when pregnant with HNO_3. The most corrosive organic solution appears to be the stream leaving the scrub section since it contains 0.40 M HNO_3. Several stainless steel types (304, 304L, 316, 316L, and 347) were tested along with one mild steel sample (AISI No. 1018 or 1020). The coupons were first rinsed in acetone and then washed in hot concentrated HNO_3. After being dried and weighed, the

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* Rohm & Haas Co., Philadelphia, Pennsylvania

coupons were placed in bottles and covered with organic. After six months, the only sample that showed any corrosion was the mild steel coupon. All of the samples, including the blank, did change color during the six months. Because the blank also changed color, it is evident that the solvent itself undergoes a change when loaded with acid. The degree of change should indicate the degree of corrosion, and in order of increasing color, the samples were 304, 304L, 316, 316L, 347, and 1018 (or 1020). The mild steel sample showed a noticable color change after 24 hours. Therefore, the organic should not be stored for any length of time if loaded with acid, and all of the materials of construction associated with the actinide removal process should be stainless steel.

IV. CONCLUSIONS

Tests using simulated columns, miniature mixer-settlers and pilot plant extraction columns with simulants as well as actual ICPP coprocessing wastes have demonstrated that a process to remove actinides to the 10nCi/gram limit from certain ICPP wastes is technically feasible. This separation can be made in a pulsed, sieve plate extraction column in a height suitable for radioactive service. The DHDECMP solvent can be used repeatedly, thus making the solvent extraction process feasible. Detailed conclusions are discussed in the following sections.

1. Column Design Basis

One trade-off in the design of an extraction process is that between column capacity and separation efficiency. By increasing the pulse column diameter and thus the capacity, the column becomes less efficient. Therefore, the greater the diameter, the larger the HTU and the taller the column needed to achieve the desired separation. In nuclear applications this is very important since column height is limited by the size of the process building. In increasing the pulse column diameter from three to eight inches, an increase in average HTU of up to 50% was observed by Sege.[40]

For plant operation, the extraction, scrub, and first strip columns would all be pulsed at 40 cycles per minute, 2.5 cm per pulse. In the extraction column, the HTU should be no greater than 0.75 metres, even considering changes resulting from scaleup. Applying this to the feed described in Table I, a 4.0 metre column (i.e. $\curvearrowleft$ 5 transfer units) should deliver a raffinate which, when calcined, contains less than 1.0nCi of actinides per gram of calcine.*

In the scrub column, trace impurities are stripped from the organic phase. In the pilot plant tests, the removal of these impurities was not studied, but rather, efforts were directed towards the effect of scrubbing on the extracted solute. Adequate performance of the scrub section in the pilot plant was evident, because of favorable comparisons with the simulated column experiments and the observation that no zirconium was measurable in the column extract. Based on the pilot plant section of 1.6 metres plus the scaleup considerations mentioned earlier, a plant scrub column section of 2.5 metres is therefore necessary.

As described in the pilot plant results, there is some evidence that the strip column floods where no mass transfer is occurring. Thus, a column plate section height of three metres is recommended for the first strip. This height is only slightly greater than that used in the pilot plant strip column. It should be

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* A series of tests to establish the effect of concentration upon HTU was made. The overall column analyses are reported in Table VI and VII. A more detailed analysis of this results will be reported by Chamberlain (see Bibliography). Tenatively, it appears that the pulse column separation efficiency improves with decreasing Ce concentration. Thus, the column heights recommended should be appropriate for this process.

adequate to strip the bulk of the actinides, lanthanides, and HNO_3 from the pregnant organic. If flooding should occur, corrective measures would include using a higher percentage of extractant (>20%) or lowering the A/O ratio. These measures both help to insure that mass transfer will occur throughout the column. The Pu complexes, which are not stripped in the first column, will be removed in the second strip column. The oxalic acid in this column however, will precipitate any lanthanides that are carried over to the second column. By increasing the A/O ratio in the first strip column, this problem could be resolved.

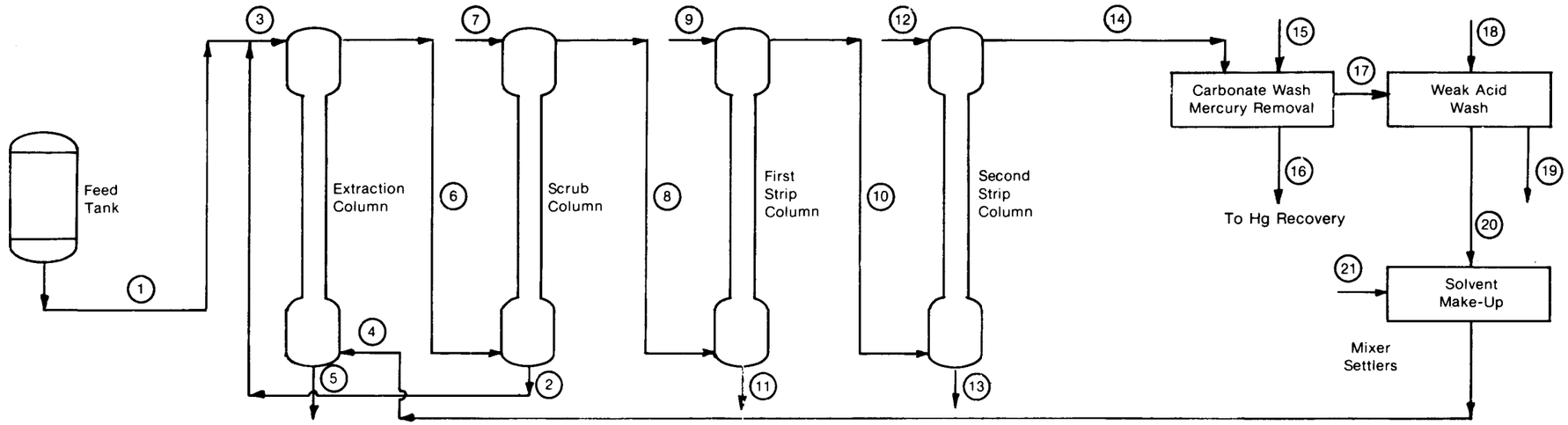
The results from the pilot plant extraction tests have indicated that the HTU is a better indicator of pulse column performance than the HETS. Treybal[41] has emphasized that the use of equilibrium stage contacts to describe a differential contractor such as a pulse column is theoretically unsound since mass transfer is differential rather than stagewise in chararcter. Consequently, the HTU was used to evaluate column efficiencies. For dilute solutions with straight equilibrium lines, such as in the extraction and scrub sections, the HTU is a logarithmic function of the HETS (see Appendix E). The suitability of efficiency measurements for several solutes over wide concentration ranges had to be established for the application of the pilot plant data to design calculations. For this type of analysis, the HTU proved to be better than the HETS for separation efficiency measurements.

The choice of diameters for each column in the plant is not as straight-forward. The diameter depends only upon the rate at which the HLLW needs to be processed. This, in turn, depends upon the implementation of the actinide removal process, the capacity of the New Waste Calcining Facility to process HLLW, and the need to dissolve calcine for the removal of actinides. Several assumptions were made in calculating column diameters: (1) the ICPP production of HLLW will be approximately 1500 m^3 per year. (2) In order to reduce the liquid inventory of HLLW currently stored at the ICPP, an additional 1550 m^3 will be processed each year until the inventory drops to 1100 m^3. (3) Once this inventory is reached, the actinide contaminated calcine will be dissolved at a rate of 225 m^3 per year. (4) The pulse columns will operate at 80% of their flooding capacity. (5) The process will operate 270 days per year. Taking these factors into consideration, the column diameters calculated are 23 cm for extraction, 14 cm for scrubbing, and 12 cm for the first strip column.

If the actinide removal process were to begin operation in 1987, it will take approximately 16 years once calcine dissolution begins to process all the calcine for the removal of actinides. If this schedule or the ICPP's flowrates were to change, then the column diameters would also change to provide a larger throughput. Implicit in these calculations is the assumption that processing of old actinide-bearing calcine can proceed only when the NWCF and the actinide removal system have spare capacity. If the calcine had to be processed within a certain time frame, then a larger actinide removal system as well as a new calciner would be required. These factors are considered in detail elsewhere.[42]

2. Material Balance Flowsheet

A result of the chemical development work by McIsaac[43,44] and the engineering studies presented in this report is the material balance flowsheet presented in Figure 14. For the extraction column, the actinide separations are based upon five transfer units. This will yield a raffinate which, when calcined, will be approximately 0.5 nCi actinides/gram calcine. For the scrub column, two



Stream		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Description		Aqueous Feed	Scrub Raffinate	Combined Feed	Organic Feed	Extraction Raffinate	Organic Extract	Scrub Feed	Scrub Extract	1st Strip Aqueous Feed	1st Strip Extract	1st Strip Raffinate	2nd Strip Aqueous Feed	2nd Strip Raffinate	2nd Strip Extract	1st Wash Aqueous Feed	1st Wash Raffinate	1st Wash Extract	2nd Wash Feed	2nd Wash Raffinate	2nd Wash Extract	Organic Make-Up			
Flow Rate	ℓ/Hr.	470	47	517	235	517	235	47	235	235	235	235	235	235	235	117	117	235	117	117	235	As Needed			
DHDECMP	Vol. %				20		20		20		20				20			20			20	20			
DECALIN	Vol. %				53		53		53		53				53			53			53	53			
DIPB	Vol. %				27		27		27		27				27			27			27	27			
H^+	M	1.62	2.55	1.70	$4x10^{-4}$	1.55	0.33	3.0	0.42	0.015	0.02	0.415	0.005	0.004	0.021				0.005	$4.2x10^{-3}$	$4x10^{-4}$				
Al^{+3}	M	0.67		0.61		0.61																			
Zr^{+4}	M	0.45	0.028	0.41		0.41	$4.3x10^{-3}$		$8.3x10^{-6}$			$8.3x10^{-6}$													
NO_3	M	2.36	2.55	2.38	$4x10^{-4}$	2.23	0.33	3.0	0.42	0.015	0.02	0.415	0.005	0.004	0.021				0.005	$4.2x10^{-3}$	$4x10^{-4}$				
B^{+3}	M	0.20		0.18		0.18																			
F^-	M	3.21		2.92		2.92																			
Hg^{+2}	M	0.002	$4.08x10^{-4}$	.002		$1.97x10^{-13}$	0.0041		0.004		0.004				0.004		0.008								
HAN[1]	M									0.05		0.05													
$H_2C_2O_4$	M												0.05	0.05											
Na_2CO_3	M															0.10	TRACE	TRACE		TRACE					
KCN	M															0.90	0.90								
U	g/l	$2x10^{-4}$	$1.18x10^{-5}$	$1.82x10^{-4}$		$5.74x10^{-28}$	$4.02x10^{-4}$		$4x10^{-4}$		$7.70x10^{-5}$	$3.23x10^{-4}$		$7.70x10^{-5}$											
Pu	g/l	$1.92x10^{-3}$	$1.05x10^{-3}$	$1.84x10^{-3}$		$3.13x10^{-12}$	$4.05x10^{-3}$		$3.84x10^{-3}$		$1.92x10^{-6}$	$3.84x10^{-3}$		$1.92x10^{-6}$											
Am	g/l	$3.63x10^{-5}$	$2.28x10^{-5}$	$3.51x10^{-5}$		$3.20x10^{-9}$	$7.72x10^{-5}$		$7.26x10^{-5}$		~0	$7.26x10^{-5}$													
Cm	g/l	$5.87x10^{-7}$	$3.08x10^{-7}$	$5.62x10^{-7}$		$7.39x10^{-10}$	$1.23x10^{-6}$		$1.17x10^{-6}$		~0	$1.17x10^{-6}$													
Np	g/l	$1.24x10^{-5}$	$1.32x10^{-5}$	$1.25x10^{-5}$		$9.87x10^{-6}$	$5.73x10^{-6}$		$3.09x10^{-6}$		~0	$3.09x10^{-6}$													
Ln	g/l	0.20	0.11	0.19		$2.52x10^{-4}$	0.42		0.399		~0	0.399													

1. HAN is oxidized to NO_x and leaves the column as a gas.

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2. Raffinate Values for Zr, Hg, U, Pu, Am, Cm, Np, and the Lanthanides are Calculated on a Basis of 5 Transfer Units in the Extraction Section and 2 Scrub Equilibrium Stages.

3. Material Balances Are Not Exact Due to Round Off Error.

Figure 14. Actinide Removal Process, Material Balance Flowsheet

equilibrium stages were used. The first strip column was patterned after the column in the pilot plant. For plutonium, which forms complexes in the organic phase, 0.05% of the Pu was assumed not to strip. This value will vary depending upon the purity of the solvent and the amount of acid degredation products formed. Because only these three operations are known in detail, the remaining material balances are only estimates. Additional tests are needed to confirm these values. The flowrates given are based upon the column diameters given earlier in this report. Changes would result if modifications in equipment size or type are specified.

3. Discussion of Process Feasibility

The solvent was used repeatedly in pilot plant and in simulated column experiments. During some of the pilot plant tests, there were times when the solvent was stored for several days loaded with HNO_3. Even under these conditions, the solvent cleanup step did an adequate job of removing acid degradation products from the organic. A solvent cleanup step using a resin ion exchange bed was used several times to remove degredation products. This step was needed only after the organic, pregnant with acid, sat for several weeks. Solvent recycle is a fundamental part of any solvent extraction system. For the actinide removal process, solvent recycle appears to be very reasonable. If this process were to be implemented, a purer DHDECMP should be used than that used in the pilot plant. Although the Hg purification technique has been demonstrated only on a bench scale, it should be used to produce the large amounts of DHDECMP required if this process is implemented.

Although most of the tests have been completed using synthetic coprocessing solution, the changes in actinide concentration, differing feed compositions, and unexpected process inefficiencies that will occur in a plant process can be controlled by changes in the column operating conditions. These include pulse frequency, amplitude, and the aqueous-to-organic (A/O) flow ratio. For example, better separations can be obtained by decreasing the A/O flow ratio in the extraction column. With the decrease in A/O flow ratio and the need to process a specific volume of solution, a different operating point on the flooding diagram would have to be used. With this system a lower frequency would increase the throughput, and the desired separation would still be acheived. Pulse columns are versatile and can be operated under various operating conditions. They can handle a variety of feeds bearing actinides. The use of different plate types could improve the capacity and separation efficiency of this process.[45] The resulting improvements may offset the lowered flooding curve which may result in the scaleup to a larger column.

For several years, a partitioning and transmutation program for nuclear waste management has been under the direction of the Oak Ridge National Laboratory (ORNL).[46] These studies were made for commercial power plant nuclear waste. One of the components of that strategy is the large scale separation of actinides from commercial nuclear fuel reprocessing wastes. While these separations have been performed countercurrently on a small scale, the pulse column tests for the ICPP as reported here are more evidence for the technical practicality of the waste management strategy.

The ORNL study states that while the separation of actinide waste is technically feasible, the actinide recycle concept is not. The collection and isolation of the actinides merely concentrates the radioactive waste problem. Routine processing creates exposure hazards to personnel. The concentrated actinides must be shielded. With respect to disposal, no federal repository now exists to receive the actinide fraction of the ICPP waste. Furthermore, the storage of the actinide-free fraction at the ICPP has never been formally proposed, much less accepted. For all of these reasons, the disposition of actinides from the ICPP process is uncertain, even though the process appears to be feasible from the technical standpoint and offers significant cost savings compared to shipping all wastes to a repository.

V. RECOMMENDATIONS FOR FURTHER DEVELOPMENT

Although development of the actinide removal process appears to have reached the point where it is technically feasible, some long-term testing using radioactive feeds should proceed. Certain aspects of the flowsheet such as Hg removal and the second strip require more development work before a fullscale plant can be built. Such development would include radioactive testing to prove the process under actual plant conditions as well as nonradioactive testing to verify equipment design. Because the basic types of equipment for the process can be estimated fairly accurately now, further testing might be completed concurrently with the conceptual design phase of a fullscale plant. Resulting changes could then be accommodated before the Title I design phase began. Additional testing could be done on new equipment types, such as centrifugal contactors or new extraction column plates.

1. Radioactive Development Work

An important verification of this process would be to test the entire flowsheet over an extended period of time on a continuous countercurrent basis using mini mixer-settlers in a hot cell. In this test, the mixer-settlers would be set up for continuous solvent flow. That is, the solvent, after the final HNO_3 wash, would be recycled to the extraction unit. The characteristics of the actinide removal process to be established in this test would be to: (1) prove the recycle of the solvent when used in radioactive service, (2) establish solvent losses and the buildup of impurities, (3) prove the operation of the second strip, since it is necessitated by the presence of radiation, and (4) verify that the solvent can continuously remove the actinides from the ICPP wastes. Such a test should last for a sufficient length of time for steady-state to be reached, perhaps a week or more. The advantage of this test is that the cost of an expensive hot pilot plant could be significantly reduced.

Prior to this test, some process information may have to be determined for the second strip and the Hg removal operations. The number of equilibrium contacts required for the second strip could be determined in a simulated column. The solvent would have to be irradiated in the presence of a Pu-bearing coprocessing solution to produce the organic plutonium complexes that are stripped by the oxalic acid. The combined Hg removal/sodium carbonate wash should also be demonstrated prior to the extended mixer-settler run.

As a result of the radioactive tests, some further solvent cleanup may have to be added to the flowsheet. This may be a resin ion exchange cleanup of the solvent, which was described in the "Pilot Plant Results" section of this report.

2. Nonradioactive Development Work

Most of the pilot plant testing has been directed towards the performance of the extraction, scrub, and first strip operations. Consequently, the majority of the information necessary for the design of these operations is presently known. The effect of mass transfer upon pulse column flooding is the major design uncertainty for this process. The design of the two strip columns needs to take this effect into account. As noted in the "Pilot Plant Results" description, problems have been encountered with flooding in the first strip column, where most of the solutes are removed from the pregnant organic leaving the scrub column. This problem did not ordinarily occur, but happened when an excessively tall column was used. It was concluded that the flooding was due to the absence of mass transfer in the upper portion of the column.

The oxalic acid strip removes residual Pu and U from the organic. There is not much mass transfer that occurs in this operation. Hence, a pulse column may not be appropriate for this operation. Cold pilot plant testing of pulse columns for this operation will determine if the desired flow rates can be obtained without flooding. If flooding is a problem, a mixer-settler would be a good choice for a contactor. Mixer-settlers provide good phase separation and mass transfer; their scale-up is reliable. Prior to any nonradioactive testing of this operation, mass transfer in the presence of radiation will have to determine the number of equilibrium contacts required.

Mixer-settlers should probably be used for the other solvent cleanup operations: solvent wash, Hg removal, and the weak $HN0_3$ wash of the solvent. None of these operations has been demonstrated on a continuous pilot plant scale. Removal of Hg from the DHDECMP has been demonstrated only in the laboratory. The probable technique for this operation would be a KCN complexation.[47] This could be a one stage operation; perhaps perfomed in the same mixer-settler as the Na_2CO_3 is. (An electrolytic separation of the Hg could follow if this were desired.) Batch solvent washes by Na_2CO_3, to remove acidic decomposition products, and by HNO_3, to neutralize Na_2CO_3 entrained in the organic, have been routinely performed on this solvent. These treatments have been done to the solvent used in the pilot plant and to that used in the simulated columns. There is no reason to doubt that these operations would not succeed. Nevertheless, some nonradioactive testing is necessary to verify the flow characteristics of process equipment. With respect to the solvent wash, a hydrozine carbonate wash[48] may be appropriate since the Na-bearing wastes may cause operating problems for the ICPP calciner.

3. Miscellaneous Process Improvements

Some process improvement could be expected to result from equipment changes. For the pulse columns, using one of the new plate types developed by General Atomic[49] would improve separation efficiency as well as increase throughput. Thus, shorter, smaller cross-sectional area columns would be feasible. For the extraction column, teflon or nozzle plates would allow an organic continuous bottom interface column to be used. This type of operation would tend to force solid and emulsified impurities to the raffinate end of the column and away from the actinide bearing organic product.

Centrifugal contactors were considered for the pilot plant experimental phase of the project. They were not purchased because of money and time constraints. Use of a centrifugal contactor for this process would be appropriate for several reasons. First, the kinetics of the extraction of the actinides are sufficiently different from those of mercury and zirconium that the differences could be exploited by taking advantage of a short contact time to extract the actinides but not the mercury and zirconium. Thus, the need for a scrub section would be eliminated or minimized. Second, the short contact time characteristic of a centrifugal contactor could significantly reduce the radiolysis damage suffered by the solvent. At the miminum, this would reduce the operating cost associated with the solvent upgrade. Third, the need for a mercury removal step and consequently the use of hazardous KCN might be eliminated. Fourth, a new technology would be developed that could offer further fuel reprocessing advantages. However, centrifugal contactors have a high initial cost, may be expensive and difficult to operate, and have known solids problems. It is questionable if a mechanically complex piece of equipment should be used in radioactive service. These problems would have to be resolved in a pilot plant program.

4. Final Disposition of the Actinide Fraction

In addition to the other development areas already discussed, the final disposition of the actinides has yet to be determined. Once the actinides have been removed from the ICPP HLLW, there are two probable options for their final disposition. These options are: (1) solidification and removal to a federal nuclear waste repository or (2) separating the actinides from the lanthanides for fission in Light Water Reactors (LWR's) and Liquid Metal Fast Breeder Reactors (LMFBR's). (The lanthanide waste would be combined with other fission product waste.) The ORNL has undertaken an extensive technical evaluation of the actinide removal scheme as a waste management strategy. These results are reported in four summary reports.[50,51,52,53] The discussions in these reports apply to all aspects of this actinide removal strategy including fuel refabrication, remote handling, and reactor physics.

One problem that needs to be resolved prior to the implementation of this process is that of the combination of the two strip raffinates. The low concentration of oxalic acid present in the second strip raffinate would precipitate only the lanthanides. The Oak Ridge reports also discuss this problem but offer a solution, which is to destroy the oxalic acid. This same destruction technique would undoubtedly be applied to the ICPP strip raffinates.

To date, only preliminary studies have been conducted on the solidification of the actinide-lanthanide mixture. In these tests a synthetic strip raffinate solution, presented in Table XI, was used. This solution is low in acid concentration and high in the concentrations of the actinide constituents. Oxalic acid was then added to this solution forming a precipitate of mixed actinides and lanthanides. As shown in Table XII, more than 99% of the Am and Pu was precipitated in each of six tests. The precipitate could then be mixed with various types of frits, formed into a glass and shipped to a federal repository. These tests are only preliminary and are not an endorsement of the method. Other types of solidification include calcination followed by vitrification of the actinide-lanthanide mixture, sorption on inorganic ion exchange media,[54] or a ceramic form of solidification.

TABLE XI

EXPECTED COMPOSITION OF ACTINIDE WASTE FRACTION SOLUTION

Component	Concentration
HNO_3	0.24 M
Hydroxylamine Nitrate	0.05 M
U	0.36 mg/ℓ
Np	trace
Pu	7.2 mg/ℓ
Am	0.12 mg/ℓ
Cm	0.0024 mg/ℓ
Rare Earths	360 mg/ℓ
Other Fission Products	trace

TABLE XII

PERCENT Am AND Pu REMOVED BY OXALATE PRECIPITATION

Run No.	Am	Pu
1	99.80	99.67
2	99.81	99.78
3	99.79	99.40
4	—	98.8
5	—	99.59
6	—	99.56

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APPENDIX A - DILUENT STUDIES

During the pilot plant tests, emulsions formed in the strip column. They were initially thought to be caused by the solvent. Specifically, it was felt that the diluent could be changed to improve column performance. Based on batch distribution results reported[1] previously for the DHDECMP system, it seemed that ketones, as a class, would be superior diluents. Three ketones, selected for high flash point, low viscosity and density, and availability, were used as diluents for batch distribution studies. The results of these batch tests are presented in Table AI. While the 2:1 decalin-diisopropyl benzene diluent gave the best distribution coefficients, the other solvents all had better coalescence times. Therefore, if the full-scale plant columns do not have satisfactory hydraulics, there are other reasonable diluents that can be used. Diluents exert a major influence upon a solvent extraction process: hydraulics, equilibrium position, and economics. Diluents for some systems can be selected on a solubility parameter concept.[2] The selection of diluents for other systems may first be made based on classes of organic compounds giving good distribution coefficients. Then the final selection may be made from within those classes of compounds giving best flow characteristics, flash point, and cost.

TABLE AI

EXTRACTION OF Am FROM Zr-Al DISSOLVER SOLUTION WITH DHDECMP

	Americium Distribution Coefficient				
20% DHDECMP (in diluent)	Extraction[a] Contact	Scrub[b] Contact	Strip Contact[c] 1	2	3
2-Octanone	6.4	1.88	0.49	0.101	0.086
4-Pentanone	8.7	2.67	0.69	0.126	0.086
3-Pentanone	7.6	2.43	0.62	0.125	0.095
2:1 Decalin-DIPB	12.1	4.81	0.37	0.073	0.070

a Equal volume organic to aqueous Zr-Al dissolver solution (O/A = 1)
b Scrub: 3 M HNO_3, O/A = 5
c Strip: 0.010 M HNO_3 - 0.05 M HAN, O/A = 1

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APPENDIX B - FLOODING DETERMINATION TECHNIQUE

Flooding tests were made to establish the volumetric capacity of the pulse columns. The results of these tests are presented in Figures B1 and B2 for the extraction/scrub and the first strip respectively. Flow ratios of 2:1 for extraction and 1:5 for the scrub sections were used in these tests. A simple column was used for the strip, where a flow ratio of 1:1 was used. For low frequencies, the pulse volume velocity (see Figures B1 and B2) describes the maximum flow to a column for a given pulsing condition. Greater flows would flood the column, i.e., the phase would short circuit the column and exit at the end to which it was fed. At higher frequencies, the flooding line had to be determined experimentally.

The flooding points for the extraction/scrub and strip columns were determined visually by a method suggested by Dr. L. Burkhart of the Ames, Iowa Laboratory at Iowa State University. For each flooding point determined, the column throughput and pulser frequency were set, and the pulse amplitude was adjusted to 2.5 cm. The column throughput was then incrementally increased until the column flooded. This was determined when the organic phase would no longer proceed up the column, and a second interface formed in the bottom disengagment section. The throughput was then reduced and adjusted systematically every 5-20 minutes. By observing the reaction of the interface position to changes in flow rate, the flooding point was determined. If the organic interface at the bottom of the column remained stable or moved upwards, the column was considered to be operating below the flooding point. A downward movement of the interface meant that the throughput was above the flooding point.

The following polynomials were then fitted to the data:

$$Y = 6.5 - .053 + 1.2\ (10^{-4})\ X^2 \qquad \text{extraction/scrub} \qquad (1)$$

$$Y = 19.9 - .189 + 4.63\ (10^{-4})\ X^2 \qquad \text{strip} \qquad (2)$$

$$Y = \ell/\text{hr}\cdot\text{cm}^2 \qquad X = \text{cm/min(2.5 cm pulse)} \qquad (3)$$

For the mass transfer tests, the flow rates were set at a percentage of flooding, usually at 80%. The flooding lines in Figures B1 and B2 were the bases used to set this percentage.

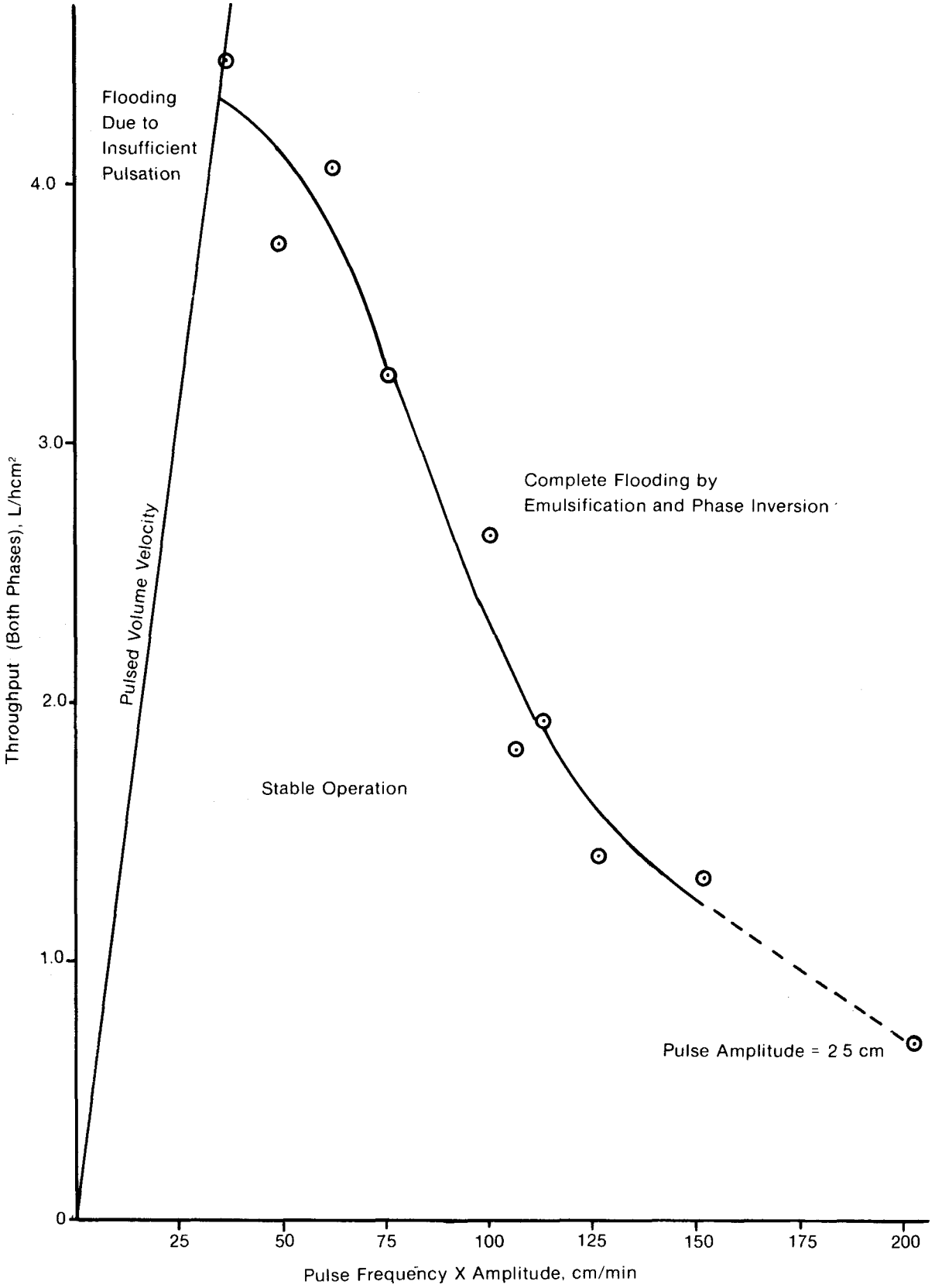

Figure B1. Flooding Curve - Compound Extraction/Scrub Column DHDECMP System

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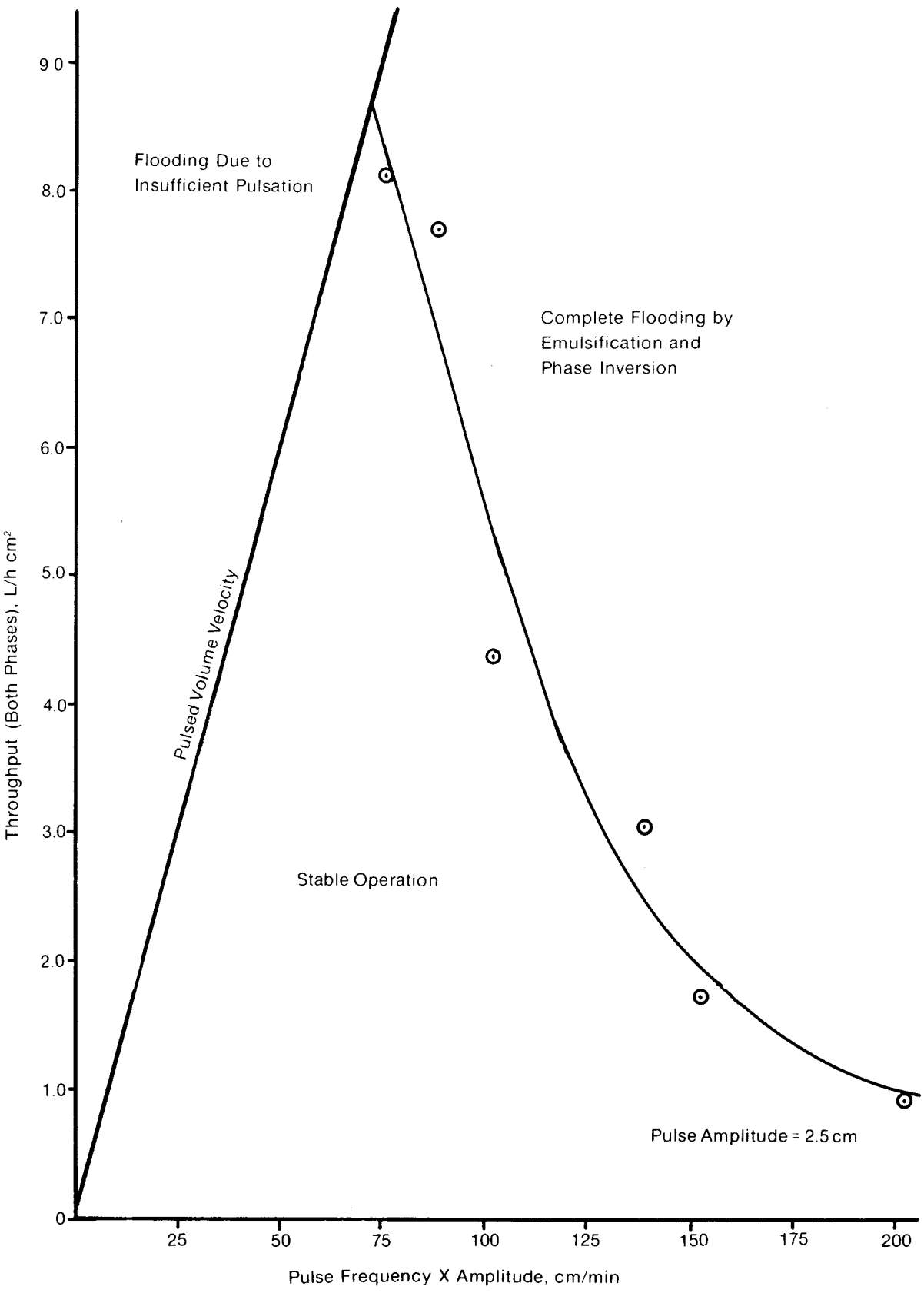

Figure B2. Flooding Curve - Strip Column DHDECMP System

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APPENDIX C - SIMULATED COLUMN TECHNIQUE

A "batch pseudo countercurrent extraction"[1,2] or a "simulated column" is a separatory funnel cascade that can be used to study a solvent extraction flowsheet, such as the one represented in Figure C1. In this figure, the aqueous feed is center-fed to an extraction/scrub column. Fresh extractant is fed to the bottom of the extraction column. This extractant is used to separate the desired solutes from the aqueous feed. Some co-extracted solutes are selectively back extracted in the scrubbing column. Solute is removed from the pregnant organic exiting the scrubbing section in the stripping section. After the proper cleanup steps, the solvent from the strip column can be used as a fresh extractant. An advantage of the simulated column is the accurate collection of equilibrium data over a wide concentration range. The major advantage of this experiment, though, is the information developed about the process on a countercurrent basis, e.g., flow ratios, equilibrium contacts, and feed concentration changes. This is a particularly attractive experiment because a material balance can be made on the system to assess overall accuracy and because the data fall in a logical pattern. Collection of the data is quick, and the experiment can be done in a small area with a minimum use of chemicals.

Figure C2 is a flow chart for a typical simulated column experiment. The circles at the bottom of the figure represent the same solvent extraction process that was shown in Figure C1. For this process there are four extraction, two scrub, and four strip stages. Each of the circles in the bottom of the figure represents an equilibrium contact. The circles in the top of the diagram represents a separatory funnel shake-out. Starting with the uppermost separatory funnel (number "1"), aqueous feed, F, scrub solution, S, and solvent, E, are added together and shaken for one and a half minutes. Once the phases coalesce, the raffinate is withdrawn and added to separatory funnel #2, where fresh solvent E_2 is added, and the shake-out procedure is repeated. Meanwhile, funnel #1 has had fresh scrub added to it. This solution is then mixed, and the phases are allowed to coalesce. This produces an aqueous phase that is contacted with new feed and the organic now present in separatory funnel #2. These transfers are repeated as shown in Figure C2. For this flow chart, organic phases move to the left, and aqueous phases move to the right.

The cascade of separatory funnels followed the cycles (rows) until a chemical steady-state was reached. Once chemical steady-state is achieved, the liquids in the separatory funnels have all the physical properties that would be encountered in a multistage solvent extraction process. Achievement of steady-state can be monitored by analyzing the raffinate from the strip-column, "SR Out." Typically, the concentration of solute in this stream rose with repeated cycles of the cascade until the values centered around a steady-state concentration. This generally took place in seven to ten cycles. Use of tracer isotopes of the extractable species ensured that the information was quickly available. For some experiments, the extract from the scrub column was used to assess the attainment of steady-state.

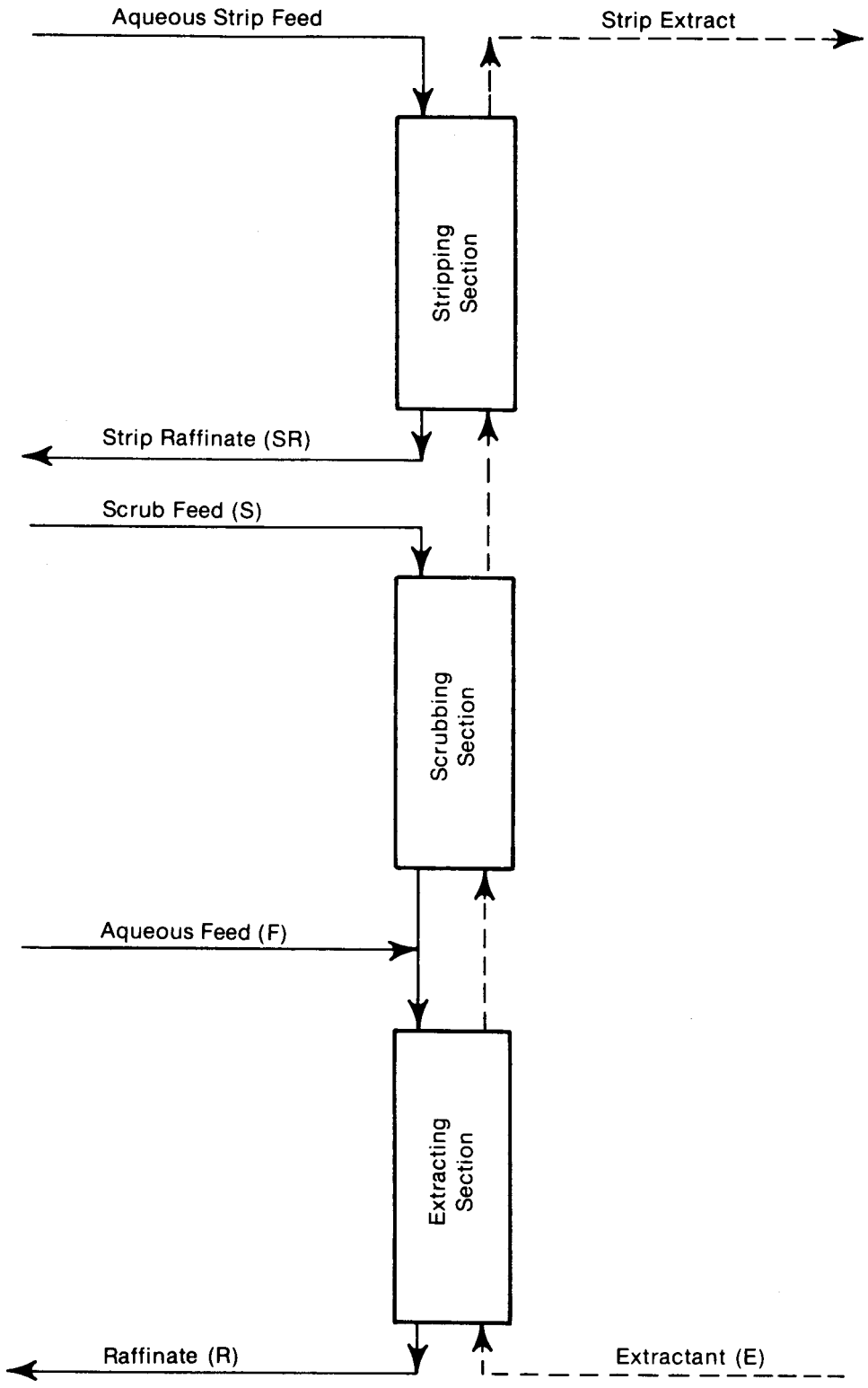

Figure C1. Solvent Extraction Flowsheet with Extraction, Scrub, and Strip.

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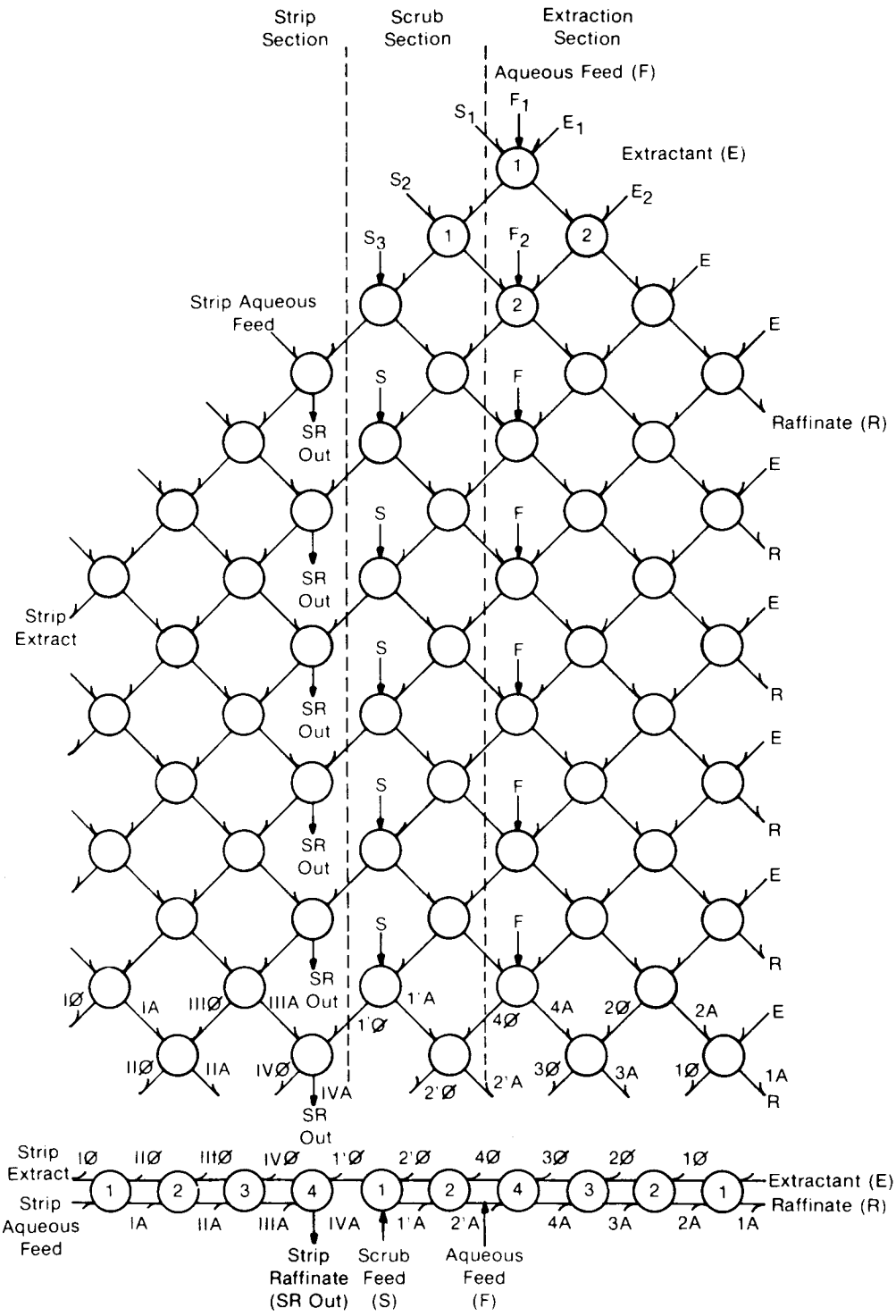

Figure C2. Batch Simulation of Fractional Extraction.

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The physical arrangement of the experiment was quite simple. Ring stands were used to hold the funnels. The organic phases remained in the same funnels throughout the sequence. The raffinate was withdrawn after the extraction contacts; the strip raffinate was withdrawn after the strip contacts. No attempt was made to control the temperature in these experiments. Generally, three or four people participated in these experiments, which lasted about six hours. A device described by Scheibel[3] can also be used for a simulated column experimental setup.

Since each row of the simulated column flowchart represents only half of the equilibrium stages, the solutions were halved upon attainment of steady-state. This produced half of the samples for the experiment. The other half of the solutions were mixed to produce the remaining samples. In the bottom of Figure C2, the arabic numbers (e.g., 1Ø and 1A) represents equilibrium extraction streams, the primed numbers (e.g. 1'Ø and 1'A) represent the equilibrium scrub streams, and the Roman numerals (e.g. IØ and IA) represent the equilibrium strip streams.

A typical set of data for a four extraction stage and two scrub stage simulated column is presented in Table CI. In this table are presented the stagewise Ce concentration, analyzed by tracer isotope and by a spectrochemical method. This experiment had a feed/solvent/scrub ratio of 2/1/0.2. These data can be analyzed by material balances, which are reported in the table. A material balance analysis considers the amount of material leaving a separatory funnel in relationship to the amount entering. The reported material balance values divide the output by the input. Obviously, the tracer analyses were more accurate than those analyzed spectrochemically.[4] Treybal[5] recommends that pilot plant material balances should close to within five percent. If not, the results should not be used to assess equipment performance. By using the results from the simulated column material balances and by comparing the tracer analyses with the spectrochemical results, the spectrochemical analytical technique for Ce was refined. Eventually, a ten percent material balance limit was used for the pilot plant results.

The linear regression curve fitting routine of the HP-67 calculator[6] was used to analyze the data from the simulated columns. For example, the samples exiting the separatory funnels were used to generate equilibrium lines. A regression of organic phase concentrations (Y) as a function of aqueous phase concentrations (X) was used to produce these lines. The data quality could also be judged by its fit to the material balance operating line. The extraction and scrub material balance operating lines would be of the form in equation 1 and 2:

$$Y = (A/O)_e (X - X_R) \quad \text{(extraction)} \quad (1)$$

$$Y = Y_E + (A/O)_S X \quad \text{(scrub)} \quad (2)$$

Y = organic phase concentration
X = aqueous phase concentration
A/O = phase ratio
Y_E = extract concentration leaving scrub section
X_R = raffinate concentration leaving extraction section

TABLE CI

COMPARISON OF CERIUM SPECTROCHEMICAL ANALYTICAL METHOD VERSUS CERIUM 144 TRACER ANALYSIS BASED ON MATERIAL BALANCES

Stage #	Cerium Concentration Based on ^{144}Ce Tracer Aqueous Ce g/ℓ	Organic Ce g/ℓ	Cerium Concentration Based on Spectrochemical Analysis Aqueous Ce g/ℓ	Organic Ce g/ℓ	Material Balance % Out Feed Basis Tracer	Spectrochemical
1	0.004	0.020	0.004	0.021	100.7	150.5
2	0.013	0.061	0.009	0.075	99.1	106.3
3	0.032	0.167	0.031	0.192	101.1	107.4
4	0.079	0.395	0.076	0.361	96.6	86.6
5	0.099	0.391	0.099	0.485	99.2	132.8
6	0.095	0.387	0.095	0.435	107.8	93.6
Aqueous Feed Concentration	0.201		0.199			
Organic Extract Concentration		0.387		0.435		
Overall Material Balance					98.6	111.5

Regressed equations of the data from Table CI gave equations 3 and 4:

$$Y = 2.23\,(X - .004) \qquad \text{(extraction)} \qquad (3)$$

$$Y = 0.387 + .06X \qquad \text{(scrub)} \qquad (4)$$

Since the experiment was set to have an extraction section phase ratio of 2.2 and because the actual raffinate concentration was 0.004 gCe/ℓ, the data appear to be quite good. Similarly, the scrub section results are mixed because the experimentally set phase ratio was 0.2 and because the extract concentration was 0.387 gCe/ℓ.

Complete results from the extraction/scrub simulated column experiments are presented in Table CII, CIII, and CIV. In Tables CII and CIII are presented the stagewise distribution coefficients (D) and phase concentrations for Am, Pu, Ce and HNO_3, respectively. In Table CIV the overall extraction and scrub distribution coefficients are presented for Am, Pu, and Ce. These distribution coefficients were calculated by a linear regression of the data in Table CII. For these regressions, the point (0.0, 0.0) was included for each equilibrium line. As a result of the simulated column experiments, it has been concluded that the distribution coefficients for Ce, Am, Pu, HNO_3 and Zr were each constant throughout the extraction and scrub sections. This is illustrated for Ce in the operating diagram, Figure C3. In addition, it was concluded that: (1) pinches for Ce, Am and Pu in the scrub section and for HNO_3 and Zr in the extraction section showed that the flow rates were reasonable; (2) co-extracted Zr can be successfully removed from the pregnant organic in two scrub contacts; and (3) that the pregnant organic exiting the scrub section was about 0.4 M in HNO_3.

The results of the Ce, Am and Pu strip simulated columns are presented in Table CV. Unlike the distribution coefficients for the extraction/scrub section, the distribution coefficients for the strip section are not constant. This is illustrated in Figure C4, the strip operating diagram for Ce. After the bulk of the HNO_3 is removed from the organic, usually in one equilibrium stage, the solute is then quickly stripped from the organic. The Ce strip data were fitted to a fourth order polynomial using a Tektronix 4051 desktop computer:

$$Y = 1.25(10^{-5}) + 1.96(10^{-2}) + 0.7486X^3 + 13.8646X^4 \qquad (5)$$

Y = Organic phase Ce concentration, g/ℓ

X = Aqueous phase Ce concentration, g/ℓ

This equation does not represent the true equilibrium relationship for Ce in the strip column, but rather it is a convenient analytical tool. This relationship was used to calculate the strip pulse column separation efficiencies for the pilot plant runs. An example of these calculations is presented in Appendix E.

TABLE CII

Am, Pu, & Ce SOLUTE PROFILES: SIMULATED COMPOUND COLUMNS

		Ce Extraction/Scrub #1			Ce Extraction/Scrub #2			Am Extraction/Scrub			Pu Extraction/Scrub		
Section	Stage[a]	Organic Phase g Ce/ℓ	Aqueous Phase g Ce/ℓ	D_{Ce}	Organic Phase g Ce/ℓ	Aqueous Phase g Ce/ℓ	D_{Ce}	Organic Phase g Am/ℓ	Aqueous Phase g Am/ℓ	D_{Am}	Organic Phase g Pu/ℓ	Aqueous Phase g Pu/ℓ	D_{Pu}
Extraction	1	.020	.004	4.59	.00104	.00027	3.85	1.76×10^{-7}	2.53×10^{-8}	6.96	2.73×10^{-6}	2.12×10^{-7}	12.9
	2	.061	.013	4.70	.0049	.0011	4.45	7.72×10^{-7}	1.11×10^{-7}	6.94	1.94×10^{-5}	1.43×10^{-6}	13.5
	3	.167	.032	5.25	.0208	.0045	4.69	2.63×10^{-6}	3.87×10^{-7}	6.79	1.19×10^{-4}	9.17×10^{-6}	13.0
	4	—	—	—	.0816	.0170	4.80	8.56×10^{-6}	1.27×10^{-6}	6.72	7.26×10^{-4}	5.44×10^{-5}	13.3
	5	—	—	—	—	—	—	2.66×10^{-5}	3.97×10^{-6}	6.71	—	—	—
	Feed	.395	.079	5.02	.3291	.0754	4.36	8.46×10^{-5}	1.30×10^{-5}	6.53	4.54×10^{-3}	3.30×10^{-4}	13.8
Scrub	3	—	—	—	.3206	.0984	3.26	8.66×10^{-5}	2.48×10^{-5}	3.48	—	—	—
	2	.391	.099	3.94	.3152	.0878	3.59	8.61×10^{-5}	2.49×10^{-5}	3.43	4.47×10^{-3}	1.21×10^{-3}	3.71
	1	.387	.095	4.06	.2998	.0762	3.94	8.13×10^{-5}	2.52×10^{-5}	3.23	4.28×10^{-3}	1.02×10^{-3}	4.20
		Aqueous Feed = 0.201 g Ce/l; Extraction A/0 = 2.2; T = 21°C; ^{144}Ce used for Ce Analyses			Aqueous Feed = 0.298 g Ce/l; Extraction A/0 = 1.2; T = 23°C; ^{144}Ce used for Ce Analyses			Aqueous Feed = 4.3×10^{-5} gAm/l; Extraction A/0 = 2.2; T = 25°C; ^{241}Am used for Am Analyses			Aqueous Feed = 2.2×10^{-3} gPu/l; Extraction A/0 = 2.2; T = 20°C; ^{239}Pu used for Pu Analyses		

a Feed stage is the point where the aqueous feed is introduced to the center-fed column. Less than 5 extraction stages or less than 3 scrub stages were used in some columns.

b A/0 = actual (not feed) aqueous-to-organic phase ratio for extraction section. For all experiments, the A/0 for the scrub section was 0.2.

TABLE CIII

HNO_3 PROFILES: SIMULATED COMPOUND COLUMNS

Section	Stage[a]	Ce Extraction/Scrub #1			Ce Extraction/Scrub #2			Am Extraction/Scrub			Pu Extraction/Scrub		
		Organic Phase, M	Aqueous Phase, M	D_{HNO_3}	Organic Phase, M	Aqueous Phase, M	D_{HNO_3}	Organic Phase, M	Aqueous Phase, M	D_{HNO_3}	Organic Phase, M	Aqueous Phase, M	D_{HNO_3}
Extraction	1	.35	1.46	.24	.28	1.60	.18	.39	1.84	.21	.35	1.62	.22
	2	.36	1.59	.23	.31	1.61	.19	.42	2.03	.21	.36	1.82	.20
	3	.36	1.58	.23	.33	1.61	.20	.43	2.05	.21	.39	1.83	.21
	4	—	—	—	.33	1.64	.20	.42	2.05	.20	.38	1.82	.21
	5	—	—	—	—	—	—	.40	2.04	.20	—	—	—
	Feed	.36	1.57	.23	.32	1.64	.20	.44	2.05	.21	.38	1.84	.21
Scrub	3	—	—	—	.37	2.63	.14	.35	3.01	.12	—	—	—
	2	.41	2.52	.16	.40	2.76	.14	.40	3.08	.13	.38	2.78	.14
	1	.41	2.80	.16	.42	2.85	.15	.41	3.10	.13	.43	2.95	.15
		Aqueous Feed = 1.54 M HNO_3 Scrub Feed = 3.03 M HNO_3 Extraction A/0 = 2.2 T = 21°C			Aqueous Feed = 1.44 M HNO_3 Scrub Feed = 2.96 M HNO_3 Extraction A/0 = 1.2 T = 23°C			Aqueous Feed = 2.33 M HNO_3 Scrub Feed = 3.09 M HNO_3 Extraction A/0 = 2.2 T = 25°C			Aqueous Feed = 1.74M HNO_3 Scrub Feed = 2.92M HNO_3 Extraction A/0 = 2.2 T = 20°C		

a Feed stage is the point where the aqueous feed is introduced to the center - feed column. Less than 5 extraction stages or less than 3 scrub stages were used in some columns.

b A/0 = Actual (Not Feed) aqueous-to-organic phase ratio for extraction section. For all experiments, the A/0 for the scrub section was 0.2.

TABLE CIV

LINEARLY REGRESSED OVERALL DISTRIBUTION COEFFICIENTS
FROM EXTRACTION/SCRUB SIMULATED COLUMNS

Solute	Extraction Section Phase Ratio $(A/0)_e$	Extraction Distribution Coefficient De	Scrub Section Phase Ratio $(A/0)_s$	Scrub Distribution Coefficient Ds
Ce	2.2	5.0	0.2	4.0
Ce	1.2	4.4	0.2	3.5
Am	2.2	6.5	0.2	3.4
Pu	2.2	13.8	0.2	3.9

NOTE: The point (0,0) was included in each of these regressions.

TABLE CV

SOLUTE PROFILES : STRIP SIMULATED COLUMNS

	Ce Strip			Am Strip			Pu Strip		
Stage	Organic Phase g Ce/L	Aqueous Phase g Ce/L	D_{Ce}	Organic Phase g Am/L	Aqueous Phase g Am/L	D_{Am}	Organic Phase g Pu/L	Aqueous Phase g Pu/L	D_{Pu}
1	0.100	0.292	0.343	1.67×10^{-5}	7.42×10^{-5}	0.226	1.65×10^{-3}	4.33×10^{-3}	0.381
2	0.00287	0.102	0.028	4.26×10^{-7}	1.81×10^{-5}	0.024	1.55×10^{-5}	1.79×10^{-4}	0.009
3	7.5×10^{-5}	3.47×10^{-3}	0.022	1.44×10^{-8}	4.37×10^{-7}	0.033	6.25×10^{-7}	3.56×10^{-5}	0.018
4	1.2×10^{-5}	1.2×10^{-4}	0.100	NM	NM	NM	4.27×10^{-7}	1.02×10^{-6}	0.42
5	NM	NM	NM	NM	NM	NM	-	-	-
	Organic Feed=0.278g Ce/l ^{144}Ce Used for Ce Analyses T = 22.5°C			Organic Feed=7.24×10^{-5} g Am/l ^{241}Am Used for Am Analyses T= 25.5°C			Organic Feed=4.28×10^{-3} g Pu/l ^{239}Pu Used for Pu Analyses T = 20°C		

NOTE:
A/O For All Experiments = 1.0
NM = Not Measureable, Solute < Detection Limit

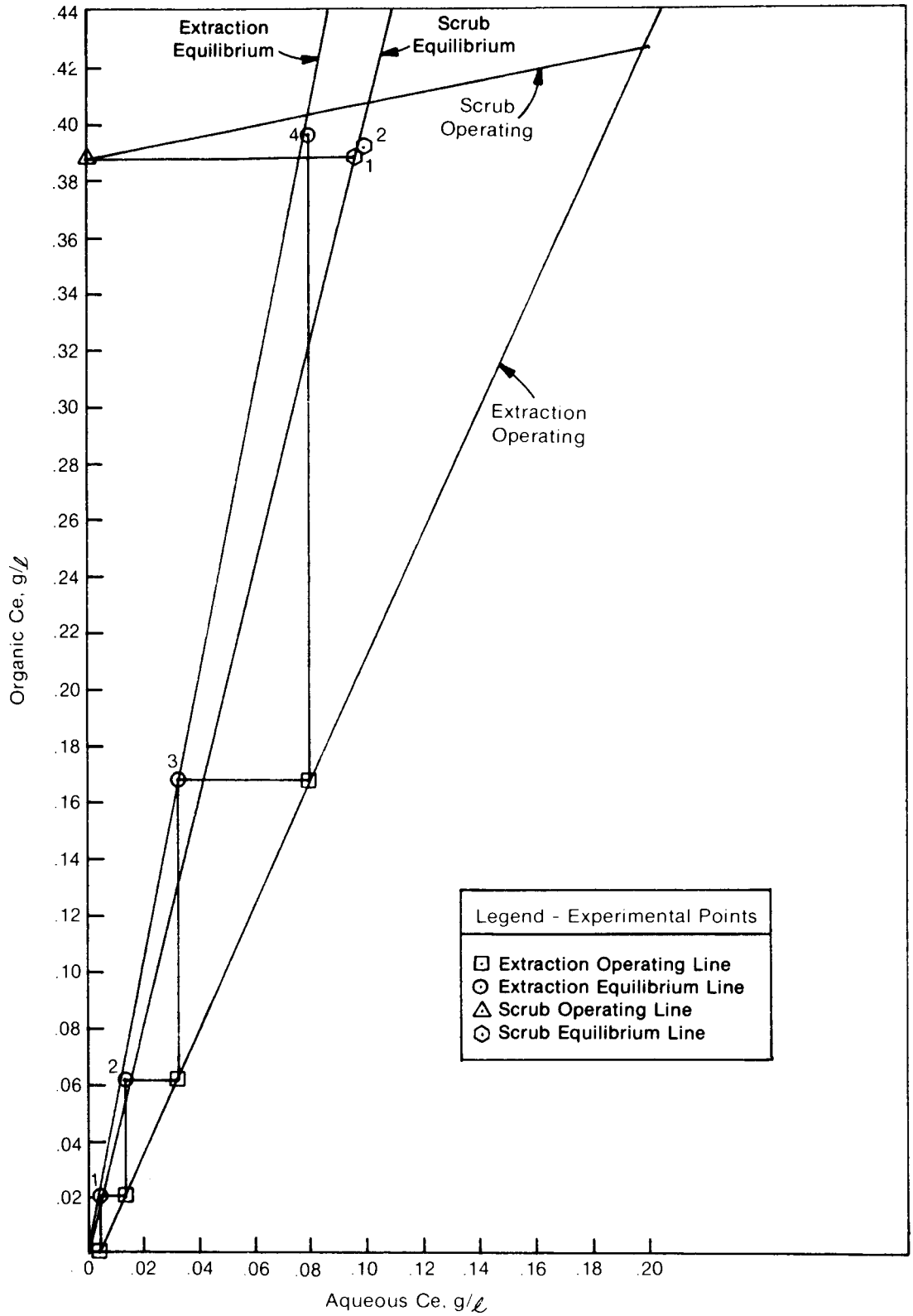

Figure C3. Ce Operating Diagram: Batch Simulated Compound Column

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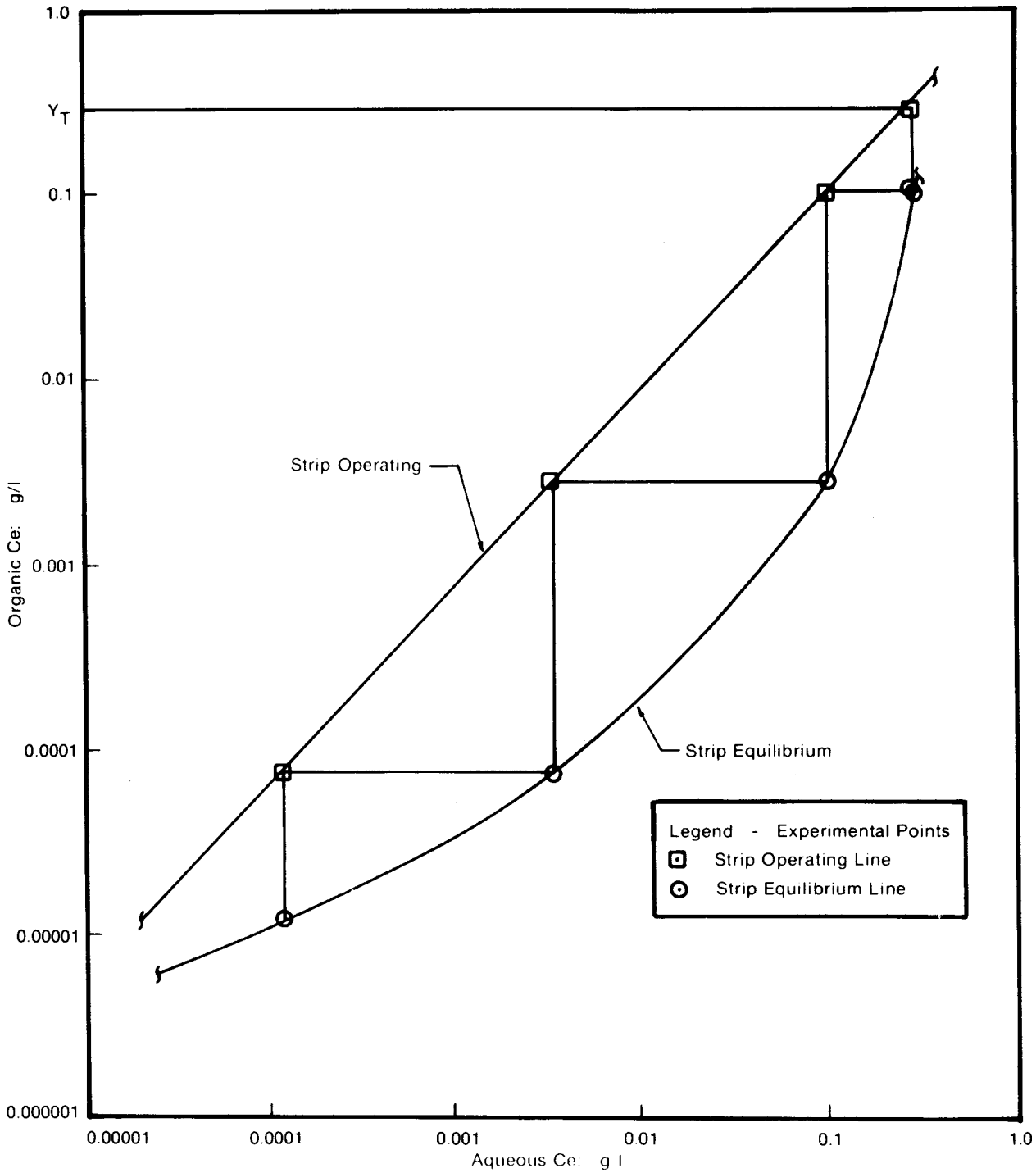

Figure C4. Ce Operating Diagram: Batch Simulated Strip Column

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4. R.W. Stone, et al The Determination of Cerium by Induction Coupled Plasma Optical Emission Spectroscopy, US DOE Report ENICO 1056, September 1980.

5. Treybal, p. 386.

6. "Curve Fitting," Standard Pac 1, Hewlett-Packard Co., 1976, pp. 03-10-03-08.

APPENDIX D - PILOT PLANT DESCRIPTION

1. Columns

Pulse sieve-plate extraction columns were used for most of the pilot plant tests. The two pulse columns used for these tests are constructed of 5.08 cm (two inch) inside diameter (I.D.) pyrex pipe with plate section heights of 6.60 metres and 2.89 metres, respectively. The taller column has two intermediate feed locations so that it can be operated as a compound column. Usually, the length of the top, or scrub section was 1.54 metres while that of the extraction section was 5.06 metres. By use of the other feed point, the scrub section could be extended to 2.87 metres and the extraction section reduced to 3.73 metres.

The sieve plates are stainless steel, with 0.31 cm (0.123 inch) diameter holes, approximately 25% free area, and are spaced 5.08 cm (two inches) apart in both columns. These stainless steel plates were wetted by the aqueous phase; therefore, the aqueous phase was continuous in the columns. The organic phase was lighter than the aqueous and flowed vertically upward in this countercurrent system. Samplers are located at intervals along both columns so pure samples of either phase can be taken independently of one another. These samplers are similar to those described by Benedict.[1]

A third column occasionally used for Na_2C0_3 washing of the organic is a 5.08 cm I.D. packed column 7.19 metres high. The packed section height of 6.34 metres is filled with 0.1 cm stainless steel Raschig rings. This column was not pulsed.

Each of the three columns has a disengaging head on either end, in which the two phases separate before leaving the column. The organic passes out through the upper disengaging head and the aqueous through the lower one. Each head consists of a section of 10.2 cm (4.0 inch) I.D. pyrex pipe attached to the column end by a concentric reducer.

2. Metering Pumps

Initial filling of the columns and subsequent feeding of the two phases to the columns during testing was provided by two sets of Milton-Roy Quadruplex Metering Pumps, Model No. D2/4-4-175SM. Each set consists of four pumps driven in tandem by one self contained motor. These pumps are positive displacement piston pumps whose flow is controlled by setting a vernier on each pump head. Whenever the motor is on, all four pumps are running but not pumping unless some setting between 0 and 100 percent has been set on the vernier. It was necessary to calibrate each pump in order to correlate pump flow rate with pump settings.

3. Pulsers

The organic phase does not normally flow upward through the sieve plates rapidly enough to be practical, so pulsers are incorporated to give an external "push" to the organic. This pulsing also improves the mass transfer characteristics of pulse columns. Parallel to each column is a 1.27 cm (0.5 inch)

I.D. pyrex pipe called a jack leg. It is connected directly to the bottom of the column and, at the top, to an air supply, through a set of valves driven by a variable speed motor. The jack leg is filled with the aqueous phase simultaneously with the initial filling of the column. When air pressure is applied through the valve at the top, the liquid is forced down the jack leg into the bottom of the column. The two phases in the column are displaced upward forcing them through the sieve plates where the buoyancy of the organic causes it to rise up just beneath the next sieve plate to await the next pulse. When pressure is released, the aqueous phase flows downward with some of it returning to the jack leg. By adjusting air pressure and motor speed, the pulse amplitude and frequency, respectively, can be controlled.

4. Accessory Items

In addition to the components described previously, the pilot plant contained a number of storage tanks used to hold solutions. Two of these tanks are equipped with stirrers and are used as mixer settlers in which the organic phase was washed after the HAN strip. Two other tanks are equipped with heating coils so solutions can be heated. Both these tanks and the columns contain thermocouples so solution temperature can be monitored. All the tanks have sight glasses so liquid levels can be watched. This also served as a useful check on flow rates through the pumps.

Reference

1. G. E. Benedict, Light Water Reactor Fuel Reprocessing Program, Quarterly Progress Report for the Period ending June 30, 1977, GA-A14511, pp 4-24.

APPENDIX E - SAMPLE HTU/HETS CALCULATIONS

In calculating column separation efficiencies by either transfer units or equilibrium stages, several different methods were employed. Each method depends upon whether: (1) the column was operated as a simple or compound system, and (2) the equilibrium lines were straight or curved. The curve fitting of the equilibrium data, generated from the simulated column tests, was done on a Tektronics 4051 desktop computer. It should be noted, however, that the fitted curves used in these calculations are only approximations and should not be taken as being absolutely correct. Numerical integrations were done with a Hewlett Packard HP-97 programmable calculator. The calculations described in this Appendix are for the mass transfer of Cerium, the actinide simulant used in the pilot plant tests. Most equations in this appendix have been adapted from the Purex Technical Manual.[1] The nomenclature for these equations is listed in Appendix F.

Method #1

Compound Column - Straight Equilibrium Lines

A compound extraction/scrub column was used in this test. Both the extraction and scrub section equilibrium lines were straight, and a pinch for Ce occurred only in the scrub section. The first calculations were to determine the organic and aqueous phase concentrations at the pinch using equations (1) and (2).

Scrub Operating Line	$Y=Y_E+(A/O)_S(X-X_S)$	(1)
Scrub Equilibrium Line	$Y=DsX$	(2)

The intersection of these two lines defines the point at which the phase concentrations no longer change. Equations (1) and (2) were equated, since the organic phase concentrations (Y) were equal. The aqueous phase concentration (X) was solved for, as in equation (3). The organic concentration at the pinch is calculated using equation (4).

$$X_{pinch} = \frac{Y_E-(A/O)_S X_S}{D_S-(A/O)_S} \tag{3}$$

$$Y_{pinch} = D_S X_{pinch} \tag{4}$$

These points are shown in Figure E1. To calculate the number of equilibrium stages in the scrub section, a stage by stage method using material balances to calclulate each stage was used. This calculation begins at the dilute end of the scrub section and moves towards the pinch. It was determined that the pinch was reached by comparing the calculated aqueous phase concentration with the pinch concentration. The pinch was reached if equation (5) was satisfied.

$$\frac{X_{pinch}-X}{X_{pinch}} \leq 0.01 \tag{5}$$

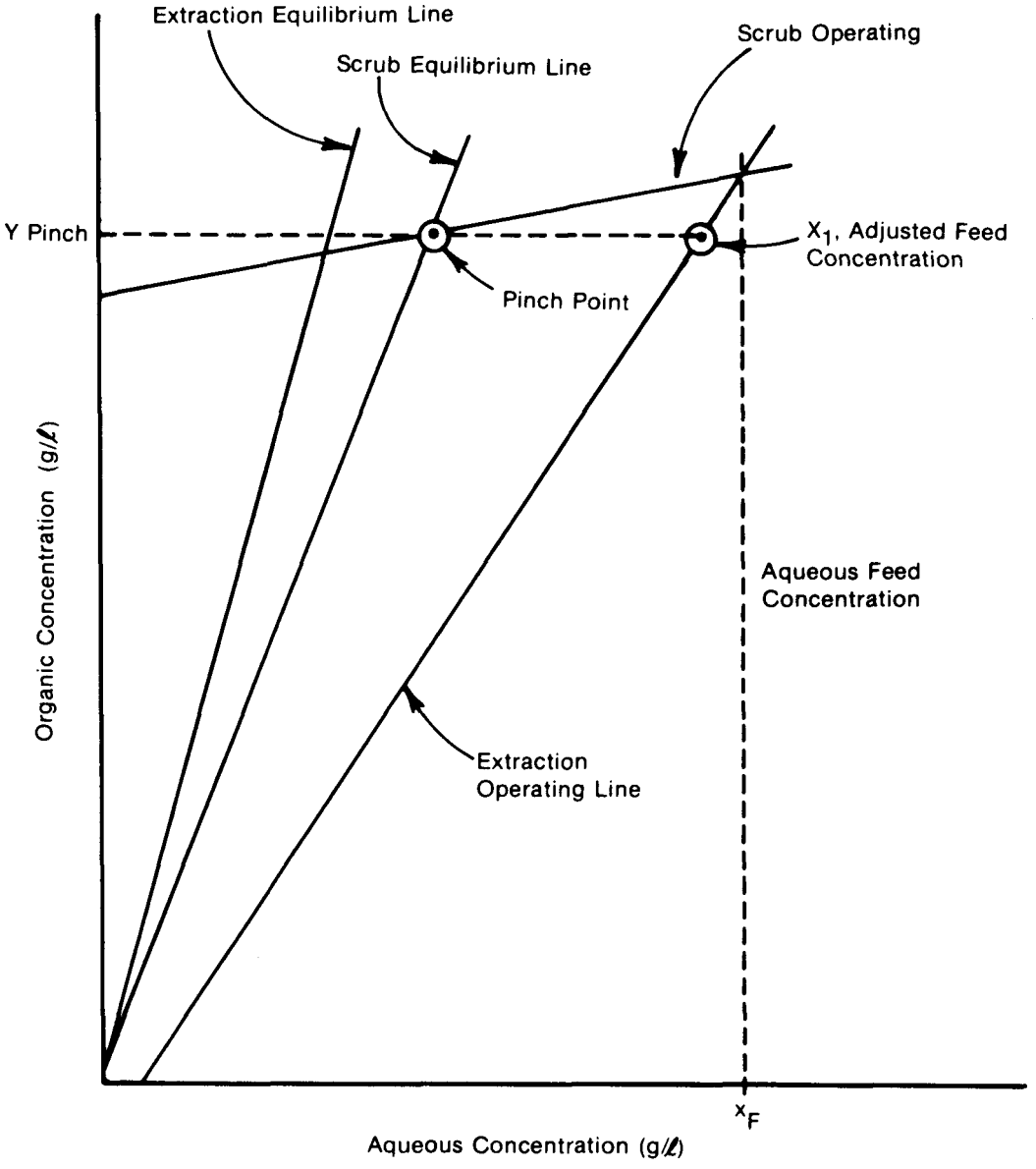

Figure E1. Compound Column McCabe-Thiele Plot

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The number of transfer units is then calculated using equation (6).

$$N_s = \frac{\ln\left[\frac{(A/O)_s}{D_s}\right]}{1-\left[\frac{D_s}{(A/O)_s}\right]} \qquad (6)$$

To calculate the height of a transfer unit (or equilibrium stage) from the number of transfer units, the height of the column section is divided by the number of transfer units (or equilibrium stages).

In order to calculate the number of transfer units and stages in the extraction section, equations (7), (8), (9), and (10) are used.

$$N_s = \frac{\ln\ (M(1-P) + P)}{\ln\ (1/P)} \qquad (7)$$

$$N_t = N_s \cdot \frac{\ln\ (1/P)}{(1-P)} \qquad (8)$$

where

$$P = (A/O)_e/D_e \text{ for extraction} \qquad (9)$$

$$M = \frac{X_1 - Y_2/D_e}{X_2 - Y_2/D_e} \qquad (10)$$

The subscripts 1 and 2 in the equations above refer to the concentrated and dilute ends of the column respectively. For the compound column calculations. X_2 and Y_2 refer to X_R and Y_T, while X_1 is calculated from equation (11).

$$X_1 = X_R + \frac{(Y_{pinch} - Y_T)}{(A/O)_e} \qquad (11)$$

This value of X_1 is the adjusted aqueous feed concentrations to the extraction section, shown in the Figure E1. (This figure shows straight equilibrium lines for both the extraction and scrub sections. The figure would look the same if the extraction line is curved.) That is, a stream of this composition results when the aqueous feed and scrub raffinate are combined. This calculation yields the overall stages or transfer units in the extraction section. If interstage concentrations are known from column sampling, equations (7) - (10) are again used with the variables X_2 and Y_2 set equal to the dilute concentrations while X_1 is set equal to the higher concentration in the aqueous phase.

Sample Calculation #1

Data:

$(A/O)_s$	= 0.194	X_F	= 0.191 g/ℓ
$(A/O)_e$	= 2.44	X_R	= 0.0003g/ℓ
D_s	= 4.00	X_S	= 0.0g/ℓ
D_e	= 5.02	Y_E	= 0.457g/ℓ
		Y_T	= 0.0004g/ℓ

Pinch Point Calculation:

EQ (3) $$X_{pinch} = \frac{Y_E - (A/O)_S \quad X_S}{D_S - (A/O)_S}$$

$$X_{pinch} = \frac{0.457 - (0.194)(0.0)}{4.00 - 0.194} = 0.120 \text{ g/l}$$

EQ (4) $$Y_{pinch} = D_S X_{pinch} \qquad = 4.0(0.120) \qquad = 0.480 \text{ g/l}$$

Stagewise calculation yields 2.00 scrub stages.

EQ (6) $$N_t = N_S \cdot \frac{\ln \left[\frac{(A/O)_S}{D_S} \right]}{1 - D_S/(A/O)_S}$$

$$N_t = \frac{2.00 \ \ln (0.194/4)}{1 - 4/.194} = 0.309$$

Scrub section height = 1.56 meters

$H_t = 1.56/N_t = 1.56/0.309 = 5.05$ meters

$H_S = 1.56/N_S = 1.56/2.0 = 0.78$ meters

This completes the scrub section calculations.

Extraction Section

EQ (11) $$X_1 = X_R + \frac{(Y_{pinch} - Y_T)}{(A/O)_e}$$

$$X_1 = 0.0003 + \frac{(0.480 - 0.0004)}{2.44}$$

$$X_1 = 0.197$$

EQ (9) $$P = \frac{(A/O)_e}{D_e} = \frac{2.44}{5.02} = 0.436$$

EQ (10) $$M = \frac{X_1 - Y_2/D_e}{X_2 - Y_2/D_e} = \frac{X_1 - Y_T/D_e}{X_R - Y_T/D_e}$$

$$M = \frac{0.197 - 0.0004/5.02}{0.0003 - 0.0004/5.02} = 894$$

EQ (7)

$$N_S = \frac{\ln\ (M(1-P) + P)}{\ln\ (1/P)}$$

$$= \frac{\ln\ (894(1-0.486)+0.486)}{\ln(1/0.486)}$$

$$N_S = 8.50$$

EQ (8)

$$N_t = N_S \cdot \frac{\ln\ (1/P)}{(1-P)}$$

$$N_t = 8.50 \cdot \frac{\ln\ (1/0.486)}{(1-0.486)} = 11.9$$

Extraction section height = 5.03m

$$H_t = 5.03\text{m}/N_t = \frac{5.03\text{m}}{11.9} = 0.42\text{m} \quad \text{HETS} = \frac{5.03}{N_S} = \frac{5.03}{8.5} = 0.592$$

This completes the extraction section calculations

Method #2

Compound Column - Curved Extraction Equilibrium Line

In this case, only the scrub equilibrium line is straight. In the extraction section, the equilibrium line is curved. The scrub section is calculated as shown in method #1, including the pinch concentrations. For the extraction section, the definition of an HTU as shown below is used for dilute solutions.

$$N_t = \int_{X_1}^{X_2} \frac{dx}{X-X^*} \tag{12}$$

For a cerium feed concentration of approximately 2.0 g/ℓ, the following equilibrium equation was used:

$$X^* = 0.0021 + 0.165\ Y + 0.0231\ Y^2 \tag{13}$$

This equation resulted from the curve fitting of simulated column equilibrium data. From the extraction operating line, we know

$$Y = (A/O)_e(X-X_R) + Y_T \tag{14}$$

Combining equations 12, 13 and 14 yields equation (15)

$$N_t = \int_{X_1}^{X_2} \frac{dx}{X - (0.0021 + 0.165((A/O)_e(X-X_R)+Y_T) + 0.0231((A/O)_e(X-X_R) + Y_T)^2)} \tag{15}$$

This equation is then integrated numerically by Simpson's Approximation on an HP-97 calculator. This method of integration is described in detail elsewhere.[2] When integrating by this method, the number of intervals is picked and the N_t is calculated. By increasing the number of intervals, the accuracy of the calculation is increased. For our purposes, the number of intervals was doubled until the change in N_t was less than 0.1%.

To calculate the number of equilibrium stages, a stage by stage method is employed. This would be analogous to stepping off stages on a McCabe-Thiele Plot except that it is done numerically. The equations (#7-10) cannot be used because the equilibrium lines are not straight.

Sample Calculations #2

Data:

$(A/O)_e$ = 2.44
X_R = 0.072 g/ℓ
Y_T = 0.0003 g/ℓ
X_1 = 2.136 g/ℓ (Calculated from pinch point; See Method #1)

Extraction Section Calculations:

NTU Equation: EQ(15)

$$N_t = \int_{2.136}^{0.072} \frac{dx}{X-(0.0021+0.165(2.44(X-0.072)+0.0003)+0.023(2.44(X-0.072)+0.0003)^2)}$$

# of Intervals	NTU	Δ%
4	6.389	
8	5.852	-8.4
16	5.711	-2.4
32	5.685	-0.46
64	5.682	-0.05

Column Height = 5.03 meters

H_t = Height/H_t = $\frac{5.03 \text{ m}}{5.682}$ = 0.885 meters

Method #3

Simple Extraction Column

For this system, there are straight equilibrium lines and no pinches. Therefore, the N_S and N_t equations (EQ (7)-(10)) can be used directly. No adjustment in the feed concentration is necessary because it is not being diluted by a scrub stream.

Method #4

Strip column Calculations

The strip column was always operated as a simple column. However, the equilibrium lines are not straight, but curved. The same technique used for the extraction section with a curved equilibrium line is used here, except that for stripping, the N_t is based on the organic concentrations. The general N_t equation for stripping with dilute concentrations is shown below.

$$N_t = \int_{Y_2}^{Y_1} \frac{dy}{Y-Y^*} \tag{16}$$

For cerium feed concentrations that are less than 0.8 g/ℓ, the equilibrium curve is given by equation (17).

$$Y^* = 1.125(10^{-5}) + 0.0196X + 0.7486X^2 - 5.7858X^3 + 13.8646X^4 \tag{17}$$

For feed concentration >2.0g/ℓ, the equilibrium line is as follows:

$$Y^* = 1.78(10^{-4}) + 0.0212X - 0.0542X^2 + 0.0423X^3 \tag{18}$$

The strip column operating line is given by equation (19).

$$X = X_F + \frac{(Y-Y_E)}{(A/O)_e} \tag{19}$$

Combining equations (19), (16), and one of the equilibrium line equations, yields an N_t equation similar to equation (15). Then using Simpson's Approximation, the valve of the N_t can be calculated numerically.

For the number of stages, the same technique used for the extraction section with a curved equilibrium line is used again (see Method #2).

Sample Calculation #3

Data:

Y_T	=	0.4615, use equilibrium equation #17
Y_E	=	0.015
X_F	=	0.0
(A/O)	=	1.0

The equation to be integrated is as follows:

$$N_t = \int_{Y_E}^{Y_F} \frac{dY}{Y-(1.25\,(10^{-5}) + 0.0196(1)(Y-0.015) + 0.7486(Y-0.015)^2 - 5.7858(Y-0.015)^3 + 13.8646(Y-0.015)^4)}$$

# of Intervals	NTU	Δ%
4	4.673	
8	3.940	-16%
16	3.705	-6.0
32	3.650	-1.5
64	3.641	-0.25
128	3.640	-0.03

Height of Strip column = 2.86 meters

H_t = 2.86m/3.640 = 0.786 meters

References

1. Purex Technical Manual, USAEC Report HW 31000, (March 1955) pp. 513-527.

2. B. Carnahan, H.A. Luther, and J.O. Wilkes, Applied Numerical Methods, New York: John Wiley and Sons, Inc., 1969, pp 73-75.

APPENDIX F - NOMENCLATURE

$(A/O)_e$	-	Extraction section aqueous/organic flow ratio
$(A/O)_S$	-	Scrub section aqueous/organic flow ratio
De	-	Extraction distribution coefficient
Ds	-	Scrub distribution coefficient
HETS	-	Height Equivalent to a Theoretical Stage
HTU	-	Height of a Transfer Unit
NETS	-	Number of Equivalent Theoretical Stages, same as Ns
Ns	-	Number of Equivalent Theoretical Stages
Nt	-	Number of Transfer Units
NTU	-	Number of Transfer Units
X	-	Aqueous phase concentration
X_F	-	Aqueous feed concentration
X pinch	-	Aqueous phase concentration at the scrub pinch point
X_S	-	Scrub feed concentration
X_R	-	Aqueous raffinate concentration
X_1, X_2	-	Aqueous concentrations, concentrated and dilute respectively.
X*	-	An aqueous concentration in equilibrium with the organic phase.
Y*	-	Organic concentration
Y_E	-	Organic extract concentration
Y pinch	-	Organic phase concentration at the scrub pinch point
Y_T	-	Organic feed concentration
Y_1, Y_2	-	Organic concentrations, concentrated and dilute respectively.
Y*	-	An organic concentration in equilibrium with the aqueous phase.