

**REMOVAL OF ACTINIDES FROM NUCLEAR FUEL  
REPROCESSING WASTES USING AN  
ORGANOPHOSPHOROUS EXTRACTANT**

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REMOVAL OF ACTINIDES FROM NUCLEAR FUEL  
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## Abstract

By removing actinides from nuclear fuel reprocessing wastes, long term waste storage hazards are reduced. A solvent extraction process to remove actinides has been demonstrated in miniature mixer-settlers and in simulated columns using actinide feeds. Nonradioactive pilot plant results have established the feasibility of using pulse columns for the process.

## Introduction

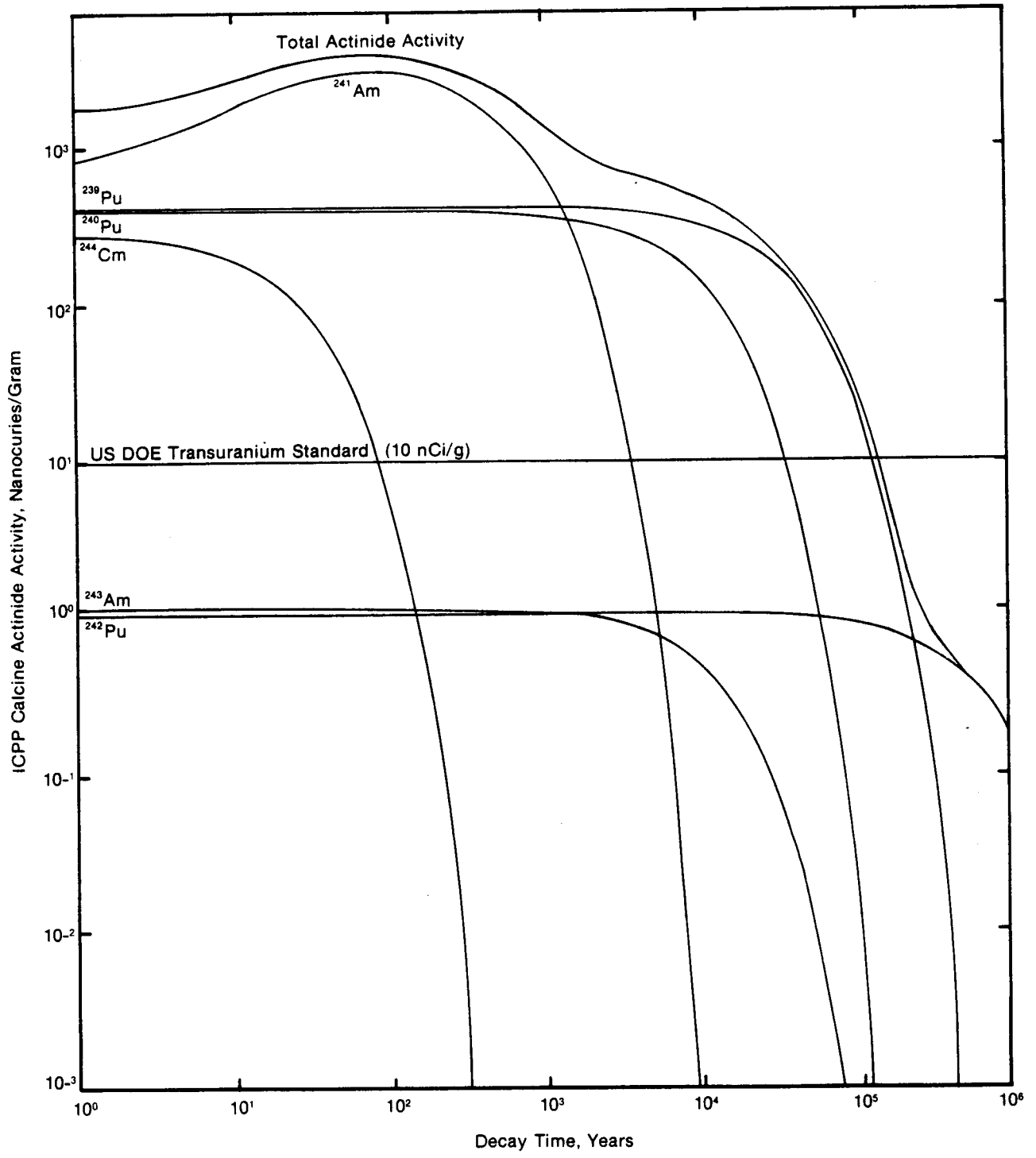
The Idaho Chemical Processing Plant (ICPP), is one of many facilities located at the Idaho National Engineering Laboratory (INEL) near Idaho Falls, Idaho. The ICPP processes irradiated nuclear fuel from test and naval reactors for the recovery of fissionable uranium (U). These fuels are highly enriched, typically to 93 percent  $^{235}\text{U}$ . During reprocessing, the fuel, including cladding, is dissolved into acidic solutions which are separated by tributylphosphate (TBP) extraction into one stream containing U and a second containing the radioactive fission products, cladding components, chemical additives, and actinides.<sup>1,2</sup> This second stream, called High-Level Liquid Waste is converted to a free flowing granular solid (calcine) by fluidized-bed calcination.

Transuranium elements are produced in a reactor largely by neutron capture in  $^{238}\text{U}$ . Because the fuels processed at the ICPP are highly enriched in  $^{235}\text{U}$ , there are relatively few actinides in the waste. A typical TBP raffinate, designated coprocessing waste, is presented in Table 1. The decay of actinides in ICPP calcine is represented in Figure 1. There is a buildup in the total actinide concentration because of the decay of  $^{241}\text{Pu}$  to  $^{241}\text{Am}$ .  $^{241}\text{Pu}$  and  $^{238}\text{Pu}$  are not classified as actinides by Department of Energy (DOE) standards,<sup>3</sup> probably because of their short half-lives of 14.6 and 89 years, respectively. Waste containing greater than ten nanocuries of actinides per gram (10 nCi/g) are classified by DOE standards as transuranic wastes. The figure illustrates that, without removal of the actinides, the waste is a transuranic waste for over 125,000 years, even though the amount of actinides in ICPP calcine is

TABLE 1  
TYPICAL COMPOSITION OF ICPP COPROCESSING RAFFINATE

<u>Macroconstituents</u>		<u>Actinides, g/l</u>	
H <sup>+</sup> , M	1.62	Total U	2.0x10 <sup>-4</sup>
Al <sup>+3</sup> , M	0.67	<sup>237</sup> Np	1.24x10 <sup>-5</sup>
Zr <sup>+4</sup> , M	0.45	<sup>238</sup> Pu	3.70x10 <sup>-4</sup>
F <sup>-</sup> , M	3.21	<sup>239</sup> Pu	1.09x10 <sup>-3</sup>
B <sup>+3</sup> , M	0.20	<sup>240</sup> Pu	2.92x10 <sup>-4</sup>
NO <sub>3</sub> <sup>-</sup> , M	2.36	<sup>241</sup> Pu	1.29x10 <sup>-5</sup>
Lanthanides, g/l	0.20	<sup>242</sup> Pu	4.33x10 <sup>-5</sup>
Hg <sup>+2</sup> , M	0.002	<sup>241</sup> Am	3.53x10 <sup>-5</sup>
		<sup>243</sup> Am	9.77x10 <sup>-7</sup>
		<sup>244</sup> Cm	5.87x10 <sup>-7</sup>

small ( $\approx 10$  ppm). (In this definition, the nCi/g is a measure of the radioactivity per mass of material.) Separation of the long half-life actinides from the fission products allows versatility in managing the radioactive wastes. Rather than transferring all waste to a distant Federal Repository, fission product wastes could be stored in existing surface facilities until they decay to an acceptable level, typically 500 years. The actinides could either be sent to a geologic repository or fissioned as fuel in fast reactors. The reduced volume of waste requiring shipment would result in a significant decrease in transportation and storage costs. The object of the pilot plant described in this paper is to obtain the engineering scale-up information necessary to establish the feasibility of building a full-scale actinide removal process.

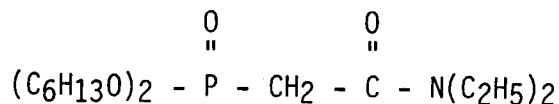


**Figure 1. Actinide Decay in ICPP Calcine**

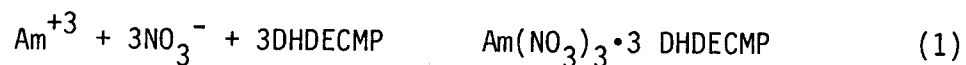
## Chemistry of the Actinide Removal Process

The development of a process to remove actinides from ICPP fuel re-processing wastes has been underway since 1973. The synthesis and purification of extractants for use in this process have been reported earlier by McIsaac<sup>4</sup> and Schulz.<sup>5</sup> In addition, these investigators have reported the effects of extractant concentration, diluent, temperature, contact time, and HNO<sub>3</sub> concentration upon extraction. The results of these studies will be briefly summarized here.

Dihexyl-N, N-diethylcarbonylmethylenephosphonate (DHDECMP) was the extractant chosen for this process. DHDECMP is a bidentate organophosphorous compound with the following structure:



The complexing and extraction of the actinide Americium (Am) can be represented by the mechanism shown in equation (1):



While the extraction of other actinides may differ in detail, they all proceed by the formation of a neutral species and are dependent upon nitrate and extractant concentrations. By adjusting the nitrate concentration of the aqueous phase, the direction of mass transfer can be controlled. For example, a high nitrate concentration causes the mass transfer to favor the organic phase (extraction) while a low nitrate concentration causes the actinides to favor the aqueous phase (stripping).



McIsaac<sup>6</sup> has also shown that the kinetics of the actinide mass transfer are fast, usually within ten seconds for a single contact.

The DHDECMP as received\* is 86 percent pure. This material 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 percent 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. This makes solvent recycle too difficult. Second, technical grade DHDECMP is too viscous and dense for use in process equipment. This DHDECMP is therefore mixed with other organics, called diluents, to produce the organic solvent used in this process. McIsaac<sup>7</sup> has found that aliphatic diluents generally give good distribution for actinides but form a second organic phase, even at low ( $\sqrt{3}M$ ) acidity. Aromatic solvents, when used as diluents, are free of the second organic phase, but result in lower actinide distribution coefficients. By using a mixed diluent of decalin and di-isopropylbenzene (DIPB), a favorable distribution coefficient without the formation of a second organic phase is attained. A 20 volume percent 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 addition, these diluents are inexpensive, and their flash points

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\* Manufactured by Bray Oil Co., Los Angeles, California

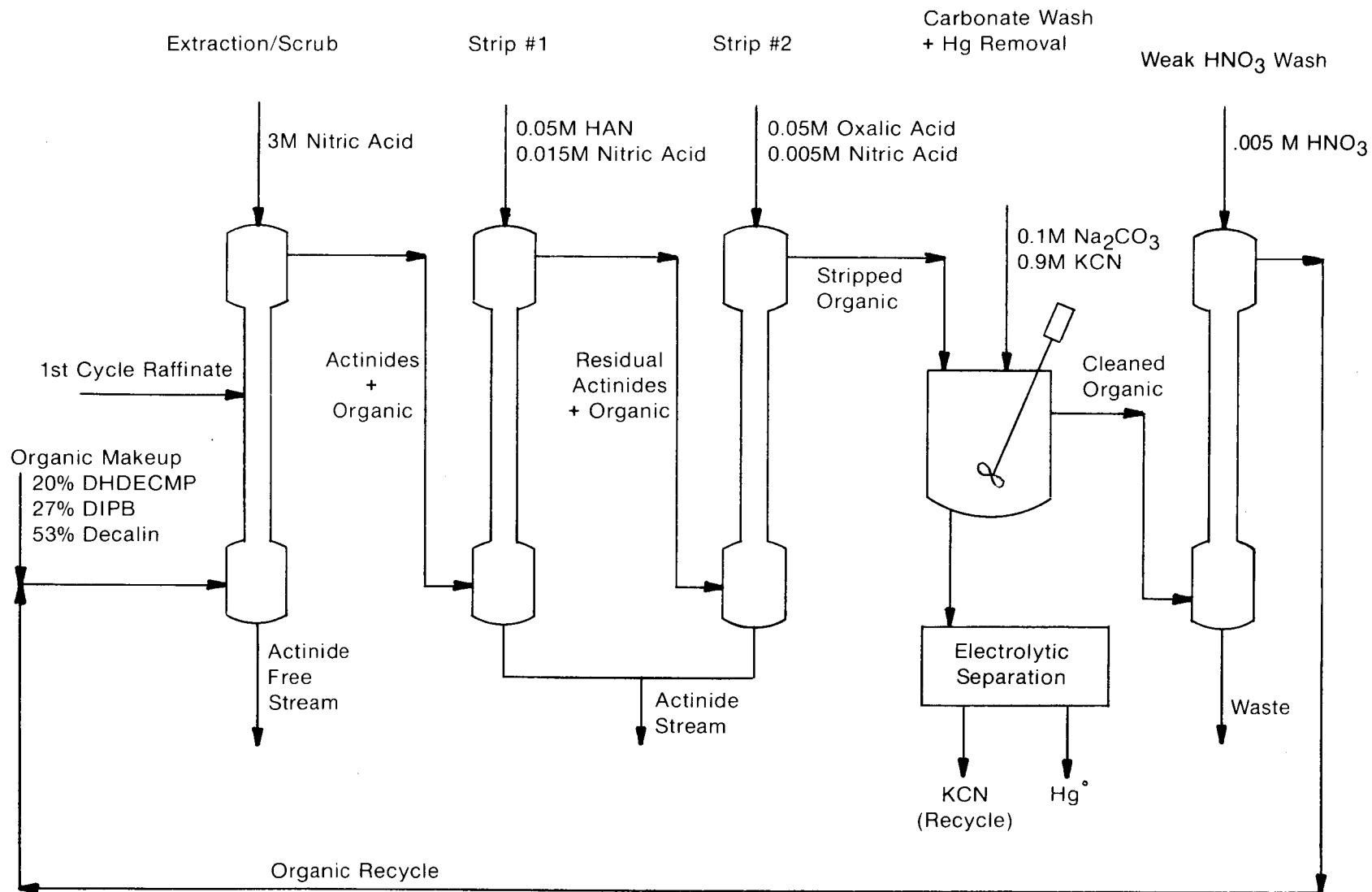
are in excess of 60°C. The DHDECMP solution will be referred to as the solvent or simply, DHDECMP.

### Process Flowsheet

The conceptual flowsheet for the actinide removal process is shown in Figure 2. The aqueous feed solution to the extraction column was described in Table 1. This feed is contacted countercurrently by the extractant, DHDECMP, in a pulsed, perforated plate extraction column. In this column, actinides and lanthanides are extracted from the aqueous phase. Impurities are extracted with the actinides and a 3M HNO<sub>3</sub> scrub section removes these impurities, mostly zirconium, from the organic. This scrub section could be operated either in a compound extraction/scrub column or as a separate scrub column.

In the second column, the organic is contacted with a hydroxylamine nitrate (HAN) and nitric acid solution which strips the actinides from the organic. Radiation from fission products and high acid concentrations cause organic degradation products to form complexes with some of the uranium and plutonium. To remove these residual actinides, oxalic acid is used in the second strip column. Oxalic acid cannot be used in the first strip column because it precipitates the lanthanides. The actinide raffinate from both strip columns will be combined and concentrated.

The remaining unit operations are needed to upgrade the solvent for reuse. Mercury, which is present in the system because of its use as a catalyst during aluminum fuel dissolution, is not removed in either strip



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Fig. 2. Conceptual Actinide Removal Process

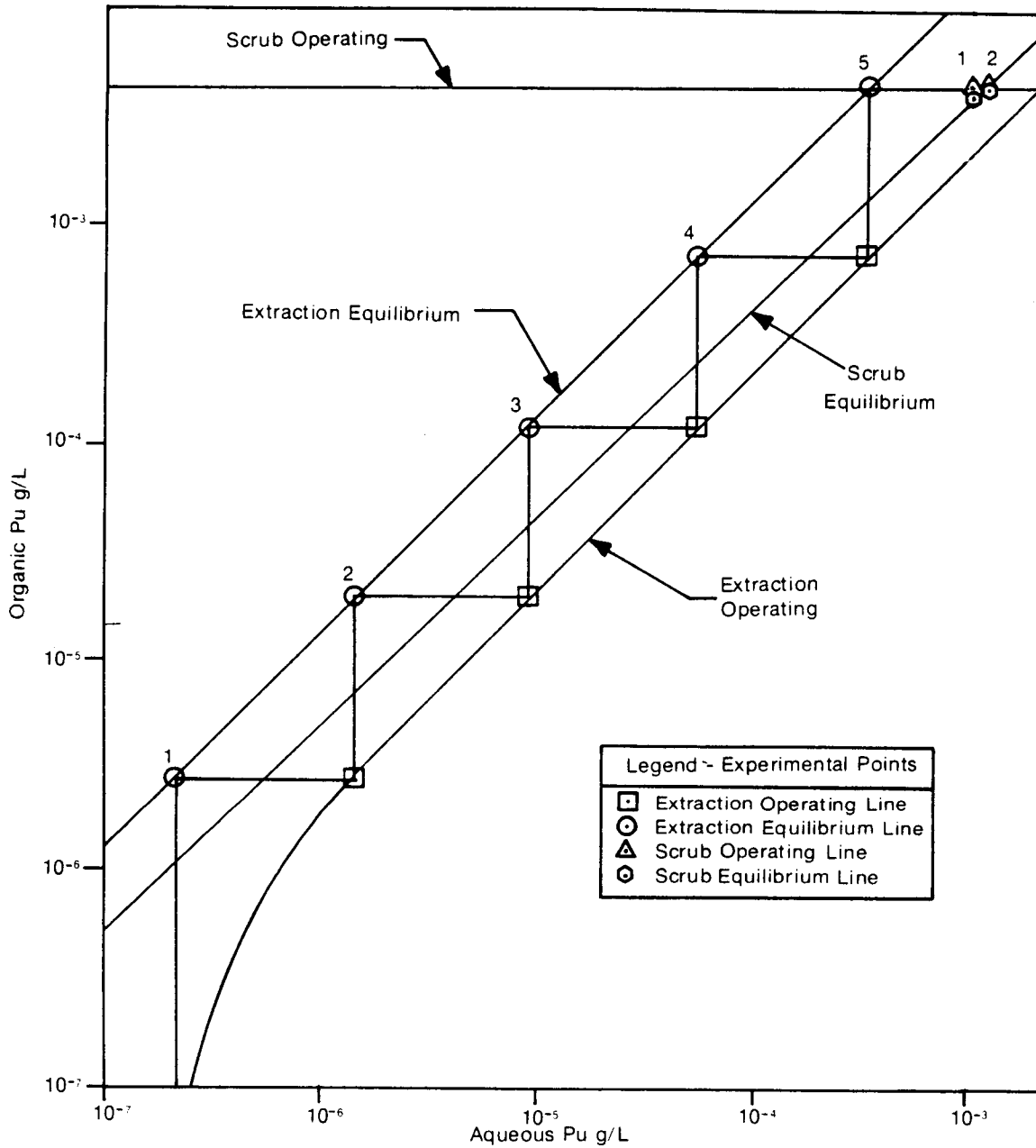
column. To remove the mercury, a potassium cyanide solution is mixed with the organic in a mixer-settler, and a mercury-cyanide complex forms in the aqueous phase. The mercury and the cyanide could be recovered in an electrolytic cell.<sup>8</sup> In the same mixer-settler, a sodium carbonate solution is added which removes any acid or radiation degradation products formed in the organic. The final polishing step consists of a dilute acid wash which neutralizes any residual carbonate in the organic.

#### Laboratory and Small Scale Simulation of the Actinide Removal Process

Flowsheet verification of this process was done in two types of laboratory experiments. In one type of experiment, actinides were extracted from actual ICPP wastes with the DHDECMP in miniature mixer-settlers.<sup>9</sup> These tests showed that Am and Pu can be removed from TBP raffinates using the DHDECMP extractant. In the second type of experiment, Am and Pu were extracted from a synthetic co-processing raffinate (a non-radioactive solution containing the same macro-solute composition as the actual co-processing waste). This experiment is known as a "batch pseudo countercurrent extraction," or a "simulated column."<sup>10,11</sup> The simulated column uses feed, extractant, and scrub which are selectively mixed and remixed in small batches to dynamically describe the stage profile of a continuous solvent extraction process. In this manner, variables such as equilibrium coefficients, extraction and scrub stage requirements, and phase ratio can be established. 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 data is quick, and the experiment can be done in small areas with a minimum use of chemicals.

The first simulated column experiments studied the extraction/scrub operation using Ce as an actinide simulant. The results showed constant distribution coefficients for Ce,  $\text{HNO}_3$ , and Zr throughout the extraction and scrub sections. An unexpected result of the second extraction/scrub simulated column was a reduction of the distribution coefficient for cerium when the feed-to-solvent flow ratio was lowered from 2.0 to 1.0. We speculate that this was due to the effectively reduced salting strength of the aqueous phase.

Over 80 percent of the actinide content of ICPP calcines is due to the isotopes of Am and Pu. Consequently, collection of equilibrium data for these solutes down to the concentration range necessary to produce "actinide-free" wastes is a major goal of this project. Because of this, Am and Pu equilibrium data for the extraction/scrub operations were collected in simulated column experiments. The Am and Pu feed concentrations were typical for those solutes in ICPP co-processing raffinates. These experiments proved that the DHDECMP extractant is capable of producing "actinide-free" wastes. The results of the Pu simulated column are presented as McCabe-Thiele operating diagrams for Pu and  $\text{HNO}_3$  in Figures 3 and 4, respectively. The important results of this experiment are: first, the distribution coefficients for  $\text{HNO}_3$  and Pu are constant. This also proved true for Am and Ce in other experiments. Second, pinches occurred for Zr and  $\text{HNO}_3$  in the extraction section, and for Pu in the scrub section. Third, two scrub stages remove the bulk of Zr from the pregnant organic. In addition, the simulated columns were an "ideal" system, particularly when contrasted to the operational uncertainties of large equipment used in pilot plants.



**Fig. 3. Pu Operating Diagram: Batch Simulated Compound Column**

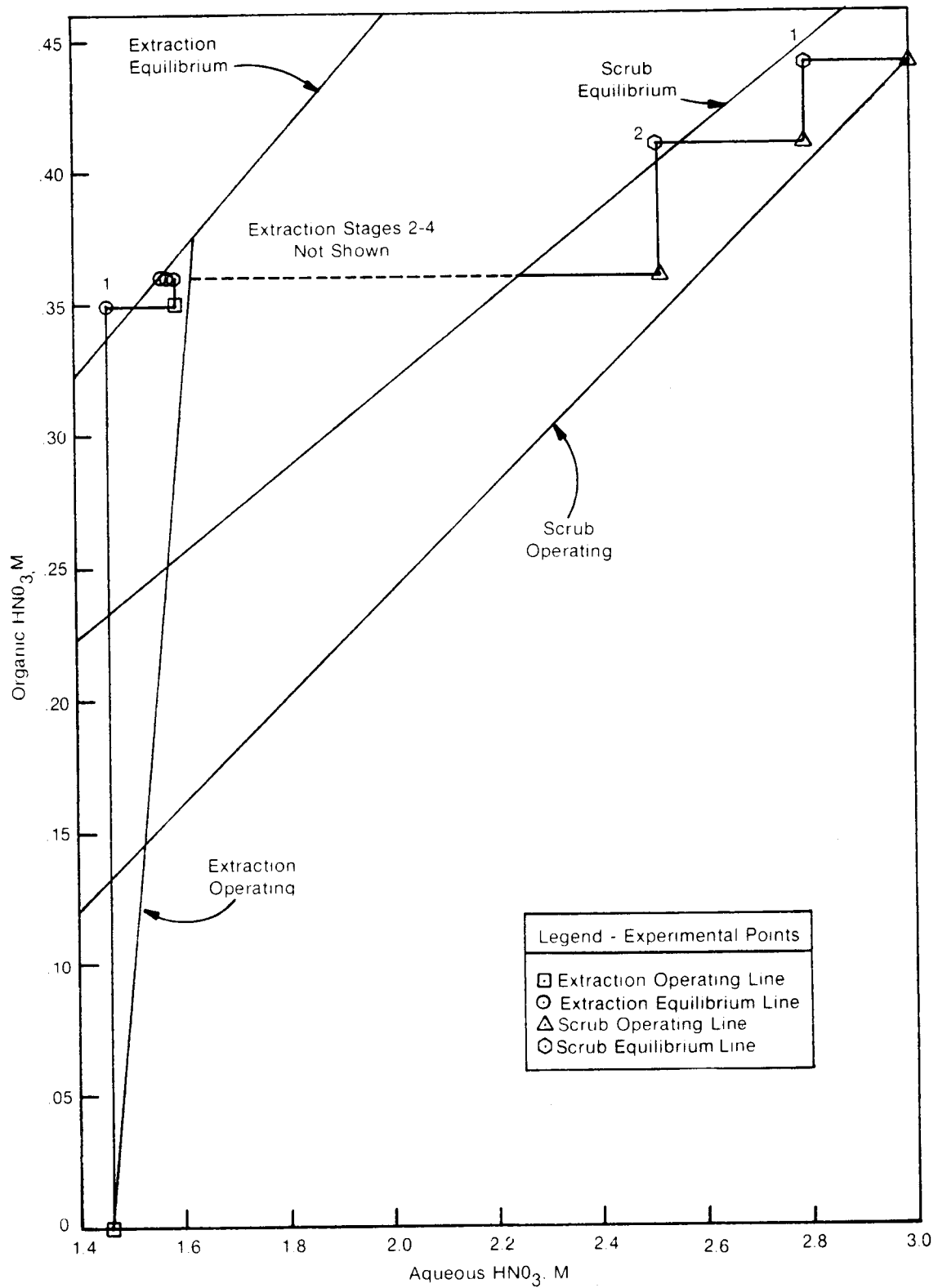


Fig. 4. HNO<sub>3</sub> Operating Diagram: Batch Simulated Compound Column

Data quality can be assessed by making a material balance on a system. Treybal<sup>12</sup> reports that pilot plant data should be discarded if the material balances do not close to within five percent. For the simulated columns the material balance always closed to within ten percent for  $Ce^{+3}$ ,  $NO_3^-$  and  $H^+$ . This limit was used for the pilot plant runs.

### Process Engineering Development Using Pulse Sieve-Plate Extraction Columns

Because of extensive operating experience with pulse columns at the ICPP and their low maintenance requirements, pulse columns were the first choice of contacting equipment for our pilot plant. The two columns used for our tests are constructed of 5.08 cm (two inch) I.D. pyrex pipe, with plate section heights of 6.60 meters and 2.89 meters, 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 is 1.54 meters while that of the extraction section is 5.06 meters.

The sieve plates are stainless steel, with 0.31 cm diameter (0.123 inch) holes,  $\sqrt{25\%}$  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 column. The organic phase was the lighter one and flowed vertically upward in this counter-current system.

Flooding tests were conducted to determine the capacity or flooding point of each column. This information was then used to set the pulser frequencies and throughputs for the remaining pilot plant work. The flooding point was determined visually.<sup>13</sup> For these tests, the column

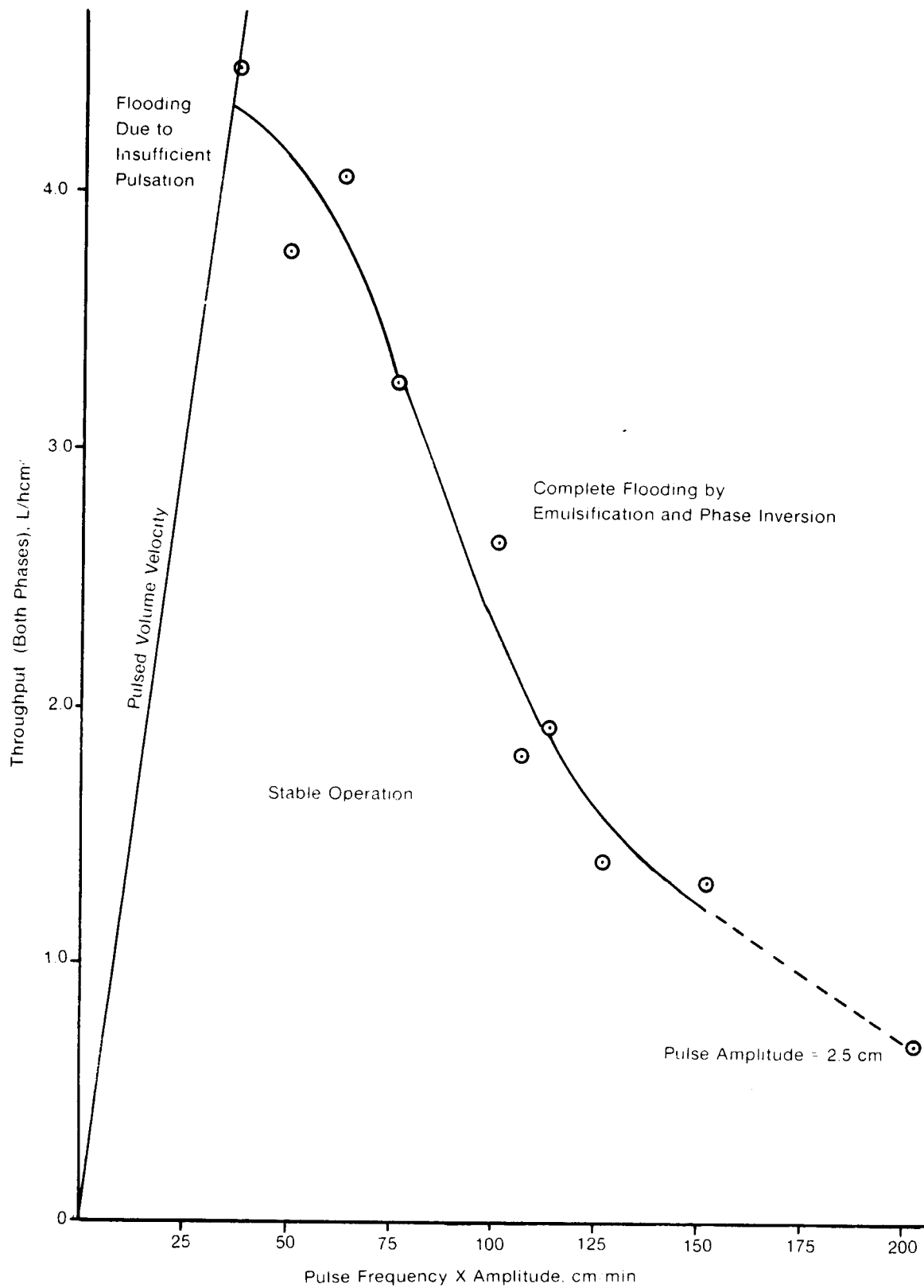


throughput and pulser frequency were set, and the pulse amplitude was adjusted to 2.5 cm. The column throughput was then increased until the column flooded, which was determined by the formation of a second interface in the base of the column. The throughput was then reduced and adjusted systematically every 5-20 minutes. By observing the reaction of the interface position to changes in flow rate, the flooding point could be determined. If the interface 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. A typical flooding curve for this system is presented in Figure 5. Column flooding throughput was plotted as a function of the pulse amplitude-frequency product. A polynomial function was fitted to these data using a least squares technique.

During these tests, it was discovered that the maximum throughput for the columns changed with time. As Long suggests,<sup>14</sup> 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. The columns, when not in operation, are 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 which occurred twice during the pilot plant tests.

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



**Fig. 5. Flooding Curve - Compound Extraction/Scrub  
DHDECMP System**

ICPP-A-4123

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 2. The solvent was analyzed after each of the steps to determine the effect of the contacts. These solvents were also compared with a 99 percent 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 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  $\text{HNO}_3$ . In our work, we have had success using A-26 resin,\*  $\text{OH}^-$  form, to purify the solvent. DHDECMP undoubtedly forms a series of acid degradation products similar to the TBP degradation products. 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 described in Figure 2 adequately clean the solvent for recycle.

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\*Rohm & Haas Co., Philadelphia, Pennsylvania

Most of the pilot plant development has used Ce as a simulant for the actinides. Ce(III) was chosen because it is a non-radioactive solute chemically similar to Am(III). Our first mass transfer tests were made to determine the time required for the raffinate and extract of each column to reach steady state. In the absence of temperature fluctuations, this time was found to be less than three hours. Thus, later tests were run using the same feed, but varying the column conditions every three hours. The results of the Ce extraction and strip tests are presented in Tables 2 and 3, respectively. Column efficiency is measured by the Height of a Transfer Unit (HTU) and the Height Equivalent to a Theoretical Stage (HETS). Percentage flooding was determined by the fitted curve of the experimental flooding data. From these tests we have found that the Ce HTU is reasonable, usually about 0.55 m. This is in the range of HTU's reported for diffusion processes.<sup>15</sup> The variation of HTU with pulse amplitude and frequency is similar to that of PUREX processing.<sup>16</sup> We have also found that the number of scrub stages is 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 a simulant for the actinides, the hydraulics and simple mass transfer of the extraction and strip operations have been established. These characteristics are similar to those reported by Sege<sup>17</sup> for the extraction of uranyl nitrate with TBP. However, the concentration of actinides in the coprocessing feed is only about one percent of the Ce concentration used in these tests. Moreover, the presence of several actinides, though chemically similar to one another, caused added uncertainties. Hafnium and zirconium are also chemically similar, yet

TABLE 2

## OPERATING AND SEPARATION DATA FOR DHDECMP EXTRACTION OF CERIUM

Run No.	Pulse Frequency (CPM)	Pulse Amplitude (Cm)	Percent of Flooding (%)	Section Phase Ratio		Stream Compositions			Extraction Section		Scrub Section	
				Ext.	Scrub (A/O)	Feed (g/l)	Raffinate (g/l)	Extract (g/l)	HTU (m)	HETS (m)	HTU (m)	HETS (m)
1	40	1.1	NM <sup>C</sup>	2.18	0.23	0.23	0.0054	0.41	0.92	1.36	4.6	0.80
2 <sup>b</sup>	40	1.1	NM	2.28	0.24	0.23	0.0127	0.45	0.90	1.29	7.9	1.43
3 <sup>b</sup>	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

<sup>a</sup> Extraction and Scrub Operated in a Compound Column

<sup>b</sup> Column section heights of 3.78 meters for extraction and 2.85 meters for scrub. All other heights are 5.06 m and 1.54 m respectively.

<sup>c</sup>NM Not measured

TABLE 3  
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 <sup>a</sup> (g/l)	Raffinate (g/l)	Extract (g/l)	HTU (m)	HETS (m)
1 <sup>b</sup>	40	1.1	NM <sup>c</sup>	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

<sup>a</sup> Feed composition represents organic feed to the strip column

<sup>b</sup> Strip section height of 6.63 meters. All other runs had heights of 2.89 meters.

<sup>c</sup> NM- Not Measured.

their separation can be made using TBP.<sup>18</sup> Therefore, chemical similarity does not ensure similar extraction behavior.

Fortunately, not only is the concentration of these actinides so low that the organic will not be saturated by them, but our simulated column experiments showed the stagewise  $\text{HNO}_3$  profile is independent of solute. Thus, it seems reasonable to assume that, for this system, column separation efficiency is independent of solute.

To confirm this assumption, a series of experiments was performed using the solutes Ce, Th, and U. Since each solute is a metal differing primarily in the electrons in its  $f$  orbital, the solutes are chemically similar. They do differ in valence states but so do the actinides in the coprocessing feeds. Thus, by using these additional simulants, the column behavior for different solutes could be studied. Unfortunately, Th formed an insoluble compound in the coprocessing solution, probably with fluoride and zirconium. A 1.5 M  $\text{HNO}_3$  feed was therefore used for these tests. To be certain that each of these solutes could be extracted from 1.5 M  $\text{HNO}_3$  using DHDECMP, simulated column experiments were made. In each case, the  $\text{HNO}_3$  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  $\text{HNO}_3$  concentration in the aqueous phase was 0.35 M. The extraction was open in each case, i.e., no pinches occurred.

Treybal<sup>19</sup> emphasizes that the use of equilibrium stage contacts to describe a contractor, such as a pulse column, is theoretically unsound since the mass transfer is differential rather than stagewise in character.

Consequently, the HTU should be used to measure column efficiencies. For dilute solutes, such as the actinides in coprocessing feeds, the HTU is a linear function of the Height Equivalent to a Theoretical Stage (HETS). However, we were interested in the suitability of efficiency measurements for different solutes over wide concentration ranges. Much of our work was concerned with the use of the HTU and the HETS as indicators of column efficiency.

Comparisons of extraction column separation efficiencies, expressed as HTU and HETS values, are presented in Tables 4 and 5, respectively. Each table has the HTU (or HETS) for the overall extraction column, sections of the extraction column, and the concentrated end of the column through a midpoint. Data are shown for different pulsing frequencies. The data for column sections were obtained using samplers which split individual aqueous and organic samples. Accurate samples should fall on the material balance operating line, determined by the column endstream compositions. 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 which occurred not only in the plate section but also in the upper disengaging head of the columns. 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. The four operating conditions were chosen solely to avoid the bias which might be associated with any particular one. ANOVA tables<sup>20</sup> were constructed to test the



TABLE 4

PULSE COLUMN SEPARATION EFFICIENCIES FOR EXTRACTION USING Ce, Th, &amp; U, BY HTU

Operating Conditions, 2.5 Cm Pulse (cycles/min)	Solute	Height of a Transfer Unit, m					Feed Point Through Section 1	Feed Point Through Section 2
		Overall Column	Section 1, 0.64 m	Section 2, 0.64 m	Section 1-2, 1.28 m	Section 3, 0.94 m		
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 <sup>#</sup>	0.20 <sup>#</sup>
	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 <sup>#</sup>	0.15 <sup>#</sup>

# 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 5

## PULSE COLUMN SEPARATION EFFICIENCIES FOR EXTRACTION USING Ce, Th, &amp; U, BY HETS

Operating Conditions, 2.5 Cm Pulse (cycles/min)	Solute	Height Equivalent To A Theroretical Stage, m					Feed Point Through Section 1	Feed Point Through Section 2
		Overall Column	Section 1, 0.64 m	Section 2, 0.64 m	Section 1-2, 1.28 m	Section 3, 0.94 m		
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 <sup>#</sup>	0.76 <sup>#</sup>
	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 <sup>#</sup>	0.53 <sup>#</sup>

# 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.

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 five percent level of significance. Since much of the data is invalid at the higher frequencies, we are not as confident of the conclusions made for these frequencies. 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 6. 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 an  $\text{HNO}_3$  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.

#### Summary and Recommendations

The major emphasis has been placed on being able to adequately understand process behavior in the extraction column. It is the actinide-free raffinate from this operation, after all, that is the true product of this process. In simulated column experiments, and more importantly in minimixer-settler experiments, it was proved that in a given number of equilibrium contacts, the actinide-free product could be produced. The

TABLE 6

PULSE COLUMN SEPARATION EFFICIENCIES FOR STRIPPING USING Ce &amp; U, BY HTU &amp; HETS

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

# Column material balance did not close to within 10%.

\* Section material balance did not close to within 25%.

pilot plant activities have been directed towards showing that a similar product can be obtained in engineering equipment. We believe that a pulse column can achieve this separation in a reasonable height. In this program, we have convincing, but not conclusive, evidence that the HTU is a better indicator of column performance than is the HETS.

Future work should consider the behavior of the strip and solvent cleanup operations. Little time has been spent on these operations. However, because the simulated columns have shown that only five stages of stripping remove the bulk of solute from the pregnant DHDECMP, complete mass transfer in a reasonable column height can be expected. The solvent cleanup operation has been demonstrated for the simulated columns but not in the pilot plant. These operations also merit pilot plant studies.

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