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A PILOT PLANT STUDY USING NON-RADIOACTIVE SIMULANTS

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ABSTRACT

Nuclear fuel reprocessing wastes generated at the ICPP contain small amounts of actinides, primarily Pu and Am. Removal of these actinides reduces the long term storage hazards of the waste. The development of a flowsheet to remove trivalent actinides is discussed in this paper. Pilot plant studies used actinide simulants. As a result of these studies, the Height of a Transfer Unit (HTU) was selected as the better measure of pulse column separation efficiency.

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering Laboratory near Idaho Falls, Idaho is a multipurpose reprocessing facility for Department of Energy (DOE) fuels containing highly enriched uranium. Fuels routinely processed at the ICPP include stainless-steel-clad fast-reactor fuels, aluminum-clad test-reactor fuels, and zirconium-clad fuels for which the enrichment before burnup varies from 50% to 93%. The stainless-steel-clad fuel is electrolytically dissolved in HNO_3, the aluminum-clad fuels are dissolved in HNO_3- $Hg(NO_3)_2$, and zirconium-clad fuels are dissolved in HF. These multi-head-end dissolver solutions provide the feed for a multiple-solvent extraction system that is composed of a first cycle of tributyl phosphate (TBP) extraction followed by two cycles of methyl-isobutyl ketone extraction(1). The uranyl nitrate product from the extraction system is denitrated in a fluidized-bed to UO_3 for shipment. Dissolved aluminum and zirconium fuels are processed concurrently. A typical raffinate from such processing, designated coprocessing waste, is presented in Table 1. This stream is solidified to a free flowing granular material, called calcine, in a fluidized bed.

The presence of small amounts of actinide elements, primarily americium and plutonium, in this calcine causes it to be classified by the DOE as a transuranic waste. Such classification could require geologic disposal of

TABLE 1

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^{-6}
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^{-5}
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}

the waste. The radioactive decay of these actinides in calcine is represented in Figure 1. The figure illustrates that, without removal of the actinides, the calcine is a transuranic waste for over 125,000 years. By removing the actinides from the calcine, the remaining fission product wastes could be stored in existing surface facilities until they decay to an acceptable level, typically 500 years. The actinide fraction could be stored geologically, or fabricated into fuel elements and fissioned as fuel in a fast reactor. Our pilot plant studies have established the feasibility of this process in pulsed extraction columns.

PROCESS CHEMISTRY

Dihexyl-N, N-diethylcarbamylmethylenephosphonate (DHDECMP) is the extractant used in this process. DHDECMP is a bidentate organophosphorous compound with the following structure:

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

The selectivity of DHDECMP for trivalent actinides is the chemical basis for this process. Schulz(2) and McIsaac have reported on the synthesis and purification of DHDECMP and the effects of extractant concentration, diluent, temperature, contact time, and HNO_3 concentration upon extraction. The complexing and extraction of the actinide Americium (Am) can be represented by the mechanism shown in equation (1):

$$Am^{+3} + 3NO_3^- + 3DHDECMP \rightleftharpoons Am(NO_3)_3 \cdot 3\ DHDECMP \qquad (1)$$

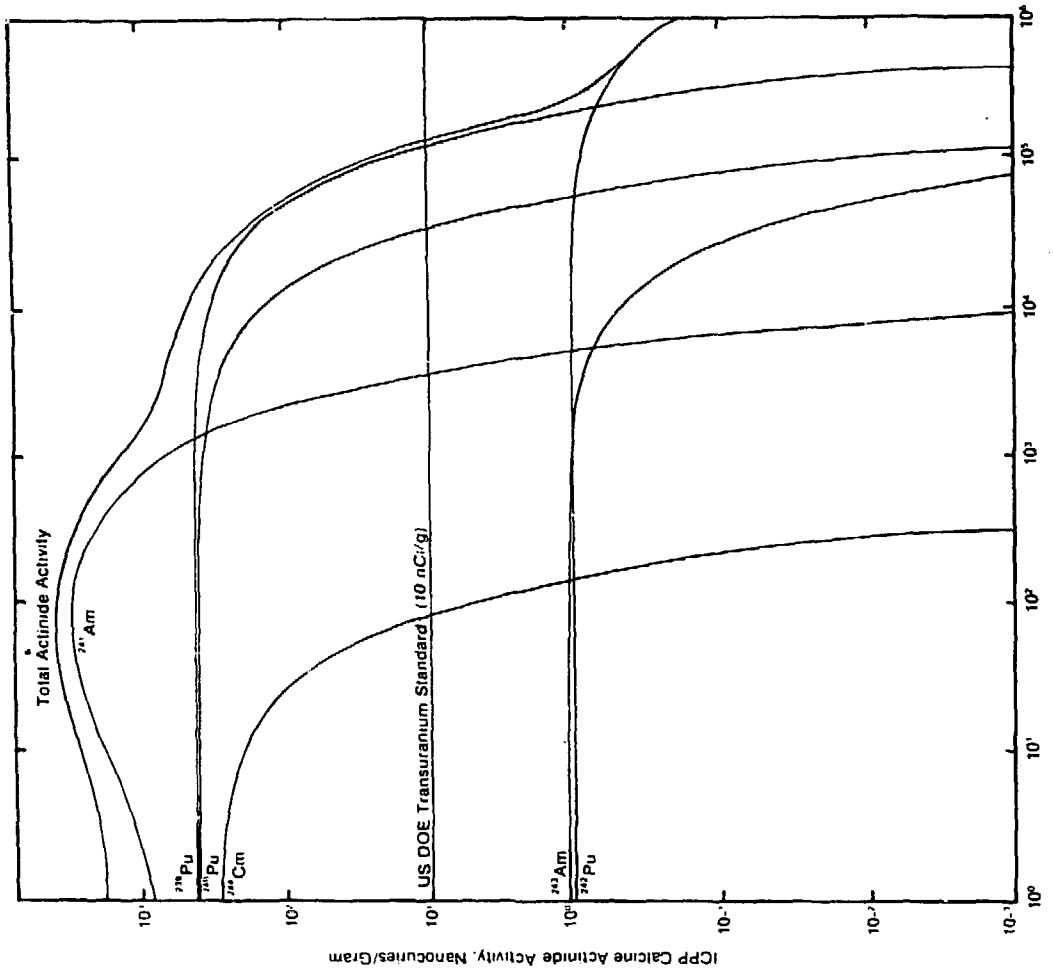

Fig. 1. Actinide Decay in ICPP Calcine

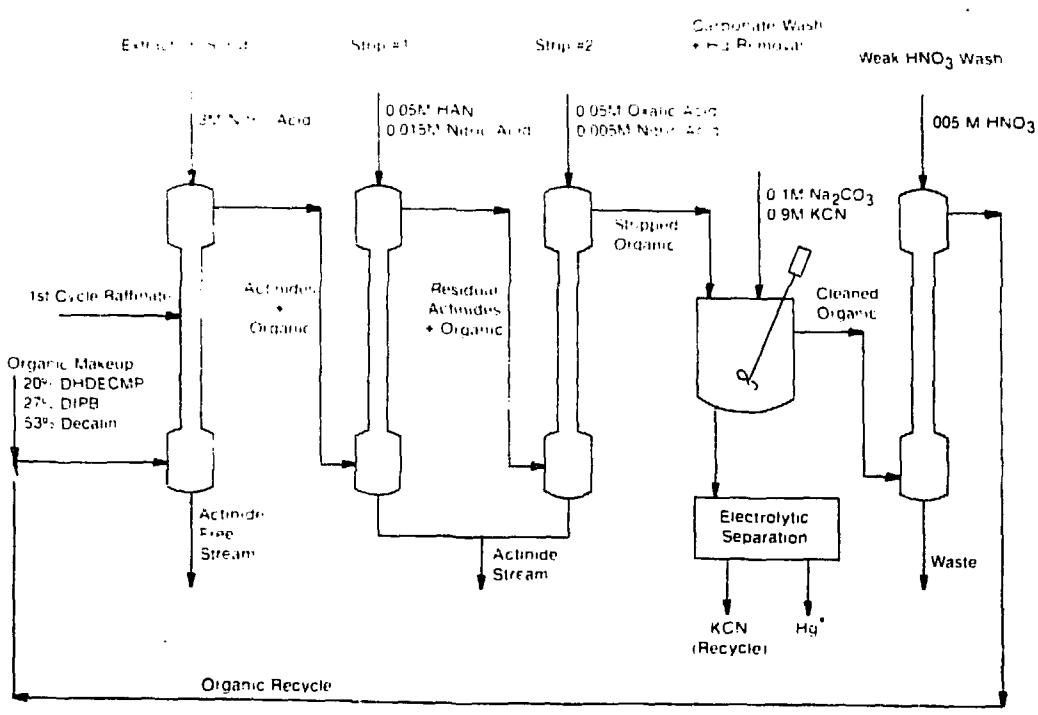

Fig. 2. Conceptual Actinide Removal Process

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. Thus, 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.

By using a mixed diluent of decalin and di-isopropylbenzene (DIPB), a favorable distribution coefficient of actinides without the formation of a second organic phase is attained. A 20 volume percent DHDECMP solution in a 2:1 solution 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 are in excess of 60°C.

PROCESS FLOWSHEET

The flowsheet of the actinide removal process is shown in Figure 2. The principal features of this process are as follows: a separation of the actinides from the TBP raffinate in column I; a stripping of the actinides from the pregnant organic in column II; a second stripping in column III to recover the Pu and U chemically unremovable in column II; removal of solvent degradation products in mixer-settler; a wash of the solvent prior to recycle to column I.

The feed solution, a TBP raffinate, is described in Table 1. This feed is contacted countercurrently by the DHDECMP solvent which removes actinides, lanthanides, and some HNO_3 from the chemically unadjusted feed. Because of its high feed concentration, a greater mass of Zr is extracted than that of the actinide/lanthanide fraction, even though its distribution coefficient is less than 0.01. For this reason, the pregnant organic is scrubbed with 3M HNO_3 to preferentially remove the Zr. Hydroxyl Amine Nitrate (HAN) reduces Pu to Pu(III) allowing most of it to be stripped in Column II along with the Am, HNO_3 and the lanthanides.

The subsequent unit operations are used to recover the solvent for reuse as an extractant, an essential feature of a solvent extraction flowsheet. Radiation from fission products in the aqueous feed promotes the formation of organic complexes of Pu which are not reduced with HAN strip solution. For this reason, a second strip, using oxalic acid ($HO_2C \cdot CO_2H$) is necessary. Hg, present as an aluminum cladding dissolution catalyst, is complexed by cyanide allowing it to be stripped away in a mixer-settler. Acidic organic degradation products are produced by the radiolytic degradation of the DHDECMP in the presence of acid, and are removed by a Na_2CO_3 neutralization in the same mixer-settler. A weak HNO_3 wash is used to polish the solvent prior to recycling to the extraction column.

SMALL-SCALE FLOWSHEET DEVELOPMENT

Much of the process chemistry was established using single separatory funnel extractions. Plant scale operations undoubtedly will operate countercurrently, so two types of laboratory experiments were performed on a countercurrent basis. A "batch pseudo countercurrent extraction," or a "simulated column," is a separatory funnel cascade(3) in which liquids are

repeatedly transferred from one funnel to another. Once chemical steady-state is achieved, the liquids in the separatory funnels have all physical properties which would be encountered in a multistage process. By using small amounts of chemicals, stagewise distribution coefficients and material balances can be determined and undesirable side effects, such as third phase formation, can be determined before costly pilot plant work is undertaken.

Over 80 percent of the actinide content of ICPP calcine is due to the isotopes of Am and Pu. Consequently, the extraction of these solutes down to the concentration range necessary to produce "actinide-free" wastes is a major goal of this project. The separation of Pu from ICPP coprocessing raffinates is represented as McCabe-Thiele operating diagrams for Pu and HNO_3 in Figures 3 and 4, respectively. These figures are representative of the data also collected for Am and for Ce, which was used as an actinide simulant in our pilot plant work. From these experiments, we concluded: (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 HNO_3 and Zr in the extraction section; (3) two stages of scrubbing remove the co-extracted Zr; and, (4) the actinide free raffinate can be produced. The pregnant organic was effectively stripped in a five stage simulated column.

Virtually all experiments in this program were performed with nonradioactive solutions containing actinides. Since the presence of β-γ activity may cause unfavorable changes in equilibrium or the formation of highly stable organic complexes, which may not follow the design flowsheet, some experiments using actual ICPP raffinates were necessary. One of us (Lyle McIssac) has used a miniature mixer-settler which is small enough to be placed in a shielded cell. This mixer-settler has six extraction stages and two scrub stages. Using one liter of ICPP coprocessing raffinate as feed, chemical steady state was reached in the mixer-settler in ten hours. The results of this test are presented in Table 2. It is evident that the actinide-free raffinate was produced. A six stage strip mixer-settler was used to remove the actinides from the pregnant organic. Oxalic acid, present in the strip raffinate, caused the lanthanides to precipitate. Consequently, provision was made in the flowsheet for two strips.

TABLE 2

RESULTS OF MINIATURE MIXER-SETTLER EXPERIMENT

	Am		Pu	
	Concentration (g/ℓ)	Calcine[a] Equivalent (nCi/g)	Concentration (g/ℓ)	Calcine[a] Equivalent (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.

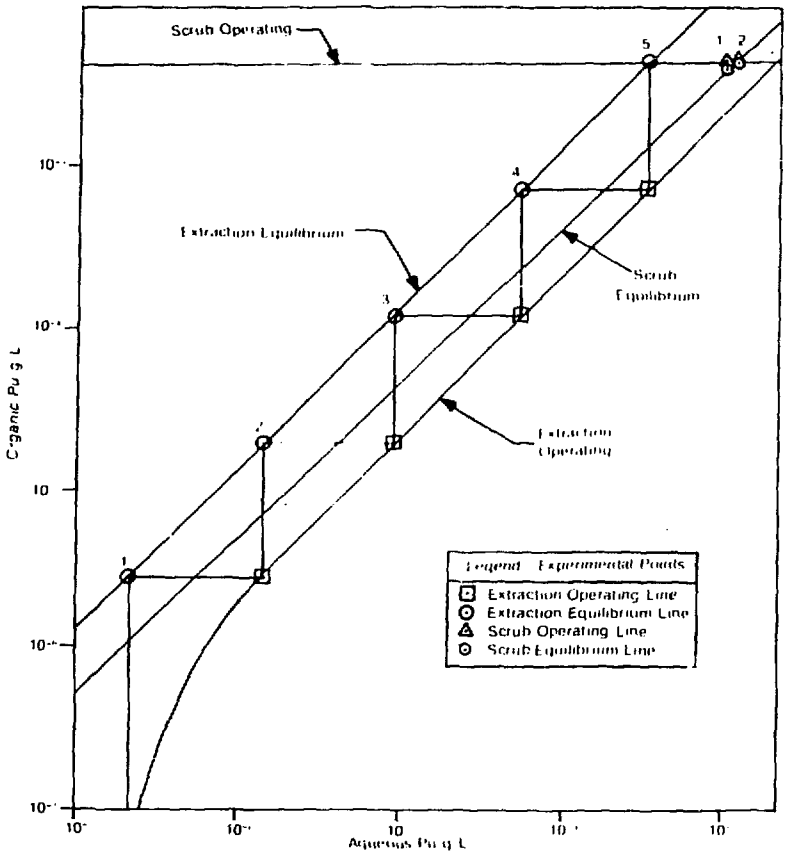

Fig. 3. Pu Operating Diagram: Batch Simulated Compound Column

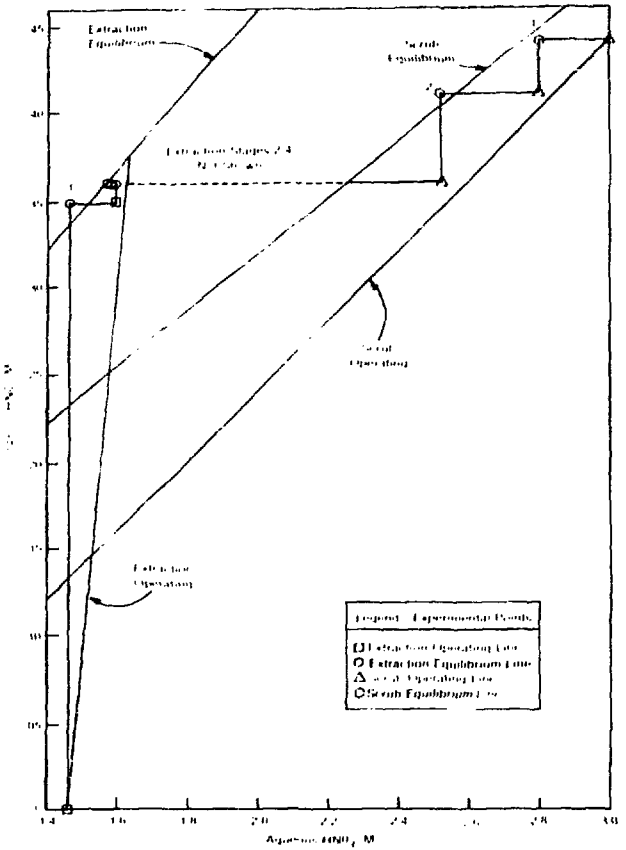

Fig. 4. HNO_3 Operating Diagram: Batch Simulated Compound Column

ACC-A-4035

ICPP-A-4534

PILOT PLANT STUDIES

The ICPP uses pulse sieve plate extraction columns for the recovery of U. Similar columns were used for pilot plant verification of the actinide removal process. Each of these columns is constructed of 5.1 cm (two inch) pyrex pipe and has stainless steel sieve plates spaced 5.1 cm apart. The plates have 0.3 cm diameter holes and have a free area of approximately 25 percent; they are wetted by the aqueous phase. The columns have samplers capable of separating individual aqueous and organic phases.

The hydraulics of this process in pulse columns have been acceptable and are described elsewhere.(4) Our pilot plant cannot be used for radioactive service. 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 non-radioactive rare earth chemically similar to Am(III). The pilot plant results of the extraction of Ce from synthetic i.e., non-radioactive, coprocessing feeds and the subsequent stripping from the pregnant organic are presented in Table 3. From these tests, we have found that the Ce Height of a Transfer Unit (HTU) for extraction is reasonable, usually about 0.55 m. This is in the range of HTU's reported for other diffusion processes.(5) The variation of HTU with pulse amplitude and frequency is similar to that of PUREX processing.(6) 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.

How applicable is this information to the extraction of actinides in pulse-columns in a plant scale actinide removal process? 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 adds uncertainties. For example, hafnium and zirconium are also chemically similar, yet their separation can be made using TBP.(7) Therefore, chemical similarity does not ensure similar extraction behavior. To study the effects of solute upon extraction behavior, we extracted Ce, Th, and U from 1.5 M HNO_3, both in simulated columns and in pulse columns. (A Th precipitate formed in the coprocessing feed preventing the use of this solution for the tests.) Ce, Th, and U are chemically similar metal solutes differing primarily in f orbital electrons. They do differ in valence, but so do the actinides in coprocessing feeds. For all tests, the solute feed concentration was 1.4×10^{-3} g moles/l. Simulated column tests proved that the extraction was not pinched, and therefore, similar. High distribution efficients of 41 and 64 for U and Th, respectively, meant that these solutes could not be analyzed after several contacts.

These same extractions were then performed in the pulse columns. Column separation efficiencies, expressed as HTU's, are presented in Table 4 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. 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

TABLE 3

OPERATING AND SEPARATION DATA FOR DNDECMP EXTRACTION AND STRIPPING OF Ce

Column[1] Section	Section Height (m)	Pulse Amplitude (Cm)	Pulse Frequency (CPM)	Percent of Flooding	Section[2] Phase Ratio (A/O)	Volume Velocity (ℓ/h·cm²)	Stream Composition g Ce/ℓ Feed[3]	Raffinate	Extract	HTU Column Section[4] (m)
Extraction	5.03	1.1	40	NM[5]	2.18	3.25	0.23	0.0054	0.41	0.92
Extraction	1.78	1.1	40	NM	2.28	3.26	0.21	0.0147	0.45	0.90
Extraction	1.78	1.1	40	NM	2.12	3.08	0.40	0.01	0.81	0.68
Extraction	5.06	2.5	15	80	2.20	3.70	0.20	0.003	0.39	0.48
Extraction	5.06	2.5	20	80	2.20	3.55	0.21	0.001	0.43	0.59
Extraction	5.06	2.5	21.4	80	2.20	3.48	0.21	0.0003	0.45	0.47
Extraction	5.06	2.5	30	50	2.20	1.77	0.24	0.0006	0.51	0.51
Extraction	5.06	2.5	30	70	2.20	2.48	0.24	0.001	0.47	0.58
Extraction	5.06	2.5	30	80	2.20	2.83	0.21	0.001	0.45	0.58
Extraction	5.06	2.5	30	90	2.20	3.18	0.24	0.001	0.51	0.57
Extraction	5.06	2.5	40	80	2.20	1.98	0.20	0.0004	0.43	0.60
Strip	6.64	1.1	40	NM	1.71	2.81	0.39	0.22	0.0003	1.71
Strip	2.86	2.5	15	80	1.00	5.81	0.35	0.37	0.02	0.98
Strip	2.86	2.5	40	80	1.00	4.58	0.45	0.42	0.02	0.90
Strip	2.86	2.5	60	80	1.00	1.60	0.45	0.44	0.001	0.46

1. Extraction and scrub operated in compound column; total column height, including scrub section of 6.6 m
2. Scrub section phase ratio (A/O) of 0.2
3. Feed composition represents aqueous feed to extraction/scrub column and organic feed to strip column
4. Ce scrub HTU's typically were 4.9 m
5. Not Measured

TABLE 4

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

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	0.28	0.23	0.32	0.18	0.70
	Th	0.35	0.22	0.20	0.21	NM	0.17	0.21
	U	0.68	*	0.22	*	NM	0.15	0.18
10	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	0.41	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.

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(8) tables were constructed to test the following null hypothesis: for each frequency, the HTU 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 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 for 20, 30, and 50 CPM. In these tests, the F values chosen were for the five percent level of significance. Similar comparisons for the Height Equivalent to a Theoretical Stage (HETS) were not as conclusive. While the data are not overly forceful, it seems that the HTU is the better method of measuring column efficiency. The HTU appears to be valid for several solutes and over wide concentration ranges.

For plant operation, the pulse columns could probably be pulsed at 40 cycles per minute, 2.5 cm per pulse. At these operating conditions, the HTU should be no greater than 0.75 m even considering changes resulting from scale-up. (Sege(9) found that HTU increased by no more than 50% with an increase in column diameter of 167%.) Applying this to the feed described in Table 1, a 7.5 meter column (i.e., 10 tranfer units) will deliver a raffinate which, when calcined, will contain less than 10 nCi of actinides per gram of waste.

SUMMARY AND RECOMMENDATIONS

Our pilot plant efforts have been largely directed to the performance of the extraction column. The raffinate from this column, an actinide-free stream, is the product of this process. While actual radioactiv feeds have been used only in a limited number of tests, the analogies drawn from the simulated column and the solute comparison tests have shown us that the process will work in actual service. It also appears that the HTU is a good indicator of pulse column operation for several solutes through large concentration differences.

The hydraulics of the first strip have been proven in the pilot plant. The mass transfer of the strip operations has been proved in bench scale experiments but not in the pilot plant. These operations need to be further established. Neverthless, it appears that the actinide removal process is feasible for ICPP feeds. Thus, the ICPP waste can be separated into two fractions, one of which is essentially nonradioactive within 500 years, and a much smaller fraction which may require geologic isolation.

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