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Uranium and Zirconium Mass Transfer Testing of 5.5-CM-DIAM Centrifugal Contactors

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URANIUM AND ZIRCONIUM MASS TRANSFER TESTING OF 5.5-CM-DIAM CENTRIFUGAL CONTACTORS*

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ABSTRACT

As part of the Consolidated Fuel Reprocessing Program of the Oak Ridge National Laboratory, compact centrifugal contactors were designed and prototypes built for the Breeder Reprocessing Engineering Test (BRET) facility with a throughput capacity of 0.1 t/d of heavy metals. While the construction of BRET has been put on hold indefinitely, development of the 5.5-cm-diam centrifugal contactors has advanced due to the contactor's broad applicability in other areas of fuel reprocessing and liquid-liquid extraction. Due to the short residence time of the process fluids in a centrifugal contactor, it was necessary to measure the mass transfer efficiency for a typical process flowsheet. This was done with depleted uranium and ^{91}Zr. The results of mass transfer tests with uranium and zirconium are reported in this paper.

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INTRODUCTION

A brief review of the centrifugal contactor literature indicates they were first used for the extraction of penicillin (1,2). Upon application to nuclear fuel reprocessing, hydrodynamic models were developed but withheld from the literature due to government classification. Presently, most countries with nuclear fuel reprocessing programs are involved to some degree with centrifugal contactor development.

The development efforts can be divided into hydrodynamic and mass transfer studies. The following recent publications concern centrifugal contactor development in the areas of hydraulics and mass transfer:

1. a study of flow over a circular weir in a centrifugal field and the characterization of the weir coefficient by Leonard et al. at Argonne National Laboratory (ANL) (3);
2. a study of the interface behavior in the separating zone by Fumoto and Kiyose of the University of Tokyo (4);
3. solvent extraction kinetic studies with uranium, ruthenium, and zirconium by Siczek et al. at ANL (5); and
4. hydraulic and mass transfer studies by Leonard et al. at ANL (6).

The test program and results presented in this paper concern the mass transfer behavior of 5.5-cm-diam centrifugal contactors. The test program objective was to measure single-stage mass transfer efficiencies and demonstrate multistage flowsheets. The single-stage tests were used to determine which of the contactor operating parameters significantly affected the mass transfer efficiency. The multistage tests were used to demonstrate low uranium loss flowsheets developed with the computer code SEPHIS. In addition, the multistage tests were used to investigate the scrub behavior of zirconium, a common fission product.

EXPERIMENTAL

The single-stage 5.5-cm-diam centrifugal contactor is shown in Fig. 1. Feed streams were gravity fed with flow rates controlled by an automated flow control valve. The feed and exit stream temperatures were measured with in-line thermocouples. Steady-state liquid samples were collected first by diverting the entire exit stream flows into sample bottles and then diverting the entire feed stream flows into sample bottles. All of the feed tanks had paddle mixers to maintain a consistent feed composition.

The multistage cascade consisted of four stages of extraction, two stages of scrub and eight stages of strip. Figure 2 is a

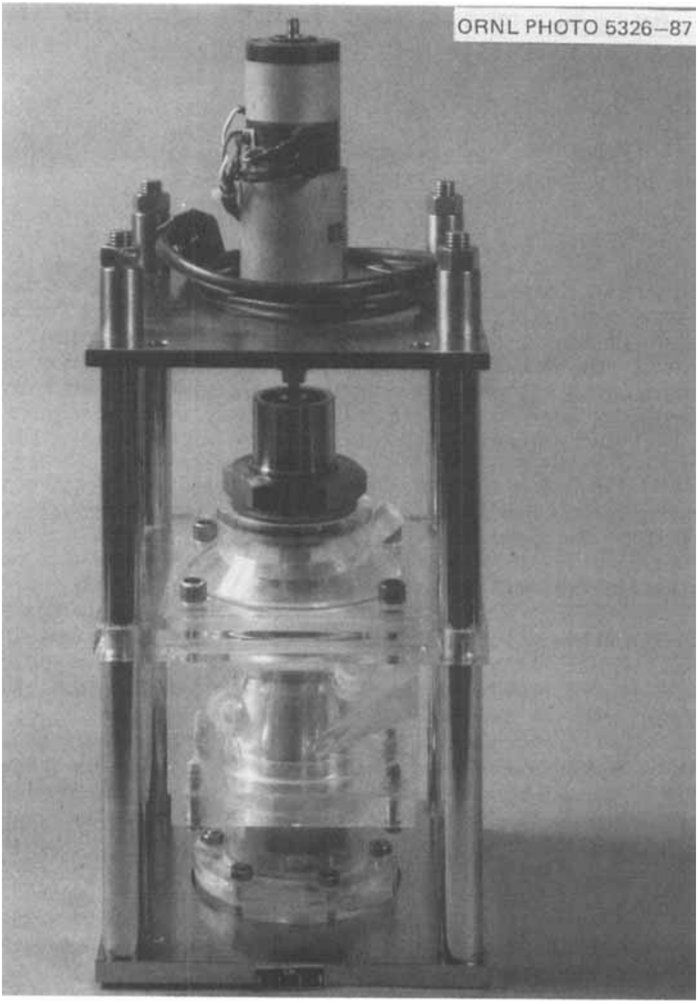

Fig. 1. 5.5-cm-diam rotor centrifugal contactor.

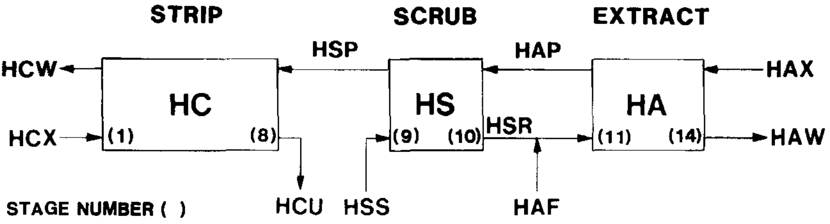

Fig. 2. Multistage cascade flow paths.

schematic of multistage cascade. All inlet flow streams other than the HAF were controlled by valves similar to those used for control during the single-stage tests. The HAF flow was controlled by a water wheel. The sample collection for the multistage system utilized solenoid valves that were operated simultaneously to minimize system perturbations during sampling. Thermocouples were located in-line between each contactor bank and in each cascade inlet and outlet stream.

The zirconium analysis was accomplished by inductively coupled plasma (ICP).

RESULTS AND DISCUSSION

Single-Stage Testing

The range of conditions used during the single-stage testing were as follows:

$2000 \le$ rotor speed (rpm) ≤ 4000
$1/3 \le$ phase ratio ≤ 3
$1/2 \le$ total flow (L/min) ≤ 2
$20 \le$ U (g/L) < 40
$1/4 <$ HNO_3 (M) $< 1/2$.

The Murphree efficiencies for the single-stage extraction tests are listed in Table 1 for the entire range of test conditions. The 100% theoretical efficiency was determined by SEPHIS (7). The uranium distribution coefficient correlations have been updated since the 1972 SEPHIS publication. The E_{MR} in Table 1 represents the extraction efficiency of the aqueous stream (raffinate) as determined directly from the aqueous stream uranium concentration. The E_{ME} in Table 1 represents the extraction efficiency of the organic stream (extract) as determined from the organic stream uranium concentration. The extraction efficiencies were calculated from the data of Table 2. The following calculations show how the Murphree efficiency was determined for a rotor speed of 2000 rpm,

Table 1. Murphree efficiencies for single-stage extraction

		Approximate total flow (L/min)								
		1/2			1			2		
Approximate phase ratio		2000	3000 rpm	4000	2000	3000 rpm	4000	2000	3000 rpm	4000
1/3	E_{MR}	87.7	87.7	83.2	87.5	80.7	79.1	--	91.9	85.4
	E_{ME}	88.6	87.9	78.7	92.4	92.4	90.4	--	96.1	92.2
1	E_{MR}	102	98.8	96.6	98.2	92.4	94.0	--	96.8	97.5
	E_{ME}	87.5	85.4	85.7	101	92.1	94.2	--	101	98.3
3	E_{MR}	97.3	93.5	68.5	96.8	96.2	94.4	--	99.0	99.6
	E_{ME}	98.9	95.0	80.4	121	116	116	--	105	100

phase ratio of approximately 1, and total flow rate of approximately 1 L/min. These conditions are shown in the first entry of Table 2.

$$U_{in} = (1/3)(46.4 + 46.4 + 46.7) = 46.5 \text{ g/L aqueous phase},$$

$$= (1/3)(0.4 + 0.4 + 0.4) = 0.4 \text{ g/L organic phase}.$$

$$U_{out} \text{ actual} = (1/3)(17.4 + 17.7 + 17.5) = 17.5 \text{ g/L aqueous phase},$$

$$= (1/3)(29.2 + 28.6 + 29.7) = 29.2 \text{ g/L organic phase}.$$

$$U_{out} \text{ SEPHIS} = 17.0 \text{ g/L aqueous phase},$$

$$= 29.0 \text{ g/L organic phase}.$$

$$E_{MR} = 100(X_{m-1} - X_m)/(X_{m-1} - X_m{}^*),$$

$$= 100(46.5 - 17.5)/(46.5 - 17.0) = 98.2.$$

$$E_{ME} = 100(Y_m - Y_{m+1})/(Y_m{}^* - Y_{m+1}),$$

$$= 100(29.2 - 0.4)/(29.0 - 0.4) = 101.4.$$

Material Balance Difference:

$$\text{Diff} = [(Q_aC_a + Q_oC_o)_{in} - (Q_aC_a + Q_oC_o)_{out}]/(Q_aC_a + Q_oC_o)_{in},$$

$$= \frac{\{[0.49(46.5) + 0.49(0.4)] - [0.49(17.5) + 0.49(29.2)]\}}{[0.49(46.5) + 0.49(0.4)]},$$

$$= 0.004.$$

Table 2. Single-stage extraction test conditions

W (rpm)	Q_{in} (L/min)		T_{out} (C)		$(HNO_3)_{in}$ (M)		TBP_{in} (vol%)	U_{in} (g/L)		Actual U_{out} (g/L)		SEPHIS* U_{out} (g/L)	
	A	O	A	O	A	O	O	A	O	A	O	A	O
2000	0.49	0.49	26.8	26.8	0.34	0.01	32.4	46.4	0.4	17.4	29.2	17.0	29.0
										17.7	28.6		
										17.5	29.7		
3000	0.48	0.49	26.9	26.9	0.34	0.01	30.7	46.4	0.4	19.2	26.5	17.0	29.0
										19.4	27.0		
										19.3	26.8		
4000	0.48	0.50	26.8	26.8	0.34	0.01	30.4	46.7	0.4	18.7	25.9	17.0	29.0
										18.9	27.5		
										18.8	28.5		
2000	0.27	0.26	26.8	26.8	0.25	0.03	32.9	42.9	0.5	16.2	23.0	16.6	26.4
										16.0	23.1		
										16.2	23.3		
3000	0.27	0.26	26.8	26.8	0.27	0.03	33.1	40.9	0.5	16.7	22.2	16.6	26.4
										17.2	22.6		
										16.7	23.0		
4000	0.29	0.26	26.4	26.4	0.27	0.03	33.0	40.6	0.4	17.5	21.9	16.6	26.4
										17.3	23.1		
										17.4	23.1		
2000	0.13	0.38	28.1	27.8	0.20	0.04	32.8	25.1	0.5	6.36	6.79	5.73	6.82
										6.03	6.76		
										6.38	6.70		
3000	0.12	0.37	28.1	28.1	0.20	0.04	32.7	25.0	0.5	7.29	6.50	5.73	6.82
										7.15	6.46		
										6.53	6.54		
4000	0.14	0.40	28.7	28.7	0.52	0.00	37.6	30.8	0.0	10.4	7.36	4.04	9.00
										12.0	7.17		
										14.9	7.19		
2000	0.57	0.20	27.6	27.6	0.11	0.04	34.3	13.9	1.0	11.3	8.18	10.9	9.09
										11.3	8.15		
										11.3	--		
3000	0.57	0.21	27.6	27.6	0.11	0.04	34.3	13.9	0.9	11.3	8.13	10.9	9.09
										11.3	8.08		
										11.3	--		
4000	0.57	0.21	27.5	27.4	0.11	0.04	34.5	13.8	1.0	11.4	7.41	10.9	9.09
										11.4	7.31		
										11.5	--		

Table 2 (continued)

W (rpm)	Q_{in} (L/min)		T_{out} (C)		$(HNO_3)_{in}$ (M)		TBP_{in} (vol%)	U_{in} (g/L)		Actual U_{out} (g/L)		SEPHIS* U_{out} (g/L)	
	A	O	A	O	A	O	O	A	O	A	O	A	O
2000	0.23	0.79	28.9	28.7	0.24	0.01	34.3	31.8	0.2	7.62	8.50	6.64	7.17
										7.33	8.66		
										7.44	8.71		
3000	0.20	0.79	29.0	29.0	0.24	0.01	34.5	32.4	0.2	7.31	8.26	6.64	7.17
										7.75	8.16		
										7.82	8.47		
4000	0.21	0.77	29.1	29.0	0.24	0.01	34.4	32.9	0.2	7.88	8.30	6.64	7.17
										8.15	8.33		
										8.23	8.20		
2000	0.76	0.24	28.2	28.1	0.24	0.01	34.1	32.4	0.2	23.2	30.6	22.0	34.6
										23.2	32.6		
										23.4	32.6		
3000	0.77	0.23	28.0	27.8	0.24	0.01	34.0	32.4	0.2	23.8	31.9	22.0	34.6
										24.0	32.1		
										24.1	31.8		
4000	0.77	0.22	28.0	27.8	0.24	0.01	34.3	32.3	0.2	24.0	31.3	22.0	34.6
										24.2	31.3		
										24.2	31.2		
3000	0.46	1.50	29.7	29.7	0.52	0.00	37.6	30.8	0.0	4.28	8.32	3.90	8.17
										4.20	8.97		
										4.02	8.51		
4000	0.46	1.52	29.6	29.6	0.52	0.00	37.6	30.8	0.0	4.02	8.20	3.90	8.17
										3.97	8.20		
										4.02	8.22		
3000	1.00	1.04	29.2	29.2	0.52	0.00	37.6	30.8	0.0	8.51	21.9	7.85	21.7
										8.62	21.9		
										8.61	22.3		
4000	1.00	1.06	29.3	29.3	0.52	0.00	37.6	30.8	0.0	8.43	20.9	7.85	21.7
										8.40	21.6		
										8.40	21.5		
3000	1.45	0.54	28.8	28.8	0.52	0.00	37.6	30.8	0.0	16.2	40.6	15.1	42.2
										16.7	40.5		
										16.2	40.6		
4000	1.46	0.53	28.7	28.7	0.52	0.00	37.6	30.8	0.0	17.5	39.1	15.1	42.2
										17.6	39.1		
										17.1	38.5		

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* - Equivalent SEPHIS output conditions are based on averaged input conditions.

Table 3. Murphree efficiencies for single-stage strip

		Approximate total flow (L/min)								
		1/2			1			2		
Approximate phase ratio		2000	3000 rpm	4000	2000	3000 rpm	4000	2000	3000 rpm	4000
1/3	E_{MR}	--	78.1	--	--	106	--	--	92.9	--
	E_{ME}	--	93.0	--	--	95.1	--	--	93.7	--
1	E_{MR}	--	97.1	--	--	89.5	--	--	95.3	--
	E_{ME}	--	98.4	--	--	99.3	--	--	96.3	--
3	E_{MR}	--	88.1	--	--	95.2	--	--	89.3	--
	E_{ME}	--	148*	--	--	183*	--	--	96.7	--

*Reflects the analytical colormetric inaccuracy due to interference from solvent degradation products.

The Murphree efficiencies for the single-stage strip tests are listed in Table 3. The E_{MR} in Table 3 represents the strip efficiency of the organic stream (raffinate) as determined from the organic stream uranium concentration. The E_{ME} in Table 3 represents the strip efficiency of the aqueous stream (extract) as determined directly from the aqueous stream uranium concentration.

The results shown in Table 1 indicate that the average single-stage extraction efficiency over the range of test conditions was (92 ± 8)% at one standard deviation (based upon the aqueous phase uranium analyses). Similarly the results shown in Table 3 indicate that the average single stage strip efficiency over the range of test conditions was (92 ± 7)% based upon the aqueous phase uranium analyses.

An Analysis of Variance (ANOVA) (8,9) indicated that the phase ratio had a significant effect upon the mass transfer efficiency at a 95% confidence level. In addition, it was concluded by General Linear Modeling (GLM) (8,10) that the phase ratio had a quadratic effect on the efficiency, yielding a maximum at approximately two (organic/aqueous). The ANOVA results also indicated that the rotor speed and total flow rate had no significant effect upon the efficiency at 90% confidence level.

It was also desired to determine from the single-stage tests if there was a significant difference between the extraction and strip efficiency. The comparison was made at a rotor speed of 3000 rpm over the complete range of phase ratios and flow rates tested. It was determined by a t-test that there was no significant difference over the range of test conditions.

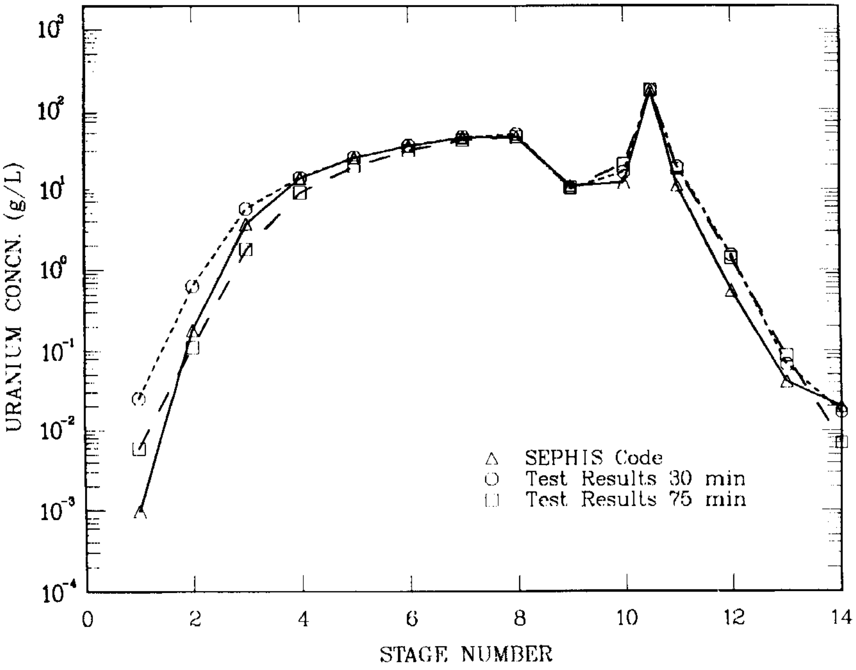

Fig. 3. Aqueous uranium concentration for low U loss test 2.

Multistage Testing

The results of the low uranium loss multistage tests are shown in Figs. 3 and 4. Figure 3 displays the aqueous phase uranium concentration profile, as determined from samples collected at 30 min after time zero, 75 min after time zero, and as calculated for theoretical equilibrium by SEPHIS. Figure 4 displays the organic uranium concentration profile for the same test as Fig. 3. The SEPHIS curves of Figs. 3 and 4 were generated from the low U1 test data of Table 4.

The single-stage efficiencies determined from the multistage tests were based on the high uranium loss test of Table 4, which maximized the reliability of uranium concentration analysis and avoided "pinch-points" at the cascade ends. It can be concluded from Table 5 that the average single-stage efficiency was approximately 90% over the entire cascade. The efficiencies were calculated one stage at a time based on the flow rate and

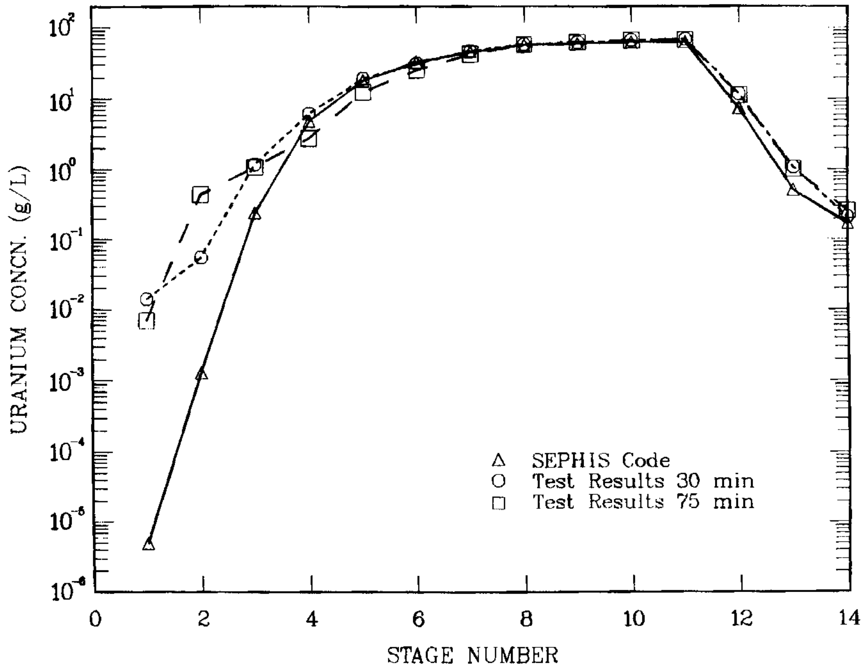

Fig. 4. Organic uranium concentration for low U loss test 2.

temperature data of Table 4 and the concentration data of Table 5. The TBP concentration in HAX was 32 vol %. The values with asterisks reflect large flow uncertainties due to the feed.

Table 6 shows the zirconium decontamination factor measured for two different low uranium loss tests shown in Table 4. The decontamination factor reported is defined as the Zr_{in}/Zr_{out} on a mass-per-time basis, where Zr_{in} is the HAF zirconium concentration and Zr_{out} is the HCU zirconium concentration, as labeled in Fig. 2. The large variation in decontamination factors reported in Table 6 (standard deviation of 85) may be attributed to at least one of the following conditions: (1) the solvent becomes saturated with inextractable zirconium, which decreases the distribution coefficient in the extraction bank and (2) analytical inaccuracy.

CONCLUSIONS

The mean Murphree stage efficiency for the extraction tests was (92 ± 8)% within one standard deviation based upon the aqueous

Table 4. SEPHIS input

Variable	Test Low U1	 Low U2	 High U
HAF:			
flow (L/min)	0.210	0.205	0.300
temp (C)	28.6	30.8	32.1
U concentration (g/L)	172.5	180.6	178.0
NO_3^- concentration ($\underline{M}$)	1.20	1.20	1.19
HCX:			
flow (L/min)	0.795	0.790	0.505
temp (C)	25.0	26.9	27.8
U concentration (g/L)	<0.001	<0.0001	<0.001
NO_3^- concentration ($\underline{M}$)	0.008	0.007	0.007
HSS:			
flow (L/min)	0.200	0.200	0.205
temp (C)	26.5	28.5	28.4
U concentration (g/L)	<0.001	<0.001	<0.001
NO_3^- concentration ($\underline{M}$)	1.42	1.41	1.44
HAX:			
flow (L/min)	0.600	0.600	0.500
temp (C)	26.1	28.1	28.0
U concentration (g/L)	0.16	0.16	0.13
NO_3^- concentration ($\underline{M}$)	0.003	0.003	0.007
TBP concentration (vol %)	31.8	31.7	31.9

Table 5. Data from high uranium loss test

Stage No.	Stage code Aq	 Org	U actual (g/L) Aq	 Org	NO_3 actual (M) Aq	 Org	Efficiency (%) Aq	 Org
-	HCX	-	<1E-3	-	7E-3	-		
1	-	HCW	1.2E+1	9.9E+0	1E-2	2E-3	80	72
2	-	-	2.5E+1	2.1E+1	1E-2	2E-3	87	103
3	-	-	3.6E+1	3.7E+1	1E-2	2E-3	88	94
4	-	-	4.6E+1	4.9E+1	1E-2	2E-3	91	96
5	-	-	5.5E+1	5.9E+1	1E-2	2E-3	83	101
6	-	-	6.4E+1	6.8E+1	1E-2	2E-3	94	82
7	-	-	7.4E+1	7.9E+1	1.3E-2	2E-3	93	81
8	HCU	-	8.4E+1	8.8E+1	9.6E-2	4E-3	76	76
	HSS	-	<1E-3	-	1.44	-		
9	-	HSP	3.0E+1	9.6E+1	1.3E+0	7.6E-2	81	70
10	HSR	-	5.9E+1	1.1E+2	1.3E+0	5.3E-2	61*	8*
	HAF	-	178.0	-	1.19	-		
11	-	HAP	1.2E+2	1.2E+2	1.2E+0	2.9E-2	149*	19*
12	-	-	1.1E+2	1.2E+2	1.2E+0	3.1E-2	83	112
13	-	-	6.9E+1	1.1E+2	1.2E+0	7.0E-1	94	88
14	HAW	-	1.6E+1	4.9E+1	1.2E+0	1.6E-1	90	78
	-	HAX	-	1.3E-1	-	7E-3		

Table 6. Zirconium decontamination factor

Test	Zirconium Concentration HAF Aqueous feed (g/min)	HCW Organic exit (g/min)	HCU Aqueous exit (g/min)	HAW Aqueous exit (g/min)	Material Balance (%)	Decontamination factor $\frac{HAF}{HCU}$
Low U1*	0.0195	0.0001	0.00013	0.0168	87	150
Low U1	0.0195	<0.0001	0.00008	0.0152	78	244
Low U2	0.0191	<0.0001	0.00006	0.0194	102	318
Average	--	--	--	--	--	240

Note: The two low U1 data sets were collected at 15 min* and 75 min into the run.

uranium concentration. The mean Murphree stage efficiency for the strip tests was (92 ± 7)% within one standard deviation based upon the aqueous uranium concentration.

The average efficiencies based upon the organic stream uranium concentrations were not significantly different from the aqueous stream results as determined by a t-test. The aqueous uranium analyses were considered more accurate than the organic because some of the organic analyses required stripping prior to colormetric analysis and an F-test indicated that the organic efficiencies of Table 1 had a significantly larger variance than the aqueous efficiencies.

The ANOVA results indicate a 95% probability of the phase ratio having a significant effect on the stage efficiency. The probability of the flow rate or rotor speed having a significant effect on the stage efficiency was less than 90%. Therefore, it was concluded the phase ratio had the only significant effect on the stage efficiency based upon the reasonable confidence level of 90% or better.

The results of the GLM indicate the effect of phase ratio on the stage efficiency is quadratic at the 97% confidence level based on a Type III error(8). It was also be concluded from the GLM that the quadratic effect had a maximum stage efficiency at a phase ratio of approximately two.

By visually examining Figs. 3 and 4 the low uranium loss test indicated SEPHIS adequately modeled the cascade performance except in the solvent exit region of the strip bank. In the region of stages 1-4, very low uranium concentrations were present. It is possible that for the condition of low uranium concentration, the effect of solvent degradation, interfacial crud, kinetic limitations, or SEPHIS distribution coefficient estimation errors may have a more pronounced effect on the mass transfer than at high uranium concentrations.

The high loss uranium test was performed in order to get an estimate of stage efficiencies in a cascade arrangement. The mean Murphree single-stage efficiency of the cascade was 90%. This efficiency was based on the aqueous phase uranium and nitric acid analysis. It is interesting to note that the mean single-stage efficiency based on the single-stage testing was (92 ± 8)% at one standard deviation for 24 data points, and based upon the multistage testing it was (90 ± 19)% for 14 data points. These efficiencies are not significantly different based upon a t-test, which is as expected.

The conclusions can be summarized as follows:

1. SEPHIS adequately modeled the multi-stage cascade uranium mass transfer for all conditions but the solvent at low uranium concentrations.

2. The average single-stage uranium mass transfer efficiency was found to be 92% over the entire range of test conditions.

3. The uranium mass transfer efficiency was found to be independent of the total flow rate and rotor speed, but maximum at a phase ratio (organic/aqueous) of two. This was only over the range of test conditions.

4. The zirconium decontamination factor for the multi-stage tests ranged from 150 to 318.

NOMENCLATURE

$$E_{ME} = \frac{Y_m - Y_{m+1}}{Y_m^* - Y_{m+1}}$$

$$E_{MR} = \frac{X_{m-1} - X_m}{X_{m-1} - X_m^*}$$

E_{ME} = Murphree extract stage efficiency

E_{MR} = Murphree raffinate stage efficiency

extract = solvent product that gained solute

feed = solution to be extracted

m = stage m

phase ratio = (organic flow rate)/(aqueous flow rate)

raffinate = residual feed that lost solute

solvent = liquid contacted with feed

X = feed and raffinate stream solute concentration

Y = solvent and extract stream solute concentration

* = equilibrium condition

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