WSRC-RP-92-1101

LATE WASH CROSS-FLOW FILTER ORGANIC BALANCE (U)

WSRC-RP--92-1101

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LATE WASH CROSS-FLOW FILTER ORGANIC BALANCE (U)

SUMMARY

A recent DOE-SR review of the results and data from the Late Washing Crossflow Filter assessment identified the fate of biphenyl as a concern in the Late Washing material balance. The concern arose because after the late washing operation only about 40% of the biphenyl remained in the irradiated precipitate and analyses of the spent wash water stream did not account for the missing biphenyl [2]. This document summarizes the results of subsequent filtration studies on the behavior and fate of all known organic precipitate feed components including biphenyl. The study employed a statistically designed material balance across a laboratory crossflow filter. Data from two separate experiments are presented here.

Results of the first study indicated no statistically significant loss of biphenyl, diphenylmercury, O-terphenyl, diphenylamine, or aniline. Results did indicate minor losses of phenylboric acid, M-terphenyl, P-terphenyl, and a significant production of phenol, believed to be due to the way in which the experiment was performed. A second experiment demonstrated no statistically significant loss of any of the organic compounds.

Authorized Derivative Classifier

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EXPERIMENTAL PROCEDURE

To close the material balance for precipitate feed organics, a precipitate feed simulant was irradiated to an absorbed dose of 1.9×10^8 rads in the 774-A cobalt-60 source. After analytical characterization of the nitrite concentration, the nitrite concentration was adjusted to 0.13 M and then the soluble potassium and cesium were re-precipitated with sodium tetraphenylborate solution. Samples were taken for organic analysis. The material was then concentrated by circulating through a laboratory sintered metal crossflow filter, removing filtrate without wash water makeup to a calculated 10 wt% insoluble solids. Batch washing was initiated by adding an aqueous solution of 0.004 M sodium tetraphenylborate equal to the permeate collected. Samples of the washed precipitate and the permeate were taken and analyzed for organic materials. In the first experiment, permeate samples were taken during the wash cycle to determine permeate concentration profiles. In the second experiment, the total permeate was collected in one container and sampled. The filter tube was then flushed and samples of the flush were taken and subsequently analyzed for organic materials.

ANALYTICAL OBSERVATIONS

The concentration of biphenyl in the permeate samples appeared to be constant with an average concentration of 27.5 ppm. In the first experiment, the soluble phenol concentration followed an exponential decline in concentration as would be expected for a continuous washing process. However, the phenol concentration of the last permeate sample was only about 23% of that detected in the slurry product. This indicates that a fraction of the phenol is trapped within the terphenylborate crystal matrix. This phenol may or may not slowly leach out during washing. No terphenyls were detected in the permeate samples and only trace amounts of phenylboric acid were detected in the initial permeate samples. This indicates that the highly water soluble phenylboric acid is extensively trapped within the solid crystal matrix and does not leach out during washing operations.

MATERIAL BALANCE

A statistical analysis was performed by T. B. Edwards of SRTC/NRTSC [3] (attached) to account for propagation of the random errors associated with the analytical and laboratory measurements. In the first experiment, the balance resulted in closure of the biphenyl, O-terphenyl, diphenylamine, aniline, and diphenylmercury at the 99% confidence interval. That is the "99% confidence interval for the unaccounted material" contained the value of zero. The "99% confidence interval for the unaccounted material" for phenylboric acid, M-terphenyl, and P-terphenyl did not include the value of zero. This indicates a systematic loss of this component or a systematic analytical error. Although the analysis indicated a significant production of phenol during the washing operation, it is likely that this error is due to the numerical method used to perform the integration used in determining the total mass of phenol contained in the permeate.

Analysis of the data from the second experiment demonstrated no statistically significant losses of any of the organic compounds. Variability was higher but acceptable (in view of the fact that it is a mass balance on components present at < 0.5 wt% in a highly complex chemical system.) in the sample analyses for the second experiment.

DISCUSSION

Due to the exponential decline in the permeate phenol concentration for the first experiment, an integration of the total amount of phenol in the permeate was performed. An estimate of the variance was made by evaluating the degree to which the analytical data fit an exponential decline. The standard deviation was calculated to be 42.3 ppm which is consistent with that of the other phenol analysis for that experiment.

The 99% confidence interval for M-terphenyl and P-terphenyl did not include zero, which indicates a statistically significant amount unaccounted for in the first experiment. These results are possibly due to the extremely low levels of these components and the lack of their presence in the analytical standards on a routine basis. No statistically significant loss was observed in the second experiment.

CONCLUSIONS

The material balance has demonstrated that:

- 1) All of the terphenyl's and the majority of the phenylboric acid (>95%) in the irradiated feed to the Late Wash facility will be retained in the product slurry.
- 2) The majority (~2/3) of the phenol in the irradiated feed will be removed with the permeate from the Late Wash facility.
- 3) Minor amounts of biphenyl will be washed out of the slurry. The amount determined by the volume of wash and the solubility of the biphenyl (25-30 PPM).
- 4) The random errors associated with the analytical methods combined with the sheer mass of material and low concentrations precludes the use of a material balance to determine the compounds responsible for the observed reduction in filter flux rates during the Late Wash filtration process.

RECOMMENDATIONS

- 1) Investigate the chemical nature of the insoluble phenol and phenylboric acid in irradiated feed.

REFERENCES

- 1) Dworjanyn, L. O. and Morrissey, M. F., "Initial Technical Basis for the Use of Spare ITP Filter in DWPF Late Washing", WSRC-RP-92-766, June 5, 1992.
- 2) Morrissey, M. F., "Late Washing Efficiency", WSRC-RP-92-1030, August 31, 1992.
- 3) T. B. Edwards, "Statistical Analysis of Mass Balance Data", SCS-ASG-92082, October 16, 1992.

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INTER-OFFICE MEMORANDUM
Westinghouse Savannah River Company

SCS-ASG-92082
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STATISTICAL ANALYSIS OF MASS BALANCE DATA (U)

Introduction

Data from the most recent Filter Tests (#3 and #4) completed at TNX were analyzed using statistical methods. The objective of this analysis was to complete a mass balance for each of the chemical compounds of interest for each of the tests.

To complete a mass balance for a test, the concentration of each compound as well as the total mass at each of four locations were used. These locations are feed slurry, product, flush, and filtrate. The material total at each of these locations is assumed known without appreciable error. The concentrations at each location are estimated based upon the experimental data. These values are used to estimate the unaccounted for mass of each compound. The uncertainty of this estimate is determined by propagating the variances of the estimates of the concentrations.

Seven samples of the feed slurry, product, flush, and filtrate were taken and analyzed. Tables 1a and 1b in Appendix A provide these data and identify the chemical compounds of interest for Test #3 and #4, respectively. Values are given in parts per million (ppm) for all concentrations except the filtrate which is in micrograms/milliliter ($\mu\text{g/ml}$).

Estimation of the Unaccounted for Mass

The following notation will be helpful in developing an appropriate model for the mass balance problem for a given compound for each of the two tests.

Let		Test #3	Test #4
x	= mass of feed slurry in grams (g)	= 7,241 g	15,238 g
y	= mass of product in grams	= 5,577 g	13,292 g
t	= mass of flush in grams	= 3,473 g	4,378 g
z	= volume of filtrate in milliliters (ml)	= 15,089 ml	36,385 ml

and

c_x	=	estimated concentration of compound in feed slurry in ppm
c_y	=	estimated concentration of compound in product in ppm
c_t	=	estimated concentration of compound in flush in ppm
c_z	=	estimated concentration of compound in filtrate in $\mu\text{g/ml}$

If u represents the unaccounted for mass of the compound in grams, then u is estimated by

$$\hat{u} = \frac{(xc_x - (yc_y + tc_t + zc_z))}{10^6} \quad (1)$$

The values of c_x , c_y , c_t , and c_z and their uncertainties are estimated from the sample data. An example is used to demonstrate the approach. If p_i , for $i=1,2, \dots, 7$, represents the seven feed slurry sample ppm values, then estimate c_x is taken as the sample average of the p_i 's. Thus,

$$c_x = \sum_{i=1}^7 \frac{p_i}{7}$$

If the sample standard deviation of the p_i 's is represented by s_p , then the standard deviation of the error of c_x is estimated by $\frac{s_p}{\sqrt{7}}$. The other concentrations, except for the phenol filtrate concentration in Test #3, are handled in a similar manner using the sample means and standard deviations in Tables 2a and 2b in Appendix A. Due to the method of filtrate sampling used in Test #3, the estimations of the phenol concentration and the associated uncertainty had to be handled differently. The details of these estimations are provided in Appendix B.

Let σ_{cx} represent the estimate of the standard deviation of the error for c_x ,
 σ_{cy} represent the estimate of the standard deviation of the error for c_y ,
 σ_{ct} represent the estimate of the standard deviation of the error for c_t , and
 σ_{cz} represent the estimate of the standard deviation of the error for c_z .

The variance of $\hat{u}$ in equation (1) is determined via a propagation of variance. The errors in the values of x , y , t , and z are assumed to be small compared with the errors in the concentrations. Data were not available to investigate bias or systematic errors in the sampling or analytical methods; these errors are assumed to be negligible. Errors in the measured concentrations are assumed to be independent. Since the error in $\hat{u}$ is a linear combination of independent, random error terms, the estimate of the standard deviation of $\hat{u}$ is given by

$$\hat{\sigma}_u = \sqrt{\left(\frac{x}{10^6} \sigma_{cx}\right)^2 + \left(\frac{-y}{10^6} \sigma_{cy}\right)^2 + \left(\frac{-t}{10^6} \sigma_{ct}\right)^2 + \left(\frac{-z}{10^6} \sigma_{cz}\right)^2}$$

A 99% confidence interval for u is given by

$$\hat{u} \pm (t_{.005, v} \times \hat{\sigma}_u)$$

where $t_{.005, v}$ represents the upper 0.5 percentile of Student's t distribution with v degrees of freedom.

Tables 3a and 3b provide an estimate of the unaccounted for mass of each compound along with a 99% confidence interval for Test #3 and #4, respectively. A negative value for the unaccounted for mass implies a processing "gain" for that particular chemical compound and a positive value a "loss." A significant "gain" for a compound would imply a bias in the sampling or analytical process for that compound while a significant "loss" indicates a bias in the measuring process or an unaccounted for deposit of the compound.

Conclusions

A confidence interval for the unaccounted for mass of each compound of interest has been determined. Some of these intervals for Test #4 are very wide compared to Test #3. This indicates a larger value for the estimate of the standard deviation, $\hat{\sigma}_u$, for $\hat{u}$. This is a result of the large variability of the concentration measurements of the samples within a location or process. Smaller confidence intervals would be expected if between sample variability could be reduced. Such a reduction may be possible via improvements in the sampling and/or analytical methods. An investigation into these methods could help identify opportunities for such improvement as well as allow for the estimation of any bias errors.

Appendix A: TABLES

Table 1a:	Filter Test #3 Data
Table 1b:	Filter Test #4 Data
Table 2a:	Filter Test #3 Sample Statistics
Table 2b:	Filter Test #4 Sample Statistics
Table 3a:	Mass Balance Results for Filter Test #3
Table 3b:	Mass Balance Results for Filter Test #4

Table 1a: Filter Test #3 Data

Unit = parts per million (ppm) for all results except Filtrate
Unit for Filtrate = micrograms/milliliter (µg/ml)

Rows	Process	Sample	Biphenyl	Phenol	Dipng	PBA	O-Ter	M-Ter	P-Ter	DIP	Aniline
1	Feed Slurry	227A	1444.8	2241.6	.	540	22.8	102	32.4	8.4	30
2	Feed Slurry	228A	1591.2	2288.4	2784	535.2	24	103.2	34.8	14.4	33.6
3	Feed Slurry	229A	1500	2222.4	2698	535.2	22.8	99.6	34.8	16.8	38.4
4	Feed Slurry	230	1534.8	2274	.	568.8	43.2	128.4	45.6	24	36
5	Feed Slurry	231	1477.2	2254.8	1881.6	522	22.8	104.4	33.6	15.6	30
6	Feed Slurry	232	1429.2	2242.8	1670.4	562.8	21.6	100.8	32.4	24	32.4
7	Feed Slurry	233	1459.2	2281.2	2457.6	578.4	22.8	99.6	27.6	20.4	34.8
8	Feed Slurry	234	1419.6	2250	1632	501.6	22.8	103.2	36	6	33.6
9	Feed Slurry	235	1419.6	2257.2	1852.8	516	21.6	100.8	33.6	19.2	30
10	Feed Slurry	236	1482	2281.2	1881.6	532.8	24	103.2	32.4	13.2	30
11	Feed Slurry	237	1474.8	2295.6	1814.4	526.8	22.8	104.4	33.6	16.8	28.8
12	Feed Slurry	238	1444.8	2223.6	1708.8	494.4	22.8	103.2	36	12	28.8
13	Feed Slurry	239	1366.8	2151.6	1632	540	20.4	91.2	27.6	8.4	19.2
14	Feed Slurry	240	1485.6	2260.8	3062.4	770.4	22.8	114	36	22.8	28.8
15	Filtrate	241	22	1807	5	23	0	0	0	4	18
16	Filtrate	242	19	1592	4	5	0	0	0	4	16
17	Filtrate	243	24	1215	18	24	0	0	0	3	17
18	Filtrate	244	22	900	3	1	0	0	0	3	0
19	Filtrate	245	23	704	0	25	0	0	0	2	0
20	Filtrate	246	49	594	6	17	0	0	0	19	0
21	Filtrate	247	26	493	9	3	0	0	0	1	0
22	Filtrate	248	26	363	22	0	0	0	0	2	0
23	Filtrate	249	20	338	4	0	0	0	0	3	0
24	Filtrate	250	21	282	6	0	0	0	0	0	3
25	Filtrate	251	24	236	15	0	0	0	0	0	0
26	Filtrate	252	63	177	12	0	0	0	0	98	0
27	Filtrate	253	19	156	9	0	0	0	0	2	0
28	Product	254	1843.2	881.8	1632	561.6	24	108	33.6	7.2	16.8
29	Product	255	1818	879.6	3264	547.2	26.4	105.6	36	14.4	12
30	Product	256	1608	808.8	2698	514.8	22.8	93.6	30	4.8	10.8
31	Product	257	1484.4	855.6	2208	596.4	25.2	100.8	34.8	12	9.6
32	Product	258	1575.6	805.2	2112	518.4	24	96	32.4	6	21.6
33	Product	259	1586.4	804	2112	511.2	22.8	94.8	31.2	8.4	12
34	Product	260	1598.4	806.4	2016	570	22.8	91.2	28.8	6	16.8
35	Product	262	1316.4	732	1440	459.6	19.2	80.4	24	4.8	8.4
36	Product	263	1408.8	708	2112	439.2	19.2	79.2	25.2	6	9.6
37	Product	264	1945.2	850.8	3552	580.4	25.2	98.4	33.6	6	10.8
38	Product	265	1599.6	846	2112	602.4	26.4	103.2	37.2	22.8	0
39	Product	266	1545.6	800.4	1824	507.6	24	92.4	31.2	15.6	9.6
40	Product	267	1883.6	798	3168	556.8	30	90	26.4	12	6
41	Flush	268	59	63	32	39	2	5	1	4	0
42	Flush	269	50	81	8	39	0	4	1	0	0
43	Flush	270	52	65	4	17	1	4	1	0	0
44	Flush	271	63	11	4	24	8	26	4	2	0
45	Flush	272	38	51	9	22	1	4	1	0	0

Table 1b: Filter Test #4 Data

Unit = parts per million (ppm) for all results except Filtrate
Unit for Filtrate = micrograms/milliliter (µg/ml)

Rows	Process	Sample	Biphenyl	Phenol	Diphg	PBA	O-Ter	M-Ter	P-Ter	DIP
1	Feed Slurry	MONSON-1	992	1174	196	190	21	75	21	2
2	Feed Slurry	MONSON-2	1528	1538	1894	189	23	83	10	32
3	Feed Slurry	MONSON-3	1724	1594	2093	669	29	93	26	17
4	Feed Slurry	MONSON-4	1729	1720	1849	749	28	97	23	43
5	Feed Slurry	MONSON-5	840	979	133	242	16	58	5	4
6	Feed Slurry	MONSON-6	369	515	2331	212	3	21	2	3
7	Feed Slurry	MONSON-7	1580	1600	2229	694	22	88	23	20
8	Filtrate	MONSON-8	17	374	6	3	0	0	0	0
9	Filtrate	MONSON-9	10	349	7	1	0	0	0	0
10	Filtrate	MONSON-10	4	373	6	12	0	0	0	0
11	Filtrate	MONSON-11	12	370	8	10	0	0	0	3
12	Filtrate	MONSON-12	8	355	7	3	0	0	0	0
13	Filtrate	MONSON-13	14	378	8	4	0	0	0	0
14	Filtrate	MONSON-14	11	353	7	4	0	0	0	0
15	Product	MONSON-15	1340	911	1874	468	33	100	38	9
16	Product	MONSON-16	1597	601	1620	153	38	116	45	19
17	Product	MONSON-17	1648	618	2470	532	41	126	52	17
18	Product	MONSON-18	1421	563	2050	473	36	108	39	47
19	Product	MONSON-19	1347	530	1193	442	28	87	24	37
20	Product	MONSON-20	1327	550	36	143	31	96	34	19
21	Product	MONSON-21	1361	637	1606	539	35	99	37	36
22	Flush	MONSON-22	0	4	11	10	0	0	0	0
23	Flush	MONSON-23	0	4	7	4	0	0	0	0
24	Flush	MONSON-24	0	0	7	0	0	0	0	0
25	Flush	MONSON-25	0	0	9	5	0	0	0	0
26	Flush	MONSON-26	0	3	5	3	0	0	0	0
27	Flush	MONSON-27	0	0	10	6	0	0	0	0
28	Flush	MONSON-28	0	0	9	4	0	0	0	0

Table 2a: Filter Test #3 Sample Statistics

Unit = parts per million (ppm) for all results except Filtrate
Unit for Filtrate = micrograms/milliliter (µg/ml)

Rows	Process	N	Mean(Biphenyl)	Mean(Phenol)	Mean(Diphg)	Mean(PBA)	Mean(O-Ter)	Mean(M-Ter)	Mean(P-Ter)	Mean(DIP)	Mean(Aniline)
1	Feed Slurry	14	1466.4	2251.8	2088.8	551.742857	24.0857143	104.142857	34.0285714	15.8571429	31.0285714
2	Filtrate	13	27.5384615	681	8.69230769	7.53846154	0	0	0	10.8461538	4.15384615
3	Flush	5	48	64.6	11.4	28.2	2.4	8.6	1.6	1.2	0
4	Product	13	1616.4	813.507692	2326.15385	534.276923	24	84.8923077	31.1076923	18.69230769	11.0769231

Rows	Process	N	Std(Biphenyl)	Std(Phenol)	Std(Diphg)	Std(PBA)	Std(O-Ter)	Std(M-Ter)	Std(P-Ter)	Std(DIP)	Std(Aniline)
1	Feed Slurry	14	54.6676673	36.6759615	511.67285	67.198646	5.57837268	8.43524787	4.27793632	15.8527741	4.53557368
2	Filtrate	13	13.1505094	546.185866	6.421119	10.4691243	0	0	0	126.6265724	7.3806747
3	Flush	5	8.51459318	10.7144762	11.7388245	10.1833197	3.20936131	9.73552916	1.3416329	1.78885438	0
4	Product	13	174.040685	51.262762	647.737839	48.6238308	2.89827535	8.68739139	4.11227057	5.39914523	5.32512188

Table 2b: Filter Test #4 Sample Statistics

Unit = parts per million (ppm) for all results except Filtrate
Unit for Filtrate = micrograms/milliliter (µg/ml)

Row	Process	N	Mean(Biphenyl)	Mean(Phenol)	Mean(Dlphg)	Mean(PBA)	Mean(O-Ter)	Mean(M-Ter)	Mean(P-Ter)	Mean(DIP)
1	Feed Slurry	7	1251.71429	1302.85714	1532.14286	420.714286	20.2857143	73.5714286	15.7142857	17.2857143
2	Filtrate	7	10.8571429	384.571429	7	5.28571429	0	0	0	1.28571429
3	Flush	7	0	0	8.28571429	4.57142857	0	0	0	0
4	Product	7	1425.85714	630	1549.85714	392.857143	34.5714286	104.571428	38.4285714	26.2857143

Row	Process	N	Std(Biphenyl)	Std(Phenol)	Std(Dlphg)	Std(PBA)	Std(O-Ter)	Std(M-Ter)	Std(P-Ter)	Std(DIP)
1	Feed Slurry	7	524.580059	436.781731	949.786016	286.321901	8.78852065	28.5572158	9.78309787	15.3083763
2	Filtrate	7	4.18045338	11.8160504	0.81649658	4.07080188	0	0	0	2.36038738
3	Flush	7	0	1.73205081	2.05886346	3.947247	0	0	0	0
4	Product	7	121.892389	129.668808	777.716407	170.86198	4.35343324	13.1384568	8.73418935	13.7189889

Total Mass - grams (except for Filtrate) - milliliters for Filtrate	Sample Avg & Std Dev - ppm (except for Filtrate) - micrograms/ml for Filtrate
Unaccounted For Mass (grams)	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	0.9152057
Sample Conc	1466.4	1616.4	48	27.5	
Sample STDev	54.7	174	8.5	13.2	0.298
Sample Size	14	13	5	13	
Degrees of Freedom	13	12	4	12	12
99% confidence interval for Unaccounted					
		0.0059		1.8245	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	0.7686987
Sample Conc	551.7	534.3	28.2	7.5	
Sample STDev	67.2	48.6	10.2	10.5	0.158
Sample Size	14	13	5	13	
Degrees of Freedom	13	12	4	12	12
99% confidence interval for Unaccounted					
		0.287		1.251	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	1.8273877
Sample Conc	2088.8	2326.2	11.4	8.7	
Sample STDev	511.7	647.7	11.7	6.4	1.474
Sample Size	12	13	5	13	
Degrees of Freedom	11	12	4	12	11
99% confidence interval for Unaccounted					
		-2.751		6.406	

Table 3a: Mass Balance Results for Filter Test #3 (con't)

Total Mass - grams (except for Filtrate) - milliliters for Filtrate	Sample Avg & Std Dev - ppm (except for Filtrate) - micrograms/ml for Filtrate
Unaccounted For Mass (grams)	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	-0.106734
Sample Conc	15.9	9.7	1.2	10.8	
Sample STDev	5.9	5.4	1.8	26.6	0.112
Sample Size	14	13	5	13	
Degrees of Freedom	13	12	4	12	12
99% confidence interval for Unaccounted					
		-0.450		0.236	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	0.0984599
Sample Conc	31	11.1	0	4.2	
Sample STDev	4.5	5.3	0	7.4	0.033
Sample Size	14	13	5	13	
Degrees of Freedom	13	12	4	12	12
99% confidence interval for Unaccounted					
		-0.003		0.200	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted
Mass(grams)	7241	5643	3473	15089	-3.3285594
Sample Conc	2251.8	813.5	64.6	982.1	
Sample STDev	36.7	51.3	10.7	44.5	0.680
Sample Size	14	13	5	13	
Degrees of Freedom	13	12	4	11	11
99% confidence interval for Unaccounted					
		-5.441		-1.216	

Total Mass - grams (except for Filtrate) - milliliters for Filtrate	Sample Avg & Std Dev - ppm (except for Filtrate) - micrograms/ml for Filtrate
Unaccounted For Mass (grams)	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-0.2763
Sample Avg Conc	1251.7	1425.9	0	10.9	
Sample Std Dev	524.6	122	0	1.2	3.083
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
99% confidence interval for Unaccounted For					
		-11.7067		11.1542	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	0.9752
Sample Avg Conc	420.7	392.9	4.6	5.3	
Sample Std Dev	266.6	170.9	3	4.1	1.760
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
	99% confidence interval for Unaccounted For				
		-5.550		7.500	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	2.4538
Sample Avg Conc	1532.1	1549.9	8.3	7	
Sample Std Dev	949.8	777.7	2.1	0.82	6.722
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
		99% confidence interval for Unaccounted For			
		-22.466		27.373	

Total Mass - grams (except for Filtrate) - milliliters for Filtrate	Sample Avg & Std Dev - ppm (except for Filtrate) - micrograms/ml for Filtrate
Unaccounted For Mass (grams)	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-0.1506
Sample Avg Conc	20.3	34.6	0	0	
Sample Std Dev	8.8	4.4	0	0	0.055
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
99% confidence interval for Unaccounted For					
		-0.356		0.054	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-0.2688
Sample Avg Conc	73.6	104.6	0	0	
Sample Std Dev	26.6	13.1	0	0	0.167
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
99% confidence interval for Unaccounted For					
		-0.887		0.349	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-0.2712
Sample Avg Conc	15.7	38.4	0	0	
Sample Std Dev	9.8	8.7	0	0	0.071
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
99% confidence interval for Unaccounted For					
		-0.536		-0.007	

Total Mass - grams (except for Filtrate) - milliliters for Filtrate	Sample Avg & Std Dev - ppm (except for Filtrate) - micrograms/ml for Filtrate
Unaccounted For Mass (grams)	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-0.1333
Sample Avg Conc	17.3	26.3	0	1.3	
Sample Std Dev	15.8	13.7	0	2.4	0.119
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
99% confidence interval for Unaccounted For					
		-0.574		0.307	

	Feed Slurry	Product	Flush	Filtrate	Unaccounted For
Total Mass	15238	13292	4378	36385	-1.7907
Sample Avg Conc	1302.9	630	1	364.6	
Sample Std Dev	436.8	129.7	1.7	11.8	2.604
Sample Size	7	7	7	7	
Degrees of Freedom	6	6	6	6	6
		99% confidence interval for Unaccounted For			
		-11.443		7.862	

Appendix B: Test #3 Filtrate Phenol Sample Results

The method of sampling the filtrate for Test #3 was different from that for Test #4. In test #3, the filtrate stream was sampled during the processing, whereas in Test #4 the sampling was performed from a container holding the filtrate after completion of the processing. The phenol results are very sensitive to the method used for Test #3; this is seen in the data in Table 1a of Appendix A. These data decrease significantly over time.

The following method was used to estimate an "average" concentration of phenol in the filtrate samples. The relationship between phenol concentration and time is represented in Figure 1 below.

Figure 1: Phenol Concentration vs Filtrate Volume

Concentration - micrograms/milliliter

Volume - milliliters

This figure shows a stable phenol concentration in the filtrate until a volume of 1663 ml had been generated at which time the concentration begins to decline like a first order exponential. Let A be the area under the curve of Figure 1; then, the relationship to the average phenol concentration, a, is estimated by

$$15089 a = A$$

To estimate the portion of area A under the exponential curve, an exponential model was fitted to the phenol filtrate sample data. This was accomplished by performing a linear fit to the natural log (LN) of these data. The results of this fit are presented in Exhibit 1.

EXHIBIT 1: LN (Phenol) versus Corrected Cumulative Permeate Volume

The estimated exponential model is given by

$$\begin{aligned}\text{Phenol Concentration at Volume } v &= e^{7.639} e^{-0.000196(v - 1663)} \\ &= 2,077.7 e^{-0.000196(v - 1663)}\end{aligned}$$

The area under the exponential portion of Figure 1, call this area A_1 , is given by

$$A_1 = \int_{1663}^{15089} 2077.7 e^{-0.000196(v - 1663)} dv = 11,363,436.5$$

The estimate of the concentration at a filtrate volume of 1663 ml is 2077.7 $\mu\text{g/ml}$. Thus, the estimate of the area under the rectangular portion of Figure 1, call this area A_2 , is given by

$$A_2 = 2,077.7 \times 1663 = 3,455,215.1$$

The total area under the curve of Figure 1 is 14,818,651.6 and thus the estimate of a , the phenol concentration for the filtrate, is 982.1 $\mu\text{g/ml}$.

The variance, σ^2 , of this estimate of phenol concentration is given by

$$\sigma^2 = \frac{\text{VARIANCE}(A_1) + \text{VARIANCE}(A_2) + \text{COVARIANCE}(A_1, A_2)}{15089^2}$$

These variances and covariances will be estimated from the results of the exponential model fitted to the phenol sample values. The root mean square error of 0.053 provides an estimate of the relative error of the phenol concentration at a filtrate volume over 1663 ml. Thus, the relative standard deviation of the error in the phenol concentration is 5.3%. This translates into a 5.3% relative standard error in the value of A_1 . For the value of $A_1 = 11,363,436.5$, the standard error is 602,262.1.

Area A_2 is based on the estimate of the intercept from the exponential fit. The standard error of the estimate of the intercept is 0.031 with degrees of freedom equal to 11. Thus, a 95% confidence interval for the intercept is given by

$$7.639 \pm t_{0.025, 11} (0.031) = 7.639 \pm 2.201 (0.031) = (7.57, 7.71)$$

where $t_{0.025, 11}$ is the upper 2.5 percentile for the Student's t distribution with 11 degrees of freedom.

Using the limits of this interval, a 95% confidence interval for A_2 is computed as follows

$$(1663 \times e^{7.57}, 1663 \times e^{7.71}) = (3,224,790 ; 3,709,392)$$

This confidence interval can be used to estimate the standard error of A_2 since 4 times the standard error is approximately the width of this interval, or

$$\text{Standard Error of } A_2 = \frac{(3,709,392 - 3,224,790)}{4} = 121,151$$

The covariance for A_1 and A_2 will be estimated by the product of the standard errors for A_1 and A_2 or

$$\text{COVARIANCE}(A_1, A_2) = 602,262.1 \times 121,151$$

Finally, the variance of the estimate of the phenol concentration is given by

$$\begin{aligned}\sigma^2 &= \frac{\text{VARIANCE}(A_1) + \text{VARIANCE}(A_2) + \text{COVARIANCE}(A_1, A_2)}{15089^2} \\ &= \sqrt{(602,262.1^2 + 121,151^2 + (121,151 \times 602,262.1), 15089^2)} \\ &= 1978\end{aligned}$$

Thus, the standard error of the estimate of the phenol concentration is given by 44.5.

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