REGULATORY OFF-GAS ANALYSIS FROM THE EVAPORATION OF HANFORD SIMULATED WASTE SPIKED WITH ORGANIC COMPOUNDS

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INTRODUCTION

The Hanford River Protection Project Waste Treatment Plant (RPP-WTP) pretreatment and immobilization process will decontaminate Envelope A, B & C supernatant liquids using cesium and technetium ion exchange columns, after strontium and transuranics (Sr/TRU) are removed via a precipitation (Envelope C only) and filtration step. The decontaminated low activity waste (LAW) will be concentrated through the LAW Melter Feed Evaporator, a forced circulation evaporator, before glass formers are added and the resulting slurry vitrified in a joule-heated, refractory-lined melter. The purposes of this work were to: 1) develop preliminary operating data such as expected concentration endpoints for flow sheet development and evaporator design, and 2) examine the regulatory off-gas emission impacts from the evaporation of relatively organic-rich Hanford Tank 241-AN-107 Envelope C waste simulant containing 14 volatile, semi-volatile and pesticide organic compounds potentially present in actual Hanford RPP waste. The latter results will be used as input into RPP-WTP environmental permits and risk assessments. This work also served as the working basis for Crawford *et al.* (Paper 108a).

EXPERIMENTAL

To minimize potential organic absorption/adsorption losses, a bench-scale thermosiphon evaporator constructed mainly of glass and polytetrafluoroethylene (PTFE) was used (Figure 1). Thermocouples and resistance temperature detectors measured the evaporator (T2), condensor (T3) and condensate (T4) temperatures, and an Incoloy® heating rod (with internal thermocouple T1) served as the heating element in this natural circulation evaporator. Pressure (PG) and temperature measurement devices as well as material addition/removal ports were secured using stainless steel fittings mounted in PTFE plugs. Feed, condensate and concentrate were introduced or removed from the system through PTFE lines and valves (V1-V3). Continuous feed addition and concentrate removal (semi-batch for condensate) was performed using peristaltic pumps equipped with a segment of Viton® tubing. Natural leak rates of as low as 0.2 mL/min (STP) were achieved for this ~5200 mL internal volume system. A measured air in-leakage was added using a mass-flow controller to create a total evaporator in-leakage (11.5 ml/min) scaled for expected air in-leakage in the full-scale plant. AN-107 simulated waste feed material (5.5 M Na) was introduced into the evaporator from 1L polyvinyl fluoride (PVF) bags, after being injected with an acetone spiking solution containing 14 target volatile, semi-volatile, and pesticide compounds to a target of 1 ppm (similar to maximum concentrations

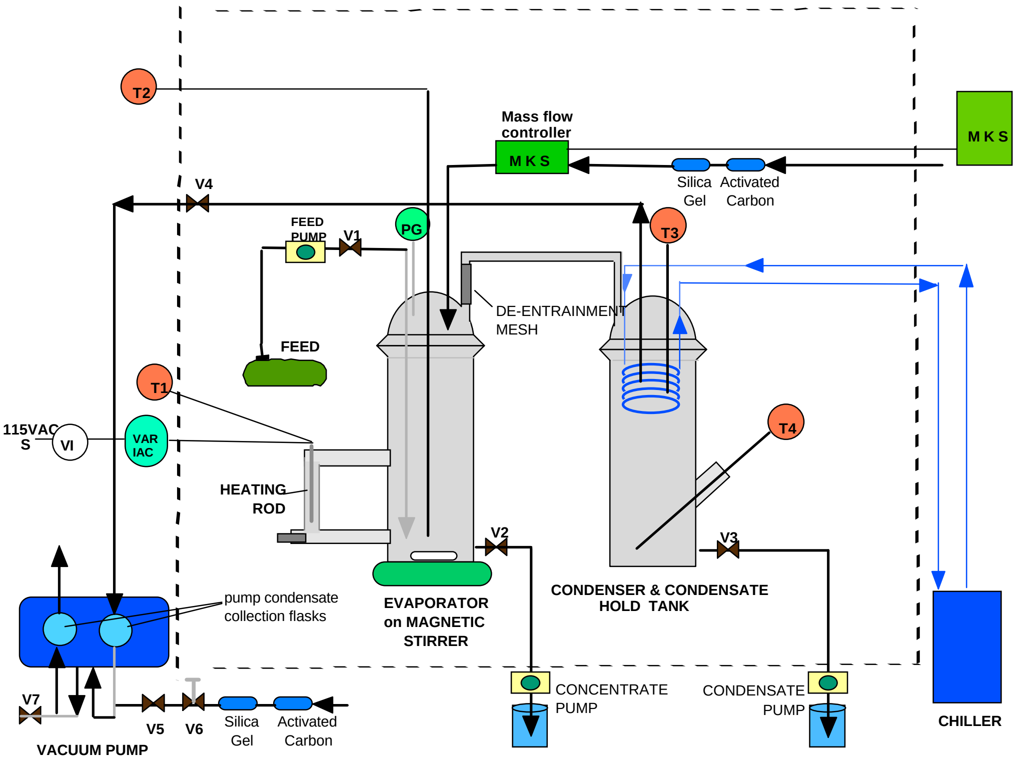

Figure 1. Evaporator System Schematic

in actual waste [Klinger *et al.*, 2000]). Anti-entrainment of liquid to >99% was achieved using a rolled stainless steel mesh mounted above the evaporator.

The total evaporator off-gas and PTFE-diaphragm vacuum pump bleed air, used to adjust evaporator pressure, were sent to a volatile organic sampling train coupled with a metering console that is designed for use for Environmental Protection Agency (EPA) SW-846 Methods 0010 and 0031 required this work. Two Tenax®-GC and one Anasorb®-747 sorbent tube were mounted in the off-gas sampler for volatiles sampling (Method 0031), and a single XAD-2® sorbent tube for the semi-volatiles/pesticide sampling (Method 0010). After an initial boildown to raise the evaporator concentration from 5.5 to 8.0 M Na, steady state operation (50 ± 3°C, 60 ± 8 mm Hg, 40 ± 1°C condensor) was performed for ~75 hours continuously, with the total run time divided equally between each off-gas sampling method. For a post-experiment material balance, regulatory liquid samples were collected simultaneously with the off-gas samples, and together were sent to a vendor laboratory for EPA SW-846 regulatory analysis.

RESULTS AND DISCUSSION

Mass balance closure on the 75 hour steady-state evaporation was to within 2% by mass overall, with closures to within 5% and 1% for the volatiles and semi-volatiles off-gas sampling portions of the run, respectively. Table 1 shows that material balance results for each of the 14 target organic compounds were generally well within the customer-approved 20-130% recovery (-30 to 80% mass closure), except 1,2-dibromoethane, 1,2,3-trichloropropane and pentachlorophenol where measured small quantities and large analytical losses are expected due to hydrolysis.

	Chemical	Mass Fed (ug)	Condensate	Concentrate	Sorbent Tube	Pump Traps	Off-gas Line Rinse	TOTAL	Mass Closure (%)
Volatiles	Benzene	55550	405	174*	49896	15*	0	50491	9.11
	4-methyl-2-pentanone (MIBK)	99928	2063*	1833*	66401	373*	0	70670	29.28
	Toluene	41386	326	235*	22736	10*	0	23307	43.68
	1,2-dibromoethane	2821	523	55*	9335	24*	0	9938	-252.25
	Chlorobenzene	45660	554	166*	17811	11*	0	18542	59.39
	1,2,3-trichloropropane	38471	2139*	6222*	0	34*	0	8395	78.18
Semi-volatiles	1,2,4-trichlorobenzene	22927*	1000	1508*	19599	130	0	22238	3.01
	Naphthalene	22021*	3712	683*	17024	448	0	21867	0.69
	Hexachlorobenzene	31574	22	22522*	0	0*	940	23483	25.62
	Pentachlorophenol	2332	0	4058	0	0*	0	4058	-74.04
	Pyrene	36140*	1699	20425*	0	28*	719	22870	36.72
	Bis(ethylhexyl)phthalate (BEHP)	40220	38	24618*	0	0	0	24656	38.70
	Benzo[a]pyrene (BaP)	56735*	0	31449*	0	0*	0	31449	44.57
Pest-icide	Aldrin	40285*	315	31449*	0	18*	0	31782	21.11
	Theoretical (each)	50518	*from SRTC Analytical Result						

Table 1. Overall Mass Balance for Each Target Organic Compound

Excellent evaporator performance was evidenced by non-detectable levels (<0.01-10 mg/L) of metals (except Si) and anions in the condensate when analyzed by induced-coupled plasma emission spectroscopy (ICP-ES) and anion ion chromatography (IC). When more sensitive analytical methods such as ICP-mass spectroscopy (ICP-MS) and pH were used, decontamination factors (DF = feed concentration/condensate concentration) of 10^5 were obtained for Cs and free hydroxide, respectively, confirming quality of performance.

The overall mass balance data indicate the feed was concentrated by a factor of 1.42 (Table 2), assuming ideal mixing and that the condensate is pure water. Combining this concentration factor with evaporator feed data, predicted species concentrations in the concentrate were calculated (Table 2). Given the estimated 10% random error in the analytical data, the actual and predicted concentrate metals and total solids concentrations match very well, being within 12% for the majority of analytes except Si and Zr. The good comparisons for the major and/or highly soluble nitrate, total hydroxide, formate and total organic carbon suggest analytical error which could account for up to 20% of the difference is not a major factor, although error in nitrite indicates the contrary. Overall, Table 2 indicates that the Envelope C simulant generally appears to behave like an ideal mixture in this concentration range,

Property/Analyte	Measured Feed (basis)		Measured Concentrate	Volume Additivity Concentrate Prediction	% Difference vs. Measured
Al (mg/L)	236	223	328	325	0.9
B (mg/L)	23	22	28.7	31.9	11.0
Ca (mg/L)	160	143	202	215	6.2
Cu (mg/L)	13	13	17.5	18.4	5.2
Fe (mg/L)	34	35	47.0	48.8	3.9
Mn (mg/L)	11	24	22.4	24.8	10.6
Mo (mg/L)		20	30.2	28.3	6.2
Na (mg/L)	125258	131057	184200	181460	1.5
Si (mg/L)	8	9.2	19.8	12.2	38.5
Sr (mg/L)	80	73	106	108	2.2
Zn (mg/L)	18	17	24.8	24.8	0.1
Zr (mg/L)	2	1.7	1.9	2.6	37.9
Chloride (mg/L)	1308	2477	1559	2680	71.9
Fluoride (mg/L)	2864	2455	3177	3766	18.5
Formate (mg/L)	7179	6636	10105	9780	3.2
Nitrate (mg/L)	145186	137961	188331	200456	6.4
Nitrite (mg/L)	38751	36145	42364	53023	25.2
Oxalate (mg/L)	1578	1306	1647	2042	24.0
Phosphate (mg/L)	1529	2349	2148	2745	27.8
Sulfate (mg/L)	5273	5297	5913	7483	26.6
Total OH^- (M)	1.395	1.421	2.059	1.994	3.2
Free OH^- (M)	0.553	0.561	0.987	0.789	20.1
Total Inorganic C (mg/L)	17512		15046	24795	64.8
Total Organic C (mg/L)	11070		17328	15674	9.5
Na (M)	5.58		8.01	7.90	1.5
Tot. Solids (wt%)	32.5		42.9	42.5	0.9
Total Mass Processed (g)	49585		37874	*Conc. Factor*	
Total Volume Processed (mL)	38860		27445	***1.42***	
Assumed Density (g/mL)	1.276		1.38	-----	

Table 2. Actual concentrate metal and anion concentrations versus prediction by volume additivity (ideal mixing behavior).

within measurement error. A similar analysis with concentrate samples taken after a “final” boildown to a “saturated” solution yielded the same results. Good comparison of simulant composition after steady state evaporation with expected Hanford waste concentrations was also found [Fiskum *et al.*, 2000]. During the “final” boildown of an aliquot of ~8.3 M Na concentrate, evaporator contents within a 1-2 minute period transitioned from a green semi-translucent liquid to a very viscous greenish-white gel at a calculated 10.1 M Na, corresponding to bulk saturation at 48.6 wt% total solids (94.6 g TS per 100 g water) at 50°C.

Modeling using the OLI Environmental Simulation Program (ESP) successfully predicted conditions suitable for steady state evaporation, predicted bulk saturation at >11 M Na, and generally correctly predicted the relative partitioning of each target organic between condensate, concentrate and off-gas (Table 3). As the model predicted a separate organic phase in all aqueous streams, secondary interactions between water and acetone (from the spiking solution) assisting dissolution of heavier semivolatiles were likely not taken into account, leading to the

		% of total feed						Condensor Vent (ug/g)
		EXPERIMENTAL DATA			OLI Model Prediction			
	Target Organic	Condensate	Concentrate	Off-gas	Condensate	Concentrate	Off-gas	
Volatile	Benzene	0.7	0.3*	*89.8*	0.4	0.0	99.5	*723*
	4-methyl-2-pentanone (MIBK)	2.1*	1.8*	*66.8*	11.9	0.2	87.9	*963*
	Toluene	0.8	0.6*	*55.0*	0.4	0.0	99.6	*330*
	1,2-dibromoethane	18.6	2.0*	*331.7*	3.5	0.1	96.4	*135*
	Chlorobenzene	1.2	0.4*	*39.0*	0.9	0.0	99.1	*258*
	1,2,3-trichloropropane	5.6*	16.2*	*0.1*	4.9	0.1	95.1	*0*
Semi-volatile	1,2,4-trichlorobenzene	4.4	6.6*	86.1	0.9	0.0	99.0	315
	Naphthalene	16.9	3.1*	79.3	2.8	0.0	97.2	274
	Hexachlorobenzene	*0.1*	71.3*	3.0	0.0	100.0	0.0	0
	Pentachlorophenol	0.0	174.0	0.0	77.8	19.4	2.8	0
	Pyrene	4.7	56.5*	2.1	88.3	6.0	5.6	0
	Bis(ethylhexyl)phthalate (BEHP)	*0.1*	61.2*	0.0	12.6	87.4	0.0	0
	Benzo(a)pyrene	0.0	55.4*	0.0	0.0	100.0	0.0	0
Pest-icide	Aldrin	0.8	78.1*	*0.0*	67.7	31.3	1.0	0

* from SRTC Analytical Result

Table 3. Experimental and OLI Model Predicted Organics Distribution as a Percentage of Each Species Fed.

exceptions pyrene, pentachlorophenol and Aldrin. By dividing total quantities of volatilized species detected in the off-gas samplers by total mass of air in-leaked (11.5 mL/min), target organic compound concentrations in the evaporator condensor vent stream as high as ~1000 ppm were found.

CONCLUSIONS

The following was found from the regulatory off-gas sampling from the evaporation of Hanford RPP Tank AN-107 (Envelope C) simulated waste spiked with 14 (1.03 ppm theoretical concentration) volatiles, semi-volatiles, and pesticide target compounds: 1) volatiles and light semi-volatiles (1,2,4-trichlorobenzene and naphthalene) almost completely exit through the evaporator condensor vent gas, 2) heavier semi-volatiles and pesticides appear to remain in the evaporator concentrate, 3) a very sharp bulk saturation transition occurs at about 10.1 M Na concentration (48.6 wt%, or 94.6 g total solids/100 g water), and 4) an OLI model can generally describe organics distribution from the evaporation of Hanford simulant.

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