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To: M. E. Stone, 999-W

From: A. S. Choi, 773-42A

Approval: ________________________________
Manager, Material Science & Engineering / SRNL

Technical Review: ________________________________
M. E. Stone, Material Science & Engineering / SRNL

REVIEW OF EXPERIMENTAL DECONTAMINATION FACTORS (DF) OF IODINE IN THE PILOT-SCALE LAW MELTER OFF-GAS SYSTEMS

1. Background

The Low Activity Waste (LAW) melters at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) will convert low-activity tank wastes containing high concentrations of sodium salts into glass for onsite disposal.[1] Much of the airborne particulates during the calcination/fusion of the feed solids will be removed by condensation and scrubbing of the melter exhaust in the Submerged Bed Scrubber (SBS) and Wet Electrostatic Precipitator (WESP) of the primary off-gas treatment system. The gases exiting the WESP enter a secondary off-gas treatment system, which includes a High-Efficiency Particulate Air (HEPA) filter, an activated carbon absorber, a Thermal Catalytic Oxidizer (TCO), a Selective Catalytic Reduction (SCR) unit, a caustic scrubber, and an exhauster. Much of the volatile organics and NO_x will be removed in the TCO and SCR, respectively. Under WTP Direct Feed LAW (DFLAW) configuration, the liquid effluents from the SBS and WESP will be collected and evaporated under vacuum with the evaporator concentrate recycled back to the LAW melter, while the evaporator condensate will be merged with the caustic scrubber solution and sent to the Effluent Treatment Facility (ETF).

Volatile radionuclides in the LAW feed that are major contributors to the long-term dose consequences for onsite disposal are ^{99}Tc and ^{129}I. The volatility of ^{99}Tc in the melter is known to depend strongly on the oxidizing potential of the melt pool (i.e., the more oxidizing the melt, the more volatile ^{99}Tc becomes).[2] How the volatility of ^{129}I is affected by the melter conditions, including the redox, is not as well understood due to insufficient data.[3] Additional melter testing at VSL has shown that the feed chemistry (e.g., simulant type and nitrate/sugar contents) and the melter operating variables (e.g., bubbler configuration and bubbling flux) have varying degrees of effects on the melter emissions, including iodine.[6] The goal of this task was to perform an in-depth assessment of the experimentally measured decontamination factors (DF) of iodine across the melter, SBS and WESP; however, the DFs for the secondary off-gas treatment system were not evaluated. The DF data reviewed came primarily from four reports issued by the Vitreous State Laboratory

(VSL) on the DM1200 and DM10 melter tests.[4-7] This report documents the results of the assessment and recommends more conservative DFs of iodine across the melter, SBS and WESP than those reported by VSL and used by Bechtel National Inc. (BNI).

2. DM1200 Test with Sub-Envelop A1 Feed

2.1. Simulant

The LAW Sub-Envelope Al simulant used in the test was based on composition data for Tank AN-105 supernatant derived from the Tank Farm Contractor Operation and Utilization Plan (TFCOUP) Rev. 3; the organics data in the TFCOUP were supplemented by other Hanford tank waste information.[4] The concentration of sodium in the simulant was increased by 2.56 % to account for the sodium added during pretreatment. The sulfate content in the simulant was also increased to account for the recycle of the evaporator concentrate to the melter assuming that 20% of sulfur in the feed is carried over to the off-gas system. The nominal composition of Sub-Envelope Al simulant was set at 8 molar (M) sodium and the resulting simulant was a solution of predominantly sodium salts of nitrite, nitrate, and carbonate, aluminum nitrate, and hydroxides of sodium and potassium.

The simulant was prepared by an off-site vendor and the as-received simulant in 55-gallon drums was unloaded into a mix tank where the required feed additives, including sugar, were added prior to use. The feed additives were selected on the basis of glass formulation studies, which included optimization with respect to sulfate incorporation, salt formation, and rheological testing.[4] Potassium iodide (KI) was added to the feed at VSL as a surrogate for iodine at the target iodine concentration of 0.1 wt% in the glass at 100% retention. The final blended feed was introduced into the melter in a batch mode that mimicked the operation of Air Displacement Slurry (ADS) pump, which is the present WTP baseline.

2.2. Melter and Off-Gas System

The DM1200 is a Joule-heated melter with Inconel 690 electrodes. The melt pool is 34" by 54" or 1.18 m^2 in surface area and is typically operated with a glass depth of about 29", which gives a glass inventory of 849 liters or approximately 2 metric tons.[4] Four top-entering bubblers were used (one in each corner) together with three bottom-electrode bubblers. The target glass temperature of 1150°C was successfully maintained for most of the glass pool during the test. The measured vapor space temperatures were between 400 - 500°C for the steady-state portions of the tests, which were slightly higher than the 400 - 450°C target. Visual observations of the cold cap indicated that melt pool coverage was nearly complete and, therefore, attempting to lower the vapor space temperature by increasing feeding or reducing bubbling would have resulted in excessive cold cap accumulation.[4]

The DM1200 off-gas treatment system included an SBS, WESP, HEPA filter, a hybrid catalytic unit (HCU), a packed-column caustic scrubber, and a High-Efficiency Mist Eliminator (HEME). The HCU includes a heater, TCO, and SCR. Note that the activated carbon absorber was not tested, while the HEME is not in the WTP baseline. Thus, the DM1200 off-gas treatment system was prototypical of the WTP LAW melter except for the missing activated carbon absorber and an extra HEME after the caustic scrubber. The off-gas treatment system was not run under the DFLAW configuration and thus did not include a recycle loop with a WTP-prototypical Effluent Management Facility (EMF) evaporator; the liquid effluents from the SBS and WESP were not recycled back to the melter.

2.3. Testing

The DM1200 was run from 2/27/02 to 3/20/02, including feed outages on 3/2/02 and 3/6/02 that lasted 2 and 12 days, respectively. The total test duration was 172 h, including time for water feeding (prior to start of feeding) and cold cap burn-off (after termination of feeding). The actual duration of slurry feeding was 158 h. The entire test can be divided into three segments. The first test segment was from the beginning of the test to the onset of 2-day feed outage, which occurred after 47.9 h into the test. There was a brief 1-hour feed outage about 23 h into the test, and the actual duration of slurry feeding for the first test segment was 42 h. The second test segment was from the resumption of feeding after the 2-day outage to the onset of 12-day feed outage, which occurred after 121.6 h into the test. The duration of slurry feeding was 69 h. The third and final test segment was from the resumption of feeding after the 12-day feed outage to the end of the test, and the duration of slurry feeding was 47 h. Additionally, the feed was spiked with three organic compounds (chlorobenzene, trichloroethylene, naphthalene) during test segments two and three for 41 h and 23 h, respectively.

2.4. Sampling and Analysis

2.4.1. *Melter Feed*

The elemental compositions of feed samples were analyzed by x-ray fluorescence (XRF) at VSL; each sample was melted in a crucible and the resulting glass was crushed before analysis. The XRF results for the major feed elements with oxide concentrations >3 wt% in glass (Al, Fe, Na, Si, Zn, Zr) were all within ±5% of the target composition.[4] It is noted that sodium was the only major element with a negative deviation at 2.15% below target, which could be due to its higher volatility during melting in a crucible. Elements in the intermediate oxide concentration range between 0.5 and 3 wt% (Ca, Cl, Mg, Ti) deviated from the target composition by greater margins. Among the minor elements (Cd, Cr, Cs, F, I, K, Ni, P, Se, S), highly volatile elements such as sulfur and halogens were under-represented in glass.[4] For example, the average concentration of iodine in the calcined feed was 0.01 wt% vs. 0.1 wt% target. Note that it is the target composition that represented the input to the mass balance calculations performed in this work, not the XRF results.

2.4.2. *Glass*

Glass samples were taken from each 55-gallon drum into which glass was discharged by an air-lift system.[4] Samples were crushed prior to analysis by XRF like the calcined feed samples.

2.4.3. *Off-Gas*

Off-gas sampling was performed primarily by Air-Tech Environmental. The sampling locations were: (1) the melter outlet in the Transition Line (TL), (2) the outlet of the SBS, (3) the outlet of the WESP, and (4) the outlet of the TCO. In addition, volatile organic sampling train (VOST) samples were taken at the inlet of the TCO and outlet of the corona (see Figure 1).[4] A summary of analytes and analytical methods used is reproduced in Table 1 from the Air-Tech report, which is attached to the VSL report.[4]

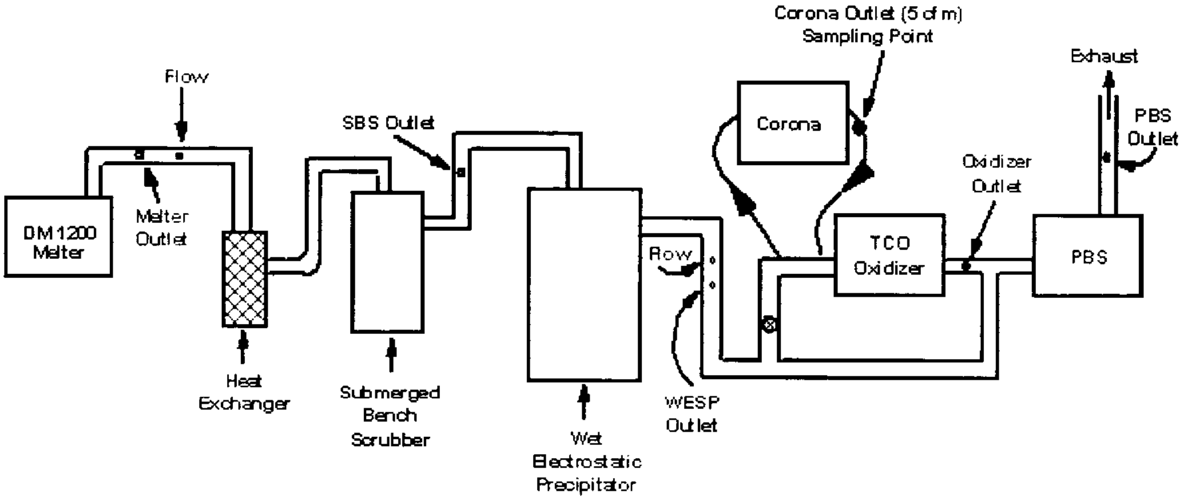

Figure 1. DM1200 Sampling Locations – Taken from Air-Tech Report.[4]

Table 1. Summary of Off-Gas Sampling and Analysis – Taken from Air-Tech Report.[4]

Parameter	**Analyte**	**Sampling Method**	**Analysis Method**
Total Particulate	Particulate matter	M-29 (Filter, Probe Rinse)	Gravimetric
Particle Size	Particulate matter	Impactor (8 filters)	Gravimetric
Halogens	Cl_2 / F_2 / I_2	Modified M-26 (Caustic Impingers)	Ion Chromatography Severn Trent Laboratories
Acidic Halogen Gases	HCl /HF /HI	Modified M-26 (Acidic Impingers)	Ion Chromatography Severn Trent Laboratories
Total Metals	See footnote 1, 2	M-29	ICPES / ICPMS
Metals (Particle size)	See footnote 1, 2	Impactor	Analysis performed by VSL
Semi-Volatile Organics	EPA Method 8270A list	EPA SW846 Method 0010	GC/MS
Dioxin/Furan/PCB	See Footnote 3	M-23	GC/MS
Volatile Organics	EPA SW 846 Method 0030	EPA SW 846 Method 0030	GC/MS
Anions from total particulate catch	See Footnote 2	M-29 (Filter)	Analysis performed by VSL

[1] Analytical methods were set at discretion of VSL. [2] Analytical targets were determined by VSL.
[3] All dioxin/furan (D/F) with chlorine at the 2, 3, 7 and 8 positions; polychlorinated biphenyls (PCBs).

A summary of off-gas sampling at the melter, SBS, WESP and TCO is given in Table 2 and Table 3 without and with organic spiking, respectively; each run number represents one continuous sampling event for a given sample type at a given sampling location. So, for each combination of sample type and sampling location there would be a new sequence of run numbers. Off-gas samples were taken using 40-CFR-60 Methods 3, 5, and 29 to determine particulate and certain gaseous fluxes. Twelve of these samples were taken with Teflon filters (M-5/M-29 TFE) to collect engineering data across the melter, SBS, and WESP. Six samples were taken with quartz filters (M-5/M-29 Quartz) to collect environmental data. The sampling trains used were identical, consisting of particulate filters and iced impingers containing acidic and basic solutions; the acidic impinger contained a 5% nitric acid/10% hydrogen peroxide solution, while the basic impinger contained a 0.2 N sodium hydroxide solution. The difference was in the method of analysis used on filters, rinses, and impinger solutions; M-5/M-29 TFE engineering samples were analyzed at VSL for all feed constituents, including iodine, while M-5/M-29 Quartz environmental samples were taken by Air-Tech using EPA Method SW-846-0060 and analyzed by Severn Trent Laboratories (STL) using Method SW-846-6010B for select metals.

Air-Tech also used a modified Method 26 (M-26A) containing two acidic (dilute sulfuric acid) and two basic (dilute sodium hydroxide) impingers and samples were analyzed by STL for volatile/semi-volatile organics and halogens. The intent was to capture acidic halide gases (HCl/HF/HI) in the acidic impinger and molecular halides ($Cl_2/F_2/I_2$) in the basic impinger, which would permit determination of total halides emission. However, maintaining the target pH particularly in the basic impinger solution throughout the sampling duration proved difficult as the high concentration of NO_x would continuously acidify the basic impinger solution, thus reducing its scrubbing efficiency. Furthermore, neither M-26 nor M-29 had been validated for iodine, and the analysis was performed under the assumption that iodine removal would be similar to those of other halogens. Three samples were taken each at the melter and TCO outlets. The first melter and TCO outlet samples were taken before the chlorine-rich organic spike, whereas the remaining two samples were taken while the feed was being spiked. The results of the analysis showed that as expected, chlorine concentrations increased when the feed was spiked with organics, while fluorine emissions seemed unaffected. Concentrations of molecular halogens were low except for I_2.

Also shown in Table 2 and Table 3 are percent isokinetic sampling data for each sampling run; per 40-CFR-60 Methods 1-5, 100% isokinetic sampling means taking a gas sample from the exhaust at the same velocity as the bulk air is flowing in the duct. A sampling run was considered to pass the QA test when the isokinetic range falls between 90 and 110%. Table 2 shows that Run 1 of the M-5/M-29 (TFE) sampling at the melter outlet failed the isokinetic test (as denoted by F/iso), while all three M-5/M-29 (TFE) sampling runs at the SBS outlet failed the QA test by wide margins. This is probably why the melter sampling data for Run 1 were excluded from the reported DFs in Table 6.2 of the VSL report.[4] By contrast, the non-isokinetic SBS sampling data were used to calculate the reported DFs in Table 6.3.

Table 2. Off-Gas Sampling Summary (No Organic Spike) – Taken from Air-Tech Report.[4]

Location	Run#	Sample Type	Date	Time	% Isokinetic	QA Test Pass/Fail
Melter	1	Dioxin/Furan/PCB	3/4/02	02:23-05:42	97	P
	1	Semi-VOST (SW 8270)	3/3/02	10:04-13:04	94	P
	1	M-5/M-29 (Quartz)	3/3/02	14:07-15:07	102	P
	2		3/18/02	14:55-15:55	105	P
	3		3/18/02	20:57-21:25	96	P
	1	M-5/M-29 (TFE)	3/1/02	12:21-12:26	85	F/iso
	2		3/3/02	17:45-17:47	110	P
	3		3/4/02	09:49-10:49	98	P
	4		3/18/02	17:17-17:27	106	P
	1	M-26A (Halogens)	3/3/02	19:19-20:19	95	P
	1	PSD	3/3/02	15:30-15:35	60	F/iso
	2		3/4/02	16:55-16:59	27	F/iso
	3		3/19/02	12:25-12:27	91	P
WESP	1A	M-5/M-29 (TFE)	3/2-3/4/02	14:10-00:42	104	P
	1B		3/4/02	01:10-13:59		
TCO	1	M-5/M-29 (Quartz)	3/3/02	06:10-07:10	108	P
	2		3/18/02	15:04-16:04	102	P
	3		3/18/02	20:45-21:45	106	P
SBS	1	M-5/M-29 (TFE)	3/1/02	12:33-12:53	74	F/iso
	2		3/3/02	16:10-16:37	132	F/iso
	3		3/18/02	17:56-18:06	77	F/iso

Table 3. Off-Gas Sampling Summary (Organic Spike) – Taken from Air-Tech Report.[4]

Location	Run#	Sample Type	Date	Time	% Isokinetic	QA Test Pass/Fail
Melter	2	Dioxin/Furan/PCB	3/4/02	09:57-10:57	94	P
	3		3/5/02	14:40-15:40	94	P
	4		3/19/02	20:35-21:35	81	F/iso
	2	Semi-VOST (SW 8270)	3/4/02	15:50-16:40	95	P
	3		3/5/02	03:29-04:29	95	P
	4		3/5/02	07:33-08:34	87	F/iso
	2	M-26A (Halogens)	3/4/02	18:31-19:30	95	P
	3		3/5/02	00:27-01:27	93	P
WESP	2A	M-5/M-29 (TFE)	3/4-3/5/02	21:35-09:41	98	P
	2B		3/5-3/5/02	10:25-22:42		
	2C		3/5-3/6/02	23:04-07:04		
TCO	1	M-26A (Halogens)	3/18/02	23:02-00:02	108	P
	2		3/19/02	17:03-18:03	101	P
	3		3/19/02	18:50-19:54	100	P
	1	Semi-VOST (SW 8270)	3/4/02	15:59-18:59	103	P
	2		3/5/02	06:45-09:45	104	P
	3		3/5/02	10:37-13:47	110	P
	1	Dioxin/Furan/PCB	3/4/02	21:06-00:06	101	P
	2		3/5/02	02:14-05:14	101	P
	3		3/5/02	14:22-17:22	104	P
	1	Carb-429	3/5/02	18:08-21:08	104	P
	2		3/6/02	01:48-03:51	96	P
	3		3/19/02	20:48-23:40	101	P

2.4.4. Liquid Effluents

One-liter samples were collected from the SBS and WESP sumps each time liquids were blown down and at the end of each test. Both dried filtered solids and filtrate underwent complete chemical analysis; direct current plasma emission spectroscopy (DCP) analysis for metals, atomic absorption (AA) for cesium, ion selective electrode (ISE) for ammonium, and ion chromatography for all other anions.[4] The only anions determined in the filtered solids were sulfate and iodide due to interference from the acids required to dissolve the filtered solids.

The sampling data showed that iodine was present in the dissolved solids (filtrate), and no detectable levels of iodine were found in the filtered solids. The concentrations of iodine in the WESP blow-down samples were in general about two orders of magnitude lower than those of the SBS blow-down samples. Furthermore, the pH of the SBS blow-down samples varied from 5 to 8 but remained mostly near 7. By contrast, the pH of the WESP blow-down samples was very acidic, ranging from 0.5 to 1.6. The cumulative WESP blow-down volume was 427 gallons vs. 2,937 gal for the SBS.

2.5. Assessment of DF Data

All condensed effluent and gaseous sample data were analyzed for the mass balance closure check in this section. The DF of element i is calculated as:

$$DF_i = \frac{\dot{m}_{i,in}}{\dot{m}_{i,out}} \tag{1}$$

where $\dot{m}_{i,in}$ and $\dot{m}_{i,out}$ are the mass flow rates of element i in and out of the melter, SBS or WESP. Each unit has two outlet streams, one condensed (glass or liquid) and one gaseous stream, and $\dot{m}_{i,out}$ refers to the latter. When either outlet stream data are deemed to have a high degree of uncertainty in terms of flow, concentration or both, they were estimated using the mass balance. Note that the reciprocal of DF is termed off-gas carryover, i.e., fraction of element i fed to the melter that ends up in the off-gas.

2.5.1. DF Across Melter

The iodine DF across the melter reported by VSL is 2.5 (Table 6.2 of Ref. 4); it was calculated by dividing the constant inlet concentration by the average of the three outlet concentrations ($\dot{m}_{I,out}$) from M-5/M-29 (TFE) Runs 2 through 4 in Table 2 (i.e., 1,586/633 = 2.5). By comparison, the mean of Ln(DF) was slightly higher at 2.57.[3] To check data variability, the DFs for each run were calculated using the reported sampling data and the results are given in Table 4. It is noted that the sampling duration of Run 2 was only 2 min, and its DF was the highest at 3.15, because the least amount of iodine was captured in the impinger solutions during the 2-min span, resulting in the lowest iodine emission rate. When the sampling duration was increased to 10 min in Run 4, the iodine emission rate was slightly higher, resulting in a lower DF of 2.83. Finally, when the sampling duration was increased to 60 min in Run 3, the DF fell to 1.9 as 66% more iodine was captured in the impingers. In terms of melter turnover, which is defined as the ratio of cumulative mass of calcined feed to the mass of glass in the melt pool, Run 3 had the highest turnover ratio of 1.2.

Table 4. Melter Emission and Iodine DF based on M-5/M-29 (TFE) Sampling Runs.

Sampling Run	2	3	4	Average
Sampling Duration (min)	2	60	10	24
$\dot{m}_{I,in}$ (mg/min)	1,586	1,586	1,586	1,586
$\dot{m}_{I,out}$ (mg/min)	503	836	561	633
DF	3.15	1.90	2.83	2.5
Melter Turnover	0.4	1.2	0.4	0.7

Not only the melter but TCO/SCR exhausts were also sampled using a modified Method 26 (M-26A) by Air-Tech and analyzed exclusively for halogens using IC by Severn Trent Laboratories (STL). Run 1 was without organic spike and Runs 2 and 3 were made with organic spike, as shown in Table 2 and Table 3, respectively. The M-26A sample results are summarized in Table 5. Also included are the total emission rates of iodine, calculated as the sum of iodine from HI and I_2. In Run 1, more iodine is shown to have exited the TCO/SCR than the melter, which seems unrealistic given that a considerable portion of iodine fed to the melter was found in the SBS blow-down samples, as shown in the next section. Thus, Run 1 could be an outlier. In Run 2 and 3, the iodine emission rates were about 50% or lower at the TCO/SCR outlet than at the melter outlet, which is the expected trend from the mass balance standpoint.

Table 5. Halides Emission Rates Based on M-26A Sampling Runs (mg/min).

Run	Organic Spike	Compound	Melter	TCO/SCR	Total I Melter	Total I TCO/SCR
1	No	HCl	< 12 .0	50.2		
		HF	10.1	< 17.4		
		HI	18.6	< 17.0		
		Cl_2	< 114	< 145		
		F_2	< 114	< 145		
		I_2	317	344	335	344
2	Yes	HCl	333	418		
		HF	34.8	< 22.9		
		HI	47.8	9.87		
		Cl_2	< 132	< 197		
		F_2	< 132	< 197		
		I_2	838	443	885	453
3	Yes	HCl	45.9	1413		
		HF	25.5	<24.5		
		HI	633	< 24.5		
		Cl_2	< 144	< 189		
		F_2	< 144	< 189		
		I_2	650	489	1,278	489

The calculated iodine DFs across the melter based on the M-26A sampling runs are shown in Table 6. The DF of Run 1 was 4.7, which is even higher than that of Run 1 in Table 4, but may be dismissed as an outlier, as described in the preceding paragraph. Incidentally, both M-5/M-29 (TFE) Run 2 and M-26A Run 1 samples were taken less than 2 h apart and both resulted in seemingly low emission rates, compared to other samples. It is also noted that the remaining M-26A samples resulted in lower DFs than the M-5/M-29 (TFE) Run 3 and 4 samples. It is stated that the M-26A had not been validated for iodine emission at the time of the DM1200 test,[4] which was attributed to the fact that the basic impingers used to absorb molecular halides became acidic due to high NO_x levels in the off-gas leading up to the SCR, thus rendering them less effective. In fact, both methods use a series of acidic and basic impingers to absorb halides and the potential for under-estimating the emission rate should apply to both. Thus, the calculated DFs in Table 4 and Table 6 should be interpreted as the upper bounds and the smallest (i.e., the most conservative) upper bound DF is 1.24 for Run 3.

Table 6. Melter Emission and Iodine DF based on M-26A Sampling Runs.

Sampling Run	1	2	3	Average
Sampling Duration (min)	60	60	60	60
$\dot{m}_{I,in}$ (mg/min)	1,586	1,586	1,586	1,586
$\dot{m}_{I,out}$ (mg/min)	335	885	1,278	833
DF	4.73	1.79	1.24	1.90
Melter Turnover	0.5	1.5	1.8	1.3

The other melter effluent is glass and the measured concentrations of iodine in glass samples are plotted in Figure 2 vs. cumulative mass of glass produced throughout the test. The concentration remained at 0.01 wt% initially until it reached its steady state value of 0.02 wt% at the cumulative glass mass of ~2,000 kg or one melter turnover. The lower initial concentration of iodine was expected because the melt pool was filled with the residue glass from the Sub-Envelop C1 test, whose feed contained much less alkali halides.

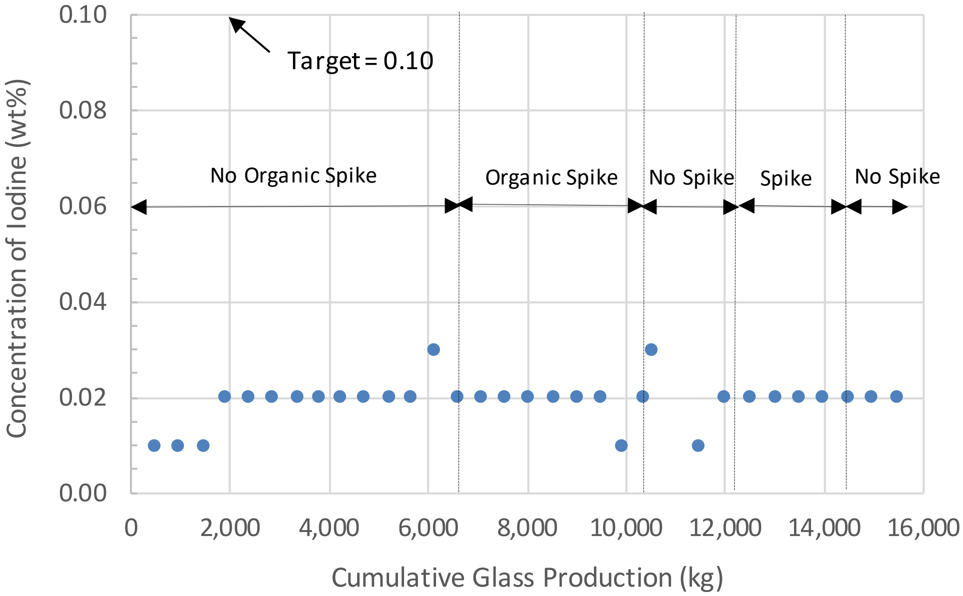

Figure 2. Iodine in Glass (wt%) vs. Cumulative Glass Production (kg).

It is noted that the iodine concentration of the initial DM1200 glass samples equaled that of the calcined melter feed samples at 0.01 wt% and yet the former increased further to 0.02 wt%. This is most likely due to the mass transfer resistances that are present in a melter but not in a crucible. First, volatile emissions are suppressed by the cold cap in a slurry-fed melter, which acts as a physical barrier for such emission. Second, volatile species must rise to the open melt surface for volatilization to occur, which is not the case for a crucible but very much an issue for large melters like DM1200, whose melt pool is constantly agitated using the bubblers to promote convective flows for increased glass production but at the cost of increased off-gas carryover including the volatile emissions.

Iodine was fed to the melter to target 0.1 wt% in glass when 100% of iodine fed is retained in glass. Thus, when the concentration of 0.02 wt% in glass is taken with 0.1 wt% target, the retention of iodine in glass becomes 20% and the remaining 80% should be in the off-gas carryover, assuming no buildup of iodine in the system, which was shown to be the case in the DM10;[5] 0.6% of iodine in the feed was found in the Film Cooler (FC) and Transition Line (TL) rinse solutions at the end of the test. Thus, the melter DF based on the glass data is calculated per Eq. (1) as: 1.0/0.8 = 1.25, which is essentially identical to the smallest upper bound DF of 1.24 for the M-26A Run 3 sample in Table 6.

Lastly, a constant iodine feed rate of 1,586 mg/min was used by VSL in all DF calculations, although the actual slurry feed rate varied from one test segment to the next. To see how large the variations were from the value used by VSL, the iodine feed rate was calculated for each test segment by multiplying the average slurry feed rate for that test segment by the calcination ratio and 0.1 wt% target iodine concentration on a calcine basis. The calcination ratio was calculated by dividing the mass of glass produced by the mass of slurry feed fed during each test segment. It turns out that the calculated iodine feed rates for all test segments varied within ±5% of 1,586 mg/min. Thus, all calculations were done in this work using the same constant iodine feed rate used by VSL.

2.5.2. *DF Across SBS*

The iodine DF across the SBS reported by VSL is 3.6 (Table 6.3 of Ref. 4); it is the average of M-5/M-29 (TFE) data for Runs 1 through 3 in Table 2 with no organic spike. To check data variability, the DFs for each run were calculated using the reported sampling data and they are shown to vary from 2.33 to 7.54 in Table 7. Besides the large variations, these results may not be the best representation of overall iodine DF for the following reasons. First, the SBS outlet concentrations ($\dot{m}_{I,out}$) for all runs were calculated using non-isokinetic sample data; deviations from the isokinetic sampling protocol were quite large. Second, Table 4 shows that the variations in the melter outlet concentrations were fairly large, ranging from 503 to 836 mg/L. Yet, the average of those melter outlet concentrations was used as the SBS inlet concentration for all runs and paired with varying SBS outlet concentrations. Third, there is a mismatch in the timing of melter and SBS sampling runs. For example, the sampling time for SBS Run 1 almost coincided with that of Melter Run 1 (see Table 2) but the latter was disqualified due to non-isokinetic sampling. Fourth, the concentration of iodine at the melter outlet (or the SBS inlet) was likely under-estimated due to the difficulties with maintaining the pH of basic impinger solutions at high NO_x concentrations, as discussed in Section 2.5.1.

Table 7. SBS Emission and Iodine DF based on M-5/M-29 (TFE) Sampling Runs.

Sampling Run	1	2	3	Average
Sampling Duration (min)	20	27	10	19
$\dot{m}_{I,in}$ (mg/min)	633	633	633	633
$\dot{m}_{I,out}$ (mg/min)	171	272	84	176
DF	3.70	2.33	7.54	3.6

Thus, it was clear that the DF must be estimated based on the SBS blow-down data, as was done for the melter DF using glass data. Figure 3 shows a plot of iodine concentration in the SBS blow-down samples vs. cumulative glass production. The iodine concentration initially increased steadily up to about 2,000 kg cumulative glass production, after which the rate of increase slowed down and appeared to level off at 450-500 mg/L. As the organic spike was terminated at ~10,000 kg cumulative glass production, the iodine concentration began to decrease below 400 mg/L and increased back to 400 mg/L as the organic spike was resumed. In essence, the overall trend appears to be similar to that of the glass samples in Figure 2. In order to estimate the fraction of iodine in the feed that was removed via the SBS liquid effluent, VSL assumed that a steady state (SS) iodine concentration in the SBS liquid was reached between 1,997 kg and 5,280 kg cumulative glass production, as shown in Figure 3, which fell entirely in the no-organic-spike period. As the organic spike began, available data became not only less numerous but scattered.

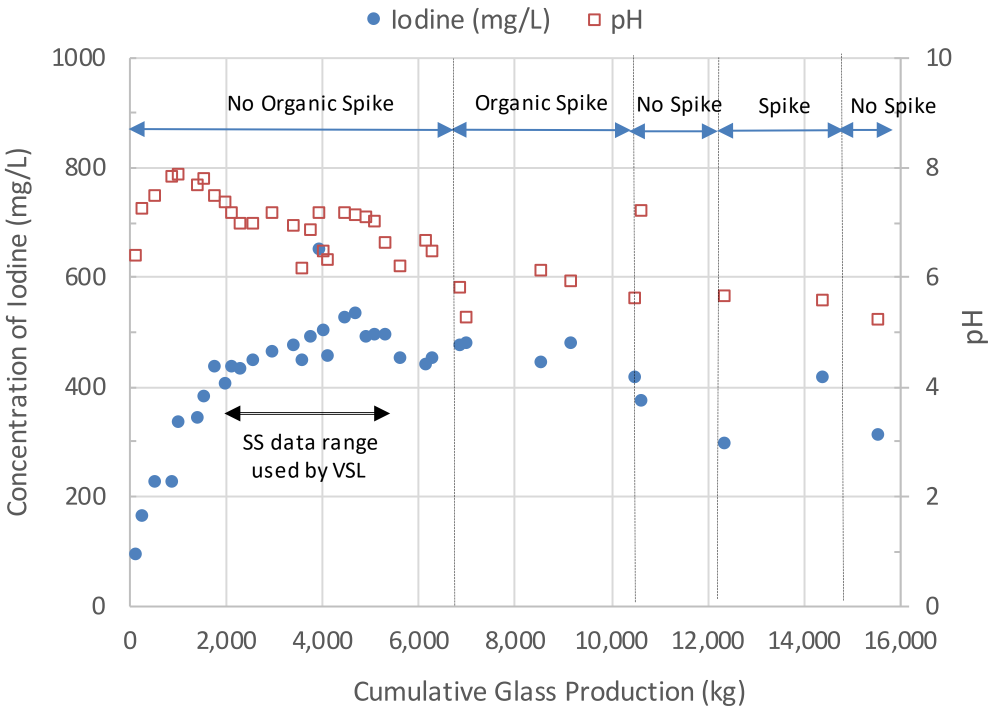

Figure 3. Iodine in SBS Blow-Down (mg/L) vs. Cumulative Glass Production (kg).

The amount of iodine removed via the SBS liquid effluent was calculated by multiplying the concentration of iodine in each blow-down sample by the volume of each blow-down, typically ~40 gallons, and summing them up over the steady state period. VSL determined that 39.36% of iodine in the feed ended up in the SBS effluent, compared to 37.3% estimated in this study. Since the difference was ~5%, it was decided to continue the calculation using the VSL value of 39.36%. Since it was already determined that 20% of iodine fed would be retained in glass, the mass balance shows that:

$$\begin{aligned} \textit{Iodine in SBS exhaust} &= 1.0 - 0.2 - 0.3936 \\ &= 0.4064 \text{ or } 40.64\% \textit{ of iodine in the feed} \end{aligned} \tag{2}$$

In terms of instantaneous flow rate, this is equivalent to: (0.4064) (1,586 mg/min) = 644.55 mg/min. Note that this is 3.7X larger than the average $\dot{m}_{I,out}$ of M-5/M-29 (TFE) Run 1-3 in Table 7. Furthermore, the average flow rate of iodine in the melter exhaust or SBS inlet was: (0.8) (1,586 mg/min) = 1,268.8 mg/min. Thus, the iodine DF across the SBS is calculated as: 1,268.8 / 644.55 = 1.97 ≈ 2.0.

2.5.3. DF Across WESP

The iodine DF across the WESP reported by VSL is 15.3 (Table 6.4 of Ref. 4); it is the average of M-5/M-29 (TFE) Run 1A/1B (no organic spike) and 2A/2B/2C (organic spike), as shown in Table 2 and Table 3, respectively. To check data variability, the average DFs for Run 1 and 2 were calculated using the reported sampling data and the results are presented in Table 8. Besides the large variability, the calculated DFs are much higher than those of the melter and SBS, which is the result of very low iodine emission rates at the WESP exit ($\dot{m}_{I,out}$). For example, the measured iodine emission rates during Run 1 averaged 5.14 mg/min or ~0.3% of iodine fed, which is equivalent to 1/125th of the emission rate in the SBS exhaust estimated in Eq. (2). Thus, much of the incoming iodine should have been captured in the WESP liquid effluent. However, VSL estimated that only 0.06% of iodine in the feed was in the WESP liquid effluent,[4] which means that the combined iodine emission rate in the WESP exhaust and liquid effluent is less than 0.4% of iodine fed to the melter vs. 40.64% estimated in Eq. (2) to be in the WESP inlet stream. This large gap in mass balance is examined further next.

Table 8. WESP Emission and Iodine DF based on M-5/M-29 (TFE) Sampling Runs.

Sampling Run	1A/1B	2A/2B/2C	Average
Sampling Duration (h)	23.6	10.8	17.2
$\dot{m}_{I,in}$ (mg/min)	175	175	175
$\dot{m}_{I,out}$ (mg/min)	5.14	17.77	11.46
DF	34.3	9.8	15.3

Figure 4 is a plot of iodine concentration (mg/L) in the WESP blow-down samples vs. cumulative glass production (kg), and the following stood out. First, the WESP liquid effluent was strongly acidic. Although not shown, the pH fell to as low as 0.5 during the test,[4] which means that the WESP liquid effluent was essentially a 0.1M nitric-acid solution. Second, the concentration of iodine in the blow-down sample remained low (less than 8 mg/L). Third, only four samples contained detectable levels of iodine, which is probably why the total iodine in the WESP liquid effluent was estimated to be so low. However, the uncertainty associated with the estimated 0.06% removal of iodine in the WESP liquid effluent is expected to be high because too few data points were available at such low concentrations.

Moreover, with 0.06% of iodine fed in the WESP liquid effluent, the WESP exhaust would contain: 0.4064 – 0.0006 = 0.4058 or 40.58% of iodine fed, which is equivalent to an instantaneous iodine emission rate of: (0.4058) (1,586 mg/min) = 643.6 mg/min. This is 56X higher than the average rate of 11.46 mg/min for the M-5/M-29 (TFE) samples in Table 8. This shows how severely the iodine emission rate could potentially be under-estimated using the M-5/M-29 (TFE) data under the conditions of the WESP exhaust, i.e., high NO_x concentrations. All this seems to indicate that available data taken directly off the WESP effluents may not be suitable for estimating the DF.

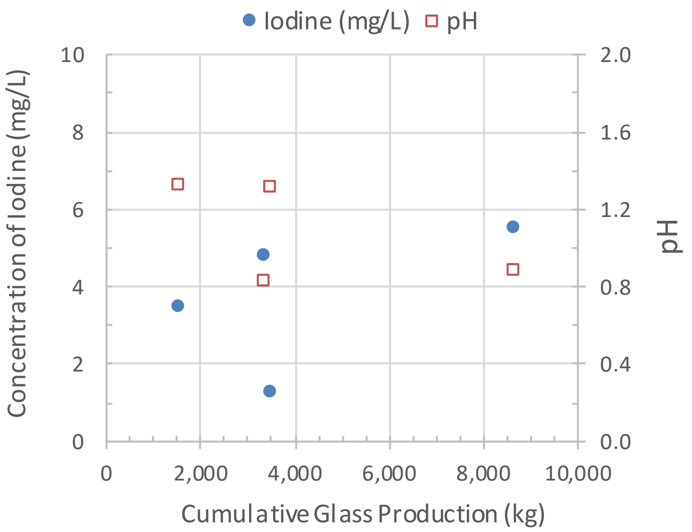

Figure 4. Iodine in WESP Blow-Down (mg/L) vs. Cumulative Glass Production (kg).

However, there are still M-26A (Halogen) data available in Table 5, which were taken at the TCO/SCR outlet. If we assume that little or no iodine is removed in the TCO/SCR, while the organics are destroyed and NO_x reduced, the measured emission rate of iodine at the TCO/SCR outlet could be taken as that at the WESP outlet. This is because the extent of under-estimating the iodine emission at the TCO/SCR outlet is likely to be minimal since the NO_x level should be quite low. Thus, it seems reasonable to take the measured iodine emission rate at the TCO/SCR outlet to be that at the WESP outlet. The iodine emission rates at the TCO/SCR outlet are re-summarized in Table 9 in terms of both instantaneous flow rates and percent iodine fed to the melter (by dividing instantaneous flow rates by 1,586 mg/min feed rate).

Table 9. Iodine Emission Rates at the TCO/SCR Outlet Based on M-26A Sampling Runs.

Run	Organic Spike	Iodine Emission	
		(mg/min)	(% Fed)
1	No	344	21.4
2	Yes	453	28.6
3	Yes	489	30.8

By taking the iodine emission rates in Table 9 as those of the WESP exhaust, the loss of iodine via the WESP liquid effluent is calculated by subtracting the sum of iodine in glass, SBS liquid effluent, and WESP exhaust from the total iodine in the melter feed:

$$\begin{aligned} \textit{Run 1:}\quad \textit{Iodine in WESP Effluent} &= 1.0 - 0.2 - 0.3936 - 0.214 \\ &= 0.192 \textit{ or } 19.2\% \textit{ of iodine fed} \end{aligned} \qquad (3)$$

It is noted that the mass balance calculations can be done using either instantaneous flow rates in mg/min or percent of iodine fed, and calculations were done here using percent of iodine fed. The inflow of iodine to the WESP is the same as the outflow of iodine in the SBS exhaust, and the latter was calculated in Eq. (2) to be 0.406 or 40.6% of iodine fed (after rounding to three decimal places). It is noted that the inflow of iodine to the WESP would be the same for all runs since the iodine in the glass and SBS liquid effluent were calculated using the sampling data averaged over the entire duration of the test. Thus, the iodine DF across the WESP for Run 1 is calculated as:

$$\begin{aligned} \textit{Run 1:}\quad \textit{WESP DF} &= 0.406/0.214 \\ &= 1.9 \end{aligned} \tag{4}$$

The mass balance calculations of Eq. (3) and (4) were repeated for Runs 2 and 3, and the results are summarized in Table 10. The calculated DFs ranged from 1.32 to 1.90 and the average DF for all runs was 1.51, which is an order of magnitude lower than the VSL-reported value of 15.3 based on the M-5/M-29 (TFE) sample data. These results and those in Table 6 seem to suggest that M-26A may be a more suitable sampling method for detecting halogens than M-5/M-29 (TFE) at high NO_x concentrations. Table 10 also shows that on average 13.8% of iodine in the feed ended up in the WESP liquid effluent, which is 230X higher than the VSL-reported value of 0.06%.[4]

Table 10. Iodine Partitioning Across the WESP (Percent of Iodine in the Feed) and Calculated DFs.

Run	Inflow	Liquid Effluent	Exhaust	DF
	(% Fed)	(% Fed)	(% Fed)	
1	40.6	19.2	21.4	1.90
2	40.6	12.4	28.6	1.42
3	40.6	9.8	30.8	1.32
Average	40.6	13.8	26.9	1.51

3. DM1200 Tests with Various Simulants

A total of eight HLW and LAW simulants, including LAW Sub-Envelop A1, were fed to DM1200 from 2001 to 2004, while varying the nitrate and sugar contents, total solids, bubbler configuration, and bubbling rate.[6] One of the objectives of these tests was to determine if off-gas emission would be affected by any of those variables. It turns out that off-gas emission (or carryover) increased with increasing nitrate/sugar contents and bubbling rate and with decreasing total solids (or increasing water content). As described earlier, all melter exhaust samples were taken in the Transition Line (TL) using the M-5/M-29 (TFE) sampling train for the sampling duration of approximately 1 h. A summary of elemental emission results is given in Table 5.1 of Ref. 6 and reproduced in Table 11 in terms of distribution of melter DF for iodine only. With no information on the feed chemistry, bubbling rate, etc. that prevailed during each sampling event included, the intent of Table 11 is to show the overall and waste-specific iodine DF trends, assuming that the effects of those parameters on the DF were still within experimental and analytical uncertainties.

For example, the measured iodine DF was less than 1.25 in 8 out of 24 HLW cases or 33.3%, while 17 HLW cases or 70.8% had DFs less than 2.0. By contrast, the measured DF of iodine was less than 1.25 in 1 out of 7 LAW cases or 14.3%, while 4 LAW cases or 57.1% had DFs less than 2.0. The overall trend of HLW DFs being lower than LAW DFs may be explained in part by the fact that the HLW feeds contain less nitrate than the LAW feeds and thus the off-gas should contain less NO_x, which means that the extent of under-estimating iodine emission would be less with the HLW feeds. It was shown earlier in this memo how to perform a mass balance not only to check the integrity of available data but to estimate missing data. No matching glass data were available to check the integrity of as-reported off-gas emission data in Ref. 6.

Table 11. Distribution of Iodine DF Across the Melter Based on M-5/M-29 (TFE) Sampling.[6]

Simulant	Number of Data Points for Test	DF					
		1.0 - 1.25	1.25<– 1.5	1.5<- 2.0	2.0<– 3.0	3.0<– 4.0	4.0<
		Number of Data Points for Indicated DF Range					
HLW AZ-101	17	6	1	3	2	1	4
HLW AZ-102	1	1	0	0	0	0	0
HLW C-106/AY-102	5	1	1	3	0	0	0
HLW C-104/AY-101	1	0	1	0	0	0	0
LAW C	4	1	1	2	0	0	0
LAW C1	1	0	0	0	1	0	0
LAW A1	1	0	0	0	1	0	0
LAW B1	1	0	0	0	1	0	0
Total HLW	24	8	3	6	2	1	4
Total LAW	7	1	1	2	3	0	0
Total HLW/LAW	31	9	4	8	5	1	4

It is noted that a total of 37 DF data points of iodine from the scaled LAW melters ranging from DM100 to DM3300 were analyzed in a 2012 study in terms of natural logarithm of DF or Ln(DF) and it was concluded that the dataset was still insufficient to adequately describe the compositional effects on Ln(DF) of iodine;[3] under normal distributions, the dataset could be represented by the mean DF of 2.4 with a standard deviation (SD) of 2.0.[3]

4. 2018 DM10 Test with Recycle

A Direct Feed LAW (DFLAW) melter test was conducted at VSL using the DM10 melter from 4/18/18 to 4/26/18 for a total duration of 200 h.[5] The main goal of the 2018 DM10 test was to demonstrate the DFLAW melter operation at the WTP with an off-gas condensate recycle loop consisting of an Effluent Management Facility (EMF) prototypic vacuum evaporator to concentrate the SBS/WESP liquid effluents; it was the evaporator concentrate that was recycled back to the melter.

4.1. Simulant

The LAW simulant used was prepared based on the AP-107 supernatant composition from the Best Basis Inventory (BBI) and the WRPS flowsheet model projections of the initial DFLAW waste feed composition.[5] The simulant was prepared and pre-mixed with the glass-forming chemicals at the vendor's facility before being shipped to VSL in 55-gallon drums. The as-received feed was blended with the recycle in batches – i.e., the evaporator concentrate collected during the processing of a given batch was combined with the next batch of as-received feed every 12 hours. The resulting batch including the recycle was further constituted with additional chemicals, including iodine (added as KI), as shown in Table 12.[5] Thus, it is important to note that the DM10 was actually run with no continuous recycle as each batch of feed was pre-mixed with the recycle from the previous batch. No recycle was added to the first batch (Batch 1), as the SBS/WESP liquid effluents had not been fully processed through the recycle loop yet. Thus, the presence of off-gas recycle in Batch 1 was simulated by adding larger quantities of key recycle species such as rhenium, iodine, chlorine, and sulfur, as shown in Table 12 and the amounts to be added were determined based on the recycle factors derived in previous VSL tests.[5] The final adjusted feed was introduced into the melter in a manner that mimicked the operation of ADS pump.

Table 12. DM10 Feed Batch Blending Ratios.

Feed Batch Number	1	2 to 15	16
Start of Feeding	4/18/2018 11:00 AM	4/19/2018 3:00 AM	4/26/2018 4:35 AM
As-Received Feed (kg)	42.6	28.3	33.1
Off-Gas Recycle (kg)	0	14.4	16.8
Boric Acid (kg)	5.759	3.759	4.39
Li_2CO_3 (g)	704	469	548
Perrhenic Acid (50 wt % Re) (g)	42.38	18.01	21.03
KI (g)	63.5	27.58	32.21
NaCl (g)	81	0	0
Na_2SO_4 (g)	6	0	0
Sugar (g)	1876	1244	1453
DI water (kg)	21.6	0	0

In order to confirm if the reported target iodine concentration of 0.1 wt% in glass at 100% attainment indeed included the recycled iodine, the entire feed preparation steps described in Ref. 5, starting from the AP-107 supernatant simulant recipe to the addition of glass forming chemicals, off-gas recycle, and trim chemicals shown in Table 12 were re-constructed in an Excel spreadsheet during this review. To do so, the available analytical data for the evaporator concentrate samples were charge-reconciled using the spreadsheet and the resulting recycle composition was blended with the next batch of as-received feed.

It turns out that the calculated maximum theoretical concentration of iodine in the Batch 1 glass was higher than the VSL target at 0.162 wt%, while that of the Batch 2 glass was also higher at 0.14 wt%. When the recycle was excluded, the maximum theoretical concentration of iodine in the Batch 2 glass was calculated to be 0.106 wt%, which is essentially identical to the VSL target. This suggests that the VSL target iodine concentration of 0.1 wt% did not include the recycled iodine and thus was not representative of the actual iodine content in each batch. Furthermore, since the batch blending ratios are identical for Batches 2 to 15, the maximum iodine concentration of 0.14 wt% calculated for Batch 2 can be considered representative of practically all batches processed throughout the test, which indicates that the iodine DF across the DM10 should be based on the maximum concentration of 0.14 wt% in lieu of the reported VSL target of 0.1 wt%.

4.2. Melter Off-Gas System

The DM10 is a ceramic refractory-lined melter with one bubbler inserted near the center of the melt surface and two Inconel 690 plate electrodes for joule-heating. It has a melt surface area of 0.021 m^2 and holds approximately 8 kg of glass.[5] The DM10 vapor space was kept under slight vacuum between -1 and -2 inches of water column ("H_2O) using an induced fan, compared to nominally at -5" H_2O during the DM1200 test, which means that the scaled rate of air infiltration into the DM10 vapor space would be less than that into the DM1200 vapor space under comparable tightness of the vapor spaces. Measured glass temperatures at two and four inches from the melter floor were 1154 and 1148°C, respectively, indicating that the target glass temperature of 1150°C was achieved. Measured average vapor space temperatures were 580 and 613°C, as measured by the exposed thermocouple and in the thermowell, respectively, indicating that the cold cap covered nearly 100% of the melt pool surface for much of the test duration.[5]

The DM10 is typically run with a dry off-gas system consisting of a filter only; however, it was fitted with a wet off-gas system for this test, which included the SBS, WESP, and a HEPA filter but without a carbon bed, TCO, SCR and caustic scrubber. The SBS and WESP used are described as suitably scaled,[5] but their designs did not appear to be prototypic of the WTP baseline. The liquid effluents from the SBS and WESP were combined and sent to a vacuum evaporator in the recycle loop, before the concentrated bottom was recycled back to the melter. The vacuum evaporator was prototypic of the WTP baseline except that it was designed to minimize the volume of liquid in the sump in order to decrease the time necessary for the system to reach steady state.[5]

4.3. Testing

A total of 16 feed batches were processed during the 200-h test from 4/18/2018 to 4/26/2018, while collecting a large quantity of glass and off-gas effluent samples throughout the DM10 off-gas system. The objectives were to determine the retention of rhenium (added as a surrogate for technetium) and other volatiles, including iodine, in glass produced from the AP-107 simulant feeds in a prototypical melter off-gas system with recycle of the off-gas effluents back to the melter. The evaporator concentrate was recycled by batch-blending it with the feed on a 12-h cycle. The test produced 345 kg of glass from nearly 800 kg of feed. The concentrations of rhenium, sulfur, chlorine and iodine were measured in the glass product at steady state in terms of percent of calcined feed. A material balance could be performed using the amounts of glass discharged and feed processed, the proportion of recycled solutions in melter feed, and the target glass composition.

4.4. Sampling and Analysis

4.4.1. Melter Feed

The elemental compositions of feed samples were analyzed by XRF or by acid digestion followed by direct current plasma-atomic emission spectroscopy (DCP-AES) on the resulting solution at VSL. Feed samples were placed into platinum/gold crucibles that were transferred into a programmed furnace for drying and fusion to form a glass. The glass samples produced from this fusion were ground to less than 200 mesh and sealed in 20-ml vials prior to analysis.

4.4.2. Glass

Glass samples were also crushed prior to the elemental analysis by XRF except for boron and lithium. Boron and lithium concentrations were determined by total acid dissolution of ground glass samples in HF/HNO_3 and subjecting the resulting solutions to DCP-AES analysis.[5]

4.4.3. Off-Gas

Melter exhaust was sampled twice, once near the beginning and again near the end of the test using the same EPA isokinetic sampling train used during the DM1200 test. The first set of melter exhaust samples taken was determined to be within the isokinetic sampling limits of 90-110% but not the second set due to anomalous instrument readouts. The WESP exhaust was sampled four times, twice near the beginning (once during the deluge and once during nominal operations) and twice near the end of the test (once during the deluge and once during nominal operations). The filtered solids and impinger solutions were analyzed using the same analytical methods used for the DM1200 samples. Off-gas was also sampled downstream of the HEPA filter for continuous monitoring of NO, NO_2, N_2O, CO, and SO_2 by Fourier Transform Infrared Spectroscopy (FTIR).

4.4.4. Liquid Effluents

Samples were collected from the SBS, WESP, and evaporator sumps each day of testing as well as at the end of the test. Samples were subjected to complete chemical analysis, which included pH, suspended solids, ion chromatography for anions, and ion selective electrode for ammonia. Filtered solids were dissolved in HF/HNO_3, followed by DCP-AES and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) analysis, while the filtrate solution was analyzed by IC, DCP-AES, and ICP-MS.

4.5. Assessment of DF Data

All condensed effluent and gaseous sample data were analyzed for the mass balance closure check in this section. When either outlet stream data are deemed to have a high degree of uncertainty in terms of flow, concentration or both, they were estimated using the mass balance.

4.5.1. DF Across Melter

The iodine DF reported by VSL for the first melter exhaust sample is 0.66 (Table 6.1 of Ref. 5). The DF less than 1 indicates that the iodine emission rate in the melter exhaust was higher than the inflow of iodine in the feed. This occurred because recycled iodine in the evaporator concentrate was not counted as part of the feed; a mass/charge balance analysis performed in this study showed that the recycled iodine amounted to 40% of the total iodine in Batch 2 feed, as discussed in Section 4.1. As in the DM1200 test, the iodine concentration in glass was shown to fluctuate between 0.01 and 0.03 wt%, and VSL estimated 0.0164 wt% to be the steady state concentration of iodine. This is equivalent to 11.7% retention of iodine in glass (= 0.0164/0.14) based on the revised iodine concentration of 0.14 wt% at 100% retention, including the recycle. Thus, the iodine DF across the DM10 is calculated using the mass balance as:

$$\begin{aligned} \text{Melter DF} &= 1.0 / (1.0 - 0.117) \text{ or equivalently} \\ &= 0.14 / (0.14 - 0.0164) \qquad (5) \\ &= 1.13 \end{aligned}$$

This calculated DF of DM10 is lower than that of DM1200 (i.e., 1.13 vs. 1.25), which may be attributed to the smaller DM10 melt pool and thus a smaller overall mass transfer resistance for iodine to migrate to the open melt surface than in the DM1200, as discussed in Section 2.5.1.

A mass balance analysis was performed by VSL by comparing the total amount of iodine fed into the melter to the total amounts measured in the discharged glass and throughout the off-gas system and associated system components and effluents at the end of the test. The results showed that iodine was distributed primarily between the glass at 16.4%, the WESP exhaust at 31.8%, and the evaporator condensate at 20.3%. It is noted that these effluent streams were not recycled back to the melter and thus represented the outlets for the overall mass balance envelop. Thus, the sum of all iodine in those effluents should be equal or close to the total iodine fed. However, the total iodine recovery, including the iodine in various sumps and rinse solutions, was only 77.8%,[5] and much of the shortfall likely resulted from the under-estimated iodine concentration in the WESP exhaust due to the potential inadequacy of the M-5/M-29 sampling in capturing iodine from highly acidic off-gas, as discussed in Section 2.5.3.

4.5.2. DF Across SBS and WESP

The DF of iodine across the SBS and WESP could not be estimated separately because:

- The iodine emission in the SBS exhaust was not monitored, i.e., no off-gas sampling.
- The SBS and WESP liquid effluents were not sampled until they were blended together in the Containment Tank.

Thus, the combined DF across the SBS and WESP is calculated using the mass balance as follows:

$$\begin{aligned} \text{Iodine at SBS Inlet} &= 1.0 \text{ (total iodine fed including recycle)} - 0.117 \text{ (iodine in glass)} \\ &\quad - (0.006)\,(0.1/0.14) \text{ (iodine in FC and TL rinses)} \qquad (6) \\ &= 0.88 \end{aligned}$$

where the reported 0.6% of iodine fed in the FC and TL rinse solutions was adjusted down by the VSL target-to-actual maximum iodine ratio in glass. The combined iodine DF across the SBS+WESP is calculated as:

$$\begin{aligned} \mathit{SBS{+}WESP\ DF} &= 0.88\ (\text{iodine at SBS inlet}) / [(0.318)\ (0.1/0.14)]\ (\text{iodine in WESP exhaust}) \\ &= 3.87 \end{aligned} \tag{7}$$

where the reported 31.8% of iodine fed in the WESP exhaust was adjusted down by the ratio of VSL target iodine to the actual maximum iodine ratio in glass. However, the calculated DF of 3.87 across the SBS+WESP is likely high for the reasons described above. If we assume that the 22.2% shortfall in the total iodine recovery (i.e., 100–77.8 = 22.2) is attributed to the under-estimated iodine in the WESP exhaust, the revised iodine in the WESP exhaust would be 54% (= 31.8+22.2) of iodine fed and the DF across the SBS+WESP is re-calculated as:

$$\begin{aligned} \mathit{SBS{+}WESP\ DF} &= 0.88\ (\text{iodine at SBS inlet}) / [(0.54)\ (0.1/0.14)]\ (\text{iodine in WESP exhaust}) \\ &= 2.28 \end{aligned} \tag{8}$$

The calculated iodine DFs across the DM10 and SBS+WESP are compared to those reported by VSL in Table 13. The reported overall DFs by VSL across the DM10+SBS+WESP are based on the average DFs across the WESP during nominal and deluge operations.

Table 13. Iodine DF Across the Melter and SBS+WESP During 2018 DM10 Test with Recycle.

	DM10	SBS+WESP	Overall	Isokinetic
VSL (4/19/2018) – Ref. 5	0.66[1]	-	5.6	102.65%
VSL (4/25/2018) – Ref. 5	0.52[1]	-	2.7	133.6%
This Work (reported WESP exhaust)	1.13[2]	3.87	4.37	-
This Work (adjusted WESP exhaust)	1.13[2]	2.28	2.58	-

[1] Excluding iodine in the recycle. [2] Including iodine in the recycle.

5. 2019 DM10 Test without Recycle

Another DFLAW melter test was conducted at VSL in 2019 using the same DM10 and off-gas system setup and the same AP-107 supernatant simulant used in the 2018 DM10 test.[7] The main goal of the 2019 DM10 test was to see if the retention of iodine in glass would be influenced by the speciation of iodine in the LAW feed. The feed was spiked with three different iodine forms; (1) iodide (I^-) added as KI, (2) iodate (IO_3^-) added as KIO_3, and (3) organic iodide added as CH_3I. DM10 was fed with each iodine-spiked feed for 36 h, and the entire test duration was divided into three equal segments. Some of the key differences between the 2018 and 2019 DM10 tests were as follows:[7]

- The recycle loop consisting of the EMF-prototypic vacuum evaporator was decoupled from the DM10 melter and off-gas system during the 2019 test - the evaporator test was run subsequent to completion of the DM10 test. By comparison, the evaporator concentrate was recycled back to the melter in batches during the 2018 test.
- The target concentration of iodine in glass for the 2019 test was set at 0.2 wt% at 100% retention vs. 0.14 wt% (or 0.1 wt% excluding the recycle) during the 2018 test.

- Isokinetic off-gas sampling was no longer pursued during the 2019 test. The partitioning of iodine in various effluents was estimated based on the mass balance of measured iodine concentrations in condensed samples, e.g., feed, glass and liquid effluents from the SBS and WESP. By contrast, isokinetic sampling results of the melter and WESP exhausts were used to estimate the partitioning of iodine during the 2018 test.

- The liquid effluents from the SBS and WESP were combined and adjusted to pH = 12 by adding 50% NaOH during the 2019 test prior to the evaporator test. By comparison, no caustic was added to the SBS/WESP liquid effluents during the 2018 test, and their pH ranged from 5.5 to 7.8.

- The WTP caustic scrubber was simulated during the 2019 test using a modified 40-CFR-60 Method 26 (Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources: Non-Isokinetic Method). A carbonate/bicarbonate buffer was used to mimic the caustic scrubber solution at pH = 9.5 followed by an impinger with a 2 M NaOH solution to capture any remaining iodine. This method was applied downstream of the HEPA filter and the resulting solutions were analyzed for total iodine. By contrast, the WTP caustic scrubber was not simulated during the 2018 test.

5.1. Sampling Results

Since both 2018 and 2019 DM10 tests were run using the same DM10 platform and the same simulant, only the key differences in the feed, glass, and liquid effluent sampling results are highlighted next.

5.1.1. Melter Feed

XRF and DCP results of the three 2019 DM10 feed samples showed that the concentration of iodine in the calcined feed averaged 0.007 wt% vs. 0.2 wt% target. Although VSL did not specify whether each feed sample represented each of the three forms of iodine added, it does not appear to be the case because the reported iodine concentrations did not vary much, ranging from 0.07 to 0.08 wt%, and the calcined feed spiked with CH_3I is expected to contain little iodine because of its high volatility. These 2019 DM10 feed sample results are compared to those of the 2018 test in Table 14. It is noted that VSL estimated that the steady state iodine concentration in glass during the 2018 test was 0.0164 wt%, which is clearly higher than that of the feed sample taken at the end of test, as expected.

Table 14. Measured Iodine Concentrations in Calcined DM10 Feed Samples.

DM10 Test	Sampling Time	Target (wt%)	Average (wt%)
2018	Beginning of Test	0.164[1]	0.02
	End of Test	0.14[1]	<0.01
2019	During Test	0.20	0.007[2]

[1] Includes iodine in the recycle. [2] Average of three samples.

5.1.2. Glass

Glass discharge from the DM10 was sampled throughout the test and analyzed by XRF. The average iodine concentrations in glass for each test segment are compared in Table 15 to that of the 2018 DM10 glass. Although the 2018 DM10 test is identified as a DFLAW melter run with recycle, it was actually run with no recycle on a batch-by-batch basis like in the 2019 test, because the entire volume of recycle collected during the processing of a given batch was pre-mixed with the next batch of feed prior to being fed to DM10. Based on this reasoning, the retention of iodine in glass when iodine was fed as KI was low at 6% during the 2018 test compared to 11.7% during the 2018 test. When iodine was fed as KIO_3, the retention of iodine in glass was slightly lower at 5.5%. However, when iodine was fed as methyl iodide (CH_3I), little or no iodine was retained in glass, which was expected because methyl iodide has a boiling point of only 42 °C.

Table 15. Measured Iodine Concentrations in DM10 Glass Discharge.

DM10 Test	Feed Iodine	Target (wt%)	Average[2] (wt%)	Retention (%)
2018	KI	0.14[1]	0.0164	11.7
2019	KI	0.20	0.012	6.0
	KIO_3		0.011	5.5
	CH_3I		<0.003	~0

[1] Includes iodine in the recycle for Batches 2-15. [2] Values reported by VSL.

5.1.3. *Liquid Effluents*

Two analytical methods were used to detect iodine in the liquid effluent samples; IC and ICP-MS. The distribution of iodine among various liquid effluents is summarized in Table 16.[7] For all three iodine forms fed, it appears that ICP-MS resulted in a closer to 100% recovery of iodine fed than IC when the glass retention results by DCP and XRF are included. This was expected as IC measures iodine ion, while ICP-MS measures total iodine. One of the key findings was that the iodine captured in the simulated caustic scrubber solution and the 2M NaOH impinger solution ranged from 50.8 to 76.6% of iodine fed with 67.3% of iodine fed being captured during the KIO_3 test, whose iodine recovery rate was closest to 100%. It is noted that these high iodine capture rates in the caustic scrubber solutions gave credence to the postulation made in Section 4.5.2; the large shortfall in the total iodine recovery during the 2018 DM10 run was attributed to the under-estimated iodine in the WESP exhaust, which resulted in the increase of iodine concentration from 31.8 to 54.0%. The next highest iodine recovery was 28.3% by the SBS+WESP liquid effluents, including the SBS sump, which subsequently became the feed for the evaporator test.

5.1.4. *Iodine Partitioning in the Evaporator*

During the 2018 DM10 run, the SBS+WESP liquid effluents were fed to the evaporator without the pH adjustment and the mass balance showed that iodine partitioned between the evaporator condensate and concentrate at a ratio of 4:1. However, when the pH of the SBS+WESP liquid effluents was adjusted from near neutral to 12.5 during the 2019 test in accordance with the current EMF operating plans, iodine became non-volatile and practically all iodine in the feed remained in the evaporator concentrate. This result is consistent with the findings from the DFLAW evaporator test conducted at Savannah River National Laboratory (SRNL) in 2019.[8]

Table 16. Iodine Distributions During 2019 DM10 Test (% Iodine Fed) – Taken from Ref. 7.

Test	KI		KIO_3		CH_3I	
% of Iodine Fed in Glass	6.0		5.5		0	
Analytical Method Used for Iodide	IC	ICP-MS	IC	ICP-MS	IC	ICP-MS
SBS Blowdowns	6.2	6.6	7.3	7.9	6.2	7.2
SBS Sump	16.2	16.1	20.4	18.7	10.4	11.4
WESP Blowdowns	1.0	1.8	0.9	1.8	0.6	1.8
Total Primary Off-Gas Solutions*	23.4	24.5	28.6	28.4	17.2	20.4
Caustic Scrubber (pH = 9.5)	57.5	70.8	45.0	60.1	9.8	52.0
2 M NaOH Impinger	4.7	5.8	5.8	7.2	5.4	6.7
Total Recovered	91.6	107.1	84.9	101.2	32.4**	79.1**

* Sum of SBS Blowdowns, SBS Sump and WESP Blowdowns. ** No methyl iodide was detected by SW-846-8260B analysis of the liquids for volatile organics; the detection limit was less than 0.003% of the total iodine in the melter tests.

5.2. Assessment of Mass Balance Results

The iodine distribution data given in Table 15 and Table 16 forms the basis for calculating the DF.

5.2.1. DF Across Melter

The DF for the KI run is calculated as follows:

$$\begin{aligned} \text{Melter DF} &= 1.0/(1.0 - 0.06) \text{ or equivalently} \\ &= 0.2/(0.2 - 0.012) \qquad (9) \\ &= 1.06 \end{aligned}$$

Eq. (9) was repeated for the KIO_3 and CH_3I runs, and the resulting DFs are compared to that of the 2018 run in Table 17. The calculated DFs for the KI and KIO_3 runs are practically identical, which indicates that glass retention was similar regardless of whether iodine was fed as iodide (I^-) or iodate (IO_3^-). As noted above, the volatility of CH_3I is high even at ambient temperature. As a result, its glass retention is essentially zero or DF = 1. Although the iodine DF fed as KI or KIO_3 seems slightly lower than that of the 2018 test, the glass retention was nearly 50% lower, i.e., 6% vs. 11.7%. It is not clear whether the fact that 40% of iodine fed during the 2018 test was recycled resulted in a higher glass retention or DF.

Table 17. Calculated Iodine DF Across DM10.

DM10 Test	Feed Iodine	Target (wt%)	Average[2] (wt%)	DF
2018	KI	0.14[1]	0.0164	1.13
2019	KI	0.20	0.012	1.06
	KIO_3		0.011	1.06
	CH_3I		<0.003	~1.0

5.2.2. DF Across SBS+WESP

The combined DF across the SBS+WESP for the KI run is calculated using the ICP-MS data in Table 16 as follows:

$$\text{Iodine at SBS Inlet} = 1.0\ (\text{total iodine fed}) - 0.06\ (\text{iodine in glass}) = 0.94 \tag{10}$$

$$\text{SBS+WESP DF} = 0.94\ (\text{iodine at SBS inlet}) / (0.94 - 0.245)\ (\text{iodine in WESP exhaust}) = 1.35 \tag{11}$$

Eq. (10) and Eq. (11) were repeated for the KIO_3 and CH_3I runs, and the resulting DFs are compared to that of the 2018 test in Table 18. As with the melter DFs, all three calculated DFs across the SBS+WESP for the 2019 test are also lower than that of the 2018 test but at a greater margin – i.e., the 2019-to-2018 melter DF ratio is 0.94 (for the KI and KIO_3 runs) vs. the corresponding DF ratio of 0.61 for the SBS+WESP. It is noted that the plenum height of the SBS above the liquid was increased before the 2019 test to reduce the carryover of droplets to the WESP,[7] and it appears that the modification did not help increase the DF.

Table 18. Calculated Iodine DF Across Melter and SBS+WESP.

DM10 Test	Feed Iodine	Melter	SBS+WESP	Overall
2018	KI	1.13	2.28*	2.58
2019	KI	1.06	1.35	1.43
	KIO_3	1.06	1.43	1.52
	CH_3I	1.0	1.26	1.26

* Based on revised iodine in the WESP exhaust.

It is also seen that the DF of the CH_3I run across the SBS+WESP is lower than those of the KI and KIO_3 runs even though the iodine concentration at the SBS inlet would have been the highest, as practically 100% of iodine fed exited the melter. It seems that this occurred because the iodine recovery in the liquid effluents of the SBS+WESP was the lowest at 20.4% of iodine fed, which suggests that methyl iodide likely exited the melter unchanged or, to a lesser extent, was decomposed to other volatile forms such as I_2 and much of iodine ended up in the SBS exhaust whose temperature was kept on average at 45 °C, just above the boiling point of CH_3I. This further suggests that the iodine recovery shortfall of 20.9% (=100-79.1) for the CH_3I run in Table 16 may be attributed to a significant portion of CH_3I that exited the simulated caustic scrubber unscrubbed.

6. Concluding Remarks

6.1. Impact of Scale on DF

The calculated iodine DFs across the DM1200 and DM10 melter and off-gas systems in this study are summarized in Table 19. It is clearly seen that the iodine DF across the melter decreases from DM1200 to DM10, and thus it seems logical from the conservative standpoint to take the lower DF of DM10 to be representative of the full-scale WTP LAW melter. However, doing so could lead to too conservative a basis for iodine emission. This is because there exists a significant scale difference between the two melters; the melt surface area of the LAW melter is estimated to be nearly 500X larger than that of DM10 and the scale difference in the melt pool volume would become even larger considering the much deeper melt pool of the LAW melter than that of DM10. As discussed above, the mass transfer resistance that iodine molecule or any other chemical form must overcome while migrating to the melt surface prior to volatilization would increase with increasing melt pool volume, which means that the retention of iodine in glass should decrease as the melt pool volume decreases. This trend was also exhibited by the lower iodine concentrations in the calcined feed samples in a closed crucible than those in the glass discharge samples from both DM1200 and DM10.

Table 19. Summary of Calculated Iodine DFs Across Melter, SBS and WESP.

VSL Test	Feed Iodine	Recycle?	Melter	SBS	WESP	SBS+WESP	Overall
DM1200	KI	No	1.25	2.0	1.5	3.0	3.75
2018 DM10	KI	Yes	1.13	-	-	2.28	2.58
2019 DM10	KI	No	1.06	-	-	1.35	1.43
	KIO_3		1.06	-	-	1.43	1.52
	CH_3I		1.0	-	-	1.26	1.26

The same scale-dependent trend is also shown in the calculated DFs across the SBS+WESP in Table 19. Regarding the difference between the DFs of the DM1200 and 2019 DM10 test with KI, it is difficult to attribute it to anything other than the obvious scale differences in the SBS and WESP designs, if they were prototypic of the WTP, from the reported data. Thus, it seems that the calculated DFs for the DM1200 test are the best available partitioning data because they are based on the data taken from the largest scale melter platform employing the most comprehensive sampling/analytical tools available at the time of testing.

6.2. Recommended DFs

The average iodine DF across the DM1200 WESP in Table 10 was further adjusted for the WTP LAW melter off-gas system using the scale-up equation:[9]

$$\begin{aligned} DF_{LAW} &= (DF_{VSL})^{1.378} \\ &= 1.5^{1.378} \\ &= 1.75 \end{aligned} \qquad (12)$$

It is noted that Eq. (12) was developed to account for the increased efficiency of the LAW WESP installed at WTP compared to the DM1200 WESP based upon design improvements including increased collection area per unit gas flow.[9]

The calculated DFs of iodine across the melter, SBS, and WESP in this work are compared in Table 20 with the BNI bases. Clearly, the calculated DFs in this work are all lower than the BNI bases. When the individual DFs are multiplied together, the differences in the overall DFs across the entire LAW melter primary off-gas system are more pronounced; the overall DF of this work is 10X lower than the BNI counterparts.

Table 20. Iodine DF Across LAW Melter, SBS, and WESP.

	Melter	SBS	WESP	Overall
BNI	2.5	3.6	4.8	43.2
This Work	1.25	2.0	1.75	4.38

Additionally, the BNI DFs are shown to increase as the melter exhaust moves through the off-gas system, while those calculated in this work show a peak at the SBS. All three DF series show the lowest DF at the melter, which was expected from the fact that the volatility of iodine or any volatile species for that matter is strongly dependent on temperature, and the temperature required to melt the LAW feed solids into glass is very high, nominally at 1,150 °C. For example, ~97% of iodine volatilized during the calcination of the nitric-acid waste of highly irradiated UO_2 at 650 °C,[10] and the main reason for the melter DF being higher than 1 during the DM1200 test was most likely the mass transfer resistances present in the slurry-fed melter such as the presence of cold cap and the transport of iodine to the melt surface. Thus, the DF across the SBS being higher than that of the melter was not unexpected. On the other hand, the BNI DF of 4.8 across the WESP seems high, considering that the WESP blow-down samples were strongly acidic, i.e., pH of ~1 or lower vs. pH of ~7 for the SBS, and thus the removal of iodine was not likely optimal at such low pH.

7. References

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Distribution:

J. Manna, joseph.manna@srnl.doe.gov
A. D. Cozzi, alex.cozzi@srnl.doe.gov
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T. J. Wagnon, todd_j_wagnon@rl.gov