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MEASUREMENT OF CESIUM AND MERCURY EMISSIONS FROM THE VITRIFICATION OF SIMULATED HIGH LEVEL RADIOACTIVE WASTE (U)

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DISCLAIMER

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ABSTRACT

In the Defense Waste Processing Facility at the Savannah River Site, it is desired to measure non-radioactive cesium in the offgas system from the glass melter. From a pilot scale melter system, offgas particulate samples were taken on filter paper media and analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The ICP-MS method proved to be sufficiently sensitive to measure cesium quantities as low as 0.135 μg, with the sensitivity being limited by the background cesium present in the filter paper. This sensitivity allowed determination of cesium decontamination factors for four of the five major components of the offgas system. In addition, total particulate measurements were also made. Measurements of mercury decontamination factors were made on the same equipment; the results indicate that most of the mercury in the offgas system probably exists as elemental mercury and $HgCl_2$, with some HgO and Hg_2Cl_2. The decontamination factors determined for cesium, total particulate, and mercury all compared favorably with the design values.

INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will be the United States' first facility to process high-level radioactive waste (HLW) into glass for storage in an off-site geologic repository. The Savannah River Technology Center (SRTC) operates the Integrated DWPF Melter System (IDMS), which is a pilot scale test facility used in support of the start-up and operation of the DWPF.[2] Specifically, the IDMS is used in the evaluation of the DWPF melter and its associated feed preparation and offgas treatment systems.

As part of non-radioactive testing of the DWPF facility prior to radioactive startup, the measurement of the decontamination factor (DF) for cesium in the melter offgas system will be performed. An experimental program was conducted in the IDMS to demonstrate the feasibility of determining cesium decontamination factors with non-radioactive cesium since non-radioactive cesium analysis techniques were believed to lack the required sensitivity.

Since SRS waste contains up to 3.2 wt% or more of mercury and the emissions of mercury must be controlled, the decontamination factors for mercury were also measured in the IDMS. This data gained from IDMS has been used to predict the emissions from the DWPF for use in environmental permitting calculations.

In addition to measuring the decontamination factors for cesium and mercury, the DF for total particulate was also measured.

IDMS FACILITY DESCRIPTION[1,2]

An overall flow diagram of the IDMS melter and offgas system is shown in Figure 1. The glass melter in the IDMS is a joule-heated slurry fed melter which melts glass at 1100-1150 °C. A slurry of HLW and borosilicate glass frit is fed via a feed tube onto the top of the glass surface in the melter. The melter is equipped with Inconel resistance heaters in the vapor space to assist in vaporization of the water in the slurry feed and to combust offgases evolved from the slurry. The melter is purged with air

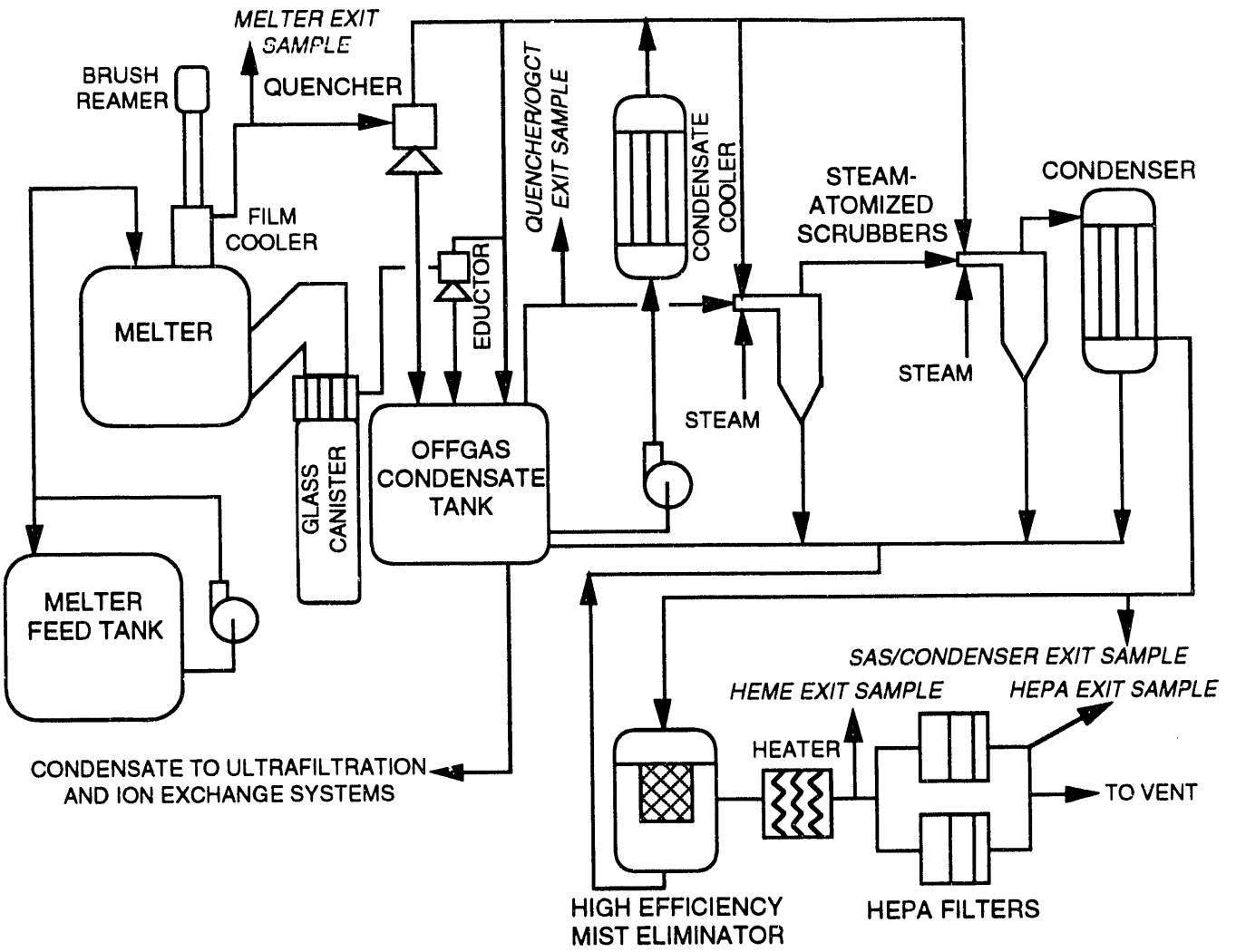

Figure 1. Integrated DWPF Melter System offgas system schematic.

and the offgas passes through the Film Cooler, which is designed to minimize particulate buildup in the offgas line and to cool the offgas from 450-725°C to less than 350°C.

After passing through the Film Cooler, the gas is then scrubbed in the Quencher. The Quencher is an ejector-venturi scrubber that reduces the gas temperature below the dew point, disengages most of the water vapor from the non-condensables, scrubs entrained glass, and allows semi-volatile particles (salts) to coalesce. The Quencher uses offgas condensate as the motive fluid. The offgas and condensate leaving the Quencher enter the Offgas Condensate Tank (OGCT) where the liquid and vapor disengage. The condensate is maintained at 40°C by a cooler.

The offgas from the OGCT is then passed through a series of two Steam-Atomized Scrubbers (SAS)[3], which remove sub-micron and micron-sized particles. The SAS removes particulates by combining water with the offgas in a region of turbulent mixing. This mixing action is created by directing a jet of steam into an enclosed cavity so as to create a region of turbulent flow along the outer boundary of the jet. Water is sprayed around the jet and mixes with the process gas. The droplets formed are then accelerated in the mixing tube where turbulence is sufficient to promote coalescence, but low enough so as not to cause significant re-entrainment of the liquid. The droplets are separated from the vapor in a cyclone separator. The SAS technology was developed and patented by the Lone Star Steel Company, which refers to the

equipment as Hydro-Sonic Scrubbers. The condensate and condensed steam are returned to the OGCT.

The offgas leaving the SASes is passed through a shell-and-tube heat exchanger that is designed to separate the condensables from the offgas and remove virtually all of any elemental mercury present. The separated condensables are returned to the OGCT. A mist eliminator (York demister) with an atomized water spray removes any suspended liquid droplets from the non-condensable gases.

The High Efficiency Mist Eliminator (HEME) consists of a densely packed glass fiber filter that is wetted continuously by an atomized water spray. There is a coarse 1.25 cm layer of 30 μm glass fiber on the face followed by a 6.4 cm layer of fine 8 μm glass fiber packed at 175 kg/m^3. The HEME was designed to operate at a 2.5 cm/sec superficial face velocity.

After passing through the HEME, the offgas is heated 10°C above its dew point to prevent condensation in the High Efficiency Particulate Air (HEPA) filters. Two HEPA filters in parallel serve as the final treatment step before the air is released to the environment. In DWPF, two HEPA filters are used in series, followed by a sand filter.

CESIUM REMOVAL[4]

The particulate samples were taken from the five points in the melter offgas system shown in Figure 1. A modified version of the EPA Method 5[5] Sampling Train was used. The offgas was sampled at as near to isokinetic conditions as possible. The process mass flowrate was measured by process flow transmitters, converted to velocity, and corrected for variations in pressure, temperature and density. The Staksamplr™ (Anderson Samplers) gas metering system was adjusted in real time to keep the sample and process velocities equal. Particulate samples were collected on glass fiber filter paper (Reeve Angel 934AH Mark 3/5 #1) with an average pore size of 0.3 μm. After leaving the filter housing, the sampled offgas passed through four chilled (0-5°C) impingers which condensed water and other condensables.

The filter samples containing the collected IDMS offgas line particulates were analyzed by ICP-MS. First, x-ray fluorescence was used to obtain an approximate value for the cesium present in each sample. The samples were then dissolved in a mixture of nitric and hydrofluoric acids, taken to dryness, and redissolved in dilute nitric acid. Additional dilutions were made to bring the cesium concentrations to levels matching the instrument's range of optimum performance. Only two dilution levels, differing by a factor of ten, were used. The total cesium per sample ranged from 0.34 to 19.2 μg and 9.18 to 948 μg for the smaller and larger dilutions, respectively. The uncertainty of the ICP-MS technique, based on duplicate analyses, ranged from 0.0 to 7.1%, with an average uncertainty of 4.4%.

Blank determinations were performed for the nitric acid, combined reagents and the filter paper. As expected, the filter paper blanks showed the highest amount of cesium and limited the sensitivity of the analyses. The average amount of cesium in the filter papers was 0.336 μg. After dissolution, roughly half of the samples analyzed left insoluble residues which were centrifuged out. The residue is believed to be associated with the filter paper medium since some of the blanks also gave a residue. In all but one sample, the residue contained less than 1% of the total cesium.

Total particulate weight was determined by weighing the filter papers on a five place analytical balance before and after sampling. For both the initial and final weight, the filter papers were dried in an oven at 110°C for at least 24 hours and were cooled in a desiccator. In some cases, the weight of the filter paper after sampling was so close to the initial weight that the DF determined was very inaccurate.

Cesium concentrations greater than the blanks were obtained from four of the five locations sampled. The HEPA exit location gave samples that were only slightly higher than the blanks, with substantial variation in the weights for a given sampling interval. The HEME exit samples were also only slightly larger than the blanks, but the weights were more consistent. Table 1 shows the cesium flowrates measured in the IDMS offgas system. This table also shows the design decontamination factors for the DWPF and the overall decontamination factors measured in IDMS. Comparison of the overall decontamination factor (without the HEPA filters) shows that IDMS achieved an order of magnitude better performance than the design basis, mainly due to the high DF for the melter. The IDMS melter has a much larger vapor space

Table 1. Design and measured cesium decontamination factors.[6]

DF across:	IDMS Cesium Flowrate (mg/min)	DWPF Design DF	IDMS Measured DF
Melter Feed	335.	-	-
Melter	2.54 ± 1.39	15.	132.
Quencher/OGCT	0.960 ± 0.560	8.9	2.7
SAS/Condenser	0.0337 ± 0.0208	50.	28.5
HEME	$1.07 \pm 0.78 \times 10^{-4}$	40.	314.
HEPA #1	$1.43 \pm 1.91 \times 10^{-4}$	422.	0.75
HEPA #2	NA	24.5	NA
Overall (without HEPAs)		2.67×10^5	31.3×10^5
Overall (without HEPAs & Melter)		1.78×10^4	2.37×10^4

volume to melt surface area ratio than the DWPF melter which may result in less entrainment of glass particles.

The DF for the Quencher/OGCT in IDMS was much lower than the design basis. It is reasonable to assume that the concentration of larger particulates at the inlet to the Quencher was smaller than assumed in the design basis since the DF of the melter was much higher than expected. The Quencher/OGCT combination is designed to remove large particulates, which are mainly entrained glass,[7] so it is not unexpected that it performed less efficiently than the design basis.

The total particulate decontamination factors determined in IDMS and the DWPF design values are shown in Table 2. The overall DF determined in IDMS is similar to the design value, but its magnitude is mainly due to the melter DF being much larger than expected. Again, the low experimental decontamination factors are due to there being less entrained particulate in offgas (melter DF = 38 times design) and also due to the difficulty in measuring small weight gains on the filter papers.

MERCURY REMOVAL

The decontamination factors for mercury were evaluated in IDMS for the Melter, Quencher/OGCT, SAS/Condenser and the HEME. The decontamination factor for mercury in the HEPA was not evaluated. Sampling of the offgas system utilized a modification of EPA Method 111,[8] which uses three scrubbers containing 4 (w/v)% $KMnO_4$ in 10 (v/v)% sulfuric acid.

Table 2. Design and Measured Total Particulate Decontamination Factors.

DF across:	DWPF Design* DF	IDMS Measured DF
Melter	69	2626.
Quencher/OGCT	<10	2.85
SAS/Condenser	50	20.6
HEME	40	8.2
HEPA #1	<500	1.43
HEPA #2	<50	NA
Overall (without HEPAs)	$\approx 1.38 \times 10^6$	1.24×10^6

* design DF values indicated are for entrainment only; semi-volatile values will be smaller

This mixture should oxidize all mercury to Hg^{+2}. Methods similar to this are described elsewhere.[9-12] The scrubber solutions were analyzed by cold vapor atomic absorption after dilution to appropriate levels. The concentrations of mercury in the scrubber solutions ranged from 16 to 63000 µg/liter. The melter feed samples were digested in a 1:1 mixture of nitric and hydrochloric acids at 95°C for 2 hours and then analyzed by cold vapor atomic absorption.[9] Direct analysis by flame AA of both the digested melter feed samples and the scrubber solutions gave erroneous results.

The offgas condensate samples were digested and analyzed according to EPA Method 245.1.[10]

Filter papers were used during sampling, but no mercury or mercury compounds were found when analyzed by x-ray fluorescence or electron microscopy. It was expected that some calomel (Hg_2Cl_2) would be found. The condensate from the OGCT was analyzed for soluble and total mercury; the ratio of soluble to total mercury varied from 0.84 to 1.00, indicating that little insoluble mercury existed. Some of the entrained glass oxides in the condensate appeared to be plated with elemental mercury. The total mercury in the condensate ranged from 1.9-11.9 mg/liter, which is well under the solubility of elemental mercury in oxygenated water (4200 mg/liter), HgO (5200 mg/liter), $HgCl_2$ (66000 mg/liter), and even calomel (200 mg/liter).[11] Hence, virtually all of the mercury was soluble resulting in there being no particulate mercury to be removed on the filter papers.

The mercury concentrations measured in the melter feed, offgas condensate and the offgas samples were checked for consistency by performing a material balance around the offgas system. For three experimental runs, the closure of the material balance was 91.6-122.5%, with a mean of 102.4%. These values indicate that the measured mercury concentrations were accurate.

Table 3 shows the decontamination factors for mercury determined in IDMS compared to those in the design basis for the DWPF. A comparison of the measured and design concentrations of mercury is also given. Examination of this table shows that the concentrations of mercury throughout the melter offgas system in IDMS were more than an order of magnitude less than in the design basis. As described elsewhere,[2] the efficiency of mercury removal in the feed preparation process in IDMS was much higher than the design basis, resulting in extremely low concentrations of mercury in the melter feed. The data in Table 3 show that, even at low mercury concentrations, the overall decontamination factor for mercury is similar in magnitude to the design basis. Moreover, because the feed concentrations were so small, the actual amount of mercury emitted was up to 20 times less than the design basis.

The mercury concentrations in the offgas were compared to the saturation concentrations for elemental Hg and $HgCl_2$. For Run 1, the concentration of mercury was about 21% of the saturation concentration for $HgCl_2$, and for Run 2, it was between that of saturated $HgCl_2$ and saturated Hg. Therefore, it appears that the mercury in the offgas may exist as a mixture of elemental Hg and $HgCl_2$. The solubility of elemental Hg in oxygenated water is approximately equal to that of HgO, indicating that elemental Hg may be converted to HgO. Hence, the condensate may also contain dissolved HgO. Since the mercury concentration in the condensate was so small, it is also possible that some of the mercury existed as calomel.

Table 3. DWPF Design and Measured Mercury Concentrations and Decontamination Factors.

DF across:	Mercury Concentration IDMS Run 1	IDMS Run 2	DWPF Design	IDMS DF	DWPF Design DF
	(mg/liter)				
Melter Feed	6.3	37.0	698		
OGCT Liquid	1.9	11.9	232		
	(ppb by volume)				
Melter Offgas	205.	1185.	58050	0.98-1.04	1.00
Quencher/OGCT	19.	249.	13930	3.32-8.38	3.92
SAS/Condenser	3.6	154.	698	1.60-4.86	21.2
HEME	1.9	34.	698	1.84-5.58	1.00
Overall				29.7-74.2	83.1

As expected, the decontamination factor for the melter was unity since mercury is not vitrified into the glass. The Quencher/OGCT DF was somewhat better than the design, but as for cesium and total particulate, the SAS/Condenser DF was lower than expected. Surprisingly, mercury was removed in the HEME where no removal was expected. The design basis assumes that most of the mercury entering the HEME is elemental mercury vapor and that it is not removed. Since the HEME is wetted by a constant stream of water, it is likely that both Hg and $HgCl_2$

in the offgas were scrubbed in the HEME.

CONCLUSIONS

The data indicate that the decontamination factors for cesium in the Melter, Quencher/OGCT, SAS/Condenser and HEME can be measured by sampling the offgas using standard filter paper sampling techniques and analysis by ICP-MS. Measurement of cesium at the HEPA exits is not possible with this technique. The decontamination factors determined in IDMS indicate that the DWPF melter offgas system components should perform at or above their design specifications for the removal of cesium, total particulate, and mercury although the performance of individual pieces of equipment may differ from the design basis.

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