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BOUNDING ESTIMATE OF DWPF MERCURY EMISSIONS (U)

by

R. A. Jacobs

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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DOE Contract No. DE-AC09-89SR18035

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Savannah River Company

WSRC-TR-92-1205TL
Revision 1

Keywords: DWPF, Hg emissions

Retention period: Permanent

cc: D. T. Bignell, 719-4A-
J. F. Ortaldo, 704-S-
K. Z. Wolf, 704-15S-
• L. F. Landon, 704-T
• D. A. Crowley, 704-1T
• D. P. Lambert, 704-1T
• J. R. Zamecnik, 704-1T
R. A. Jacobs, 704-T-
SRTC Records (4)

October 28, 1993

D. B. AMERINE, MANAGER/DEFENSE WASTE PROCESS FACILITY
WESTINGHOUSE SAVANNAH RIVER COMPANY

ATTENTION: W. D. Kimball, 704-S (5)

BOUNDING ESTIMATE OF DWPF MERCURY EMISSIONS (U)

H₂ flammability control and elevated Formic Acid Vent Condenser exit temperatures due to NO_x reactions have lead to changes in Chemical Process Cell (CPC) operating conditions. Accordingly, bounding (maximum) mercury emissions estimates have been previously updated for the Late Wash/formic acid¹ process based upon the new operating requirements, IDMS (Integrated DWPF Melter System) experience, and development of an NO_x/FAVC model which predicts FAVC exit temperatures. The previous estimates (Revision 0 of the attached document) have been revised to reflect our standard basis of 100% attainment for bounding emissions estimates and also to reflect the Batch 1 CPC cycle time of 100 hours. Using very conservative assumptions and maximum purge rates, the maximum calculated Hg emissions are approximately 130 lbs/yr with a peak rate of 0.035 lbs/hr. A range of 100 to 120 lbs/yr is conservatively predicted for other operating conditions. These estimates are approximately the same as previously transmitted. DWPF permitted Hg emissions are 175 lbs/yr (0.02 lbs/hr annual average).

Any questions about the report should be directed to R. A. Jacobs - extension 5-6431.

E.W. HOLTZSCHEITER
MANAGER/DWPTSECTION

C. T. Randall, 704-T
Authorized Derivative Classifier

AUTHENTICATED:

SIGNATURE
DATE

¹ Insufficient data exist to revise these calculations for the Late Wash/nitric acid process with ammonia scrubbers. However, emissions for LW/nitric acid are expected to be somewhat lower because of NO_x scrubbing by the ammonia scrubbers which will reduce or eliminate the FAVC temperature excursions.

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Savannah River Company

INTER-OFFICE MEMORANDUM

WSRC-RP-92-1205

Revision 1

Keywords: DWPF, Hg emissions

Retention period: Permanent

cc: D. A. Crowley, 704-1T
L. F. Landon, 704-T
D. P. Lambert, 704-1T
J. R. Zamecnik, 704-1T
SRTC Records (4)

October 28, 1993

TO: E. W. HOLTZSCHEITER, 773-A

FROM: R. A. JACOBS, 704-T

BOUNDING ESTIMATE OF DWPF MERCURY EMISSIONS (U)

Summary and Conclusions

Purges required for H₂ flammability control and verification of elevated Formic Acid Vent Condenser (FAVC) exit temperatures due to NO_x reactions have lead to significant changes in Chemical Process Cell (CPC) operating conditions. Accordingly, mercury emissions estimates have been updated based upon the new operating requirements, IDMS (Integrated DWPF Melter System) experience, and development of an NO_x/FAVC model which predicts FAVC exit temperatures.¹ Using very conservative assumptions and maximum purge rates, the maximum calculated Hg emissions is approximately 130 lbs/yr. A range of 100 to 120 lbs/yr is conservatively predicted for other operating conditions. The peak emission rate calculated is 0.027 lbs/hr. The estimated DWPF Hg emissions for the construction permit are 175 lbs/yr (0.02 lbs/hr annual average).²

Discussion

Background

Two factors which have substantial impact on predicted Hg emissions are the air flows in the CPC and the exit temperature of the FAVC. The discovery in the IDMS of H₂ generation by noble metal catalyzed formic acid decomposition and the resultant required dilution air flow has increased the expected instantaneous CPC air flow by as much as a factor of four.³ In

C. T. Randall, 704-T
Authorized Derivative Classifier

L. F. Landon, 704-T
Peer Reviewer

addition, IDMS has experienced higher than design (10°C) FAVC exit temperatures during certain portions of the operating cycle. These temperatures were subsequently attributed to the exothermic reaction of NO to NO₂. Moreover, evaluation of the DWPF FAVC indicated it was undersized and unless modified or replaced, routine exit temperatures would be in excess of design.

Subsequent experimentation, both small scale and large scale, has verified H₂ generation rates and required maximum operating air dilution flows.³ Also, a combination kinetic, empirical model has been developed to predict the CPC offgas temperature exiting the FAVC which takes into account the residence time in the riser/mist eliminator.¹

There are two other sources of Hg emissions in DWPF. The melter offgas flow from the Offgas Condenser (OGC) is significant and contributes approximately half of the total Hg emissions. The other source is the Salt Cell Vent Condenser (SCVC) which also contains small amounts of Hg; estimated to be a maximum of two lbs/yr.

Calculations

Assumptions and Notes

General

- All streams (FAVC, OGC, and SCVC) are assumed to be saturated at all times with elemental Hg at the condenser exit temperature. This should be an extremely conservative assumption for the FAVC since Hg is steam stripped from the SRAT (Sludge Receipt and Adjustment Tank) and SME (Slurry Mix Evaporator) for only about one-third of the cycle time and since it is likely that Hg is not evolved when the melter is idling. This conservative assumption allows for the possibility of significant Hg aerosol collection on the FAVC and OGC high efficiency mist eliminators (HEMEs) which then evaporates at a later time when Hg is not being evolved.
- The streams are also assumed to be saturated with water vapor at all times.
- Hg vapor pressure is calculated by the equation

$$\log p \text{ (mm Hg)} = 8.0866 - \frac{3227}{T(^{\circ}\text{K})}$$

derived from Hg vapor pressure data for the a temperature range of 0 - 100 °C.⁴

- Water vapor pressure is calculated by the equation⁵

$$\log p \text{ (mm Hg)} = 8.07131 - \frac{1730.63}{233.426 + T(^{\circ}\text{C})}$$

- Attainment is 100% or 8760 hr/yr
- CPC operating pressure is 740 mm Hg abs.

Melter Offgas

- Offgas flows per CPES material balance⁶
- Offgas emissions are

Annual OGC Hg Emissions*Air flows*

OGFC Cooling Air	425
OGFC Dilution Air	0
Backup Film Cooler Air	350
TV Lens Purge	60
Melter Air Inleakage	100
Seal Pot Purge	20
Bubbler Purge	15
Can Bellows Inleakage	40
Pour Spout Siphon Break	15
Melter Control Air	550
Control Air to Ejector	40
OGCT Air Inleakage	<u>105</u>

Emissions @ 10°C

Total OGC air flow - ppH	1720
Total OGC flow - lbmol/yr	526070

Total OGC Hg emissions - lbs/yr 69.9

SCVC Offgas

- Maximum Hg emissions can be quickly estimated by ratioing to the maximum allowable benzene emissions which are 36 tons/yr. At 10°C, the vapor pressures of benzene and Hg are 45.4 mm Hg and 0.00049 mm Hg, respectively. The maximum Hg emissions would be

$$\frac{72000 \text{ lbs benz/yr}}{78 \text{ lbs benz/lbmol benz}} \times \frac{0.00049 \text{ mm Hg}}{45.4 \text{ mm Hg}} \times 200.6 \frac{\text{lbs Hg}}{\text{lbmol Hg}} = 2.0 \text{ lbs/yr}$$

CPC Offgas

- FAVC exit temperature estimates
 - nitric acid SRAT flowsheet in use
 - maximum NO_x evolution equals maximum for formic acid flowsheet at 0.4 gpm formic acid (insufficient IDMS runs to develop correlation)
 - high nitrite sludge (0.25 - 0.35 M)

- SRAT condenser exit temperature at 50°C (design)
 - FAVC exit temperature at 10°C except during NO_x evolution
 - negligible CO₂ evolution during peak NO_x evolution
 - 250 lbs/hr total air inleakage total for other vessels which vent to FAVC (MFT, PRBT, SMECT, and MWWT)
 - In cases 1-3, SRAT condenser to FAVC line size is 6"; 3" in cases 4 and 5
 - FAVC exit temperature estimated by model documented in Reference 1
- Duration of NO_x peak is 2 hours/100 hour batch cycle; NO_x is zero at all other times |
 - Offgas flow rates are peak values at maximum NO_x evolution
 - Peak CO₂ evolution is 300 lbs/hr; duration of two hours/cycle; zero at all other times
 - SRAT and SME air purges are on 100% of the time (equivalent to 100% attainment) |

Case	SRAT air purge	SME air purge	Comments
1	1150	225	Original rad ops design basis
2	575	225	SRAT air @ 50%
3	575	575	SRAT @ 50%, SME at 575 if H ₂ evolution in SME comparable to SRAT
4	225	225	~5X reduction in H ₂ rate (HNO ₃ flowsheet); assume SME H ₂ comparable to SRAT
5	115	115	~10X reduction in H ₂ rate; assume SME H ₂ comparable to SRAT

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- Maximum CPC and total emissions are

Annual DWPF Hg Emissions

Standby flows (0% => 0 hrs/yr) - Temp = 10°C					
Total air leakage - pph	375	375	375	375	375
Operating flows (100% => 8760 hrs/yr) - Temp = 10°C					
	Case 1	Case 2	Case 3	Case 4	Case 5
SRAT air purge - pph	1150	575	575	225	115
SME air purge - pph	225	225	575	225	115
Other air leakage - pph	250	250	250	250	250
CO ₂ (for 2 of 86 hrs) - pph	300	300	300	300	300
NO _x (for 2 of 86 hrs) - lbmol/hr	4.805	4.805	4.805	4.805	4.805
FAVC temp during NO _x - °C	23.0	25.5	22.3	35.5	39.2
Hg emissions					
Emissions @ 10°C - no NO_x					
Standby flow - lbmol/yr	0	0	0	0	0
Operating flow: air - lbmol/yr	412324	266425	355233	177617	121794
Operating flow: CO ₂ - lbmol/yr	896	896	896	896	896
Total flow - lbmol/yr	418399	270671	360592	180750	124228
Hg emissions @ 10°C - lb/yr	55.6	36.0	47.9	24.0	16.5
Emissions during NO_x evolution					
Operating flow: total - lbmol/yr	8228	5573	7170	4039	3022
Hg emissions - lb/yr	3.5	2.9	2.8	4.7	4.7
CPC Hg emissions - lbs/yr	59.0	38.8	50.7	28.7	21.2
OGC Hg emissions - lbs/yr	69.9	69.9	69.9	69.9	69.9
Max SPC Hg emission - lbs/yr	2.0	2.0	2.0	2.0	2.0
Total DWPF Hg emissions - lbs/yr	130.9	110.7	122.6	100.6	93.0

Peak Hg Emissions Rate

- The peak emissions can be estimated using the peak CPC rate (4.7 lbs/hr from Cases 4 and 5 above) for 2 hrs per 100 hr cycle plus the constant rate from the Melter Offgas Systems (69.9 lbs/yr for 8760 hrs/yr).

$$\text{Peak Hg rate} = \frac{4.7 \text{ lbs/yr}}{\frac{8760 \text{ hrs/yr}}{100 \text{ hrs/cycle}} \cdot 2 \text{ hrs peak/cycle}} + \frac{69.9 \text{ lbs/yr}}{8760 \text{ hrs/yr}}$$

$$= 0.035 \text{ lbs/hr}$$

Quality Assurance

Spreadsheet calculations were verified by hand calculations. Assumptions, bases, and calculations were reviewed by L. F. Landon.

References

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