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BOUNDING ESTIMATE OF DWPF MERCURY EMISSIONS (U)

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INTER-OFFICE MEMORANDUM

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SRL Records (4)*

October 9, 1992

TO: E. W. HOLTZSCHEITER, 773-A

FROM: R. A. JACOBS, 704-T *R.A. Jacobs*

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. DWPF permitted Hg emissions 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 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

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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 75% or 6570 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

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

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/86 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 (as noted) are on at all times during attainment period (75% of the time) but off during non-operating periods (25% of the time); during non-operating periods, baseline air inleakage is 375 lbs/hr total (includes SRAT and SME)

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 (25% => 2190 hrs/yr) - Temp = 10 °C
 Total air leakage - pph 375 375 375 375 375

Operating flows (75% => 6570 hrs/yr) - Temp = 10 °C

	<u>Case 1</u>	<u>Case 2</u>	<u>Case 3</u>	<u>Case 4</u>	<u>Case 5</u>
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
CO2 (for 2 of 86 hrs) - pph	300	300	300	300	300
NOx (for 2 of 86 hrs) - lbmol/hr	4.805	4.805	4.805	4.805	4.805
FAVC temp during NOx - °C	23.0	25.5	22.3	35.5	39.2

Hg emissions

Emissions @ 10°C - no NOx

Standby flow - lbmol/yr	28319	28319	28319	28319	28319
Operating flow: air - lbmol/yr	359585	232347	309796	154898	106216
Operating flow: CO2 - lbmol/yr	1042	1042	1042	1042	1042
Total flow - lbmol/yr	393820	264988	343408	186568	137276
Hg emissions @ 10°C - lb/yr	52.3	35.2	45.6	24.8	18.2

Emissions during NOx evolution

Operating flow: total - lbmol/yr	9567	6480	8337	4697	3514
Hg emissions - lb/yr	4.0	3.4	3.3	5.5	5.4

CPC Hg emissions - lbs/yr	56.3	38.6	48.9	30.2	23.7
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	128.2	110.4	120.8	102.1	95.5
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Quality Assurance

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

L. F. Landon, 704-T
 Peer Reviewer

References

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4/1/1993

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