Selective Catalytic/Non-Catalytic Reduction Conference

SCR Operation Optimization: SO_3 Removal to Optimize Catalyst Life & NH_3 Distribution in Wastewater

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Agenda

- INTRODUCTION
- NH_3 SLIP DISTRIBUTION
- SCR'S INCREASED SO_3
- SO_3:NH_3 MOLAR RATIO
- WASTEWATER TREATMENT
- ECONOMICS
- CONCLUSION

Introduction

- Last Year's Paper
  - SCR catalyst life → limited NH_3 slip to ~2 ppm to prevent ammonium bisulfate (ABS) deposits in air heater
  - NH_3 slip is removed in air heater deposits, on ESP ash & in FGD slurry
  - NH_3 is soluble & eventually will end up in a wastewater discharge
- Last year's Recommendation
  - Install SO_3 removal system before air heater, to balance NH3 distribution between ESP & FGD
  - NH_3 slip sampling for NH_3 balance, especially air heater wash water
  - Determine critical ABS deposition number ("Radian" number), by increasing NH_3 slip to cause deposits

NH3 SLIP DISTRIBUTION

- ABS
  - ABS vapor forms at temperatures >600 F
  - SO_3 below 400 F is mostly H_2SO_4 vapor → 50% at ~600 F and 90% at 400 F
  - ABS condensate or aerosol forms from 330 F to 360 F F → higher temperatures at higher SO_3 & NH_3 concentrations
  - ABS is a viscous liquid → "sticky"
  - Temperature drop required for condensing ABS → such as an air heater
  - Condensate or aerosol formation completed at ~320 F → very low SO_3 & NH_3 (< 1 ppm)
  - Molar Ratio - SO_3:NH_3 = 4.7 SO_3 ppm per ppm NH_3

NH3 SLIP DISTRIBUTION (continued)

- Air heater
  - Radian developed a thermodynamic & kinetic model for AS & ABS formation in regenerative air heaters (1982)
  - Radian Equation for ABS deposition number:
    - SO_3 ppm x NH_3 ppm x[$T_{(IFT)}$ - $T_{(rep)}$]
    - Where "$T_{(rep)}$" is a combination of air heater gas exit temperature & cold-end metal temperature
  - Preliminary literature survey showed a "break point" at 5,000 to 7000 for the Radian number from minimal ABS deposits to "increase in pressure drop" deposits
  - NH_3 slip Guidelines → from literature review & typical Molar Ratios
    - Low sulfur – 6 ppm
    - Medium sulfur – 4 ppm
    - High Sulfur – 2 ppm

NH3 SLIP DISTRIBUTION (continued)

- Air Heater (continued)
  - Acid Dew Point – higher ADP from increased SO_3 may also increase ash deposits in air heater
  - Literature shows that some ABS deposits may decompose in combustion air side of air heater
  - Worst case - 2 ppm slip at end of catalyst life & for 12 months operation → up to average ~3,000 ppm NH_3 in wash water

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NH3 SLIP DISTRIBUTION (continued)

- ESP
  - Flue gas conditioning reaction
  - Byproduct Ash – can evolve NH_3 when mixed with cement (high pH) → 100 ppm NH_3 in ash is typical limit
  - Worst case – 2 ppm NH_3 slip at end of catalyst life to fly ash
    - Wet Sluice to Pond → up to ~2 ppm in sluice water
    - Dry Conveying to Landfill
      - Ash → up to ~ 175 ppm (adsorbed on ash)
      - Leachate → up to ~150 ppm (for a 1 year active cell)

- FGD
  - Residual NH_3 after air heater & ESP absorbed in FGD
  - Byproduct gypsum (wallboard) →
  - Worst Case – 2 ppm NH_3 slip at end of catalyst life to FGD
    - Open Loop – up to ~10 ppm
    - Closed Loop - up to ~100 ppm

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SCR`s INCREASED SO3

- Impact
  - SCR ~ doubles boiler SO_3 → up to 50+ ppm for high sulfur coal
  - Visible plume → at > 15 to 20 ppm SO_3
  - Acid Dew point (ADP) corrosion → ADP ~300 F for high sulfur coal
- Removal Economics
  - Very few SO_3 removal systems → limited cost & operational experience – see Gavin papers
  - Boiler injection only removes boiler SO_3 – not SCR SO_3
  - Assume hydrated lime system after SCR
    - Process Design – lime stoichiometry ~3
    - Capital - ~$10 per KW → ~ $0.15 per MWH
    - O&M – lime at $100 per ton → ~ $0.15 per MWH
    - Total → ~ $0.3 per MWH

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SO3:NH3 MOLAR RATIO

- SO3
  - Boiler + SCR SO_3
  - High (3.0%) → 25 + 25 = 50 ppm
  - Medium (1.7%) → 14 +14 = 28 ppm
  - Low (<1%) → 6 + 6 = 12 ppm

- SO_3:NH3 Molar Ratios
  - For typical "end-of-life" catalyst → 2 ppm NH_3
  - 1 molar SO_3 :NH3 = 4.7 NH3 ppm per ppm SO_3
  - ABS formation impacted by Molar Ratio → higher driving force results in lower temperature drop. For 95% formation completion:
    - At 1.0 MR → ~75 F
    - At 0.5 & 2.0 MR → ~45 F
    - At 5.0 MR → ~40 F

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SO3:NH3 MOLAR RATIO (continued)

- Cases
  - Without SO_3 removal & 2 ppm NH3
  - With SO_3 removal & 2 ppm NH3
  - Early catalyst replacement → 1 ppm NH_3
  - Late catalyst replacement → 4 ppm NH_3
- ABS Deposition Number (“Radian” Number)
  - ABS deposits (measurable pressure drop) in air heater start around a “Radian” number of ~5,000 to 7,000

$SO_3:NH_3$ MOLAR RATIO (continued)

		W/O SO_3 Removal	WITH SO_3 Removal	EARLY Catalyst	LATE Catalyst
NH_3	End of Catalyst Life	2	2	1	4
SO3	High Sulfur	50	5 to 10	50	50
Molar Ratio	SO3: NH_3	~5	1 to 2	~10	~2.5
ABS	Deposit # (add washes)	~6500 (1)	~1200 (0)	~3200 (0)	~13,000 (2)
Air Heater	NH_3 Removal	~30%	~10%	~40%	~20%
	Wash Water NH_3 ppm	~750	~500	~1100	~400

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SO3:NH3 MOLAR RATIO (continued)

		W/ SO_3 Removal	W/O SO_3 Removal	EARLY Catalyst	LATE Catalyst
ESP	NH_3 Removal	~70%	~70%	~60%	~70%
	Sluice Water ppm	Up to 1.2	Up to 1.2	Up to 1.0	Up to 1.2
	Dry Ash ppm	Up to 120	Up to 120	Up to 100	Up to 120
FGD	NH_3 Removal	0	~20%	0	~10%
	Open Loop ppm	0	Up to 2	0	Up to 1
	Closed Loop ppm	0	Up to 20	0	Up to 10

SO3:NH3 MOLAR RATIO (continued)

- Medium Sulfur Coal
  - Less removal in air heater → lower MR
  - Only Early Catalyst has no FGD wastewater treatment
  - Only Late Catalyst has additional air heater washes
- Low Sulfur Coal
  - Same removal in air heater & ESP – 10% & 70%, respectively
  - All cases need WWT for FGD to maintain byproduct sales

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WASTEWATER TREATMENT

- Conventional Options
  - Mechanical → result in a NH_3 off-gas or a concentrated-NH3 liquid
  - Biological →
  - ABS deposits result in just a different waste for further treatment
- Quantity (gpm /MW)

Air Heater Wash Water	<0.5
Ash Landfill Leachate	<0.5
FGD Blowdown (closed loop)	NA (only entrained liquid)
FGD Blowdown (open loop)	~2
Ash Sluice (~0.5% slurry)	~14
NPDES	~20

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WASTEWATER TREATMENT (continued)

- Comprehensive Treatment
  - Byproduct recovery from wastewater
  - Increase wastewater pH, strip NH_3 & absorb NH_3 in concentrated sulfuric acid → an ABS byproduct fertilizer(liquid)
- Economics
  - Air Heater → $2 per KW & $0.04 per MWH
  - Ash Landfill Leachate → $2 per KW & $0.04 per MWH
  - FGD Blowdown (open loop) → $5 per KW & $0.08 per MWH
  - Ash Sluice → $18 per KW & $0.25 per MWH
  - NPDES → $22 per KW & $0.35 per MWH

ECONOMICS

- Catalyst Life
  - Catalyst = ~10% of SCR cost → ~$10 per KW
  - For 20,000 hours (2 ppm NH_3) → ~$0.17 per MWH (base)
  - Early (1 ppm NH_3) at 15,000 hours → +$0.05 per MWH
  - Late (3 to 4 ppm NH_3) at 25,000 hours → -$0.04 per MWH
- Byproduct Sales
  - For every $10 per ton for disposal, loss of byproduct sales (from a high sulfur coal) due to NH3 contamination → cost is ~$0.35 & $0.65 for fly ash & gypsum
- Air Heater Washing
  - Washing Crew (for high pressure washing) → ~$0.05 per MWH
  - 50% Loss of Load for 3 days → ~$0.05 per MWH
  - Total cost per additional washing → ~$0.1 per MWH (annualized)

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ECONOMICS (continued)

	W/O SO_3 REMOVAL	WITH SO_3 REMOVAL	W/O SO_3 REMOVAL	W/O SO_3 REMOVAL
CATALYST REPLACEMENT	BASE	BASE	EARLY	LATE
SO_3 REMOVAL	0	0.3	0	0
WWT – ASH LEACHATE				
WWT – AIR HEATER	0.04	0.04	0.04	0.04
WWT – FGD (open loop)	0	0.08	0	0.08

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ECONOMICS (continued)

	W/O SO_3 REMOVAL	WITH SO_3 REMOVAL	W/O SO_3 REMOVAL	WITH SO_3 REMOVAL
CATALYST REPLACEMENT	0	0	+0.05	(0.04)
AIR HEATER WASHING	0.1	0	0	0.2
BYPRODUCTS ASH	0	0	0	0
BYRPODUCTS FGD	0	0	0	0
TOTAL	0.14	0.42	0.09	0.28

Conclusions

- Wastewater Treatment
  - All SCR may require wastewater treatment for the air heater wash water
- SO_3 Removal
  - For high sulfur coal, the cost of additional air heater washings & wastewater treatment is significantly less than the cost of SO_3 removal
- Catalyst Life
  - Early catalyst replacement cost ~ air heater WWT cost
  - Earlier catalyst replacement eliminates the need for SO_3 removal (high sulfur coal)

Recommendations

- SO_3 measurements
  - Before and during SCR operation – determine where SO_3 is formed and removed
  - During SCR operation – determine whether percent removal or ppm removed is constant with increased SO_3
- NH_3 measurements
  - Wash air heater after first ozone season and collect wash water samples to estimate NH_3 in air heater. Monitor NH_3 slip (at SCR outlet) and NH_3 in fly ash → determines NH_3 slip distribution
  - After first ozone season, increase NOx removal to increase NH_3 slip – to point where deposits are formed in air heater to determine plant specific Radian number