REINHOLD ENVIRONMENTAL Ltd.

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power generation group

"Upstream" FGD Wastewater Treatment

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Reinhold Environmental 21st APC Round Table & Expo
Louisville, KY
July 14 - 15, 2014

Agenda

- Introduction
- Combustion Additives
- Sorbent Injection
- AQCS Equipment Operation
- WFGD Additives
- Conclusion

Introduction

Federal Effluent Limitation Guidelines (ELG) will require control of Hg, As, Se, and nitrate-nitrite in FGD

Environmental Protection Agency

40 CFR Part 423

Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Proposed Rule

FEDERAL REGISTER

Other local regulations may exist with different limits or additional constituents

Introduction

Mass balance

- In = out

All inputs and outputs throughout combustion and flue gas path processes can affect what is treated by the FGD wastewater system

- Combustion
- Additives
- Reagents and sorbents
- Disposal and purge streams

Introduction

Constituents of Concern – Hg, As, Se

Generally released in the gas phase during the combustion process

Hg

- Partitioning between vapor and particulate depends on various factors
  - Concentration, combustion, halogen content, and downstream devices
- Hg^0 gas
- Hg^{2+}
  - adsorb on solid
  - soluble in liquid, can be precipitated

Introduction

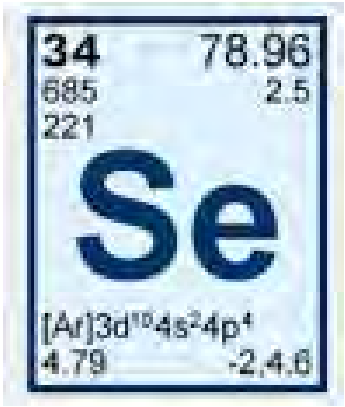
As

- Gas phase condenses on fly ash particles
- As^{3+}
  - soluble in liquid, can be precipitated
- As^{5+}
  - largely retained in WFGD solids
  - soluble in liquid, can be precipitated

Introduction

Se

- Se^{2+} bound to solids
- Se^{4+}
  - largely retained in WFGD solids
  - soluble in liquid, can be precipitated
- Se^{6+}
  - soluble in liquid, difficult to precipitate
- Appears to behave similar to Hg



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Combustion and Combustion Additives

Combustion Effects

- LOI/UBC – excess carbon can adsorb Hg, resulting in less Hg in the FGD wastewater

Refined coal

- Hg
  - Hg emissions are reduced through oxidation and capture in WFGD, but results in greater concentration in wastewater
- As
  - Calcium in the product binds As in solid form, so it doesn't get to the wastewater
- Se
  - No effect

Combustion Additive

Mitagent™

- Hg
  - Positive effect on Hg capture due to increased oxidation
  - Reduces the halogen required, so the halogen is reduced in the wastewater
- As
  - No effect
- Se
  - Reduces Se in gas, likely results in less in wastewater

Effect of Combustion Additive on Hg Oxidation

PRB unit with ESP

Br Addition Rate (ppm dry)	% Oxidized Hg w/out Mitagent	% Oxidized Hg w/ Mitagent
0	37	38
35	Not Tested	56
60	47	75
100	63	84

*Leads to greater Hg capture

Effect of Combustion Additive on Emissions

PRB unit with SCR, ESP, CDS, FF

Additive Injection Rate	Gas phase selenium lb/Mbtu	Gas phase arsenic lb/MBtu
Baseline	3.95* 10 E -6	2.32 *10 E -6
100 ppm of $CaBr_2$ solution	4.91 * 10 E -6	2.20 * 10 E -6
30 lb/hr Mitagent + 70 lb/hr S-SORB III+ 100 ppm of $CaBr_2$ solution	3.69 * 10 E -6	1.76 *10 E -6

*** Reduces gas phase Se**

Halide Addition

Halide can be introduced through specific injection for Hg oxidation or can be from brominated PAC

- Any injected halogen will make its way to the FGD wastewater
- In water, these can form THM's

Oxidizes Hg for capture in WFGD, which goes to wastewater

Increases overall Se concentration in flue gas and WFGD, speciation impact not known

No known impact on As

Effect of Halide Injection on Selenium

Eastern bituminous unit with SCR, ESP, WFGD

Test	Gas Phase Se ESP Inlet Avg (ug/dscf)
Baseline	5.33 x 10-6
w/ Bromine Injection	2.14 x 10-5
% Increase	301%

WFGD samples collected during this period also show increased Se

Effect of Halide Injection on Selenium

PRB unit with SCR, ESP, WFGD

Test	Gas Phase Se SCR Inlet Avg (ug/dscf)	Gas Phase Se WFGD Inlet Avg (ug/dscf)
Baseline	5.76 x 10-5	1.6 x 10-5
w/ Bromine Injection	6.4 x 10-5	3.8 x 10-5
% Increase	11%	137%

* Increases gas-phase Se

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Sorbent Injection

PAC and Amended Silicates

- Adsorbs Hg^{2+} from flue gas
- Br from BPAC ends up in wastewater
- No impact on Se

DSI

- Reduces As and Se through reactions
- No impact on Hg
- Can increase Br required for Hg oxidation

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AQCS Equipment Operation

SCR

- Oxidizes Hg, reducing halogen needed
- Excess NH_3 slip likely contributes to increases in nitrites/nitrates

ESP

- ESP performance/oxidizer formation may affect WFGD ORP, which affects speciation and liquid/solid phase partitioning
- Some improve Hg oxidation, improving capture
- No testing yet on As and Se speciation impacts

FF

- Captures more particulate bound Se

WFGD Operation

ORP

- Results from high concentration of strong oxidizers
- In the absence of additives, drives Hg speciation and partitioning
  - High ORP ⇒ less Hg in WFGD solids
  - More Hg is fed to the wastewater system
- Drives As speciation
  - High ORP ⇒ more As^{5+}
- High levels of oxidizers with high ORP drives perchlorate and persulfate formation
  - Negatively impacts bio-reactor performance

WFGD Operation

ORP

- Drives Se speciation
  - High ORP ⇨ more Se^{6+}
  - Se^{4+} is removed by phys-chem system
  - Se^{6+} not readily removed in phys-chem systems and requires biological treatment
  - Forced oxidation may increase Se^{6+}

WFGD Effluent

Reactions in wastewater stream continue while in transit to treatment

Buffering capacity of the solids is removed

Strong oxidants may react to produce acid in the liquid phase, lowering the pH

- may result in added costs to the plant as more alkalinity must be added in treatment for neutralization

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WFGD Additives

Sulfide additives for mercury

- Prevents re-emission by precipitating Hg, sub-saturating WFGD slurry to permit more Hg^{2+} capture
- Lowers ORP
  - Drives speciation
- Precipitates Hg^{2+} and As^{3+}, so less goes to wastewater
  - Reduced As^{3+} by ~30-60%

WFGD Additives

Sorbents

- PAC is an alternate to sub-saturate Hg in WFGD slurry

Other additives

- Flocculent (for dewatering improvement) probably does not impact WWT
- DBA lowers pH which tends to oxidize, but specific testing not performed
- Other reducing agents in development, testing required

Effect of WFGD Additive on Speciation

Eastern unit bituminous with SCR, WFGD

- Data still being analyzed
- Certain additives appear to result in more Hg^{2+} precipitation than others
- Certain additives appear to result in more As^{3+} precipitation than others
- Certain additives appear to result in more Se^{6+} than others
- Will be presented at the MEGA Symposium

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Conclusion

Coal additives, WFGD additives, and other operational parameters affect the mass flow of Hg, As, and Se in the WFGD effluent

It is possible to reduce the amount of these constituents that require treatment

- Coal additives lower the gas-phase concentrations of Hg, As, and Se ⇨ lower concentration in WFGD effluent
- WFGD additives precipitate Hg and As ⇨ lower concentration in WFGD effluent
- Controlling WFGD chemistry can lower concentrations in effluent
- Managing upstream AQCS equipment can decrease negative effects

Conclusion

Reducing the amount of the elements of concern going to the wastewater treatment system should result in:

- lower operating costs (less chemical addition)
- more margin in system performance, providing flexibility
- higher availability for sensitive systems, such as bioreactors

Operational optimization can help with maintaining steady conditions to WWT, also improving operability

power generation group

THANK YOU! QUESTIONS?

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