Wastewater Treatment and Zero Liquid Discharge Technologies: Overview and New Developments

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Presentation To:
McIlvaine Hot Topics - Control and Treatment Technology for FGD Wastewater
Thursday August 15, 2013, 10:00am CDT
Topics To Be Covered

• Overview of ELG Regulations
• FGD Wastewater Treatment
  – Properties of FGD wastewater
  – FGD WWT System Design Considerations
• Discussion of ZLD technology
• Summary and Lessons Learned
Overview of Regulations

• What are ELG’s?
  – National standards established by EPA to specify control levels for liquid discharges from power plants
  – Approximately 1,100 power plants covered by regulations
  – Implemented through National Pollutant Discharge Elimination System (NPDES) program

• History of ELG’s:
  – Rules first issued in 1974 Clean Water Act
  – Revised in 1977 and 1982
  – No changes in last 30 years
Proposed New Effluent Limitation Guidelines

• New regulations expected to be implemented between 2017 and 2022 through 5-year NPDES permit cycle
• Based on BACT standards
• Standards different for existing and new sources
• Four preferred alternatives for regulation of existing discharges and one preferred alternative for new sources
• Regulations will establish new limits for mercury, arsenic, selenium, and nitrate-nitrite in FGD wastewater
## ELG Limits for FGD Wastewater

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<tr>
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<th>Daily Max</th>
<th>Monthly Average</th>
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<tbody>
<tr>
<td>Arsenic, total</td>
<td>8 ug/l</td>
<td>6 ug/l</td>
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<tr>
<td>Mercury, total</td>
<td>242 ng/l</td>
<td>119 ng/l</td>
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<tr>
<td>Selenium, total</td>
<td>16 ug/l</td>
<td>10 ug/l</td>
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<tr>
<td>Nitrate/Nitrite as N</td>
<td>0.17 mg/l</td>
<td>0.13 mg/l</td>
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Voluntary Incentive Program – Two Tier Program

**Tier 1:**
Two additional years to comply with regulations in exchange for dewatering and closing all CCR impoundments (except for leachate)

**Tier 2:**
Five additional years to comply in exchange for eliminating all discharges
  - Requires amount of wastewater generated to be reduced and reused
  - Cooling water discharges are excluded from requirement
FGD Wastewater Treatment
FGD Wastewater Background

- Wastewater a result of need to purge chlorides from scrubber
  - Corrosion of alloy materials
  - Ability of scrubber to obtain acceptable limestone utilization

- Ways that chlorides are purged from scrubber
  - Free moisture in FGD byproducts
  - Low solids purge stream

- Characteristics of FGD wastewater
  - Suspended solids
  - Major species: Ca, Mg, Na, SO3, SO4 and Cl
  - Trace species: As, B, Br, F, I, Hg, Se, Mn
  - Heavy metals
  - Nitrogen (nitrates and nitrites)
  - ORP: Can affect oxidation state of Se and Hg
• Composition depends on:
  – Properties of fuel, reagent and makeup water
  – FGD process design and operation

• Wastewater from FGD can be saturated with gypsum. Can lead to scaling in WWT filtration and evaporation equipment
Design and Operation of FGD Can Affect Wastewater Properties

- Forced oxidation versus natural or inhibited oxidation
  - ORP
  - Amount of free moisture in byproducts
- High versus low chloride – Can affect sulfate levels and degree of gypsum supersaturation
- Operation
  - Filtercake wash?
  - Filtercake free moisture
Design Considerations for WWT Treatment

• Concentration limits for pollutants in effluent
• Design chloride level for FGD
  – Function of inlet flue gas conditions, makeup water properties and corrosion resistance of building materials
  – Determines the volume of purge water required
  – Economic trade-offs between cost of materials and volume of purge need to be evaluated during design phase
• Purge stream should be as low in suspended solids as possible and should not be diluted
• Properties of wastewater need to be considered in design of WWT system: pH, temperature, ORP, composition, degree of supersaturation
Theoretical Scrubber Cl⁻ Blowdown Rate

Assumptions: 600 MW; Fuel HHV – 12,000 Btu / lb; Heat Rate – 10,500
Discussion of ZLD Technology
ZLD Treatment Options

- Deep well injection
- Evaporative thermal process
- In duct evaporative process
- Wastewater spray dryer
- Non-thermal process
Deep Well Injection

- Deep well injection:
  - Waste must be treated before injection
  - Lower capital and O&M costs
  - Higher environmental risk
  - Not an option in some regions
Evaporative Thermal ZLD

- Evaporative thermal process:
  - Brine concentrator for initial concentration of wastewater
    - Reverse osmosis treatment
    - Thermal evaporative (e.g., Vertical tube falling film)
  - Crystallizer
  - Removal of suspended solids and Ca^{++} required prior to treatment
  - High capital and energy requirements
  - Dissolved salts present in FGD wastewater, like CaCl₂, hydrolyze at high temperature and become acidic and corrosive
  - Fairly complex operating and maintenance requirements
Block Diagram for Evaporative Thermal ZLD
Wastewater Evaporation System

- Direct injection of wastewater into ductwork
- Salts collected with fly ash in particulate control device
Wastewater Spray Dryer

- Addition of wastewater to small spray dryer installed in flue gas slipstream bypassing air heater
- Salts collected with fly ash in particulate control device
Overview of Non-Thermal ZLD Process

• Fixation and Blending for Disposal in Landfill:
  – Mixture of scrubber solids (e.g., gypsum), fly ash, lime (if required) and waste water to produce a cement-like product suitable for disposal in landfill
  – Non-thermal technology
  – No pretreatment of wastewater
  – Has potential to eliminate all discharges from plant (operate as ZLD plant)
  – Low capital and operating costs
  – Reduce quantity of ash available for resale
  – Should be preferred option due to low cost and simple O&M
Typical Composition of Stabilized Byproduct
- 30-35% gypsum
- 30-35% fly ash
- 30-35% purge water
- 2-4% lime
Mix FGD wastewater with scrubber solids (gypsum or sulfite), fly ash, and lime (if necessary) to produce a stable and fixated waste material.

Place fixated waste material in dry landfill.

Return leachate and contact water to FGD.
Approach for Tier 1 and Tier 2 Incentive Compliance
Approach for Tier 1 and Tier 2 Incentive Compliance
Validation and Development Testing for Non-Thermal ZLD Process

• Scrubber slurry to be evaluated:
  – Gypsum
  – Calcium sulfite inhibited and natural oxidation
  – Inhibited mag-lime
  – High chloride levels

• Fly ash to be evaluated:
  – Class C
  – Class F
  – Ash with PAC
  – Ash with brominated PAC

• Blending tests followed by:
  – Compressibility testing
  – Permeability/leachability testing (LEAF)
Parting Thoughts

1. Have good understanding of FGD process chemistry to improve ability to predict properties of purge water and capability of FGD system to process miscellaneous plant wastewater
2. Have a reasonable and accurate design basis for fuel, inlet flue gas properties, reagent and water
3. Operate and optimize FGD system to reduce and minimize quantity of wastewater and to produce a consistent purge stream in terms of volume and properties
4. Optimize plant water management to reduce volume of process streams
5. Consider full range of load conditions and fuel properties in design
6. Operate CCR Handling and transport to minimize volume of leachate and contact water
THANK YOU

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