Worldwide Pollution Control Association

WPCA-Duke Energy FGD Wastewater Treatment Seminar

March 7, 2013

WPCA

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Treatment and Discharge of FGD Liquid Wastes

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Topics To Be Covered

- Overview of regulations
- Properties of FGD wastewater
- FGD design and operation
- Design considerations for WWT
- Discussion of technology
  - Physical-chemical treatment
  - Biological treatment
  - Constructed wet lands
  - Zero liquid discharge technology
- Summary and lessons learned

Overview of Regulations

- Current Regulations for plant liquid discharges to surface waters:
  - Rules first issued in 1974 Clean Water Act
  - Revised in 1977 and 1982
  - No changes in last 30 years
  - Implemented through National Pollutant Discharge Elimination System (NPDES) program
- EPA currently revising Effluent Limitation Guidelines (ELG) for power plants:
  - New regulations expected to be implemented between 2014 and 2019 through 5-year NPDES permit cycle
  - Based on BACT
- Some state limits as low as: 1.3 – 12 ppt – Hg; 10 – 100 ppb - Se

Scope of New ELG Regulations

- FGD wastewater
- Fly ash transport water
- Bottom ash transport water
- Collected leachate and runoff from dry landfills containing CCR
- Flue gas Hg control wastes (e.g., ACI)

FGD Wastewater

- 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 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

FGD Wastewater (continued)

- 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 and processes

FGD Design and Operation 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

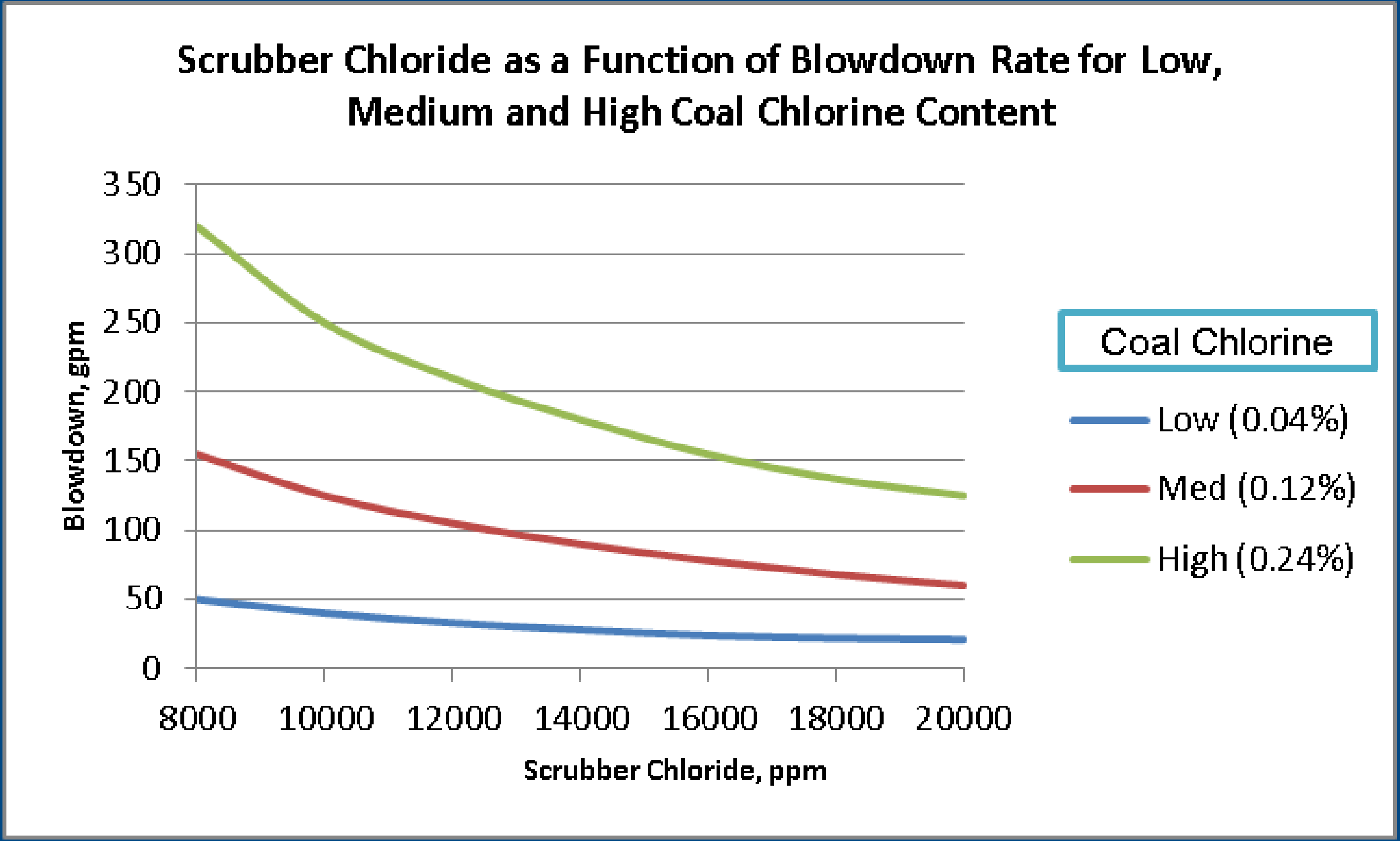
What is ORP

- Measure of redox potential of slurry. Indication of if environment is oxidizing or reduced. Also indication of how strongly oxidized or reduced
- ORP determined by:
  - Process: forced oxidized versus natural or inhibited oxidation
  - The quantity of a number of reduced sulfur species and sulfur – nitrogen species
  - Trace transition metals
- ORP can:
  - Determine form of selenium (selenite versus selenate)
  - Determine oxidation state of mercury
  - Can affect solubility of Mn which is thought to be a cause of under deposit corrosion of duplex SS and higher grade alloys

Design Considerations for WWT Treatment

- Effluent limits
- Design chloride level for FGD
  - Function of inlet flue gas conditions, makeup water properties and corrosion resistance of building materials
  - Determined the volume of purge water
  - 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

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Discussion of Technology

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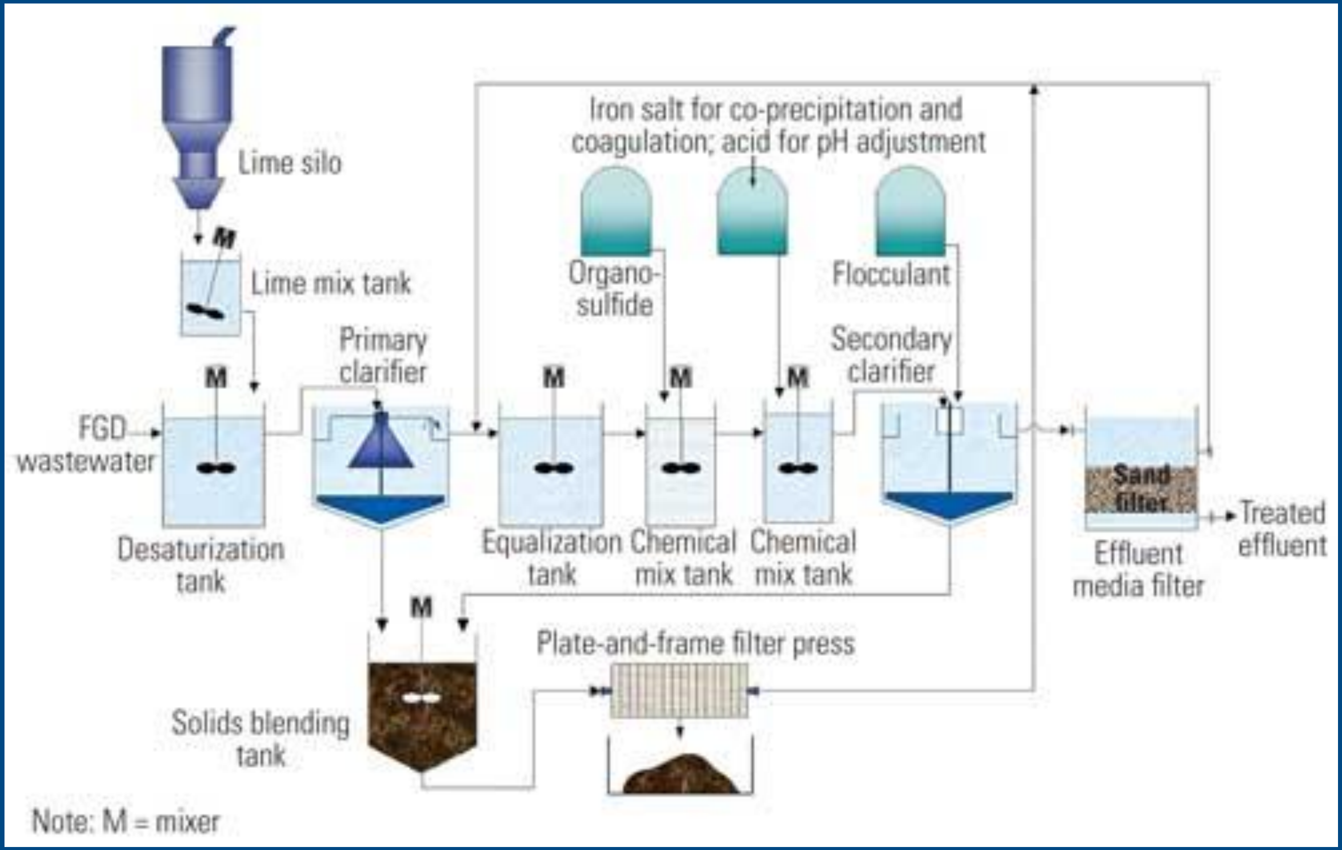
WWT Treatment Options

- Physical-chemical treatment
- Biological treatment
- Constructed wet lands
- Zero liquid discharge technology

Overview of Physical-Chemical Treatment



Source of flow diagram – CH2MHill

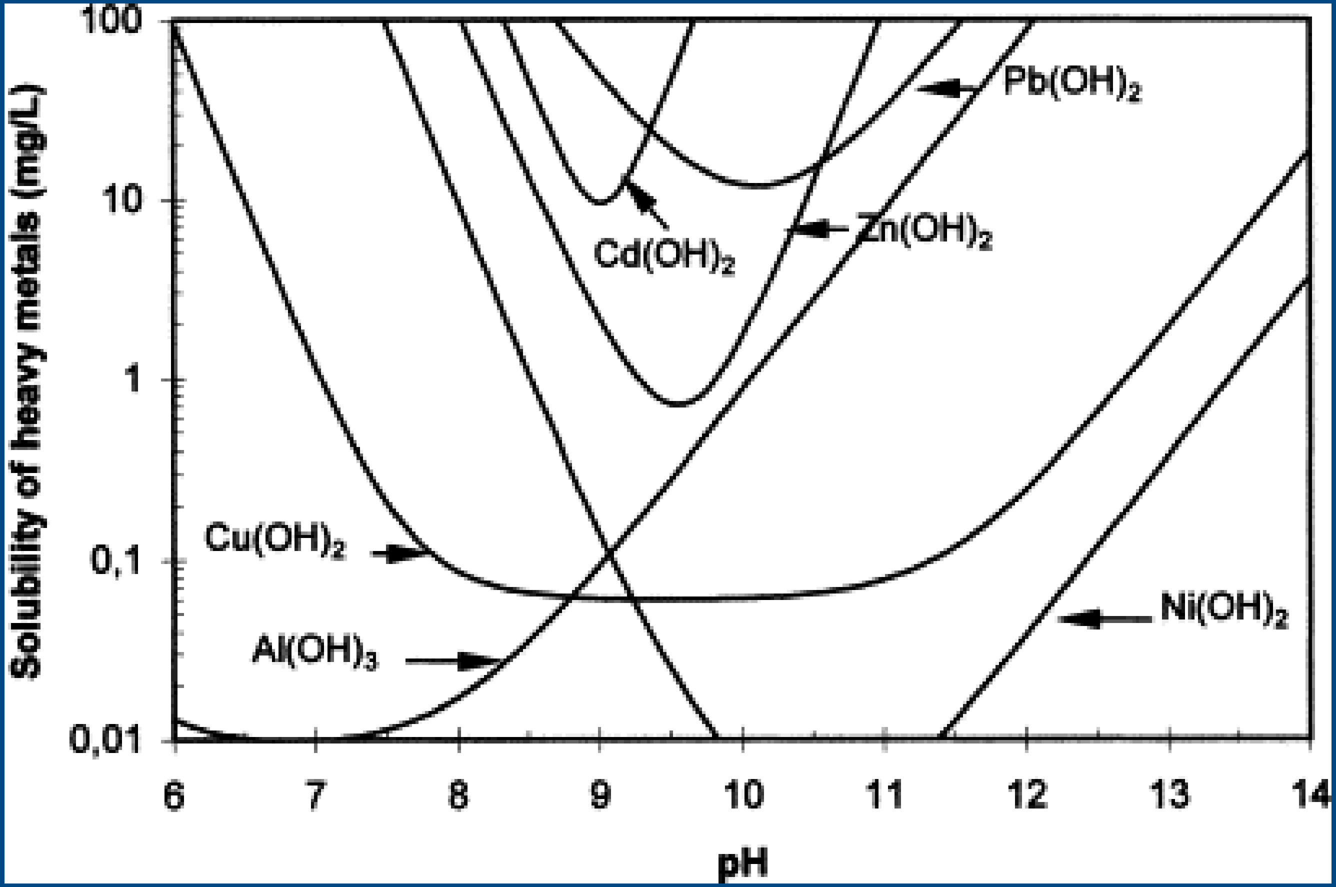
Discussion of Treatment Steps

1. Desaturation
    a. Raise pH to about 8.5 to precipitate gypsum
    b. Do not want to get too high on pH and precipitate all of the Ca and Mg
    c. Retention time – about 30 minutes
    d. Sludge from first clarifier recycled to provide seed solids (nucleation sites)
2. 1^{st} Clarifier
    a. Remove fine gypsum and other suspended solids
    b. Design similar to FGD sludge thickener
    c. Common to add flocculent to improve settling
    d. Targeting 10 to 20 wt.% in underflow
    e. Typical overflow rate – 0.5 gpm/sft

Discussion of Treatment Steps (continued)

3. Equalization Tank
   a. Used to provide consistent flow and composition to chemical treatment steps
   b. May be located upstream of desaturation tank or close to scrubber depending on number and location of influent streams
4. Chemical Treatment Tanks
   a. Metals removed by precipitation as metal-hydroxide or metal-sulfide (example - mercury-sulfide [cinnabar])
   b. Metal-sulfides precipitate so rapidly that they are too fine to settle
   c. Sulfide is bonded with large organic molecule – organo-sulfide
   d. Ferric chloride is dosed at high concentration and precipitates
   e. Metals co-precipitate with the iron and are removed (example – selenite)
   f. Retention times in chemical treatment tanks typically 10 – 15 minutes

Solubility of Metal Hydroxides



Discussion of Treatment Steps (continued)

5. 2nd Clarifier
   a. Used to settle precipitated metals to a solids concentration of 10 to 20 wt.%
   b. Typical overflow rate – 0.33 gpm/sft
   c. Lamella clarifiers are an option if space is limited
   d. Polymers (coagulant and flocculent) often added to facilitate settling
6. Effluent media filtration
   a. Used to remove un-settled suspended solids and metal precipitates
   b. Filters will need to be back-flushed
   c. Control of gypsum RS is important because filters are prone to scaling
7. Ion-exchange technology
   a. Sometimes used for challenging treatment applications (example – B removal)
   b. Very prone to scaling. Should not be regenerated with H2SO4

Discussion of Treatment Steps (continued)

8. Sludge dewatering
   a. Filter presses most common
   b. Work best at feed solids concentration of 10 to 20 wt.%
   c. Typical dewatered solids concentration 60 to 70 wt.%
   d. Sludge transported and disposed of in dry landfill

Overview of Biological Treatment

- Biological treatment (SBR) are located downstream of phys-chem treatment
- Needed to remove BOD/COD, NO3, Selenate and B
- Activated sludge process – need to maintain population of anaerobic bacteria to treat waste water
- Anaerobic bacteria reduce selenate and ionic Hg to elemental forms where they are no longer soluble
- Process typically more challenging for O&M
  - Problems with high or low temperature
  - Problems with high salinity
  - Works best with consistent influent flow and influent properties, does not work well as a batch operation

Constructed Wetlands

- Wastewater flows through microbial and bacteria rich material such as compost
- Requires a large area for treatment
- Novel vertical flow design is being evaluates as means to reduce size
- At some point the bacteria rich material needs to be removed and disposed

Overview of Zero Liquid Discharge Technologies

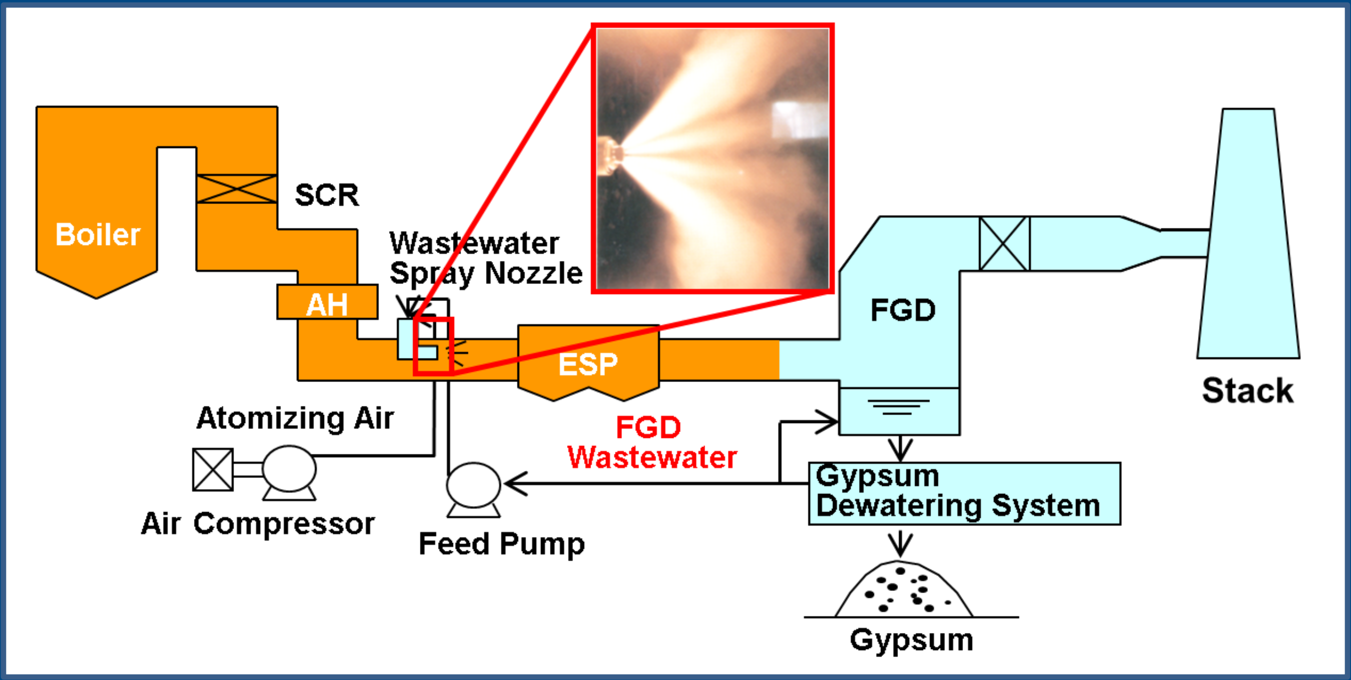
- Deep well injection:
  - Waste must be treated before injection
  - Lower capital and O&M costs
  - Higher environmental risk
  - Not an option in some areas
- Evaporative Thermal System:
  - Typical system – R.O. brine concentrator followed by crystallizer
  - Removal of suspended solids and Ca^{++} required prior to R.O. system
  - High capital and energy requirements
  - Dissolved salts present in FGD wastewater, like CaCl2, hydrolyze at high temperature and become very acidic and corrosive
  - Fairly complex operating and maintenance requirements

Overview of Zero Discharge Technologies (cont.)

- Fixation and Blending for Disposal in Landfill:
  - Mixture of scrubber sludge, fly ash, lime (if required) and waste water to produce a cement-like product suitable for disposal in landfill
  - Non-thermal technology
  - Low capital and operating costs
  - Reduce quantity of ash available for resale
  - May be preferred option due to low cost and simple O&M

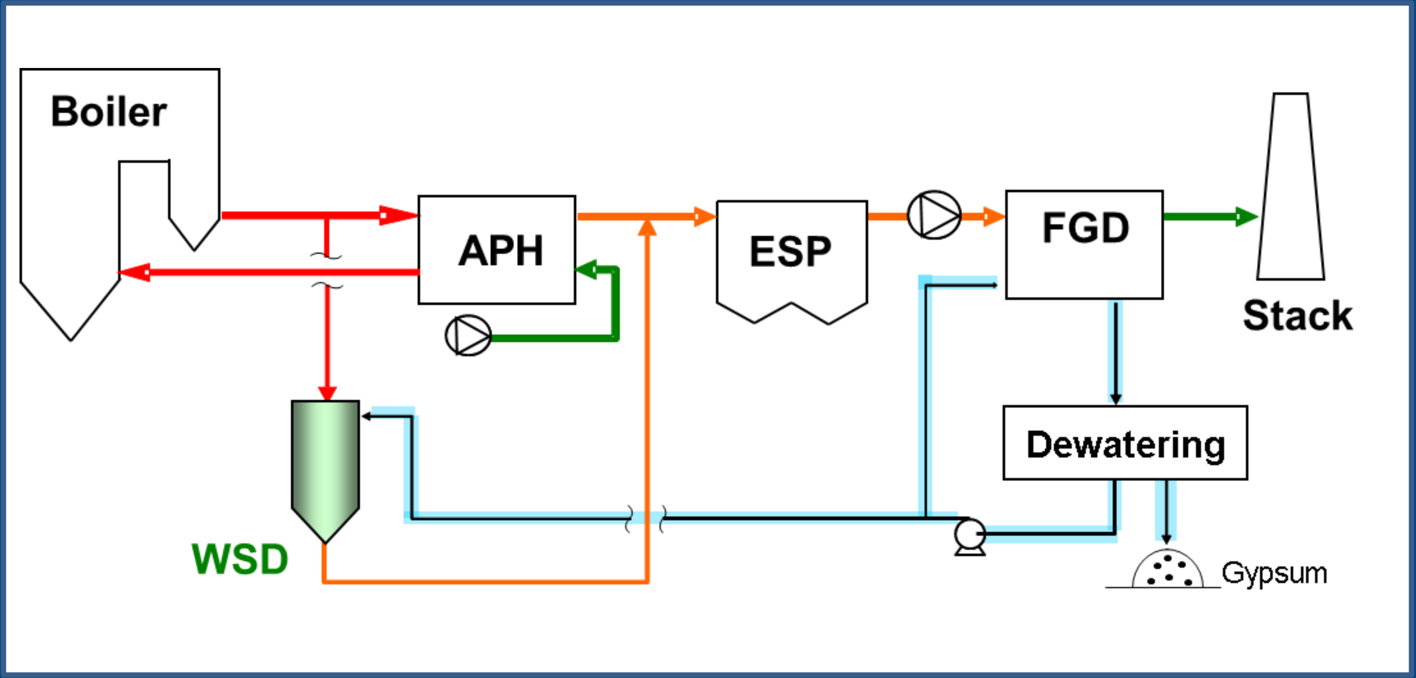
Overview of Zero Discharge Technologies (cont.)

- **Wastewater Evaporation System (WES)**
  - Direct injection of wastewater into ductwork
  - Salts collected with fly ash in particulate control device



Overview of Zero Discharge Technologies (cont.)

- **Wastewater Spray Dryer (WSD)**
  - Addition of wastewater to spray dryer installed in slipstream bypassing air heater
  - Salts collected with fly ash in particulate control device



Summary and Lessons Learned

1. Have good understanding of FGD process chemistry to improve ability to predict properties and wastewater
2. Have a reasonable and accurate design basis for fuel, inlet flue gas, reagent and water
3. Operate and optimize FGD system to reduce and minimize quantity of wastewater
4. Operate and optimize FGD to generate a consistent influent stream in terms of flow and properties
5. For FGD systems not producing wallboard spec gypsum, operate dewatering system to purge maximum amount of chlorides recognizing that some, but not all, of the chloride will come back with leachate

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