McIlvaine Hot Topic Hour
Evaporation and Crystallization of FGD Wastewater

September 3, 2009
Innovative Process Solutions
Utilizing Evaporation & Crystallization as Core technologies
ZLD for FGD as practiced today

A2A S.p.A. (formerly Endesa Italia)
- Monfalcone Power Plant, Italy
- 336 MW Coal-Fired w/ LSFO Scrubber (MHI)
- ZLD Operational Summer 2008
- Dry Cake for Landfill Disposal

Lime-Soda Softener

Brine Evaporator
Brine Crystallizer
Three Major Unit Operations

- A Softening System to reduce the overall solids and hardness content down to a level that is manageable for the evaporation system.

- A Falling Film Evaporator (MVR) to remove the major portion of water from the FGD purge stream.

- A Crystallizer (usually steam, can be MVR) to finish the process by removing the remainder of the water.

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Chemicals

FGD Purge

Softening System

Power

Evaporator

Steam

Crystallizer

Salts

Sludge

Recovered Water
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Salts
Requires chemicals, power & steam, produces sludge
Softening aids crystallization

**Softening** FGD wastewater with lime and soda ash substitutes sodium ions for most of the calcium and magnesium ions.

CaCl₂ and MgCl₂ have very high solubility – **difficult to crystallize out**. Softening changes the chemistry of FGD wastewater to NaCl, which crystallizes easily.
Softening Reactions

- \( \text{Mg}^{+2} + \text{Ca(OH)}_2 \)  
  \((\text{lime})\)  
  \(\rightarrow\)  
  \(\text{Mg(OH)}_2 \downarrow + \text{Ca}^{+2}\)  
  \((\text{sludge})\)

- \( \text{Ca}^{+2} + \text{Na}_2\text{CO}_3 \)  
  \((\text{soda ash})\)  
  \(\rightarrow\)  
  \(\text{CaCO}_3 \downarrow + 2 \text{Na}^{+1}\)  
  \((\text{sludge})\)
Soften the FGD purge - create a NaCl based chemistry

FGD purge CaCl2-MgCl2 Chemistry

Lime and Soda Ash

Softening

FGD purge CaCl2-MgCl2 Chemistry

CaCO3-MgOH2 sludge

NaCl Chemistry

Brine Concentrator

Electric Power

Recovered water

Evaporator Blowdown

NaCl Crystallizer

Steam and/or Electric Power

Centrifuge or Filter

Salt (NaCl)

Pretreatment

Primary Water Recovery

ZLD section
What’s new?

No pretreatment – Crystallizer based on industrial CaCl₂ production

No Pretreatment

Primary Water Recovery

ZLD section

FGD purge CaCl₂-MgCl₂ Chemistry

Electric Power

Recovered Water

CoLD™ Crystallizer

Steam and/or Electric Power

Centrifuge or Filter

Salt CaCl₂ & MgCl₂

Recovered Water

Brine Concentrator

Evaporator Blowdown

No Pretreatment

Primary Water Recovery

ZLD section
Requires power and/or steam, no chemicals, reduced sludge
Two Options for Evaporation of FGD Wastewater

Option 1: Pretreat FGD Wastewater Using Lime-Soda Ash softening
- Replace Ca and Mg with Na
- Chemistry is based on NaCl

Option 2: Evaporate FGD Wastewater Directly
- Chemistry is based on CaCl₂ and MgCl₂
At atmospheric pressure, the boiling point curve chases the solubility curve.
By lowering the pressure, the boiling point is lowered and a solid phase can form.
Crystallization of high solubility salts at Low Temperature and Deep Vacuum
What is the CoLD™ Process?

- A conventional forced circulation crystallizer fitted with a vacuum system.
- Energy for evaporation can be provided by a conventional indirect heat pump, using a refrigerant fluid.
- Alternately, energy for evaporation can be provided by steam, and low temperature sink can be provided by chilled water.
- Low operating temperature lowers the solubility of the dissolved salts, so they crystallize at a lower concentration.
- CoLD™ Process suited for waste streams containing highly soluble salts (e.g. FGD and IGCC blowdown, produced water, landfill leachate).

Confidential to HPD
Steam Driven CoLD™ Crystallizer
Indirect Heat Pump CoLD™ Crystallizer
Advantages of New HPD Process

- No softening required => No chemicals required, no sludge produced.
- A stable, solid product is produced directly using only electric power.
- Chemical costs are eliminated and solids disposal costs are greatly reduced.
- Energy costs are still low.
- Complexity and footprint of equipment are greatly reduced.
- Materials of construction can be reduced.
Result of CoLD™ Process ZLD
Economic comparison of FGD ZLD Options

Facility Comparison

- ZLD #1: 350 gpm capacity, Softening, Evaporator, Crystallizer
- ZLD #2: 350 gpm capacity, Evaporator, CoLD™ Crystallizer

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<tr>
<th></th>
<th>ZLD #1</th>
<th>ZLD #2</th>
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<tbody>
<tr>
<td>Cap - Amor</td>
<td>$5.4MM</td>
<td>$5.4MM</td>
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<tr>
<td>O&amp;M</td>
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<tr>
<td>$/gal</td>
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NPV savings of $88MM over 15 yrs at 7% discount rate
Thank You

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