GE Water & Process Technologies

RCC® Thermal Products & ZLD

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Agenda

GE Water & Process Technologies RCC®
Thermal Products Group

Technology
- Background
- Projects

People
- Team
- Expertise

ZLD System Design
- FGD
- ZLD System Technical Design

Review & Questions

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Technology

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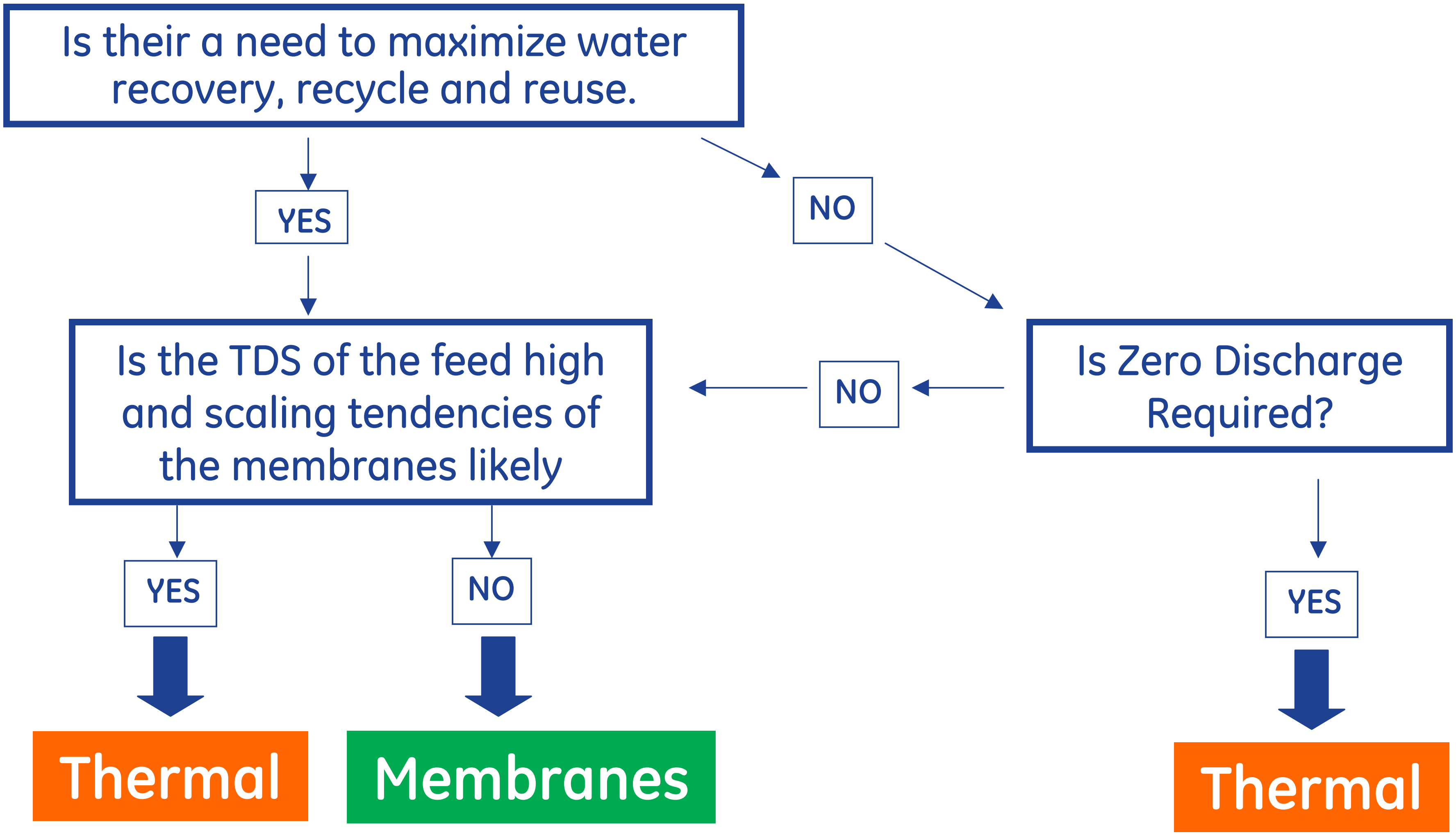
ZLD Design Considerations

- Maximize water recovery
- Wastewater minimization / achieve ZLD
- Disposal or use requirements for by-products and concentrates
- Reuse quality and quantity requirements
- Capital vs. energy costs
- Materials of construction

Why and When do you use Thermal?



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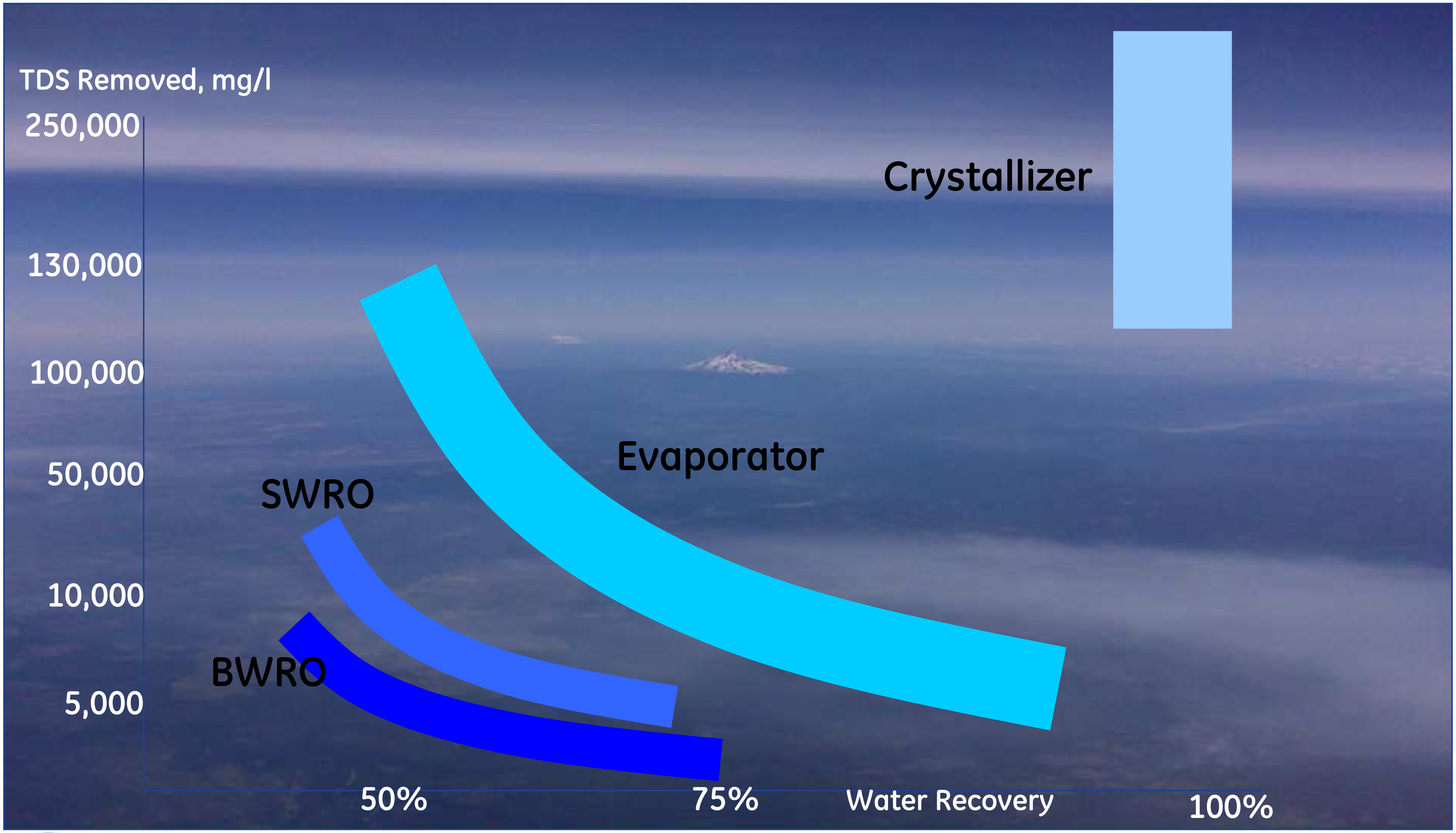
Application of Desal Technology:
Salt Removal and Recovery in Frac Water



Background

GE W&PT is the world leader in ZLD for thermal wastewater treatment with 85% market share. This combined with over 45 years of ZLD system experience provides customer confidence in ZLD system design and performance.

ZLD Waste Streams

- Cooling tower blowdown
- Demineralizer waste
- Process wastewater
- Ash pond blowdown
- Scrubber blowdown
- Plant drains
- Produced water
- Boiler blowdown
- Reverse osmosis reject
- Electrodialysis reject
- Mine drainage
- Salty effluents
- Landfill leachate

First with ZLD in the following industries:

- Power
- Synthetic fuels
- Primary Metals Processing
- Microelectronics
- Chemical
- Pulp & Paper
- Coal Mining
- Battery Manufacturing
- PVC Manufacturing
- Uranium Mining
- Petroleum & Petro Chemical
- Oil Refining
- SAGD Heavy Oil Recovery
- Co-generation
- Fertilizer
- Solid Waste (leachate and secondary sewage effluent)
- Coal Liquification
- Ethanol Production

First ZLD in Power Plants

HUNTINGTON, UT
1974

SAN JUAN, NM
1974

NAVAJO, AZ
1974

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First ZLD in Synthetic Fuels

SASOL, South Africa

1983

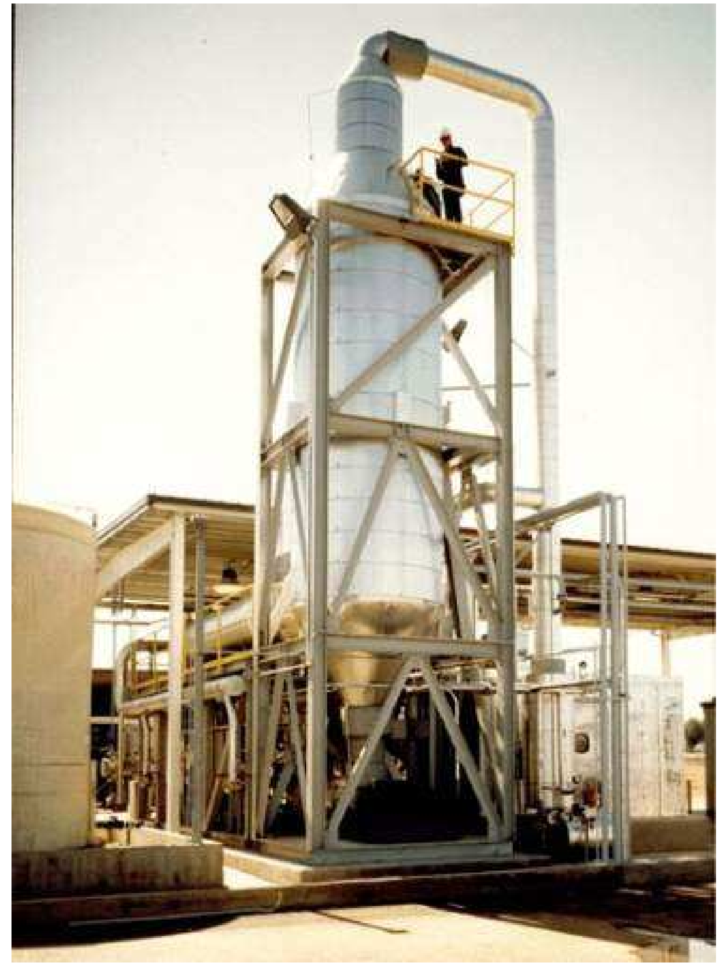
First ZLD in Microelectronics

IBM, AZ
1985

INTEL, AZ
2001

First ZLD in Chemical Plants

KERR MCGEE, NV
1989



AEROJET, CA
1990

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First ZLD in Oil Refineries

CADEREYTA / PEMEX, Mexico

1998

MADERO / PEMEX, Mexico

1999

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GE Water & Process Technology
RCC® Thermal Products

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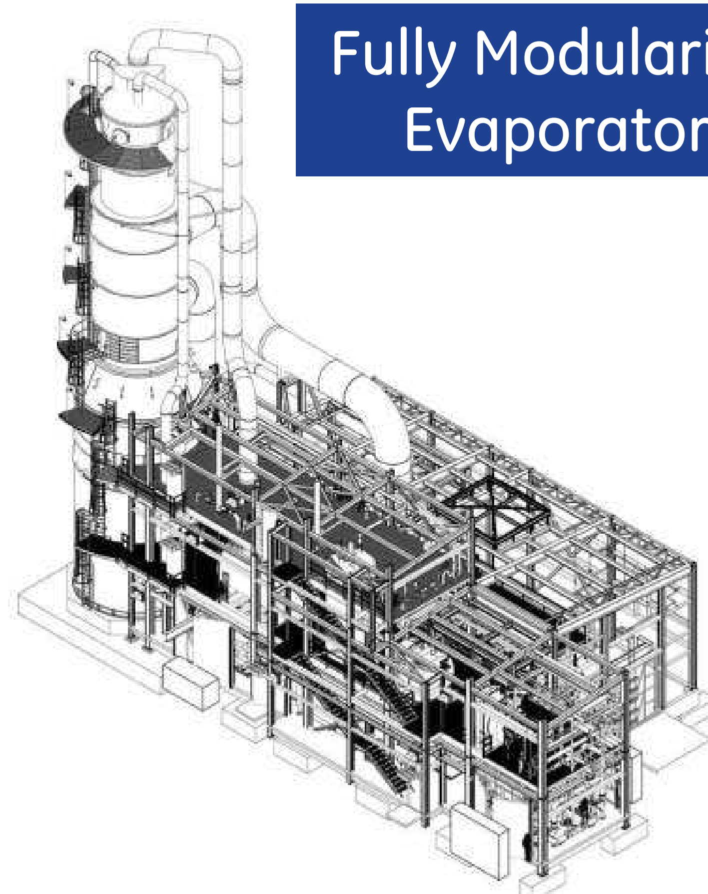
GE RCC® Thermal Products & ZLD Summary

- World leader in zero liquid discharge (ZLD) technology
- 40 years of thermal waste water re-use experience
- Over 150 operating evaporator and crystallizer units
- Supplied over 85% of all ZLD systems
- Replaced or modified 1/2 of the remaining 15%

GE RCC® Thermal Products Design Expertise

- Integration into the plant water balance
  - Consider all unit operations chemistry requirements
  - Perform technical and cost trade studies
- Evaluate reliability and design/operation risk issues
  - Solids characteristics
  - Operation and Maintenance
- Performance guarantees
- Continuing customer support

Fully Modularized Evaporators



People

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Thermal Team

The Thermal Products team is a highly qualified team of personnel with the specialized skills required for this business.

This staff includes:

- Commercial
- Engineering
  - Process
  - Application
  - Mechanical, electrical and instrumentation
  - and control design
- Project Management
- Procurement
- Product Management
- Finance
- Operations support and Quality Control
- Laboratory scientists and technicians

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ZLD design requires qualified personnel and management discipline to maintain control

GE W&PT - RCC® Thermal Products staff has evolved under the ownership and corporate discipline of Boeing, Halliburton, Ionics and now GE.

- Designing to detailed specifications.
- Interfacing with large AE's like Bechtel, CH2M Hill, WorleyParsons, Fluor, Black & Veatch, Stone & Webster, etc.
- Working with U. S. federal and local government organizations.
- Working with foreign governments.

ZLD design requires qualified personnel and management discipline to maintain control

Inexperience can lead to problems

You need to have

- Understanding the limits of the design and the chemistry
- Knowledge of proper material selection for longevity in a corrosive environment
- Experience in working with U. S. federal and local government organizations.
- Experience in working with foreign governments and with construction in countries around the world

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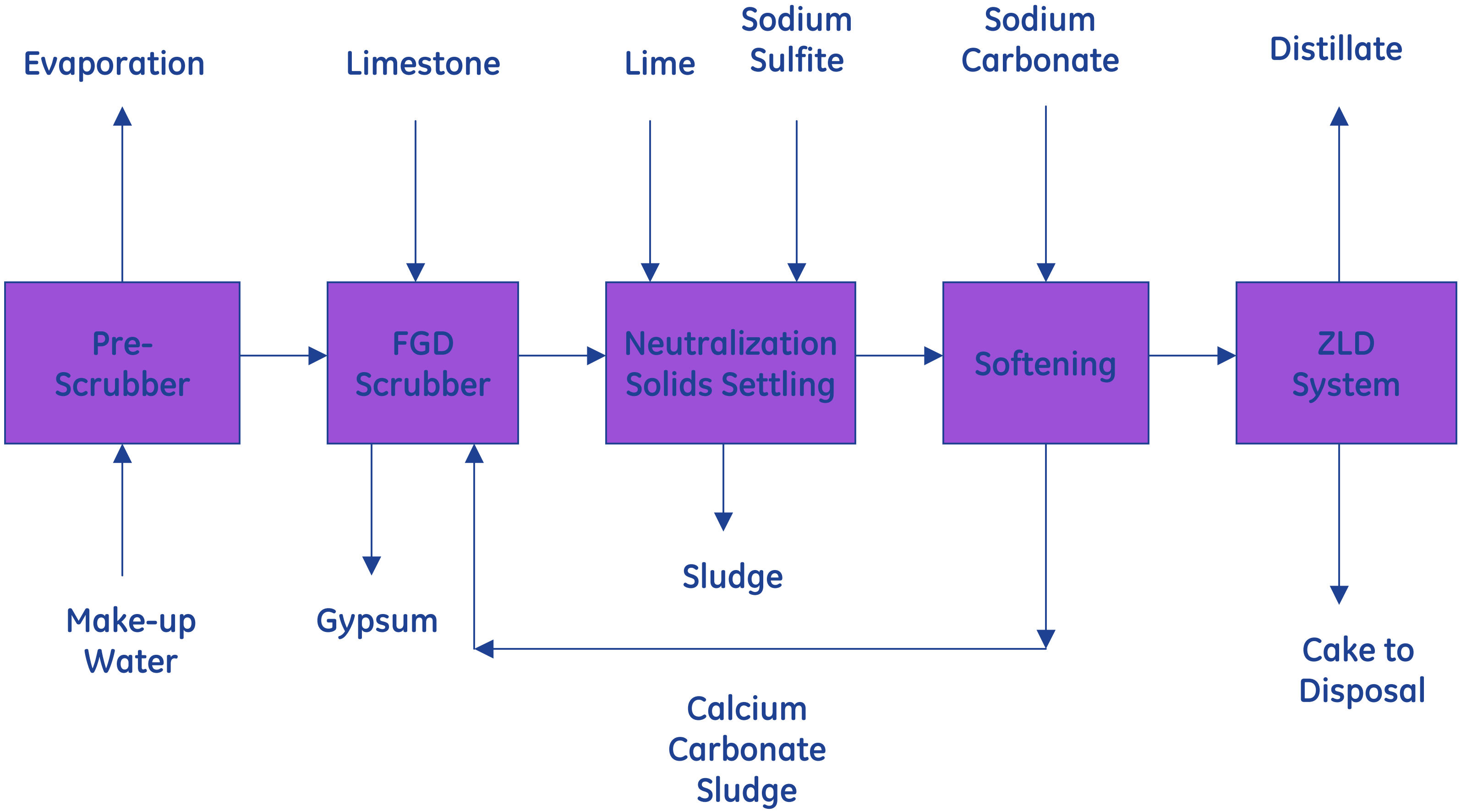
ZLD System Design

Flue Gas Desulfurization (FGD) Scrubber Blowdown Treatment

FGD Scrubber Blowdown Treatment Overall Flow Schematic



Typical FGD Blowdown Analyses

Calcium	4,000 – 20,000 mg/l
Magnesium	200 – 5000 mg/l
Sodium	75 – 1200 mg/l
Boron	10 – 400 mg/l
Chloride	10,000 – 40,000 mg/l
Fluoride	30– 200 mg/l
Nitrate	300– 1,400 mg/l
Sulfate	1500– 8,000 mg/l
pH	4 – 7
TDS	30,000 – 65,000 mg/l
COD	100 – 150 mg/l

Operational Challenges
FGD Blowdown Treatment

Gypsum scaling feed HX & deaerator

$CaCl_2$ & $MgCl_2$ buildup in crystallizer

Glauberite formation in Brine Concentrator

Seed recycle to maintain proper seed level

Feed pH control

Volatility of ammonia & boron

Foaming in BC and crystallizer

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FGD INSTALLATIONS

APS, Four Corner Station, NM

PSNM, San Juan Station, NM

Texas Utilities, Monticello Station, TX

Matsushima Power Station, Japan

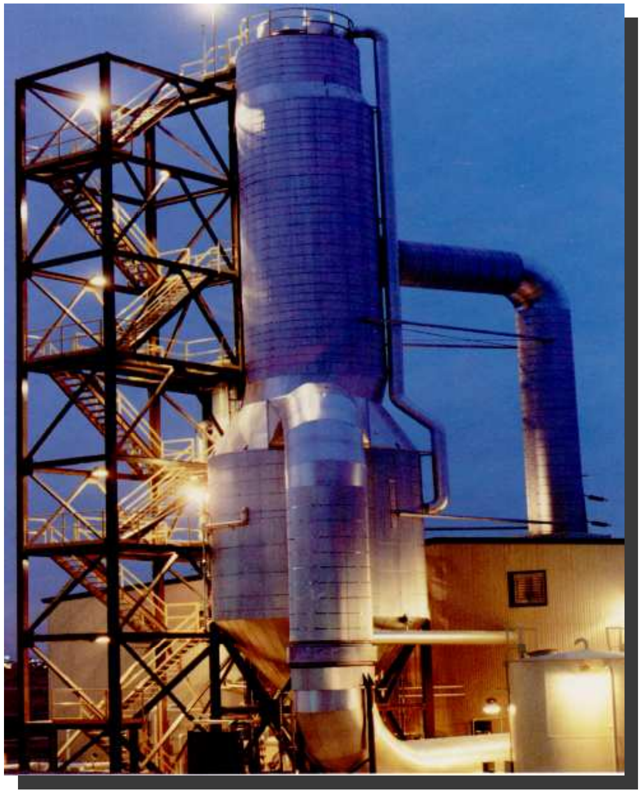
NYSEG, Milligan Station, NY

APS Four Corner Station, NM

400 gpm Brine Concentrator

Installed in 1979

Treats FGD scrubber blowdown, cooling tower blowdown



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San Juan Station, NM

Overall System Capacity – 3300 gpm

4 BCs installed 1974-84

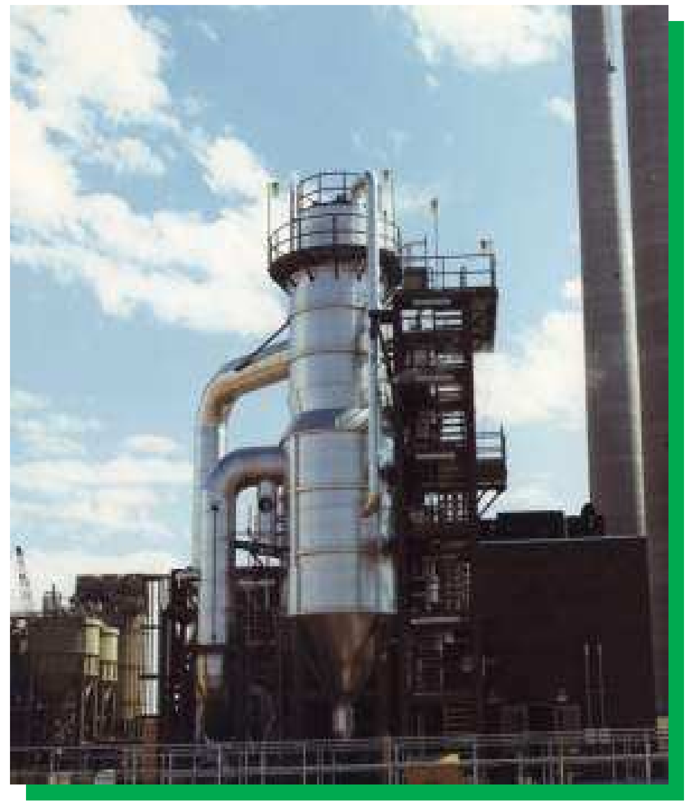
Treats FGD scrubber blowdown, ash-system runoff, demineralizer regeneration wastes, cooling tower blowdown

Monticello Station, TX

250 gpm Brine Concentrator

Installed in 1982

Treats mixture of FGD scrubber + cooling tower blowdown



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Matsushima Power Station, Japan

5 gpm Brine Concentrator

Installed in 2006

Treats FGD scrubber blowdown

NYSEG Design Feed Chemistry

Sodium	250 mg/l
Potassium	30 mg/l
Calcium	17,000 mg/l
Magnesium	60 mg/l
Chloride	30,000 mg/l
Sulfite	60 mg/l
Sulfate	980 mg/l
Boron	20 mg/l
pH	6.5
TDS	48,380 mg/l

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GE Can Meet the Challenges of ZLD Treatment of FGD Blowdown

FGD Blowdown Treatment since 1974

- Five installations treating FGD blowdown
- Extensive operational database

Can meet unique ZLD challenges

- Heat exchanger scaling
- Chloride salt buildup in crystallizer
- Glauberite formation
- Seed recycle
- pH control
- Ammonia and Boron carryover

ZLD SYSTEM Technical Design

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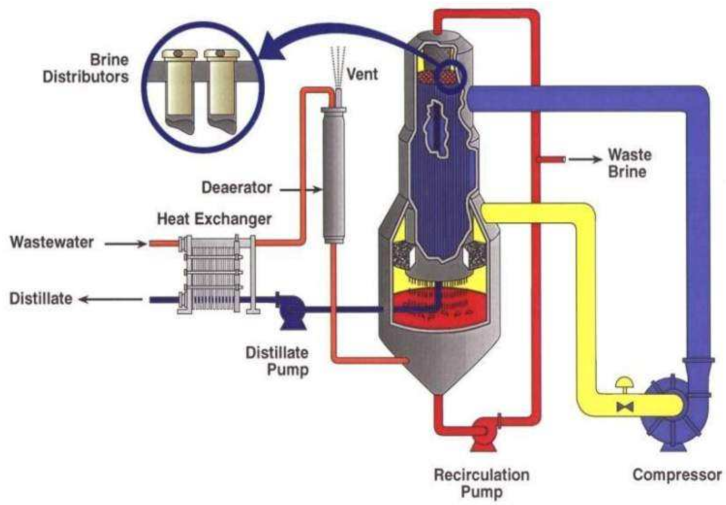
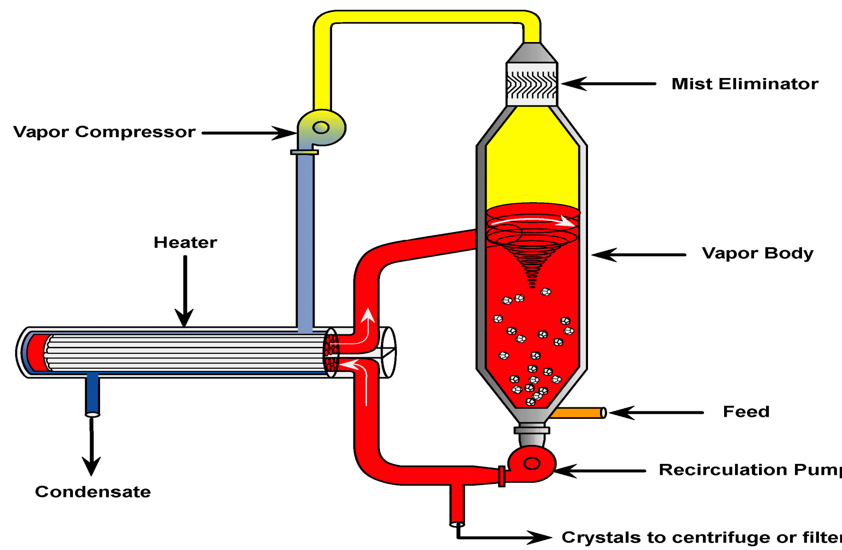
Evaporator and Crystallizer Technology Summary

Evaporator



Crystallizer



ZLD is achieved through the combination of evaporation followed by crystallization

Technology

Zero Liquid Discharge by Evaporation

- Seeded Slurry Brine Concentrator
- Crystallizer with solids separation

Zero Liquid Discharge (ZLD)

What is Zero Liquid Discharge?

- No water is discharged from the plant
- Clean water is recycled for reuse
- Solids are discharged (landfilled)

Evaporation Technology

Basic Definition: Water is evaporated concentrating the solids to a brine

Many types of evaporators

- Falling film, forced circulation
- How far to concentrate?

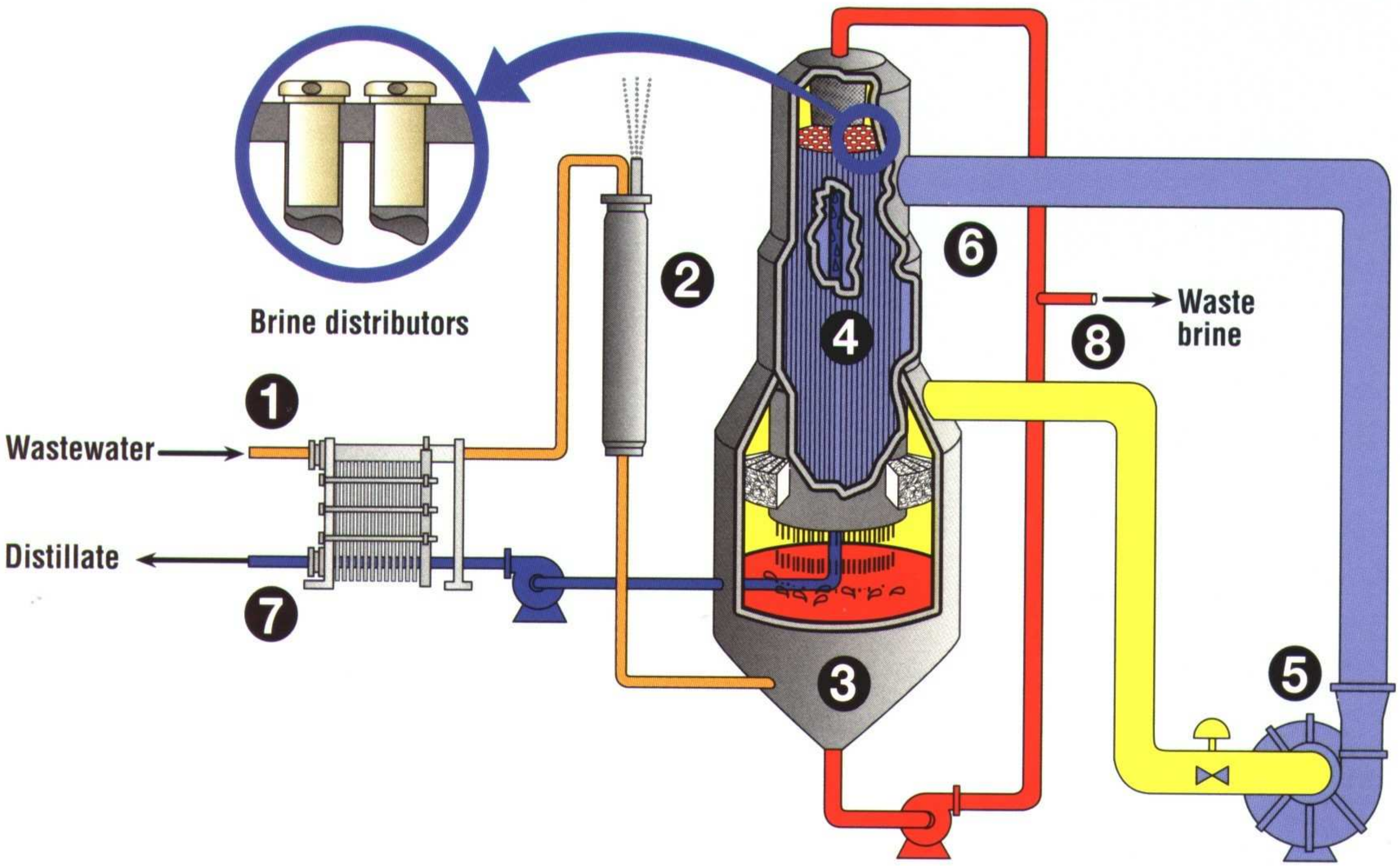
Why evaporation?

Crystallization Technology

Basic Definition: The components dissolved in water are turned into solid material (crystals) by removing the water

Why choose a crystallization process?

Brine Concentrator Schematic



Brine Concentrator Description

1. The wastewater enters a feed tank (not shown) where the pH is adjusted between 5 and 6 for deaeration, decarbonation, and residual H_2S removal. The acidified wastewater is pumped through a heat exchanger that raises its temperature to the boiling point.

2. Wastewater passes through a deaerator, which removes non-condensable gases such as oxygen, carbon dioxide, and volatile organics.

3. Hot feed combines with the brine slurry in the sump. The brine slurry is constantly circulated from the sump to a floodbox at the top of a bundle of heat transfer tubes.

4. Some of the brine evaporates as it flows in a falling film down through the heat transfer tubes and back into the sump.

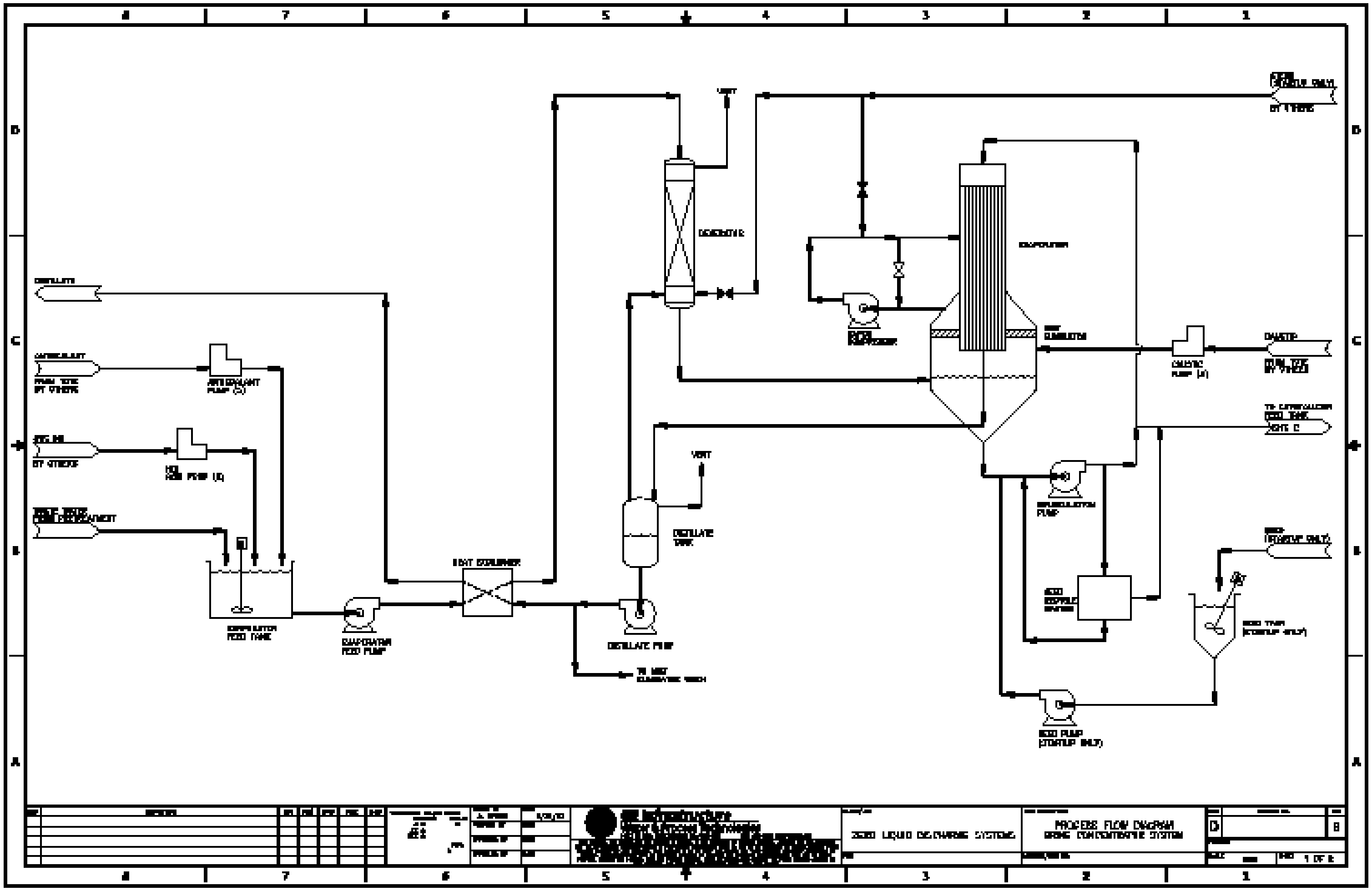
5. The vapor passes through mist eliminators and enters the vapor compressor. Compressed vapor flows to the outside of the heat transfer tubes.

6. Heat from the compressed vapor is transferred to the cooler brine falling inside the tubes, causing some of the brine to evaporate. As the compressed vapor gives up heat, it condenses as distillate.

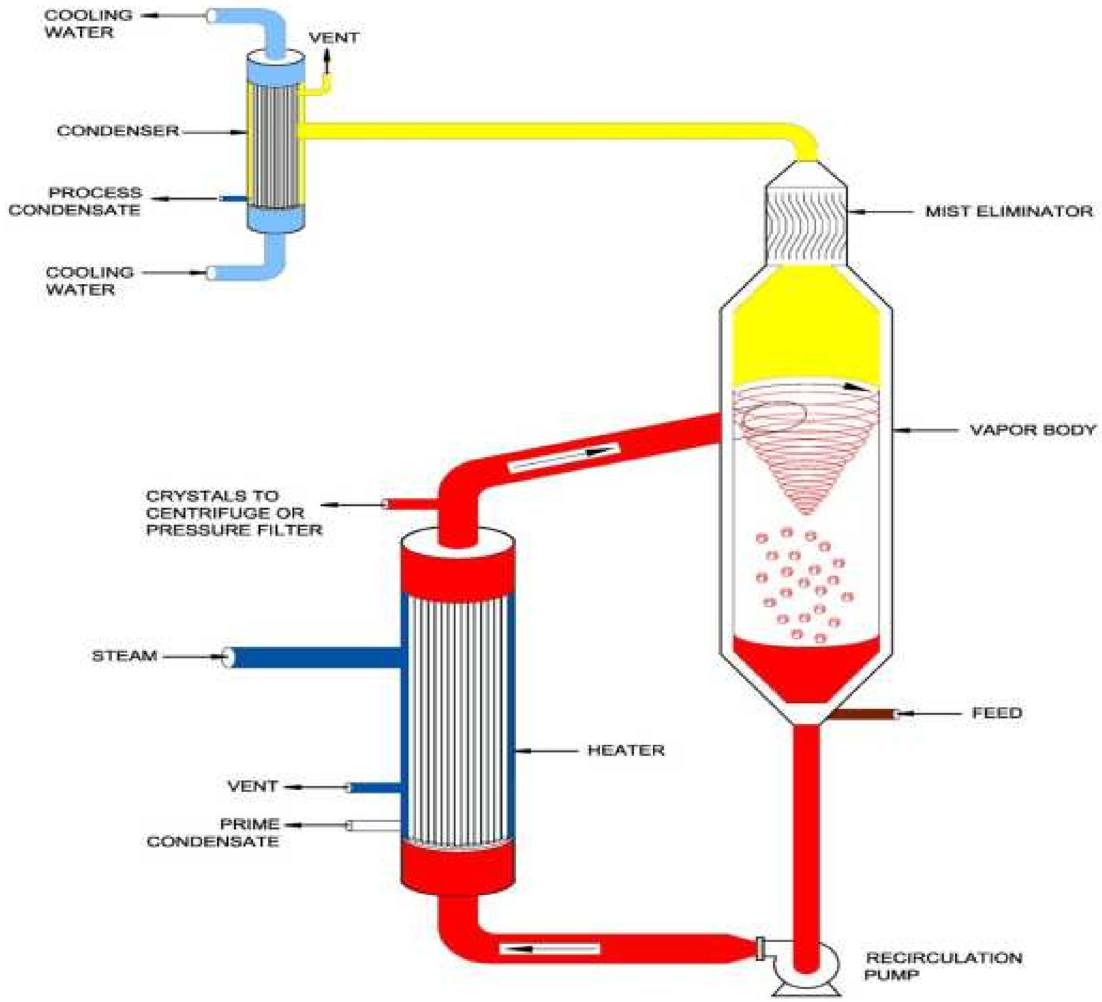
7. The distillate is pumped back through the heat exchanger, where it gives up heat to the incoming wastewater.

8. A small amount of waste brine is blown down from sump to control the brine density.

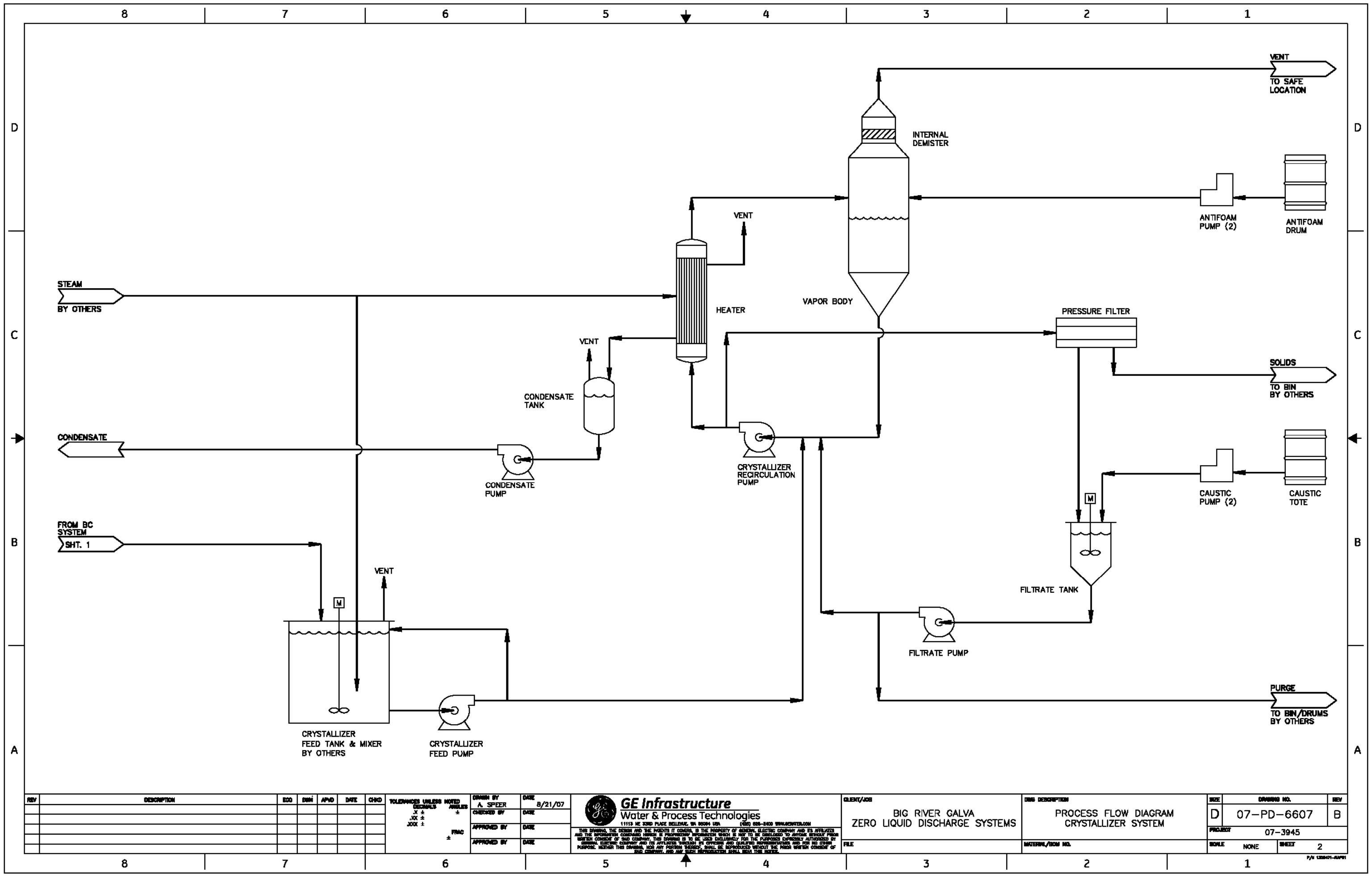
Brine Concentrator PFD



Crystallizer Schematic – Forced Circulation



Crystallizer PFD



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Chemistry

Salt solubilities

Units of Measure

pH and Alkalinity

Deaeration and Decarbonation

Seeded slurry chemistry requirements

Concentration factor

The Chemistry Elements

Positive Ions (Cations)

- Calcium, Ca^{++}
- Magnesium, Mg^{++}
- Sodium, Na^{+}
- Potassium, K^{+}
- Iron, Fe^{+++}
- Metals, Ammonia, H^{+}

Negative Ions (Anions)

- Sulfate, SO_4^{--}
- Chloride, Cl^{-}
- Nitrate, NO_3^{-}
- Phosphate, PO_4^{---}
- Alkalinity
- Hydroxide, OH^{-}

Compound Formations

Not Very Soluble

- $CaSO_4$
- Silica (taken as SiO_2)
- CaF_2
- $Ca_3(PO_4)_2$
- $CaCO_3$

Soluble

- NaCl
- Na_2SO_4
- $MgSO_4$

Very Soluble

- $CaCl_2$
- $MgCl_2$

- Suspended solids (compounded already)

What Can Affect Solubility

- Concentration (obvious)
- pH
- Temperature
- Chemical additions
- Special Organics (polymers)

Solids Measurement

Total Dissolved Solids (TDS) – weight of solids that are in solution

Total Suspended Solids (TSS) – solids can be filtered or settled out of solution

Decarbonation

Convert alkalinity, bicarbonate (HCO_3) and carbonate (CO_3), to carbon dioxide with acid addition

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$ (dissolved gas)

CO_2 gas is stripped with steam in the deaerator

Eliminates carbonate to prevent calcium carbonate precipitation

Deaeration

Water contains dissolved oxygen, O_2

Oxygen in brine can lead to corrosion

Remove oxygen along with carbon dioxide and other inert gasses in deaerator by steam stripping

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Brine Concentrator

Boils feedwater and recovers the condensed vapor (distillate)

Features

- Floodbox with nozzle - evenly distributes brine
- Brine Strainer - catches large solids
- Distributors - creates thin film of brine
- Condenser
- Sump
- Equalization Line - balances pressure between Floodbox and Sump
- Mist Eliminators - trap brine particles

$CaSO_4$ Seeded Slurry Process

Ca++ and SO_4-- ions come out of solution

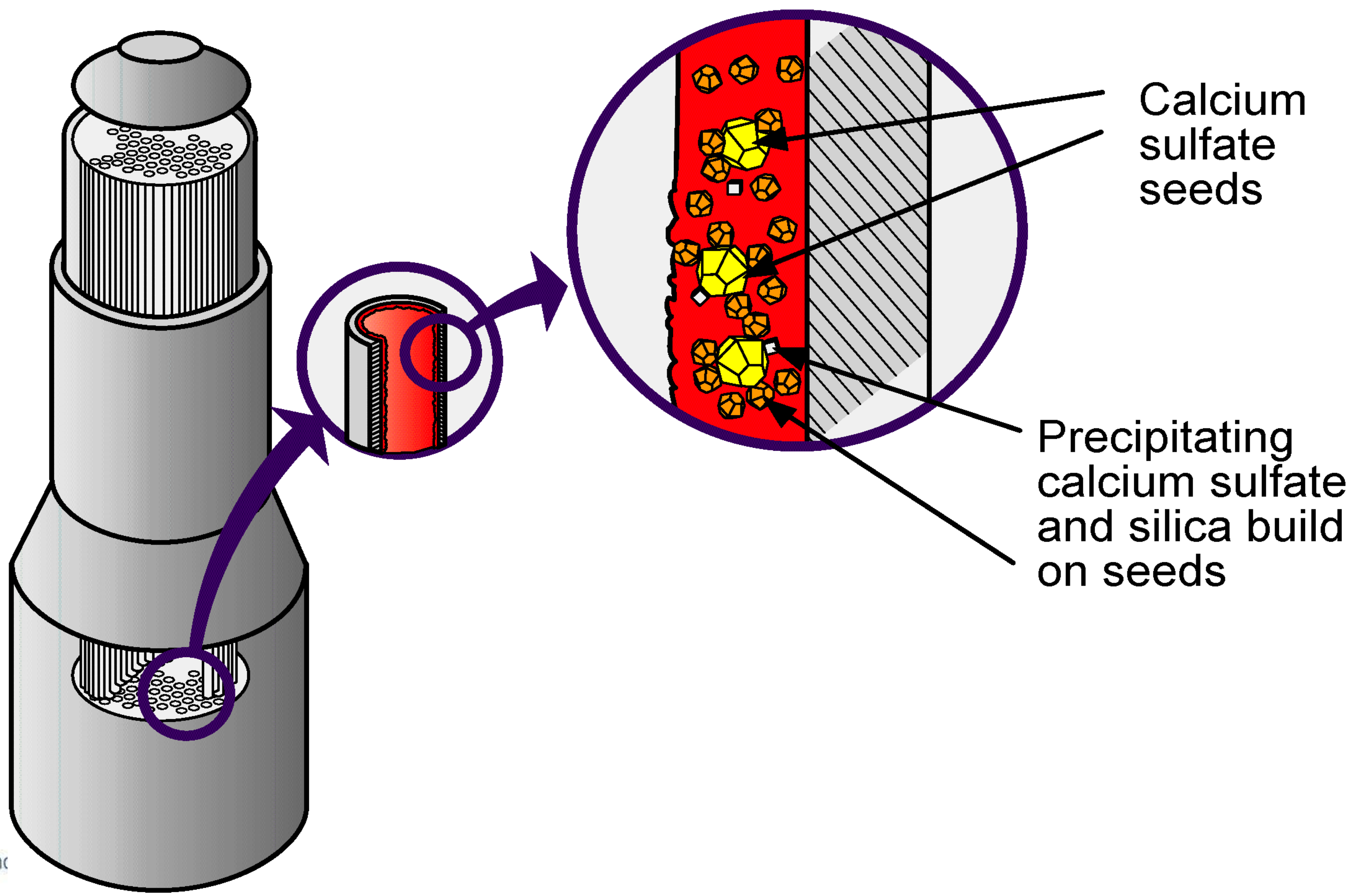
The new $CaSO_4$ 'likes' existing $CaSO_4$

Existing seed has large surface area

The BC has metal surface area

Preferential precipitation – sufficient calcium sulfate is required (in comparison to other insoluble impurities such as silica) to promote precipitation on "seed" crystals instead of heat transfer surfaces

Seeded Slurry Technology



Chemical Additions

Hydrochloric Acid – HCl

Sodium Hydroxide – NaOH

Antifoam

Antiscalant

Limits of Concentration

The amount of SS (can plug) * *This is case for design chemistry*

BC chemistry (TDS) is often limited by the double salt formation called Glauberite

Corrosion limit (Chloride, Cl)

If Glauberite/Corrosion not a limit, then the more soluble salts limit (almost a crystallizer)

Crystallization Process

All solids in water must come out in filter cake – All solids? How?

- More solids salts form from:

  Na, K, Mg, Cl, SO_4
- Compounds formed (as suspended solids):

  Na_2SO_4, NaCl, $MgSO_4$, KCl, K_2SO_4
- Very soluble salts such as $MgCl_2$ or $CaCl_2$ removed with the brine

ZLD SYSTEM - Review

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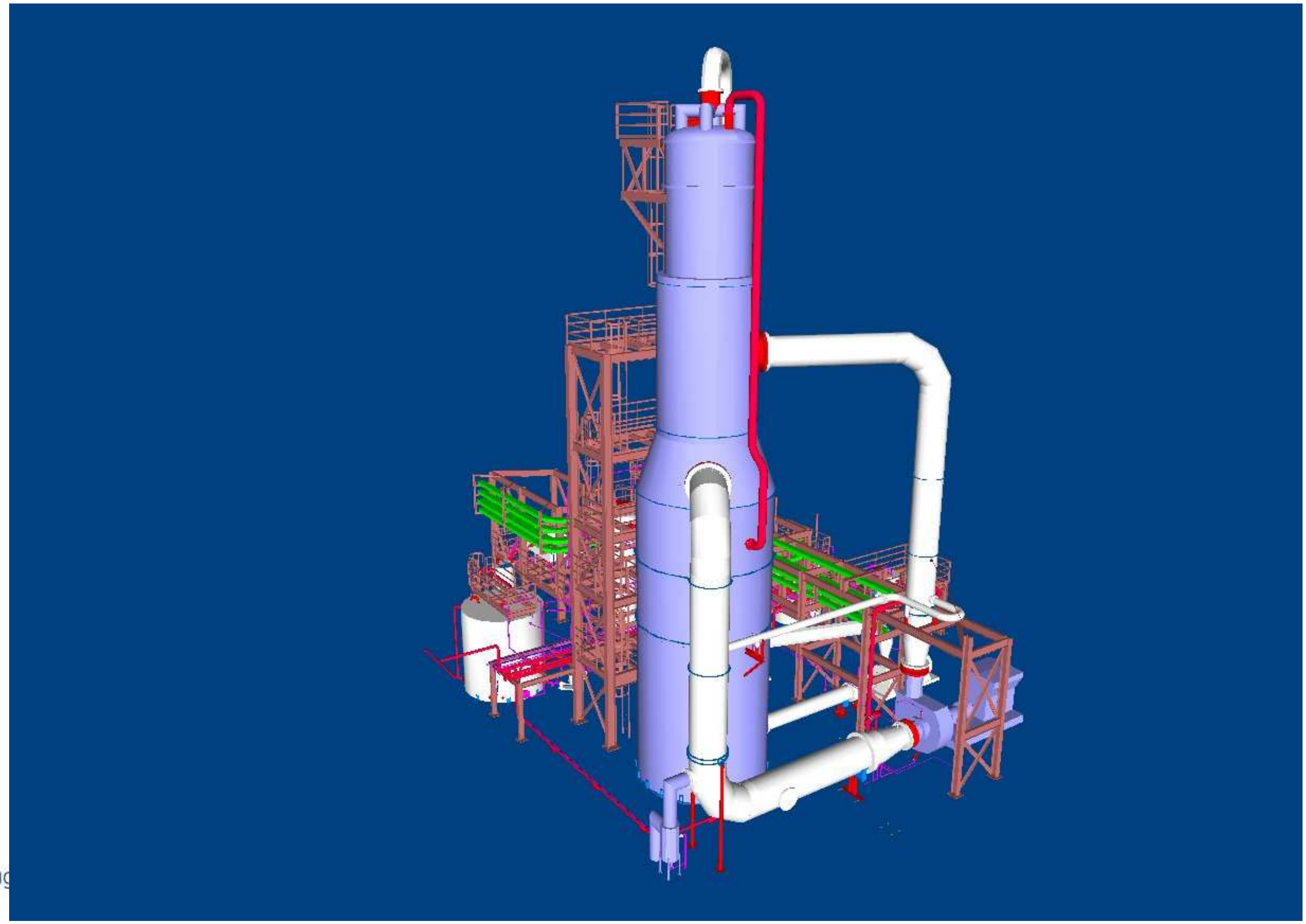
Brine Concentrator



Brine Concentrator Basics

Evaporation process using a vapor compression cycle (most efficient) or steam

Seeded slurry technology (RCC pioneered)

Falling film type of evaporator for best efficiency

- Why evaporation?
- How far to concentrate?

Evaporation Technology

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Questions

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