Minimal Liquid Discharge and Brine Management in Industry

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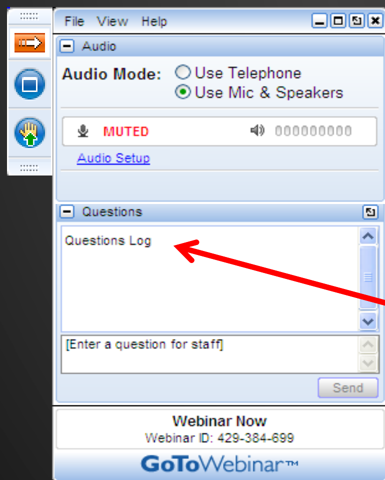
How to Participate Today



- **Audio Modes**
  - Listen using Mic & Speakers
  - Or, select "Use Telephone" and dial the conference (please remember long distance phone charges apply).
- **Submit your questions using the Questions pane.**
- **A recording will be available for replay shortly after this webcast.**

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Today's Moderator

- Framing the technology landscape
- Highlighting some results and activities from solid technology providers

Steven J. Gluck,LLC
Technology Assessment

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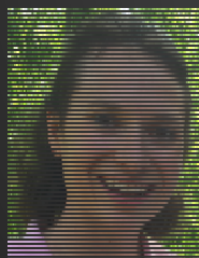
Today's Speakers



Andrea Larson, PE
Siemens Water Solutions

Tina Arrowood
DOW

Daniel Bjorklund
Aquatech International

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What we won't cover

- Sustainability drivers
- Municipal applications
- Technologies on the horizon or newly introduced by small players

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Process Flow Overview

- Objective is water "fit for use"
- Solids, Organics, Inorganics

Application options within the PFD

- Solids
  - Screening
  - Filtration
  - Density based methods
- Salts
  - Evaporation
  - Reverse Osmosis
- Organics
  - Biological oxidation
  - Chemical oxidation
  - Absorption or separation

Today's Selected Technologies

- Siemens Water Solutions
- Dow Water and Process Solutions
- Aquatech

Innovations by companies with solid records of delivery
Addressing the efficient use of water

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People make the technical solutions

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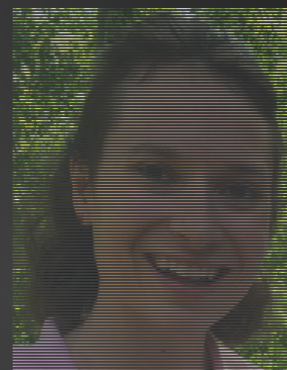
Andrea Larson, P.E.
Siemens Water Solutions

- BS in Chemical Engineering from Michigan Technological University in 2008
- Currently a research and development project engineer for water treatment in the oil and gas industry.
- Developing technologies specifically for reuse



andrea.larson@siemens.com

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Pretreatment for Industrial Reuse

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Drivers for industrial reuse

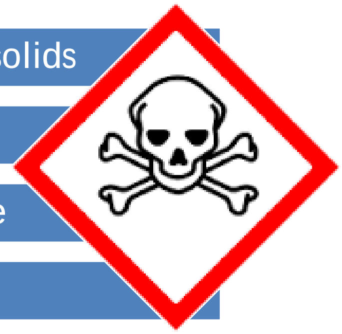
- Tight discharge limits or restrictions on discharge volume
- High cost of water purchase/discharge vs. cost of wastewater treatment
- Discharge permitting issues
- Water availability
- Public image

Steps for brine management

Pretreatment → Reverse osmosis → Evaporation → Crystallization

Constituents in industrial wastewater

- Total dissolved solids
- Metals
- Oil & grease
- Organics
- Suspended solids
- Odor



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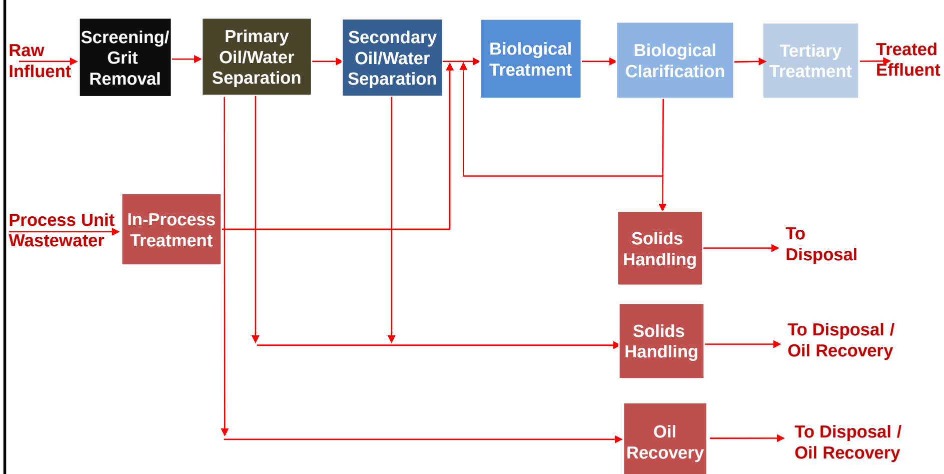
Typical refinery water treatment



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Typical requirements for reverse osmosis

Refinery Wastewater Post Deoiling

- COD 300-1000 mg/L
- BOD 125-350 mg/L
- TSS 30-75 mg/L
- O&G 20-50 mg/L
- Phenols 5-30 mg/L

Reverse Osmosis Feedwater

- COD – as low as possible
- TOC – membrane manufacturers recommend <3 mg/L
- O&G < 0.1 mg/L
- SDI < 5 – lower the better
- Turbidity < 0.5 NTU for long-term, reliable operation

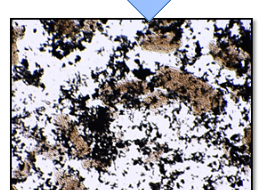
Pretreating for reuse

Deoiling
- Removes free oil

Biological treatment
- Treats biodegradable organics
- Converts organic and ammonia nitrogen to nitrogen gas

Carbon treatment
- Adsorbs recalcitrant organics
- Adsorbs metals
- Adorbs VOCs and odor

PACT combines biological and carbon treatment



Case Study:
Chinese Refinery Reuse with PACT / WAR

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Treatment

- Deoiling
- Two PACT® trains
  - 500 m^3/hr salty stream discharged
  - 500 m^3/hr oily stream pretreated for reuse
- Common onsite carbon regeneration sys
  - Zimpro® wet air regeneration
- Treatment requirements for direct r...e
  - Cooling tower make-up
  - Total N removal
  - COD

China's discharge requirements
- COD < 50 mg/L
- Ammonia < 5 mg/L
- Hydrocarbons < 3 mg/L
- Phenols <0.3 mg/L

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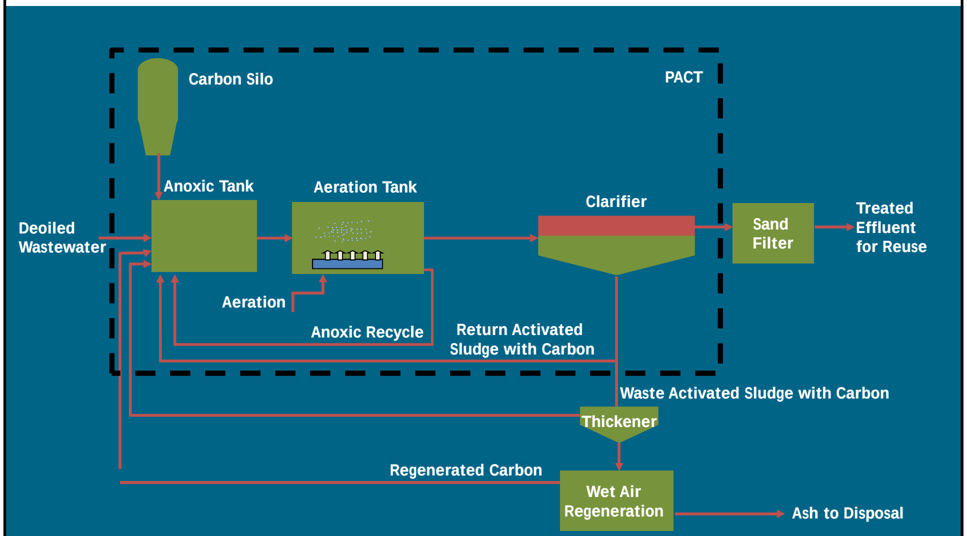
Process Flow Diagram



Factors for successful treatment

Summary

- Drivers for reuse increasing, leading to development of technologies for reuse
- Systems can be designed for reuse of difficult-to-treat industrial wastewaters, in this case study PACT / WAR
- Multiple steps are required for removal of various contaminants
- Steps can be combined to increase operability, lower the footprint, and reduce overall treatment cost

Tina Arrowood
Principal Research Scientist

DOW

- PhD Organic Chemistry, University of Minnesota, 1999
- 18 yrs of industrial science research and development experience including: process chemistry, catalyst development, process scale up, and water related projects
- Currently leading research projects in reverse osmosis membrane development

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RO/NF Membranes: Making More from Every Drop

Industrial Wastewater Treatment

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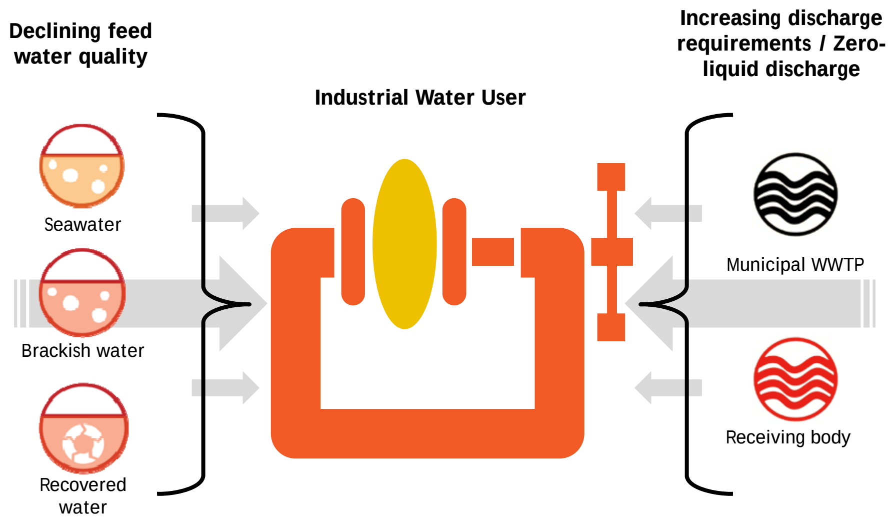
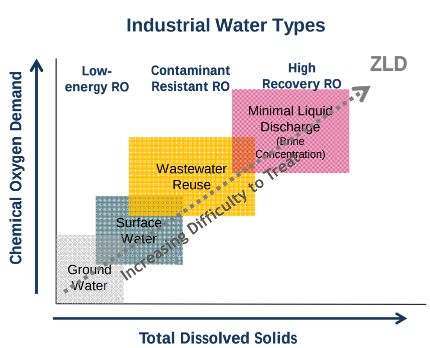
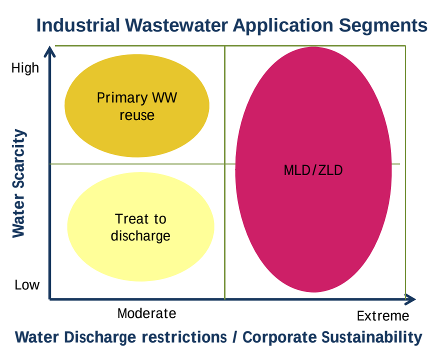
Industrial Water Users Are Being Squeezed on Both Ends



Industrial Water and Wastewater

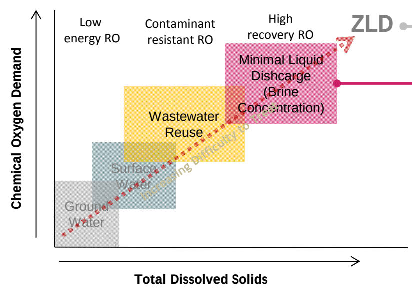




- Industrial plants are turning to wastewater to supplement fresh water feeds.
- Higher contamination levels and TDS create a more challenging water treatment environment
- Two main drivers for choice of wastewater treatment are water scarcity and discharge regulations.
- Stringent discharge regulations are needed to drive the implementation of expensive ZLD processes

28

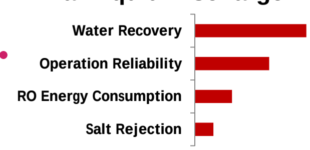
Challenging Water Treatment Improvement Needs



Zero-liquid Discharge Needs

1. Reduced over all cost of ZLD
2. Reduce the waste salts from ZLD

Minimal Liquid Discharge RO Needs



29

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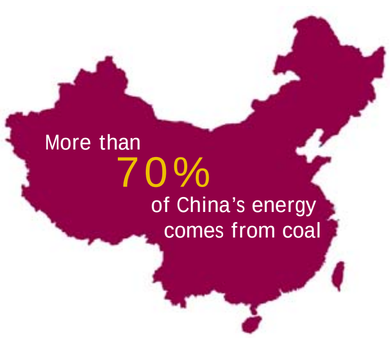
Case in point: coal production in China



Coal resources are located in the North part of China – **its most water-stressed region**

90% coal resource but

21% water resources

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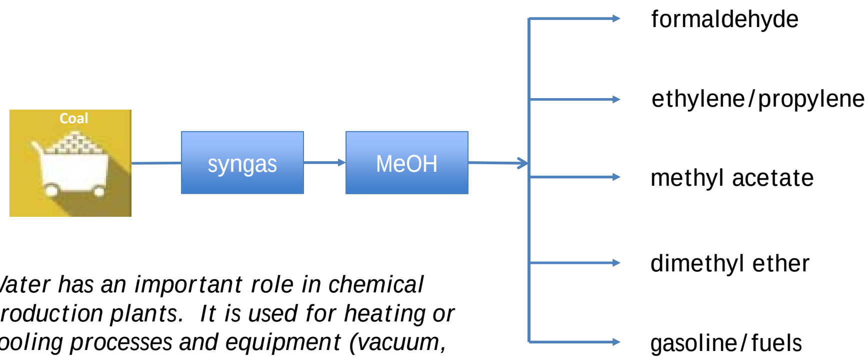
Coal to Chemical



Water has an important role in chemical production plants. It is used for heating or cooling processes and equipment (vacuum, steam, extraction, rinsing, condensing).

Approximately 5-6 units of water are used for each unit of product produced.

- 1-1.5 barrels of water per barrel of product (ZLD water management)

https://www.netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/ctl-water-use

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Coal to Chemical Plant Water Treatment: RO systems

Difficulty to treat →

Demineralization	Primary wastewater reuse	Minimal Liquid Discharge
Feed: River water, reuse water	Feed: Cooling tower blowdown, Demin. RO Reject, process WW	Feed: Wastewater reject, IER regen., High TDS WW
UF+RO(2 pass)+IER	UF+RO	UF+IER+RO(2 stage)
Product: Boiler make up	Product: cooling tower make up, process water, demineralization plant	Product: Cooling tower make up, feed to demineralization plant

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Coal to Chemical Plant Water Treatment: RO systems

Demineralization

- Feed TDS: 500-800 mg/L
- Capacity: 1050 m^3/h
- 1st Pass RO
  - 210 m^3/h * 5
  - 31:16 (6)
  - 20 LMH
  - 75% recovery
- 2nd Pass RO
  - 190 m^3/h * 5
  - 18:6 (6)
  - 32.3 LMH
  - 90% recovery
- Low Energy BWRO

2130 Elements

Primary wastewater reuse

- Feed TDS: 1000-2000 mg/L
- Capacity: 1560 m^3/h
- 1st Pass RO
  - 156 m^3/h * 10
  - 24:12 (6)
  - 19 LMH
  - 70% recovery
- Contaminant Resistant RO

2160 Elements

Minimal Liquid Discharge

- Feed TDS: 5000-8000 mg/L
- Capacity: 630 m^3/h
- 1st Pass RO1
  - 105 m^3/h * 6
  - 18:9 (6)
  - 17 LMH
  - 70% recovery
- 1st Pass RO2
  - 59 m^3/h * 3
  - 12:6 (6)
  - 15 LMH
  - 65% recovery
- Contaminant Resistant, High Recovery RO

1296 Elements

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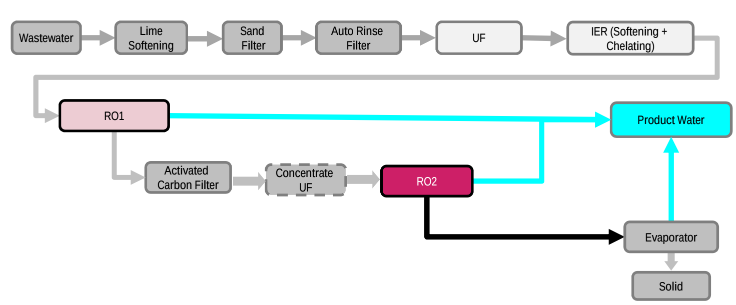
Coal to Chemical Company A: Minimal Liquid Discharge/ZLD

MLD feed: TDS: 8250 mg/L, COD ~100 mg/L
(~65:35 mixture of NaCl & Na_2SO_4)



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Coal to Chemical Company A:
MLD System Design Considerations

RO1

Technical Design Challenges
- ✓High Biofouling Fouling due to high feed COD.
- ✓ High CIP frequency of RO system

Technical Solution at start up (2014)

Capacity (m^3/h)	Recovery (%)	Element Model	Qty of Element
630	70%	BW30XFR-400/34i (interstage booster pump)	972

Advanced technology now available

Capacity (m^3/h)	Recovery (%)	Element Model	Qty of Element
630	70%	FORTILIFE™ CR100 (interstage booster pump)	972

Advanced benefit:
→ Reduce CIP frequency by up to 30-50%

RO2

Technical Design Challenges
- ✓RO reject to 80,000 mg/L TDS for low evaporator CAPEX.
- ✓High fouling due to high feed water COD
- ✓Minimize system OPEX.

Technical Solution at start up (2014)

Capacity (m^3/h)	Recovery (%)	Element Model	Qty of Element
175.5	65%	1st stage : SW30HRLE-370/34i 2nd stage: SW30ULE-400i	324

Advanced technology now available

Capacity (m^3/h)	Recovery (%)	Element Model	Qty of Element
175.5	>66%	1st stage : FORTILIFE™ XC70 2nd stage: FORTILIFE™ XC80	324

Advanced benefit:
→ Achieve RO reject >80,000 mg/L
→ Reduce CIP frequency
→ Reduced evaporator OPEX

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Coal to Chemical Company A:
Estimated DOW FILMTEC™ FORTILIFE™ RO Element Impact

MLD feed: 900 m^3/h; TDS 8250 mg/L
~65:35 mixture of NaCl and Na_2SO_4

	# of Modules	Array	Feed Pressure (bar)
RO1	162	18:9 (6)	15(+7)
RO2.1	72	12 (6)	38
RO2.2	18	6 (6)	52

ROSA Simulated Results

	Standard FILMTEC™ Element Offering	Advanced FORTILIFE™ Element Offering
RO1 (70% recovery)	BW30XFR 400/34	FORTILIFE CR100
RO2 (Stage 1)	SW30HRLE 400/34	FORTILIFE XC70
RO2 (Stage 2)	SW30ULE 440	FORTILIFE XC80
Vol. of Water to evaporator	93.3 m^3/h	89.7 m^3/h
Combined Perm TDS	254 mg/L	378 mg/L
Conc. TDS	77,800 mg/L	**80,500 mg/L**
Annual evaporator energy OPEX[1]	$2,985,000	$2,870,000
Annual evaporator energy savings	benchmark	**$115,000** ✓

[1]Evaporator energy cost: $4/m³ feed; hours operation: 8000 h/y

Plus… less chemical cleaning costs and lost productivity due to fouling

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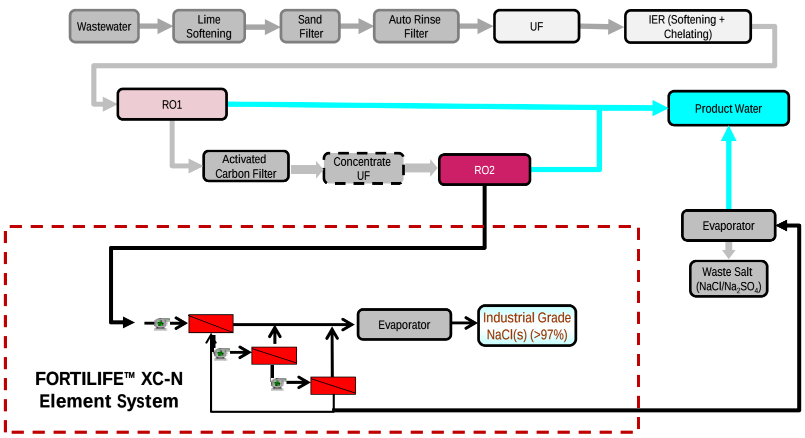
Coal to Chemical Plant A:

2016 upgraded MLD system with brine recovery

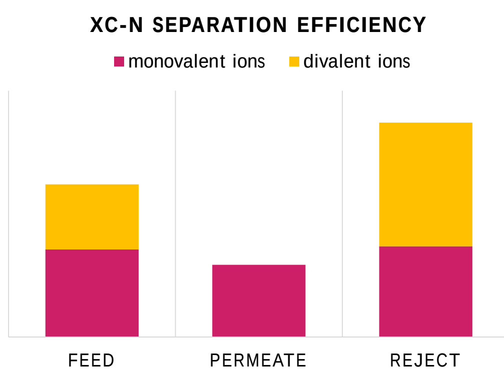


- Reduce landfill costs and improve ZLD sustainability

Coal to Chemical Plant A:

Brine recovery demonstrated performance

- 3 Stages of FORTILIFE™ XC-N elements
- Feed TDS: 50,000-75,000 mg/L
- Recovery: 60-75%
- Max feed pressure: <30 bar



- Excellent divalent ion rejection to create a purified monovalent brine solution

38

Coal to Chemical Plant A:

Calculated impact of salt recovery on cost of ZLD

RO Reject

95 m^3/h
TDS: 72,800 mg/L
(~65:35 $NaCl:Na_2SO_4$)

Option 1: RO reject → evaporator (no salt recovery)	
Water recovery OPEX ($/y)	$ 2,835,000
Landfill Costs ($/y) ($150/ton)	$ 8,940,000
Total cost ($/y)	**$ 11,775,000**
# trucks of salt landfilled / day	7.2 trucks

Option 2: RO reject → evaporator (with salt recovery)	
FORTILIFE™ XC-N recovery	60%
Water/salt recovery OPEX ($/y)	$ 3,175,000
Landfill Costs ($y) ($150/ton)	$ 4,588,000
Industrial grade salt rev. ($/y) ($0.08/kg)	$2,104,000
Net Cost ($/y)	**$ 5,659,000**
# truck of salt landfilled / day	3.7 trucks

Savings w/ salt recovery	**$ 6,116,000**
% savings	**52%**
less # of trucks/d to landfill	**3.5 trucks**

Evaporator energy cost: $4/$m^3$ feed; hours of operation: 8000 h/y

Summary

- Membrane based **Minimal Liquid Discharge** processes play an important role to **economically manage high water recovery** and disposal needs of ZLD
- RO and NF Elements **"designed for the challenge"** of high recovery water treatment provide improved operability and system OPEX savings
- DOW FILMTEC™ FORTILIFE™ XC-N Elements can **reduce the amount of salt requiring landfilling** while also offset some of the cost of ZLD by enabling brine recovery

Thank You!

Talk to Dow about MLD

www.dowwaterandprocess.com/contactus

Daniel Bjorklund
Aquatech International

Mr. Bjorklund is a Chemical Engineer from the University of Wisconsin with over 30 years of process engineering experience and 20 years of experience in the design of evaporation systems.

As the Vice President of Industrial Concentration for Aquatech he supervises a team of engineers that specialize in evaporation systems. These systems include produced water evaporation systems for enhanced oil recovery, shale gas and coal seam gas applications, as well as ZLD systems for various applications such as FGD blowdown treatment, XTL, IGCC and other applications requiring ZLD solutions.

ZERO LIQUID DISCHARGE

What is Zero Liquid Discharge?

- A water treatment process employed to recycle and reuse virtually all of the wastewater produced by a facility
- A Zero Liquid Discharge facility is an industrial plant without discharge of wastewaters from the plant boundary

Why Zero Liquid Discharge?

- Increasing regulation on the discharge of wastewaters from facilities
- Tightening of wastewater disposal options
- Increasing disposal costs
- Growing public environmental and resource scarcity concerns
- Corporate initiatives to reduce water foot print and increase sustainability

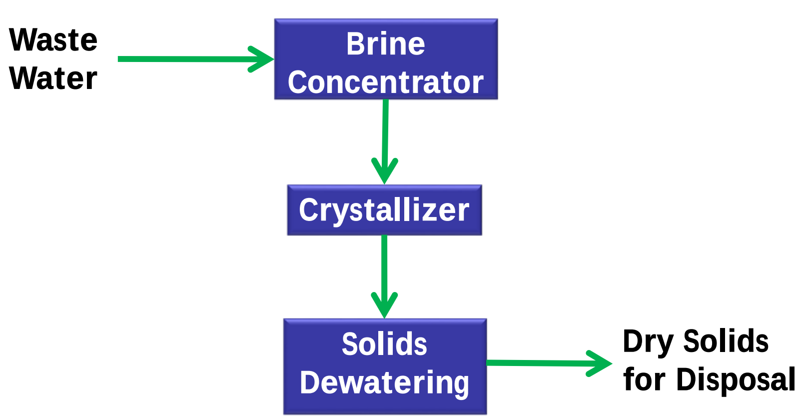
Where is Zero Liquid Discharge Used?

- **Power**
  - CTBD (Cooling Tower Blow Down) Waste water
  - FGD (Flue Gas Desulfurization)
  - Integrated Gasification Combined Cycle (IGCC)
  - Recycle/ Reuse
- **Oil & Gas**
  - EOR Produced Water
    - Steam Flood
    - Cyclic Steam Stimulation (CCS)
    - Steam Assist Gravity
  - Shale Gas
  - Coal Seam Gas
  - Gas to Liquids (GTL)

Where is Zero Liquid Discharge Used?

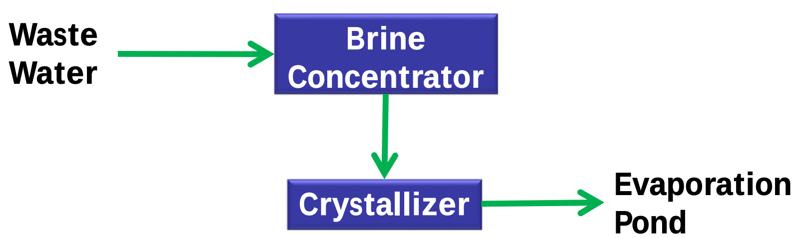
- **Gasification**
  - Coal to Chemicals (CTX)
  - Biomass
  - Other
- **Petrochemicals**
- **Mining**

Typical ZLD Plant Configurations



Typical ZLD Plant Configurations

Typical ZLD Plant Configurations



Evaporator Types

- **Falling Film Brine Concentrator**
  - o Seeded – scaling services
  - o Non-Seeded – non-scaling services
- **Forced Circulation Evaporators/Crystallizers**
- **Energy Supply Alternatives**
  - o Mechanical Vapor Recompression (MVC)
  - o Steam
    - Direct
    - Thermocompressor
    - Multiple Effect

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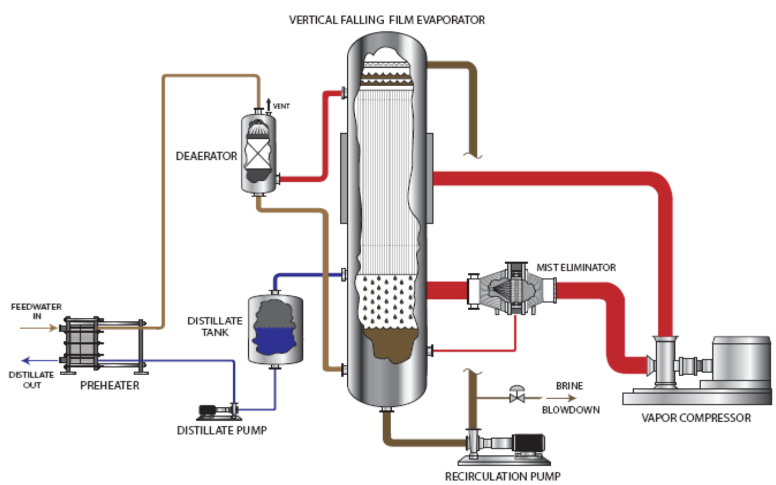
What is a Brine Concentrator?



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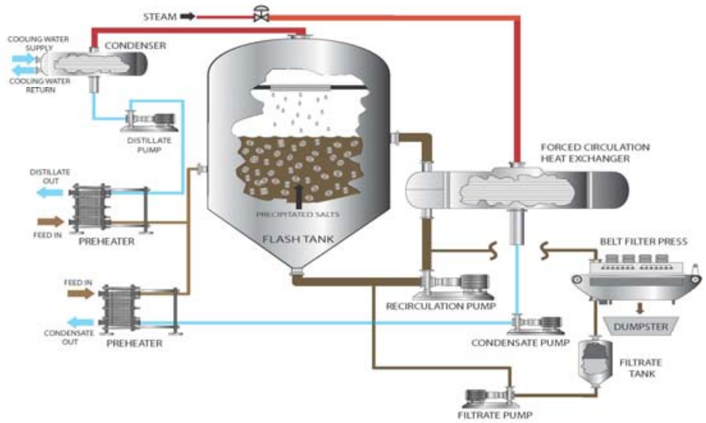
What is a Crystallizer?



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Evaporator Comparison

FALLING FILM

- Generally used to concentrate brine solutions to 12% to as high as 25% TS
- Lower specific energy than forced circulation evaporators
- Lower OPEX/GPM of evaporation
- Unseeded system used for non-scaling applications
- Scaling applications use techniques such as seeded slurry to control scaling

FORCED CIRCULATION

- Generally used to concentrate brine blowdown from upstream pre-concentrator
- Higher specific energy than falling film evaporators
- Higher OPEX/GPM of evaporation
- Crystallizer applications
- Generally resistant to scaling

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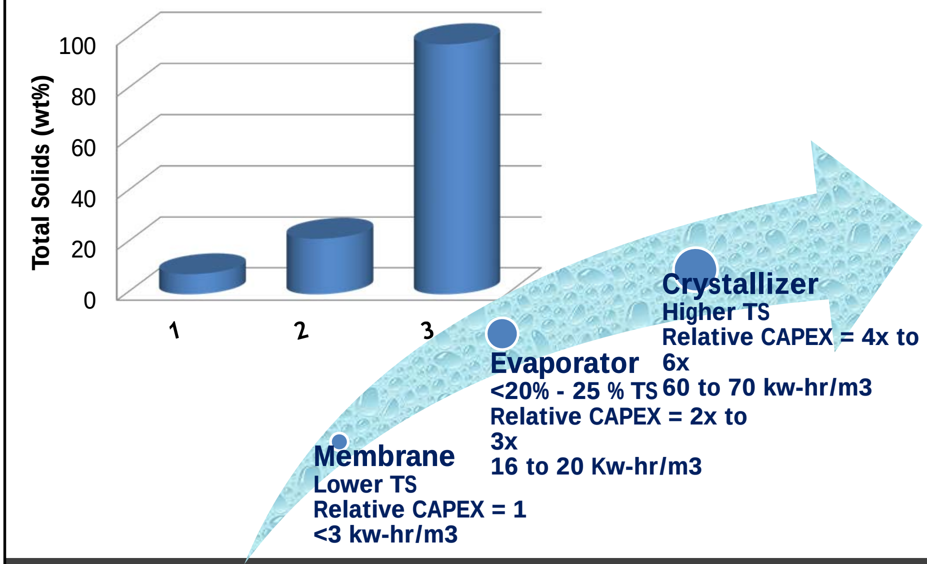
Concentration Technologies Comparison



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Typical ZLD Plant

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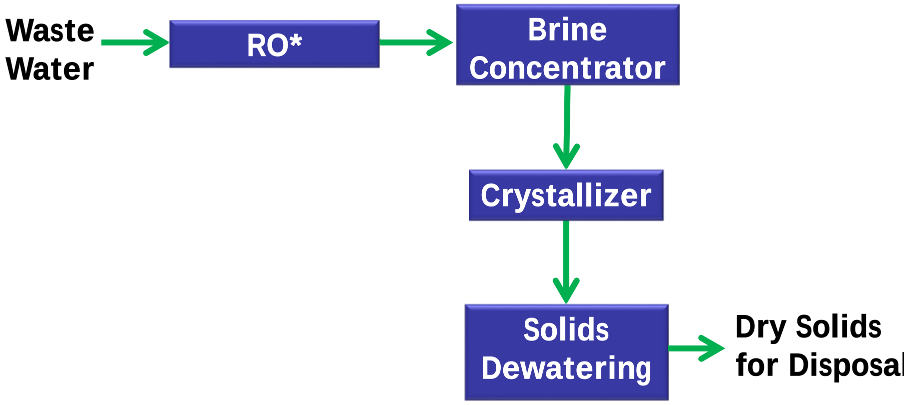
Membrane Pre-concentration



* *High Efficiency RO (HERO™) Pre-concentrator reduces CAPEX and OPEX by reducing the size of the Brine Concentrator*

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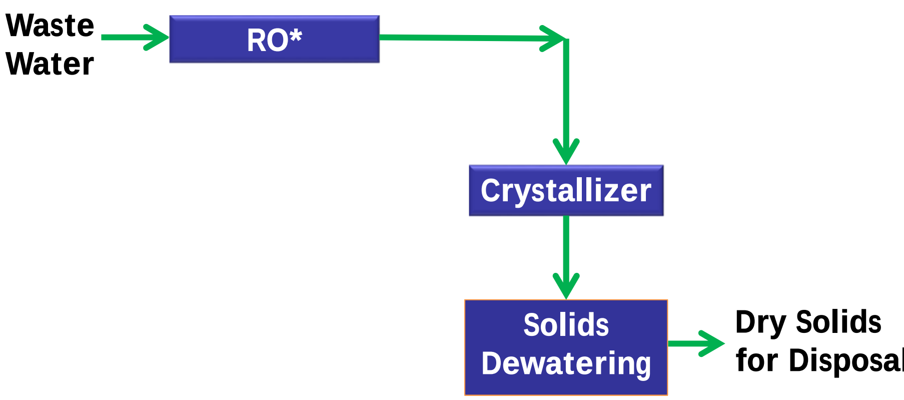
Membrane Pre-concentration



* *High Efficiency RO (HERO™) Pre-concentrator reduces CAPEX and OPEX by eliminating the Brine Concentrator*

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ZLD Success Factors

- **Careful consideration of waste water chemistry**
  - ✓ Prior experience with similar water chemistry
  - ✓ Bench-Top study where experience is lacking and if water is available
  - ✓ Computer modeling using proprietary software and third party software such as OLI
  - ✓ Pilot studies can be done if water is available and if considered early in the project schedule

An sound water chemistry design basis is key to successful ZLD design

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ZLD Success Factors

- **Relevant experience of ZLD supplier**
  - ZLD system design is intellectual property of the supplier and generally not available from text books, journals or Wikipedia
- **Relevant experience of operations team and proper man-power assignment**
  - There is a general shortage of ZLD system operations expertise
  - Training of the operations team prior to start-up and during the first year of operation is critical
  - Supervision assistance by the ZLD system supplier during the first year of operation is recommended

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ZLD Success Factors

- **Metallurgy**
  - Optimization of CAPEX
- **Operating parameters i.e. pH, conc. factors, etc.**
- **Conservative Design Margin**
  - Experience shows that actual chemistry will deviate from design chemistry

Once properly designed and staffed, operating issues are straight forward

China CTX ZLD Case Study

Aquatech has executed 6 CTX ZLD Projects in the China Market

- ✓ *Yuntianhua, China*
- ✓ *Tuke, China*
- ✓ *Shenhua Xinjian, China*
- ✓ *Shenhua Ningmei, China*
- ✓ *Tuke Mining, China*
- ✓ *Gansu Honghui Energy and Chemical Co., China*

What is CTX?

- CTX is the process for gasification of coal to various products such as alternative fuels and chemicals such as methanol, ammonia, fertilizers and olefins to name a few.
- Coal gasification is the process of producing syngas, a mixture consisting primarily of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and water vapor (H_2O) from coal and water, air and/or oxygen.

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China CTX ZLD Drivers

- China is actively encouraging the growth of coal-to-chemicals in a bid to reduce its dependence on expensive imported natural gas.
- These plants have high water demands and the regulations have made wastewater recycle/reuse mandatory for such facilities.
- Although these wastewaters lend themselves well for biological treatment, the stream generated after further concentration through recycle/reuse systems require a ZLD configuration to comply with regulations.

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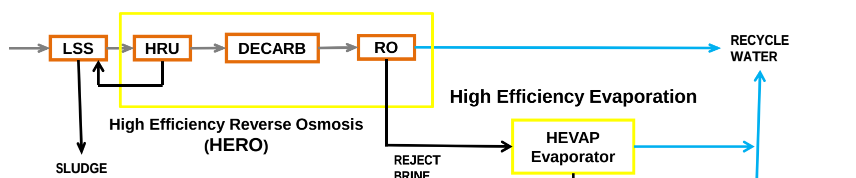
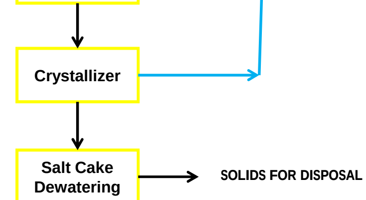
680 KTA CTX Project
Inner Mongolia China

- A fully integrated and automated system developed for the CTX market
- Highly efficient ZLD system supplied utilizing AquaEZ™ technology
  - HERO™ High Efficiency Reverse Osmosis
  - HEVAP™ High Efficiency Evaporation
  - Crystallizer and centrifuge to produce and harvest salts

AquaEZ™ ZLD Process





Pre-concentrating HERO reduces CAPEX and OPEX by significantly reducing the size of the Evaporator

HEVAP Evaporator reduces CAPEX and OPEX
- **High pH evaporation allows for optimized metallurgy and elimination of corrosion risk**
- **Non-scaling brine feed ensures clean heat transfer surface and efficient heat transfer**
- **Split sump evaporator reduces power consumption**
- **Significantly higher reliability and availability rating as compared to conventional Seeded Slurry Evaporator systems.**

Water Recycle

- The CTX wastewater stream has high scaling and fouling potential due to the presence of hardness, organic species, ammonia, silica, etc.

- The wastewater stream is first concentrated by the HERO™ system achieving high recovery of low TDS permeate for reuse by the CTX facility.

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Water Recycle

- HERO™ is a proprietary process that is designed for applications where the feed water is high in both organic and inorganic foulants. The operating environment of a HERO™ system eliminates scaling and fouling.
- The result is that an AquaEZ™ system requires less downtime for cleaning than a conventional RO based system.

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Zero Liquid Discharge

- The concentrated brine from the Water Recycle system is further concentrated in the ZLD system. The system is comprised of a HEVAP™ evaporator for brine concentration and crystallizer to achieve ZLD.

- The concentrated HERO™ reject brine is non-scaling. The HEVAP™ evaporator is designed to operate without scaling and lower power consumption compared to conventional evaporators typically used.

Zero Liquid Discharge

- The Crystallizer is the final brine concentration step. As concentration occurs, salts are precipitated, grown into crystals and harvested by a centrifuge. The dry salt is taken for suitable disposal.

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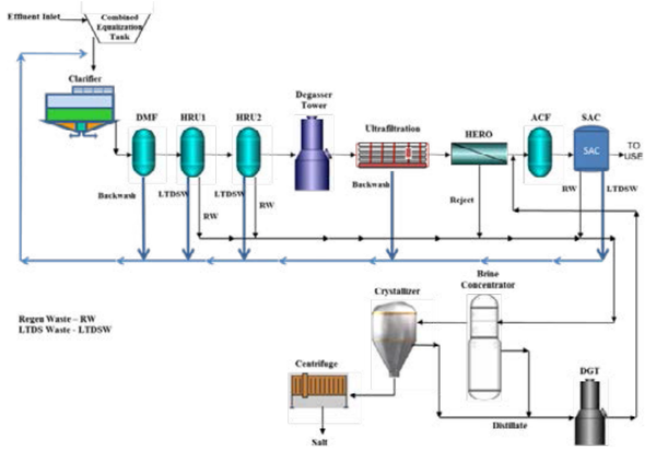
SYSTEM FLOW DIAGRAM



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DESIGN WATER ANALYSIS: COMPOSITE STREAM		
Parameters	**Units**	**Composite Feed**
pH	---	6.5-8.5
Total Dissolved Solids	mg/L	~6057
Chemical Oxygen Demand	mg/L	149.6
Hardness as CaCo$_3$	mg/L	880
NH3+ - N	mg/L	13.4
Fluorides as F	mg/L	25
Silica as SIO$_2$	mg/L	91
Bicrabonate as HCO$_3$	mg/L	136
Chlorides	mg/L	1465
Sulphates	mg/L	737
Sodium	mg/L	2241
Nitrate as NO$_3^-$	mg/L	549.2
Calcium	mg/L	160
Magnesium	mg/L	96
TOC	mg/L	63.4
TSS	mg/L	22

TREATED WATER ANALYSIS		
Parameters	**Units**	**Outlet Concentration**
Turbidity	NTU	< 3
Total Dissolved Solids	mg/L	≤ 200
Total hardness, as CaCO$_3$	mg/L	≤3
Total alkalinity as CaCO$_3$	mg/L	≤20
BOD	mg/L	< 0.5
COD	mg/L	< 5
TOC	mg/L	≤2
Fluoride	mg/L	< 0.5
Chloride	mg/L	≤ 30
Sulphate	mg/L	≤ 30
Nitrate nitrogen	mg/L	≤ 50
Silica	mg/L	<1
Phosphate	mg/L	<0.02
Sodium	mg/L	<35
Aluminum	mg/L	<0.01
Copper	mg/L	<0.01
Manganese	mg/L	<0.01
Zinc	mg/L	<0.01

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China CTX ZLD Drivers

- Earlier generation of such facilities were permitted to have an evaporation pond as a means for final disposal to comply with ZLD requirement.
- New regulations disallow evaporation ponds and encourage/require recovery and reuse of harvested salts (i.e. selective salt recovery).
- Selective salt recovery technologies are under development and commercialization.
- While recycle and reuse of wastewater is practiced globally in many markets, the China CTX ZLD market will be at the forefront of development of technologies for recycling salts for beneficial reuse.

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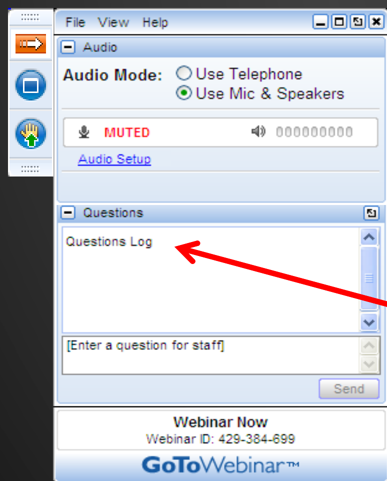

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