QP REFINERY WASTE WATER TREATMENT CHALLENGES AND THE ZERO LIQUID DISCHARGE (ZLD) INITIATIVE

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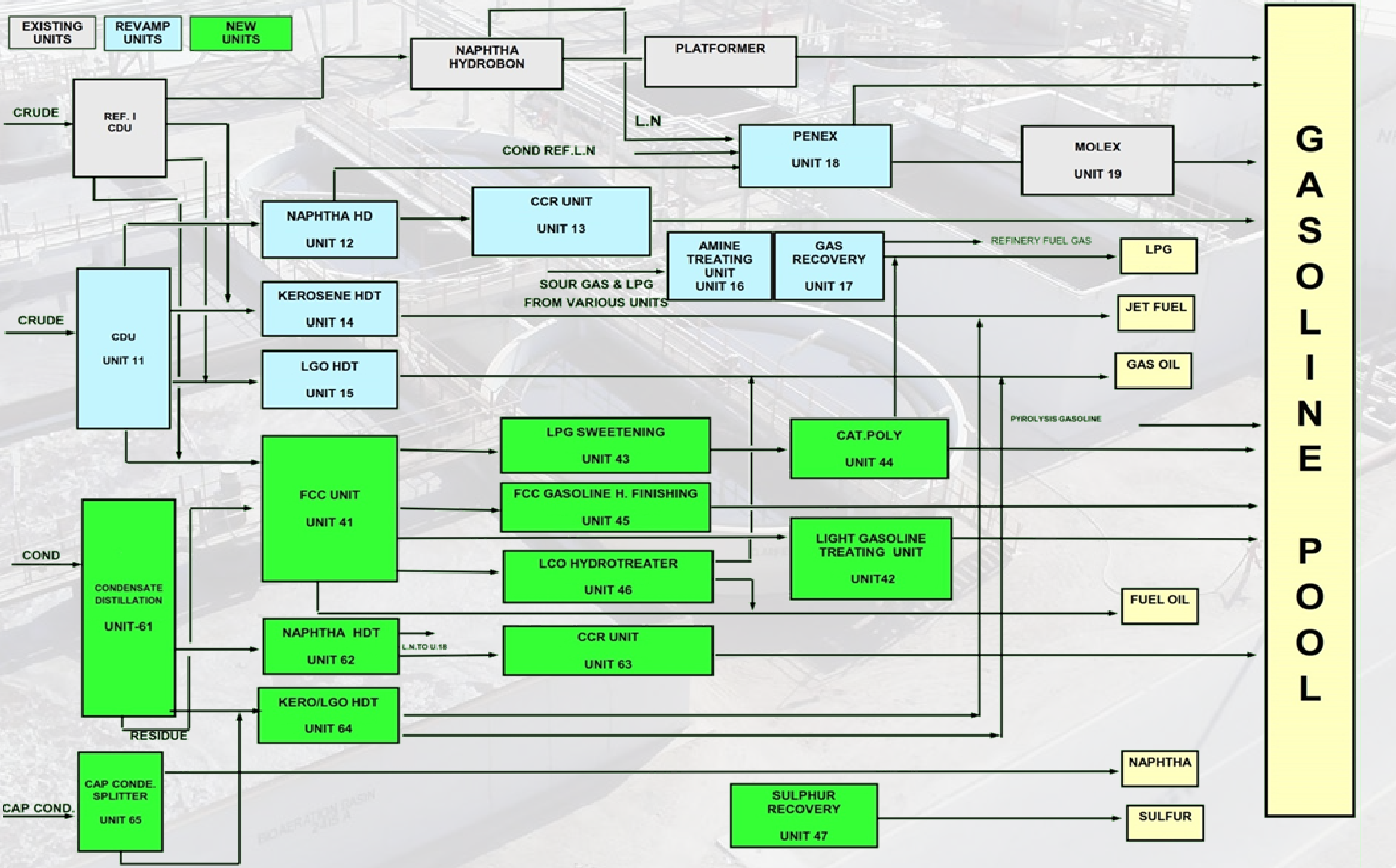
Scheme of Presentation

- General Overview of QP Refinery, Mesaieed.
- Challenges in Treatment
- Existing Waste Water Treatment Facilities
- Capacity Expansion and Upgradation of WWTP
- MoE Legislation for ZLD for Industries & Impact on QP Refinery on Waste Water Disposal
- ZLD Initiative & Technology Evaluation
- Economics of ZLD
- Recycling/ Reuse

QP Refinery Mesaieed - Qatar

- Qatar Land Crude: 80,000 BPD
- Condensate (North Field): 27,000 BPD
- Stabilized Condensate (Dukhan): 30,000 BPD
- Total Production: 137,000 BPD
- Products: Gasoline, Jet A1, LGO, LPG, DCO, FO,
- Naphtha, Sulphur

QP Refinery Overall Process Scheme



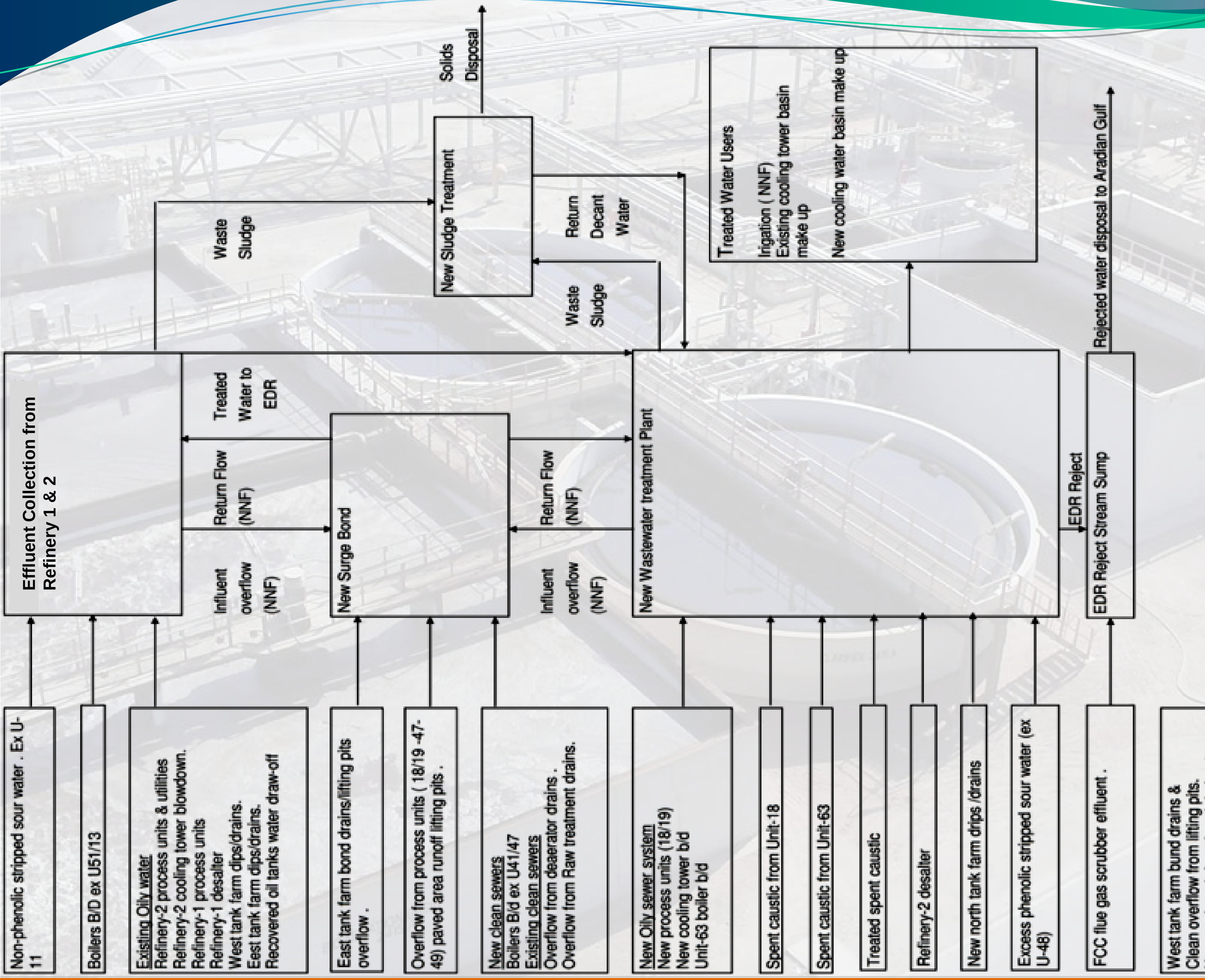
Satellite image of Refinery with WWTP Facilities

Raw Water Quality from KHARAMAA

Parameter	Value Range	Parameter	Value Range
Conductivity	400 - 500		
P&M Alkalinity (m/g/l)	0 – 10; 80 - 100	Bicarbonate (m/g/l)	80 - 110
Total Hardness as $CaCO_3$) (m/g/l)	80 - 100	Sulphate (m/g/l)	04-Jun
TDS (m/g/l)	240 - 305	Chloride (m/g/l)	40 - 70
Sodium (m/g/l)	25 - 40	Carbonate (m/g/l)	0 - 10
Potassium (m/g/l)	0.4 - 2	Nitrate (m/g/l)	0 – 0.1
Calcium (m/g/l)	25 - 50	Silicon Dioxide (m/g/l)	0.1 – 0.4
Magnesium (m/g/l)	02-Oct	Chlorine (m/g/l)	0 – 0.2
Iron (m/g/l)	0.2 – 0.4	Phosphate PO_4^{2-} (m/g/l)	0.3 – 0.4

Water Costs per Year: 3 million US$

Block Flow Diagram of Refinery Effluent Collection System



Challenges for Waste Water Treatment

- **Problem Streams**
- Spent Caustic
- Sour water
- Desalter effluent
- Boiler Blow down & Condensate
- Cooling Tower Blowdown
- Oily Sludge from dewatering of Tanks

Parameters of Concern

- Free Oil & Emulsified Oil
- COD & BOD
- Ammonia
- Phenols
- Sulphides
- Total Suspended Solids

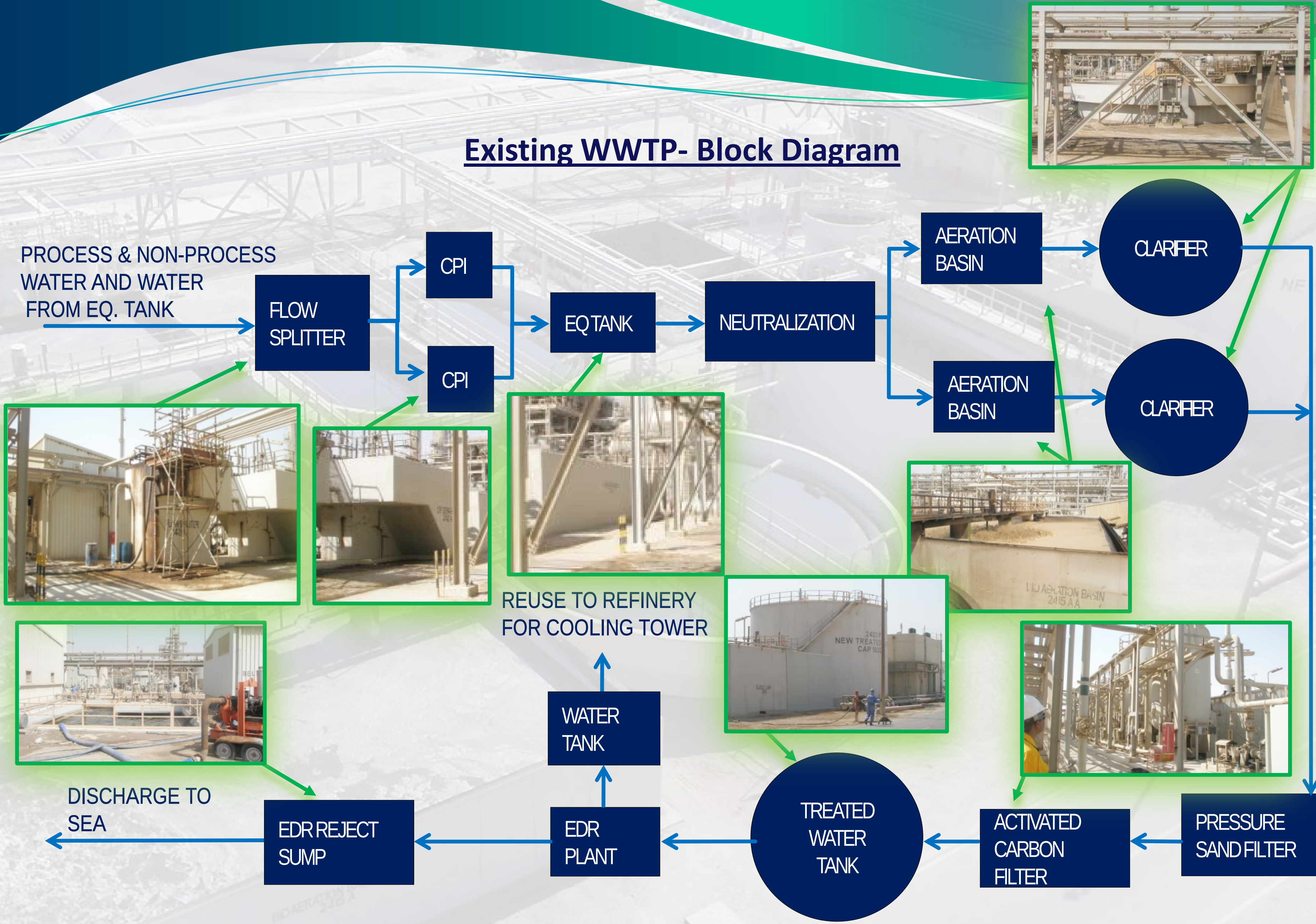
Significant Effluent Flows to WWTP

Desalter effluent, cum/hr	30	Treated Spent Caustic, cum/hr	0.5
Boiler Blowdowns, cum/hr	15	Non Phenolic Stripped Sour Water, cum/hr	7
Boiler Condensate, cum/hr	4.5	Phenolic Stripped Sour Water, cum/hr	10
Cooling Tower Blowdown, cum/hr	30	LAB effluent, cum/hr	0.8
Site Steam traps, cum/hr	5	Steam System Feed water treatment, 15cum/h	15
Sludge Treatment return liquor, cm/hr.	22	Tanks Dewatering & Misc. Streams, cum/hr	16

Effluent Quality Values for Existing WWTP – Design Basis

PH	7-9	Phenol (mg/l)	20
BOD (mg/l)	400	Sulphide (mg/l)	25.6
COD (mg/l)	900	TSS (mQ/l)	500
Oil (mg/l)	300	Ammonia	22

Existing WWTP- Block Diagram



Treated Water Quality from WWTP

Parameter (Maximum values)	Treated Water Design Value for existing WWTP and proposed new WWTP
pH	6 – 9
BOD (mg/l)	20
COD (mg/l)	100
Phenol (mg/l)	0.5
Sulphide (mg/l)	0.1
TSS (mg/l)	15
Ammonia (mg/l)	3
Oil (mg/l)	0.5
Total Dissolved Solids (mg/l)-Max	2500

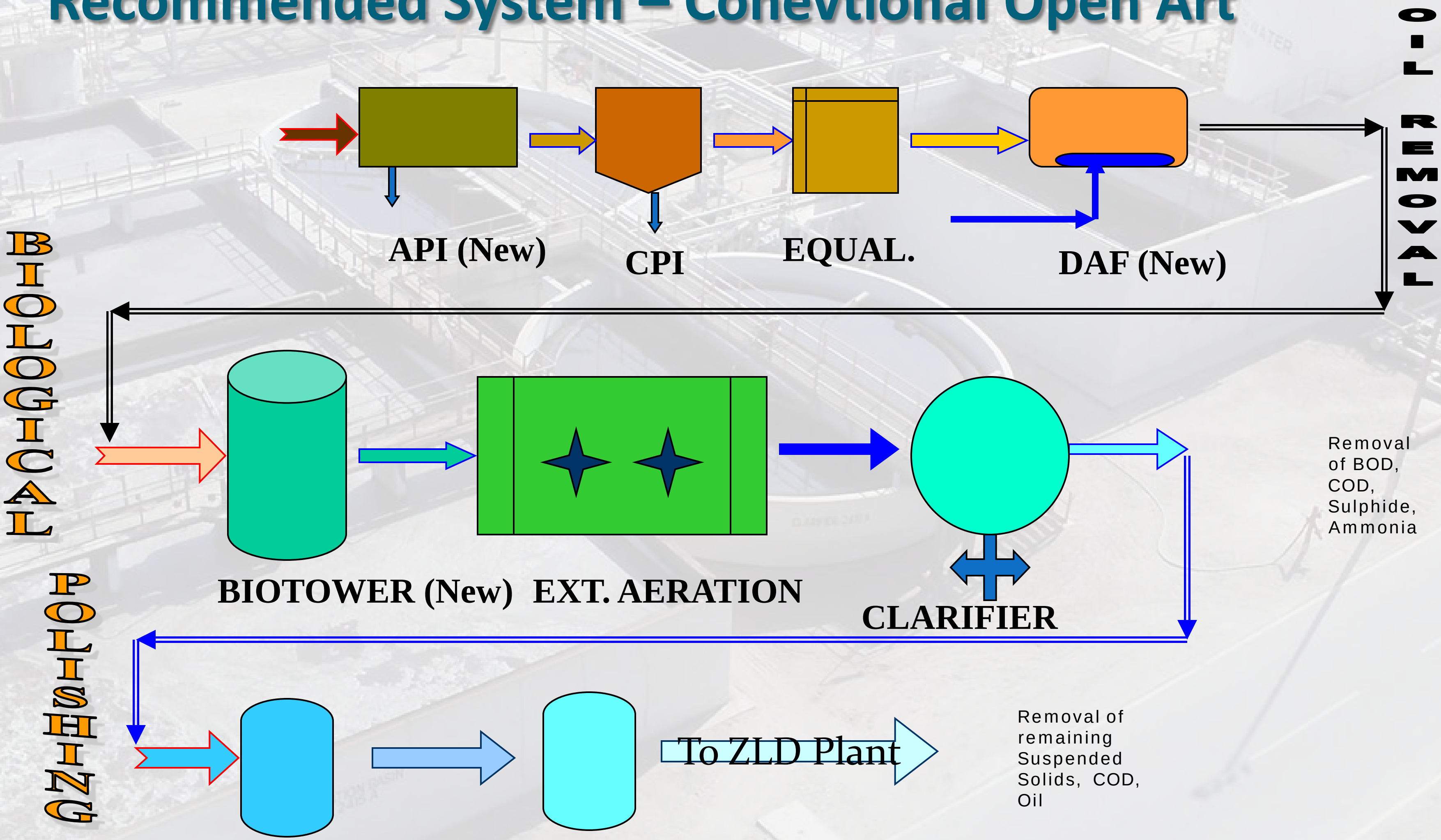
Comparative Study of Technologies for New Train of WWTP

- Three generic types of treatment schemes were evaluated
  - Scheme 1 : Based on conventional open-art systems
  - Scheme 2 : Biological system based on Sequential Batch Reactors (SBR)
  - Scheme 3 : Biological and filtration system based on Membrane Bioreactor (MBR)

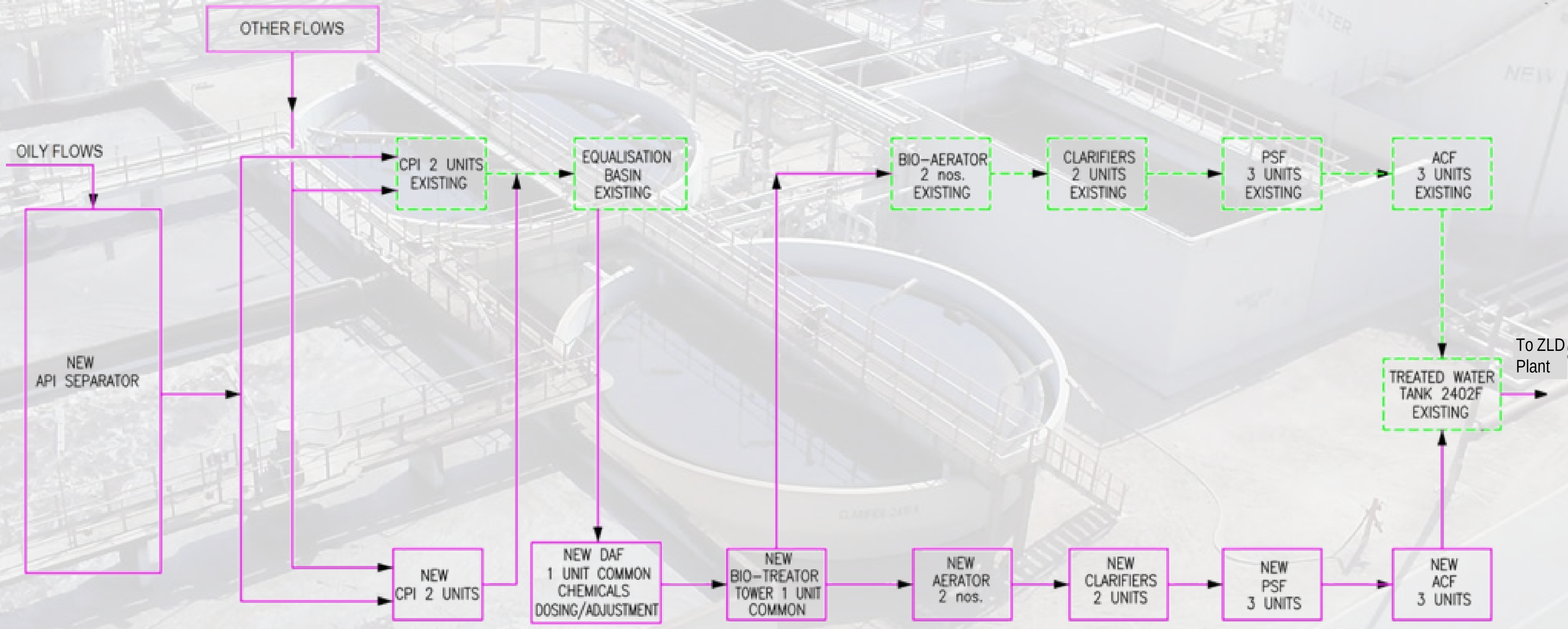
Effluent Quality Design parameter for New WWTP

Parameter	Original Design Parameters Existing WWTP	New Design Parameters - Based on actual laboratory data
pH	8.6-11	7.2-8.7
BOD (mg/l)	241	400
COD (mg/l)	462	900
Oil (mg/l)	51	300
Phenol (mg/l)	20	20
Sulphide (mg/l)	1	25.6
TSS (mg/l)	66	500
Ammonia (NH3) (mg/l)	6	22

Upgradation of Existing WWTP & New WWTP Train
Recommended System – Conevtional Open Art



Existing & Proposed WWTP Scheme – Conventional



Treated Effluent Quality from Existing Upgraded/ New Proposed WWTP

Parameter	Expected Values
pH	6-9
BOD (mg/l)	<20
COD (mg/l)	<100
Oil (mg/l)	<0.5
Phenol (mg/l)	<0.5
Sulphide (mg/l)	<0.1
TSS (mg/l)	<1.0
Ammonia (NH3) (mg/l)	<3
Total Dissolved Solids (mg/l)-Max	2500

BELCO Treated Effluent Expected Quality

Parameter	Expected Values
pH	7.0
Total Dissolved solids mg/l	50000
COD (mg/l) from Sulphites	10
Ammonia (mg/litre)	1000
Normal Flow rates(m3/h)	18
Design Flow (m3/h)	26.918

Need for Zero Liquid Discharge

Objectives

To meet Qatar MoE regulations which stipulate…*"No discharge of liquid effluents to the sea"*

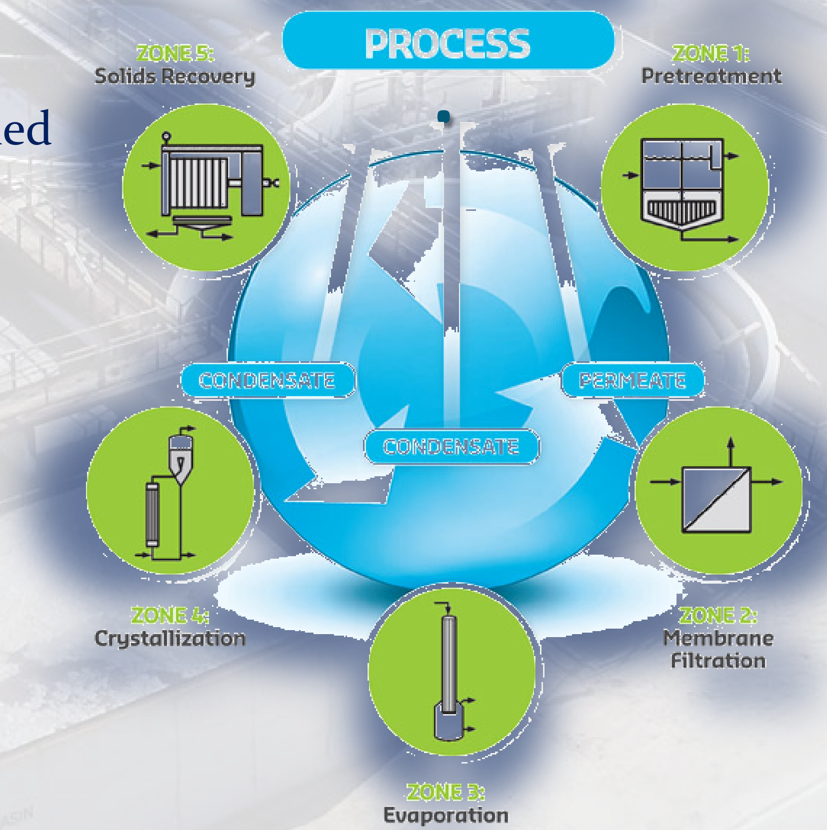
Recycling/ Reuse of ZLD produced water in Refinery.

Streams to be treated

- Treated effluents from WWTP (proposed and existing) – Maximum Designed Capacity 312 Cum/hr.
- Treated effluents from Flue Gas Scrubber (BELCO Unit); maximum 27 cum/hr.

Zero Liquid Discharge Definition & Simplified Process

ZLD is broadly defined as separation of an aqueous waste to its water and solid components.



(Figure Coutesy Degremont)

ZLD System means that no treated liquid wastes leaves the boundary of facility; and is recycled/reused within the facility. Solids disposed as waste.

Zero Liquid Discharge Concept

1. Zero Liquid Discharge (ZLD) focuses on:
   - Economic recovery of water (up to 99% overall)
   - Removal of contaminant as solid waste
2. Membrane systems are selected for water recovery
   - WWTP treated effluent (TDS <2,500 mg/L)
   - Industry standard
3. Brine Concentration systems are selected to convert high TDS reject to solid waste
   - Membrane brine reject (TDS ~50,000 mg/L)
   - BELCO treated purge (TDS 50,000 to 150,000 mg/L)

ZLD Technology Evaluation

- **Membrane Systems**
- Reverse Osmosis (OR)
- Electrolytic Dialysis Reversal (EDR)

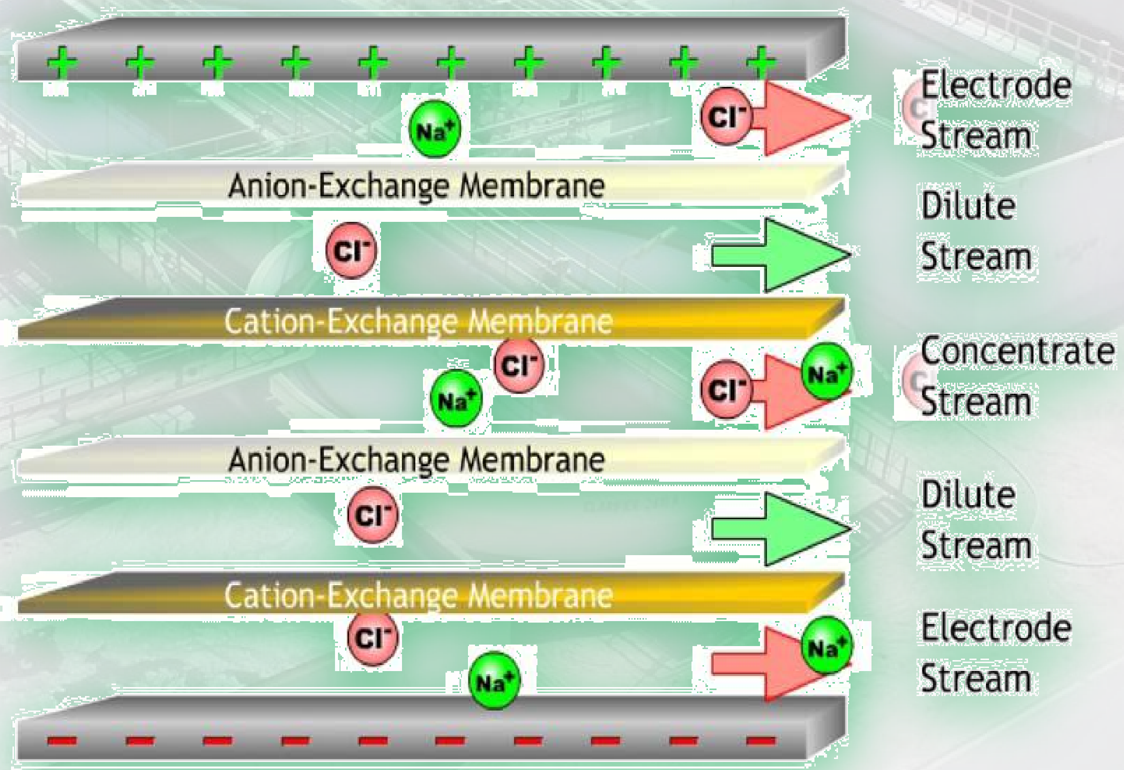
- **Thermal Evaporation Systems**
- *Brine Concentrators; MVR/MVC//MEE*
- *Crystallizers*

Pre - treatment for Membrane Systems

- Oxidation and precipitation of metals:
- Pre-filtration anti-scalants
- Ultra-filtration
- Softening
- Dosing
- Degassing

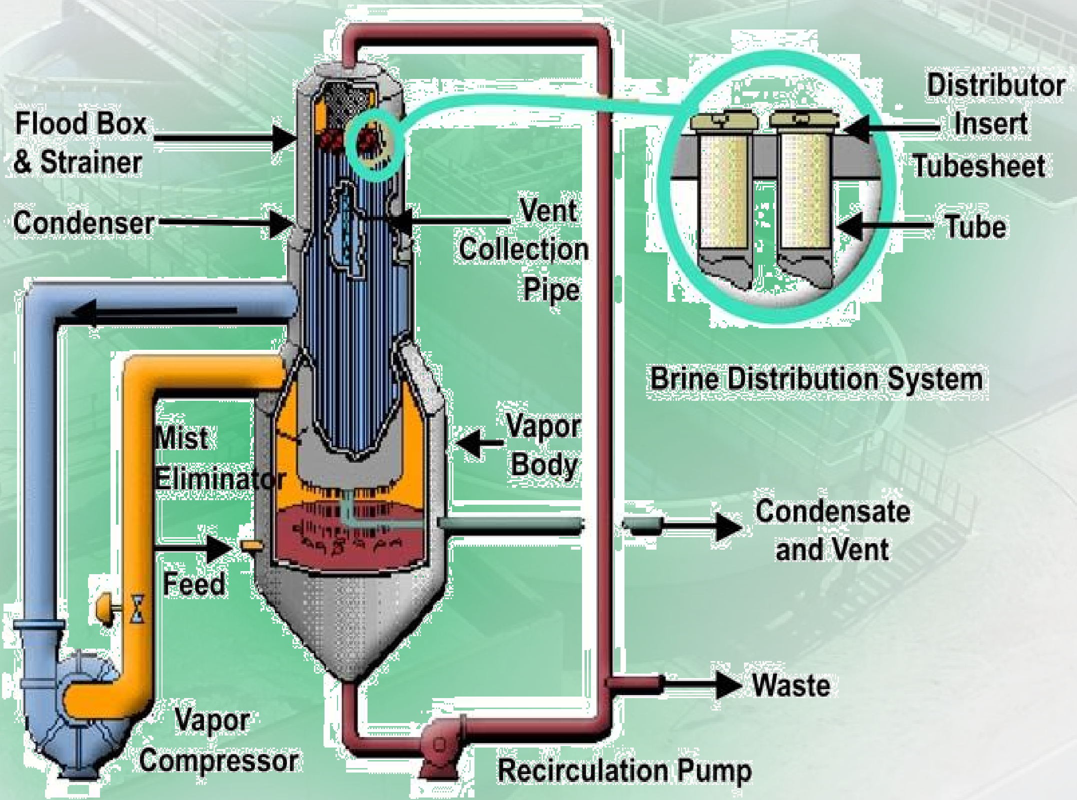
Schematic of Electrodialysis Reversal (EDR)

Electro mechanical separation process that allows selective passage of ions in a solution. Anions passes through anion exchange membrane while cations pass through positively charged ions.



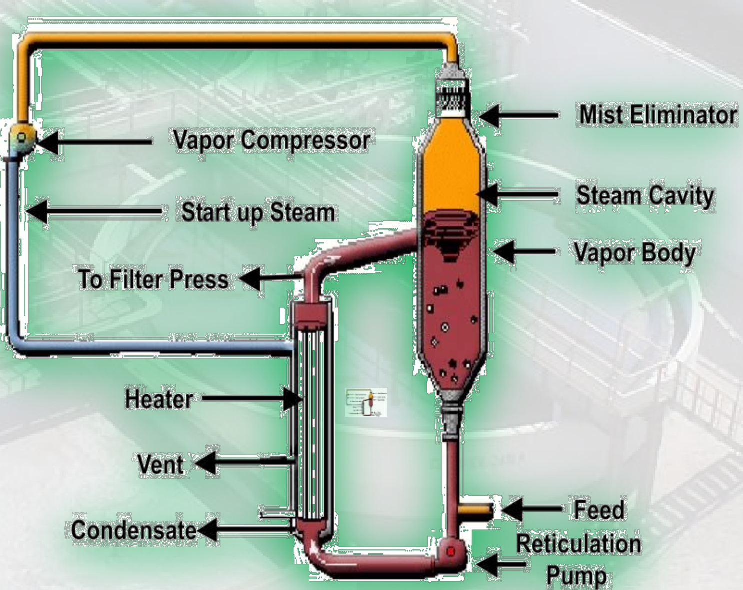
(graphics courtesy of GE)

Schematic of Brine Concentrator



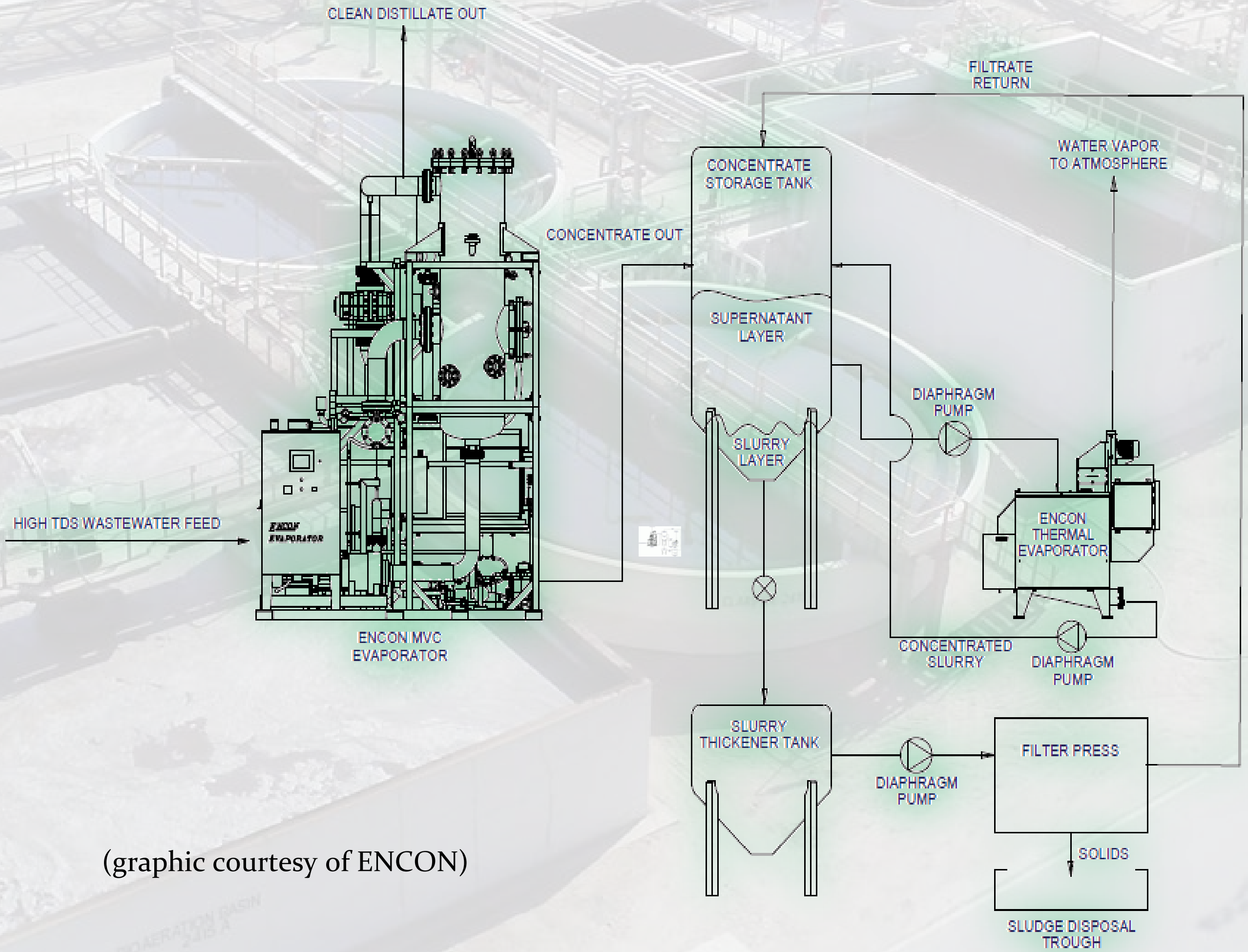
(graphic courtesy of GE)

Schematic of Brine Crystallizer



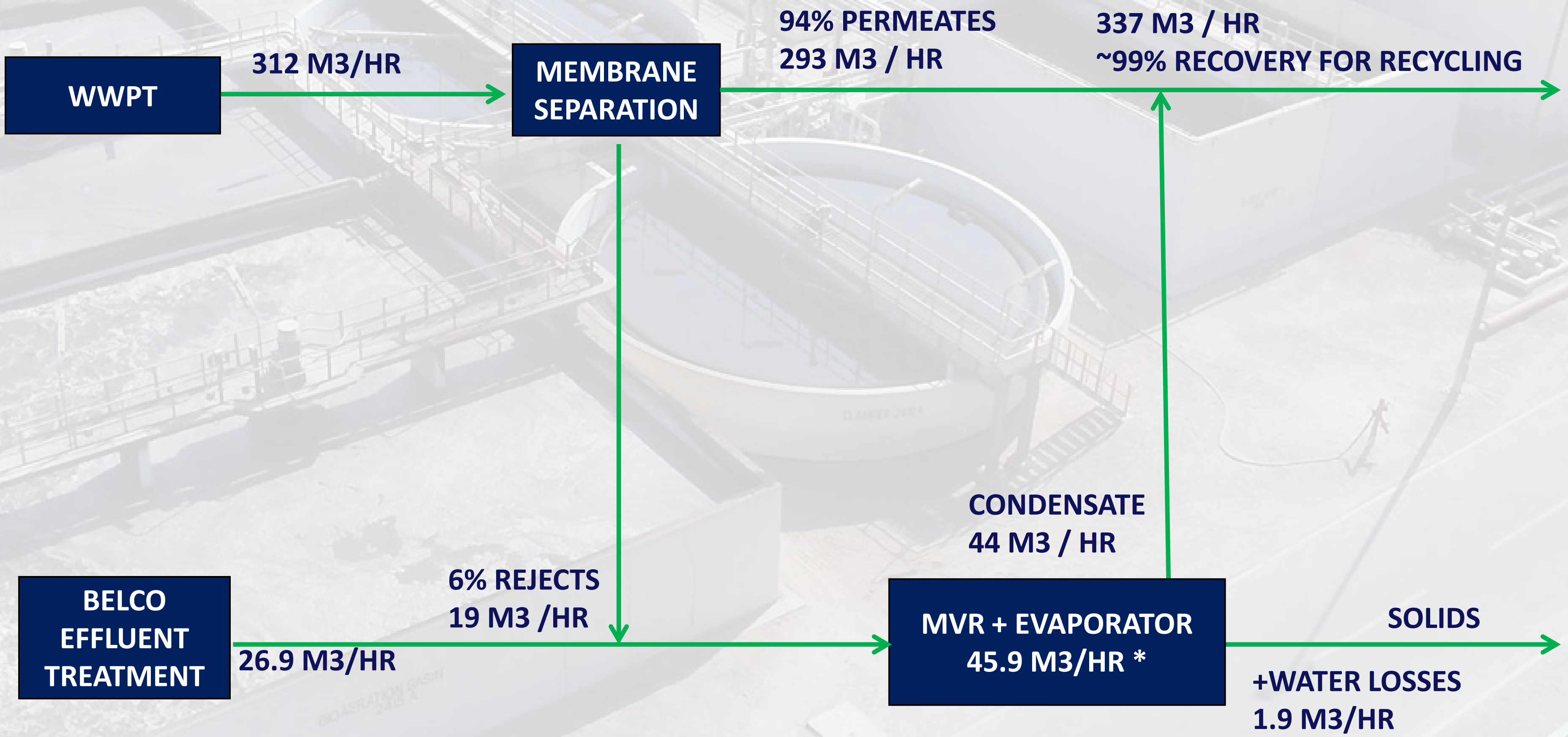
(graphic courtesy of GE)

Schematic Layout of MVC with Evaporator

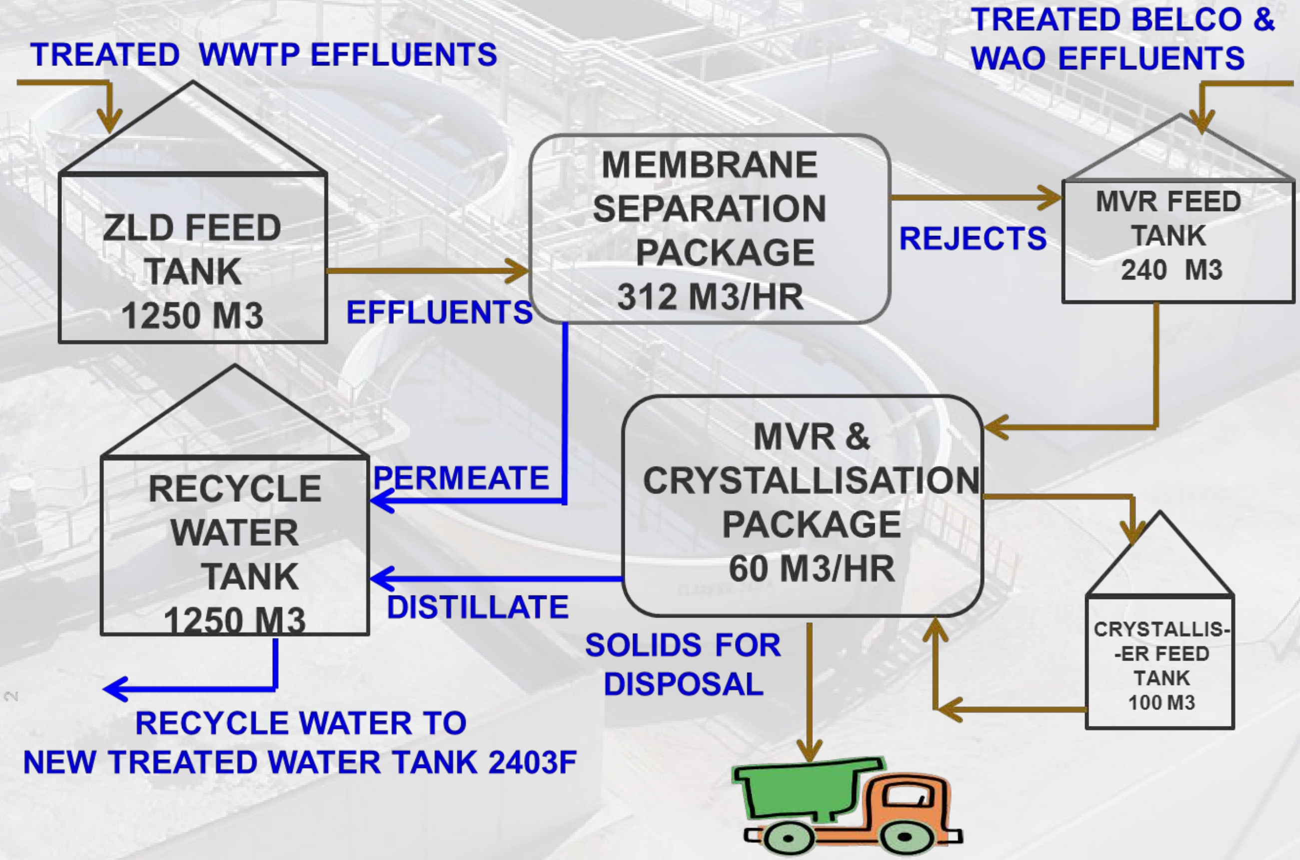


(graphic courtesy of ENCON)

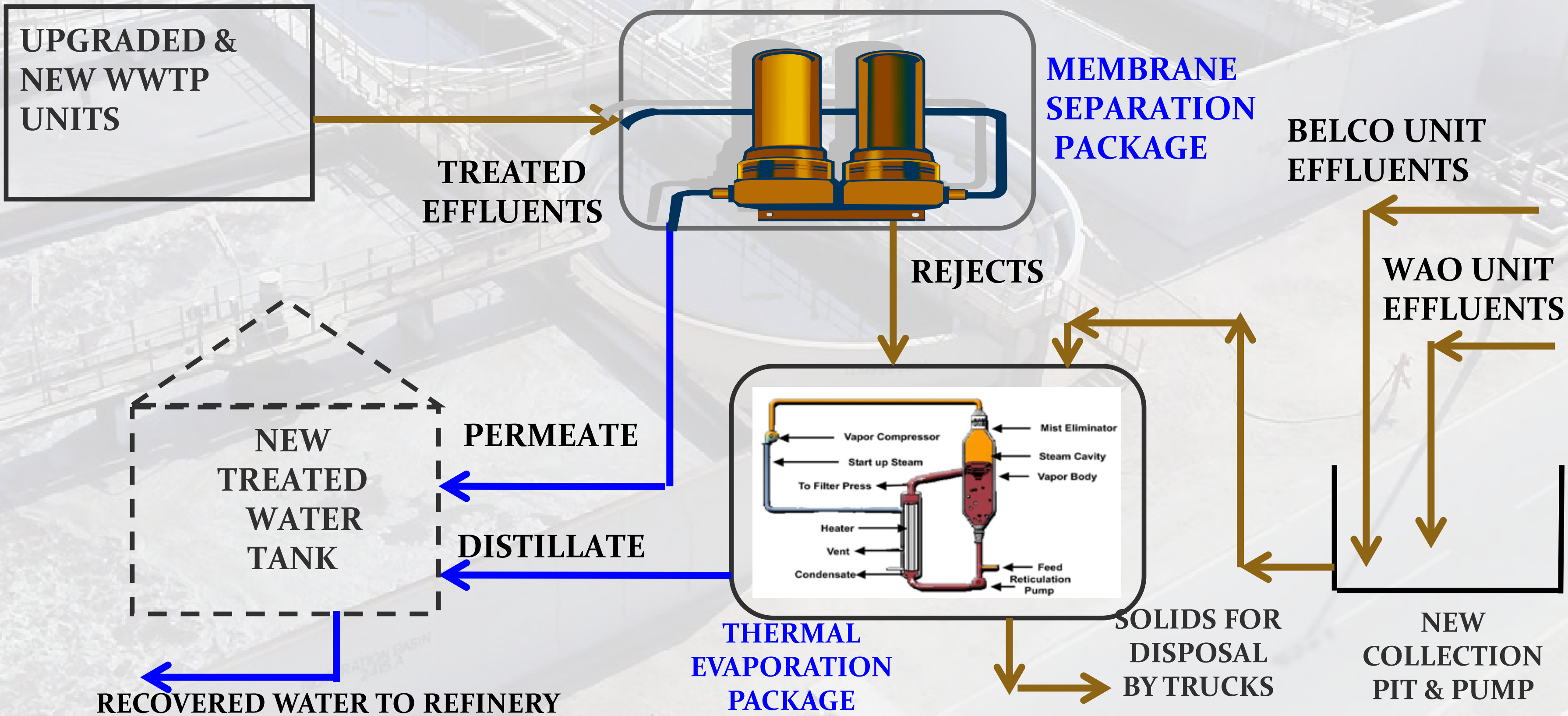
Overall ZLD Scheme Block Diagram



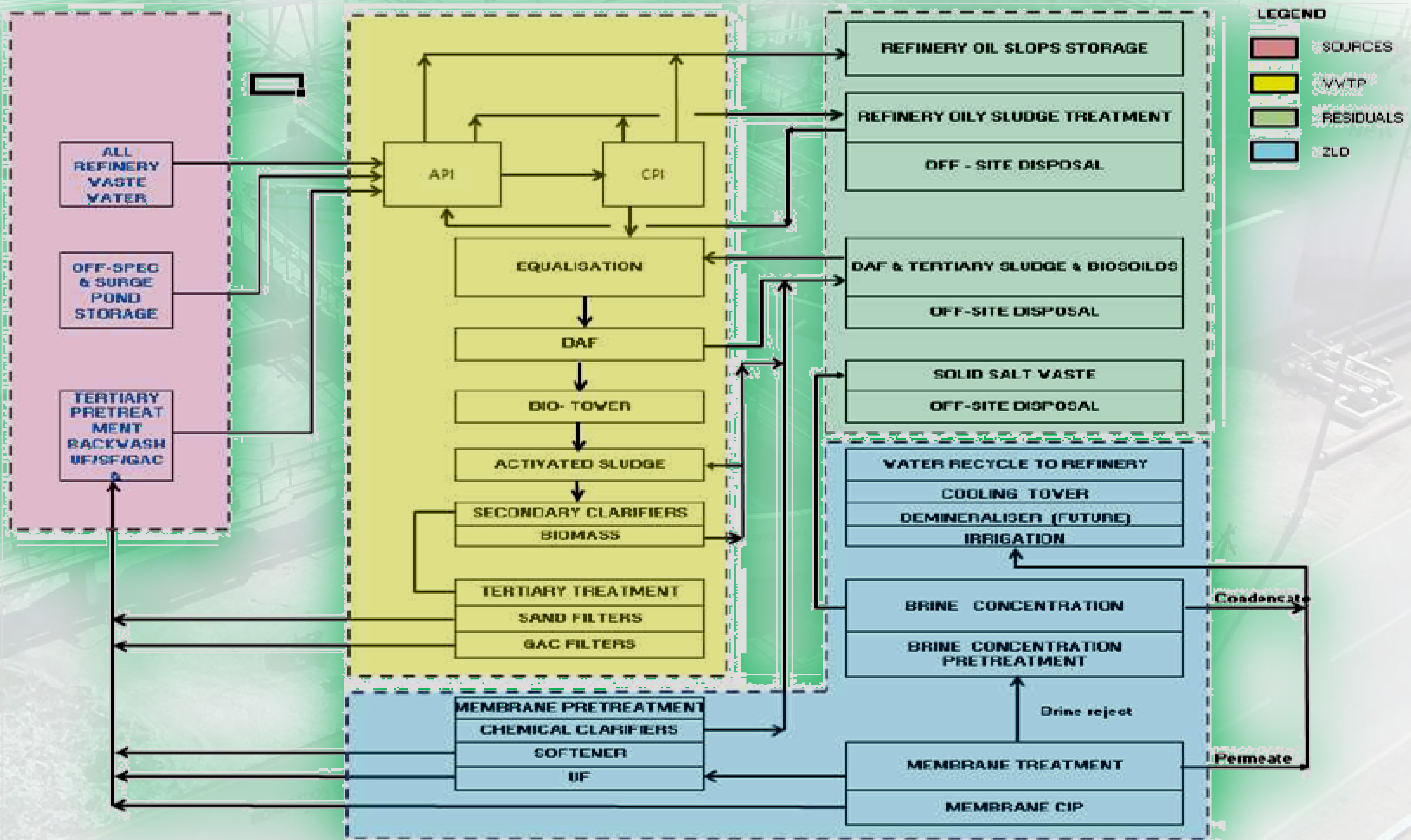
ZLD – Overall Scheme Schematic



INTEGRATION OF WWTP, BELCO & WAO WITH ZLD



Overall Waste Water Treatment , ZLD and Recycling Scheme



ZLD Treated Water Quality

Parameter	Expected Values	Parameter	Expected Values
pH	6.5-7.5	Total Suspended Solids (mg/l)	<2
Temperature normal ºC	35	Chlorides (mg/l)	80
COD (mg/l)	<20	Total Iron (mg/l)	0.05
Oil & Grease (mg/l)	<0.5	Bicarbonate (mg/l)	<10
Silica as SiO2 (mg/l)	<2	Sodium (mg/l)	60
Turbidity NTU	< 5	Sulphate (mg/l)	<50
Total Dissolved Solids (mg/l	<200	Flouride (mg/l)	0.3
Nitrate (mg/l)	< 5	Magnesium (m3/l)	<15

Proposed Uses of ZLD Treated Water for Recycling

Proposed Uses in Refinery	Consumption, m3/hr.
Old Cooling Tower make-up	85
Boiler Demineralization Plant Feed water	140
Other process uses & Irrigation	Balance

ZLD Economics

- ZLD has a high Capex and Opex Costs with ball park figures of around 60 million US$ and 14 million US$ respectively; for a multistage RO and thermal evaporator/ crystallizer.
- Annual savings in water costs; as replacement to Kharamaa water; is around 3 million US$.
- NPV for the ZLD Project over a 25 year project life turns out to be negative.

Conclusion

1. Best Evaluated Available Technology (BAT) for ZLD
   - Multiple Stage Reverse Osmosis for brackish water recovery. Recovers maximum water from WWTP effluents leaving a small concentrated stream (6% by volume) to be treated in Thermal Evaporation Unit.
   - Mechanical Vapor Recompression with Crystallizer for brine & BELCO treated effluent recovery & solid salt removal.
2. 99% recovery of reusable water
3. Highly capital intensive . Net Present Value (NPV) is negative. Cost saving in water costs 3 million US$
4. QP committed to implement the ZLD Project.

Q & A