1

Fundamentals of Produced Water Treatment in the Oil and Gas Industry

Upstream O&G Subcommittee of Industrial Wastewater Committee (IWWC), WEF with Produced Water Society (PWS)

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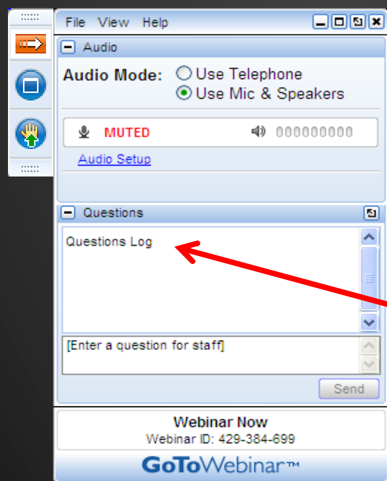
How to Participate Today



- **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

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Presentation Outline with Speakers

A) **Introduction to Produced Water (PW) Management:** *F. Morris Hoagland*

B) **Life Cycle of PW with Regulatory Issues:** *Jill E. Cooper*

C) **PW Management-Market & Treatment:** *Hossain Azam & F. Morris Hoagland*

D) **PW-Characters and Preliminary Treatment Technologies:** *Paul Sun*

E) **Recycling PW:** *F. Morris Hoagland*

F) **Advanced Produced Water Treatment:** *F. Morris Hoagland*

G) **Questions and Answers (Q & A):** *All Speakers*

5

Introduction to Produced Water Management

F. Morris Hoagland, P.E.
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& Produced Water Society
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6

Outline

- Conventional vs. Unconventional Wells
  - Conventional Wells
  - Produced Water Production
  - Produced Water Treatment
  - Water Flooding
- Unconventional Wells
  - Flowback water
  - Produced water
  - Treatment and disposal

Produced Water?

- Produced Water (PW) is ancient water
- In geological formations that were once the bottom of seas
- PW comes up with the oil & gas production
- In recent years PW management has become a greater problem

Why?

Hydrocarbon Production

Two basic kinds of oil & gas production

Conventional

- Porous formations
- Primary method for over 150 years

Unconventional

- Production from tight formations
- Recent technology - Shale Plays

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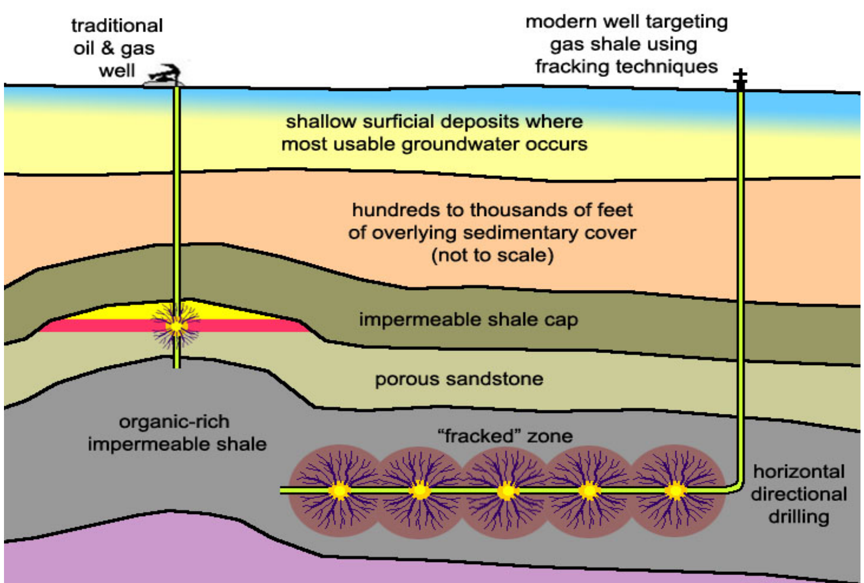
Conventional vs. Unconventional



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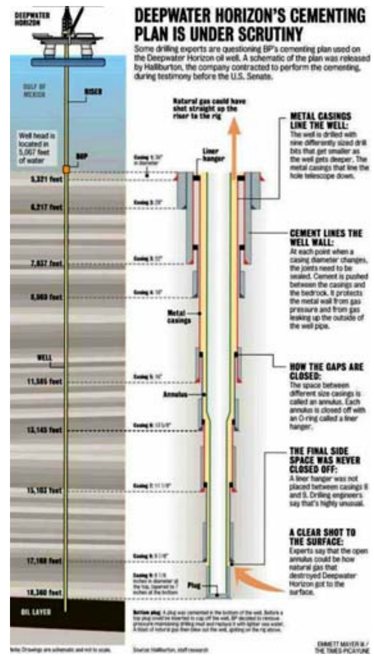
Example: Conventional Well

Water depth 5,000 feet

Note: this example is the Macondo Well drilled by the Deep Water Horizon

18,000 feet of sedimentary rock to reach pay zone

A deep water well like this might cost $100,000,000



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PW from Conventional Wells

- Initially mostly oil produced
- Eventually more water as well matures
  - Stripper wells 10 bbl water/bbl oil
  - Oman 20 bbl water/bbl oil
- Offshore treated PW water goes overboard
- On shore most PW reused in water floods

PW has not been a big problem for conventional wells

1 barrel = 42 gallons

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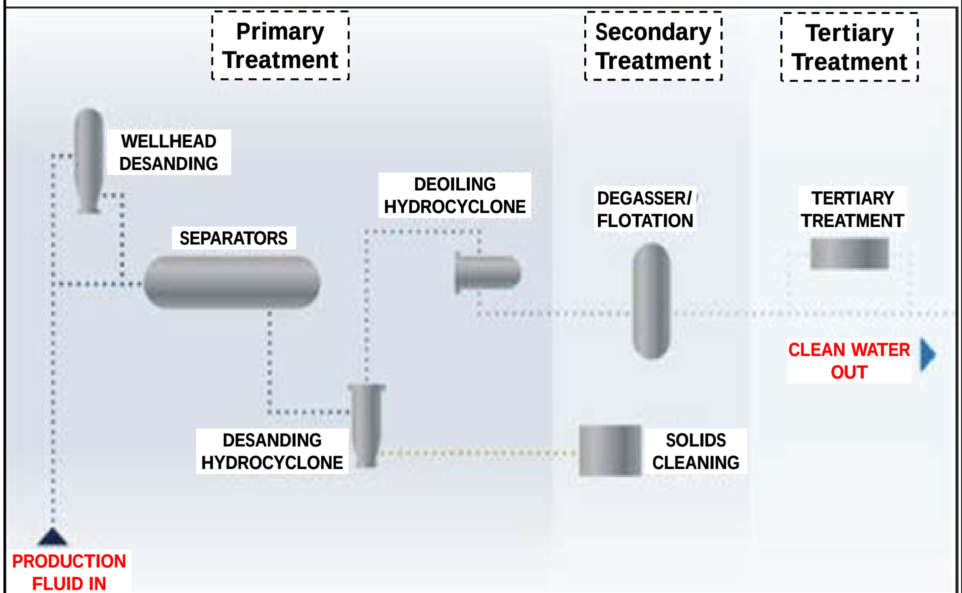
Conventional PW Treatment



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PW Treatment from Conventional On-Shore Wells

- Minimal treatment
- Separation of oil and solids in battery tanks
- Pumped to injection wells for water flooding

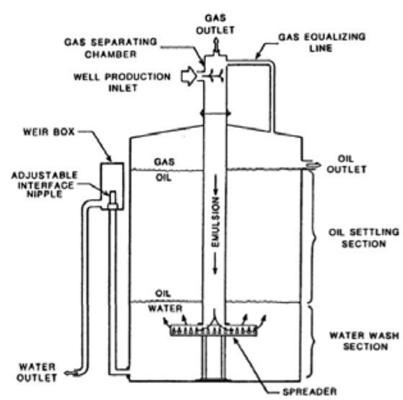

Fig: 6-9. Typical gunbarrel settling tank with internal flume

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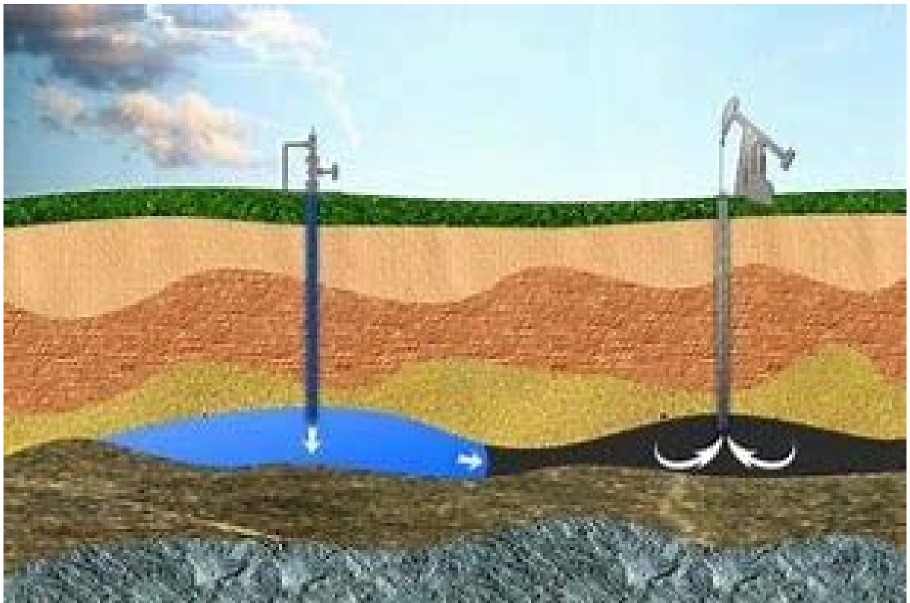
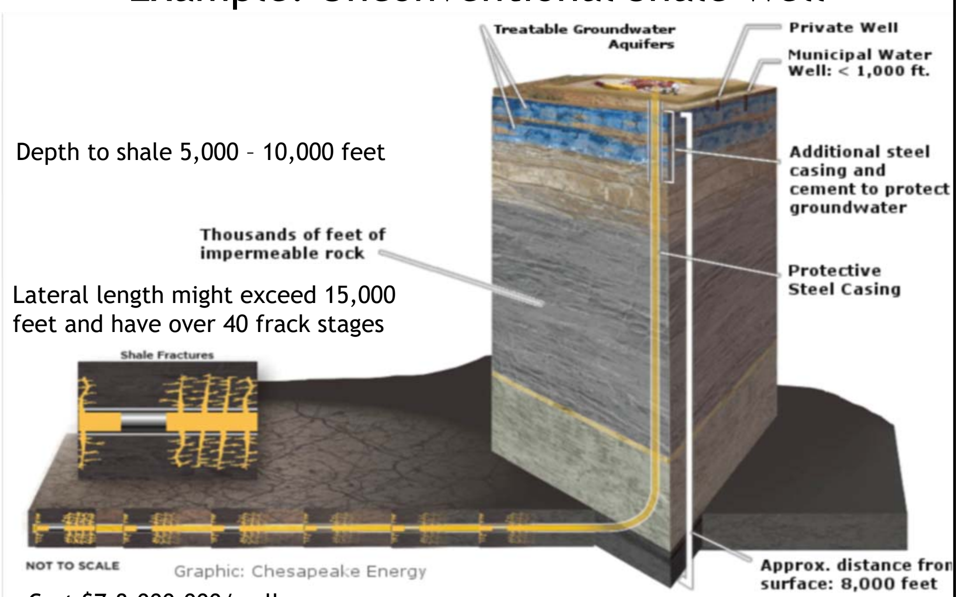
Conventional Wells PW Water Flood



15

Example: Unconventional Shale Well



Depth to shale 5,000 – 10,000 feet

Lateral length might exceed 15,000 feet and have over 40 frack stages

Cost $7-8,000,000/well

16

PW Unconventional Wells

- Much less PW vs. conventional wells
  - Haynesville Shale - <1 bbl water/boe
  - Marcellus Shale – 2-4 bbl water/boe
  - Delaware Shale – 8-10 bbl water/boe
- Initially high "flowback" water (1-month)
- PW at low rate over life of well

Most PW disposed of SWD, some recycled for completions

1 barrel = 42 gallons

17

PW Unconventional Wells

Flowback water - water was used to Frac

- 100,000 – 500,000 bbls of water used
- 5 – 70 % returns as Flowback water
- Most comes back in first month
- Highly contaminated
  - Fracking chemicals
  - Proppant sand
  - Shale formation fines

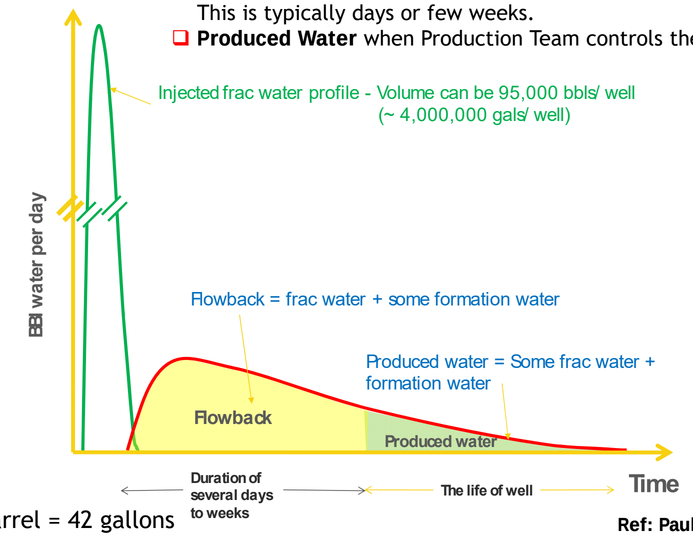
PW comes slowly over the life of the well

1 barrel = 42 gallons

18

Flowback and produced water

- **Flowback Water** as long as Completion Team controls the well. This is typically days or few weeks.
- **Produced Water** when Production Team controls the well.



1 barrel = 42 gallons

Ref: Paul Sun, WEFTEC, 2014

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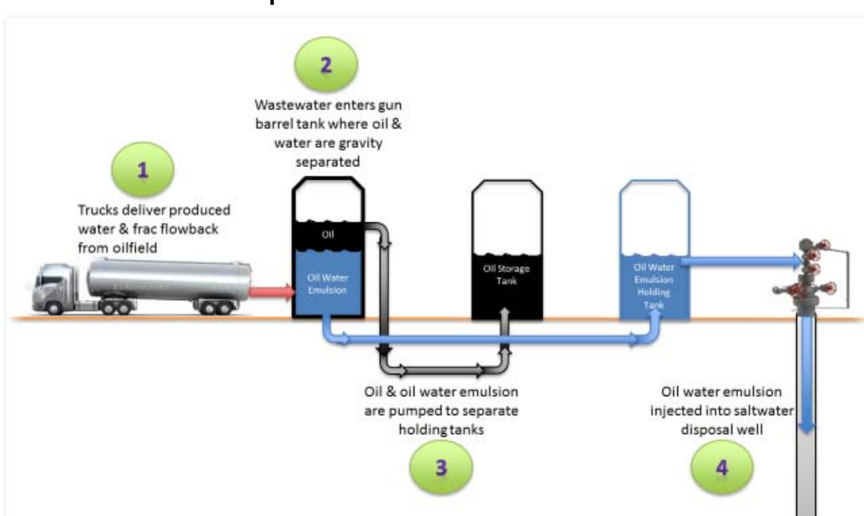
Unconventional PW Disposal

Most water is disposed of in SWDs



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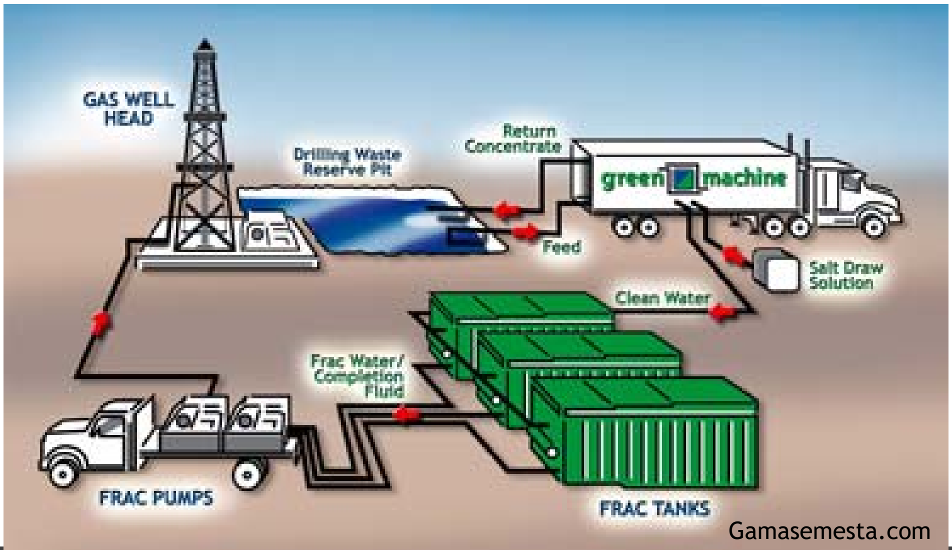
Unconventional PW Treatment

Some water is recycled for more completions



Gamasemesta.com

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APPENDIX

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Flowback Water Contaminants

- Salts 10,000 – 250,000 ppm depending on formation
- Shale fines <0.5% declining rapidly
- Proppant and proppant fines <0.5%
- Polymer – High MW friction reducers or guar-base
- Surfactant – promotes hydrocarbon wetting of fractured rock face
- Biocide – used to prevent bacterial souring of formation
- Breaker – oxidizer to break viscosity building polymers

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Fluids Used in Well Operations

- Drilling Mud – water based and oil based
- Completion Brines – Heavy brines to keep pressure on the formation until ready to produce the well
- Stimulation Fluids – primarily acids and solvents
- Hydraulic Fracturing – Polymers to build viscosity to carry proppants, surfactants, biocides, breakers

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Life Cycle of Produced Water with Regulatory Issues

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25

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Life Cycle of Produced Water with Regulatory Issues

Overview

- Water in Upstream
- Water as a Product
- Regulatory Issues
- Collaboration and Research

26

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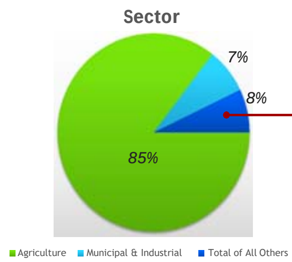
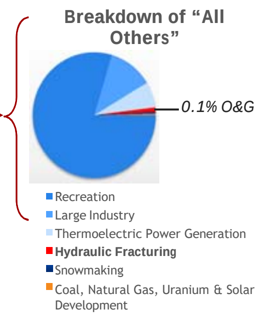
Water in Upstream

- Wells will typically produce energy for 30 years
- Colorado OGCC projected that water usage for oil and natural gas is about 0.08% of total water use in Colorado
- US EPA projected nationwide upstream water use is >1% of total water use





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Source: Colorado Oil & Gas Conservation Commission 2010

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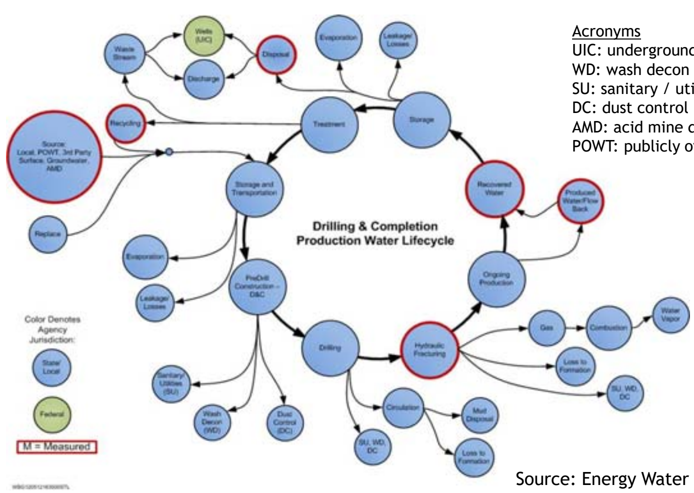
Water in Upstream: Life Cycle in Upstream Operations



Acronyms
UIC: underground injection control
WD: wash decon
SU: sanitary / utilities
DC: dust control
AMD: acid mine drainage
POWT: publicly owned water treatment

28

Source: Energy Water Initiative

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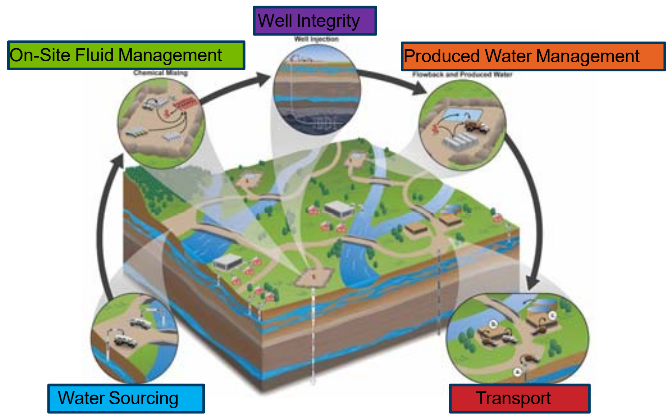
Water in Upstream: Stages of Water Management



Source: JISEA: Jordan.Macknick@NREL.GOV   Figure adapted from EPA 2015

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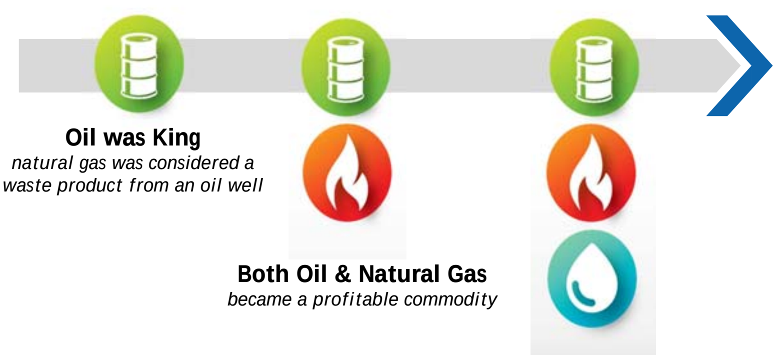
Water as a Product



Oil was King
natural gas was considered a waste product from an oil well

Both Oil & Natural Gas
became a profitable commodity

Produced or Formation Water
can it also become a Useable by-product?

30

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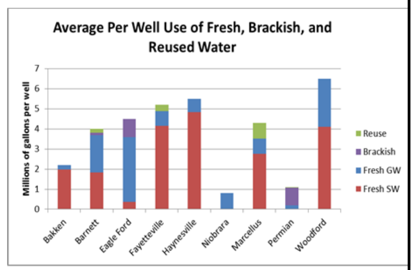
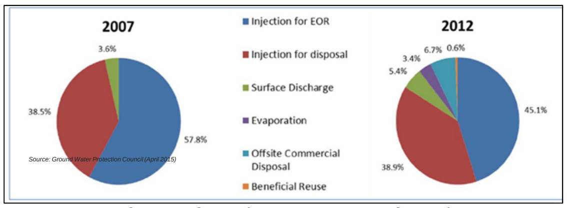
Water as a Product: Produced Water Management

- Generated from most producing oil and natural gas wells in the U.S.
- Cost of managing the water is a key consideration to producers
- Every play has a different "water profile"
- They "get what nature gives them"



Source JISEA: Jordan.Macknick@NREL.GOV

Data collected from: (Freyman 2014; Taylor 2012; Nicot et al. 2014; Nicot et al. 2012; Scanlon, Reedy, and Nicot 2014; Louisiana Ground Water Resources Commission 2012; EPA 2015a; BHP Billiton 2014; Hansen, Mulvaney, and Betcher 2013; Goodwin et al. 2014)



31

Source: Groundwater Protection Council

1 barrel = 42 gallons

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Water as Product: Produced Water as Part of the Solution

- **Opportunities**
  - Water sourcing, management and disposal
  - Not a significant user of water compared to other sectors
  - Bring "trapped water" to the surface -net gain to the system
  - Collaboration to achieve progress
- **Actions necessary to maximize opportunities**
  - Laws and regulations that support beneficial reuse of water
  - Improvements in water treatment technologies
  - Reduced cost of water treatment
  - Entities interested in accepting the treated water

32

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Water as Product: Energy Water Initiative (EWI)

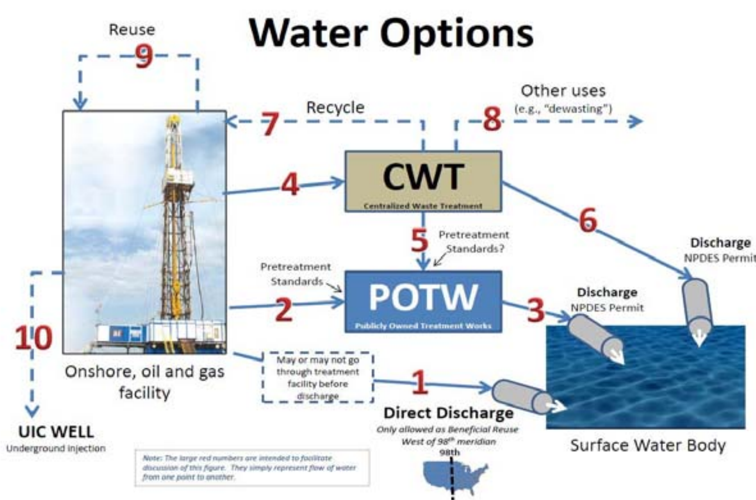
INDUSTRY TRENDS		BENEFITS
Improving Fracturing Chemistry	➡	Increasing use of non-fresh water
Innovation in Treatment Technology	➡	Increasing feasibility of produced water reuse
Increasing Water Conveyance Systems	➡	Reducing truck traffic
New Water Storage Designs	➡	Provides flexibility and reliability when using non-fresh water
Increasing Transparency	➡	Improves relationships with stakeholders
Dedicated Water Staff	➡	Improves water management, planning technical support and performance

Source: EWI: 2015 Case Study Findings

33

33

Regulatory Issues: Federal



Source: American Petroleum Institute

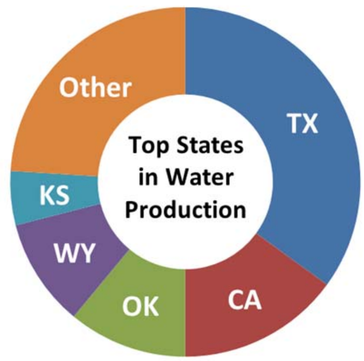
34

34

Regulatory Issues: States

States set requirements

- Permit usually not needed for:
  - Use of produced water or
  - Reuse of flowback water
- Permit is needed for discharge to surface
- Permit may be needed if provided to another user



Source: Veil, J. "U.S. Produced Water Volumes and Management Practices in 2012."

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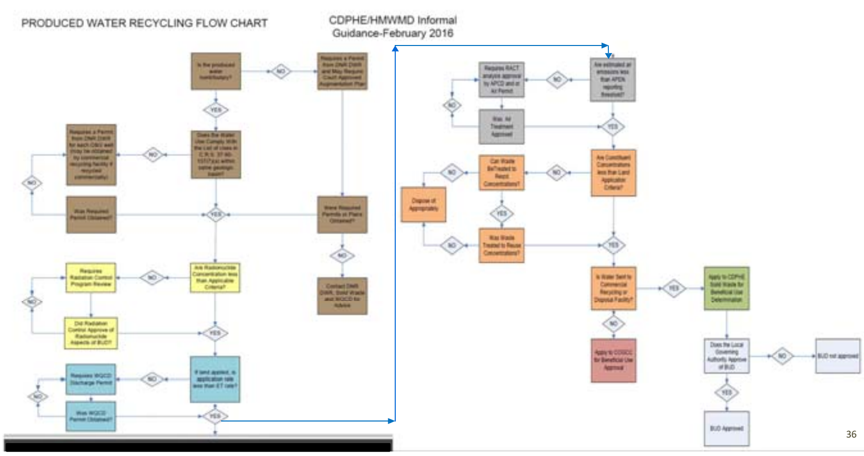
35

Regulatory Issues: Colorado Produced Water Recycling



36

Example of complexity of state process

Source: HMWMD, CDPHE

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Collaboration and Research: Water Knowledge Sharing

Industry is working together on:

- Water on demand design
- Water lifecycle evaluation
- Water risk assessment
- Water data management
- Water recycle technology

37

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Collaboration and Research: National Academy of Sciences

WORKSHOP ON
Use of Flowback and Produced Waters:
OPPORTUNITIES AND CHALLENGES FOR INNOVATION

http://nas-sites.org/uhroundtable/past-events/water-workshop/

38

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Thank You!

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39

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39

PW Management: Market & Treatment

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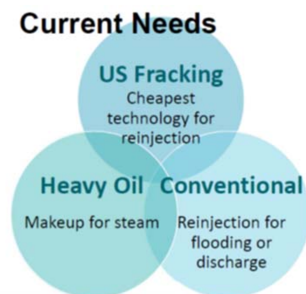
40

Outline

- Importance of PW Treatment
- Market in US Upstream O&G
- Shale Play Water Market
- Treatment Options



Ref: Andrea Larson, WEF Workshop on Produced Water, WEFTEC, 2018

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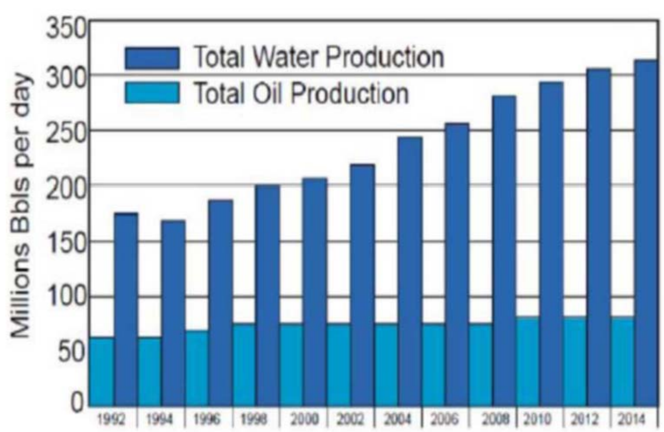
Importance of PW Treatment



Source: S. Robertson & Jahsen NEL 4th Produced Water Workshop

1 barrel = 42 gallons

Ref: Andrea Larson, WEF Workshop on Produced Water, WEFTEC, 2018

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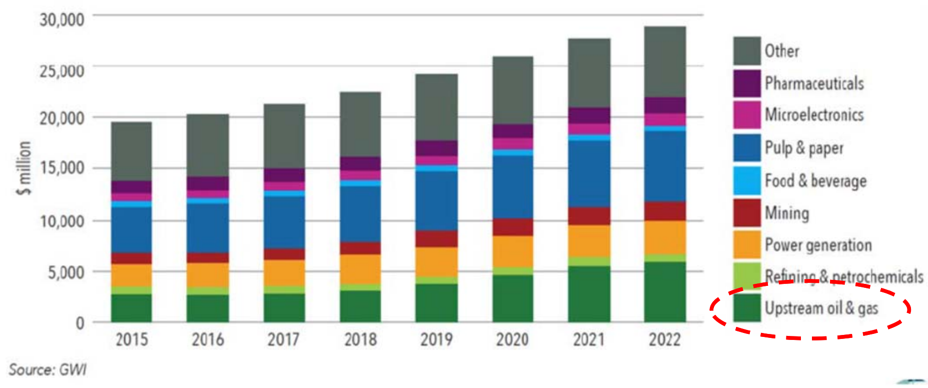
42

Industrial Water & Wastewater CapEx



Ref: Tom Pankratz, WEF Workshop on Produced Water, WEFTEC, 2018

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43

Upstream Sludge Management

Sector ($m)	2015	2016	2017	2018	2019	2020	2021	2022
Utility	6,570.2	6,908.0	7,391.3	7,893.8	8,068.9	8,491.1	8,921.4	9,545.5
Industrial	1,346.6	1,425.5	1,482.5	1,576.7	1,661.5	1,771.8	1,884.6	1,973.0
Upstream oil & gas	77.9	76.7	57.8	65.5	71.3	96.5	129.3	128.0
Refining & petrochemicals	24.1	24.9	25.9	26.6	24.5	26.7	31.5	29.4
Power generation	107.4	121.2	132.8	147.3	152.5	168.0	172.1	188.1
Mining	38.1	33.7	35.8	39.8	47.4	53.5	53.5	54.2
Food & beverage	542.2	581.4	624.8	673.0	720.6	768.4	817.3	870.2
Pulp & paper	70.6	71.0	71.0	72.1	72.5	72.8	73.3	73.9
Pharmaceuticals	54.9	58.2	63.9	68.2	72.5	78.1	83.5	88.7
Microelectronics	71.6	76.9	81.0	86.2	93.5	92.2	98.8	106.0
Other industries	359.8	381.3	389.5	398.1	406.7	415.7	425.2	434.5
Total	**7,916.8**	**8,333.6**	**8,873.8**	**9,470.6**	**9,730.4**	**10,262.9**	**10,806.0**	**11,518.5**

Ref: GWI from Tom Pankratz, WEF Workshop on Produced Water, WEFTEC, 2018

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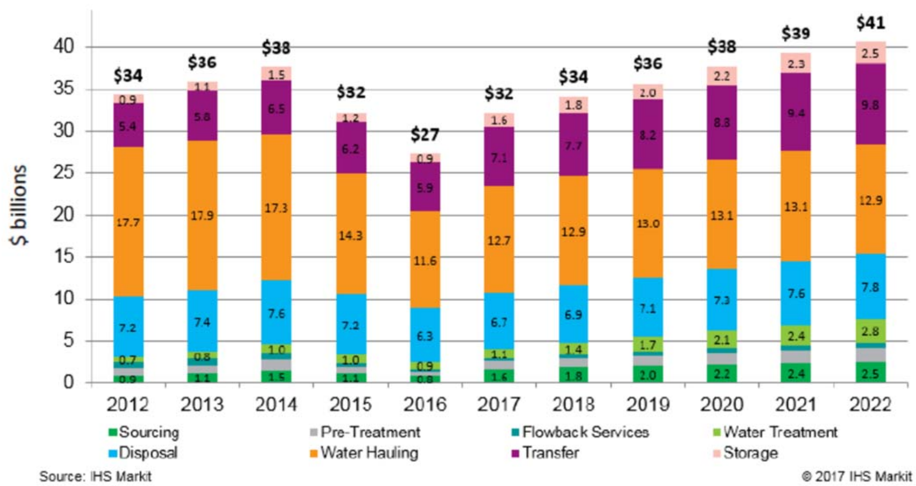
44

US O&G Water Services by Sector



Ref: Tom Pankratz, WEF Workshop on Produced Water, WEFTEC, 2018

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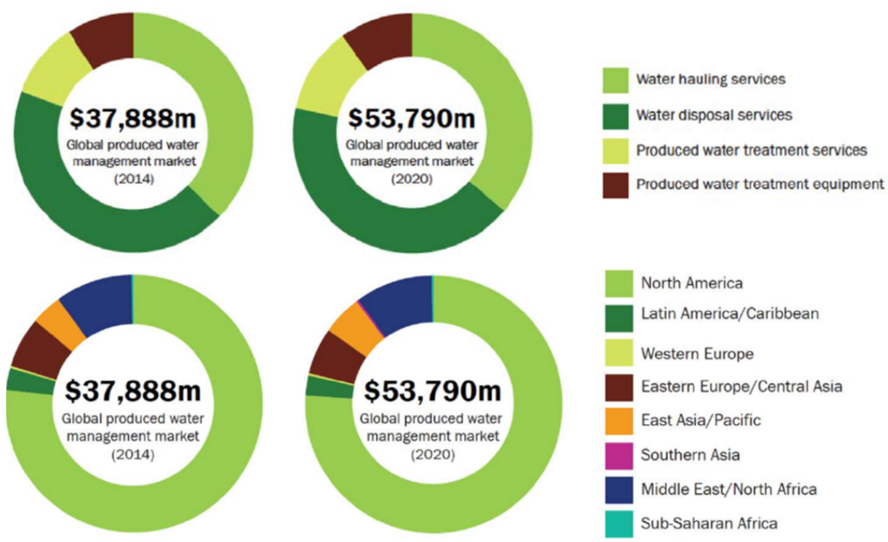
45

O&G Water Services by Sector & Region



Ref: GWI from Tom Pankratz, WEF Workshop on Produced Water, WEFTEC, 2018

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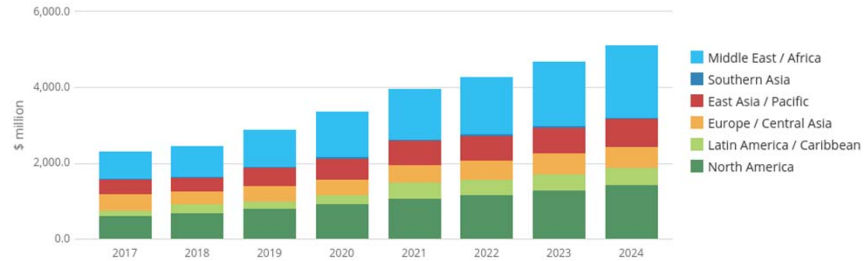
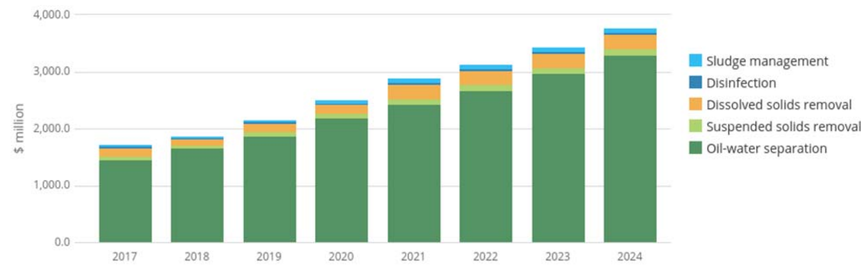
46

Upstream CapEx by Region & Technology





Courtesy: GWI/Produced Water Society

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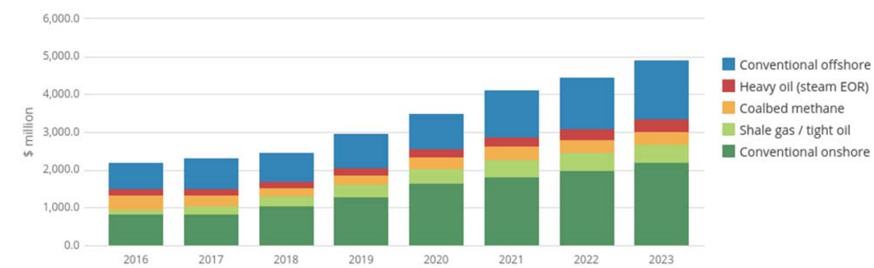
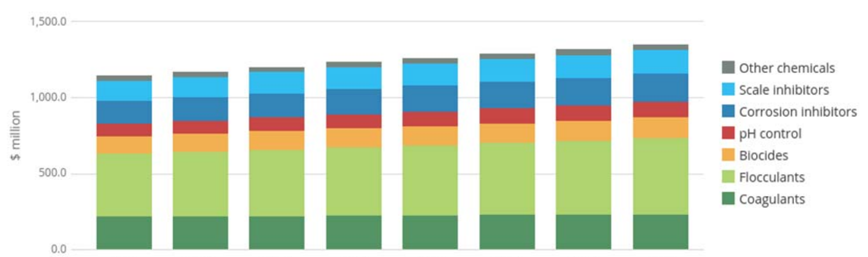
47

Upstream CapEx by Resource & Spending by Chemical





Courtesy: GWI/Produced Water Society

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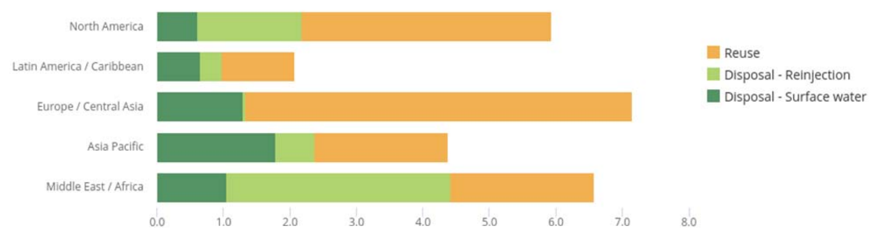
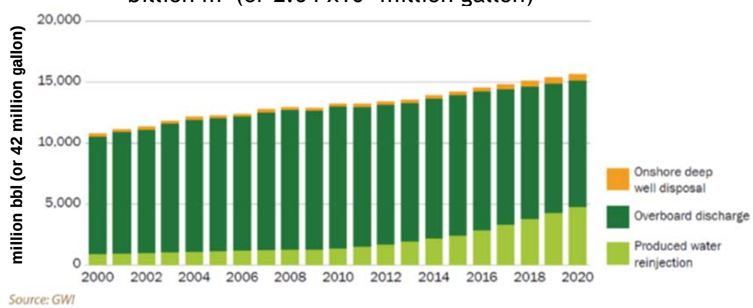
48

PW Volumes by Disposal Options & Off-Shore PW



billion m^3 (or 2.64 x10^5 million gallon)



Courtesy: GWI/Produced Water Society

Ref: Andrea Larson, WEF Workshop on Produced Water, WEFTEC, 2018

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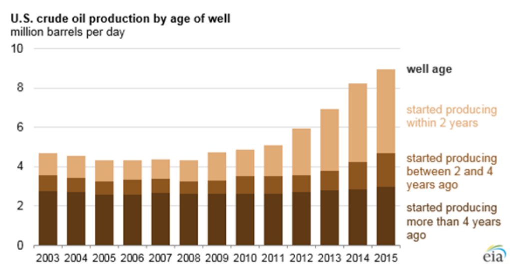
49

Shale Play Water Market

- Huge quantities of water required
- Challenges sourcing water
- Some water recycled, a long way to go
- Treatment has changed a lot
- Midstream investment changing the market
- Opportunities all along supply chain



Source: U.S. Energy Information Administration: Drilling Info & EIA-914 survey

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Shale Play Water Cycle

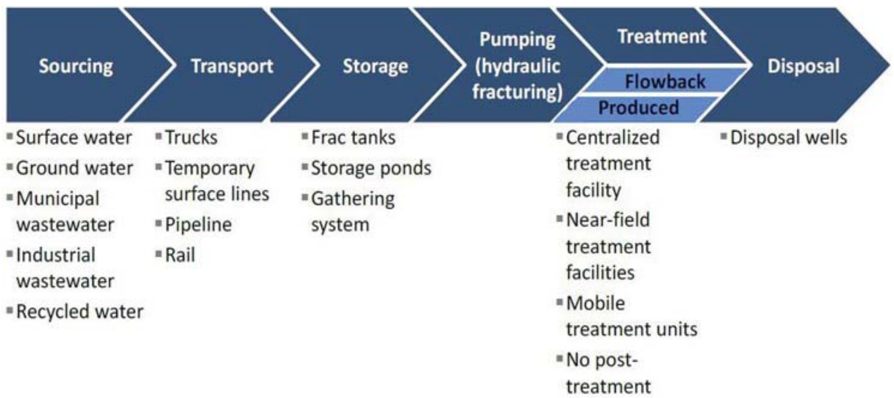

Figure 1. Oilfield water management life cycle (PacWest 2012)

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51

Shale Play PW: Disposal Options

- Dispose produced water in salt water disposal wells
- Recycle produced water
- Treat produced water for beneficial reuse

PA: 8 disposal wells
- 90% of the water is recycled
- Trucking to OH & WV may cost \$10/bbl

TX: >14,000 disposal wells
- Even when it is less expensive to recycle
- About 10% of water is recycled

1 barrel = 42 gallons

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Fracking PW: Water Treatment

Vast changes in quality of water required
- Initially fresh water was required
- RO, evaporation, crystallizers, etc.

Now modified fracking chemistry packages
- Marginal quality waters
- High TDS recycle waters
- Deep brackish water aquifers

Disposal
- Virtually no treatment

Recycling
- Chlorine Dioxide
- Electrocoagulation
- Floc & Drop
- Filtration for TSS
- Biocides

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Shale Play PW: Cost & Water Trends

Truck transportation ($1-3/bbl)
- Higher risk with Noise and congestion
- Road damage

Pipeline ($0.15-$0.25/bbl)
- Requires large investment
- Long term contracts

- More water used per well
- Companies desire to cooperate (share water)
- More pipelines to treatment or disposal wells
- Planning for larger scale infrastructure
- Mid-Stream companies will control the water

1 barrel = 42 gallons

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Contaminants: Water Treatment Challenges for PW

Hydrocarbon Recovery Strategy	Field Location	Fluid Characteristics	Disposal Options & Regulation	Contaminants/ Challenges
Primary	Onshore	Moderate gravity	Disposal well	***Large solids, oily solids***
Primary	Offshore	Wide range	Overboard	***TOG, toxicity***
Primary	Near shore	High GOR	Reuse, Surface discharge	***TOC, COD, BOD***
Water flood	Onshore	Moderate gravity	Flood	***Solids, oily solids, iron compounds***
Water flood	Onshore	Low gravity	Flood	***Oily solids***
Water flood	Offshore	Not relevant- seawater used	Flood	***Solids, oxygen, H_2S***
Steam flood	Onshore	Heavy oil, bitumen	Recycle	***Silica, hardness, TOC***
Chemical EOR	Onshore	Various	Polymer makeup	***TSS (polymer), TDS***
Shale	Onshore	Gas, light oil	Disposal well	***Sourcing water, transportation & storage***
Shale	Onshore	Gas, light oil	Reuse/Recycle	***TSS, TDS***
Coal Bed Methane	Onshore	Gas, light oil	Evaporation, Surface discharge	***Desalination for surface discharge (may be)***

Ref: Produced Water by John Walsh

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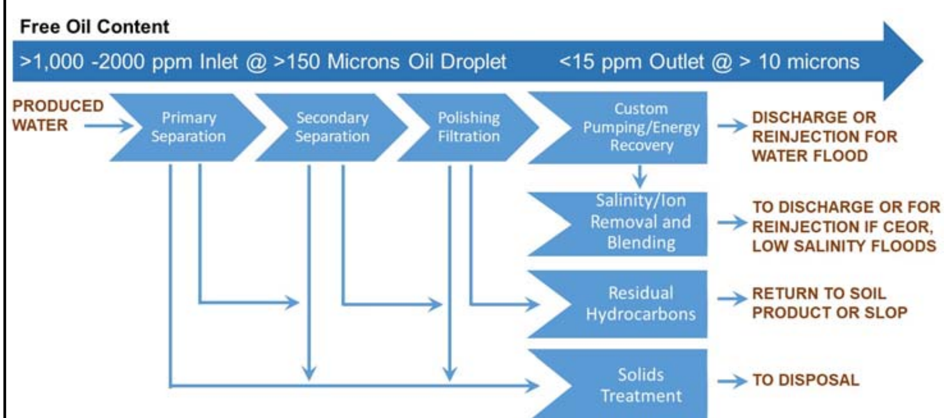
55

Produced Water Treatment



Ref: Lisa Henthorne & Chris Catalanotto, WEF Workshop on Produced Water, WEFTEC, 2018

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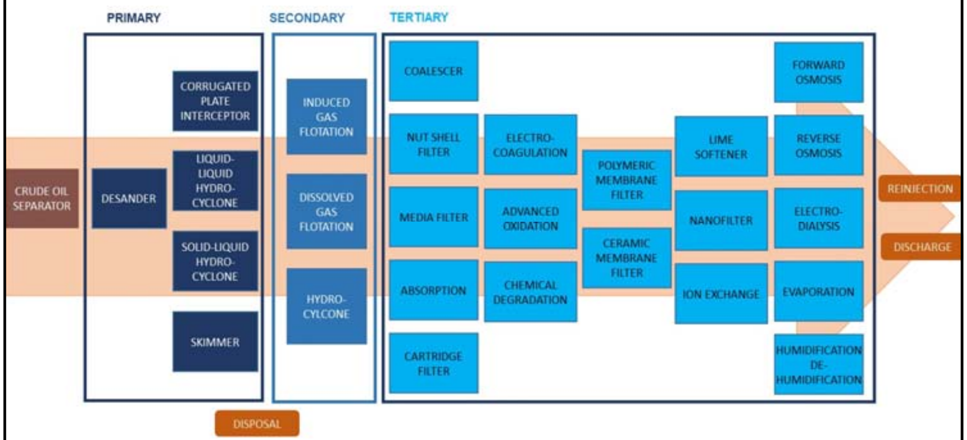
56

Produced Water Treatment



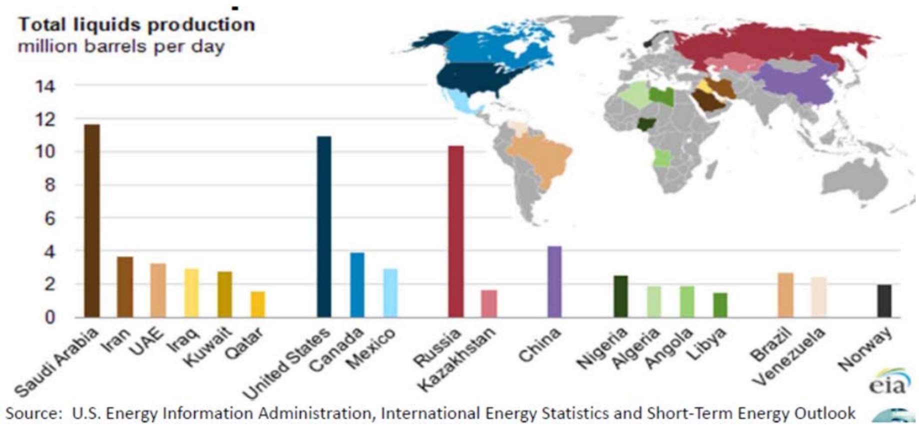
Ref: Lisa Henthorne & Chris Catalanotto, WEF Workshop on Produced Water, WEFTEC, 2018

57

APPENDIX

58

Where is produced water?



1 barrel = 42 gallons

Ref: Andrea Larson, WEF Workshop on Produced Water, WEFTEC, 2018

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59

Produced water - important characters and current preliminary treatment technologies - oil/solids/water separation

Paul T. Sun, PhD, PE
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60

OUTLINE

1. INTRODUCTION
2. IMPORTANT PARAMETERS - oil
3. IMPORTANT PARAMETERS - suspended solids
4. APPLICATIONS - conventional vs unconventional
5. BASIC THEORY
6. IMPORTANCE OF PARTICLE SIZE
7. COAGULATION & FLOCCULATION
8. GRAVITY SEPARATION
9. CENTRIFUGAL SEPARATION
10. FLOTATION PROCESSES
11. FILTRATION PROCESS
12. SUMMARY

APPENDIX

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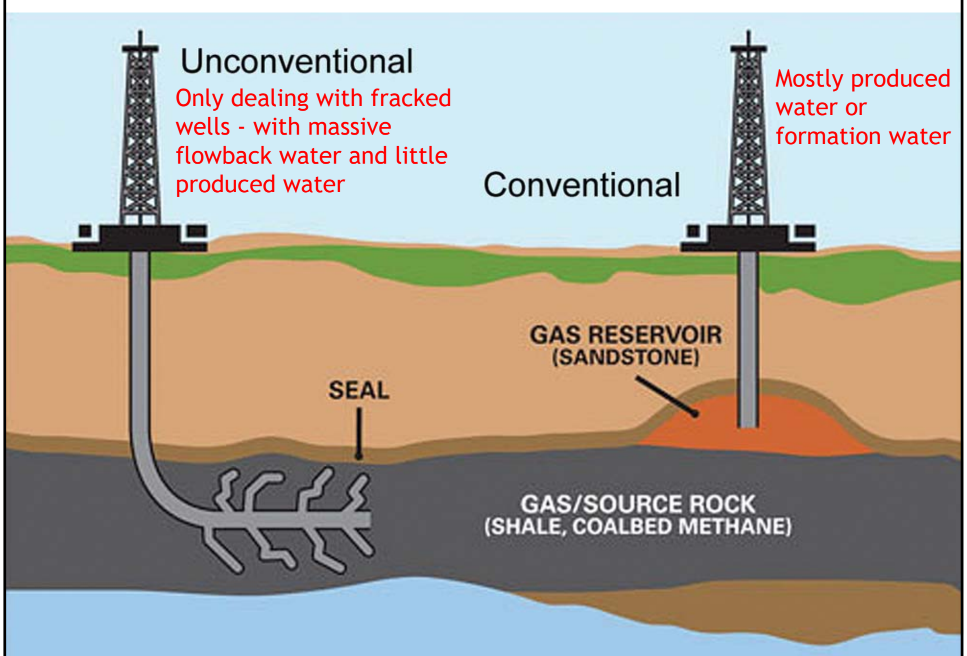
61

INTRODUCTION



62

INTRODUCTION

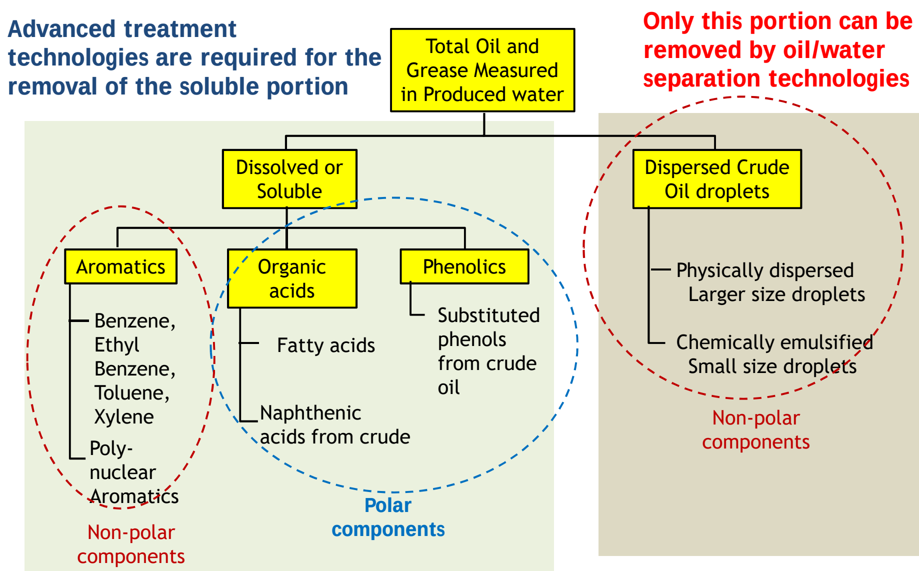
The most important parameters for produced water oil/solids/water separation

1. **Conventional produced water:**
   - Highly salty formation water - TDS (50,000 to 250,000 mg/L)
   - Oil in water after Free Water Knock Out (FWKO) - usually not heavily emulsified,
   - Low TSS concentration - mostly formed at the surface (scaling particles, precipitated sulfur or FeS, asphaltenes formed sticky deposits). They should be dealt with by chemical means in front of treatment,
   - Oil in water dominating wastewater - flotation based treatment
2. **Unconventional produced water (flowback and produced water from frac)**
   - Highly salty formation water but flowback water can be different,
   - Oil in water heavily emulsified with fracturing debris and chemicals (gum), although the produced oil itself is lighter,
   - Lots of suspended solids mixed with oily material. Requiring chemical coagulation to separate the heavier flocs for cleanup,
   - Stabilized solids/oil mixture dominating wastewater - Coagulation and solids liquid separation, either settling or DAF

63

IMPORTANT PARAMETERS - Oil

"Oil and grease" in conventional produced water



64

IMPORTANT PARAMETERS - Oil

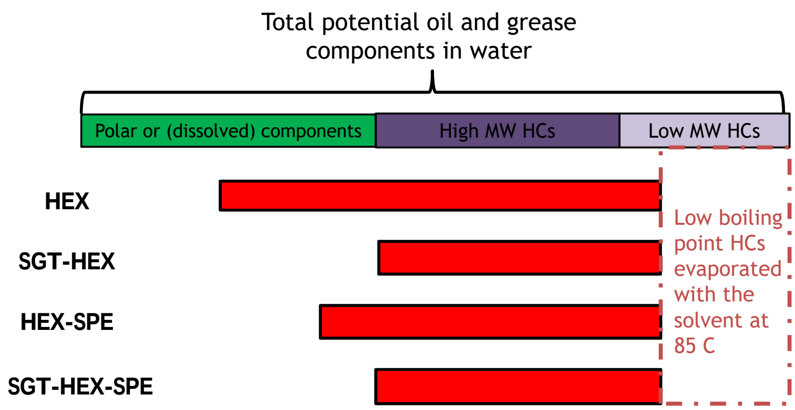
The "oil and grease" measurement techniques has changed for the past 30+ years due to the problems of "method dependent parameter" - the results don't necessary represent " oil " components in the sample.

1. EPA Method 1664 B Hexane Extractable - HEX : Low pH (2) extraction with solvent, N-hexane then evaporate solvent at 85C and gravimetrically measure of residue. Will capture HCs, naphthenic acids, substituted phenols and vegetable oil.
2. EPA Method 1664 B HEX with silicate gel treatment - HEX SGT: In HEX measurement before evaporation, the solvent is subjected to silicate gel adsorption of non-polars. Will only capture mineral oil (hydrocarbon)
3. EPA Method 1664 B Solid Phase Extraction - SPE : The acidified water sample will pass through a carbon18 solids phase extract pad. The loaded pad will be eluted with N-hexane. The eluted solvent will be evaporated at 85C and the residue will be gravitational determined. Some naphthenic acids will be captured.
4. EPA Method 1664 B SPE with silicate gel treatment - SPE SGT: In the SPE determination, prior to evaporation, the solvent will be subjected to silicate gel treatment to remove non-polars.

65

IMPORTANT PARAMETERS - Oil

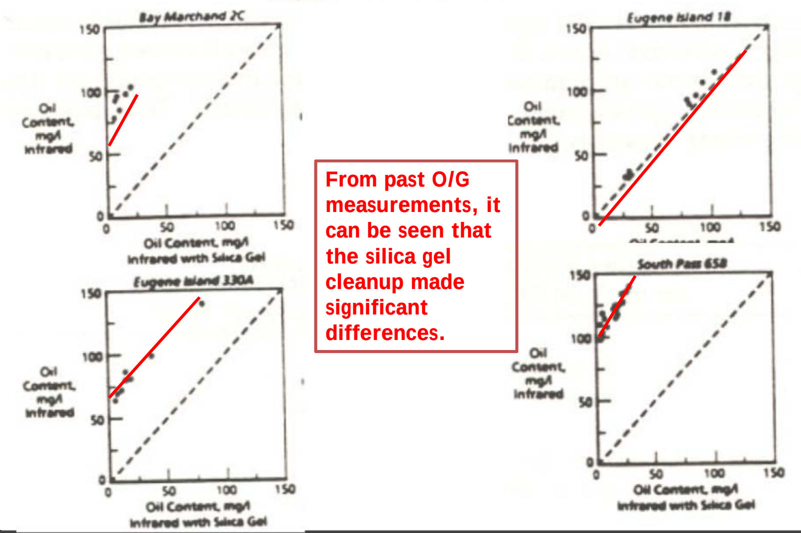
Typical measurement results with different 1664B Methods
When the polar components are large, the discrepancies are higher



66

IMPORTANT PARAMETERS - Oil

Figure 9. Correlations of infrared versus infrared with silica gel analyses of produced brine samples.[9]



From past O/G measurements, it can be seen that the silica gel cleanup made significant differences.

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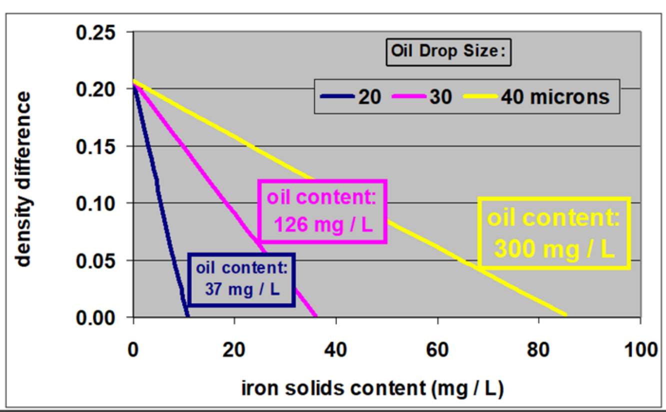
67

IMPORTANT PARAMETERS - Suspended Solids

TSS measurement can be misleading:

1. Brine water can impact TSS measurement if highly salty water got left behind on the filter paper during measurement without being rinsed "clean" by specified DI water rinses.
2. Part of oil droplets will be measured as TSS, so how can you interprete TSS in oily conventional produced waters?
3. Oil/solids emulsion making the physical separation process more difficult



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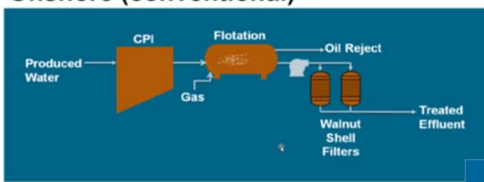
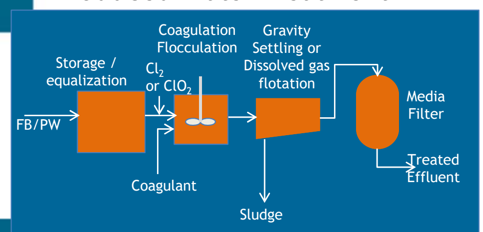
APPLICATIONS - conventional vs unconventional

Typical Produced Water Treatment – Onshore (conventional)

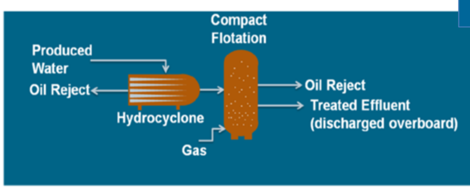


Treatment targets are not well defined, except for offshore discharge which is 39 mg/L of oil but using what measurement method ?

Typical unconventional Produced Water Treatment



Typical Produced Water Treatment - Offshore



Ref: Andrea Larson, WEF Workshop on Produced Water, WEFTEC, 2018

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BASIC THEORY

Gravity separation based on Stoke's law

The bigger the particles, the better ~ R^2

The more Δρ (lighter oil or heavier solids), the better

The larger centrifugal force

$$V = \frac{2 \cdot (\rho_{p-}\rho_w)\, g\, R^2}{9 \cdot \mu}$$

The small the viscosity, the better; higher temp.

V= settling or floating velocity, m/s
ρ = density, kg/m³
μ = viscosity of water, Kg/m/s
g = gravity or centrifugal acceleration , m/s²
R = Radius of particle, m

For an oil droplet with 100 micron diameter, 20 C, and Δρ= 0.3, the raising velocity, V is ~ 10 cm/min or 6 m/hr

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IMPORTANCE OF PARTICLE SIZE

Nominal cut off point of droplet size that can be removed for different processes - Not necessary applicable to individual cases

TABLE 5-1 Particle Size Removal Capabilities

Technology	Removes Particles Greater Than Size Indicated (in microns)
API gravity separator	150
Corrugated plate separator	40
Induced gas flotation without chemical addition	25
Induced gas flotation with chemical addition	3-5
Hydrocyclone	10-15
Mesh coalescer	5
Media filter	5
Centrifuge	2
Membrane filter	0.01

Source: Frankiewicz (2001).

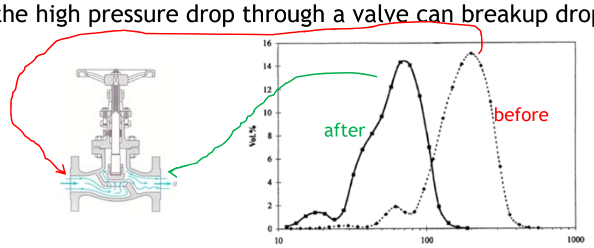
Frankiewicz, T., 2001, "Understanding the Fundamentals of Water Treatment, the Dirty Dozen – 12 Common Causes of Poor Water Quality," presented at the 11th Produced Water Seminar, Houston, TX, Jan. 17-19.

71

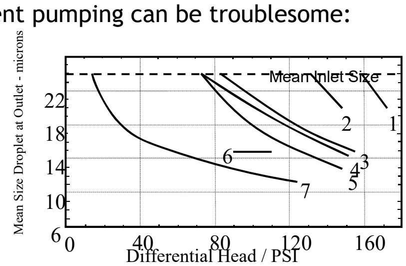
IMPORTANCE OF PARTICLE SIZE

Particle / droplet size is the most important parameter for separation - so carefully maintaining the size by not shearing them

1. Beware the high pressure drop through a valve can breakup droplets:



2. Influent pumping can be troublesome:



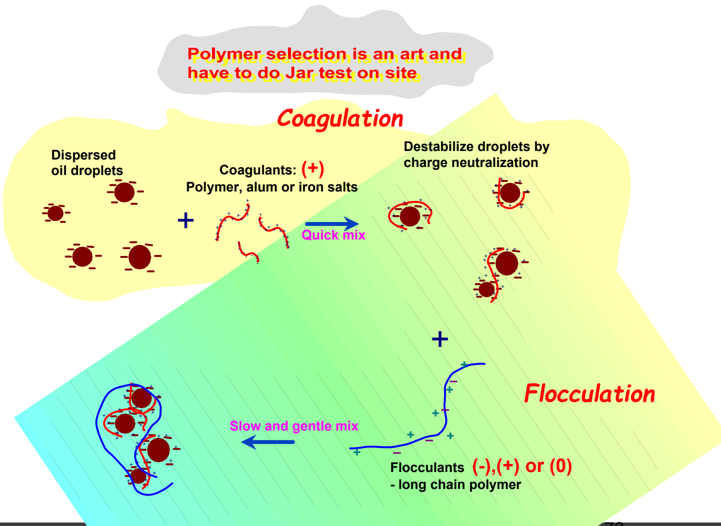
Legend

1. Progressive Cavity
2. Small Progressive Cavity
3. Twin Lobe
4. Sliding Rotary Vane
5. Lg. Progressive Cavity
6. Single Stage Centrifugal
7. Twin Screw

72

COAGULATION & FLOCCULATION

The coagulation/flocculation process works well in brine water, still jar test is the only way to select the right chemicals and dosage



73

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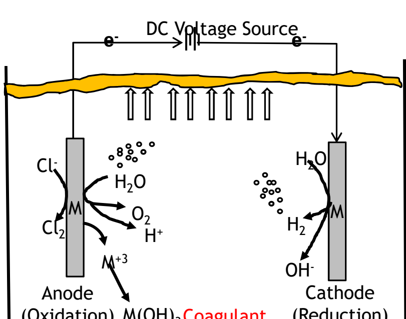
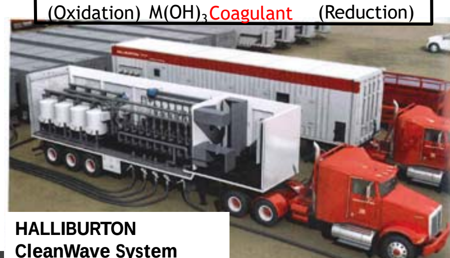
COAGULATION & FLOCCULATION

Electro-coagulation





HALLIBURTON CleanWave System

Advantages:

- This process combines coagulation and gas bubble flotation in one unit. No chemical makeup and feeding are required, except the solutions for pH adjustment.
- Coagulant usage is more efficient and the control of chemical dosing is simpler.
- Good for mobile temporary systems treating high salt water.
- Additional chemical reactions due to pH change, such as some Ca, Mg, Si, Ba, Sr precipitation, may be beneficial.

Disadvantages:

- pH adjustment to above 9.5 is required to destabilize the colloid system so that separation can take place.
- Electrode fouling is a difficult operational issue
- The combined mechanisms are not easily optimized for individual reactions.
- Capital cost is higher than conventional chemical addition.
- Specially trained operational staff is required.
- Producing combustible gas mixture and will complicate safety issues.
- Sludge production is high due to divalent cation precipitation.
- Little advantage if used in fixed centralized treatment plants

74

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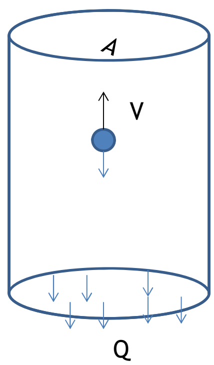
GRAVITY SEPARATION

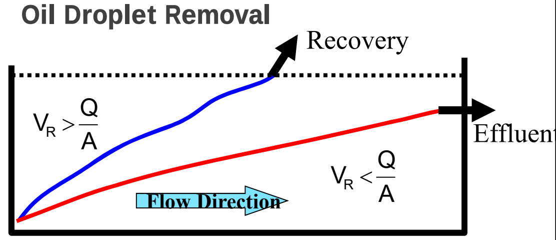
Gravity separation - based on over flow rate, Q/A

Q = Flow Rate
A = Cross Sectional Area of Separator

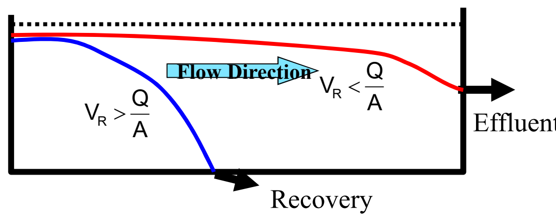
Q/A units are $m^3/m^2/day$



Oil Droplet Removal



Solid Particle Removal



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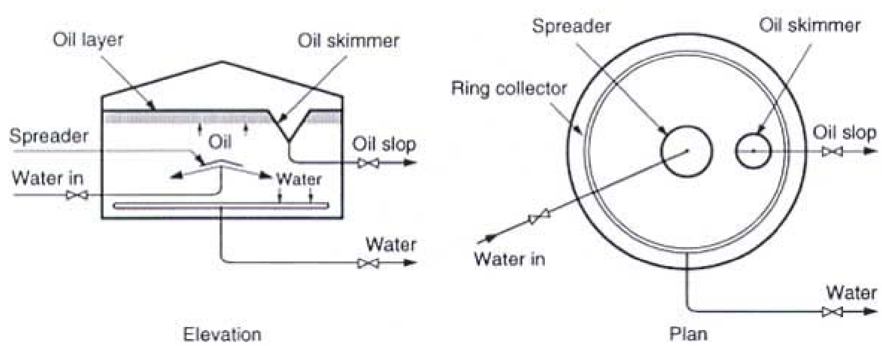
75

GRAVITY SEPARATION

Onshore conventional oil separation / skimming tank



These tanks can't handle too much solids coming in. Periodical de-sludging can be a difficult operation.

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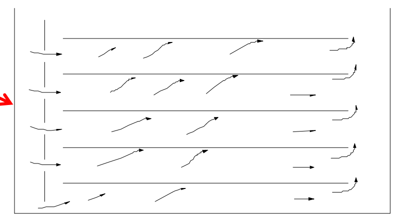
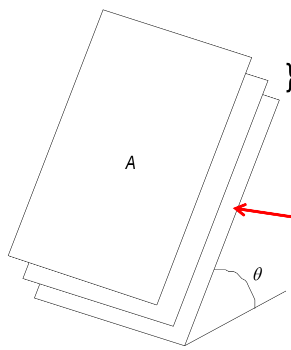
76

GRAVITY SEPARATION

Parallel & Corrugated Plate Separators or CPI

- Since horizontal surface area is the key parameter, API capacity can be increased several-fold by stacking multiple plates:





- Solids and oil removal is difficult with multiple horizontal plates, so the plates are placed at an angle.
- Effective surface area = n A cos(θ)

77

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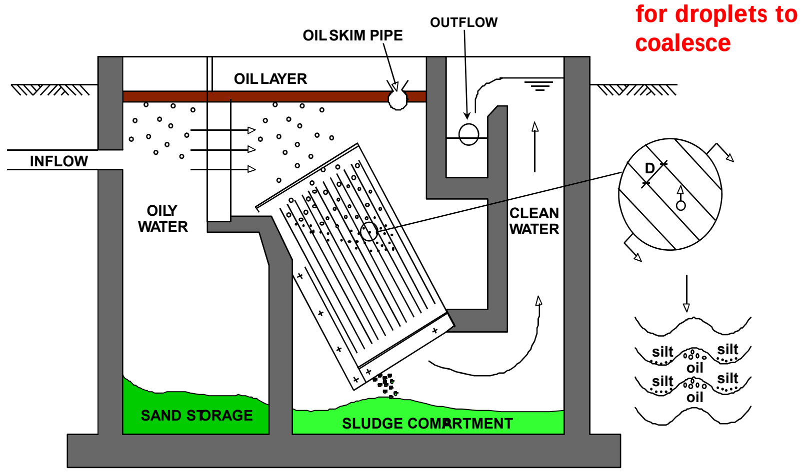
GRAVITY SEPARATION

CPI (corrugated plate interceptor) - plugging problem when applied to unconventional

100% removal of oil globules≥ 60 µm ?

Also provide opportunities for droplets to coalesce



78

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GRAVITY SEPARATION

API and CPI Comparison

API

- Maintenance on Moving Parts
- Normally below ground and large area to cover
- Large area required
- Can take large amount of oil spill
- Less operator attention in oil skimming and sludge removal
- Less plugging problem
- Better in handling free oil
- More sludge storage space

CPI

- No Moving Parts
- Can be easily covered and above ground construction
- Small foot-print (1/3 of API)
- Not much free oil storage - poor oil spill response
- More frequent oil skimming - difficult to set weirs
- Plate pack can be plugged
- Better handling of smaller size droplets
- Less sludge storage space

Typical Effluent Quality: 150 ppm TSS and 200 ppm O&G

79

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79

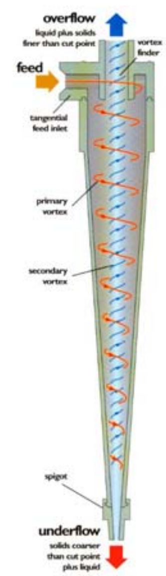
CENTRIFUGAL SEPARATION

Hydrocyclones

Using hydraulic induced centrifugal force to separate oil or solids from water, but not oil and solids

$$V = \frac{2 \cdot (\rho_{p-}\rho_w)\, N g\, R^2}{9 \cdot \mu}$$

- N can be up to 1000
- Solids removal cyclones will not remove dispersed oil (unless entrained with solids)
- Typically treat to 30 microns
- Smaller units can treat to 10 micron



80

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CENTRIFUGAL SEPARATION

Hydrocyclones

Desander is usually the first unit in flowback water treatment to separate out the sand, proponent, debris due to fracking

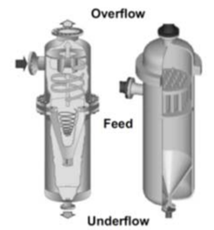
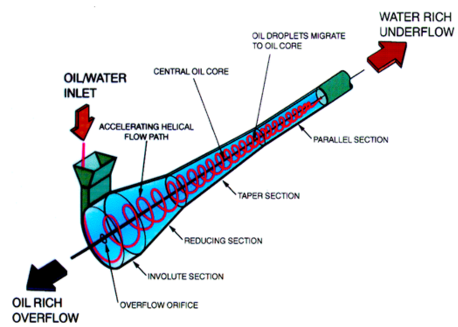


Fig. 3—Schematic drawings of vessel-style (left) and liner-style (right) desanders.

Only large sand particles or debris are separated, oil and water are discharged in overflow

Long and narrow oil water separation hydrocyclone are used in offshore produced water treatment - due to low solids load and lower footprint



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81

FLOTATION PROCESSES

Classification of flotation equipment

1. Induced gas flotation
   - Mechanically induced gas bubbles formation (Turbine mixer induced)
   - Hydraulically induced gas bubbles formation (Educator jet induced) - sometimes call dispersed gas (misleading DGF)
2. Dissolved gas flotation
   - High pressure dissolution of gas (air or nitrogen) into water and then releasing the pressure to form precipitated gas bubbles
   - Specially designed pump to accomplish the dissolution precipitation operation
3. New micro bubble generation through high shear pump

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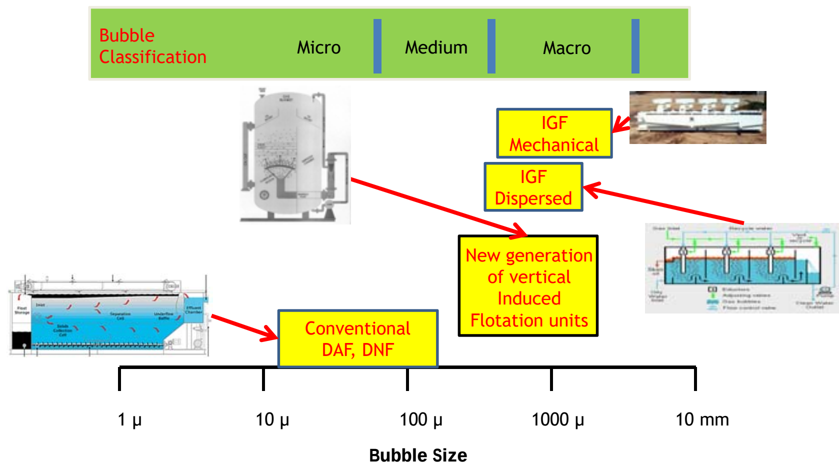
82

PRIMARY TREATMENT - FLOTATION PROCESSES

Flotation processes are characterized by the gas bubble size used in the separation



Flotation Units available in the market

83

FLOTATION PROCESSES

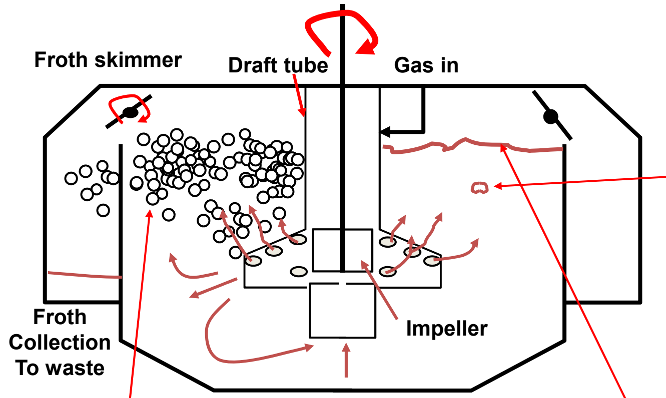
In flotation, one tries to produce bubble/oil coalescent so that the particle sizes are increased and density differences are also improved for separation

$$V = \frac{2 \cdot (\rho_p - \rho_w)\, g\, R^2}{9 \cdot \mu}$$

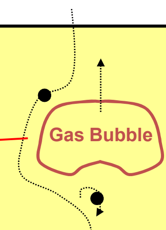
84

FLOTATION PROCESSES

Induced Gas Flotation: Important Variables



- Generate larger gas bubbles (500 to 1500 µm)
- Collect oil particles and form a stable top froth layer
- The froth layer is scrubbed into the waste trough
- High froth production 3 to 5% of the wastewater flow

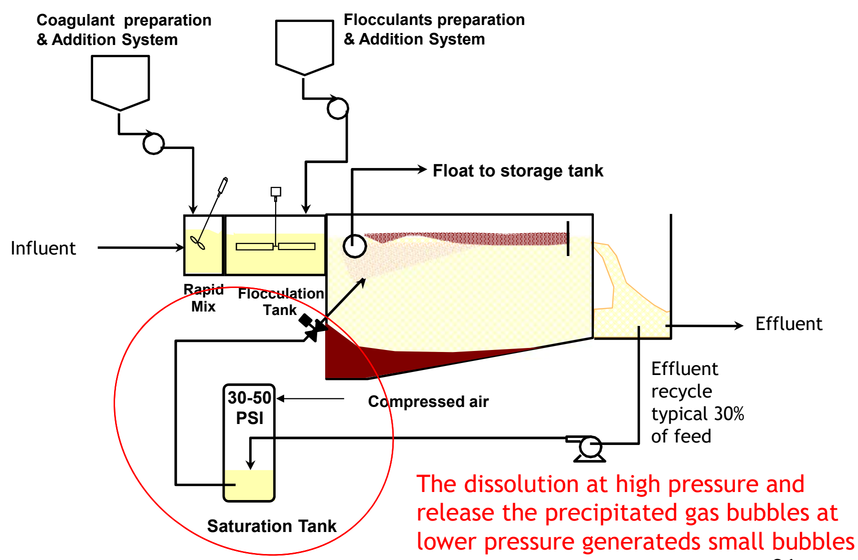


- Large bubbles make the collection of small oil droplets difficult. Chemical destabilization of the oil colloids is a more important process requirement.
- Stable froth layer may not be easily maintained

85

FLOTATION PROCESSES

The Dissolved Air Flotation (DAF) System

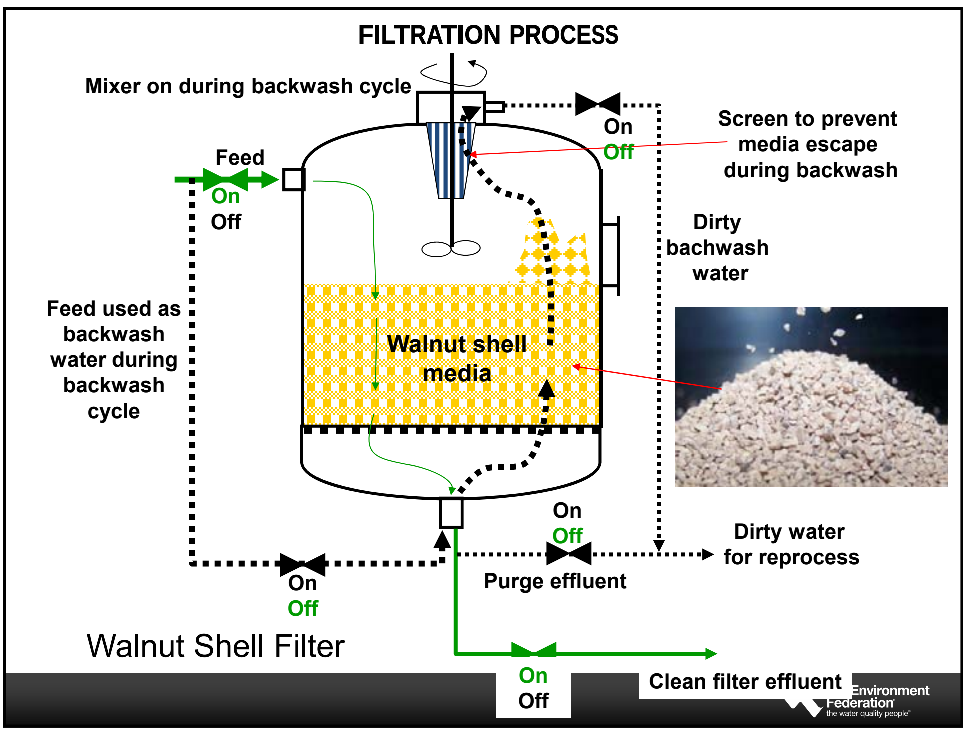


86

86

Parameter	Dissolved Gas Flotation	Induced Gas Flotation	Comparison
Bubble Diameter, µm	50 to 100	500 to 1000	DAF with small bubbles and higher collection efficiency
Overflow rate: * Conventional - * New innovation	2 to 5 gpm/sq ft 10 to 15 gpm/Sq ft	5 to 10 gpm/sq ft	The IGF is smaller than conventional DAF, but the newer DAF is getting close
Gas flux, SCFM/sq ft	0.05 to 0.2	2 to 5	IGF require more gas volume
Velocity gradient, G, per sec	60 to 80	450 to 1600	IGF is a mixing vessel, while DAF is a quiesent separator
Hydraulic resident time * per cell, min * total, min	10 to 20 10 to 20	1 to 2 4 to 8	
Recirculation ratio: * External * Internal	0.3 to 1.0 none	None 5 to 8	
Collision Efficiency	0.04 to 1	0.001 to 0.02	DAF is more effficient due to smller bubbles
Coagulant / Flocculant	Low or high M.W. cationic polymer and Inorganics based on application, need flocculation fo buildup floc sizes	Generally low M.W. cationinc polymers without flocculation	
Comments	Good for emulsified oil/solids unconventional and refinery wastewaters	Good only for oily produced water with low solids	

87



88

Walnut shell filter

1. The crushed walnut shell media (3 mm size) is light (1.4 sp.gr.), (12/20 mesh size) oleophilic (adsorb oil), and with high modulus of elasticity (withstand rigorous backwashing). It removes oil mostly without chemical destabilization.

2. Its influent oil content should be limited to < 100 ppm. Higher oil content will plug the filter and demand frequent backwash. Free oil fed into the filter will render the unit useless for oil removal.

3. For normal EP produced water treatment:
   - Designed overflow rate: 8 to 15 gpm/sq. ft.
   - Media depth: 4 to 6 ft.
   - Backwash frequency: once /day without air scouring & w/ only feed water
   - Backwash flowrate: same as feed rate, making inflow turndown difficult; If inflow flow is reduced, the backwash rate may not be enough. 15 minutes duration.
   - Media attrition rate: 5% per year
   - Backwash volume: small, 1% of processed water volume.
   - Oil content of treated effluent: < 10 ppm

4. It should be used as tertiary oil removal device for treating direct discharge quality effluent to the receiving waters in EP produced water applications. Not good for solids.

5. Its use in refinery WWTP to replace DAF is "overkill", yet its response during upsets is not adequate to protect the downstream biological systems.

6. Smaller foot print but high capital cost than flotation units.

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89

SUMMARY

Treatment processes	Application areas	Comments
Gravity separation	1. FWKO onshore and offshore conventional 2. Unconventional separators	Small FWKO for offshore and larger API separator for onshore, equalization/separation for unconventional
CPI Separators	Offshore oil solids separation and sometimes onshore conventionals	Used on offshore platforms due to its small footprint. Not used in unconventional due to plugging
Hydrocyclone	1. Desander cyclones used in most all cases, 2. Deoil hydrocyclones are only used in offshore applications.	Deoil hydrocyclones are not cost effective in onshore applications , it requires high pressure drop and low TSS in feed.
Chemical coagulation for destablization of colloids or emulsions	Applicable in most cases	Most of oil, oily solids are stablized in the produed water. Destablization is necessary
Flocculations - gentle mixing for building up large flocs	Only for the treatment of unconventional with DAF or gravity settling	IGF, hydrocyclones, filtration may need coagulation but usually do not need flocculation.
Induced Gas Flotation	Used both onshore /onshore conventionals but not for unconventionals	IGFs are not suitable for complex solids/ oil emulsion; such as unconventionals or refinery wastewaters
Dissolved Gas Flotation	Not used in offshore applications	large footprint and requires good coagulation and flocculation tanks
Walnut Shell Filters	Used both offshore / onshore conventionals but not frequently used for unconventionals	Good for removal of last small amount of oil (polishing). For unconventional, multimedia media filtration is more appropriate.

90

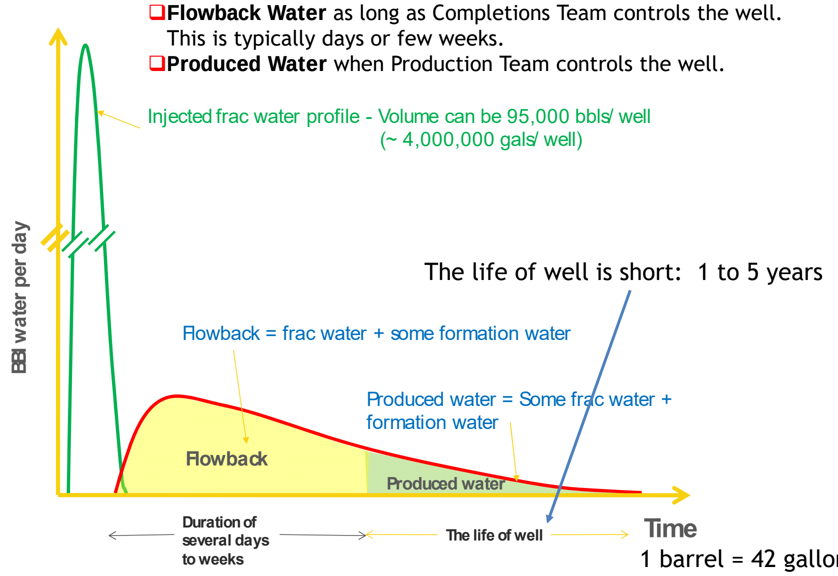
Appendix

91

INTRODUCTION

Flowback and produced water definition

- **Flowback Water** as long as Completions Team controls the well. This is typically days or few weeks.
- **Produced Water** when Production Team controls the well.



1 barrel = 42 gallons

92

IMPORTANT PARAMETERS - Oil

There are several versions of EPA Method 1664B and using what method is decided by the regulatory agencies, but one can make intelligent argument for a better selection

1664B

1 L Sample acidification w/ HCl to pH <2

↓

Extraction with n-Hexane 3 times each w/ 30ml of HX

↓

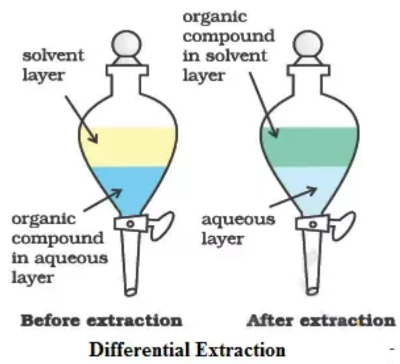
Collect solvent and dry at 85 C

↓

Quantify the residue by gravimetric measurement → **1664B HEX** **Not called oil and grease measurement anymore**

1664B CU (special permit required) for samples with high conc. of sulfide or/and thiosulfate

Cleanup solvent due to Sulfur interference, using Copper catalyst



93

IMPORTANT PARAMETERS - Oil

1664B-SGT (Silica Gel Treatment of the Solvent)

1 L Sample acidification w/ HCl to pH <2

↓

Extraction with n-Hexane 3 times each w/ 30ml of HX

↓

Collect solvent and cleanup with added silica gel absorbing polar components

↓

Filter out the silica gel granules from solvent

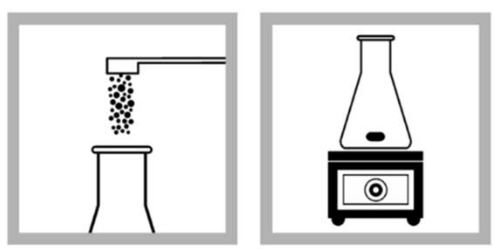
↓

Dry the cleaned solvent at 85 C

↓

Quantify the residue by gravimetric measurement → **SGT-HEX**

Using silica gel granules to remove polar components from the hexane solvent



5. Add 3 (± 0.3) g of silica gel to each 100 mg of HEM:

6. Add a stir bar to the flask. Stir for 5 minutes.

94

IMPORTANT PARAMETERS - Oil

1664B-SPE (solid phase extraction)

1664B-SPE = 1664B proven equivalenc

1 L Sample acidification w/ HCl to pH <2

↓

Vacuum filtering through a solid phase extraction pad

↓

Discard the filtered water

↓

Elute the loaded SPE pad with approx. 50 ml Hexane

↓

Drying solvent at 85C

↓

Quantify the residue by gravimetric measurement

↓

HEX-SPE
Or SGT-HEX-SPE

C18 Solid phase extraction pad

Discard the water phase

Collect the solvent and quantify

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IMPORTANT PARAMETERS - Suspended Solids

1) 1 liter of brine water with 200,000 mg/L of dissolved salt without TSS contains 200,000 mg of salt,
2) If only 0.5 ml of the brine water got left behind on the filter paper in TSS determination due to incomplete rinsing with DI water in the procedure, the dissolved salt left on the filter paper can be 0.5ml/1000ml X 200,000 mg/L = 100 mg,
3) The reported TSS concentration can be at least 100 mg/L due to poor analytical practice, in reality it should be ZERO.

Which one of these lab filtration setups can potentially contribute more to the rinse problem?

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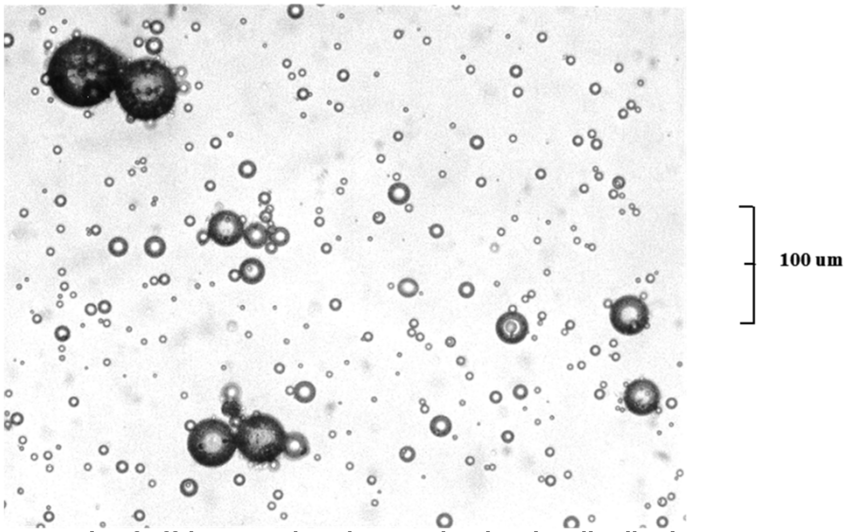
IMPORTANCE OF PARTICLE SIZE



Example of offshore produced water droplet size distribution - note very few solids particles presents

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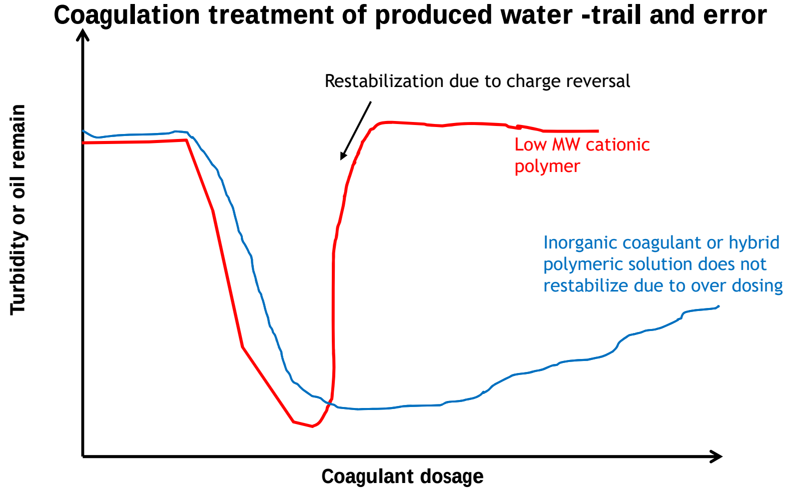
COAGULATION & FLOCCULATION

Coagulation treatment of produced water -trail and error



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COAGULATION & FLOCCULATION

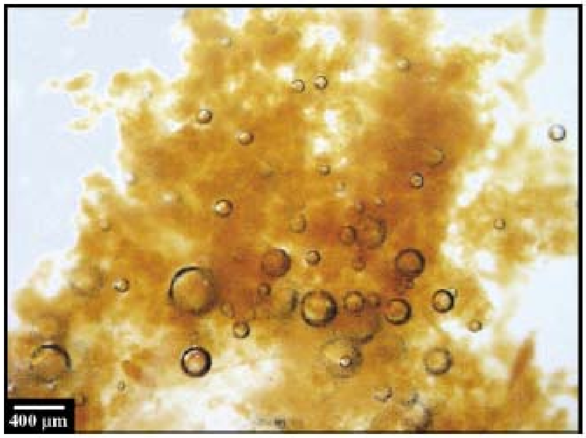

Fig. 5. Bubbles being entrapped inside flocs (colloidal iron precipitates, Fe $(OH)_3$).

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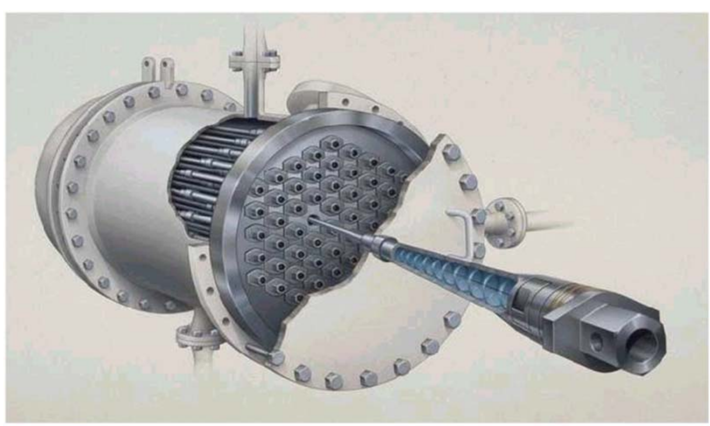
CENTRIFUGAL SEPARATION

And L/L hydrocycles are difficult to turn down and can be plugged by incoming solids, need backwash and cleanup. ΔP 100 to 150 PSI



Packaging of many liners within a single pressure vessel. This figure shows the reject header.

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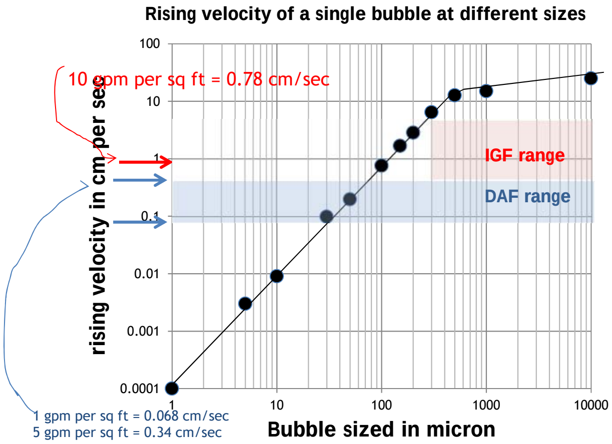
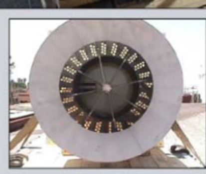
FLOTATION PROCESSES

Rising bubble velocity provides us a guide for the separation of the bubble/floc particles - The real rising velocity of a bubble/floc mixture would be different.



101

FLOTATION PROCESSES



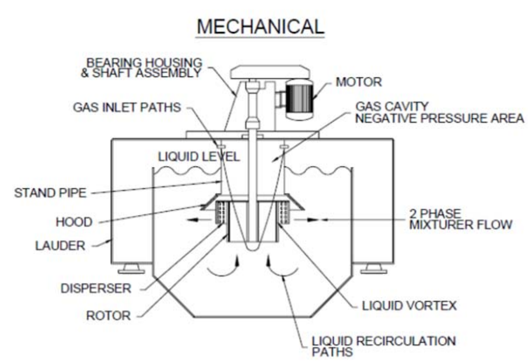


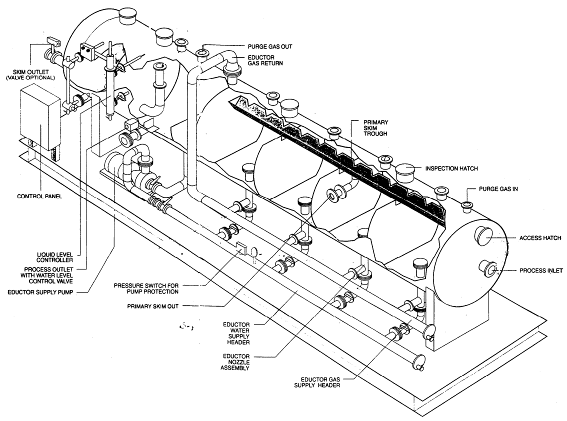
Figure 1a. Mechanical system.

Siemens Water Solutions

102

FLOTATION PROCESSES

Induced Gas Floatation Unit



With (IGF), nitrogen or nature gas is entrained and mechanically mixed with water via a recirculating pump and an eductor. Fine bubbles up to 1500 μm in size is formed and rises to surface rapidly.

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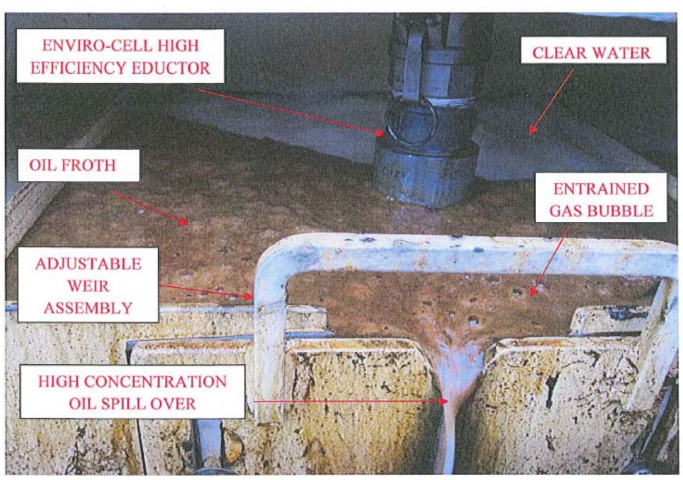
FLOTATION PROCESSES



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FLOTATION PROCESSES

Note the intensive mixing and large oily flocs on the surface of an IGF unit

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FLOTATION PROCESSES

- **The high salt content and high temperature of the produced water tends to reduce the solubility of gases in water, thus the dissolved gas flotation has to work harder (more external recycle and more pressure) to get more gas bubble generated.**
- **However, the induced gas flotation does not have this limitation, actually high salt environment will help generating smaller bubble. (but not to the level of microbubbles).**

Thus, DGF and IGF each has its own application niche.

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FLOTATION PROCESSES

Micro-Bubble Flotation (MBF™)

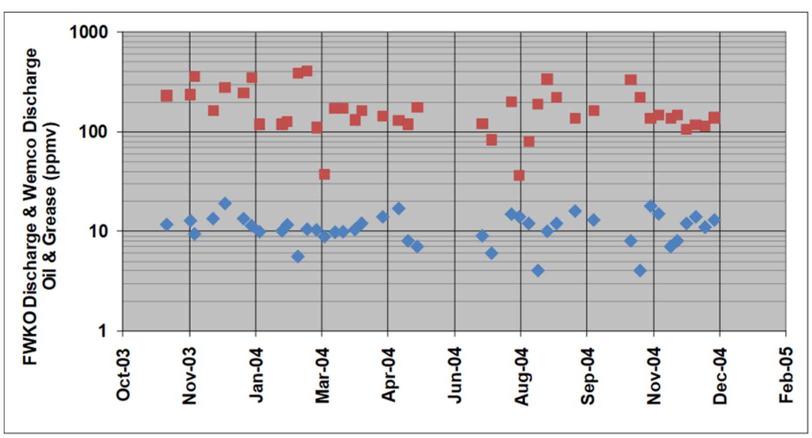
ONYX-MB IMPELLER

The vendor claims the system is dispersed not dissolved.

107

FLOTATION PROCESSES

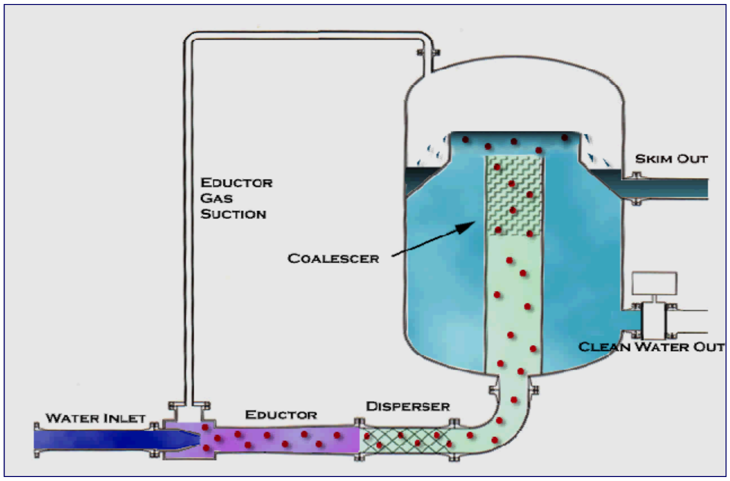
Performance of offshore IGF operation



108

FLOTATION PROCESSES

Beware it is also called a DGF or Dispersed gas flotation, but not Dissolved gas flotation. There are significant differences



Unicel IGF design

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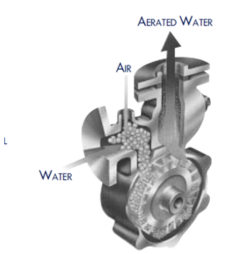
FLOTATION PROCESSES

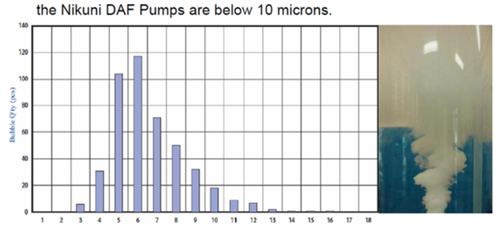
The dissolution / precipitation formed "white cloud"

The New DAF pump



Bubble Test Results

- Testing has proven that the majority of microbubbles produced by the Nikuni DAF Pumps are below 10 microns.



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Recycling Produced Water

F. Morris Hoagland, P.E.
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Email: morris.hoagland@hotmail.com

111

Outline

Recycling PW

- Focus on shale play (fracking)
- Where recycling is working
- Why so little recycling
- What quality required to recycle
- Mid-Stream – Paradigm shift

112

Recycling Produced Water

- Conventional wells water flood or overboard discharge
- Primarily a shale play issue (unconventional wells)
  - Some recycle
  - Mostly disposal in SWD

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Produced Water?

Water produced in upstream – Produced Water?

Initially Flowback Water

- First 3-4 weeks after completion (fracking)
- High flow rate drops quickly
- Highly contaminated

Longer term – Produced Water

- Natural formation water
- Primary contaminant is TDS
- Lower flow rates

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Produced Water Recycling

- It depends on where you are.

For tight formations (shale plays)

- In Pennsylvania only 8 UIC disposal wells

>90% is recycled into oilfield applications

- In Texas there are >8,000 UIC disposal wells for O&G waste disposal

~ 10% is recycled

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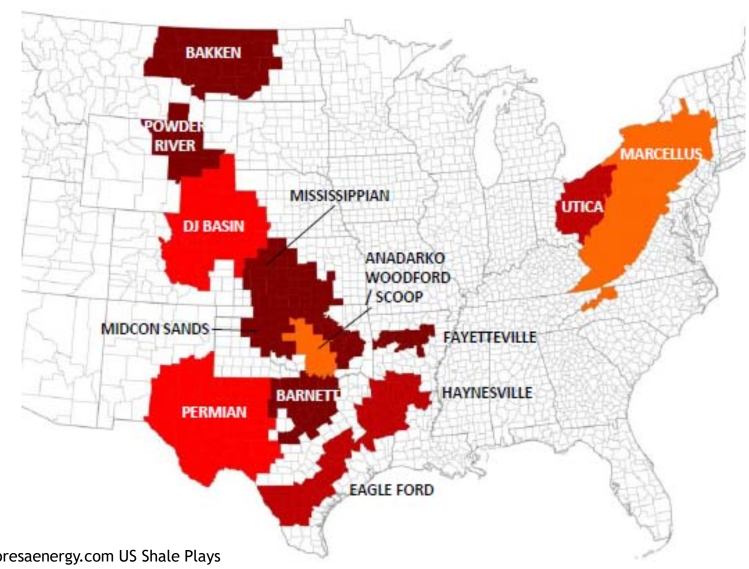
Most Active Shale Plays



Source: empresaenergy.com US Shale Plays

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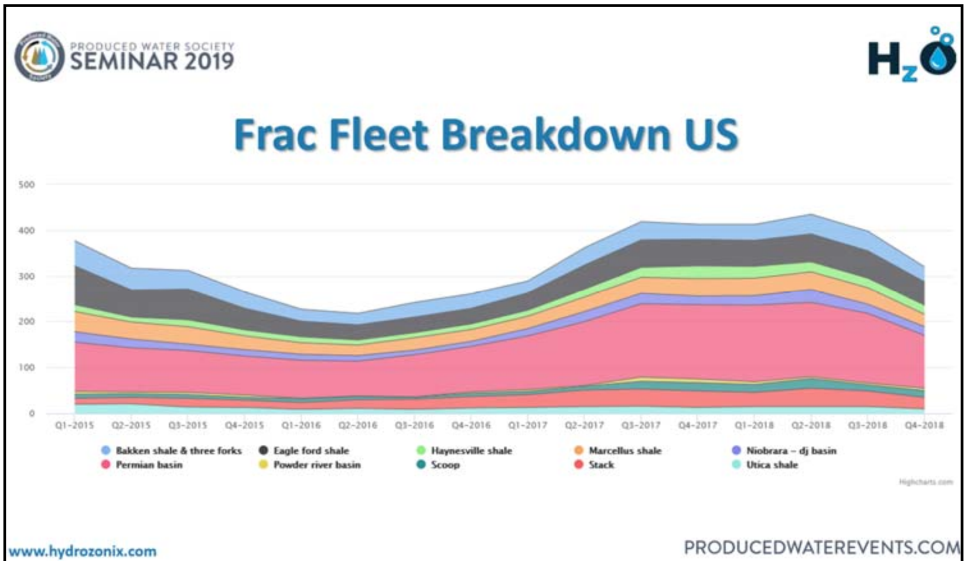

- Close to half the on USA shore shale play activity is in the Permian Basin

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Produced Water Recycling

The bigger picture (on shore operations)

Permian Basin example

- Most PW comes from conventional wells
  - 70% of PW is recycled for water flooding (conventional wells)
  - 30% is disposed of in UIC salt water disposal wells
- Unconventional wells (shale play)
  - 10-15% recycled for completions (more fracking)
  - 85% is deep well injected

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Produced Water Recycling

Early fracking operations required fresh water

Innovative completion chemistry allows use of high TDS waters

Now often recycle is lower cost

Why not recycle more?

- Easier to dispose of water in UIC (SWD) wells
- Recycle requires more infrastructure and planning
- Property owners want to sell their water to the operator

119

Required Water Quality?

Produced Water Reuse Standards

Slickwater Fracs – 5 different Operators

Constituent	A	B	C	D	E
Chlorides (ppm)	140,000	100,000	N/A	85,000	N/A
Total Hardness (ppm)	50,000	NA	N/A	20,000	Calcium 2000 Magnesium 2000
Sulfides (ppm)	0	0	0	0	0
Iron (ppm)	25	10	10	10	10
Oil (ppm)	100	50	40	10	N/A
TSS (ppm)	100	100 micron	50	5 micron	N/A
pH	6.5-7.5	6-8	6.5-7.5	6-7	6-8
Bacteria (cfu/ml)	100	0	0	1000 GHB 100 SRB 100 APB	10,000

120

Water Quality for Reuse?

Today every operator has their own internal standards

New Mid-Stream businesses will "impose" a standard

- Oil in water 10 ppm
- TSS 50 ppm (10 micron max)
- Iron 10 ppm
- Bacteria 100 cfu/ml
- H_2S 0 ppm (when in source water)

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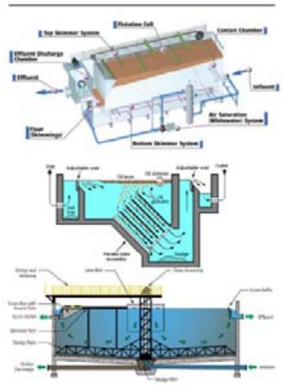
121

PW Recycle Treatment

Step 1:
Oxidation

Step 2:
Oil/Solids Control



Step 3:
Solids Polishing

Step 4:
Biocide Treatment

HYDROZONIX

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Mid-Stream – A Paradigm Shift

Mid-Stream companies investing heavily

- Pipelines
  - Takes trucks off the road
  - Logistics cost <$0.25/bbl vs. $1-2.00/bbl for trucks
- Water storage impoundments
- Centralized water treatment – low cost
- SWD wells to dispose of excess water
- Brackish water wells for excess requirements

1 barrel = 42 gallons

123

Mid-Stream – A Paradigm Shift

Mid-Stream companies investing heavily

- Takes water management burden off of operator
- Lowers unit cost of water
- Operators want to invest in E&P, not water management

Mid-Stream business drives more water reuse

- Operator pays them to take dirty water
- Operator buys back water for completions

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Disposal Remains a Key Option

- Midland side of Permian Basin 1-2 bbl water/bbl oil
- Delaware side of Permian Basin 8-10 bbl water/bbl oil
- At best 75% of water generated in shale operations to recycle
- Still huge quantities of water will go to disposal

1 barrel = 42 gallons

125

What will move Industry to recycle more?

- Biggest change is <u>Mid-Stream</u> water management
- New restrictions due to seismic events
- Regulatory incentives
- Beneficial reuse – requires low TDS waters
  - Desalination not currently cost effective
  - New innovative technologies? (thermodynamics limit)

126

Appendix

127

Flowback Water

- Variable TDS (salts)
- Polymers (raise viscosity)
- Surfactants
- Breakers (breaks up polymers)
- Biocides
- Proppant (sand and fines)
- Shale fines

128

Fluids used for Unconventional Wells

- Drilling Mud (water based and oil based)
- Completion Brine (maintain pressure)
- Stimulation Fluids (acids and solvents)
- Hydraulic fracturing fluids
  - Friction reducer
  - Surfactants
  - Biocides
  - Breakers

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Advanced Produced Water Treatment

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130

Outline

Advanced Treatment of Produced Water

- Why use Advanced Treatment
- Advanced Treatment Technologies
- Conclusion

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Treating Produced Water for Beneficial Reuse

- Already reviewed conventional water treating
  - Clean water for reuse/recycle in the oilfield
  - Remaining TDS (salts) - water unsuitable outside oilfield
- Lots of technologies to remove TDS – all expensive
  - Energy cost is primary barrier
  - Exotic materials required - corrosion
- Emerging technologies - closing the cost gap

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Treating Produced Water for Beneficial Reuse

Why is important to close this cost gap?

- SWD (deep well injection) getting more expensive
- Induced seismicity (i.e. Arbuckle – Oklahoma)
- Over pressured disposal formations (i.e. San Andres – Permian)
- Turn negative public perception into a positive perception

133

What is Goal of Advanced Treatment

- Removal of dissolved salts required for reuse or discharge
- Produce freshwater from the high saline FB/PW - residual concentrated brine water to disposal or further drying
- Selection of desalination technology dependent on the salt concentration of the influent water

Courtesy: Paul Sun

134

Treating Produced Water for Beneficial Reuse

Four technologies making progress

- Forward Osmosis
- Membrane Distillation
- Capacitance Deionization
- Humidification Dehumidification

135

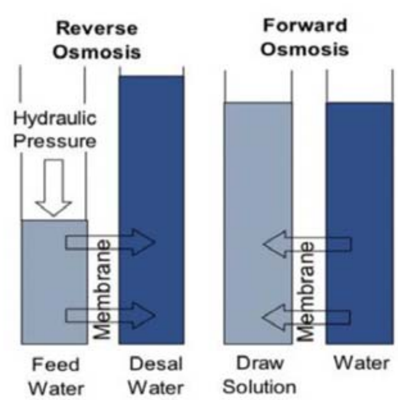
Forward Osmosis

RO uses high pressure to overcome osmotic pressure

- High cost for pumping energy

FO uses osmotic pressure

- High concentration "draw" fluid "pulls" water through membrane
- Low pumping pressure
- Requires energy to regenerate draw solution



Source: National Univ. of Singapore, CIRA

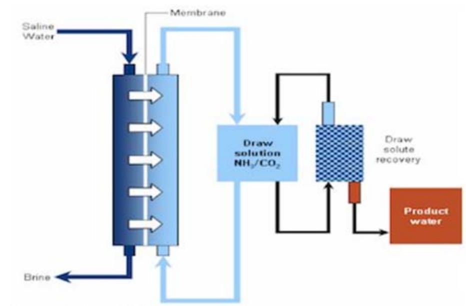
136

Forward Osmosis

FO using ammonium bicarbonate draw solution

- Low heat breaks $(NH_4)HCO_3$ into NH_3 + CO_2 and water
- NH_3 + CO_2 degas leaving water
- Gases NH_3 + CO_2 are passed over catalyst to regenerate draw solution

Lower energy required



Source: Modern Water

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Membrane Distillation

Membrane Distillation is a breakthrough technology with unique characteristics

- ***It can treat almost any water source***
- ***It runs on low-grade heat***
- ***It produces pure distillate***
- ***It has high recovery ratios***

aquaver

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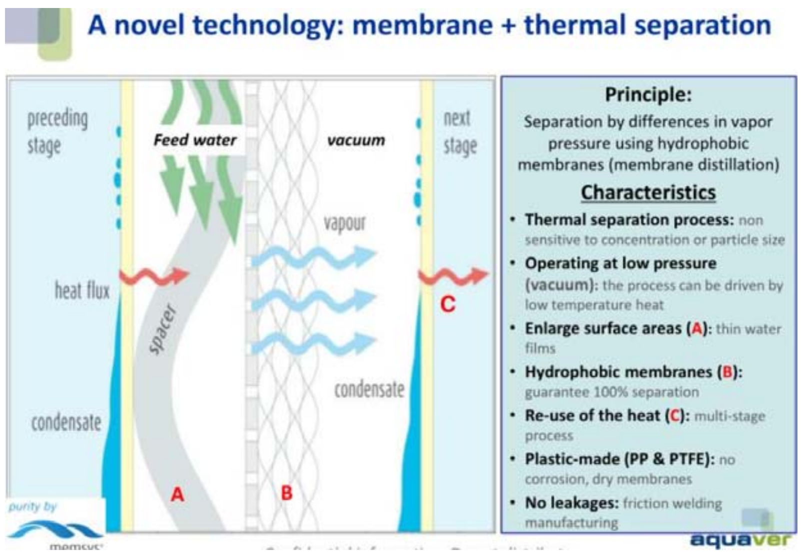
138

Membrane Distillation



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Membrane Distillation

- Efficient compact spiral-wound distillation modules
- Recover heat of condensation lowers energy requirement
- Chemical pretreatment not required
- Low pressure system reduces capital cost
- Not sensitive to dry running and fouling
- Minimal scaling issues due to operating temperatures below 80^0C (176^0F)

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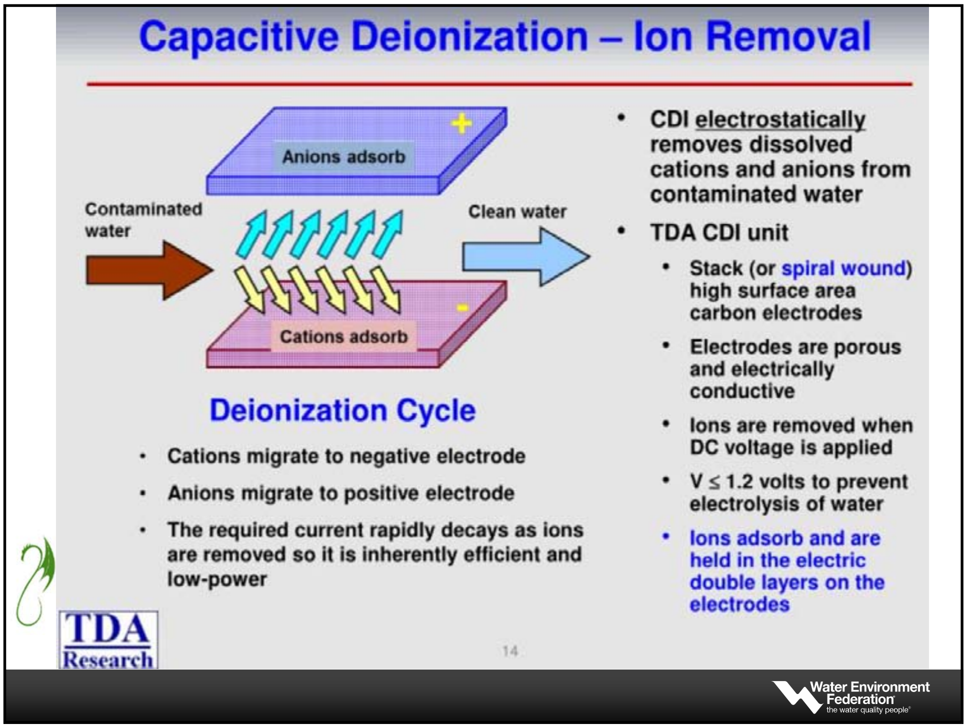
Capacitive Deionization – Ion Removal
Anions adsorb
Contaminated water
Clean water
Cations adsorb
Deionization Cycle
Cations migrate to negative electrode
Anions migrate to positive electrode
The required current rapidly decays as ions are removed so it is inherently efficient and low-power
CDI electrostatically removes dissolved cations and anions from contaminated water
TDA CDI unit
Stack (or spiral wound) high surface area carbon electrodes
Electrodes are porous and electrically conductive
Ions are removed when DC voltage is applied
V ≤ 1.2 volts to prevent electrolysis of water
Ions adsorb and are held in the electric double layers on the electrodes
TDA Research
14
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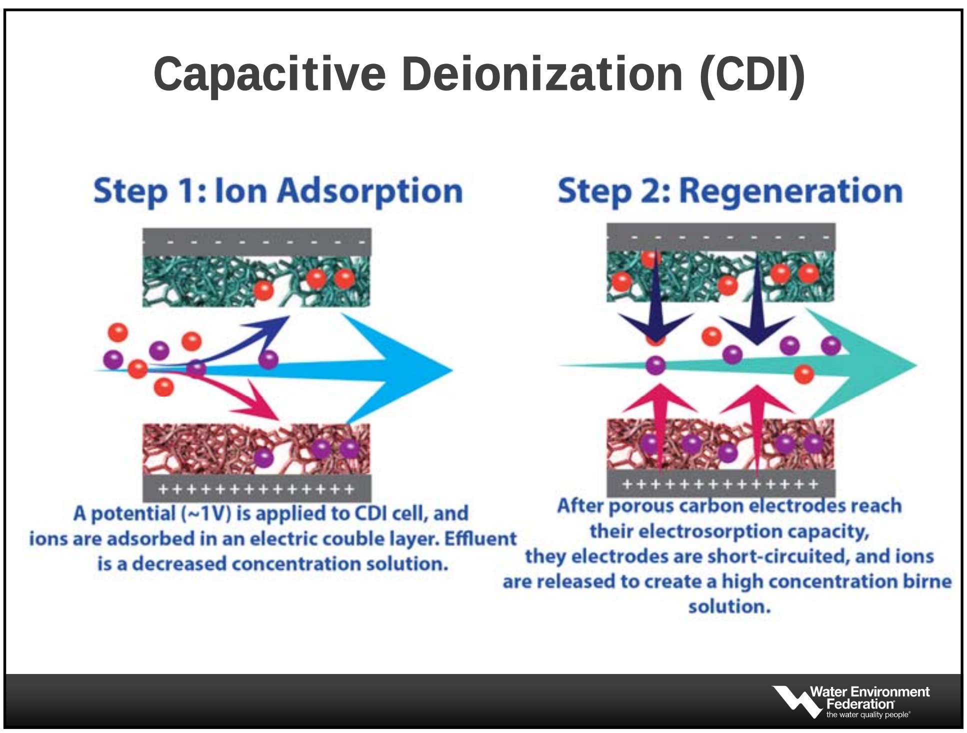
141


Capacitive Deionization (CDI)
Step 1: Ion Adsorption
Step 2: Regeneration
A potential (~1V) is applied to CDI cell, and ions are adsorbed in an electric couble layer. Effluent is a decreased concentration solution.
After porous carbon electrodes reach their electrosorption capacity, they electrodes are short-circuited, and ions are released to create a high concentration birne solution.
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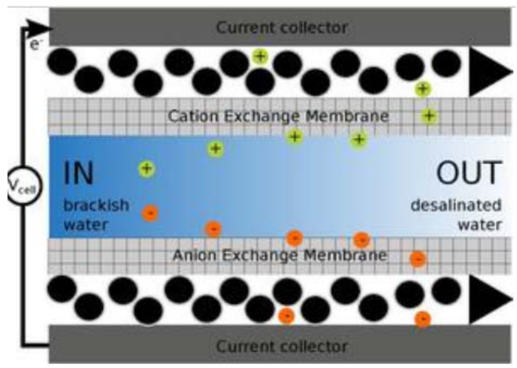
142

Capacitive Deionization (CDI)

- Uses DC current to remove charged dissolved ions from water
- Delivers deionized water suitable for surface discharge or other beneficial uses
- Lower energy than thermal or vapor recompression processes
- Requires pre-treatment to remove organics



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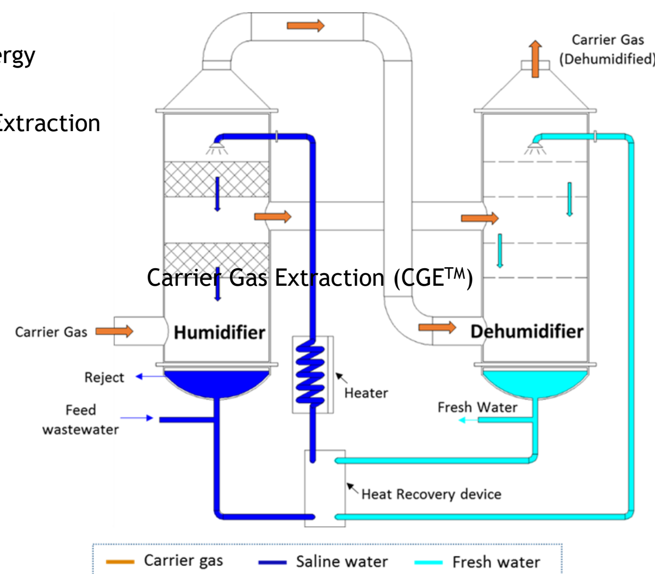
Humidification Dehumidification (HDH)

Gradiant Energy Services

Carrier Gas Extraction (CGETM)



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Humidification Dehumidification (HDH)

Novel use of carrier gas to desalinate:

- Bubble column device provides excellent direct contact - use of partial pressure concept using carrier gas
- Elimination of metallic evaporator and condenser
- Decoupling of valuable heat transfer surface from the sacrificial separation surface leads to reduced pretreatment requirement
- Thermodynamic balancing reduces energy consumption.
- Low temperature operation allows for use of waste heat to eliminate thermal energy costs

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Other Technologies

- Mechanical Vapor Recompression (MVR)
- Evaporation
- Crystallization
- Ion Exchange

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146

147

Questions?

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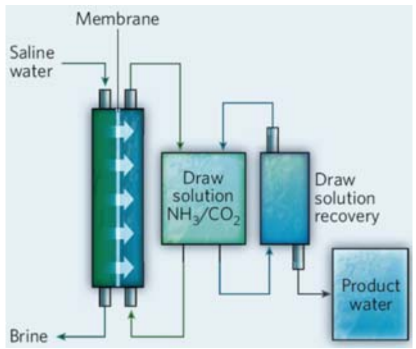
148

Forward Osmosis



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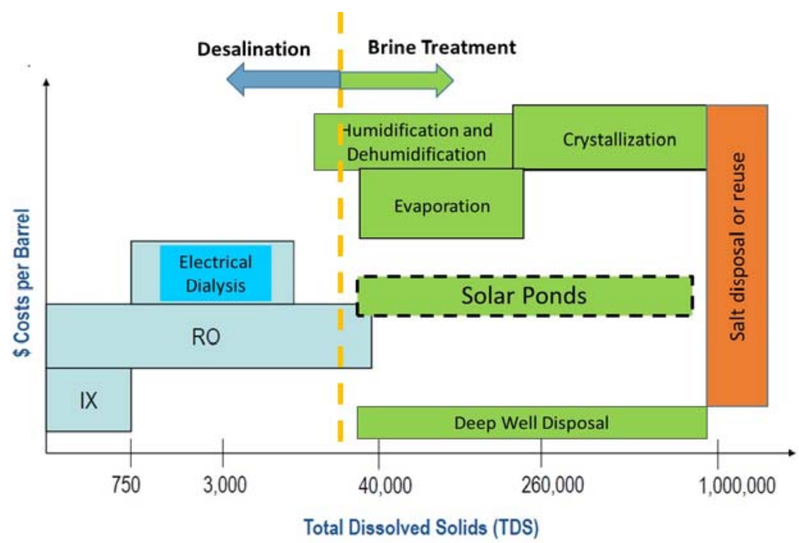
149

Motivation for Advanced Treatment



Courtesy: Paul Sun

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150

Reverse Osmosis

- The reverse osmosis process applies high inlet pressure to overcome the osmotic pressure of the brine water so that water molecules can be pushed through the semi permeable membrane while the salt molecules are rejected.

- Under current full-scale setup, the maximum pressure can be economically applied to commercial available RO membrane is approximately 80 Bars (or1200 psi), which translates to a maximum brine concentration of 70,000 to 80,000 mg/L as NaCl. As the inlet salts get more concentrated the water recovery is reduced to accommodate the upper pressure limit. This limited the application range of this desalination technology at inlet salt concentration at about 40,000 mg/L at 50% water recovery.

Courtesy: Paul Sun

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Reverse Osmosis

- The RO technology also requires significant pre-treatment :

1. Suspended solids removal to below 1 mg/L, and SDI < 5, usually a microfilter or ultrafilter is proceeding the RO units.
2. No ferrous or ferric iron concentration.
3. Biodegradable organic removal to prevent biological growth on the membrane surface
4. Silicate can limit the water recovery due to its low solubility at neutral pH, high pH RO system can extend the silicate limit
5. Divalent cations, such as Ca, Mg, Sr, and Ba can form precipitation when its solubility limits with carbonate or sulfate ions are exceeded during water passage and salt reject through the membrane process. Some cases pre-removal of hardness required,
6. Low pH and addition of anti-scalants are practiced to further prevent fouling of the membrane.

Courtesy: Paul Sun

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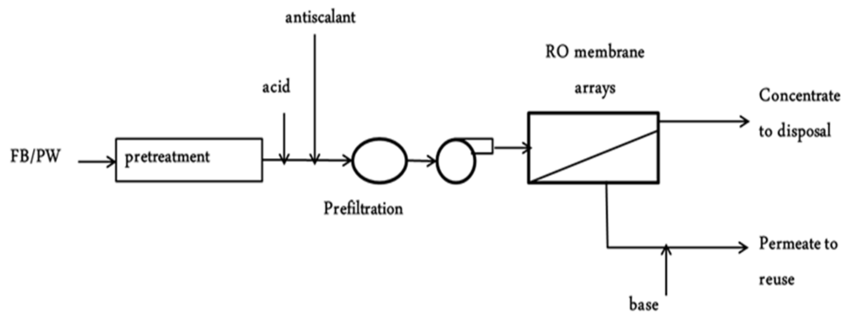
152

Reverse Osmosis Treatment Process



- Normally a freshwater of less than 500 mg/L of total dissolved solids can be produced by the RO process treating FB/PW,
- The rejected brine stream has to be disposed of in a deep well or to be further dewatered by using evaporator/crystallizer.
- RO membrane will not remove dissolved gases, such as CO_2 (at low pH) or NH_3 (at high pH), the removal of boron can be low at acidic or neutral pH conditions.

Courtesy: Paul Sun

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RO Boron Rejection: pH dependent

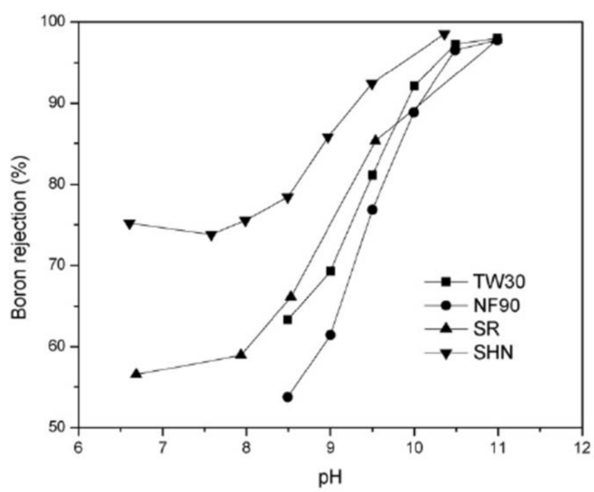

Fig. 11. The dependence of boron rejection on pH of solution for different membranes.

Courtesy: Paul Sun

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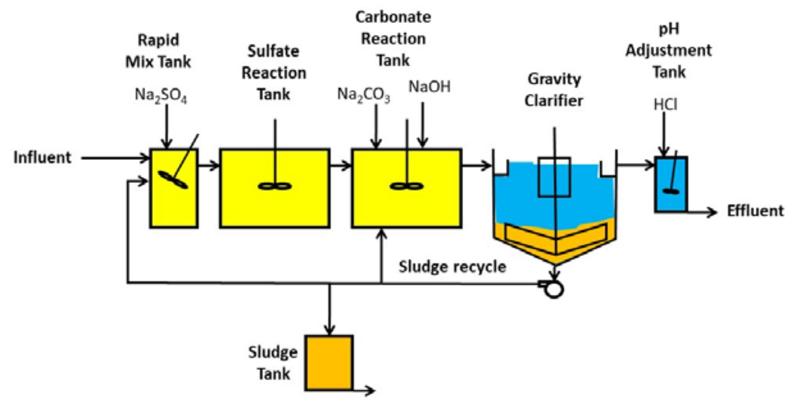
Reverse Osmosis Treatment Process (presence of Ba^{2+}, Ca^{2+} etc.)



- Excess sludge mass will be removed from the system to be dewatered and disposal. Due to the formation of $BaSO_4$ sludge, this sludge mixture would more than likely to pass the hazardous waste characterization test, the TCLP, and can be disposed off in an ordinary landfill. This system is represented by the Veolia's Multiflo Process. This compact process is very cost effective in reducing Ba, Sr, Ca, and Mg divalent ions.

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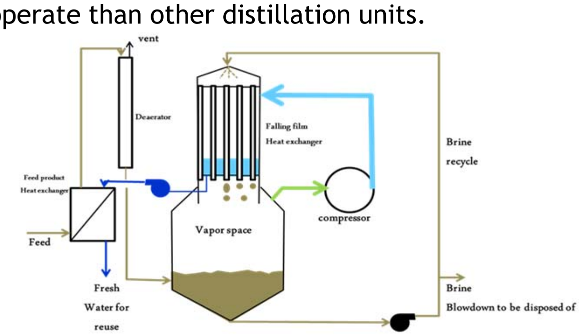
155

Mechanical vapor recompression evaporator

- Mechanical vapor recompression (MVR) evaporator uses vapor recompression by a gas compressor as the main driver for water evaporation.
- Its application range is from 20,000 to 250,000 mg/L of NaCl concentration. It is the most economic thermal desalination process for the small flow (< 4000 m^3/day) application.
- it is energy efficient (2 to 5 kWh per bbl of water treated), robust, and easier to operate than other distillation units.



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156

Mechanical vapor recompression evaporator

- It can be used to concentrate the salt up to 250,000 mg/L (the NaCl crystallization condition). Salt precipitation on the heat exchanger surface (the scaling point) also limit the application of this technology. Pre-removal of the divalent ions (Ca, Mg, Sr, and Ba) may be required in some cases.

- Boiling point elevation - Due to the special water chemistry of different FB/PW, the increase of boiling point of the brine can be unpredictable. For an efficient MVR operation, the boiling point elevation is limited to 6.5 ^{o}F. Some of the compounds in the wastewater, such as some organics, $CaCl_2$, $MgCl_2$ may cause significant brine boiling point elevation. They may need special handling.

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157

Mechanical vapor recompression evaporator

- **Foaming possibilities** - Vendor experiences are important in prevent foaming from becoming a big operational issue. The following levels of organics are listed by some manufacturers to be restricted in the evaporator for foam prevention. Addition of anti-foaming agents or removal of organics at the pretreatment are the possible preventive steps:
  1. VOC (volatile organic carbon) < 1,000 mg/L
  2. TOC (total organic carbon) < 1,500 mg/L as acetic acid
  3. Oil and grease < 50 mg/L
- **Ammonium removal is poor** – Ammonium will be boiled over to the vapor side of the evaporator. Its removal in such an evaporator is poor, further ammonium removal of the produced fresh water may be necessary, if its presence is not acceptable for reuse or discharge.
- **Volatile organics carryover** – Some volatile organics in the feed, such as methanol, will be carried over to the condensate stream. In some states when product de-listing regulation applies, the removal of these organics and ammonium is required. This can be accomplished by using a steam stripper after the MVR

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158

Mechanical vapor recompression evaporator

- There are several demarcation points in the design of MVR
  1. The brine blowdown Cl- concentration: 36,000 mg/L belong that stainless steel can be used to construct the main body, above that level more exotic (expensive) material will have to be used, increase the CAPEX significantly
  2. The boiling point elevation to be kept below 10F so that cheaper fan can be used for the recompression process, this usually limit the brine concentration to be below 100,000 mg/L of TDS. Above this level higher pressure compressor will have to be used.
  3. The upper limit of brine blowdown TDS is about 270,000 mg/L to prevent NaCl precipitation on the heat exchanger, even the low corrosion material and compressor are used in the MVR design.
  4. These two limits of TDS in the blowdown brine with the incoming feed water TDS, determines the % water recovery and % blowdown.

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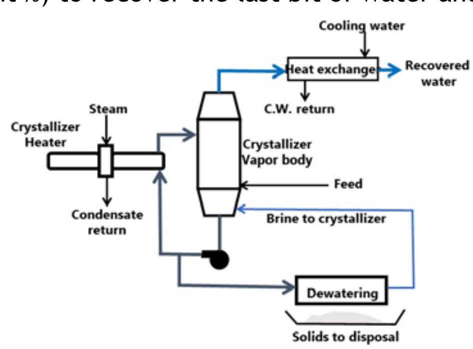
159

Crystallizers

There are two types of crystallizers being used in treating the concentrated brine solutions:

- Thermal Atmospheric Crystallizer
- Vacuum crystallizer using refrigerant

- Thermal atmospheric crystallizer - a thermal atmospheric crystallizer is used to further concentrate the inlet brine from 200,000 to 300,000 mg/L of salt as NaCl or (20 to 30 weight %) to recover the last bit of water and produce salt cake
- A forced circulation crystallizer:



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160

Crystallizers

- Crystallizer is easier to operate when the salt concentration and composition is suitable and easy to precipitate. These include NaCl which precipitates out at about 27 to 30 wt. %. This can make the crystallizer proceed without having to deal with high boiling point elevation.
- When there are more soluble salts present in high concentrations; e.g., $CaCl_2$, $MgCl_2$ and other organic salts, their high solubility (75 wt. % in the case of $CaCl_2$) can elevate the boiling point of the brine to approximately 350 ^oF, this makes the operation of the forced-circulation crystallizer more expensive.
- In addition, at the higher temperature, $CaCl_2$ can be hydrolysed to produce HCl in the vapor phase which will cause severe corrosion. Very expensive noble alloys are required to form the reactor vessel and heat exchanger surfaces.

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161

Crystallizers

- These factors make this process difficult to apply in crystallizing brines from FB/PW evaporation. To correct this problem:
  1. high pH operation has been used to assist the precipitation of $Mg(OH)_2$ or $Ca(OH)_2$ in the crystallizer at lower Ca or Mg concentration by adding caustics directly to the crystallizer body.
  2. the pretreatment of the feed brine by using secondary treatment processes to replace of Ca, Mg ions with Na becomes necessary.
  3. one can follow the crystallizer with a spray dryer. But the energy use for the dryer can be as high as 230 kWh per bbl of water evaporated
- All of these alternative ways for final brine disposal have limitations and challenges.

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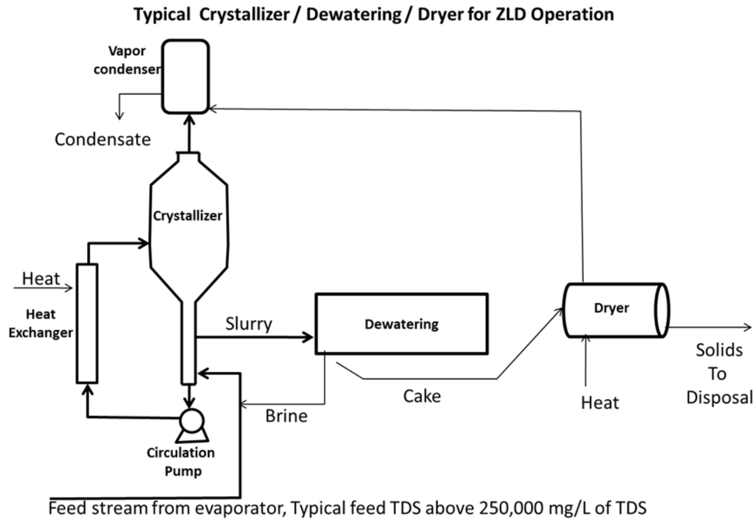
162

Crystallizers



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163

Vacuum Crystallizers

- A newly developed low pressure and low temperature evaporator by HPD of Veolia Water is targeting the highly soluble Ca or Mg chloride brine.
- At low temperature, these chloride salts can precipitate out of solution at lower concentration. For example, $CaCl_2$ solubility is 75 wt. % at 350 ^oF vs. 56 wt. % at 115 ^oF. At the lower concentration, the boiling point elevation is reduced from 135 to 56 ^oF. This makes the evaporation more economical if a deep vacuum can be applied to the crystallizer (0.5 psi).
- Next figure shows the schematics of a low temperature crystallizer. A closed loop heat pump employing a liquid refrigerant provides the cooling of the system and heating for evaporation at this low temperature, 130^oF.

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164

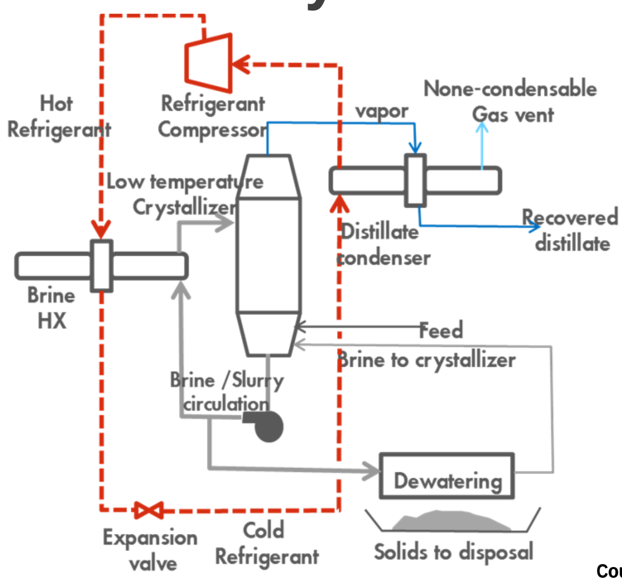
Vacuum Crystallizers

- The electric energy is approximately 12 kWh per bbl of water produced.
- One of the issues of disposal of calcium or magnesium chloride salts is that these salts are hygroscopic (water absorbing). The dry chemicals should be kept in an air-tight container. This increase the cost its handling and disposal
- None of the crystallizers has been installed strictly for the dealing with FB/PW yet. They are special equipment and should be treated carefully.

Courtesy: Paul Sun

165

Vacuum Crystallizers



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166

Deep Well Disposal

- Deep well disposal is usually the most cost-effective way for brine disposal. If it can be located safely and nearby.
- Deep well location evaluation:
  1. Injection zone depth, confining geological structure, porosity,
  2. Injection zone geochemistry and groundwater chemistry,
  3. Long term water storage capacity.
  4. Risk of inducing seismicity
- Deep well injection is tightly regulated in the USA by EPA's Underground Injection Control (UIC) Program to protect underground source of drinking water (TDS < 10,000 mg/L). One can inject brine into Class I or Class II wells.

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167

Deep Well Disposal

- Class I well has injection zone below the lowermost formation containing a underground source of drinking water (USDW) within ¼ miles of the well bore.
- Class II wells can receive oil and gas industry produced waters
- The deep well construction is strictly regulated
- The deep well is closely monitored for leakage or fracturing of receiving zone
- However, once the restrictions are met, deep well can remove the brine permanently, and is economic to operate

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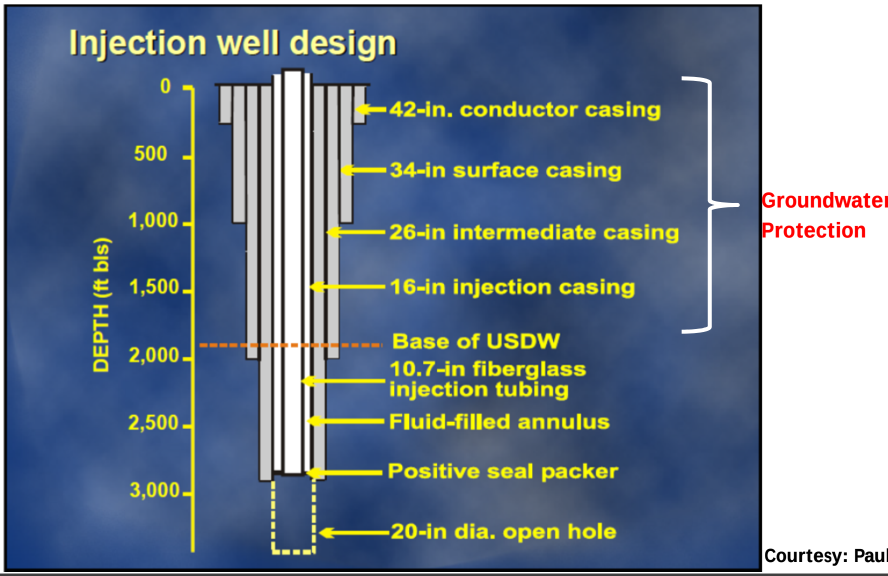
168

Deep Well Disposal



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169

Deep Well Disposal

- Important method of disposal when dispose of concentrated brine from RO or evaporator when scaling is the limiting factor for these treatment schemes,
- Detailed understanding of brine chemistry to design a pretreatment program to prevent scaling in the injection zone,
- Prevent carbonate and sulfate scaling of Ca, Sr, and Ba at injection zone pressure and temperature and compatibility with the formation zone water.
- Prevent silica precipitation at zone pressure and temperature,
- Prevent solids formation due to oxidation of sulfide or ferrous ions,
- Evaluation of injection fluid and rock interactions to prevent clogging
- The least treatment is to remove suspended solids to prevent well clogging.

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170

Questions?

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171