Key Considerations for Frac Flowback / Produced Water Reuse and Treatment

NJWEA Annual Conference – Atlantic City, NJ

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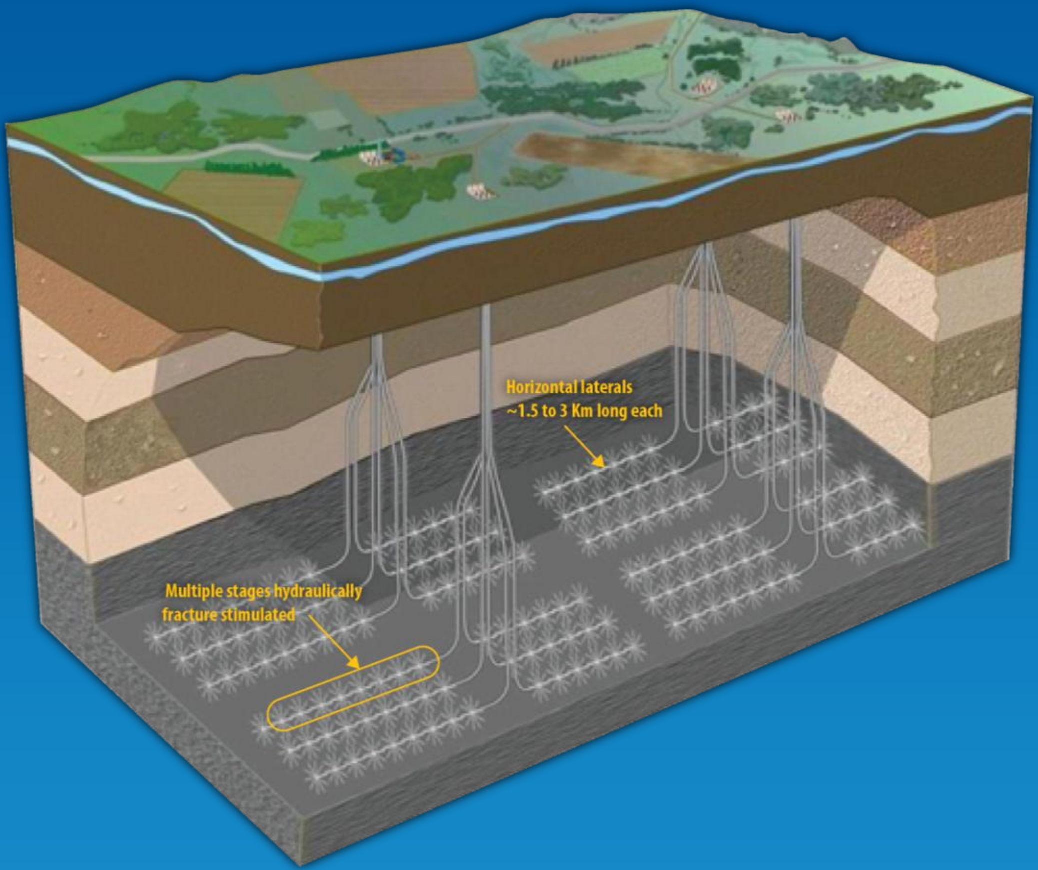
Today’s Agenda

- Overview of Hydraulic Fracturing Process
- Water Quality
- Treatment Alternatives

Hydraulic Fracturing

- Frac Method: Typically slick water frac
- Wells: 4 to 8 wells per pad
- Frac Water Volume: 4 to 6 million gallons per well (95k to 142k bbl)
- Flowback: 15 – 35% return



Source: ALL Consulting. *Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives*, July 2003.

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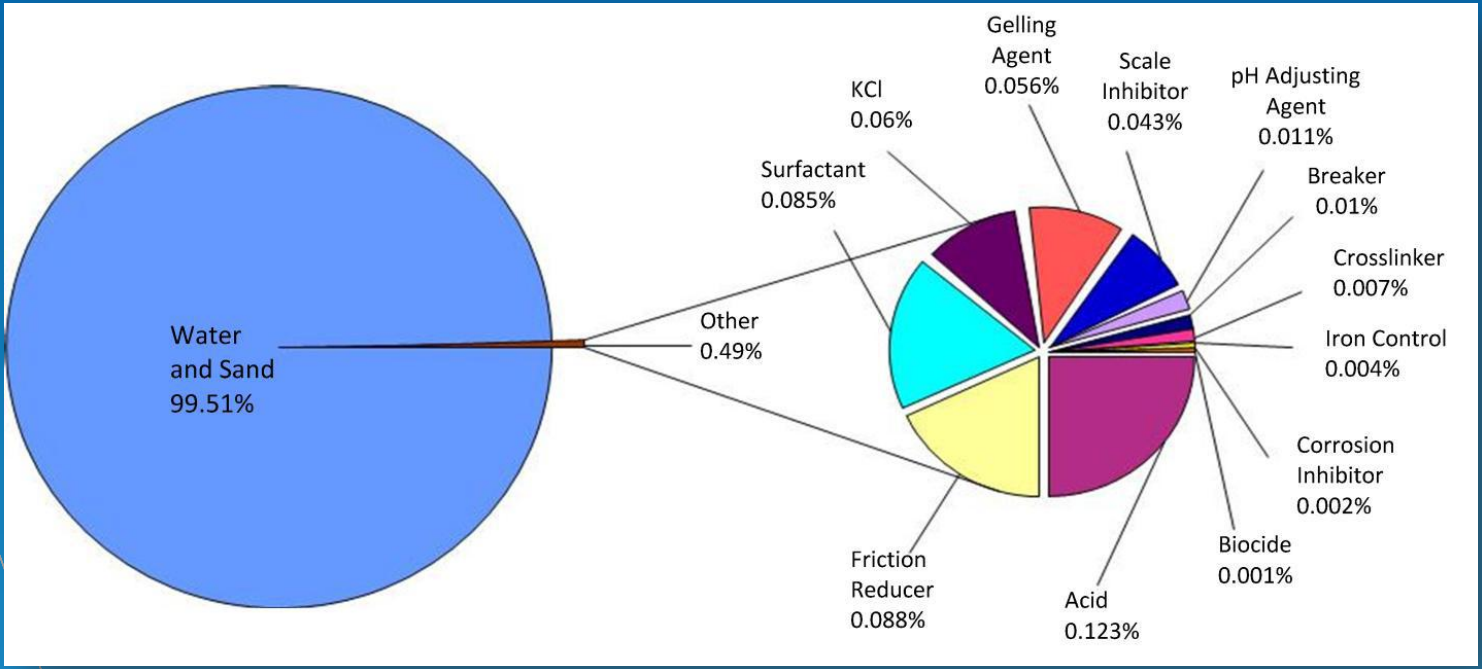
Composition of a Fracturing Fluid

- Fracturing solution consists of sand and water
- Additives include biocides, corrosion inhibitors, O2 scavengers, friction reducers, surfactants, etc.



Reference: All Consulting 2009

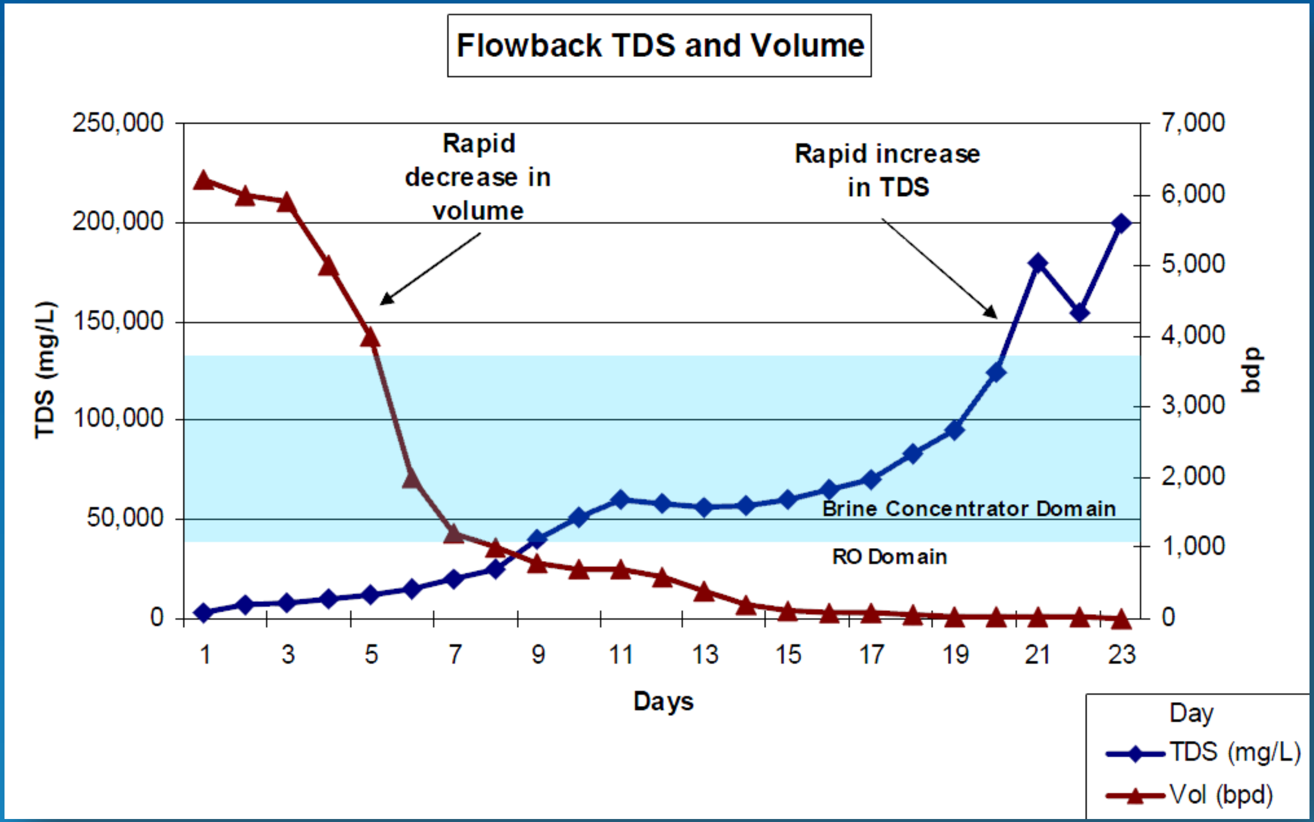
Frac Flowback Water Quality

All values in mg/L

Parameter	Feed Water	Flowback
pH	8.5	4.5 to 6.5
Calcium	22	22,200
Magnesium	6	1,940
Sodium	57	32,300
Iron	4	539
Barium	0.22	228
Strontium	0.45	4,030
Sulfate	5	32
Chloride	20	121,000
Methanol	Neglible	2,280
TOC	Neglible	5,690
TSS	Neglible	1,211
TDS	<500	182,273

Typical Flowback Characteristics

The longer Frac water is in the formation, the higher the TDS levels may become.



Source: Siemens AG 2009

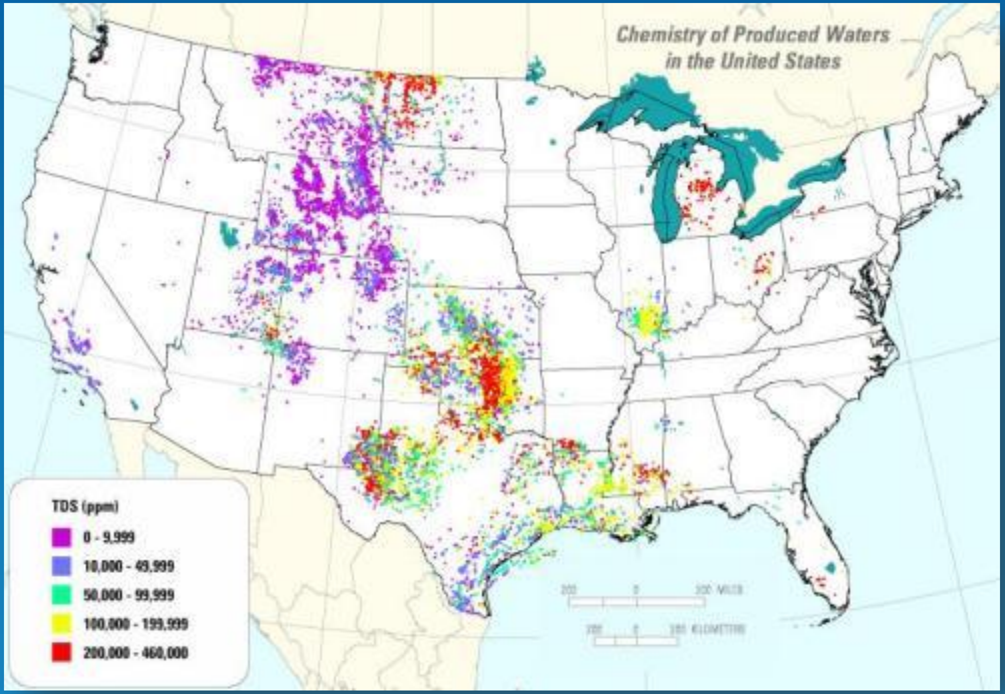
Wide Variation in Frac Flowback Chemistry

Parameter	Frac 1	Frac 2	Frac 3	Frac 4
Barium	7.75	2,300	3,310	4,300
Calcium	683	5,140	14,100	31,300
Iron	211	11.2	52.5	134.1
Magnesium	31.2	438	938	1,630
Manganese	16.2	1.9	5.17	7.0
Strontium	4.96	1,390	6,830	2,000
TDS	6,220	69,640	175,268	248,428
TSS	490	48	416	330
COD	1,814	567	600	2,272

All values in mg/L
Ref: ProChemTech International, Inc.

Total Dissolved Solids from the Produced Water Database in the United States

- Typical Produced Water TDS Levels – Selected Areas
  - Powder River CBM – 1,200 mg/l
  - San Juan CBM – 4,500 mg/l
  - Greater Green River – 8,000 mg/l
  - Eagle Ford Shale – 20,000 mg/l
  - Fayetteville Shale – 25,000 mg/l
  - Barnett Shale – 60,000 mg/l
  - Woodford Shale – 110,000 mg/l
  - Haynesville Shale – 120,000 mg/l
  - Permian Basin – 140,000 mg/l
  - **Marcellus Shale – 180,000 mg/l**



Source: USGS

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Key Water Management Concerns

- Wasting water and general water resource concern
- Surface water quality impacts
- Shallow groundwater quality impacts
- Long-term soil damage from salinity
- Transportation – 100,000 bbl = 770 trucks

BOTTOM LINE:

- Huge unconventional gas resources are driving development; and water solutions are key
- Water quality concerns leading to more treatment and reuse
- Solutions can be simple to very complex – ***Reduce, Reuse, Recycle*** are key goals

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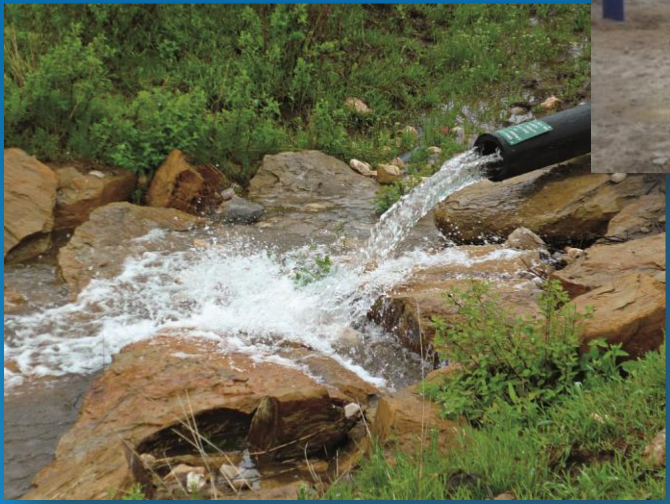
Design Basis
Critical First Step

- Feed Water Volume
- Feed Water Quality
- Treated Effluent Requirements
- Site Specific Considerations

Flowback / Produced Water Treatment Solutions

- Treatment for Reuse Without TDS Removal
- Treat for Reuse / Discharge with TDS Removal



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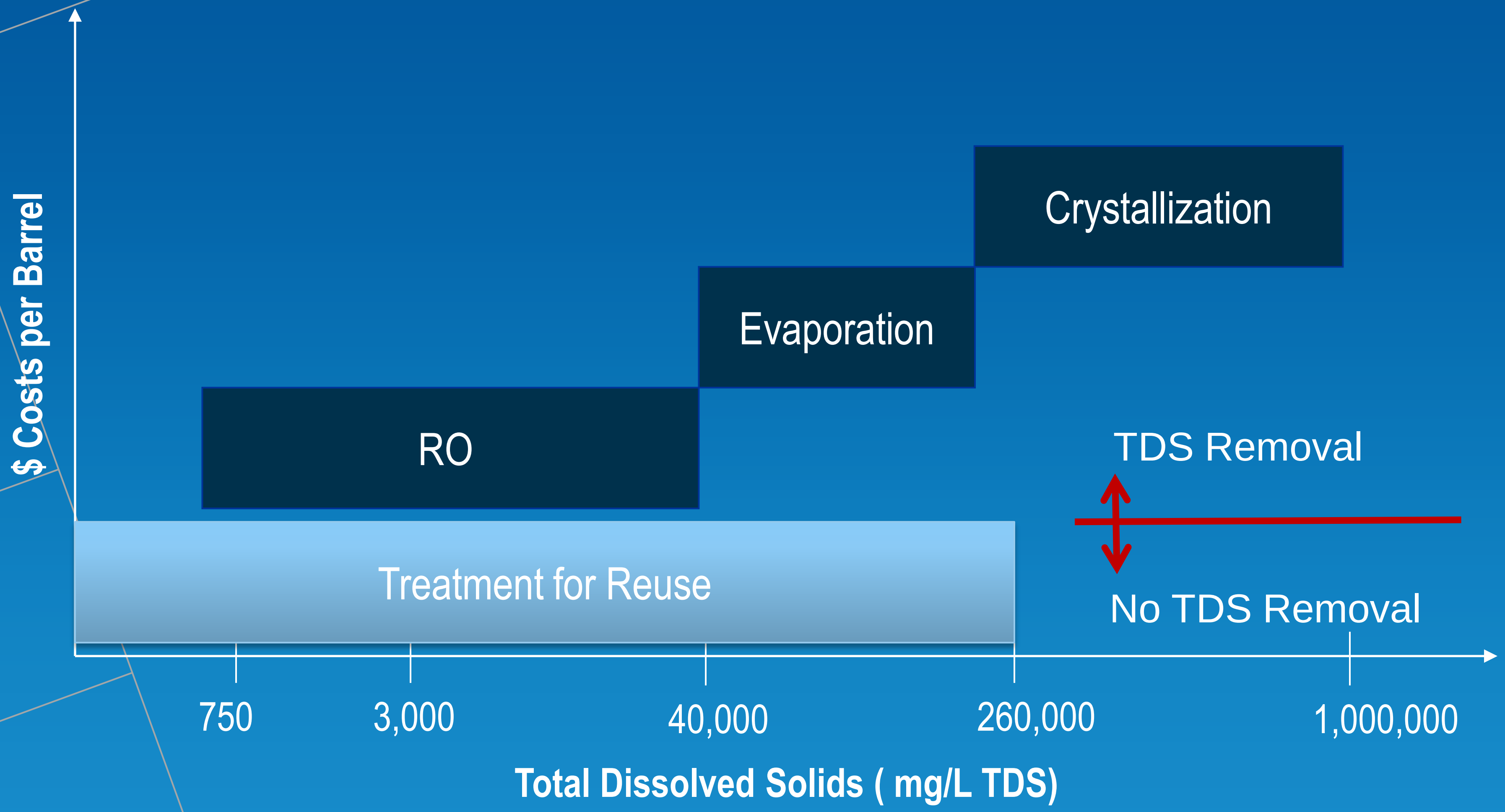
TREATMENT FOR REUSE WITHOUT TDS REMOVAL

Range of Applicability vs. Cost



Example Feed Water Quality

- Water May Also Contain:
  - Polymers
  - Other Organics
  - Radium
  - Other Inorganics (e.g., boron)

Parameter	Feed Water
pH	6.09
Bicarbonate	144
Calcium	11,595
Magnesium	690
Sodium	33,250
Iron (diss)	76
Barium	2,775
Strontium	3,633
Chloride	81,000
TSS	295
TDS	132,265

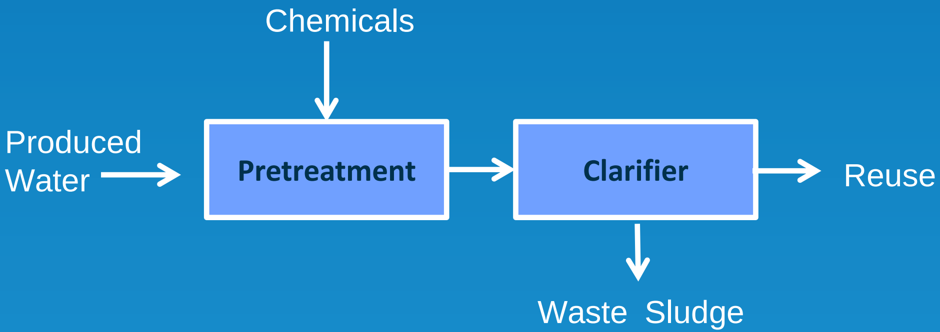
Example Treatment Requirements

- pH: 6.5 to 7.5
- Iron: < 10 mg/L
- TSS: < 50 mg/L
- Bacteria: None
- Treatment Residuals: Non-hazardous
- Mobile system required (5,000 to 10,000 BWPD)

Keys Design Considerations

- Water Chemistry
  - Presence of organics, oxygen, and nutrients
    will result in bacteria growth!
  - Precipitation of barium sulfate
    will tend to adsorb radium, which may cause the sludge to become hazardous

- Treatment Selection
  - Efficient solids / liquid separate required (small footprint)
  - Sludge management
  - Chemical consumption / dosing



Treatment Technology Options

Technology	Bact.	CH3OH	O/G	DRO	GRO	TA	HCO3-	TH	Ca	Mg	Fe	Ba	St	SO4	Cl	TDS	TSS	Poly mers
API Separators			X															
Dissolved Gas Flotation				X	X													
Activated Carbon			X	X	X													X
Nut Shell Filters			X															
Organi-Clay Adsorbants			X															
Chemical Oxidation	X										X							X
UV Disinfection	X																	
Biological Processes			X	X	X													
Air Stripper					X	X	X											
Chemical Precipitation								X	X	X	X	X	X	X				
Lime/Soda Softening	X					X	X	X	X	X	X							
Clariifers																	X	
Settling Ponds																	X	
Ion Exchange								X	X	X	X	X	X	X	X	X		
Multi- Media Filtration																	X	
Membrane Filtration	X																X	
Greensand Filters	X										X							
Cartridge Filters																	X	
Reverse Osmosis						X	X	X	X	X				X	X	X		
Evaporation								X	X	X	X	X	X	X	X	X		
Steam Stipping		X		X	X													
Acidification						X	X											

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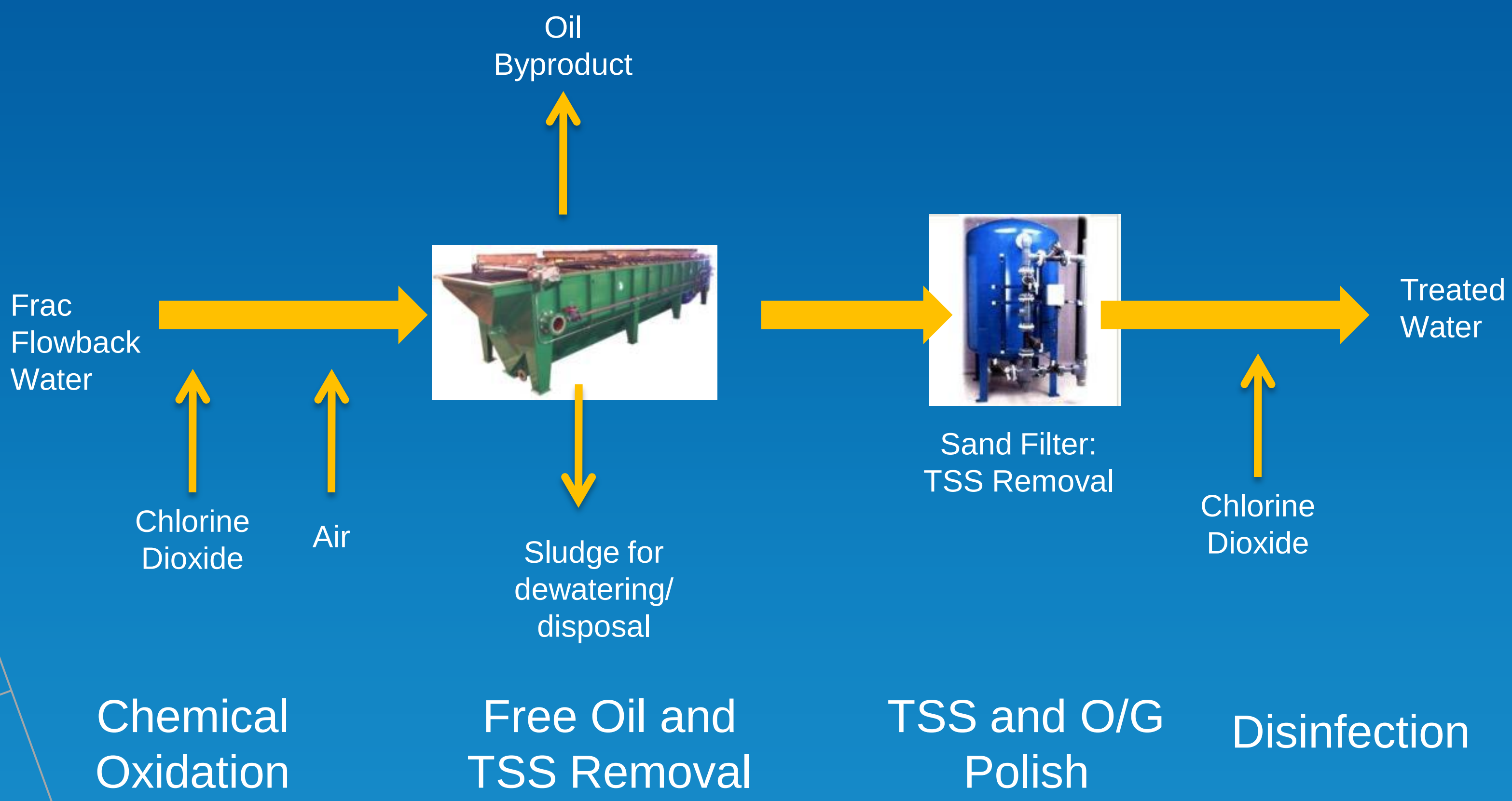
Example of Reuse Treatment Solution Without TDS Removal



Step 1. Chlorine Dioxide Oxidation

- Chlorine dioxide is strong oxidant that provides selective chemical oxidation
- Breaks oil / grease emulsions
- Destroys friction reducers and other chemical additives
- Kills Bacteria
- Oxidizes reduced compounds, such as Fe, Mn, Sulfide, etc.
- More efficient than bleach – does not react with ammonia and many other organics

Ref: Sabre Technologies

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Step 2. Dissolved Air Flotation

- Fine bubble diffusion floats oil / grease and TSS to top
- Skimmer potentially recovers saleable oil
- Covered designs also available for VOC emission control
- Skid-mounted design

NOTE: Dissolved Gas or Induced Gas Flotation may also be considered

Ref: Pan America Environmental Website

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Step 3. Multi-Media Sand Filtration

- Conventional sand filter removes TSS before reuse
- Acid or carbon dioxide addition ahead of filter to reduce pH and eliminate calcium carbonate scaling
- Periodically backwashed with filtered water. BW returned to front of system.
- Chlorine dioxide disinfection of final product water

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Summary of Reuse Treatment *Without TDS Removal*

- Simplest and least expensive form of treatment
- Multiple technology and design options available
- Reduces fresh water makeup requirements and off-site disposal costs
- Applicable only if drilling operations that need frac flowback water are on-going
- Bench and pilot-scale testing recommended to select best treatment options and minimize cost

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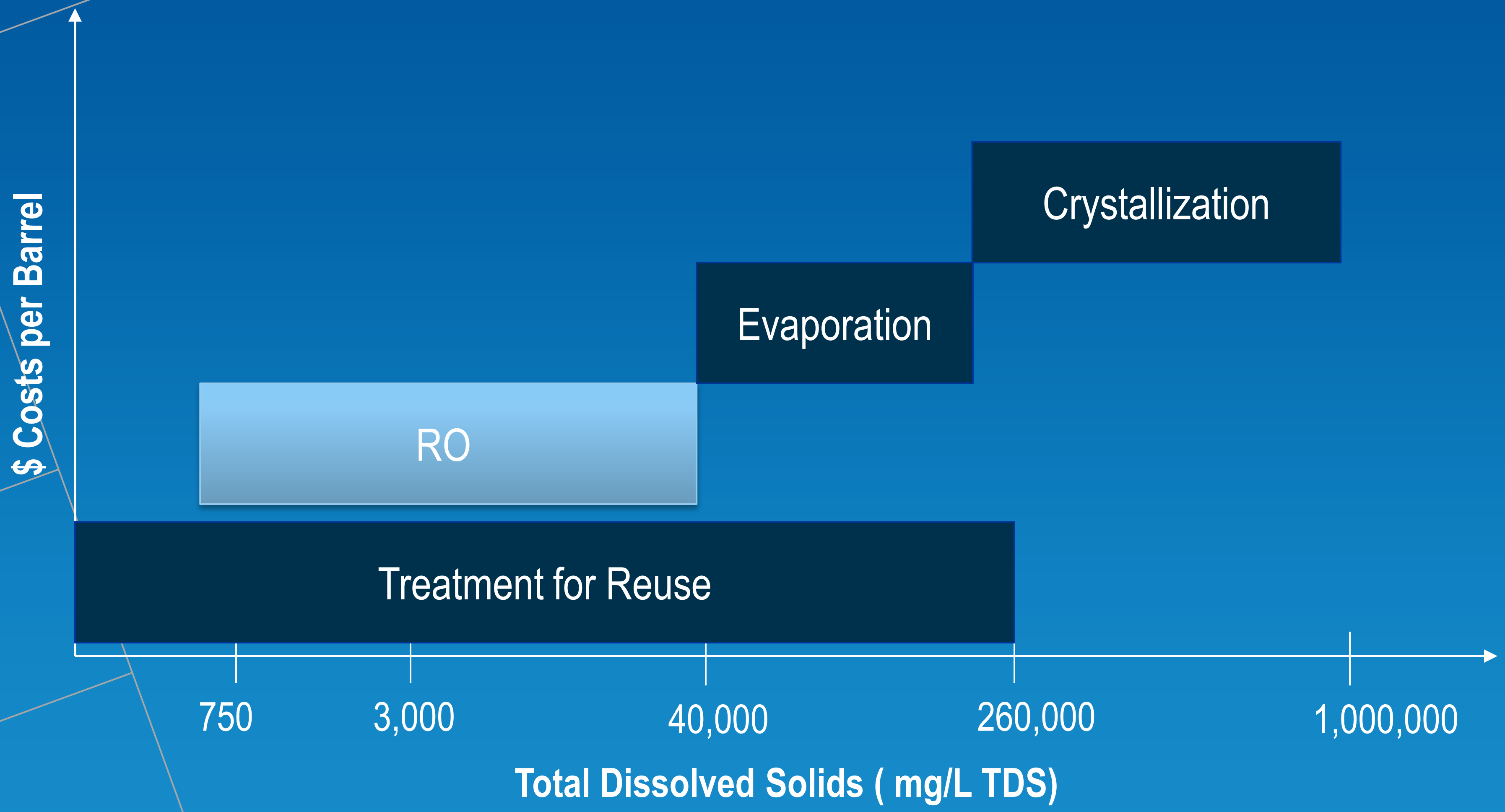
TREATMENT OPTIONS FOR TDS REMOVAL

Viable TDS Removal Alternatives

- Membrane Treatment
- Evaporation
- Crystallization

Range of Applicability vs. Cost



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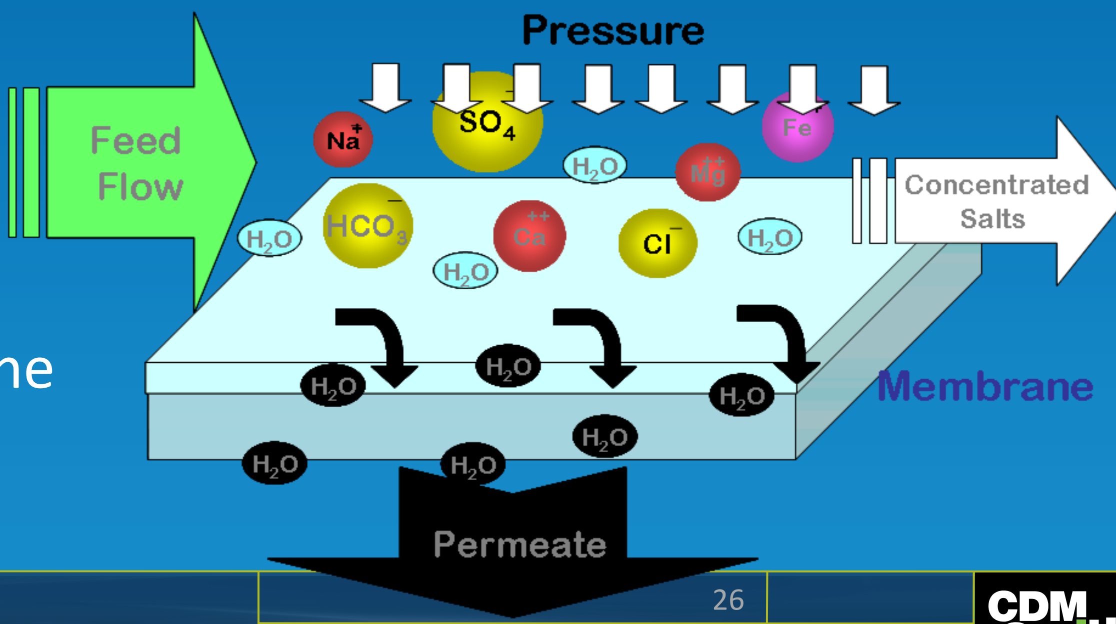
Reverse Osmosis

- Membrane separation technology that removes dissolved solids (TDS) from water
- Membrane is semi-impermeable - allowing only water to pass; 99%+ of all ionized species are rejected
- Non-selective treatment process
- Degree of <u>all</u> ion rejection is dictated by size and charge
- NF is a loose RO membane



Reverse Osmosis (continued)

- Maximum concentrate TDS is approx. 80,000 mg/L
- Energy costs are 1/10th to 1/15th the cost of mechanical evaporation
- Skid-mounted, compact design
- Operating pressures up to 1200 psig
- Multiple membranes and manufacturers available

Historical Problems with RO Treatment for Produced Water

- Limited success due to inadequate pretreatment, resulting in fouling and scaling from:
  - Calcium Hardness
  - Iron
  - Barium and Strontium
  - Silica
  - Microbiological Growth
  - Organics
  - Silt and Suspended Solids

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Scale Forming Salts

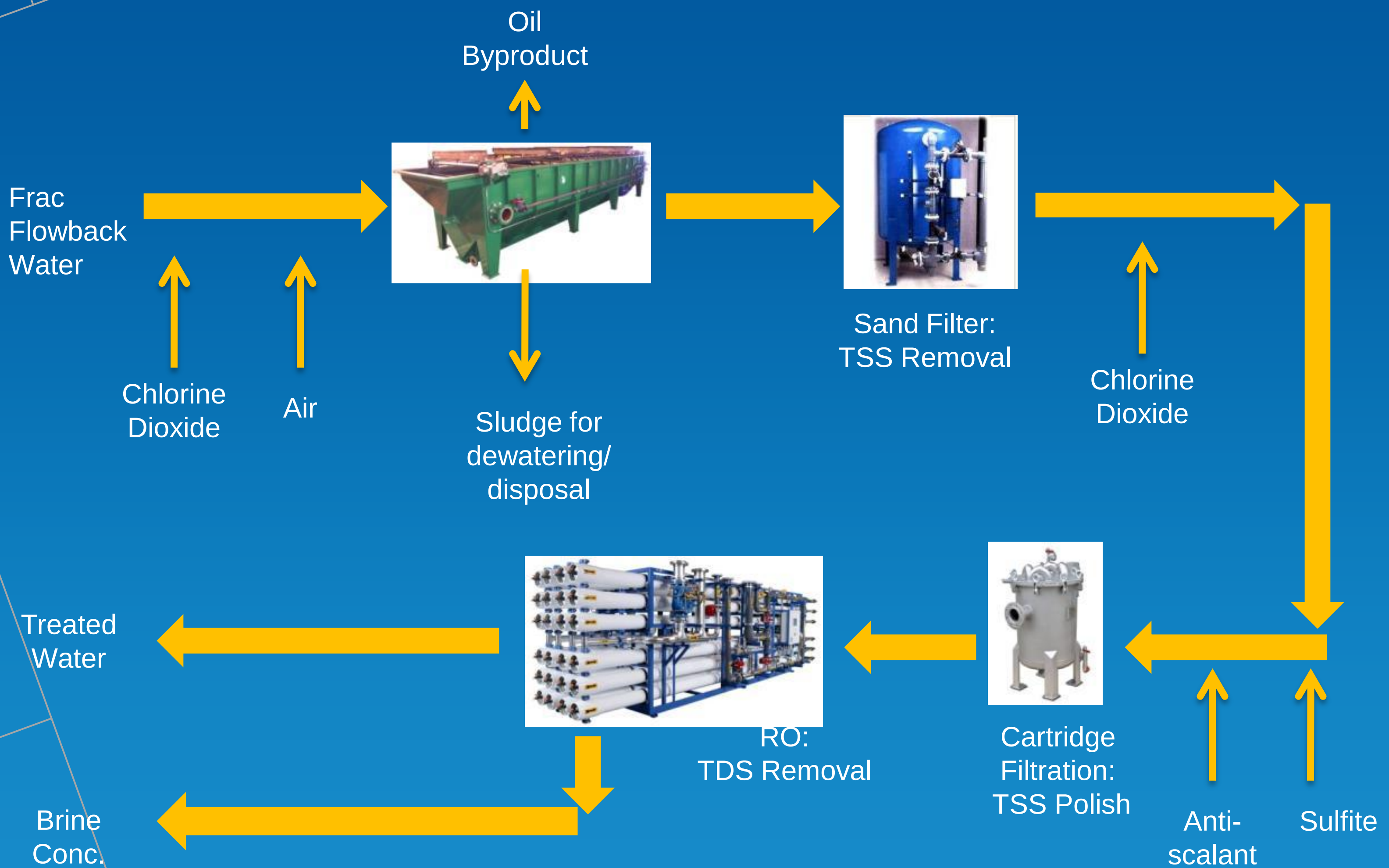
Salt	Saturation Concentration (mg/L)
Calcium Carbonate ($CaCO_3$)	8
Calcium Fluoride (CaF_2)	29
Calcium Orthophosphate ($CaHPO_4$)	68
Calcium Sulfate ($CaSO_4$)	680
Strontium Sulfate ($SrSO_4$)	146
Barium Sulfate ($BaSO_4$)	3
Silica, amorphous (SiO_2)	120

Key to Success: Efficient Pretreatment

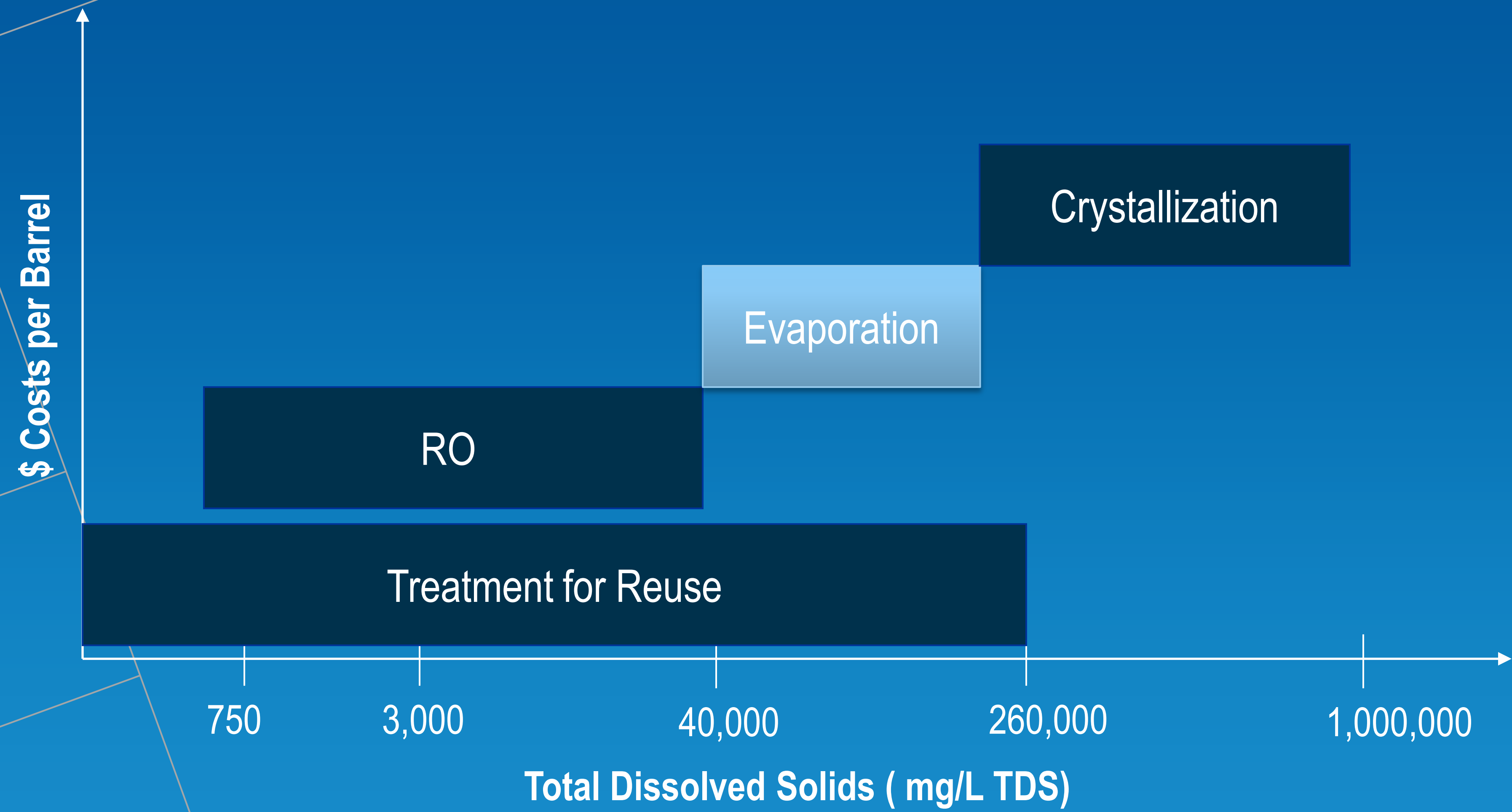
- Pretreatment Steps:
  - Organics removal (oil / grease, polymers, etc.)
  - Efficient management of hardness and metals
  - Particulate removal
  - Bacteria control

Result: Better pretreatment leads to less membrane fouling, higher water recovery and a lower cost of brine disposal

Example Treatment Solution for TDS Removal



Range of Applicability vs. Cost



Evaporation

- Ideal TDS Range of Feed Water is 40,000 to 120,000 mg/L
- Produces high quality distillate and liquid brine concentrate
- Brine concentrate requires further treatment or disposal (max TDS concentration is approx. 260,000 mg/L)
- Evaporation systems more energy intensive than RO
- Most evaporation systems cannot handle any solids

Types of Evaporation Systems

- Forced Circulation
- Falling Film
- Rising Film
- Agitated Thin Film
- Plate and Frame

Selection Considerations

- Chemical Composition of Feed Stream
- Scaling / Fouling Potential
- Foaming Potential
- Materials of Construction
  - Chloride concentrations
  - Temperature

Economization

- Multiple Effects
  - Vapor From Each Effect is used in the Next / Previous Effect Depending on Set-up to Reduce Steam Use
- Vacuum
  - Reduces Boiling Point
  - Maximizes Efficiency When Used in Concert With Multiple Effects
- Mechanical Vapor Recompression
  - Recompresses the Vapor to Reduce Steam Use
  - Usually Uses Just One Effect

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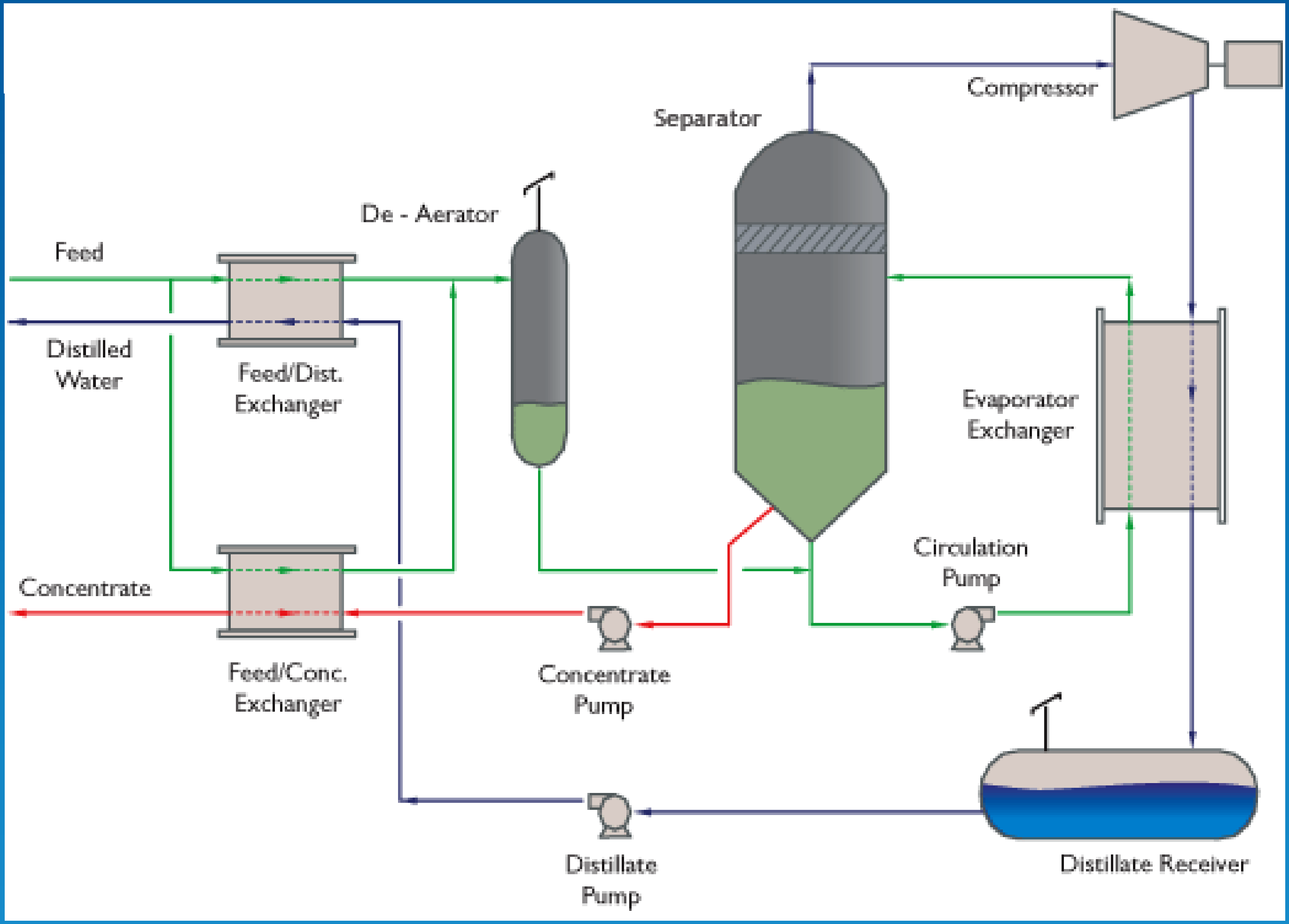
MVR Evaporator

Most Economical for this Application



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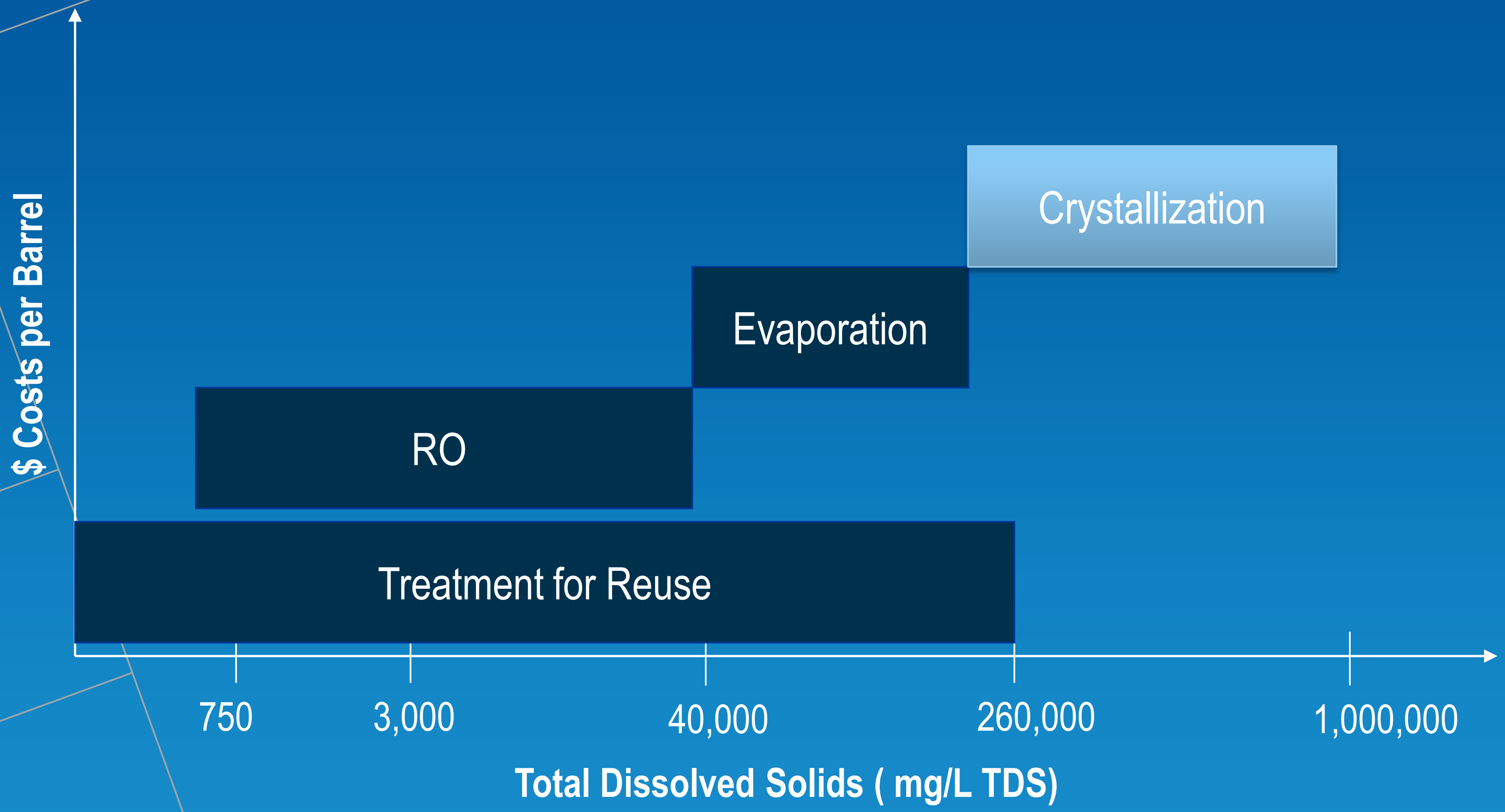
Range of Applicability vs. Cost



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Crystallizer

- Complex system capable of producing purified salt <u>products</u> from impure solutions
- Multiple Types of Crystallizers available
- Principals of Crystallization include:
  - Evaporation to form supersaturated solution
  - Nucleation and growth of salt crystals
  - Harvesting, washing and drying of salt crystals

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Application of a Crystallizer in the Marcellus

- Crystallizer Products:
  - Calcium Chloride Liquid
  - Sodium Chloride Dry Salt
  - Distilled Water

Parameter	Feed Water
pH	6.09
Bicarbonate	144
Calcium	11,595
Magnesium	690
Sodium	33,250
Iron (diss)	76
Barium	2,775
Strontium	3,633
Chloride	81,000
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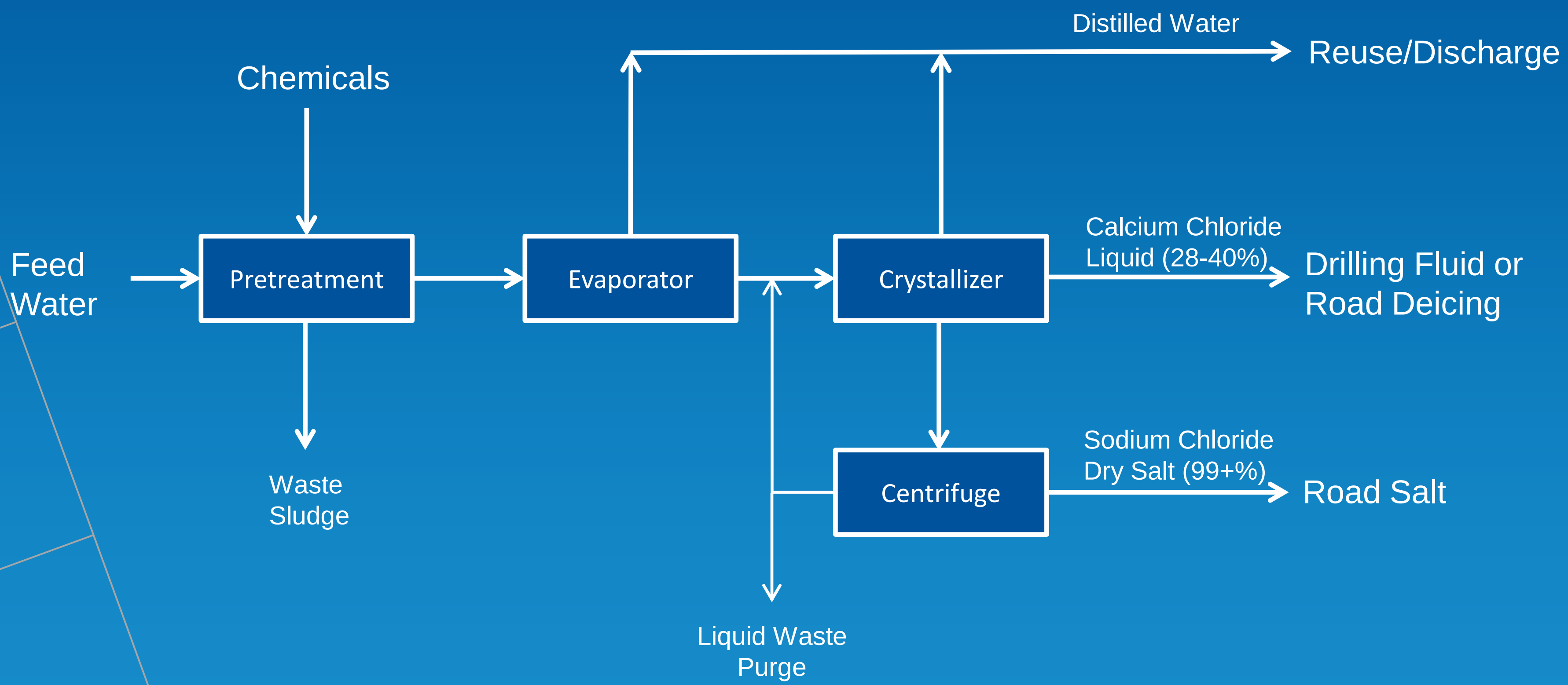
Crystallizer Block Flow Diagram



Key Considerations

- Proper Design
- Feed Water Management
- Economics – Byproduct Chemical Sales (ASTM specifications)

TDS Treatment Options Summary

- RO membranes have found little use in the Marcellus
- Evaporation technology using Mechanical Vapor Recompression most common form of TDS Treatment
- Crystallization technology is complex but can be cost effective with sale of commodity chemical byproducts
- All technologies generally produce some amount of waste brine that requires disposal

Questions and Answers

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