Produced Water Chemistry in Petroleum Basins

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ESal Engineered Salinity

Powering the Energy Transition of Tomorrow with Green Technology

Outline of Talk

I. The Oil Business is the Water Management Business
   - Conventional
   - Shale

II. Water Chemistry Analysis
   - Major Solutes Trends and Controls

III. Beneficial Uses Revisited
   - Wettability and Oil Production
   - Wettability and Carbon Sequestration

Produced Water

Oil & gas plays across the United States produce over 66 million barrels of water daily, many with high Total Dissolved Solids (>300,000 mg/L).

Oil and gas produces much more water than it consumes.

How does the industry deal with the water?

Well Types - Regulation

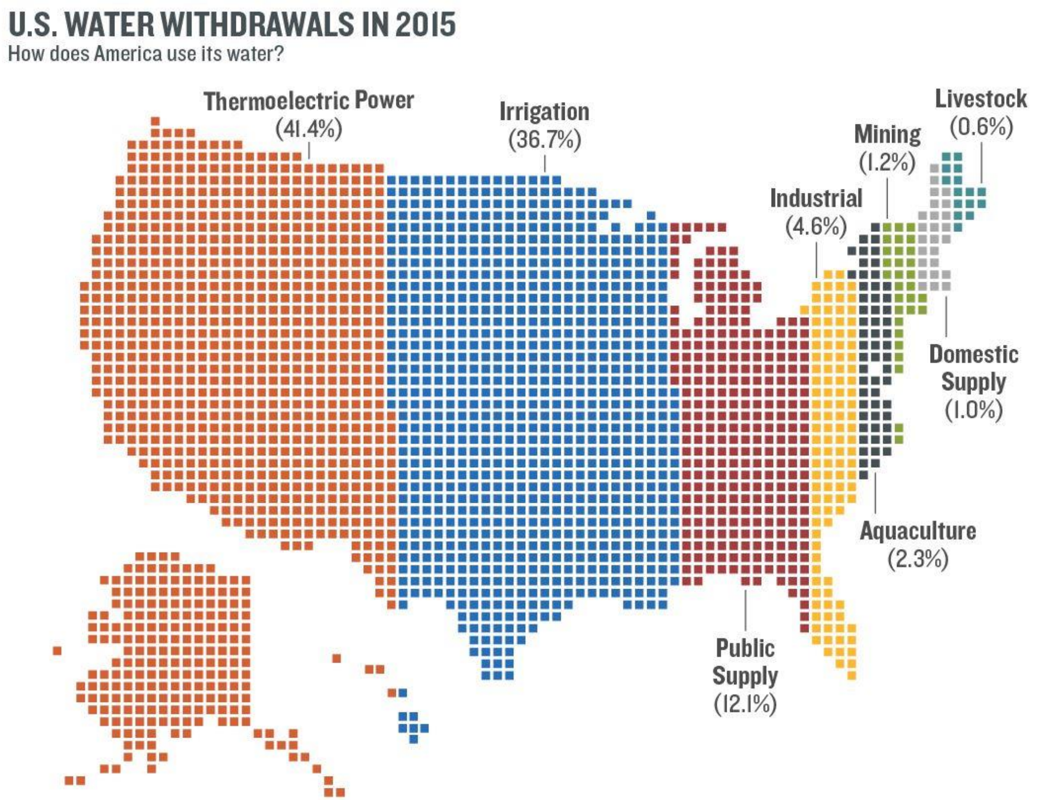
Wells are regulated by EPA as Underground Injection Control Wells (UIC)

Many States have primacy (State regulations meet or exceed EPA regulations)

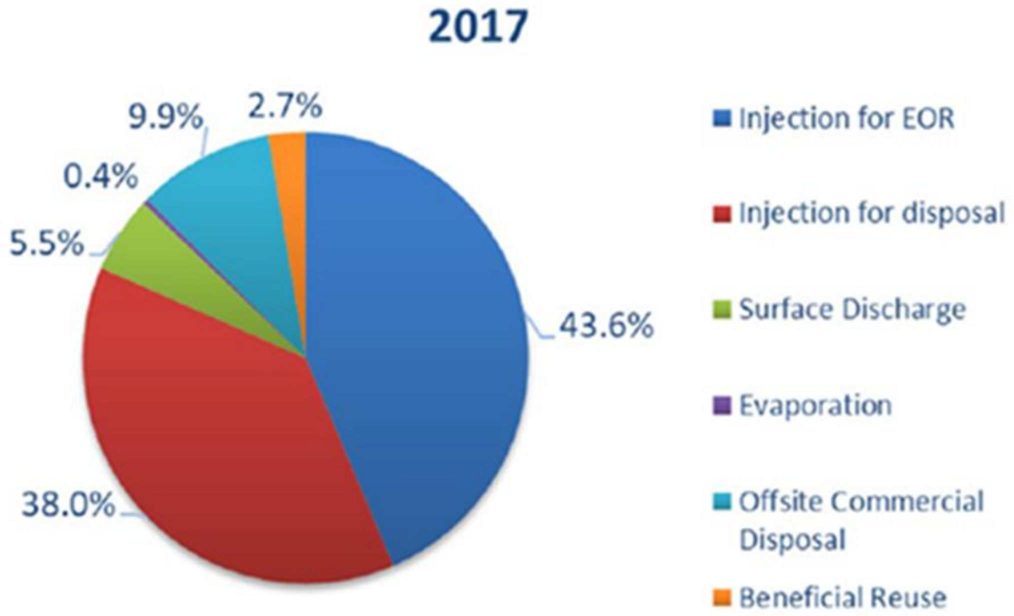
Class 1 – Hazardous Waste and non-Haz in deep wells
Class 2 – Oil and Gas Injection
Class 3 – Dissolution of subsurface Minerals for Extraction
Class 4 – Shallow wells for injection of hazardous materials above or below USDW
Class 5 – Non-hazardous fluids above or below USDW
Class 6 - CCS

Water in the USA

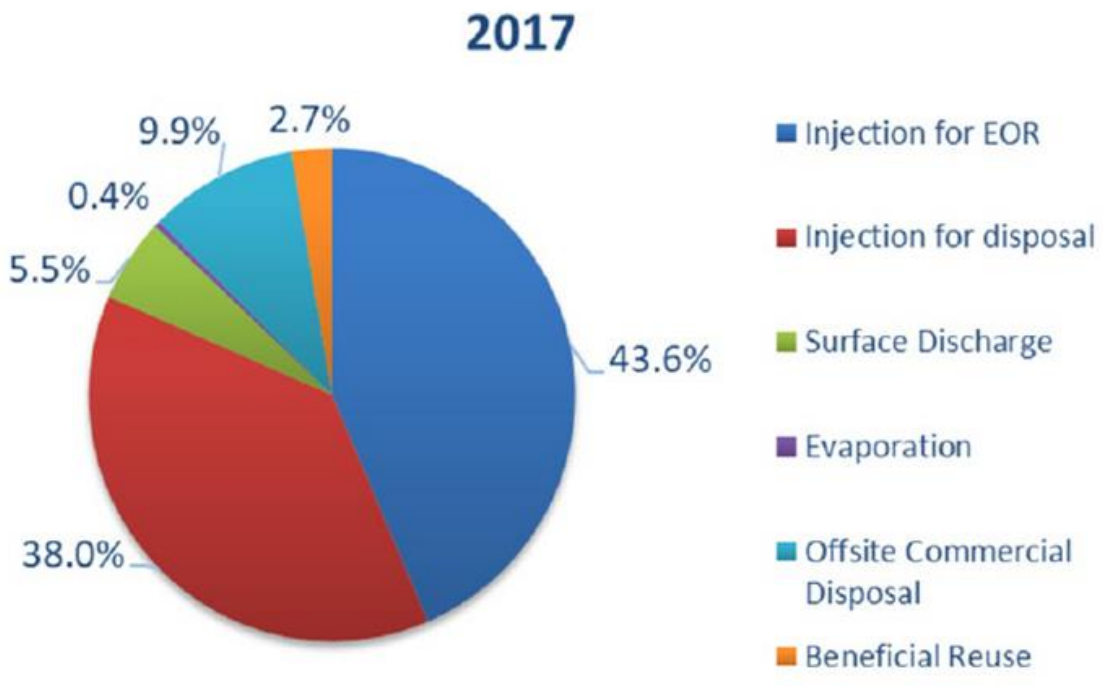
- US Water Use (2015) = 322 billion gal/day
- US Produced water (2017) = 2.81 billion gal/day



Source: Dieter et al. (2018) Estimated Use of Water in the United States in 2015. USGS Circular 1441.



The oil business is the water business

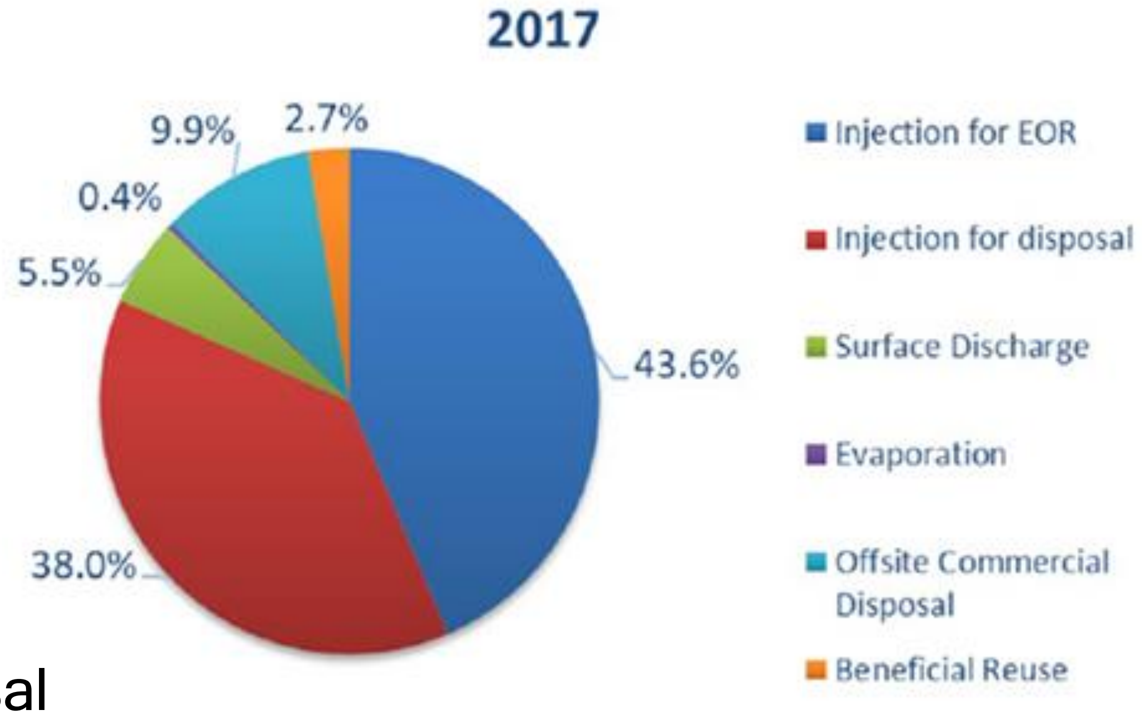


Veil 2019

- US Oil Production (2017) = 4.165B bbl/year
- US Produced water (2017) = 24.4B bbl/year
- Average Water Cut = 85.4%
- Lower in Shale
  - 50% increase in oil generated 15% increase in produced water volume since 2012
- Cost to manage = $0.01 to $5/bbl
- Typical Class II disposal is $0.75-$3.00/bbl
- Shale 5-15% of D&C costs

The oil business is the water business

- Conventional
  - Variable Quality
  - Mostly Closed Loop (reinjection during waterflood)
  - Mild Regulation
  - Localized Environmental Damage
  - Minimal Treatment
  - Major Cost is lifting
- Shale
  - Variable Quality
  - Requires Disposal
  - Requires Treatment
  - Major costs – lifting, treatment and disposal



Injection Triggers an Earthquake

Large volumes of extremely salty brine, and chemicals, come back up gas and oil wells (*left and right, respectively*). Companies often inject this wastewater down a shaft (*blue*) into a deep layer of porous rock for permanent disposal, which can trigger an earthquake (*inset diagrams below*).

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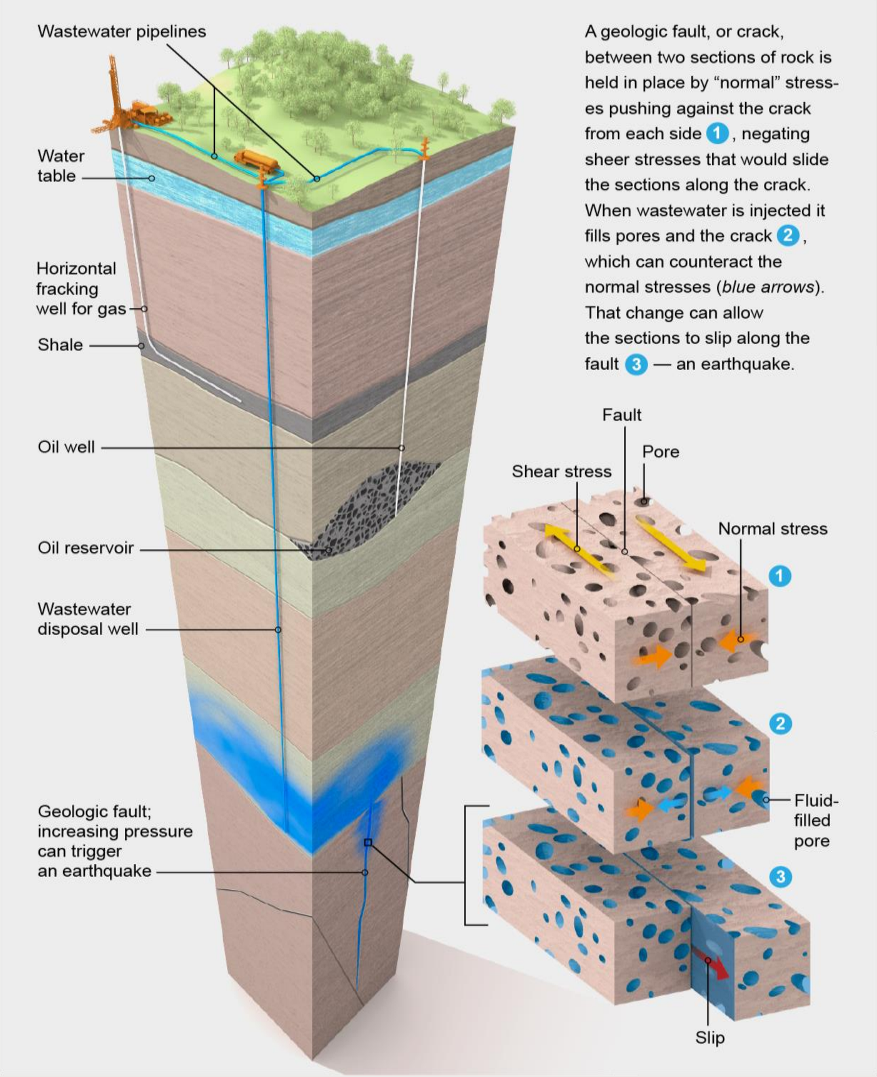

The oil business is the water business

Conventional Oil fields – most produced water is recycled (waterfloods)

Shale - produced water cannot be recycled into the source formation

80% of produced water from shale is disposed by injection, water management is 5-15% of cost of well

Disposal by injection can cause seismic activity

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Produced Water

- Produced water is an expense for the industry
- Can we turn this expense into an asset?
- A key is beneficial use – which is using the produced water in a manner that is deemed beneficial by the State.
- Groundwater is ‘owned’ by the State
- Case law linked surface and groundwater as a single resource in CA
- This legal structure makes life interesting for producers who can have liability without ownership
- CO has created a third class of water – fossil water – as a work around

Produced Water Chemistry
Beneficial Uses = Basin Scale Ecosystems

Legal Issues – who owns the water?
State Law Varies by State

1 – Absolute Dominion – 11 States – (belongs to surface owner)
2 – Reasonable Use – 17 States – (on site use)
3 - Correlative Rights – 5 States – (can use off site but reasonably)
4 – Beneficial Purpose – 2 States – (use for benefit but can't impact)
5 – Prior Appropriation) – 13 States – (1st to use gets it but not all – US West)

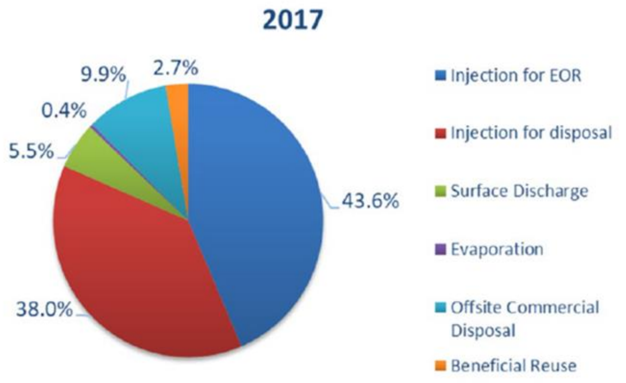
Private properties are recognized but not absolute
Rules are changing

From Water Systems Council

Produced Water Chemistry
Beneficial Uses = Basin Scale Ecosystems

Only 2.7% Used for

- Agriculture
- Aquaculture
- Stream flow augmentation
- Industrial use
- Municipal use
- NG production (CBM)



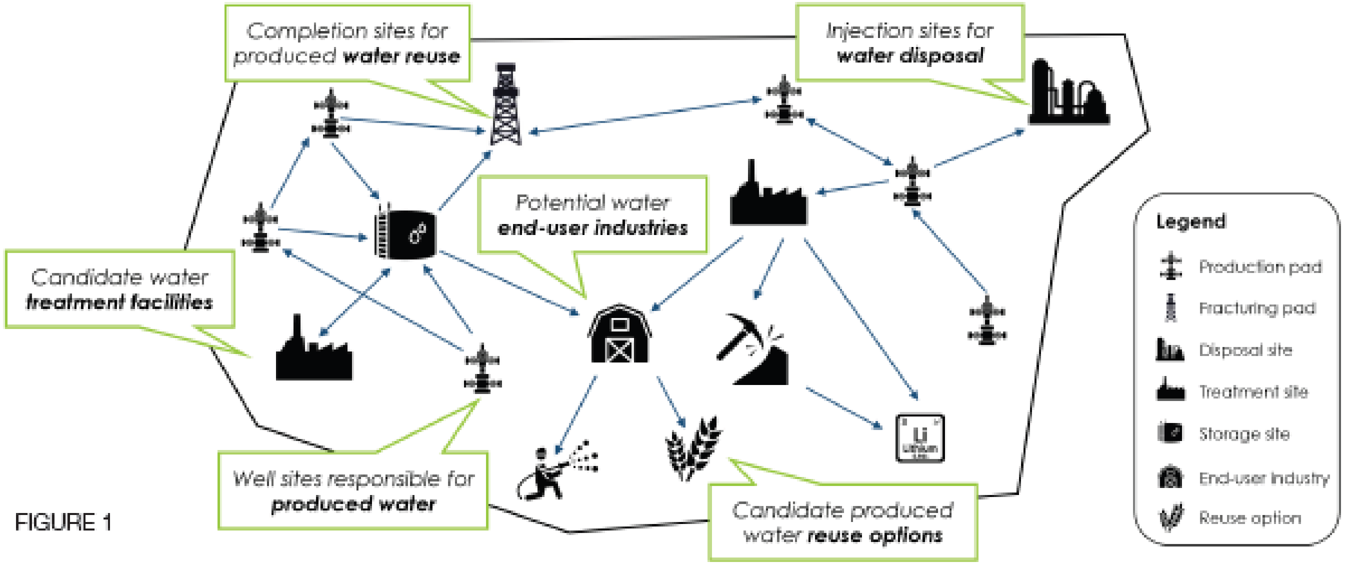


FIGURE 1

From DOE - NETL


Questions?
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- Produced Water Chemistry
  - Controlled by initial composition, burial diagenesis and water-rock reactions
  - Temperature (burial history and geothermal gradient)
  - Geology
    - Stratigraphic Architecture
    - Mineralogy

Major Solutes

Na, K, Ca, Mg, HCO_3, Cl, SO_4

Minor Solutes

Li, B, Si, Fe, Mn, Ba, Sr, Br and I

Isotopes

O, H, C

Dissolved Gases

N_2, CO_2, H_2S, CH_4

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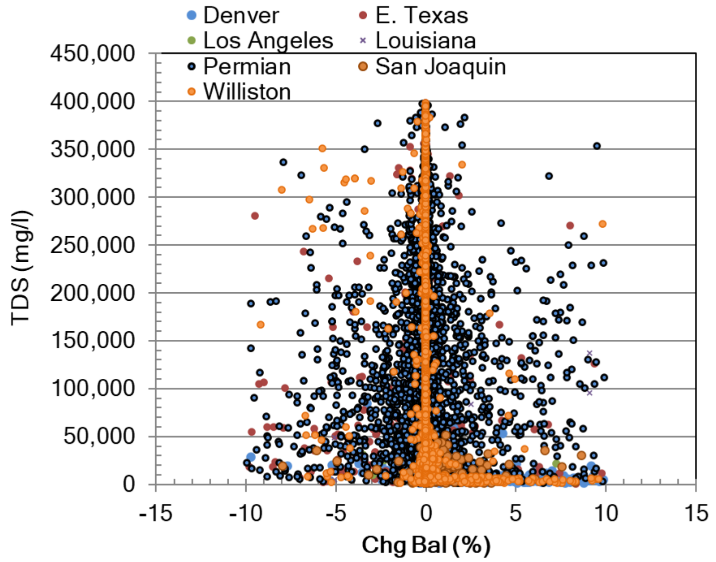
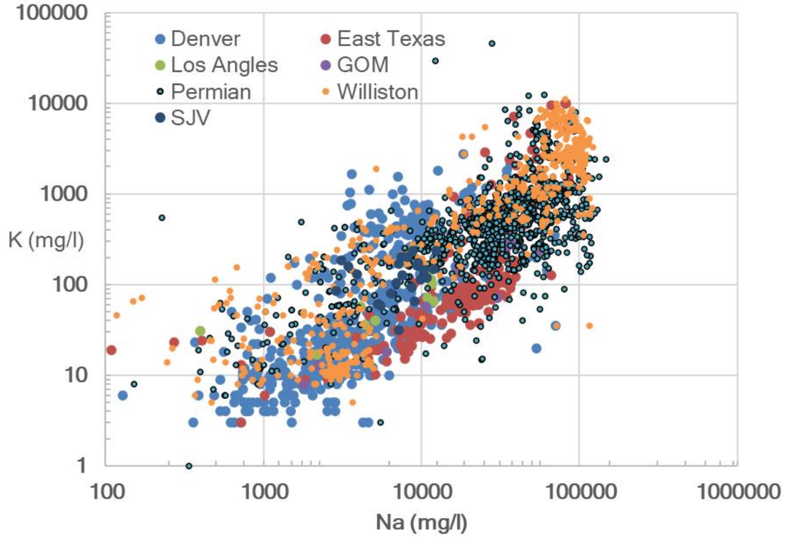
Data Preparation for USGS Produced Water Database

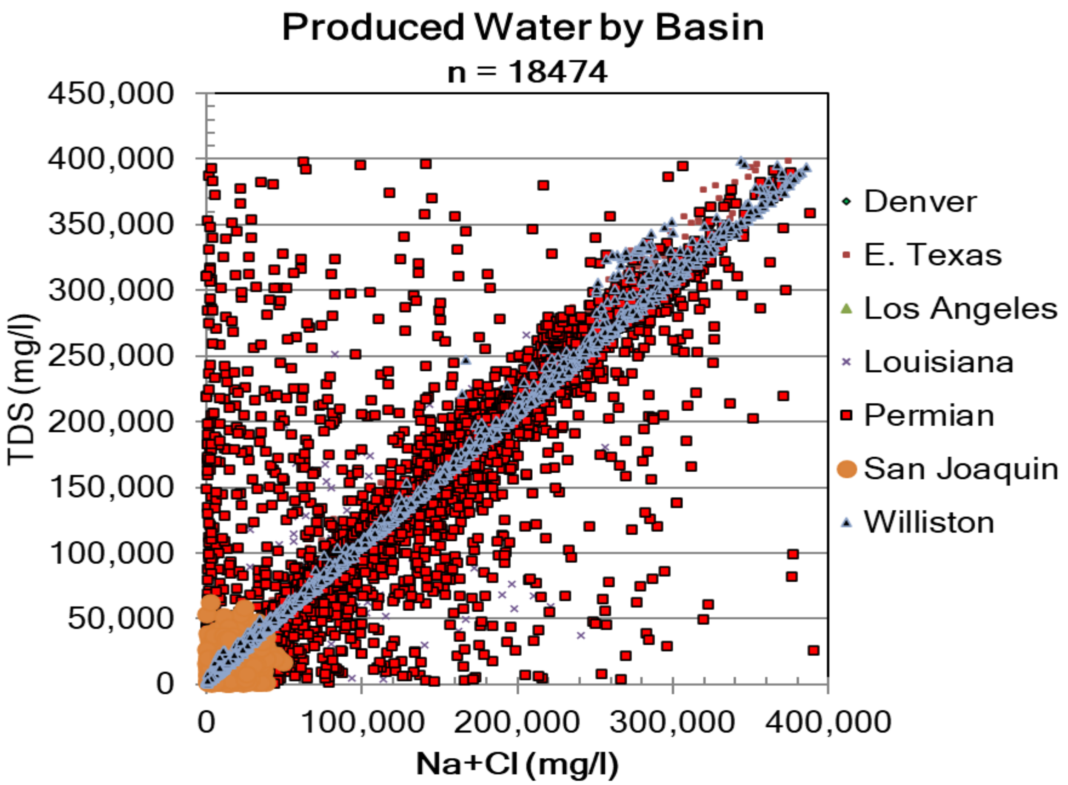
- Goal - Identify Major Solute Trends in several basins
- Remove samples with too many missing values
- Charge Balance < ±10% as QC/QA criteria
- Examine trends to further remove samples
- Temperature - often missing - estimate from sample depth
- pH - essential variable but often inaccurate
- Evaluate trends to estimate missing parameters

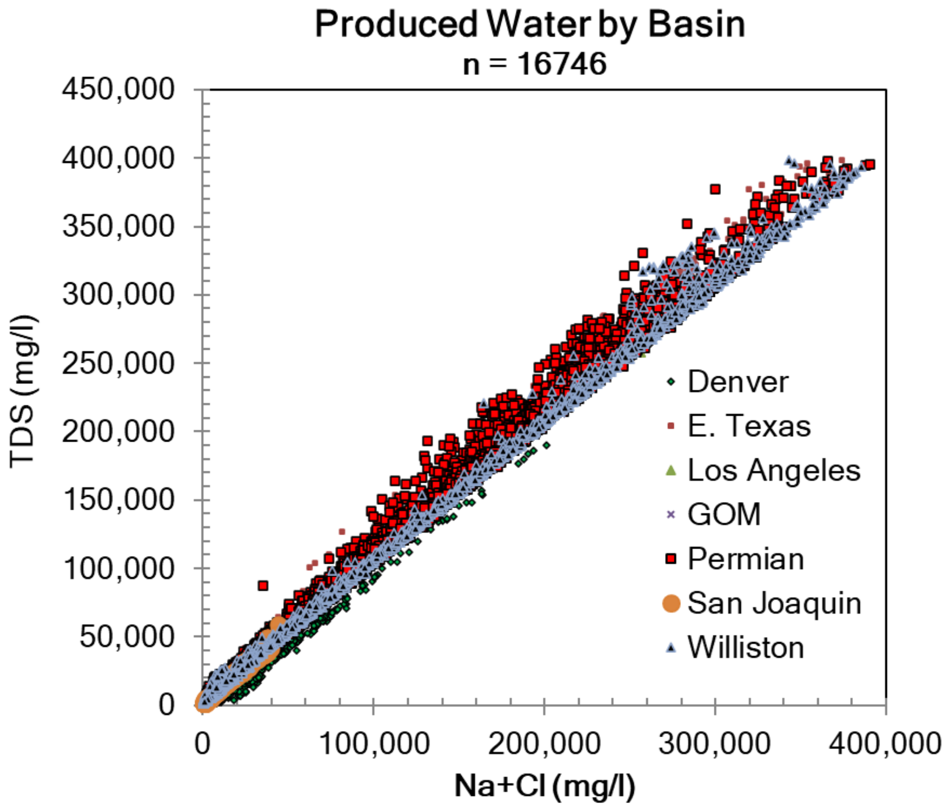




Example - Remove obvious problem analyses

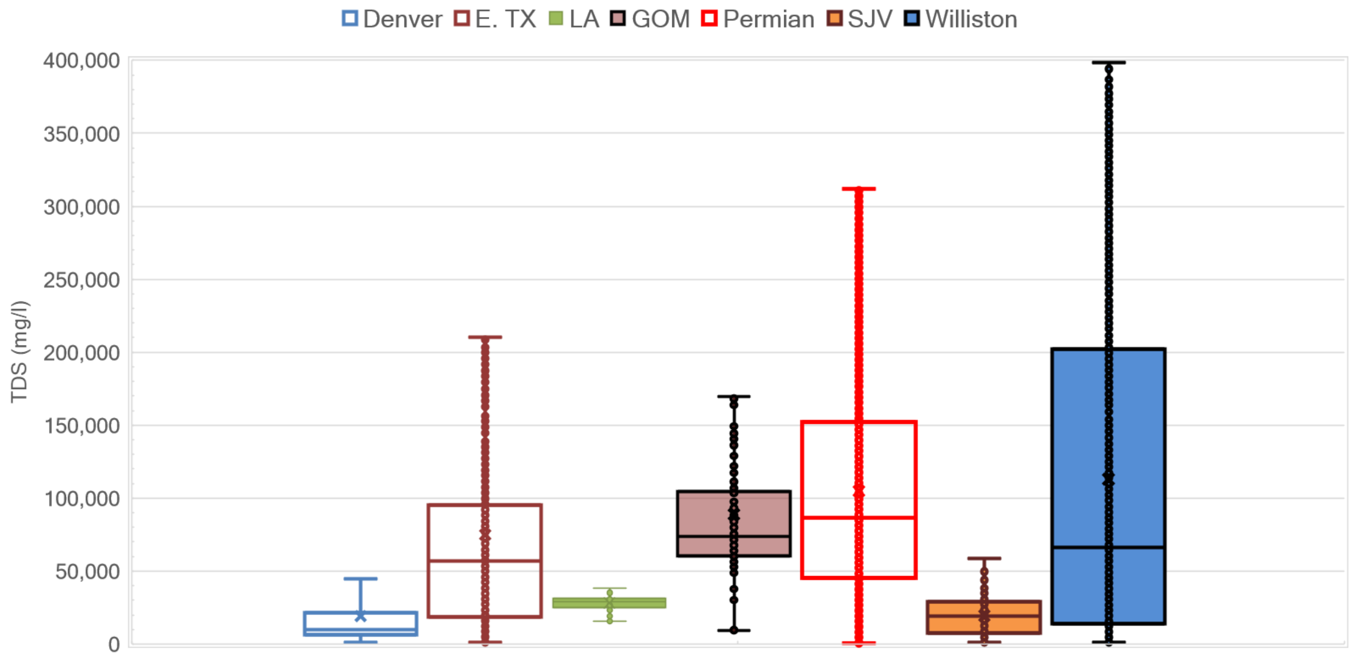
❖90+% of solutes are Na and Cl





Evaluate Basic Trends in Selected Petroleum Basins

- Denver
- East Texas
- Los Angles
- GOM
- Permian
- San Joaquin Valley
- Williston



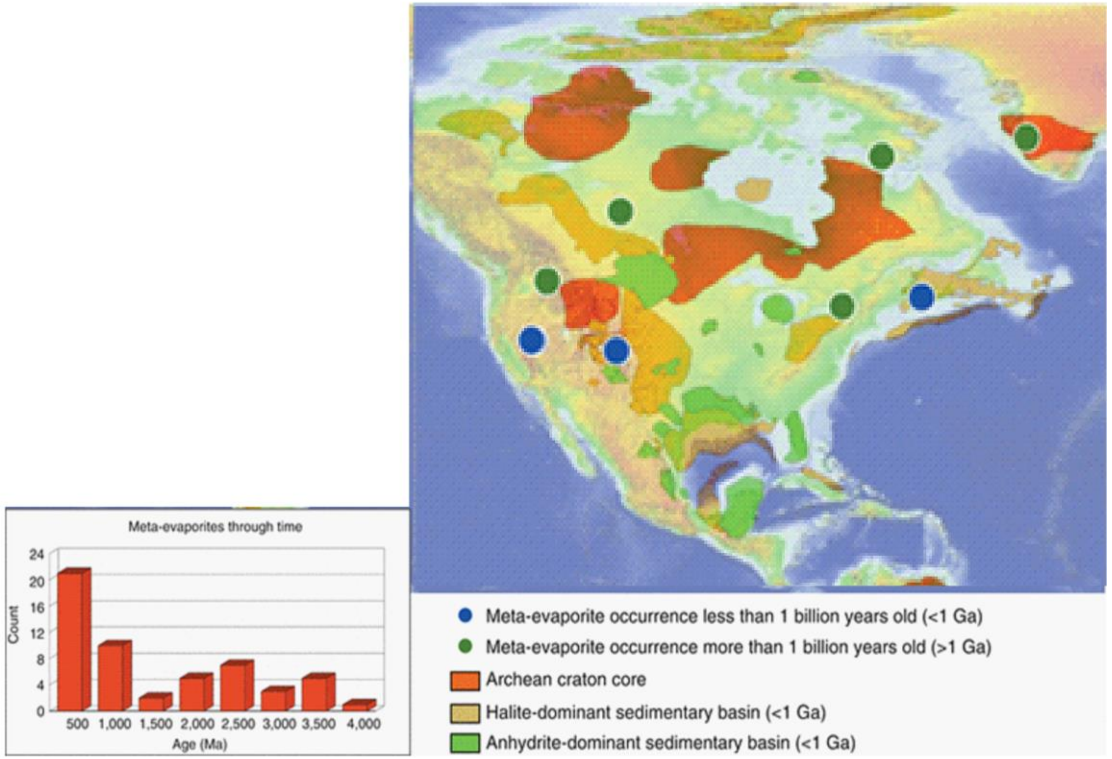
- Younger - Clastic Dominated
- Older - Clastics, Carbonates and Evaporites

Basin	n	Na/K	Na/Ca	Ca/Mg	Cl/SO4	Oldest	Max TDS
Denver	1332	732	108	4	135	Upper Cret.	201,058
E. Texas	1715	1263	13	15	943	Tri-Jurassic	398,904
Los Angles	329	224	31	26	4616	Upper Cret.	257,889
GOM	275	1291	20	3	6463	Tri-Jurassic	225,025
Permian	10939	249	16	52	243	Carboniferous	397,572
SJV	238	97	44	11	1292	Early Cret.	58,839
Williston	1938	473	26	60	133	Cambrian	398,317

meq/L

mg/L

Na, K, Ca, Mg, HCO_3, Cl, SO_4

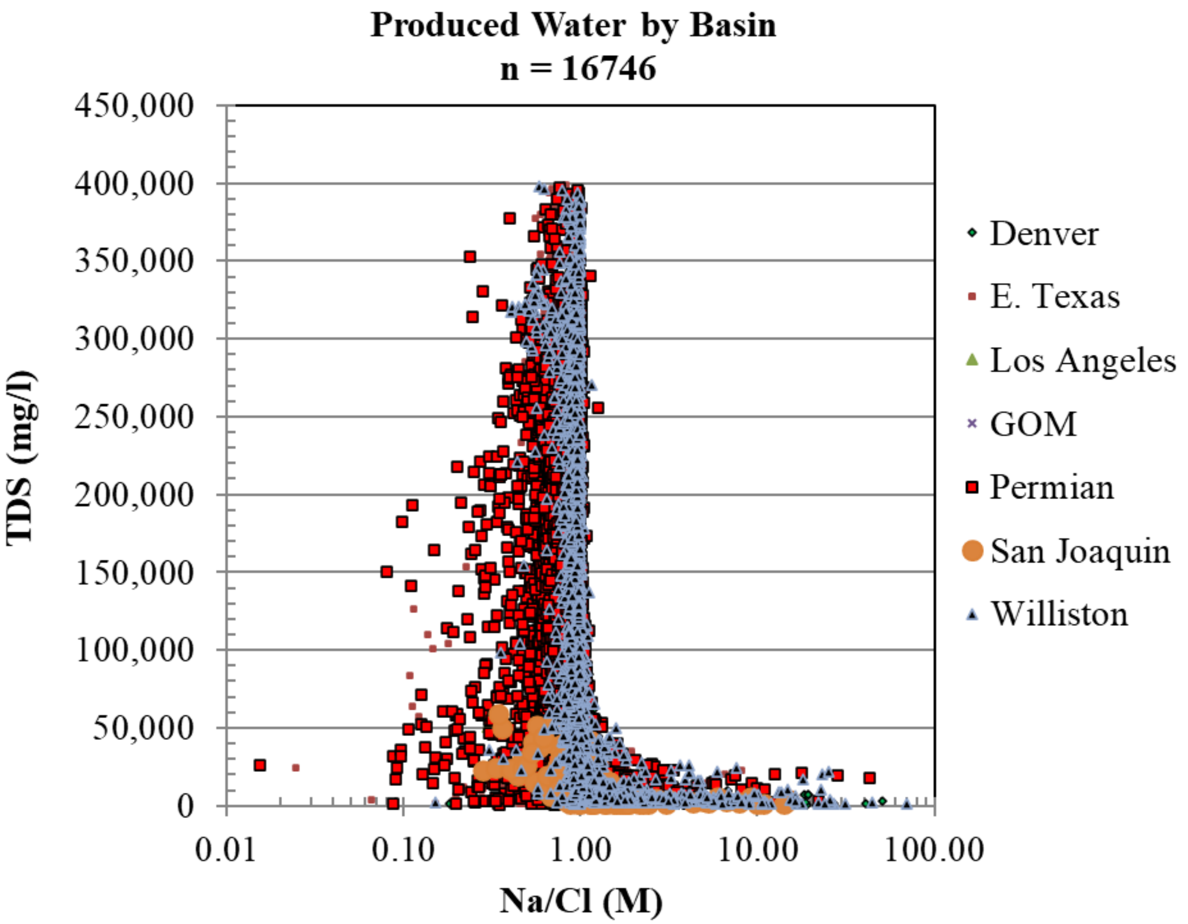


- Initial water is fresh or marine
- Pore water water can increase initial Na and Cl by
    1) evaporation in enclosed basins
    2) evaporation in lakes and ponds
    3) contact with salt deposits
    4) mixing with more saline adjacent strata

❖Na can be altered by rock-water interaction

❖Chloride is conservative except during salt formation

Na, K, Ca, Mg, HCO_3, Cl, SO_4



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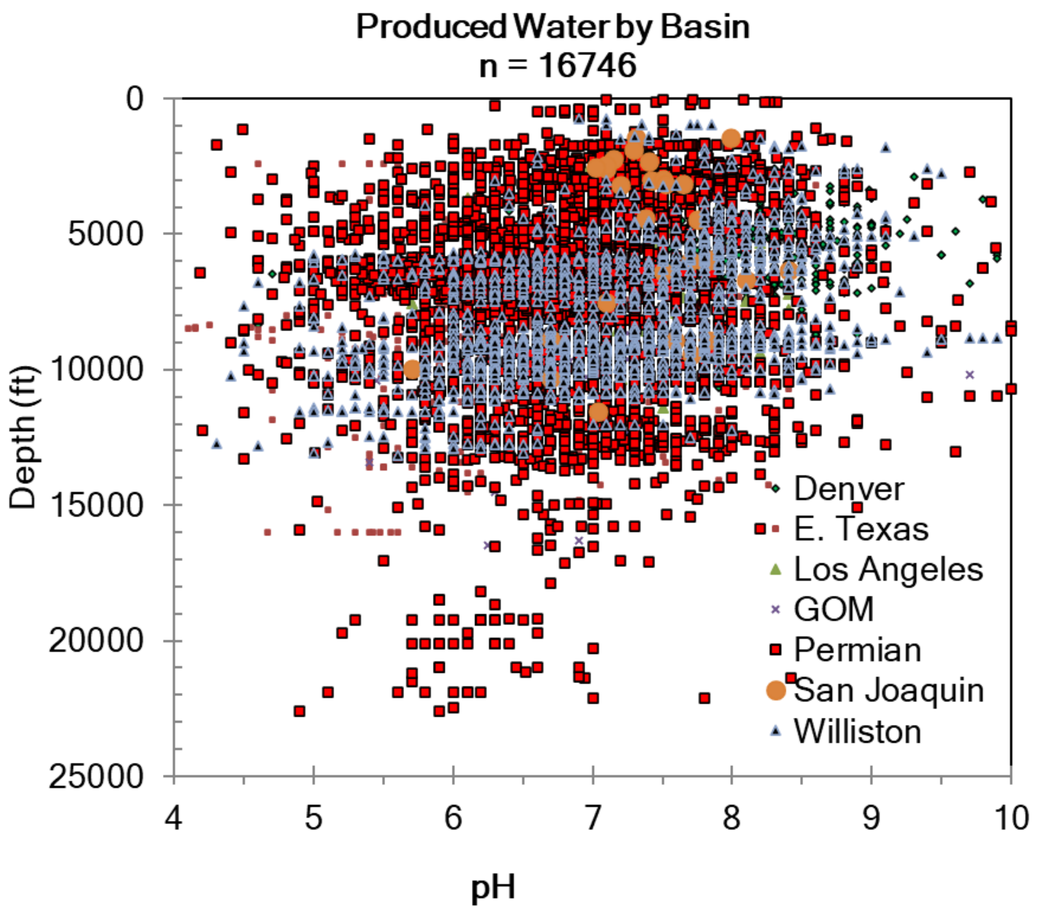
mg/L

Produced Water pH

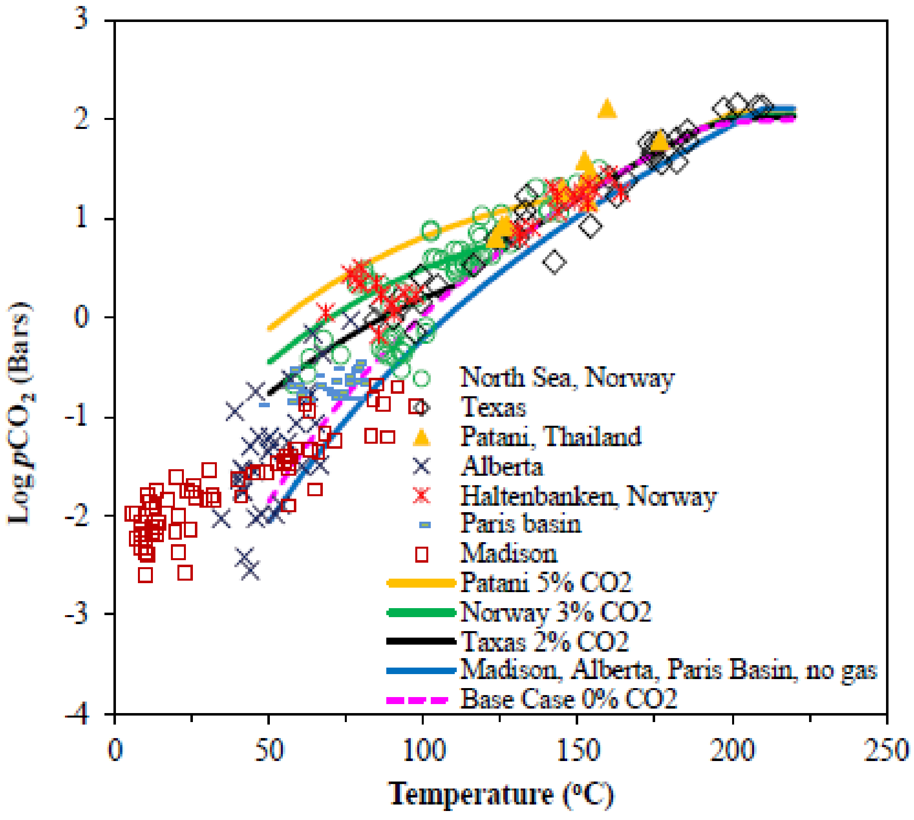
pH changes during production

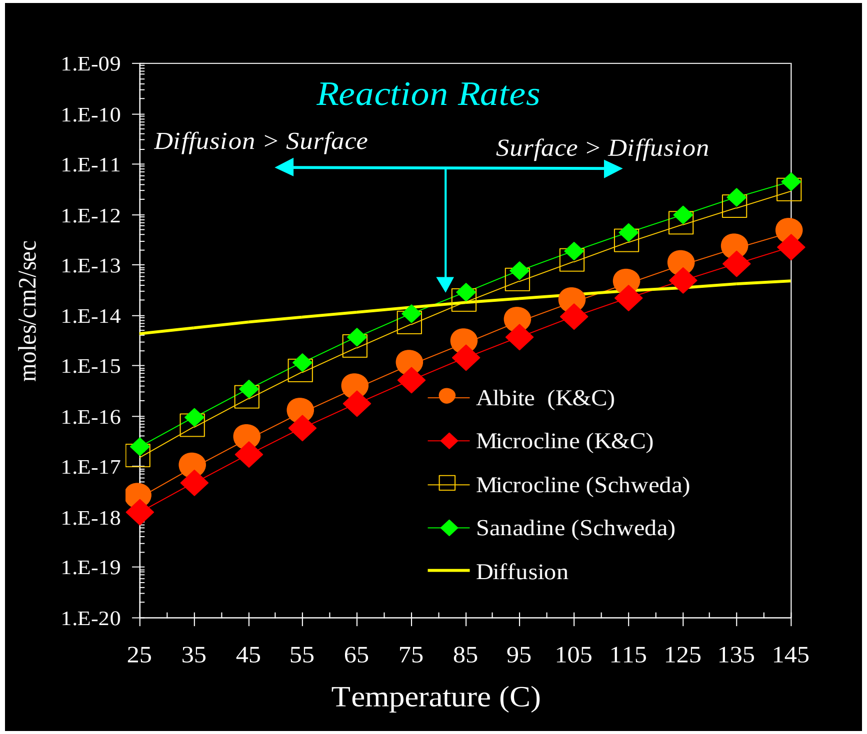
- Result of pressure change and exsolution of CO_2
- pH and pCO_2 is controlled by mineral equilibrium with feldspars, clays and carbonates in reservoir



pH systematically becomes more acidic with higher temperature (depth)

pCO_2 = pH

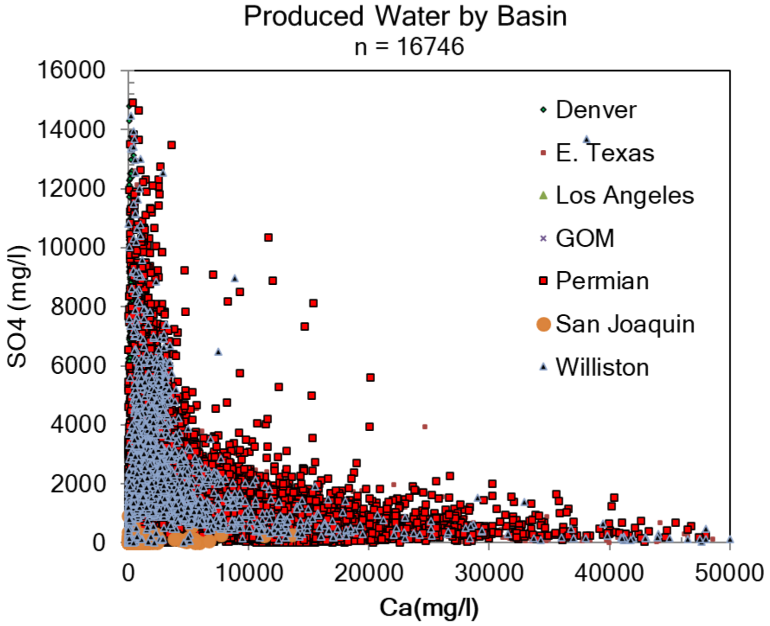


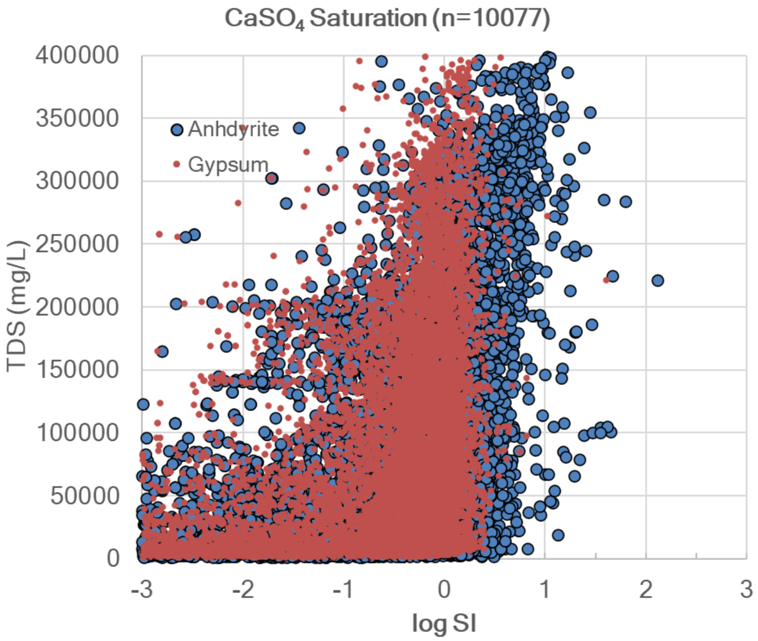


Controlled by mineral equilibrium with feldspars, clays and carbonates

Na, K, Ca, Mg, HCO_3, Cl, SO_4

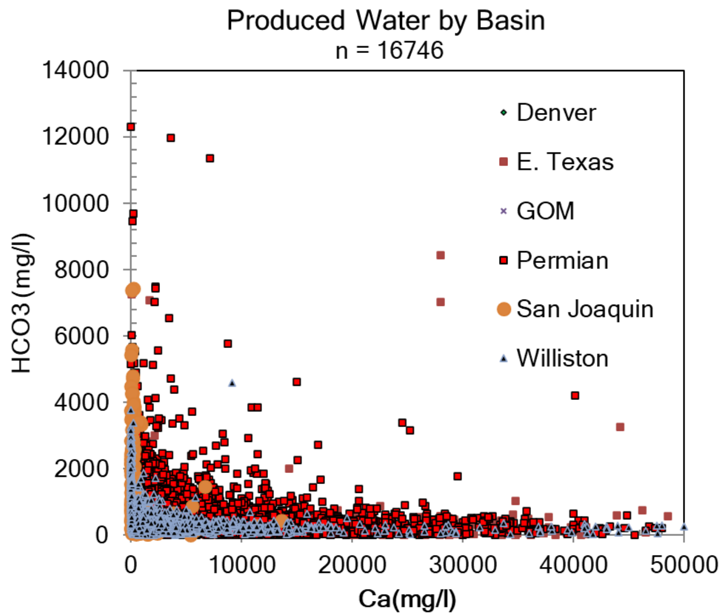
- Ca and SO_4 relationship?
- Ca-sulfate is relatively insoluble
- Check $CaSO_4$ solubility
- Gypsum and Anhydrite
- $Ca^{++} + SO_4^{2-} = CaSO_4$





Na, K, Ca, Mg, HCO_3, Cl, SO_4

- Measured pH is likely too alkaline – shifted during production
- Ca, Mg carbonates are relatively insoluble
- Calcite and Dolomite
- Retrograde Solubility
- $Ca^{++} + CO_3^{2-} = CaCO_3$ (forms scale during production)
- $Ca^{++} + Mg^{++} = CaMg(CO_3)_2$



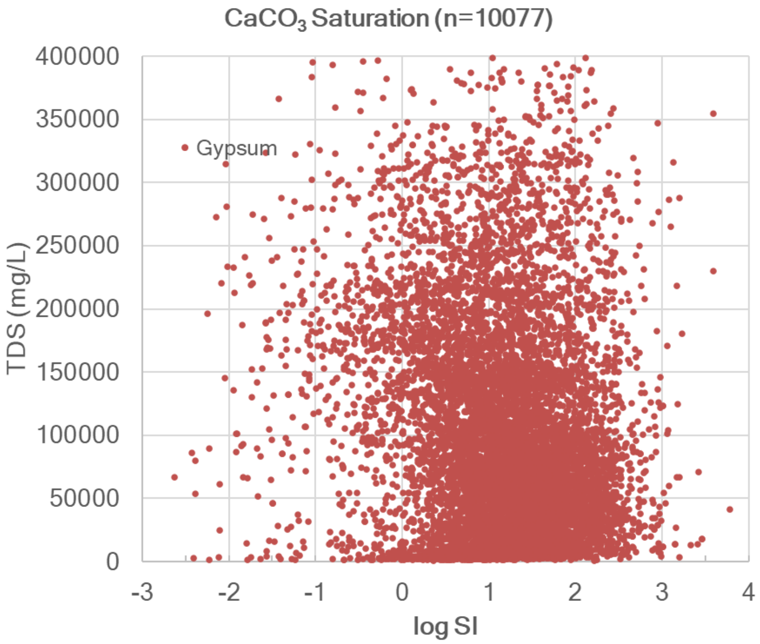
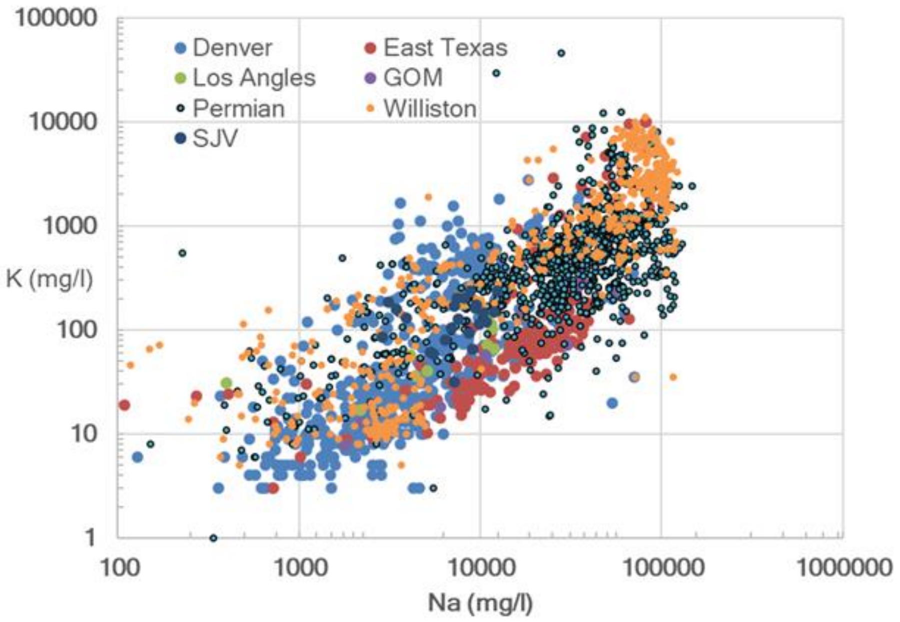


Figure 1-5 Blocking of a pipeline due to the growth of r

Controls on produced water major solutes

- Na and Cl are mostly controlled by initial composition, depositional environment and exposure to salt
- pH, Ca, Mg, HCO_3 and SO_4 are controlled by equilibrium with minerals (Calcite, Dolomite, Gypsum and Anhydrite) and changes during production.
- K is somewhat related to Na but is a minor solute.




Questions?
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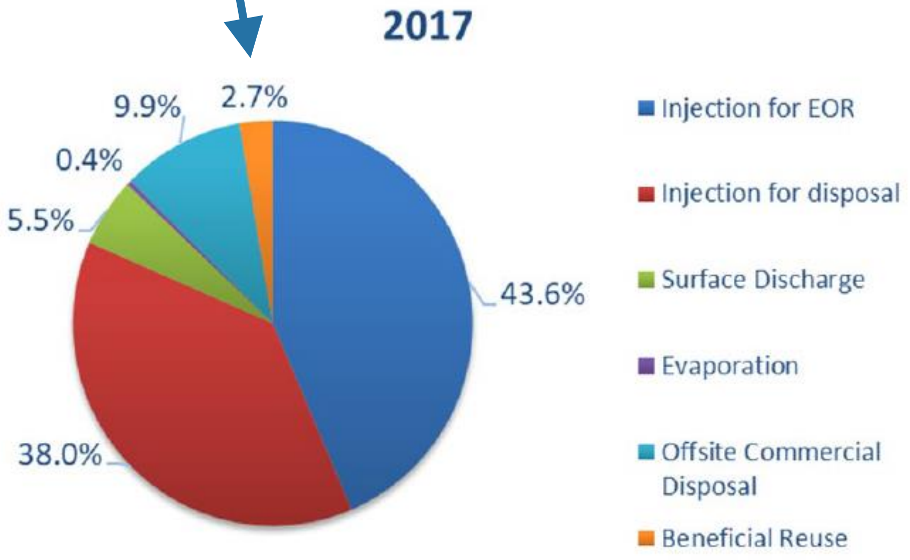
Legal Issue - groundwater is owned by the State

Produced Water Chemistry
New Beneficial Uses

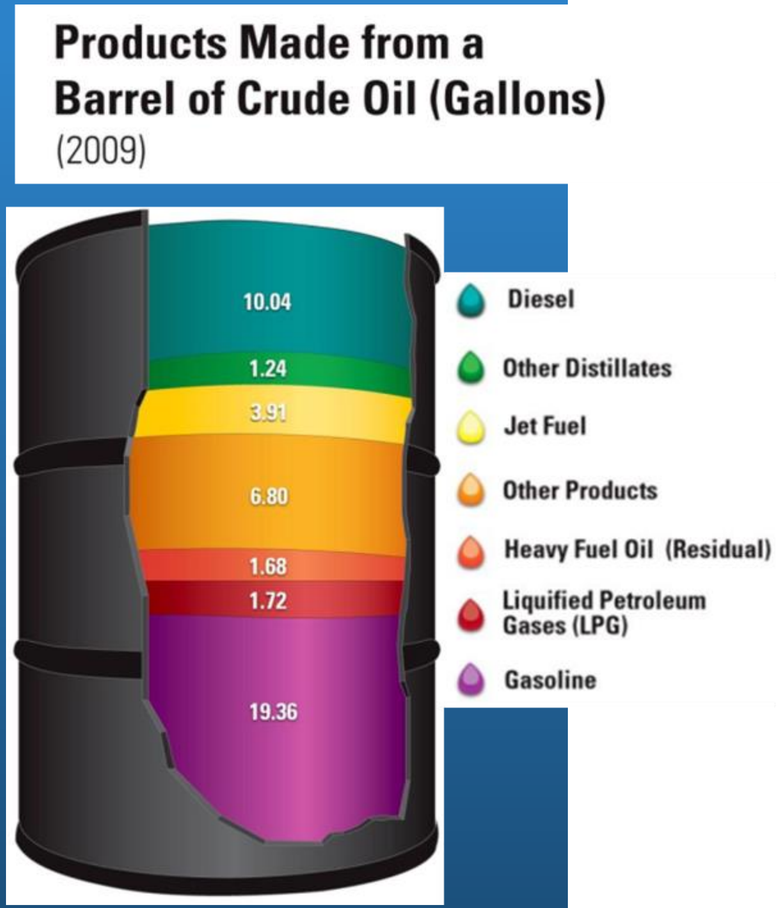
Agriculture
Aquaculture
Stream flow augmentation
Industrial use
Municipal use
NG production (CBM)



<u>Improved Oil Recovery</u>

CO_2 sequestration

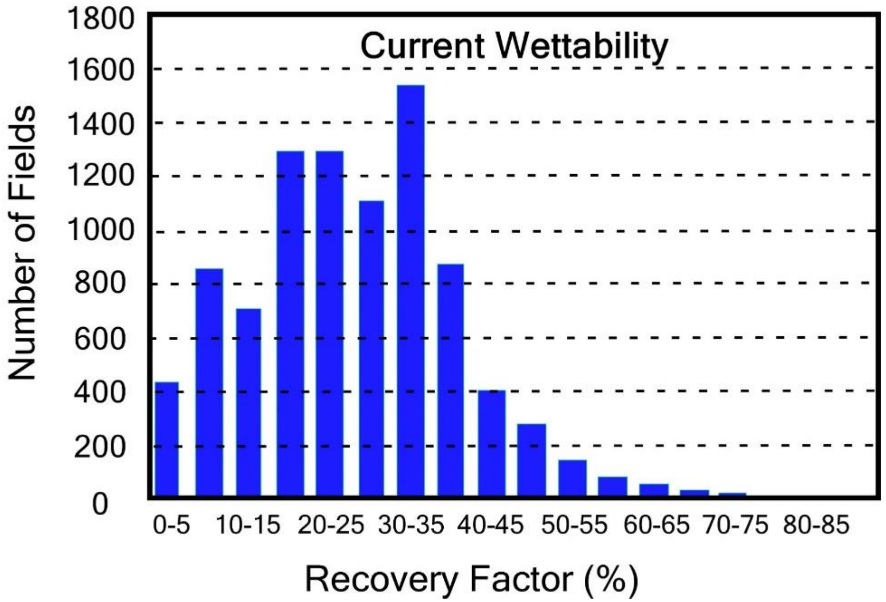
One man’s garbage is another man’s gold



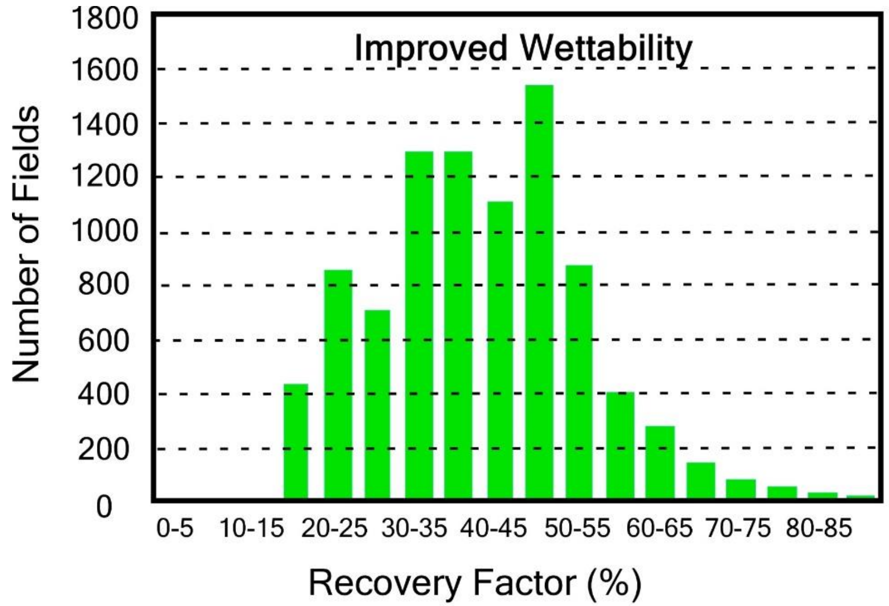
What if the produced water you pay to dispose could increase recovery in another field?

What if the produced water you pay to dispose could be reused in the next well?

The Goal



800 Billion More Barrels from existing resources



- Current world average recovery is 32% of OOIP.
- Wettability is major control on oil mobility during waterflood.
- Reservoir wettability is the chemical equilibrium between rock, water and oil.
- <u>Changing water chemistry can improve wettability in many reservoirs</u>.
- Lab and field experience show 5-15% increase in recovery is reasonable.

Challenge

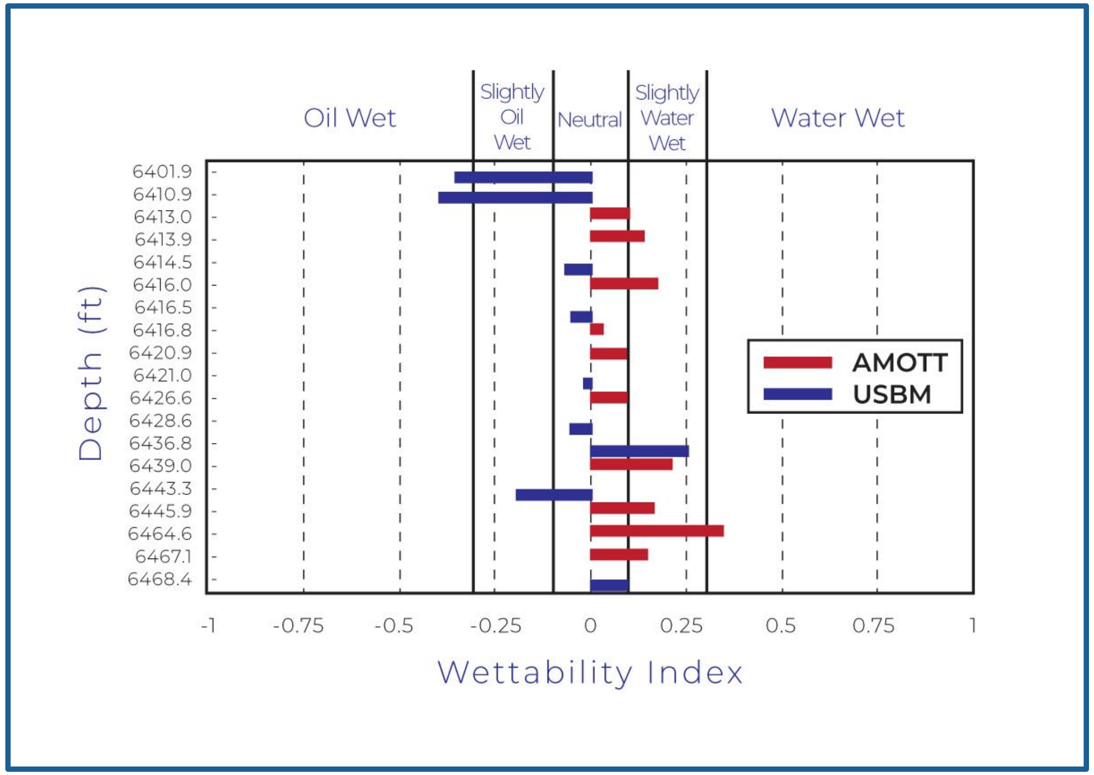
Global average recovery is 35%, much less in shale

What do fields with greater recovery have in common?

Examples
Ghawar - Carbonate - 50%
Ekofisk - Chalk - 50%
Prudhoe - Sadlerochit SS - 55%
East Texas Oil Field - SS - 80%

All have neutral wettability

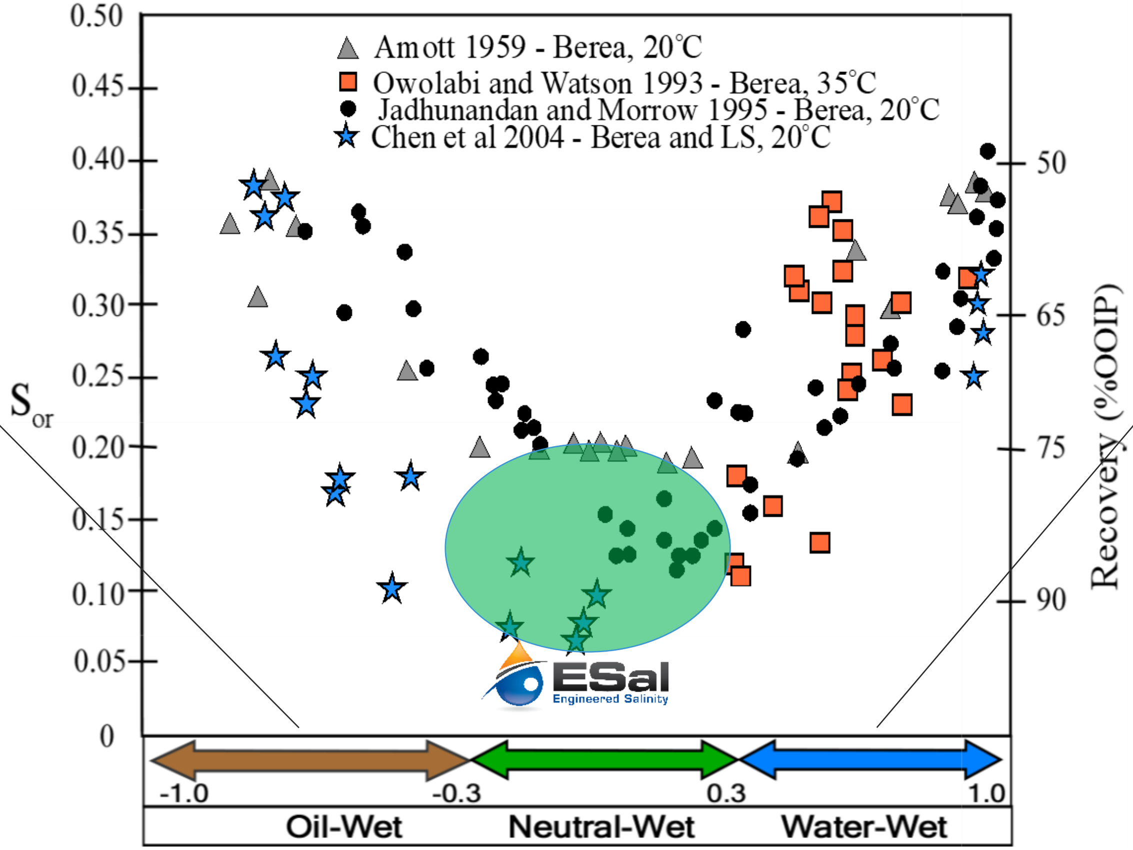
Ghawar Field



Wettability and Recovery

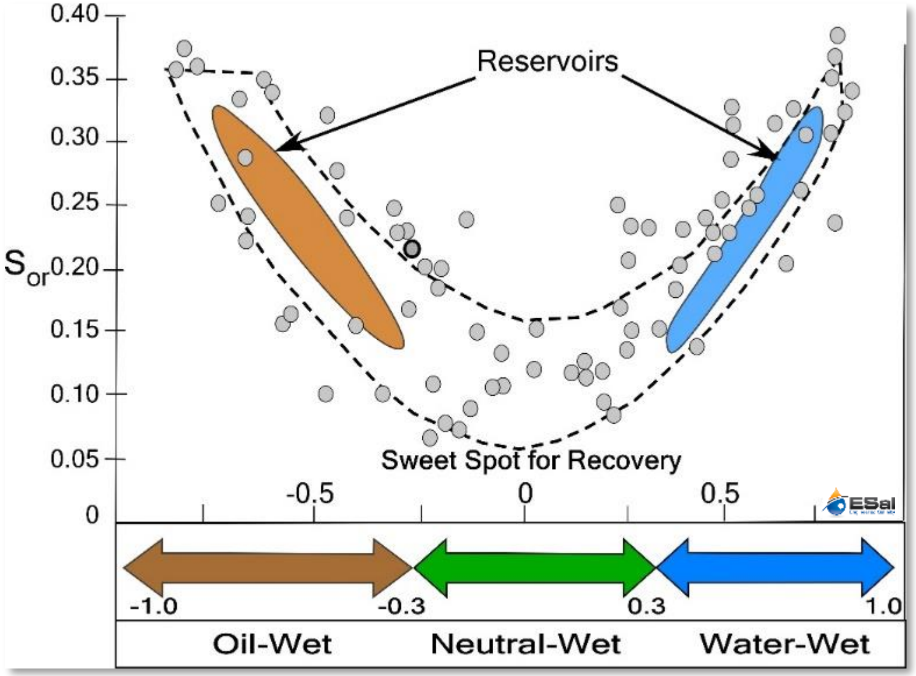
Oil adheres to the rock

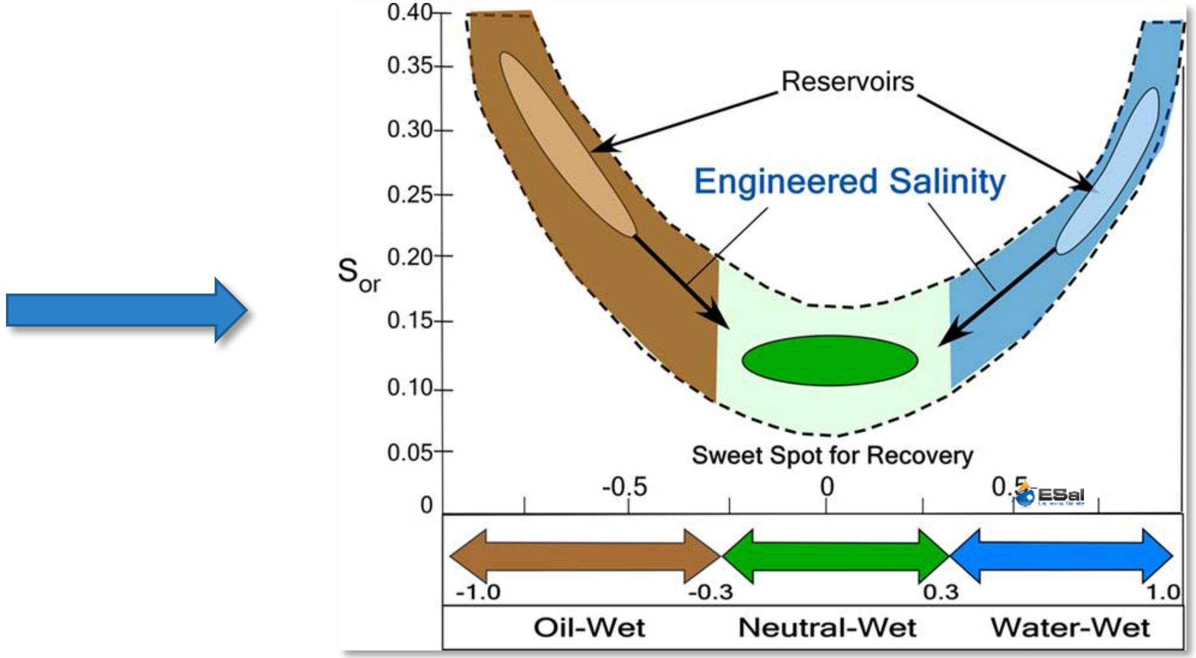
Oil can't move through water-wet pore throats



Oil and water move equally at neutral-wet conditions
Equal number of water-wet and oil-wet pore throats

Wettability Control by Salinity





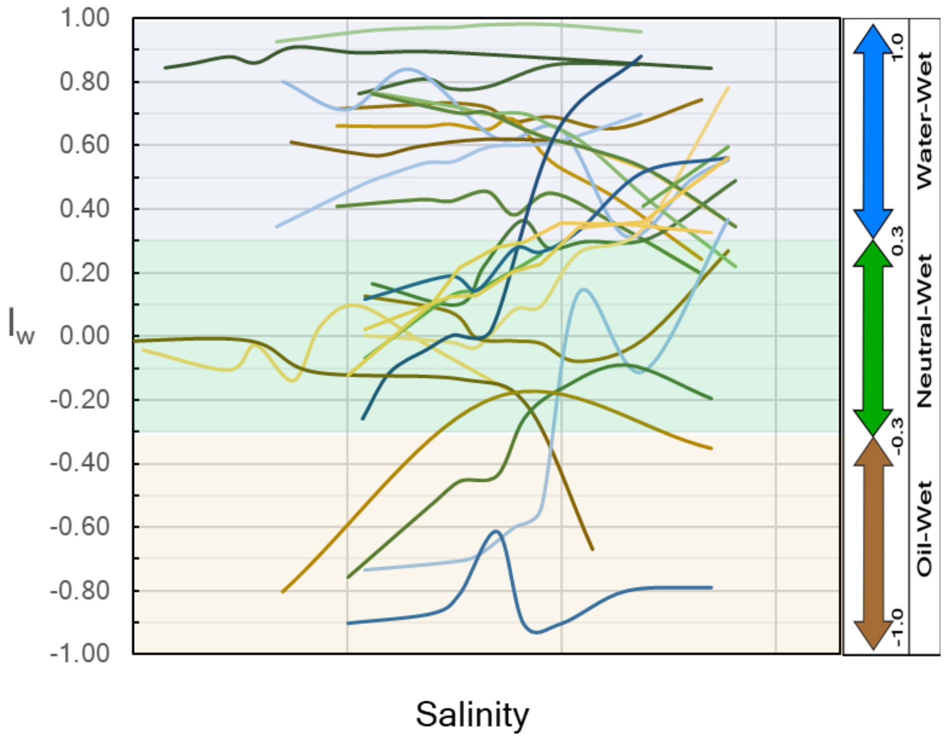
Oil recovery is the best at neutral wettability - equal numbers of oil and water-wet pore throats

Changing salinity alters wettability in many reservoirs to increase oil production

Proven Science

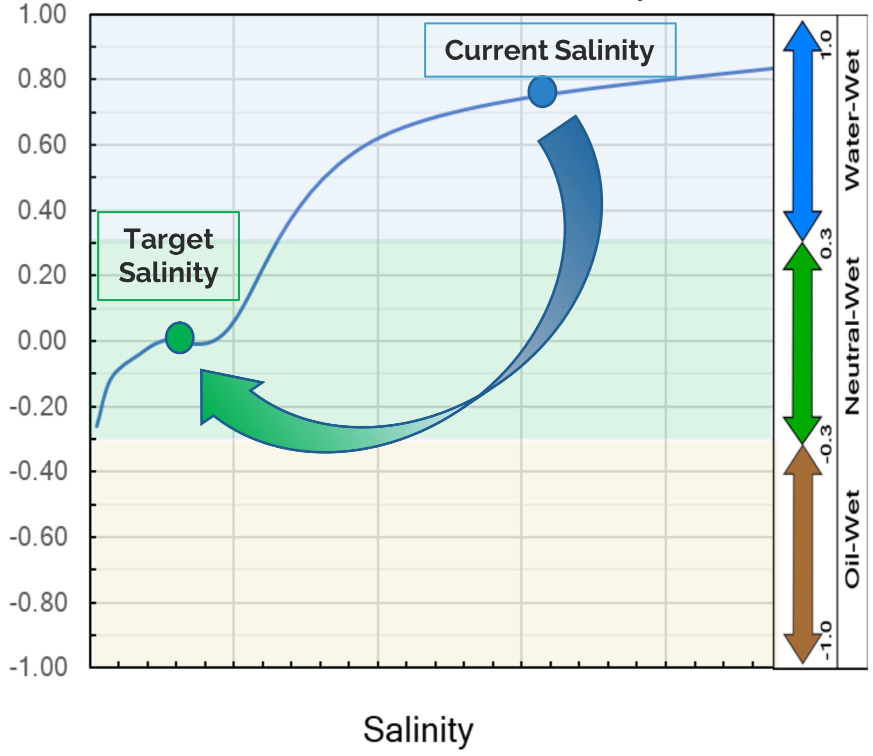
Every field is unique and requires a tailored solution

These lines show how wettability changes as salinity is altered for a variety of fields



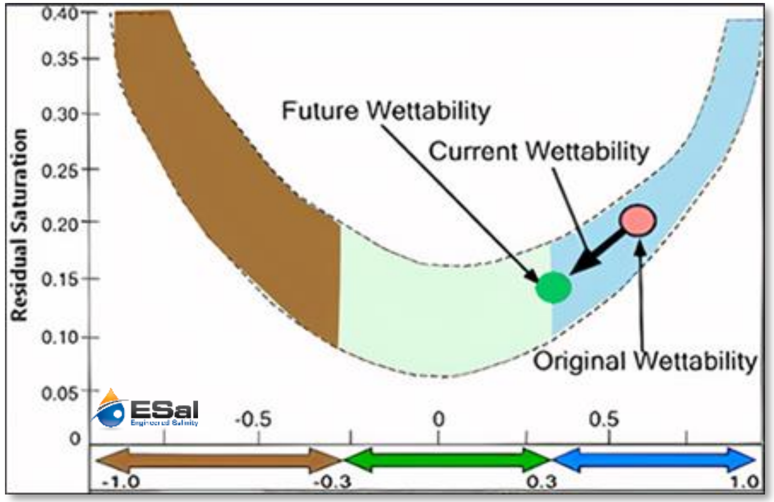
Best Zone for Production

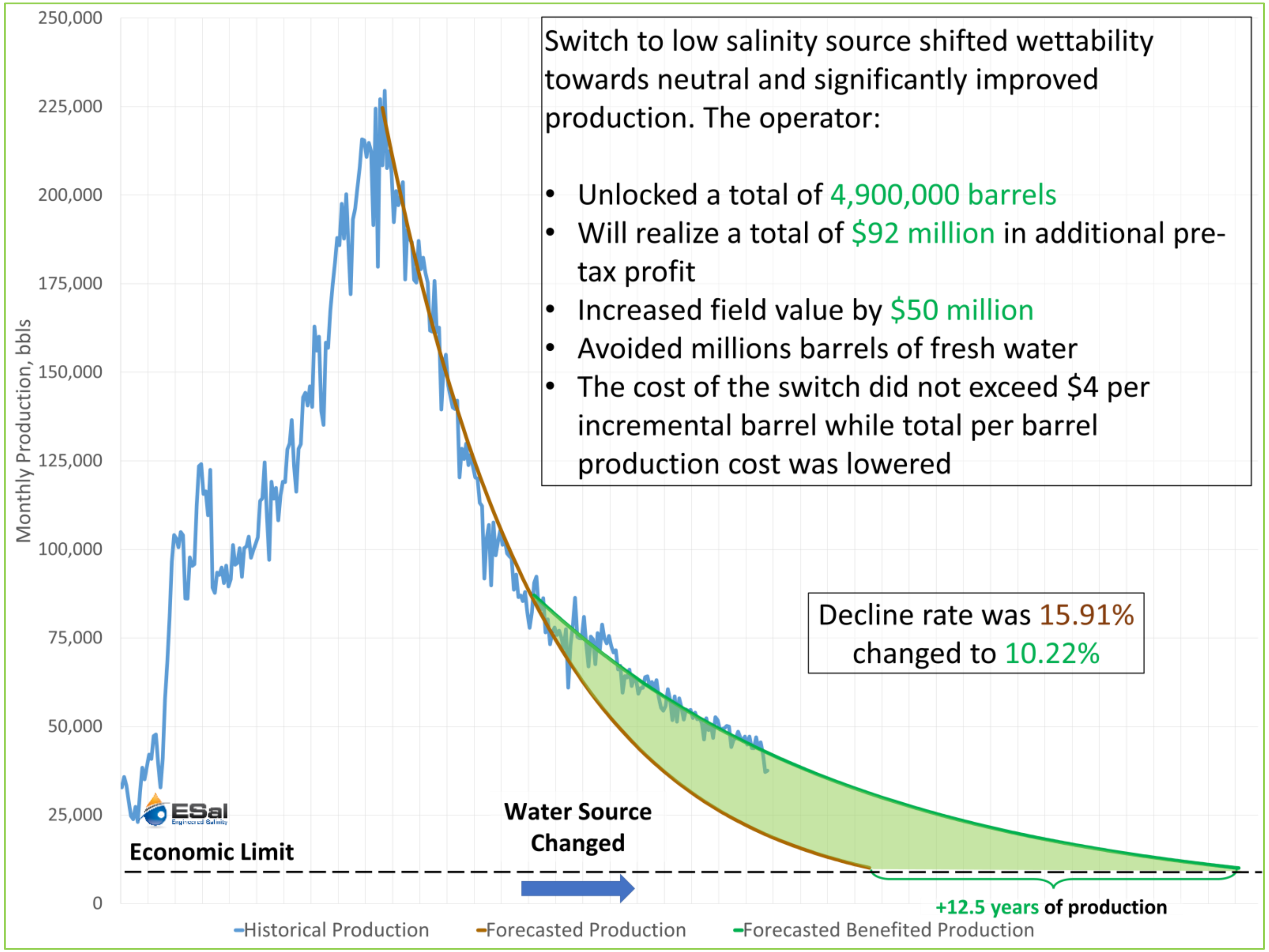
ESal tells you where you are today and where to go to maximize recovery



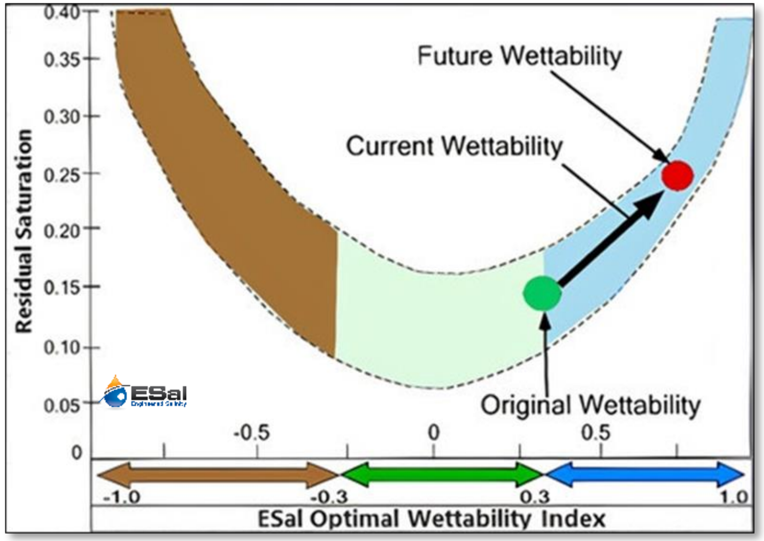
Just as each lock needs the right key, each field needs the right water
ESal matches each field with its RightWater™ solution

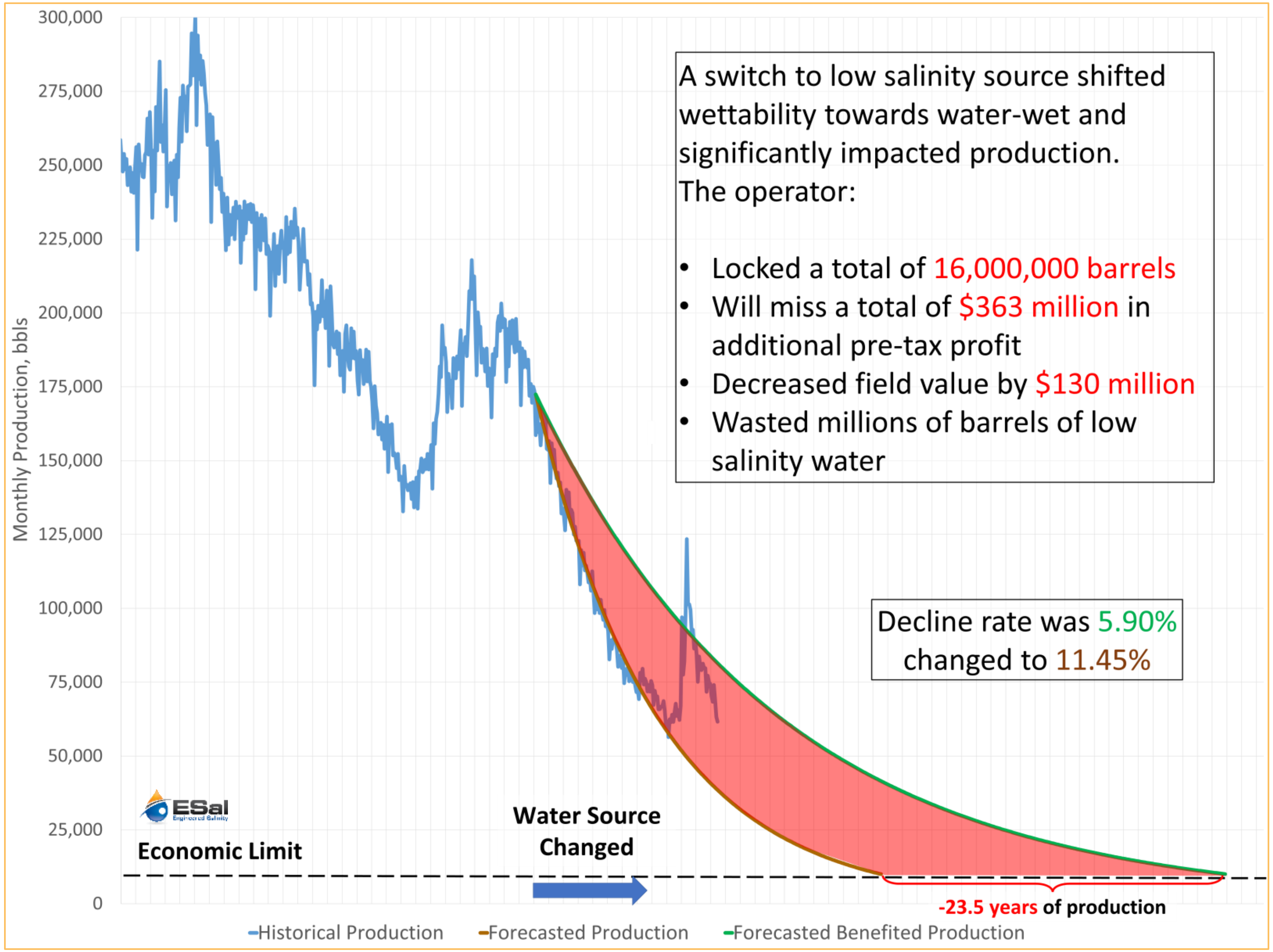
Economic Case History: Example of Positive Result





Economic Case History: Example of Wettability Damage





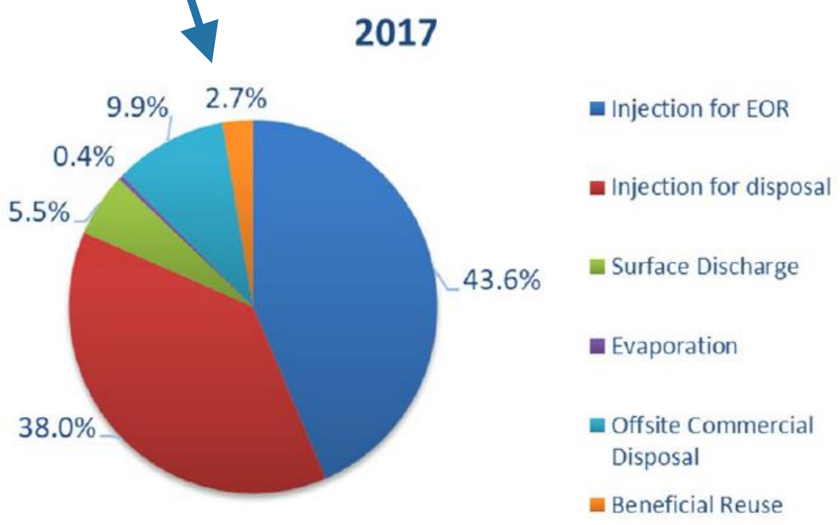
Legal Issue - groundwater is owned by the State

Produced Water Chemistry Beneficial Uses

Agriculture
Aquaculture
Stream flow augmentation
Industrial use
Municipal use
NG production (CBM)

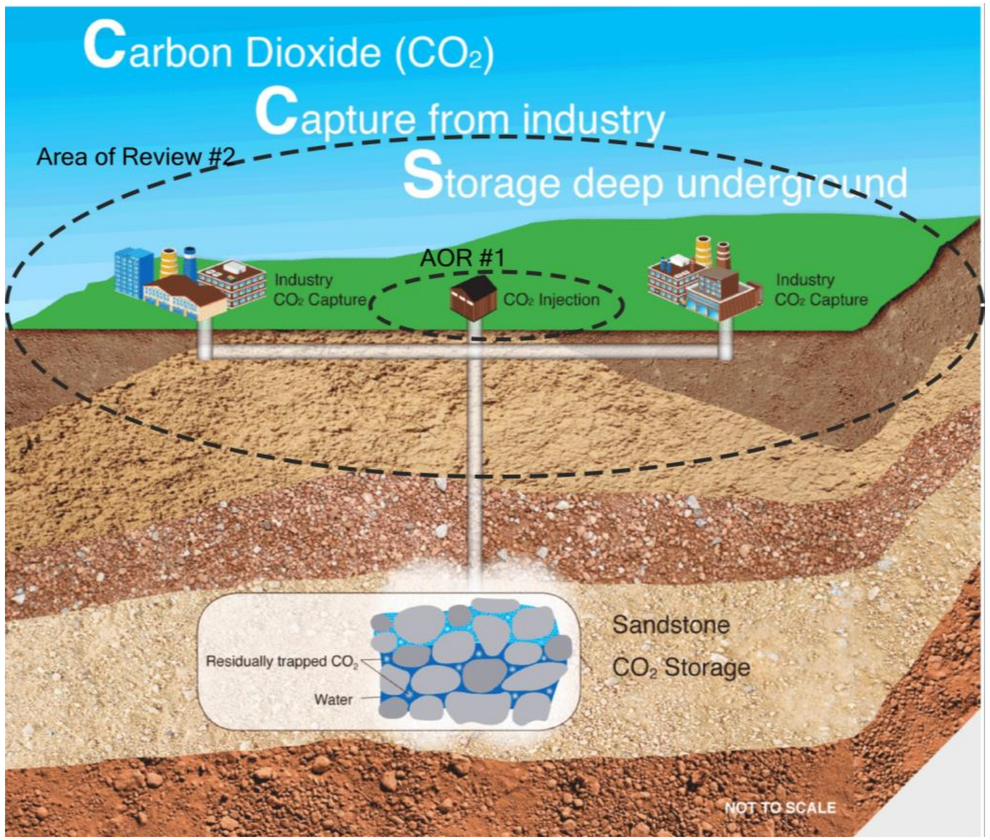
Improved Oil Recovery

<u>**CO_2 sequestration**</u>



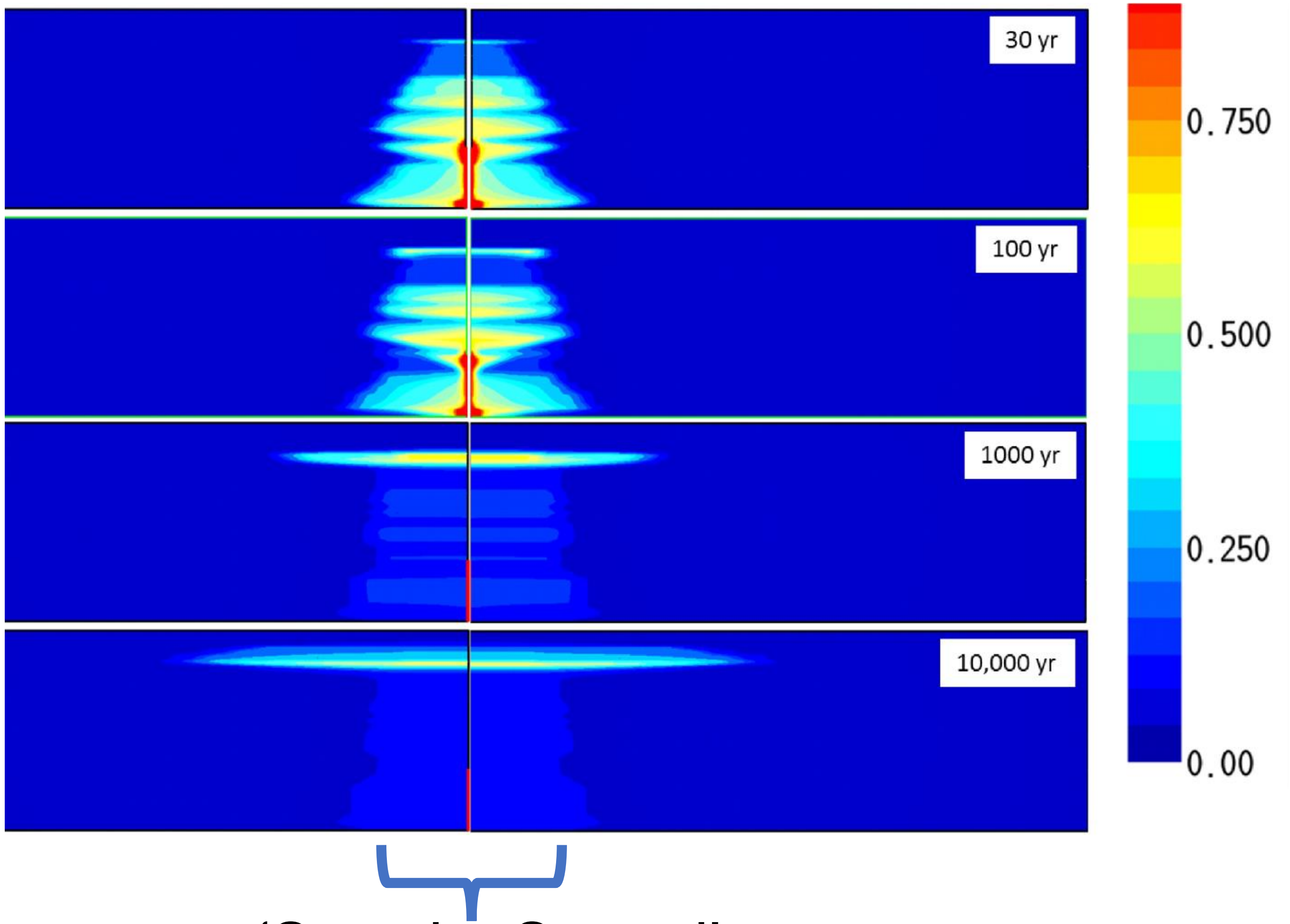
Carbon Sequestration

- Trapping Mechanisms
  - Stratigraphic
  - Capillary Trapping
  - Solubility
  - Mineralization
- One ton of CO_2 = 17.4 barrels of water
  - Average Coal-fired Power Plant emits 3MM tons/year
  - 52MM barrels of space needed to sequester the CO_2
- Injection of Management of Produced Water
  - Pressure Management (AOR)
  - Fluid Volume Management
  - Prediction of Salinity



Carbon Sequestration (Wettability Control)

- Trapping Mechanisms
  - Stratigraphic
  - Capillary Trapping
  - Solubility
  - Mineralization
- Capillary Trapping is controlled by Wettability
- Enhance Storage Capacity
  - Manipulate water chemistry to maximize storage capacity
- Enhance Residual Trapping
  - Manipulate water chemistry to counter CO_2 buoyancy and increase trapping



'Stop the Spread'

Conclusions

- The oil business is the water business
- Beneficial uses of produced water are available but only a small volume of the total is utilized
- Produced water handling and treatment can be expensive especially for produced water from shale plays
- Major solutes in produced water are result of:
  - Initial composition
  - Rock-water equilibrium at higher temperatures (>60C)
- Produced water can be valuable in increasing oil recovery and improving CCS storage capacity and CO_2 trapping

Questions?

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