EOS Remediation

a Redox Tech company

EVO Use in Hard Water aquifers: Implications and Strategies for Successful Substrate Distribution

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Sixth International Symposium on Bioremediation and Sustainable Remediation Technologies

Experience you can Rely on, Products you can Trust™

About Presenter

- Juan Fausto Ortiz Medina, Ph.D.
  - Email: jfortiz@eosremediation.com
  - PhD in Environmental Engineering, North Carolina State University
- Experience
  - Environmental Microbiology
  - Environmental Biotechnology
  - Development of new products for water and soil remediation

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About EOS Remediation

- Founded in 2002 and based in North Carolina, USA.
- Leader of emulsified vegetable oil (EVO) technology.
- Constantly improving our science-based remediation products:
  - Improve transport
  - Provide optimal nutrients
  - Reduce fouling
- Acquired by Redox Tech in 2023 to broaden our remediation expertise and technologies.

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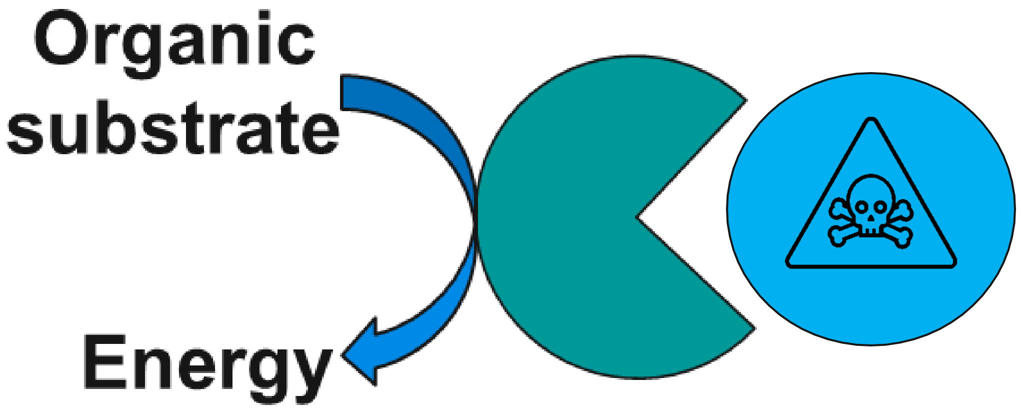
Target Contaminants for Bioremediation using EVO

- Chlorinated Solvents
  - Ethenes (PCE, TCE)
  - Ethanes (TCA)
  - Methanes (CT)
- Explosives (TNT, RDX, HMX)
- Nitrate (NO_3^-)
- Perchlorate (ClO_4^-)
- Hexavalent chromium [Cr(VI)]
- Radionuclides (TcO_4^-, UO_2^{+2})
- Acid Mine Drainage



Presentation objectives

- Challenges of using EVO in hard water
  - Higher oil retention
  - Nutrient sequestration
  - Potential fouling

- Solutions to overcome effects of hard water and optimize EVO injection

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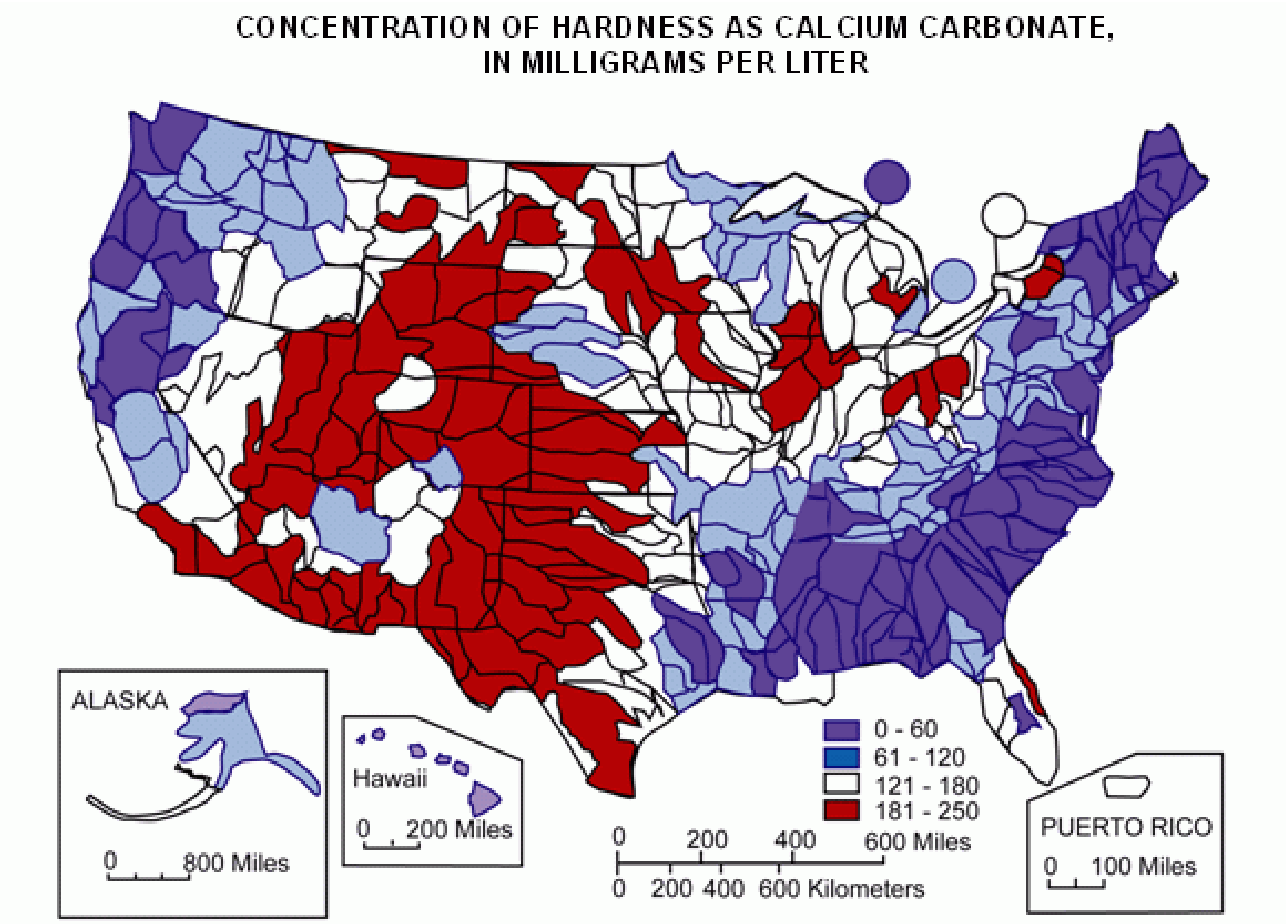
Water Hardness

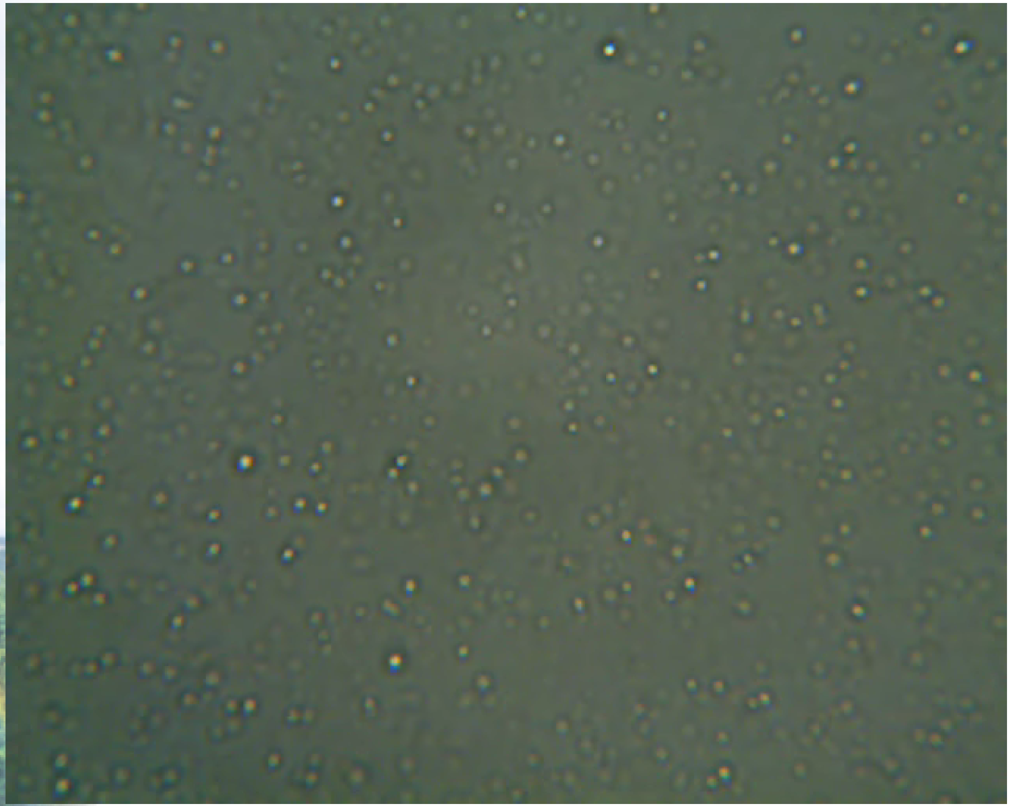
- High concentrations of divalent ions (mainly Ca^{2+} and Mg^{2+})
- Typical definitions:
  - Soft: 0-60 mg/L as $CaCO_3$
  - Moderately hard: 61-120 mg/L as $CaCO_3$
  - Hard: 121-180 mg/L as $CaCO_3$
  - Very hard: >180 mg/L as $CaCO_3$



Source: U.S. Geological Survey

Long-lasting substrate: Emulsified vegetable oil (EVO)

- Soybean oil emulsion, homogenized to form microscopic oil droplets.



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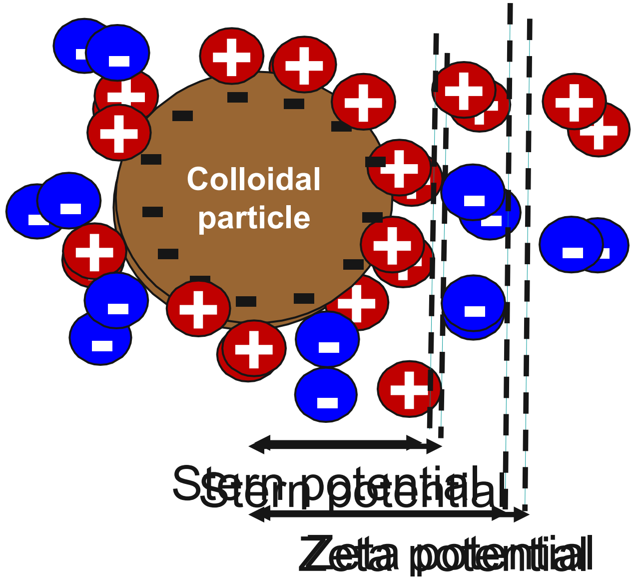
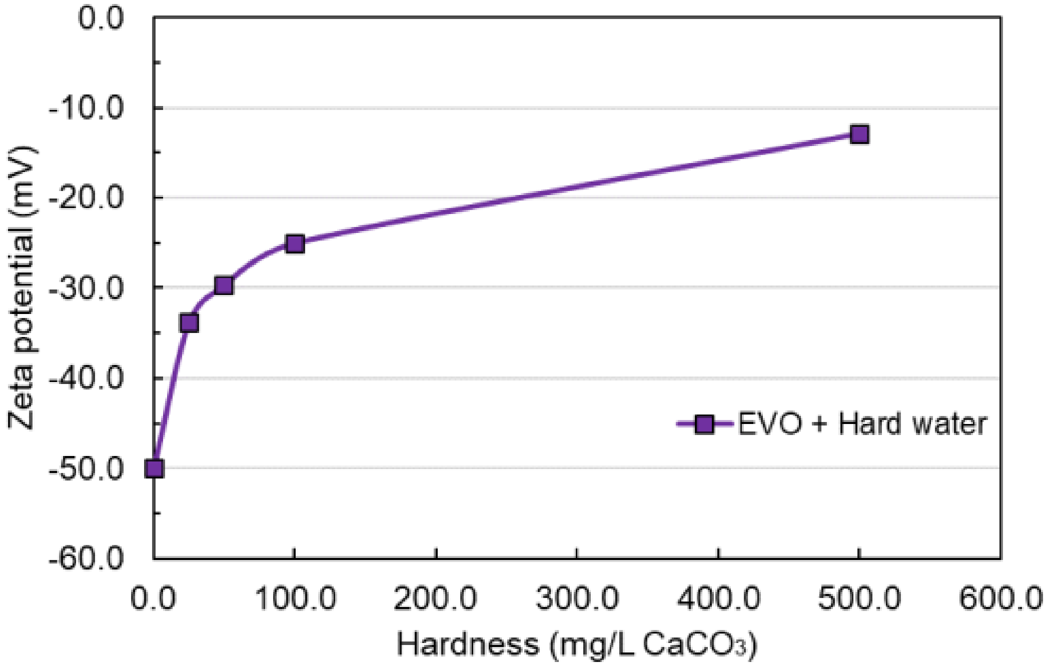
Zeta potential changes due to hard water

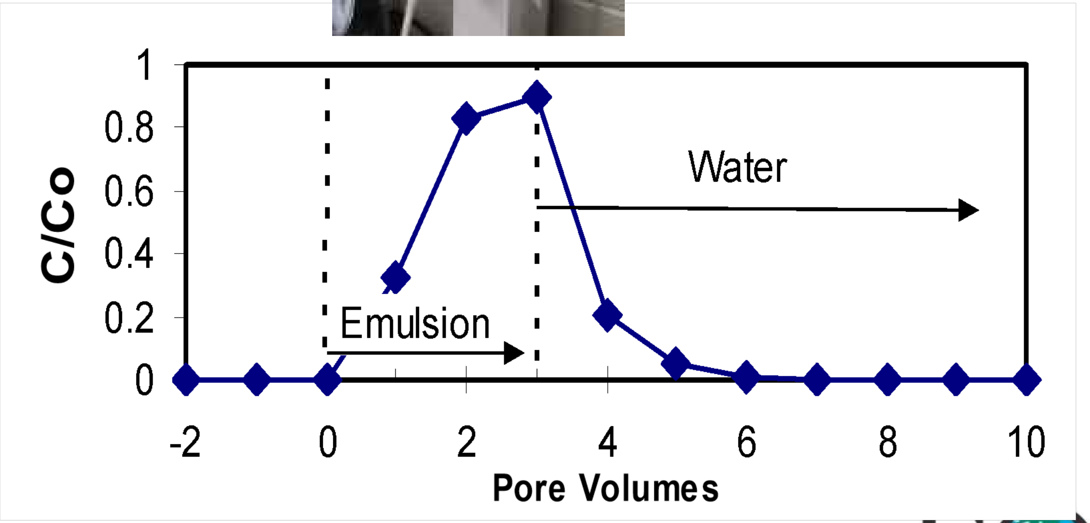
- Zeta potential (ζ) estimates charges that move along with each suspended particle (oil)
- Higher | ζ | ⟶ more likely to repel each other
- Higher concentration of divalent ions result in double layer compression which decreases | ζ |





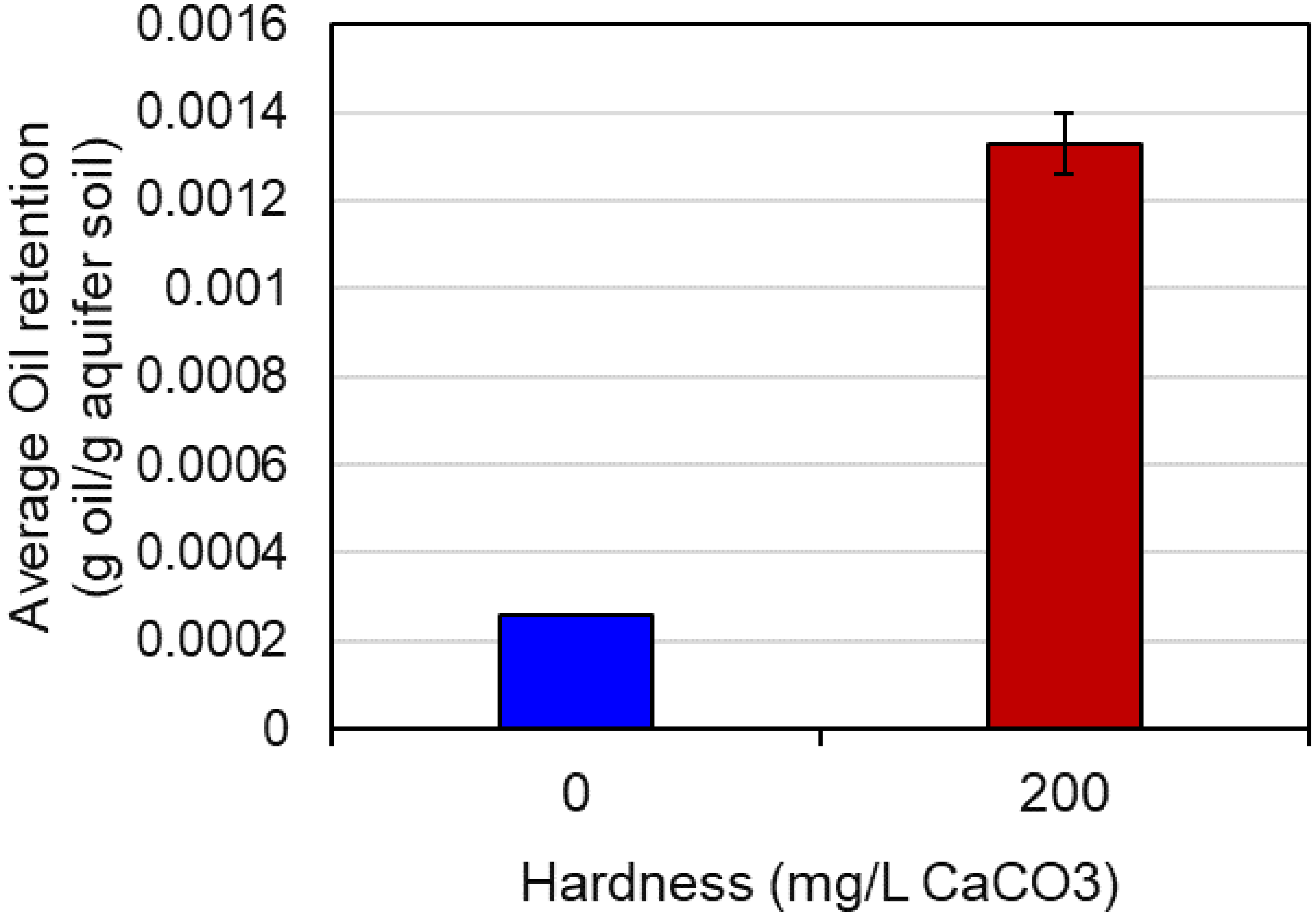
Oil retention to estimate distribution effectiveness

- Column tests are used to estimate maximum oil retention (OR_M) in aquifer.
- 3 PV of diluted EVO + 3 PV chase water.
- Typical values range from 0.0004 (coarse grained sand) – 0.01 (clayey sand) g soil/ g aquifer material



Coulibaly and Borden (2004)

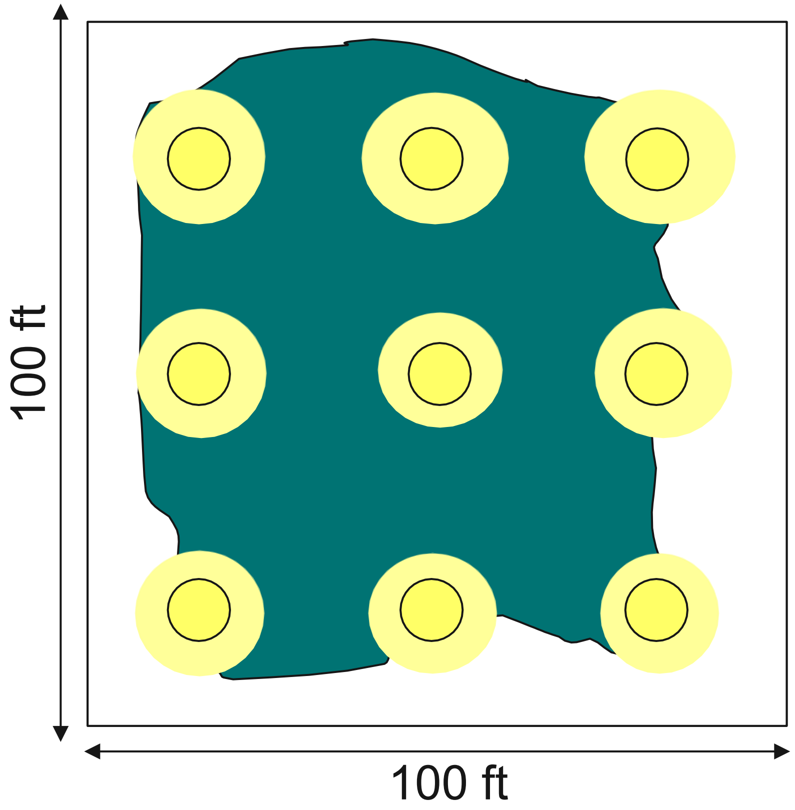
Higher $CaCl_2$ = Higher oil retention



Very hard water increases oil retention by at least 4 times

Why is Good Oil Distribution Critical?

- Higher retention demands more oil (or more chase water) to achieve proper distribution and an acceptable influence radius.
- Soybean oil hydrolysis
    - 1 glycerol ($C_3H_8O_3$)
    - 3 long chain fatty acids (LCFA)
    - Fermentation releases both H_2 and acetate
- H_2 is required for reductive dechlorination (DCE and VC conversion to ethene), and it does not travel far from retained oil.



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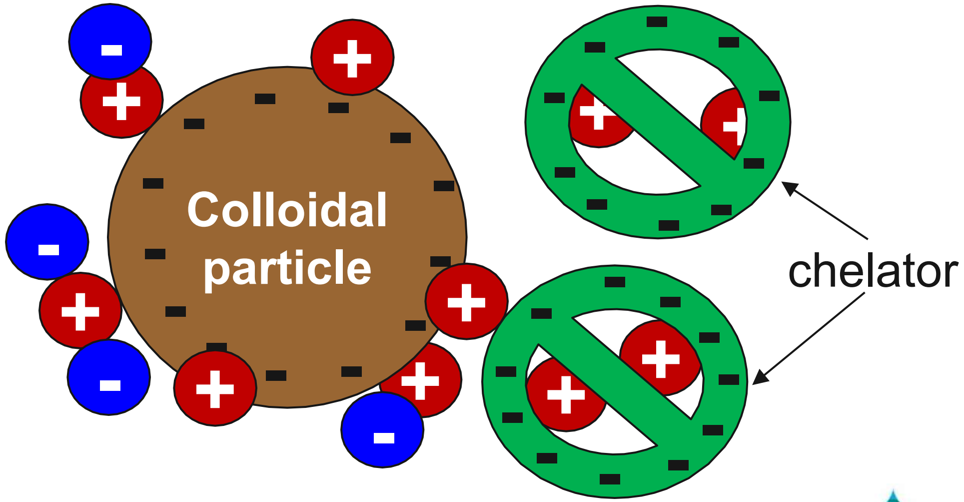
Solutions to decrease oil retention

- If possible, calculate OR_M accurately.
- Dilute substrate injection with additional chase water
  - Typical goal: 2% v/v EVO
- Soft water can be used
  - Simple, divalent cations will be diluted
  - May pose significant additional cost depending on the source of water.
- Use of chelators
  - Small concentration added will capture divalent ions and restore $|\zeta|$



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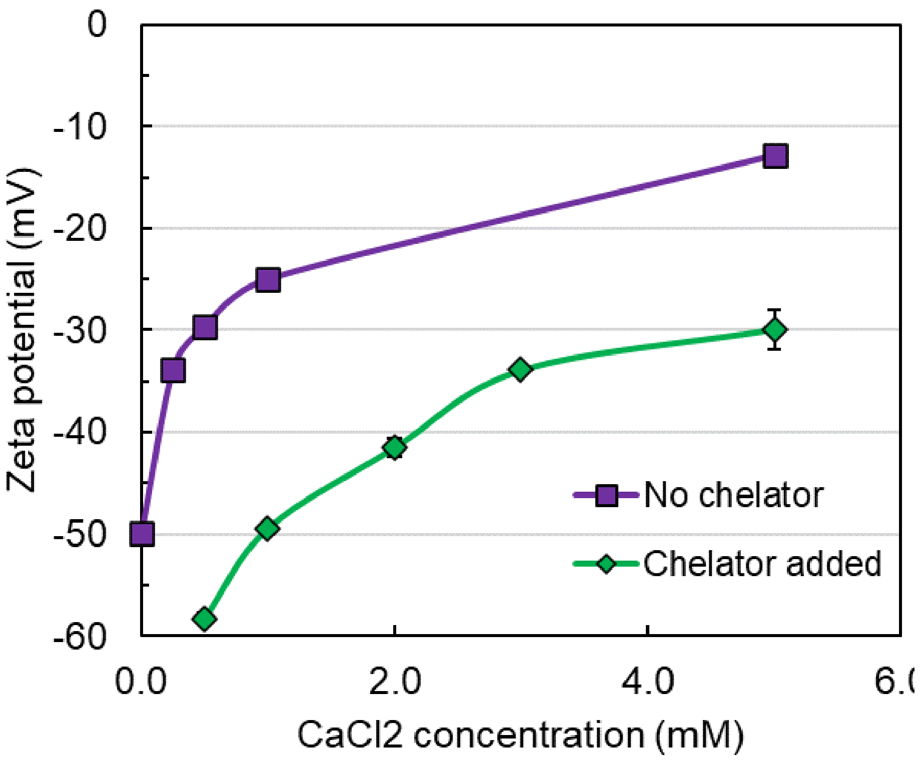
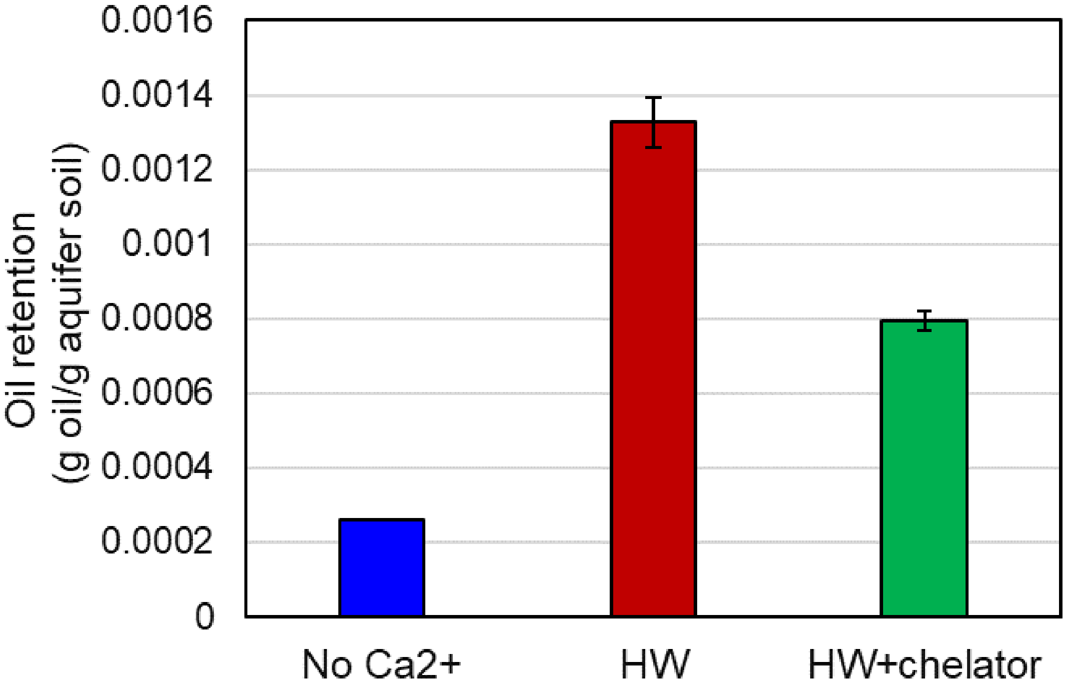
Chelator addition to improve EVO mobility

- Addition of a biodegradable chelator (1:1 molar ratio, chelator:$CaCl_2$) increases | ζ |, reduces oil retention and slightly improves soil permeability





Downside: Chelator may not be cost effective to remove all Ca^{2+}

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Sequestration of nutrients (phosphate) by hard water

- As P is a macronutrient, sufficient concentrations must be present when C substrate is added
- Redfield ratio C:N:P = 106:16:1
- Potential need to add additional nutrient solution (e.g. PLUS) alongside EVO.

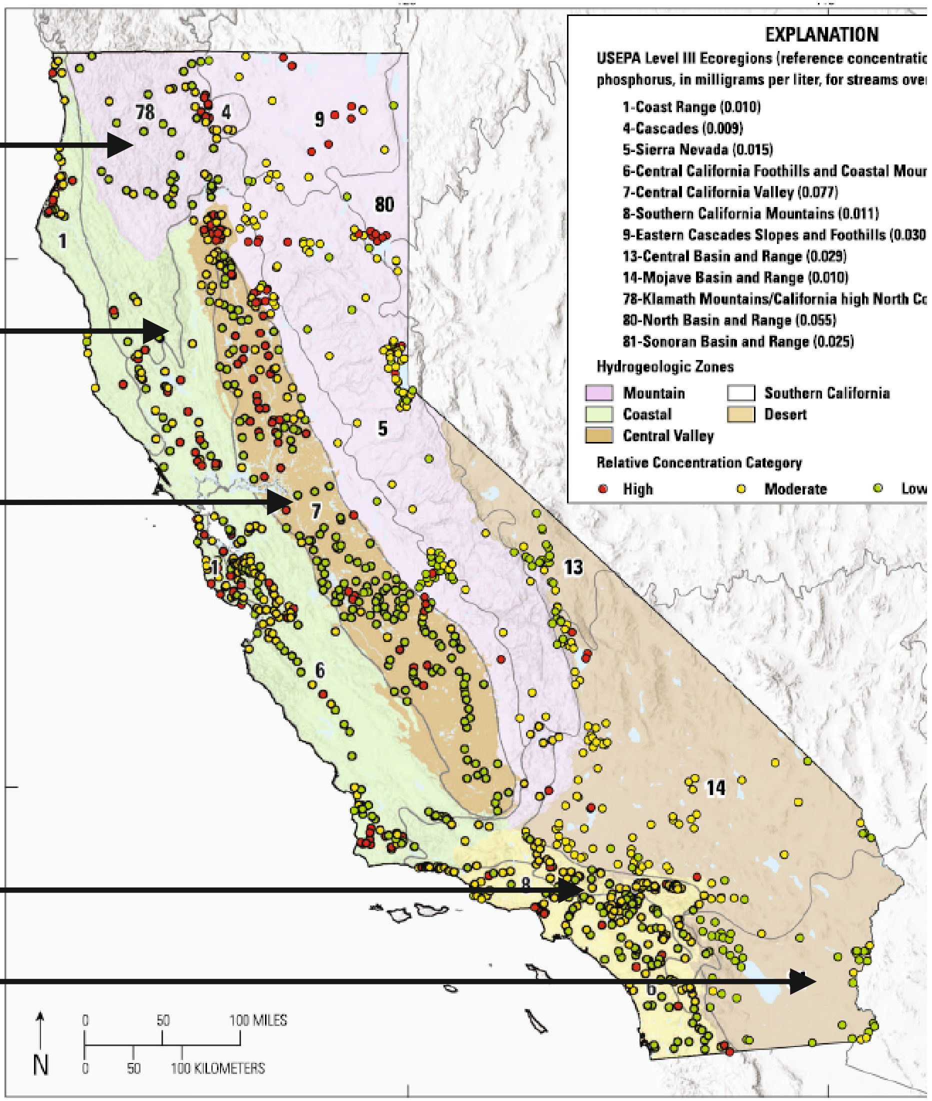
Mountain zone: 0.030 mg/L – P

Coastal zone: 0.052 mg/L – P

Central Valley: 0.055 mg/L – P

SoCal: 0.036 mg/L – P

Desert: 0.016 mg/L – P



Kent et al. (2020)

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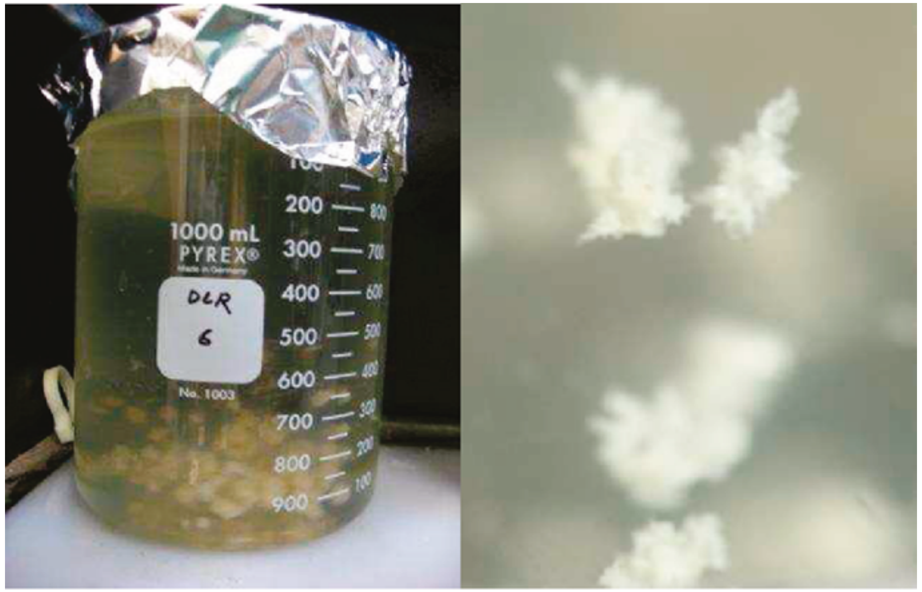
Fouling due to hard water

- Biofouling
  - Growth of undesirable microorganisms
  - More noticeable close to injection wells and zones with electron acceptors such as O_2 and NO_3^-
- Chemical (scaling)
  - LCFA precipitates with Ca^{+2}, Mg^{+2}, Fe^{+2}, Mn^{+2} , forming soap scum.
  - Essentially immobile → low bioavailability

$$2C_{17}H_{35}COO^{-} + Ca^{2+} \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow$$

Solubility: 0.4 g/L

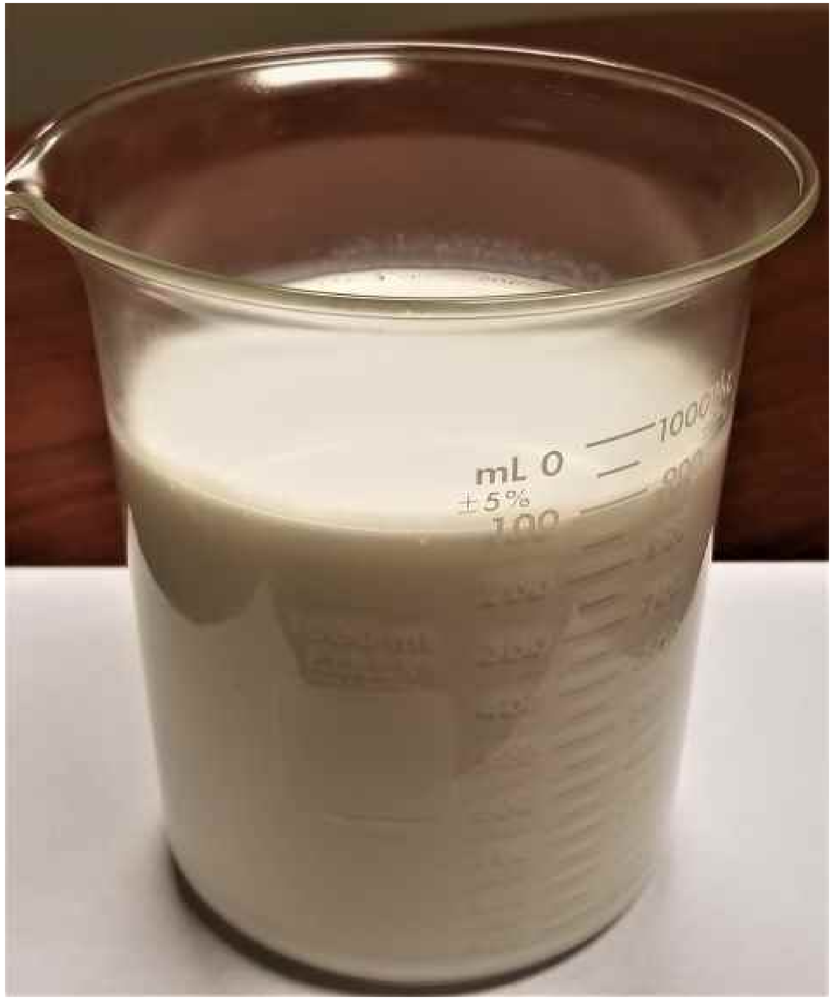
Hardness threshold ~66 mg/L $CaCO_3$



Xe et al. (2011)

Fouling prevention: Use of alternative substrates

- Other substrates may pose a viable alternative to EVO if conditions frequently favor gunk formation.
- ABC – Olé by Redox Tech:
  - Consists of emulsified fatty acid esters: no free fatty acids to interact with Ca^{2+}
  - Lower surface tension and viscosity: no chase water needed
  - Fermentation begins immediately: no need to wait for hydrolysis to occur
- Substrate choice will ultimately depend on needs: long-lasting substrate vs. potential fouling/distribution limitations.



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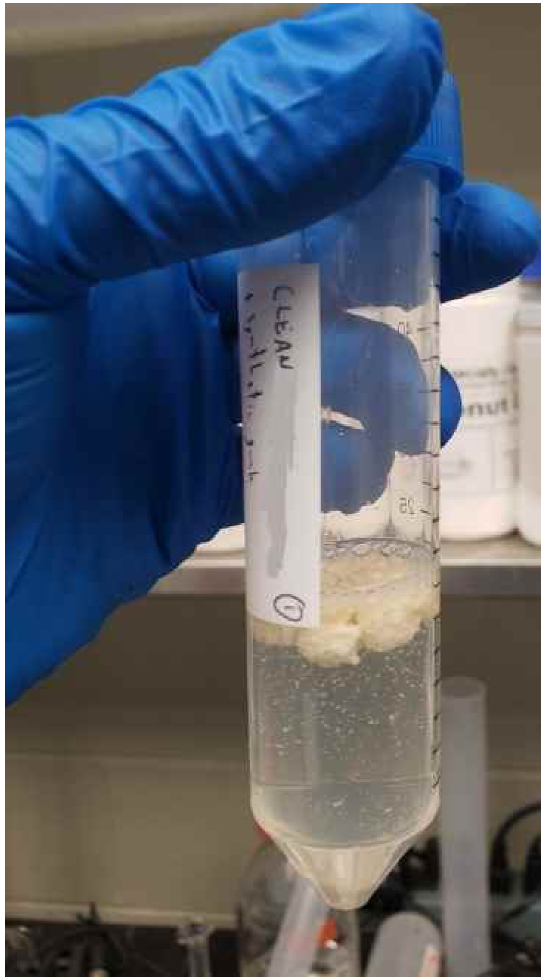
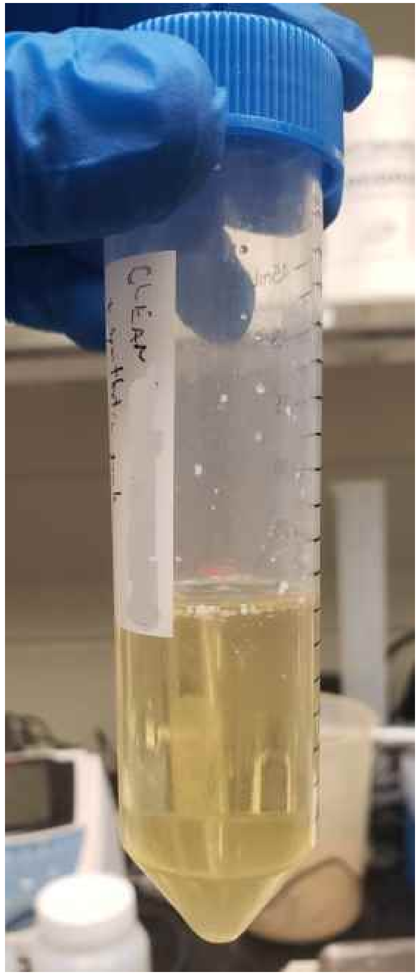
Solutions to remove fouling

- Addition of chemicals to destroy fouling materials
- EOS CLEAN:
  - Chelator:
    Capture divalent ions
  - Organic solvent:
    Solubilize scum/oil-based materials
  - Detergent:
    Emulsify oil particles, break biofilms





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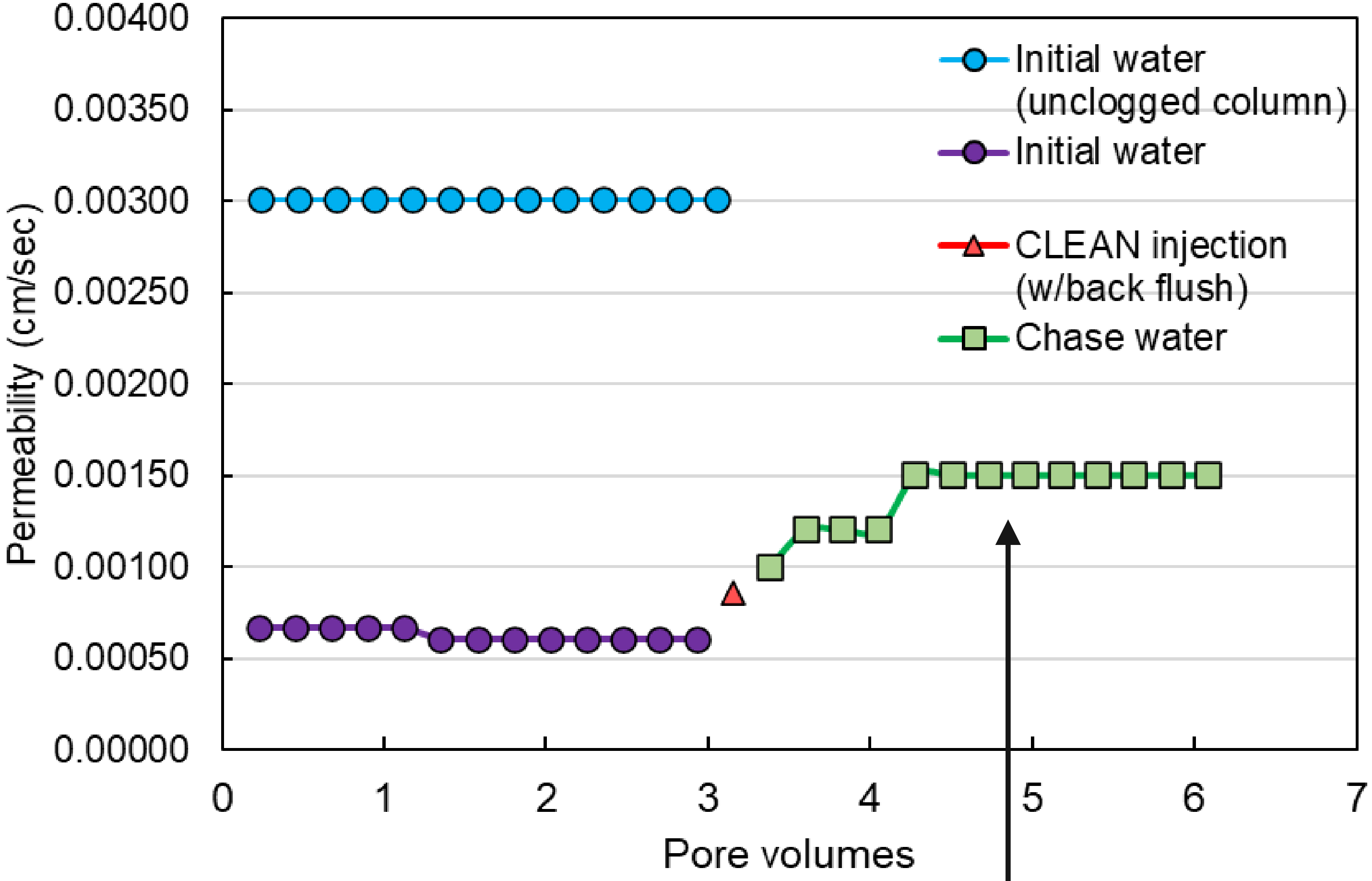
Removing synthetic gunk (potassium oleate) using CLEAN

- ¼ column filled with potassium oleate + soil
- 3 PV water, 0.5 PV CLEAN, backwash, then 3 PV chase water

  * 1 PV=~50 mL



1/2 original permeability recovered

Removing synthetic gunk (potassium oleate) using CLEAN

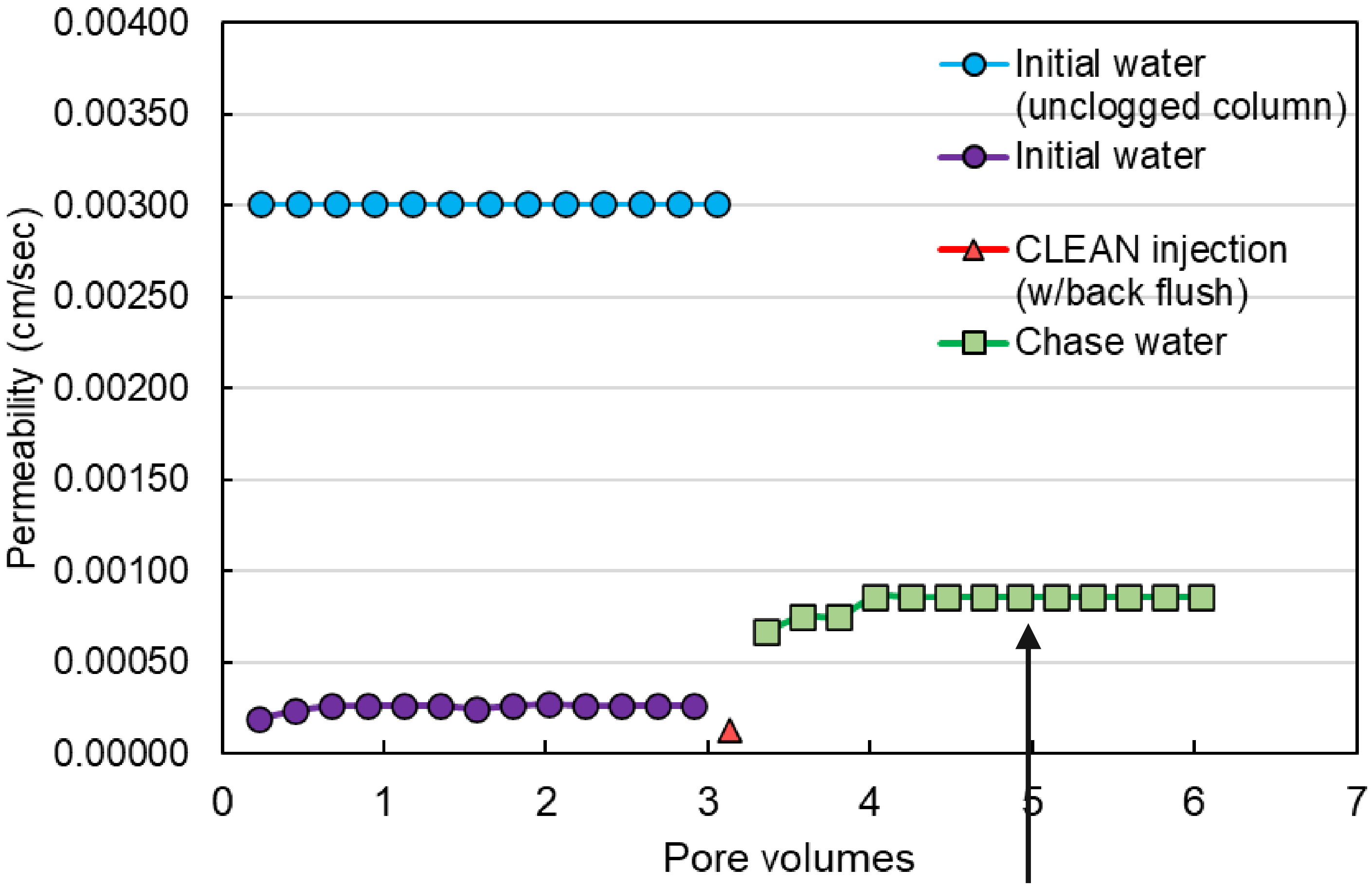
Observed Dissolution of gunk layers:

Before CLEAN injection

During CLEAN injection and backwashing

After chase water was injected

Removing injection site ‘gunk’ using CLEAN



- ¼ column filled with gunk from an injection well+ soil
- 3 PV water, 0.5 PV CLEAN, backwash, then 3 PV chase water

* 1 PV=~50 mL

1/3 original permeability recovered
In both cases, permeability increased ~3-fold

Removing injection site 'gunk' using CLEAN

Observed Dissolution of gunk layers:

Before CLEAN injection

During CLEAN injection and backwashing

After chase water was injected

- Gunk is complex, several solutions/treatments may be needed to completely restore injection conditions

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Rehabilitation of injection wells using CLEAN

- Remediation site to remove chlorinated compounds
  - 2009: Molasses injection
  - 2013: EVO (2% v/v)
  - 2018: 2nd EVO injection (2% v/v)
- During second injection event, permeability decreased substantially
  - Recovered fouling material suggested fouling due to hard water conditions
    - (2,200 mg Ca^{2+}/kg solid material, 60% dry solids, 40% moisture)
- Mixing solid material with concentrated CLEAN (1:6, solids:CLEAN) broke material in 3-5 minutes
- Pilot test suggests a 5x increase in flow rate
- Full-scale rehabilitation ongoing

Conclusions

- Hard water must be considered as an important variable when injecting EVO to treat contaminants
- Effects of hard water:
  - Increase EVO particle size and oil retention (higher EVO demand)
  - Capture of essential nutrients (phosphate).
  - Formation of fouling material
- Pre-treatment to remove hardness is desirable
  - Use of chase water
  - Chelators
  - Use of alternate substrates
- Restoring products (e.g. EOS CLEAN) to movilize oil/ destroy fouling can help in rehabilitating injection points

Questions

Thank you!

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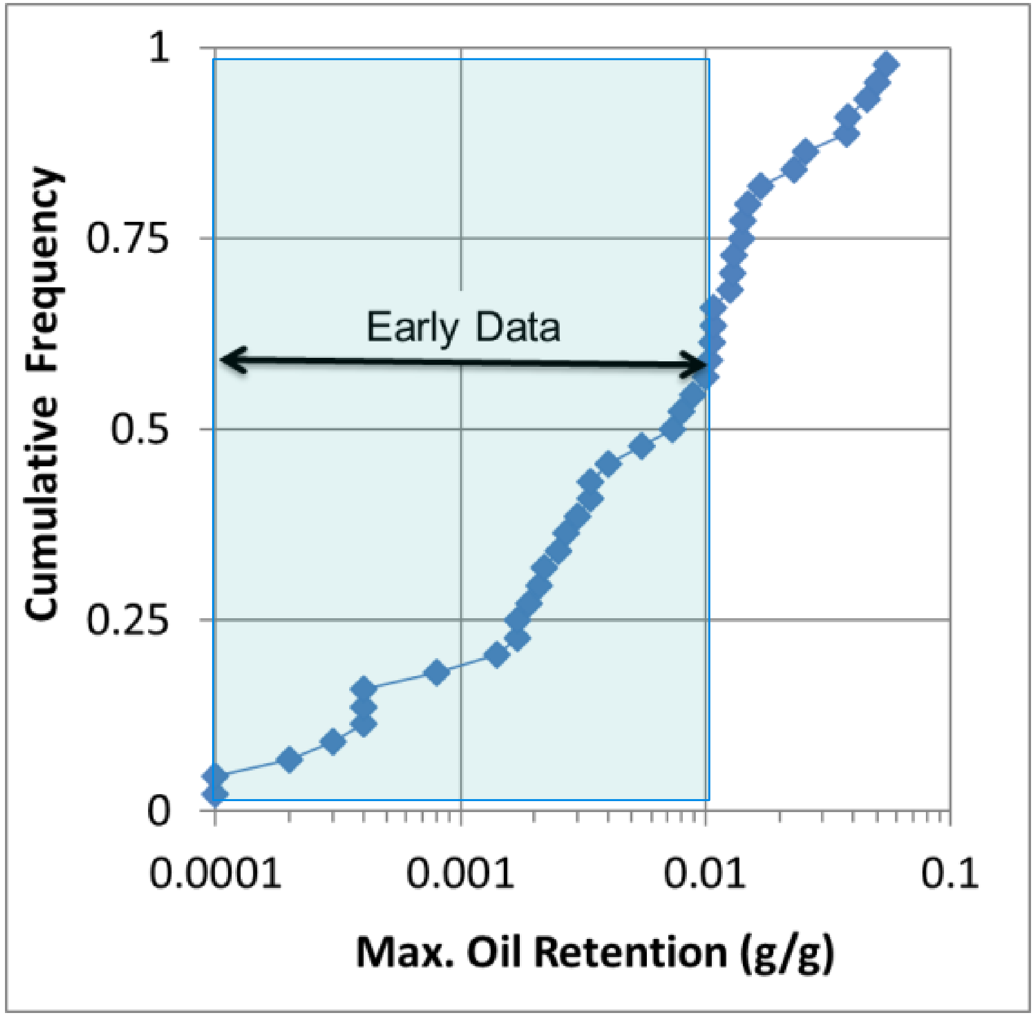
Supplemental slides

Early Measurements of Maximum Oil Retention (OR_M)

Aquifer Material	Emulsion	Test Condition	Maximum Retention (g/g)	Reference
Fine clayey-sand	Homemade	Lab Column	**0.0054**	Coulibaly and Borden, 2004
Fine clayey sand amended with kaolinite	Homemade	Lab Column	**0.0061**	Coulibaly and Borden, 2004
Fine clayey sand amended with kaolinite	Homemade	Lab Column	**0.0095**	Coulibaly and Borden, 2004
Clayey sand alluvium	EOS® 598B42	Lab Column	**0.0037**	Borden, 2007a
Low K, weathered rock	EOS® 598B42	Field (estimated)	**0.0030**	Borden et al., 2007
Coarse grained sand and gravel	EOS® 598B42	Field (estimate)	**0.0004**	Kovacich et al., 2007
Medium grain sand	EVO	Lab Column	**0.0024**	Konzuk et al., 2006

Factors Limiting Treatment – Under-Estimate Maximum Oil Retention

- New data shows some sites with very high oil retention
- Cause not completely understood



Thanks to Microbial Insights for most data!

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Factors Limiting Treatment – Under-Estimate Maximum Oil Retention

- Hard Water
  - High Ca^{+2}/Mg^{+2} → low zeta potential
  - Low zeta potential → higher oil retention
- At hard water sites, measure oil retention with groundwater from site
- Note: buffer / base addition increases hardness

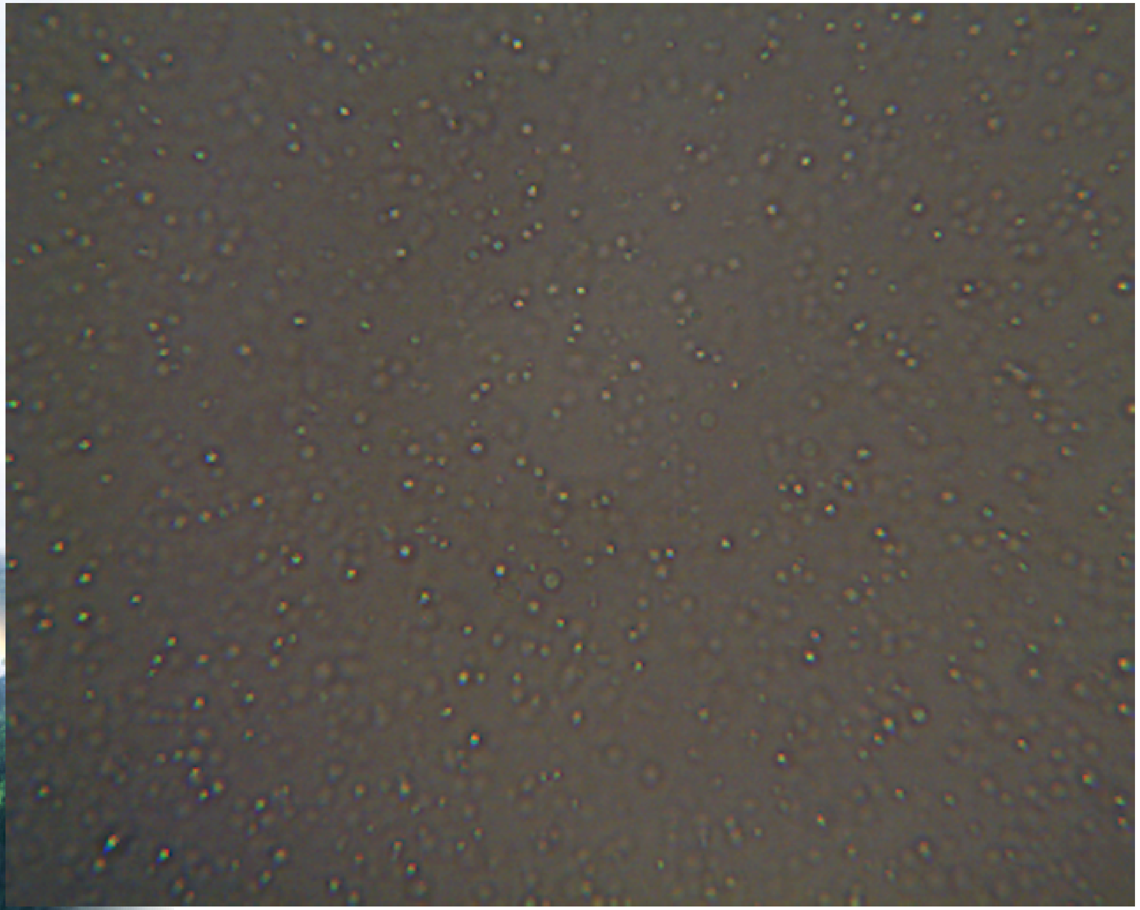
Zeta Potential

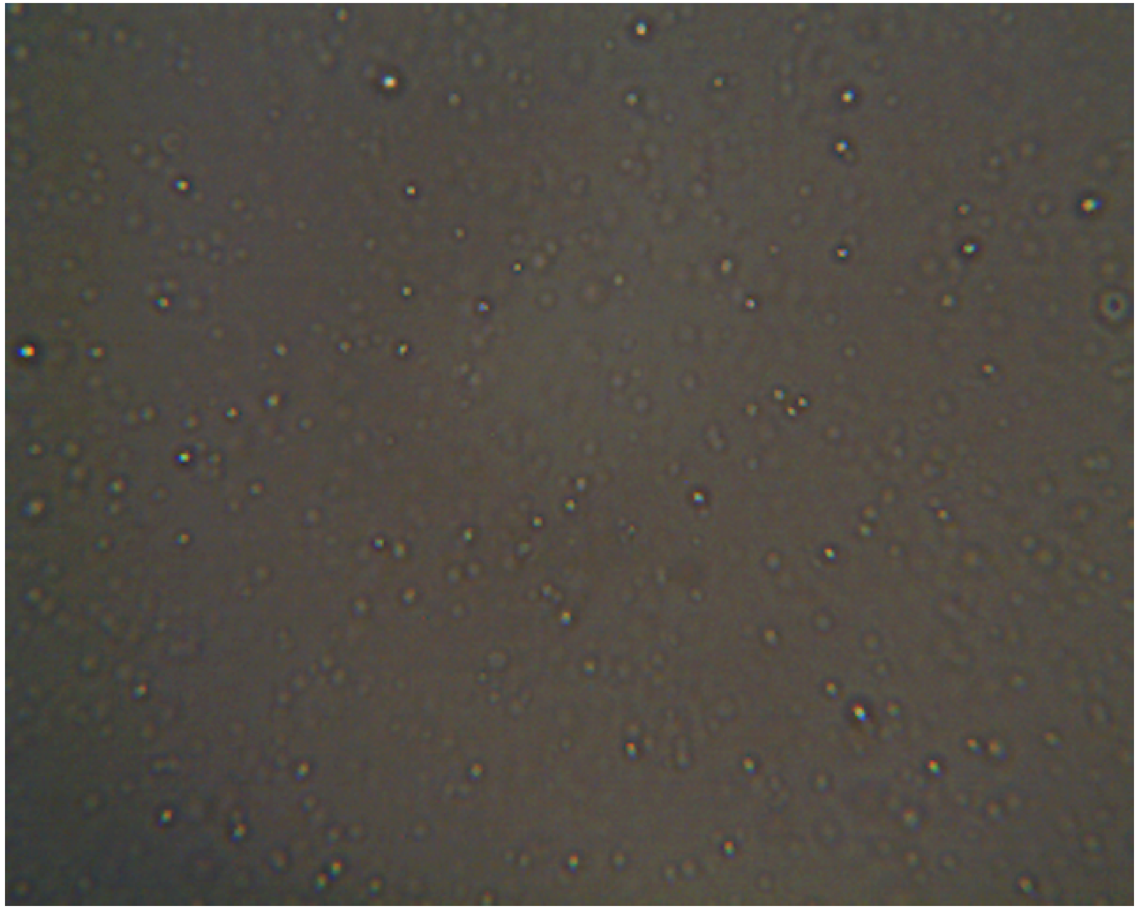
Colloid	Zeta Potential (mV)	
	DI Water	$CaCl_2$
SA17 (15-23’)	-29.4	-8.5
SA17 (30-40’)	-22.3	-7.5
OU2 (37-40’)	-29.9	-12.2
EOS 598B42	-43.0	-10.3

EVO Retention

Colloid	Oil Retention (g oil /g soil)	
	DI Water	$CaCl_2$
SA17 (15-23’)	0.003	0.013
OU2 (37-40’)	0.014	0.038

Changes in particle size due to hardness





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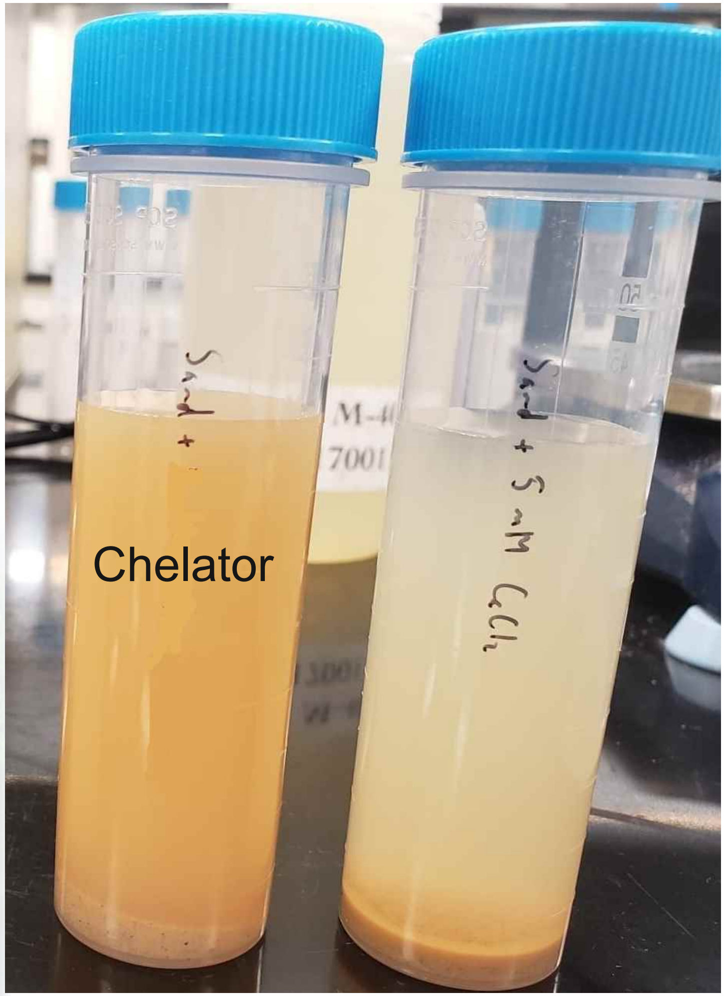

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Sequestration of nutrients (phosphate) by hard water

- Ca^{2+} reacts with ions such as phosphate. Minerals such as hydroxyapatite are formed, which sequester phosphate and potentially cause scaling.