Impact of Surface Tension, Zeta Potential, and Droplet Size on Transport of Traditional and Zero Water EVOs

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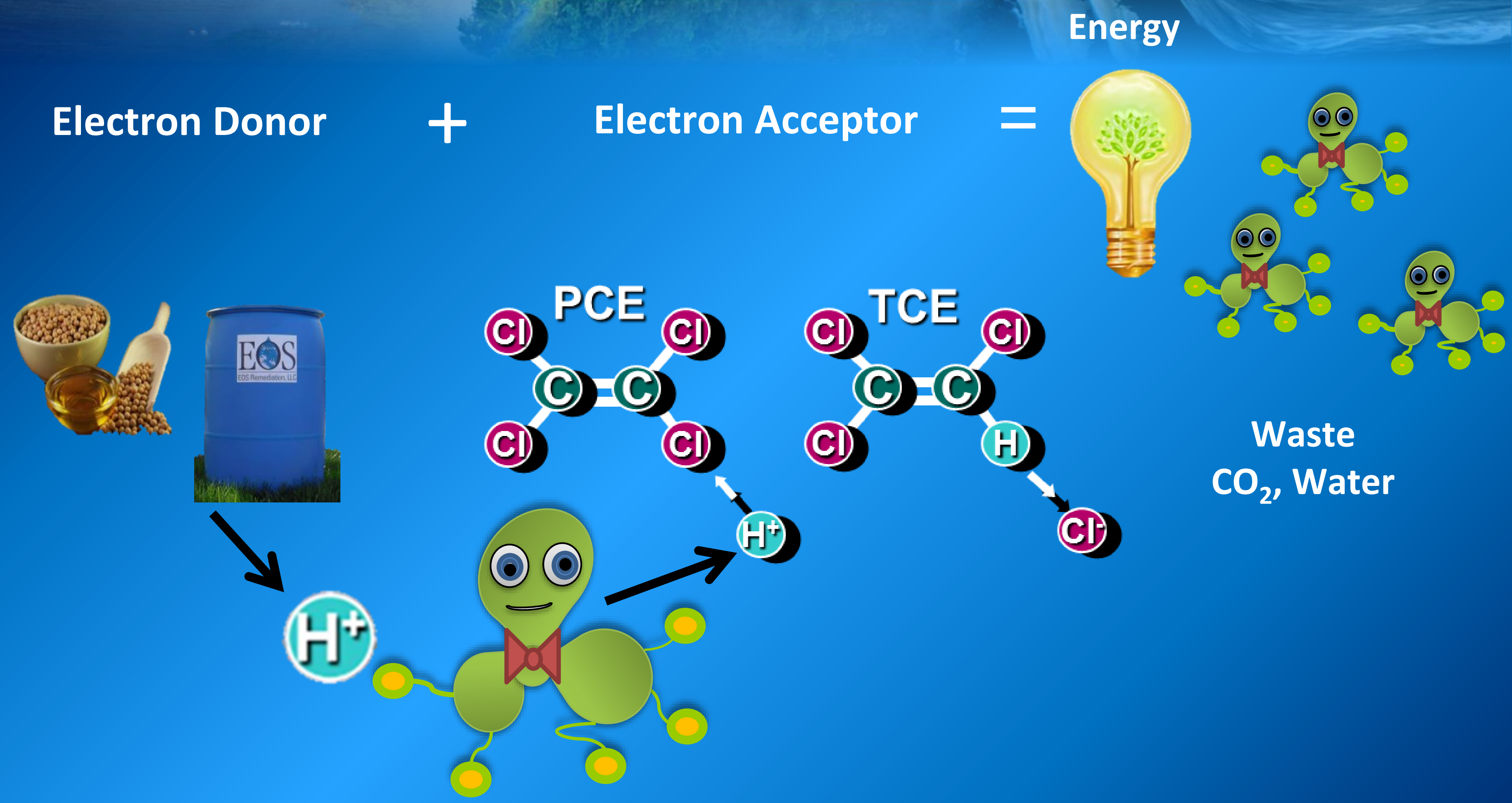
Enhanced Bioremediation



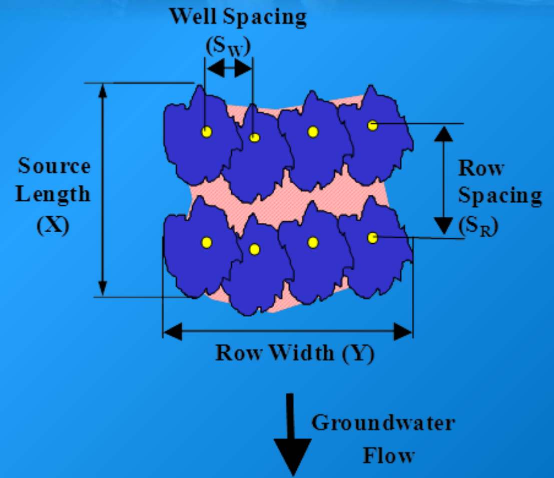
Choosing the Right Substrate

Some considerations to take into account:

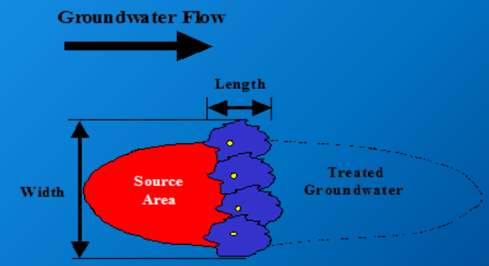
- Source Treatment or Bio-Barrier
- Lithology and Heterogeneity dictates distribution
- Groundwater Velocity
- Substrates Degrade at Various Rates
  - Soluble Substrates - Typically short life (weeks to months)
  - Emulsified Vegetable Oil (EVO) – Typically long life (years)
- Subsurface Retention Varies Based on:
  - Lithology
  - Characteristics of the substrate

Design Considerations

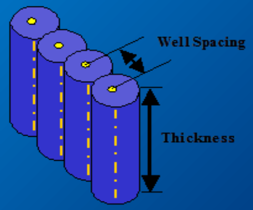
- Treatment zone dimensions
  - Width perpendicular to flow (x)
  - Length along GW flow direction (y)
    - Contact time (velocity of GW)
  - Effective vertical height (z)



- Amount of oil
  - Oil required for biodegradation, including competing e- acceptors
  - Oil droplet retention by sediment



- Number and spacing of injection wells



Design Considerations

Oil requirement

Mass of oil = $x * y * z * ne * \rho_B * O_R$

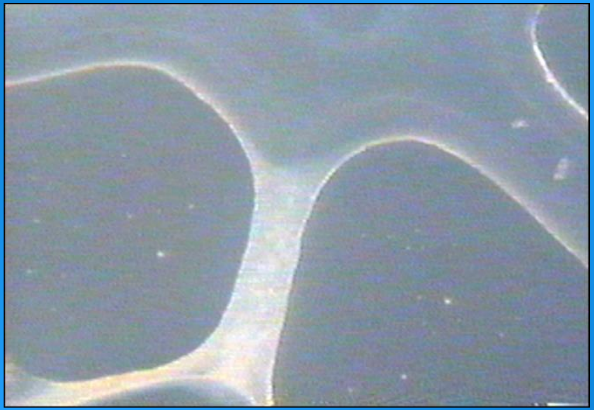
x	= Treatment zone length parallel to GW flow (ft)
y	= Design width perpendicular to GW flow (ft)
z	= height (ft)
ne	= Effective porosity (unit less)
ρ_B	= Sediment bulk density (lb./ft^3)
O_R	= Oil retention (wt./wt.)

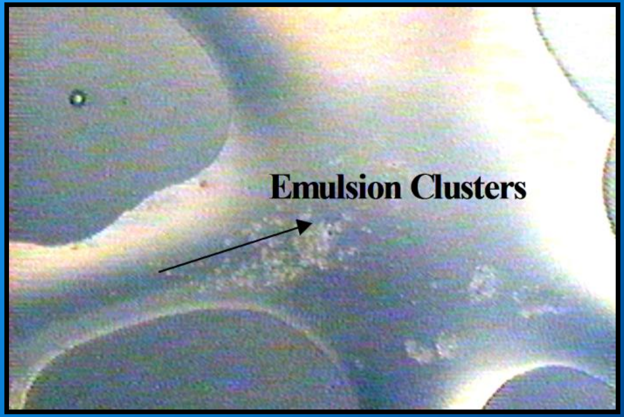
Oil Retention: the amount of oil that sorbs to an aquifer grain

What is Oil Retention

Oil retention is a function of

- Droplet size
- Zeta potential of sediments and droplets
  - Most clays have a net negative charge
  - Negatively charged droplets will have lower retention
- Surfactant type
  - Non-ionic typically have lower sorption
  - Ionics have higher sorption (lecithin sorption is very high)





Colloidal Transport of ‘Insoluble’ Particles

- Small particles / droplets (<5µm) easily pass through most pores (30-100µm)
- Particles / droplets are retained when they stick to sediment surfaces
- To be retained:
  - Droplet must first ‘bump’ into sediment
  - Properly charged space must be available
  - Droplet must attach

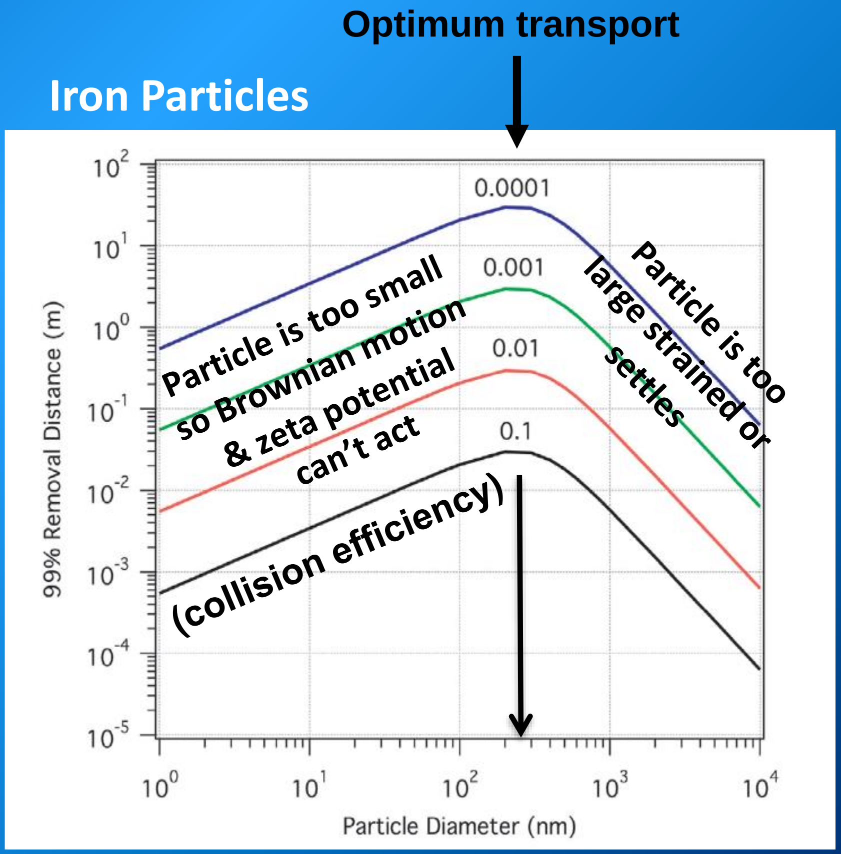
Collision Frequency vs Diameter

Three Processes Effect Collision of a Particle in Typical Porous Environmental Media

- Brownian Motion
- Straining/Settling
- Physiochemical attraction (Zeta Potential)

Collision Efficiency

The graph illustrates particle transport as a function of size with changes in collision efficiency.



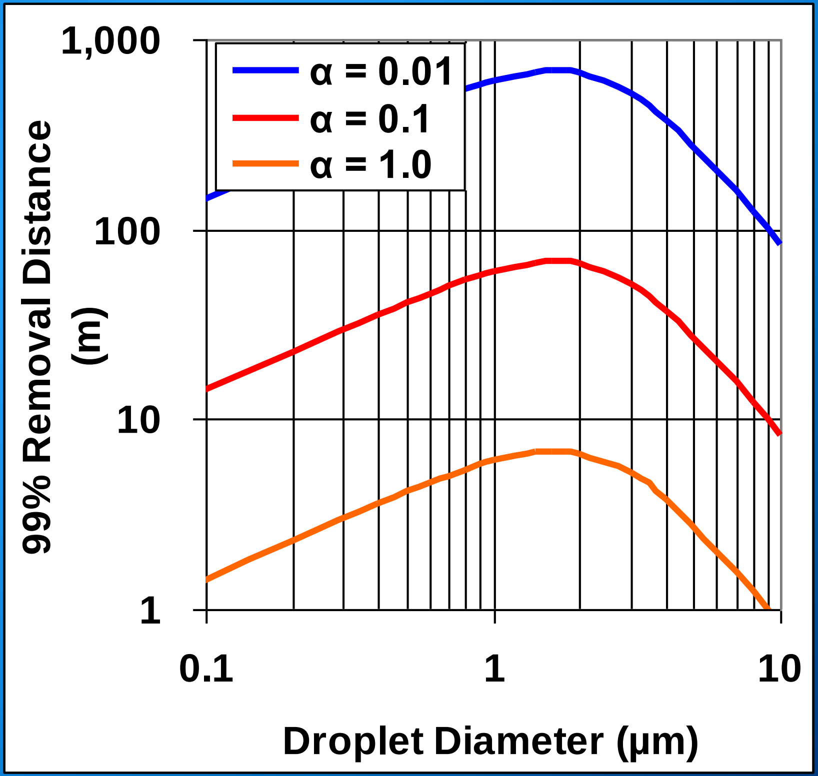
Tratnyek and Johnson, Nanotoday, 44-48, 2006

Collision Frequency vs Diameter

Similar work by Coulibaly (2006) with emulsified oils showed:

- Peak travel distance is at 1-2 µm droplets
- Transition from collision driven to "floating" rather than settling
- Distance is directly dependent on collision efficiency (α) and droplet size

Oil Droplets



Ionic Strength and Oil Retention

	SA17 B Zone		SA17 C Zone
	D.I.	$CaCl_2$	$CaCl_2$
Influent End	0.05%	0.76%	3.79%
Middle	0.18%	1.27%	4.94%
Effluent End	0.57%	1.96%	4.74%
Average	0.27%	1.33%	4.49%

Retained oil content in column tests with D.I. water and 200 mg/L $CaCl_2$.

Greater ionic strength in groundwater can impact oil retention. Consider measuring for:

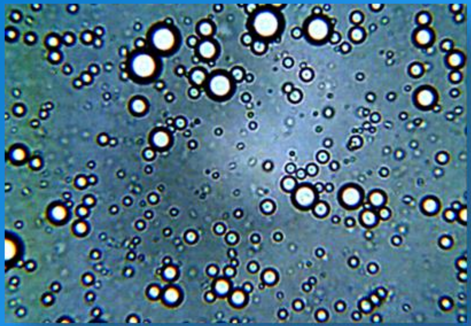
Ca^{2+}
Mg^{2+}
Fe^{2+}

From: Draft ESTCP report

Substrate Properties

<u>Properties of "water-less" oil products</u>
(EOS 100)

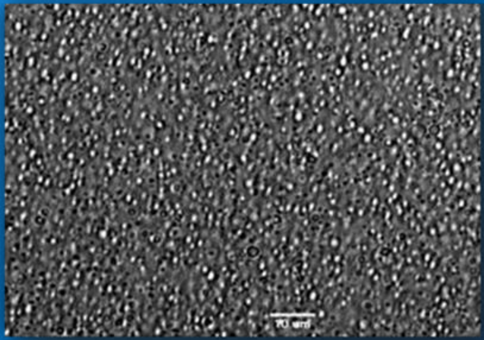
- High vegetable oil content (~80 to 95% by wt.)
- Emulsifiers and other additives
- Once mixed with water have a large droplet diameter (~5-10 microns)



Mean Droplet 5-10 microns

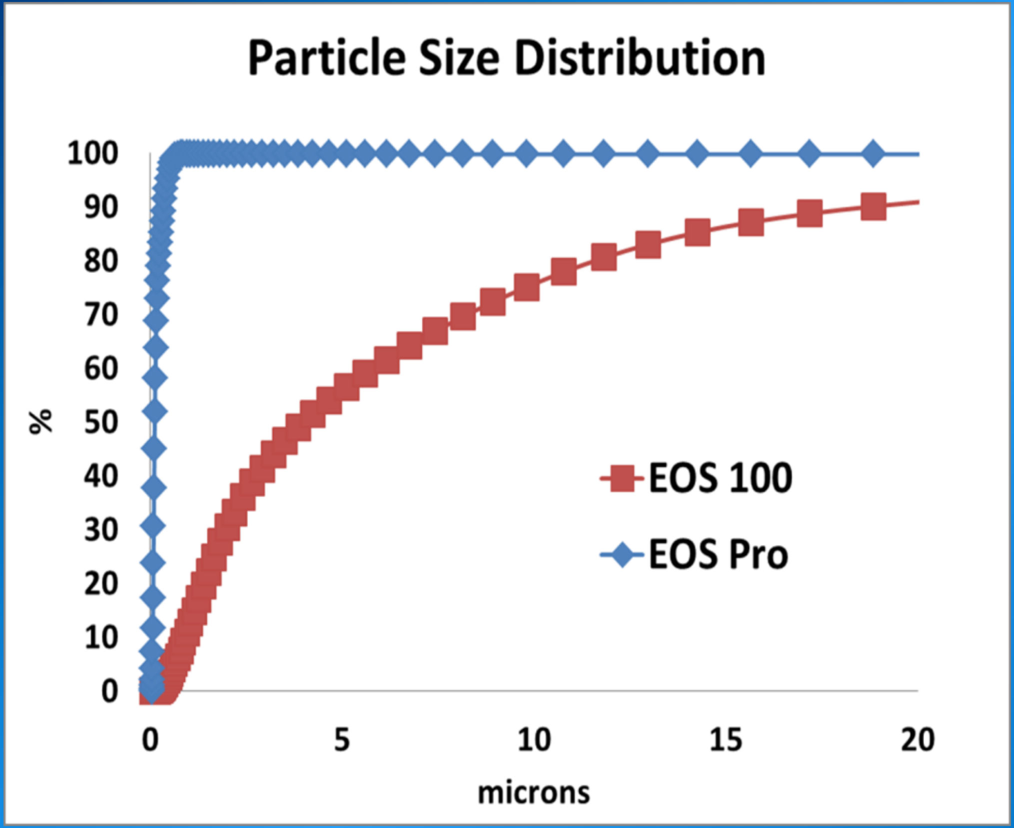
<u>Properties of traditional EVO products</u>
(EOS Pro)

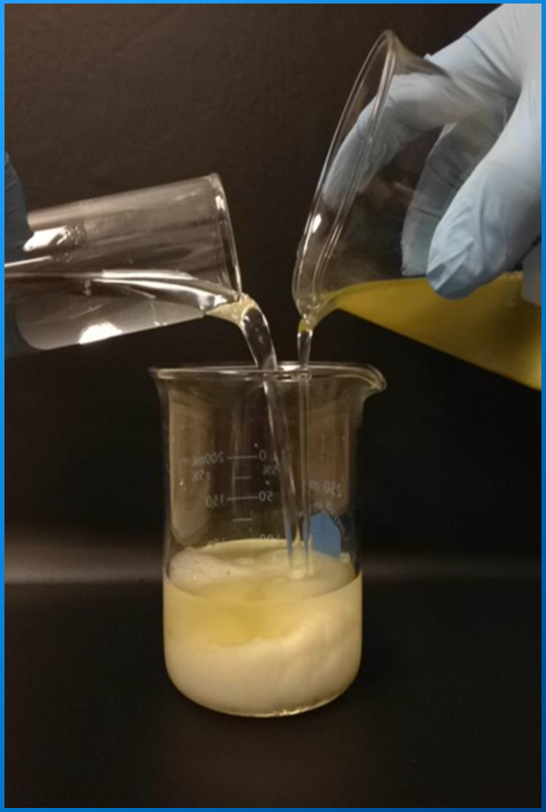
- Low to medium vegetable oil content (45%-60% by wt.)
- Include nutrients or vitamins
- Droplets as delivered ~1 micron



Mean Droplet ~ 1 micron

Particle Size Distribution

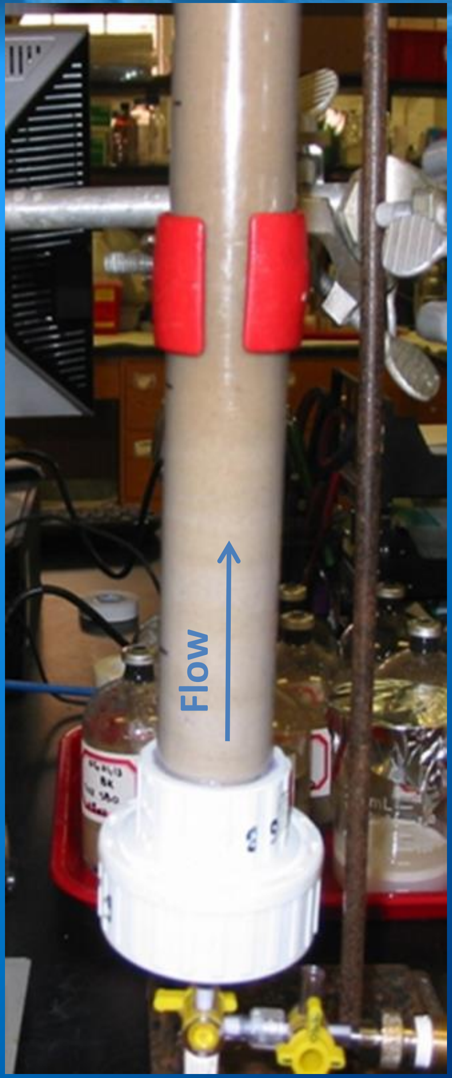




EOS 100 Suspension

Column Studies: Oil Retention

- Column studies were conducted to compare:
  - Traditional vegetable oil emulsions (EOS Pro) to water mixable oils (EOS 100)
  - Measured the effective oil retention on two different types of soil:
    - Silty sand (field sand) **K= 30 ft/day**
    - Clean sand (washed masonry sand) **K= 100 ft/day**

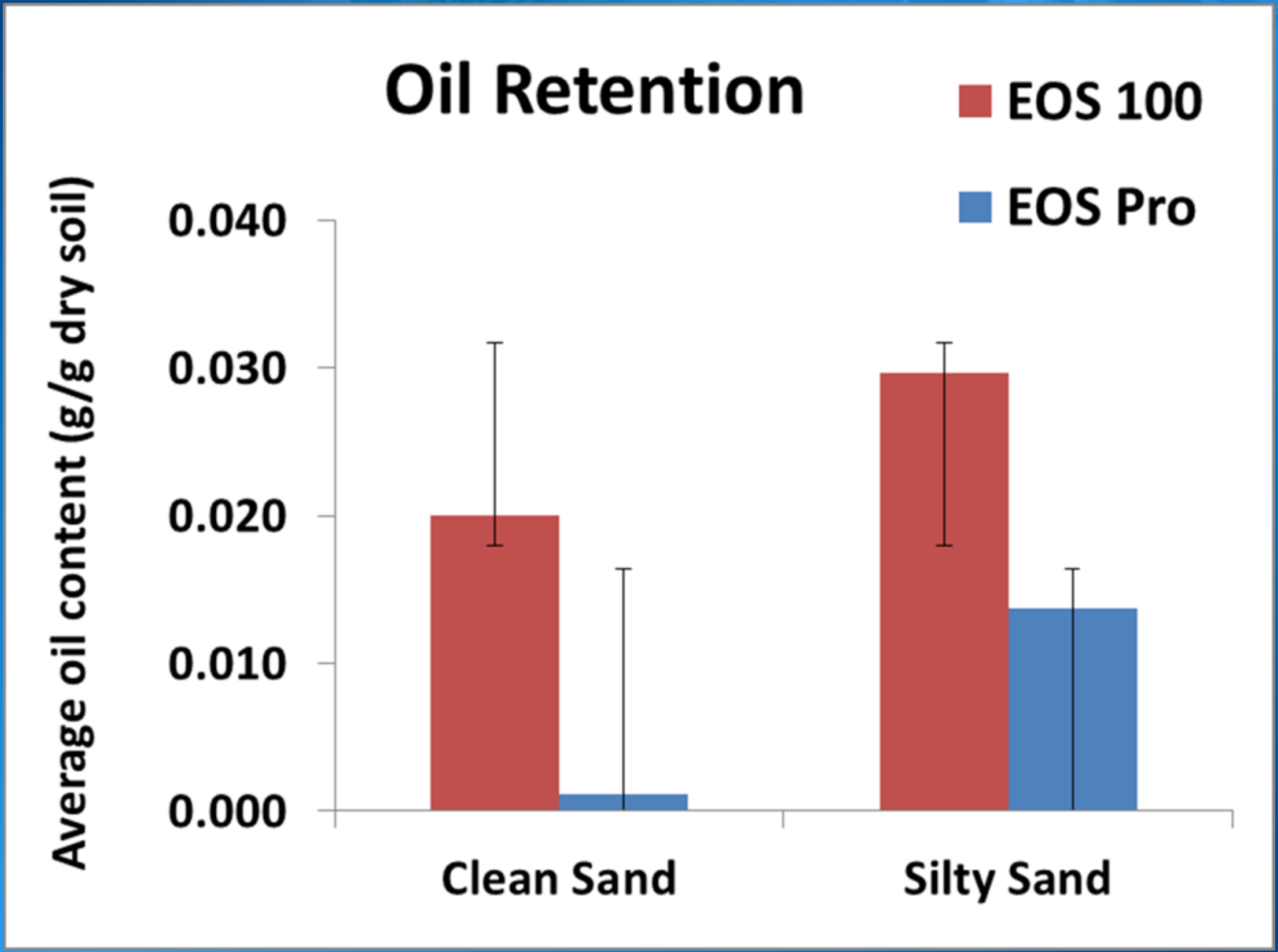


Column Studies: Oil Retention

Column Testing Process and Analysis

- Columns were packed with sand
- Developed by flushing with water until constant pressure drop
- Three pore volumes of diluted emulsion (1:10 EOS to water) were injected per column
- Columns were monitored for permeability loss (clogging)
- The columns were flushed with three pore volumes of chase water to remove un-retained emulsion
- Columns were sectioned and soil was analyzed for oil retention

Oil Retention Results



Project Cost Impact & Life Cycle

Results from the column studies were applied using the ESTCP Emulsified Oil Design Tool (ER-0626):

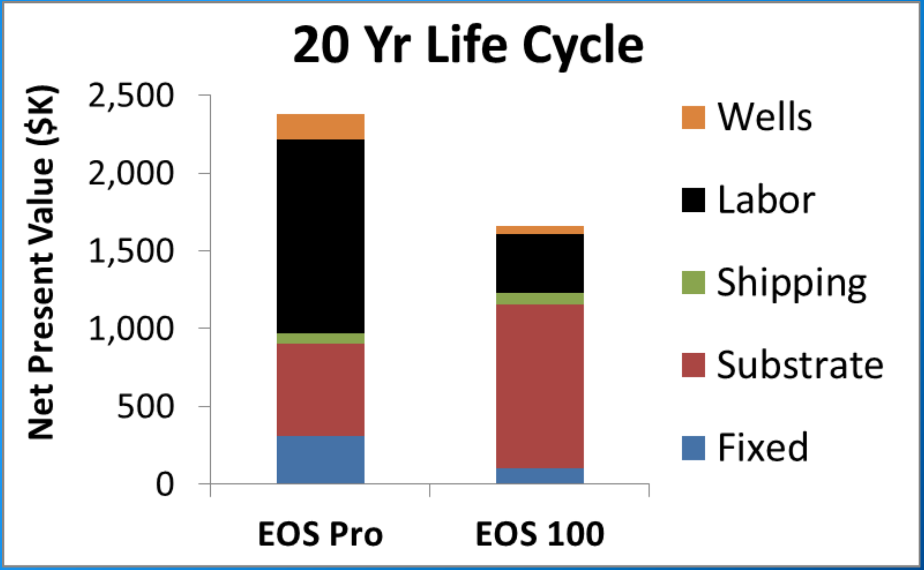
- Barrier Treatment Design
  - 200 ft wide
  - 10-40 ft bgs
  - 20 yr. life-cycle
  - 25% effective porosity
- Two Design Cases
  - Silty Sand: seepage velocity = 0.48 ft/day
  - V = (30 ft/day * 0.004 ft/ft)/0.25
  - Clean Sand: seepage velocity = 1.6 ft/day
    - V = (100 ft/day * 0.004 ft/ft)/0.25

http://www.serdp-estcp.org/Tools-and-Training/Environmental-Restoration/Groundwater-Plume-Treatment/Emulsion-Design-Tool-Kit

Life Cycle Cost Analysis

Clean Sand: seepage velocity = 1.6 ft/day

Comparison	EOS Pro	EOS 100
Contact Time (d)	> 60	> 60
Maximum Oil Retention (lb./lb.)	.001	.005
Reinjection Interval (yrs.)	1.5	5



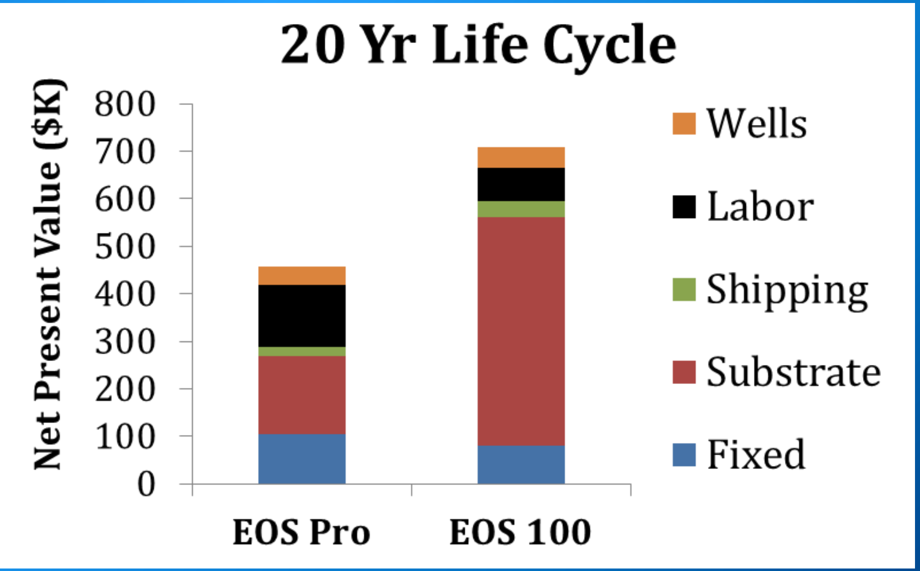
Clean Sand Barriers:

- Overall lifecycle costs are higher than for silty sand
- Cost savings realized by using larger droplet size EOS 100

Life Cycle Cost Analysis

Silty Sand: seepage velocity = 0.48 ft/day

Comparison	EOS Pro	EOS 100
Contact Time (d)	> 60	> 60
Maximum Oil Retention (lb./lb.)	0.003	0.015
Reinjection Interval (yrs.)	5	10



Silty Sand Barriers:

- Overall lifecycle costs are lower than clean sand barriers
- Cost savings realized by using smaller droplet size EOS Pro

Conclusions

Size Matters

- 1-2 µm emulsified oil drops are optimum for transport in most aquifer settings (effective porosity 5-20%).
- Larger oil droplets provide increased retention
  - High Velocity Aquifers (> 0.5 ft/day)
  - Coarse Grained Matrices (effective porosity >20%)
  - Fractured Rock
  - Bio-Barriers
- Lifecycle costs are dependent on:
  - Site specific conditions (geology, groundwater velocity, etc.)
  - Substrate selection – low vs high oil retention

Questions?

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