Pilot Scale Testing of Swellable Organo-Silica-Nanoparticle Composite Materials for the *in situ* and *ex situ* Remediation of Groundwater Contaminated with Chlorinated Organics

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Introduction

New type of sol-gel derived material: Swellable organically modified silica

Metal nanoparticles composite materials

Application: *in situ* and *ex situ* groundwater remediation of **chlorinated solvents TCE, PCE**.

Bench-scale and **pilot scale**

Commercially Produced as Osorb

Osorb is a highly structured glass which instantaneously swells when it comes in contact with a wide range of Organic molecules

Gasoline
Natural gas
Acetone
Ethanol
Pharmaceuticals
Solvents

Osorb does <u>not</u> swell in water

Four unique aspects of SOMS aka “Osorb”

No other material does these 4 things:

1 - Instantly swells.

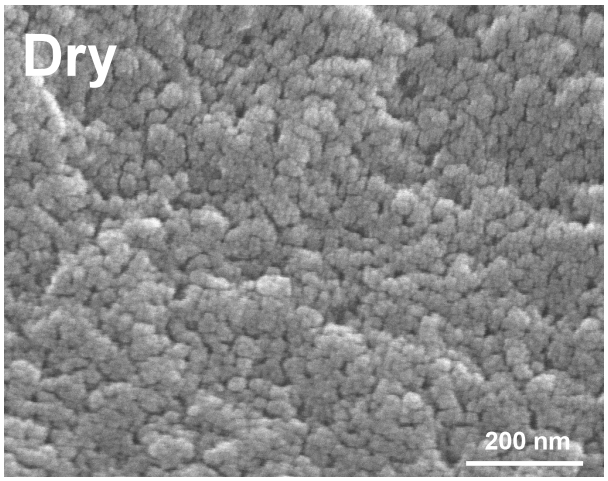
2 - High mechanical energy (100N/g)

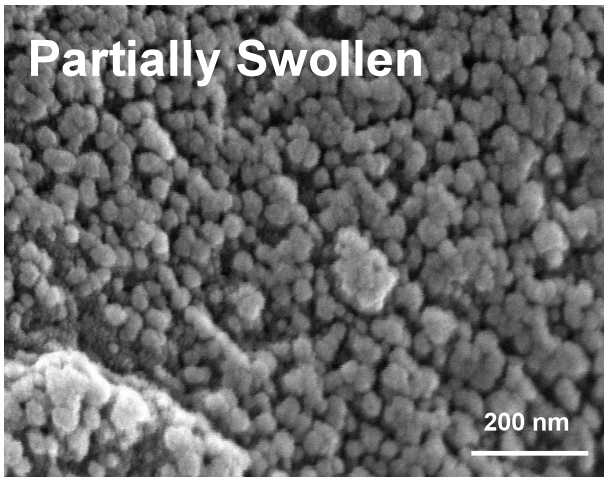
3 - Completely reversible with heat.

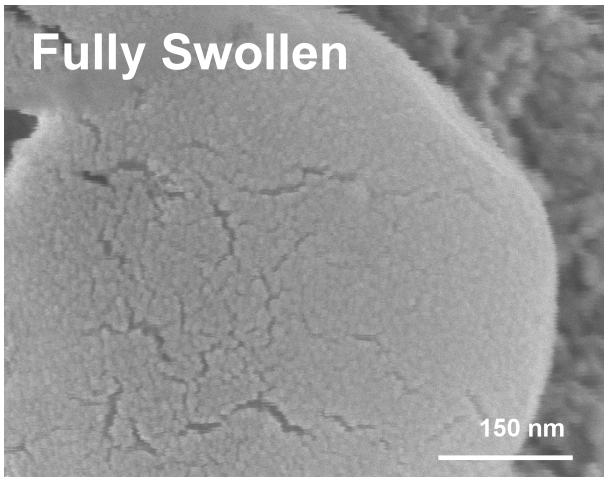
4 - Can contain 6-8x it’s own weight.

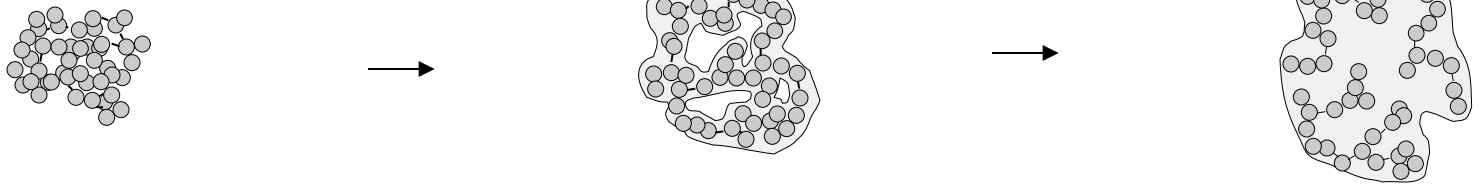
Nanoscale Morphology

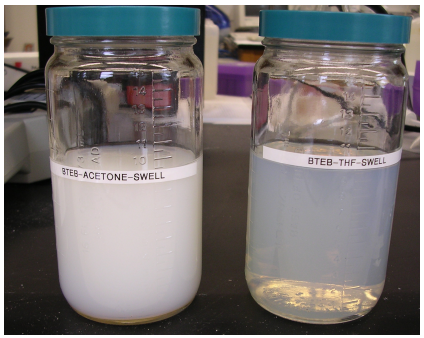
Flexibly tethered array of silica nanoparticles

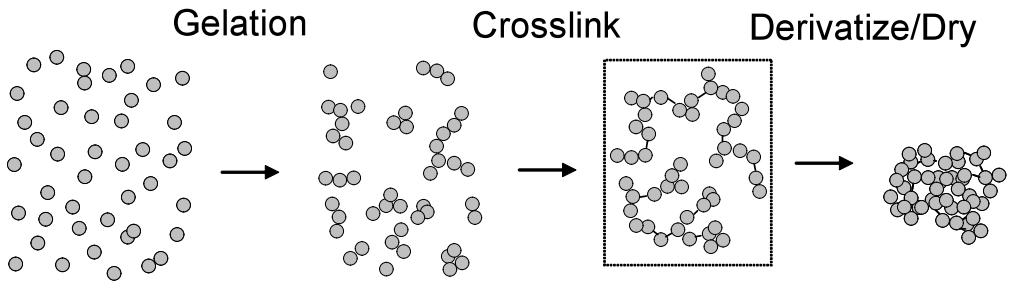






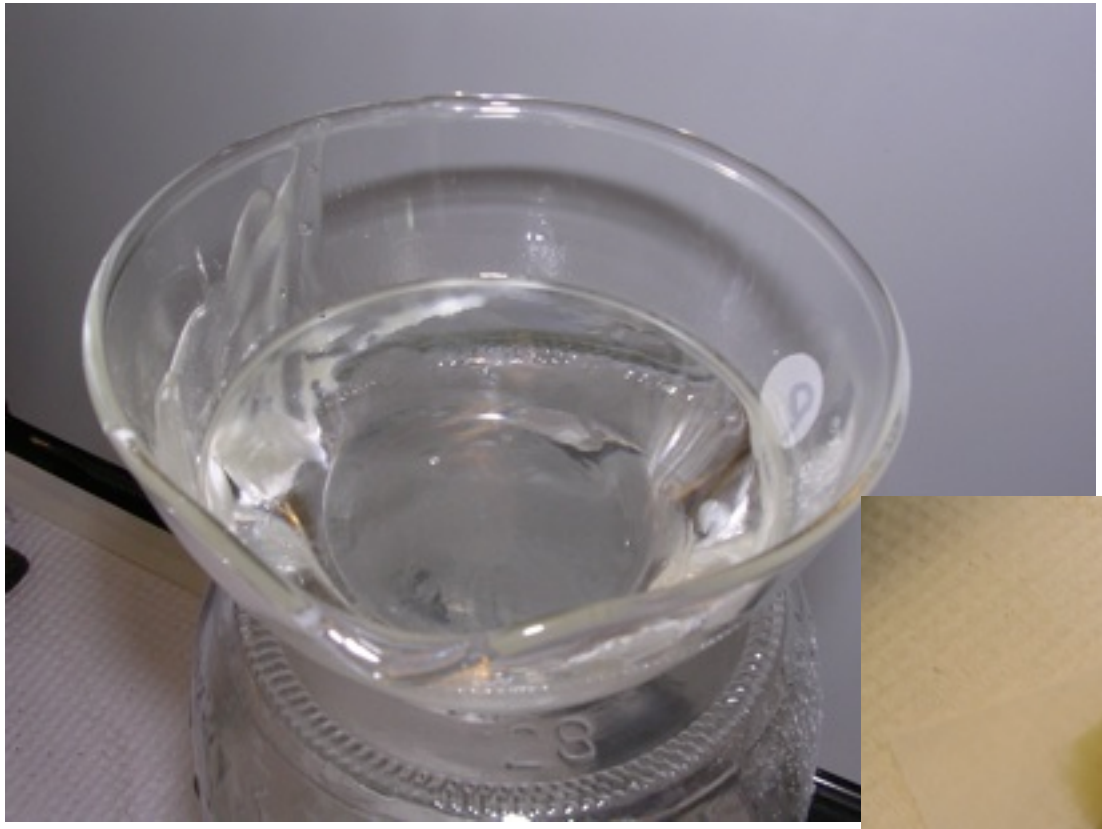




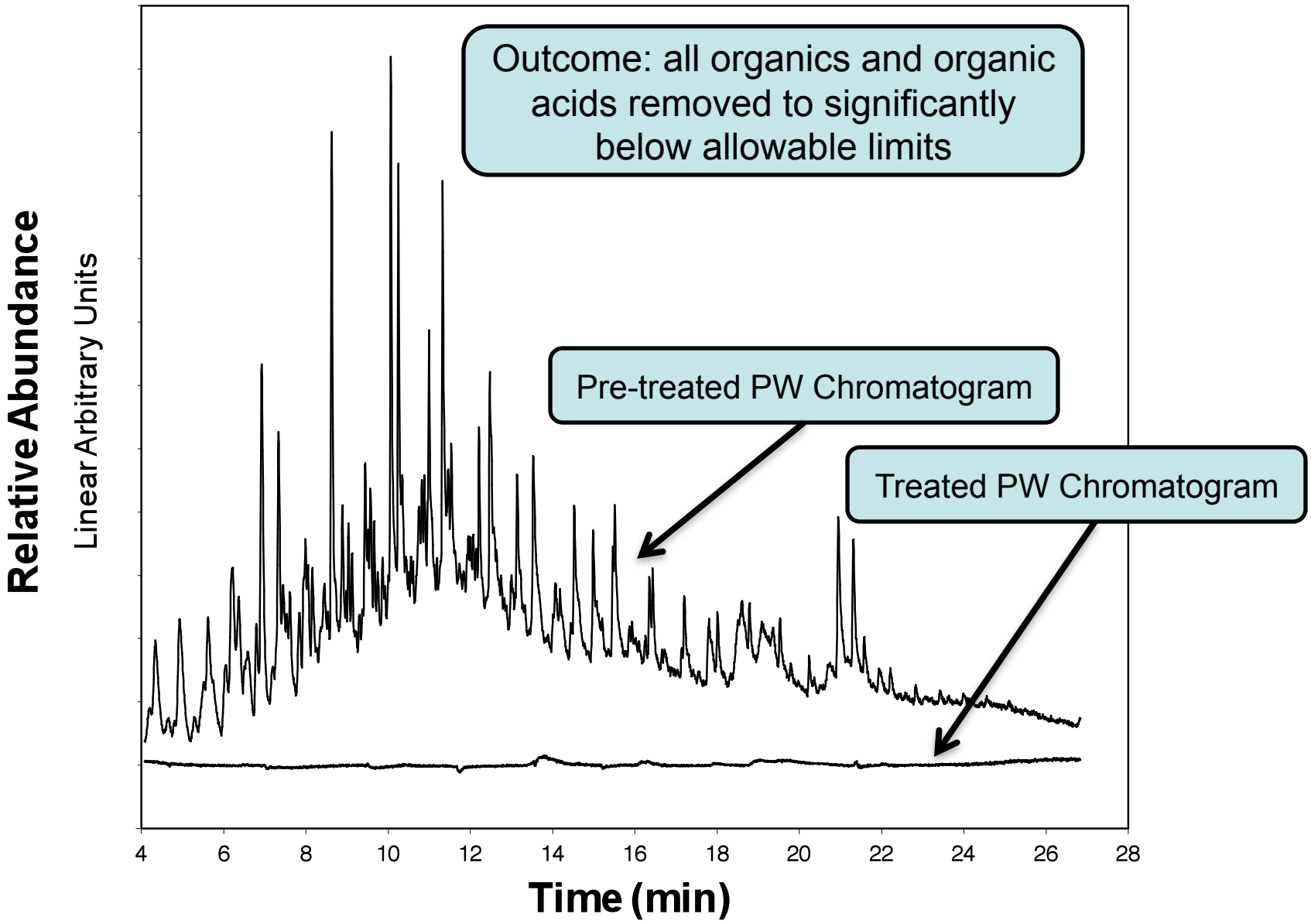


Oil Spill Clean-Up Demo

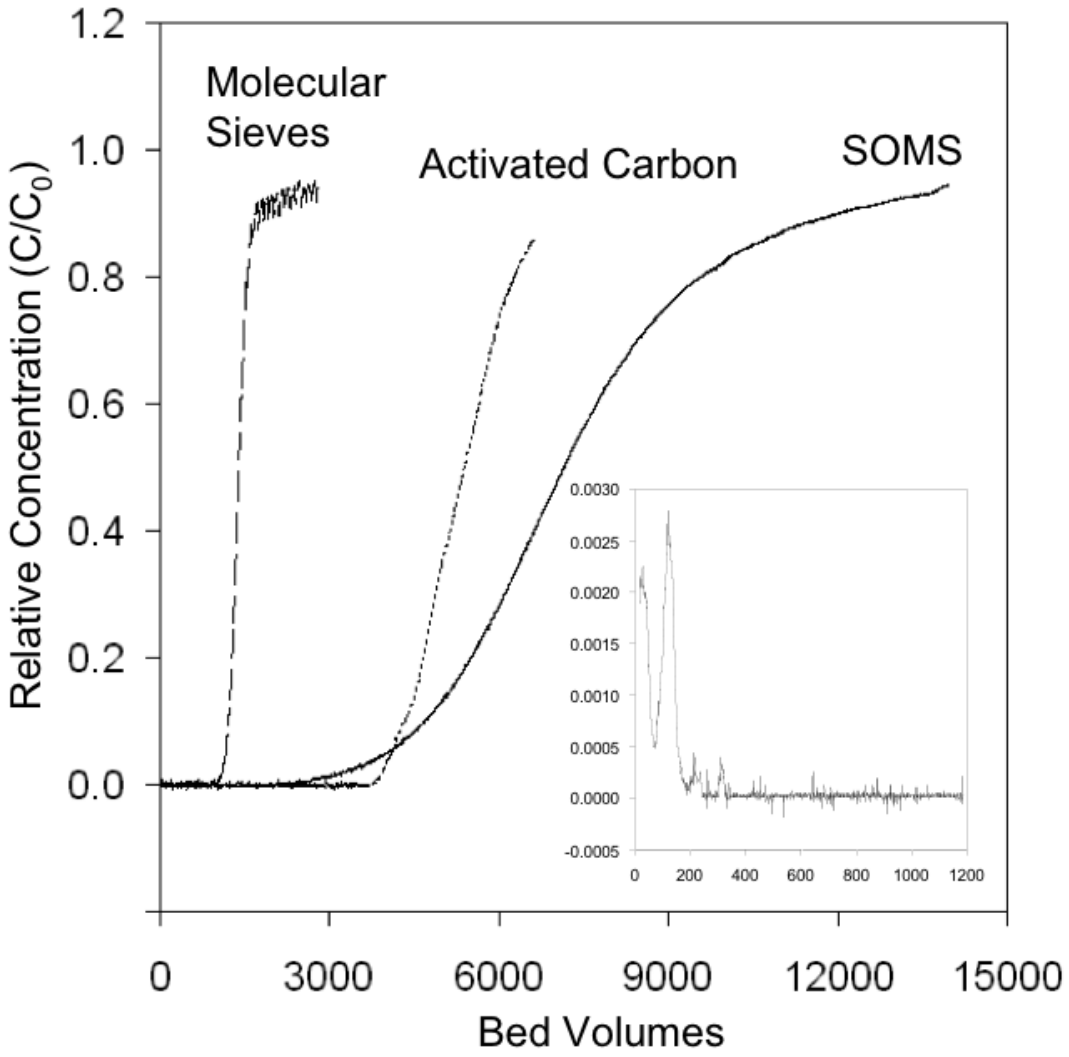
Extraction of gelled Osorb is easy



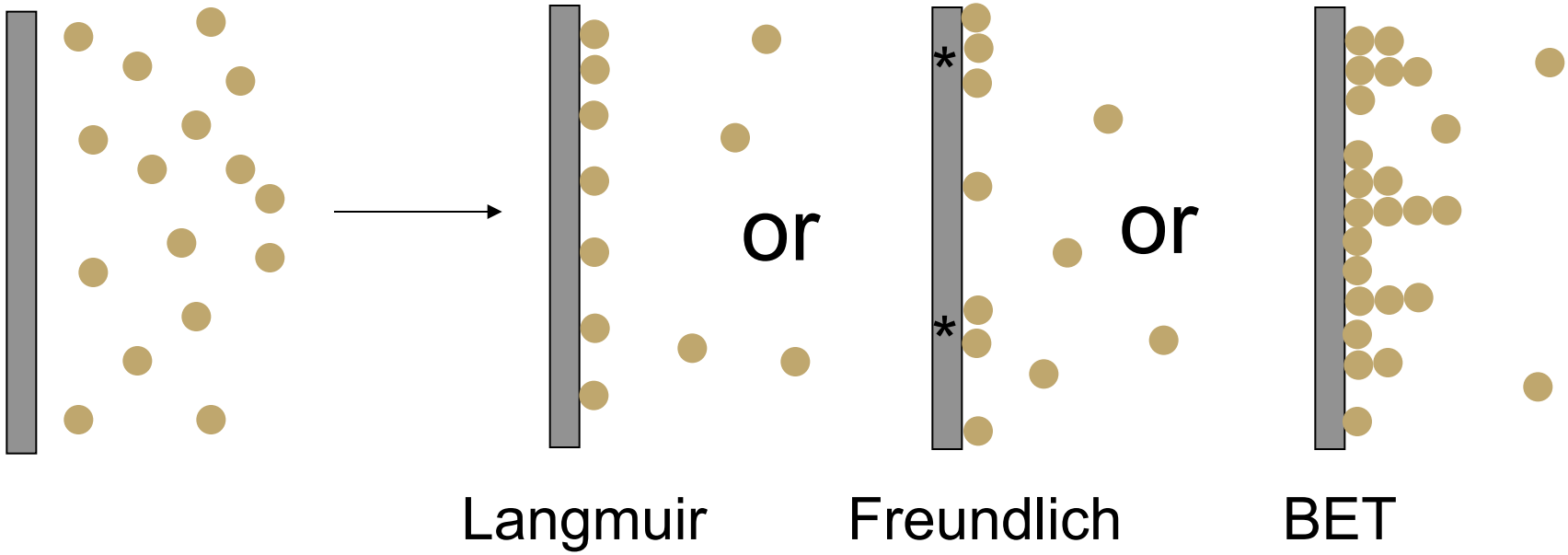
Produced Water



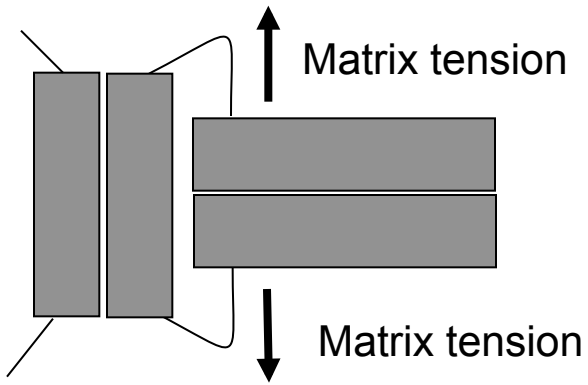
PCE Breakthrough Curves



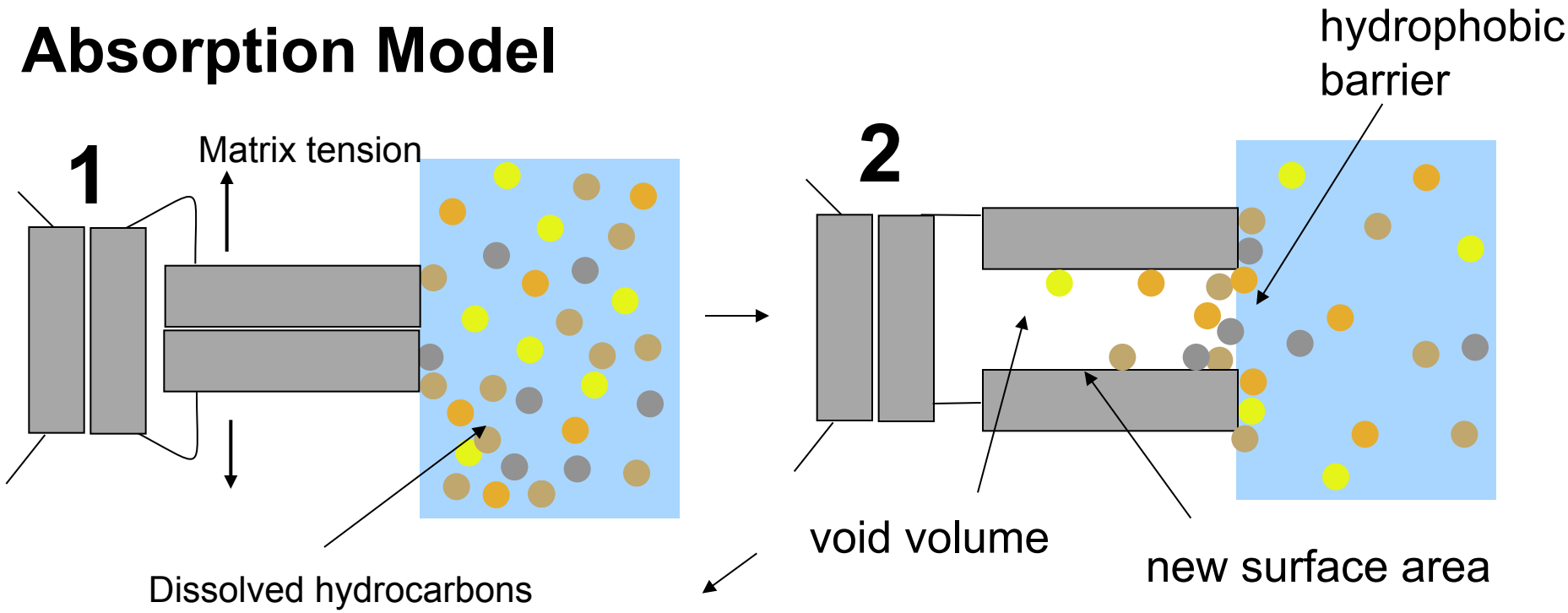
Classical Models for Adsorption



SOMS is a tiny machine to capture molecules

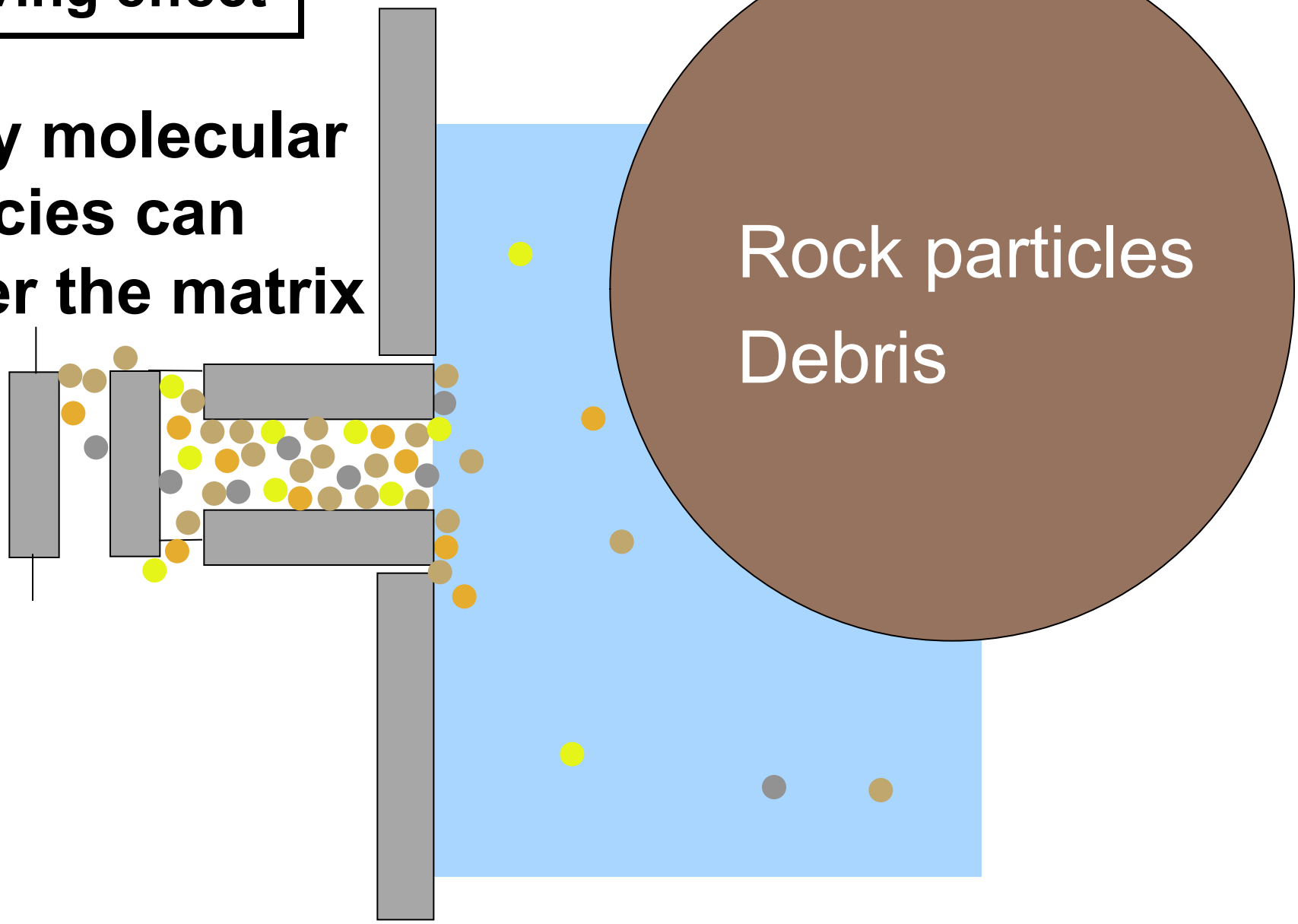


Absorption Model

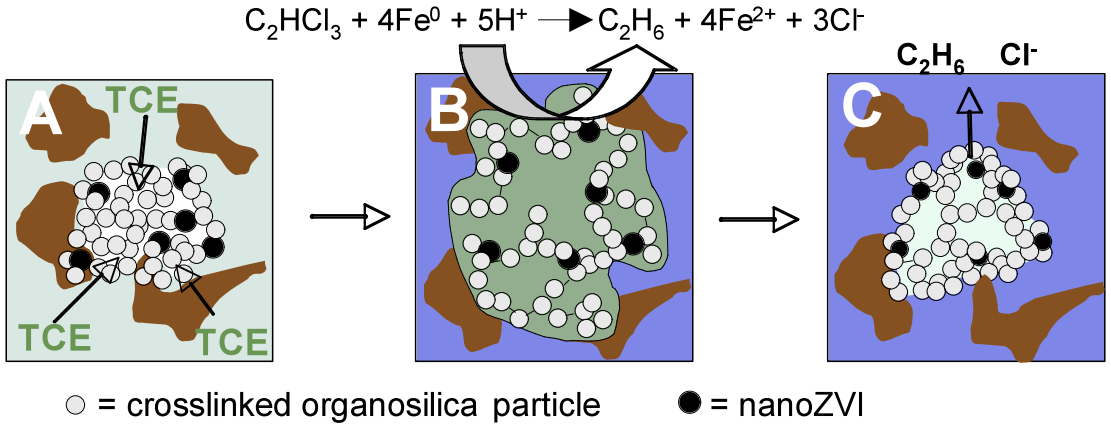


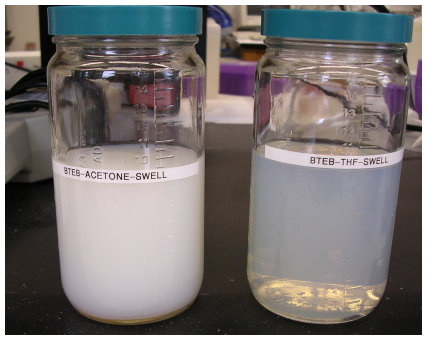
Sieving effect

Only molecular species can enter the matrix

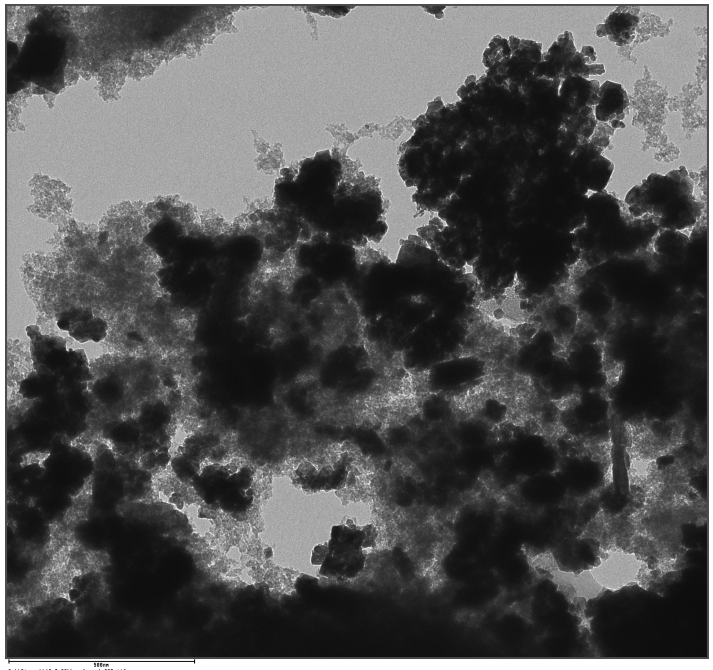


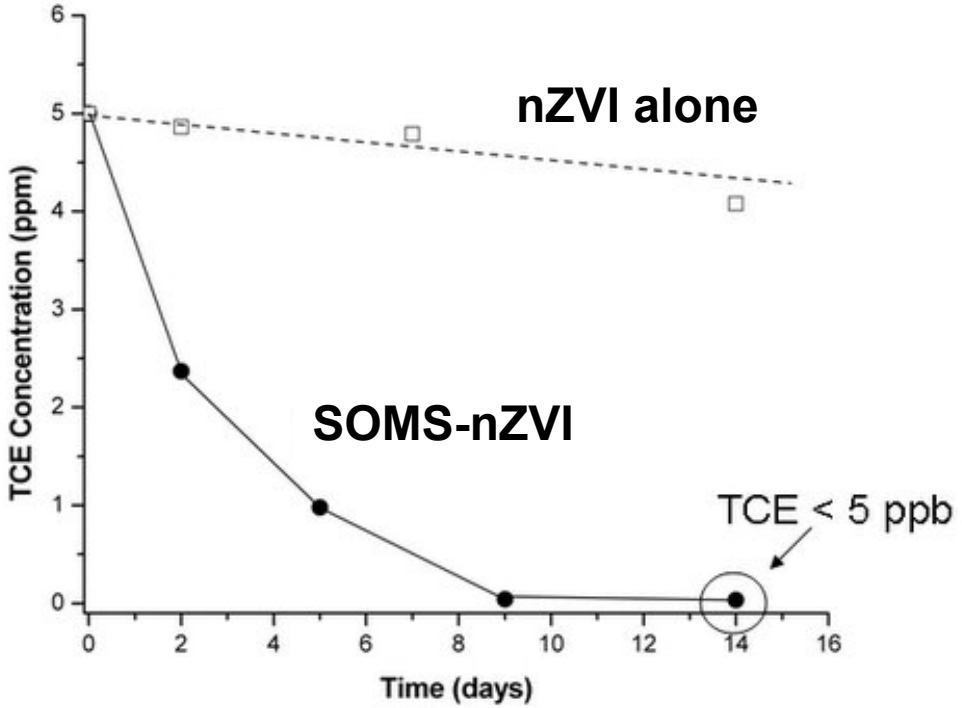
Groundwater Remediation: nZVI Composites

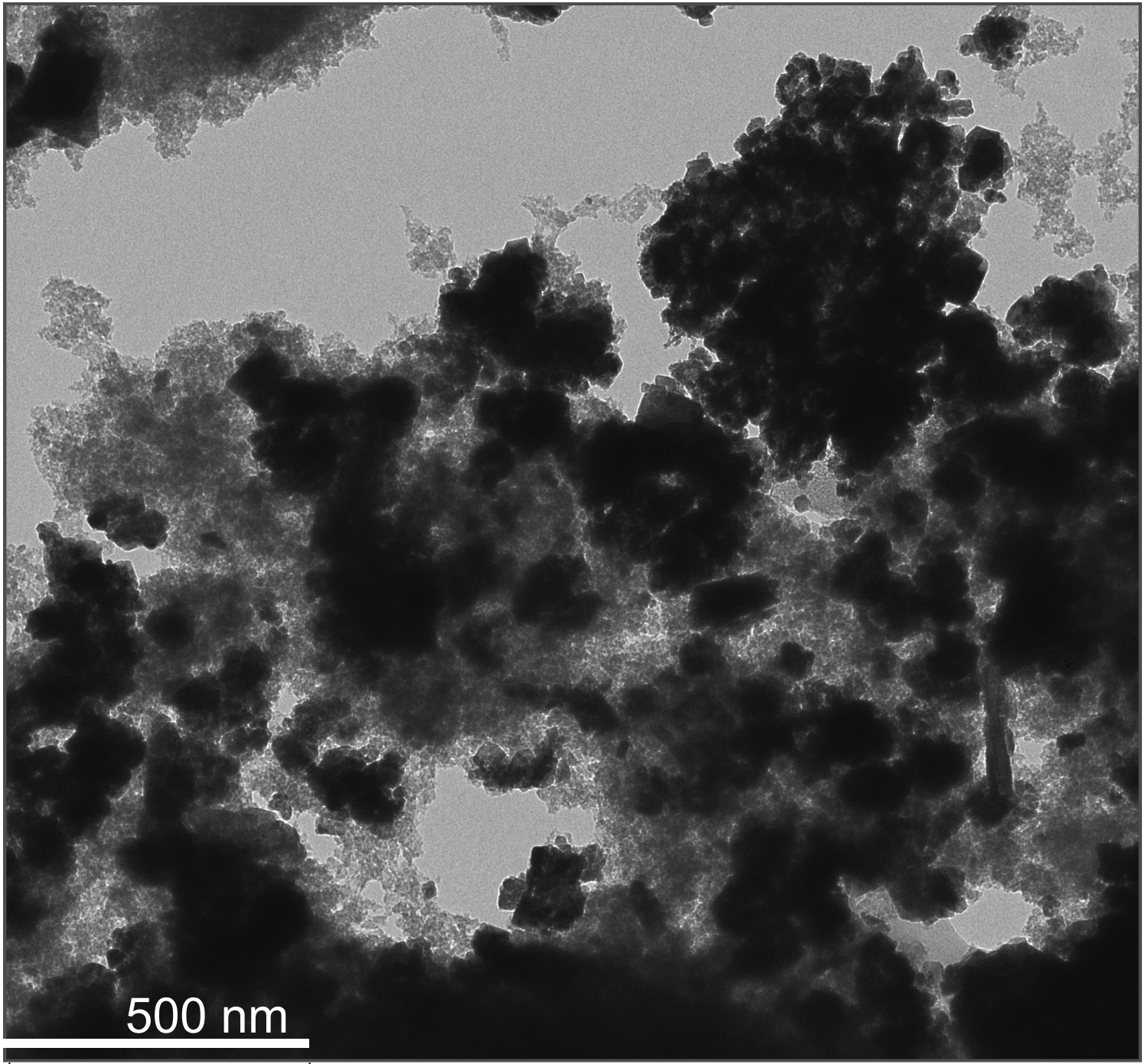




Toda RNIP nZVI







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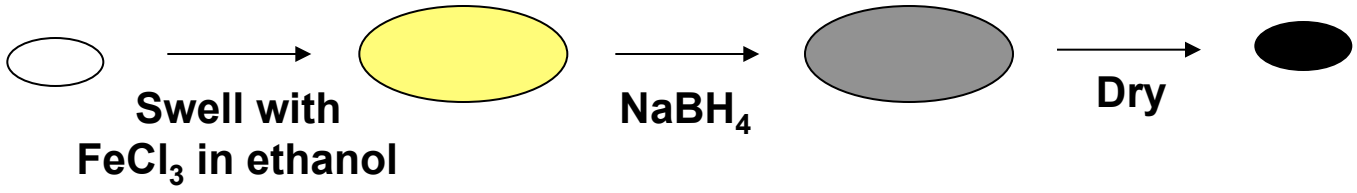
Mag (k) = 20.0
Mean = 168.2
Devi = 146.17

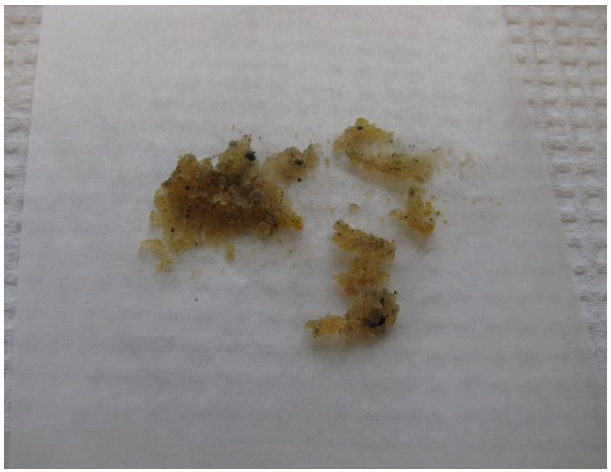
Groundwater Remediation: nZVI Composites

RNIP – addition before gelation
1000ppb → 7 ppb in 3-5 days

nZVI formation in glass



TEM: nZVI < 4 nm



Reactivity:
1000ppb → 0 ppb, 10 min

Pilot Testing: nZVI Composites

SOMS-nZVI(*RNIP*) materials

3 Pilot Tests in central Ohio

Approved by Ohio EPA
Army Corp of Engineers

Pilots run in conjunction with lab testing and matching samples run at independent labs.

Pilot Testing: nZVI Composites

Glass is ground into micron-sized particles

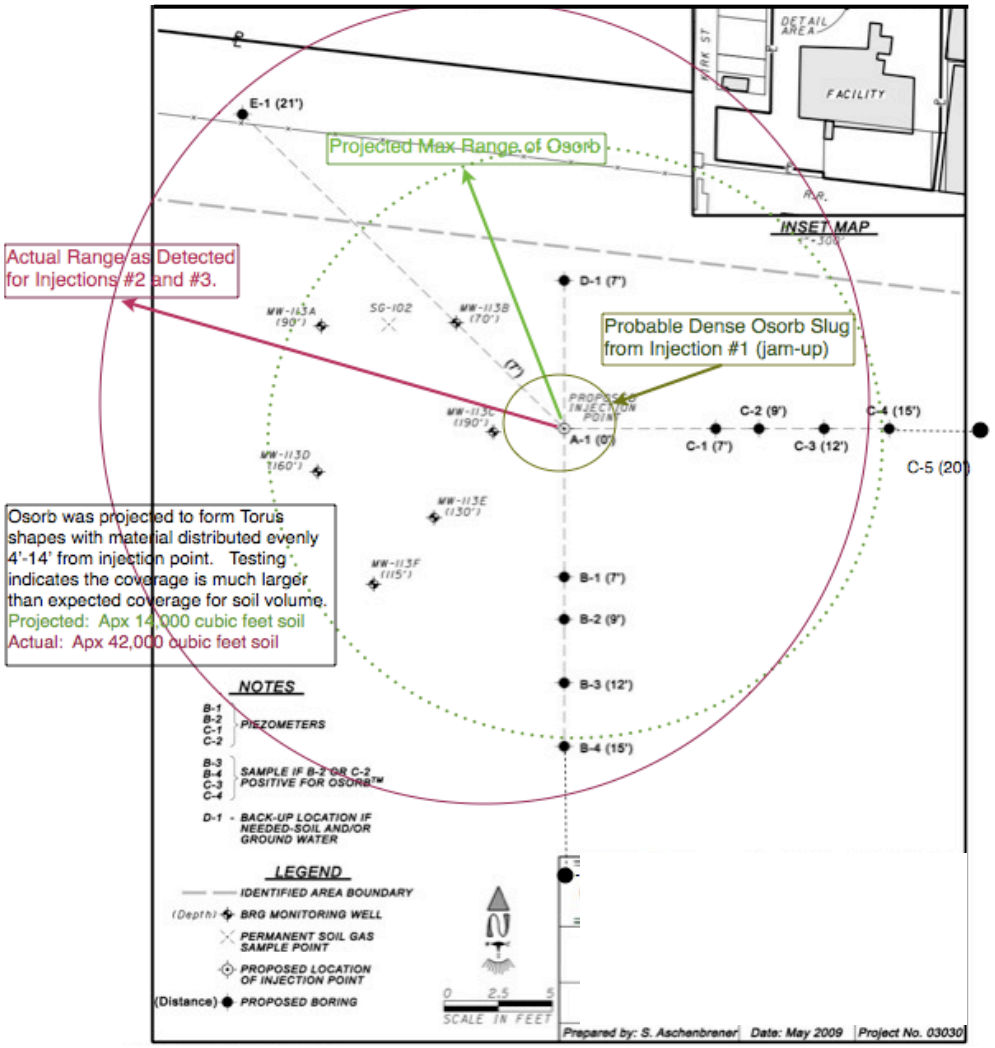
Slurry is made in water with surfactants
(sodium lauryl sulfate, polysorbate)

Sub-surface injection

Three different injection strategies have been used

Pilot Testing SOMS-nZVI (Phase I)

Central Ohio, 1200 ppb TCE 40'-120', Plume 3x1 miles.
Sand gravel aquifer, 6% fines, high flow 10-20 cm/day



Phase I:
20 kg SOMS-nZVI (500 g nZVI)
Single injection site
injected with citric acid and surfactant, tracer SOMS

GeoProbe injection

40-90 % reduction across 44,000ft^3

bounce back to 50% after 35 days (nZVI depletion)

Phase II, III underway, IV planning

Monitoring Well Results

	Well-Feet						
	113A-34’	113B-12’	C7-7’	C9-9’	B7-7’	B9-9	E1-21’
Hist.Avg**	1020	930					1100
7/20	980	900	510*	970	910	890	1050
7/23	695	780	340	474	295	500	780
7/28	580	770	320	261	270	249	720
8/3	835	323	180	220	249	230	600
8/20	820	320	210	98	238	100	597
9/3*	1058	670	370	390	220	340	650
9/20	925	710	325	210	180	280	590

ABS Materials calculated Nano-Iron should burn out apx 10/1/2009

Rebound expected and found:

12/10	1100	750	560	445	205	310	NS

Overall Best Reduction Detected at each MW 7/23-9/3

%	45%	66%	61%	91%	76%	88%	41%

*NWS Station in Coshocton records 17.59 inches of rain between 8/23 and 9/2 2009.

* Well C7’s pre-injection sample had head space and is lower than actual.

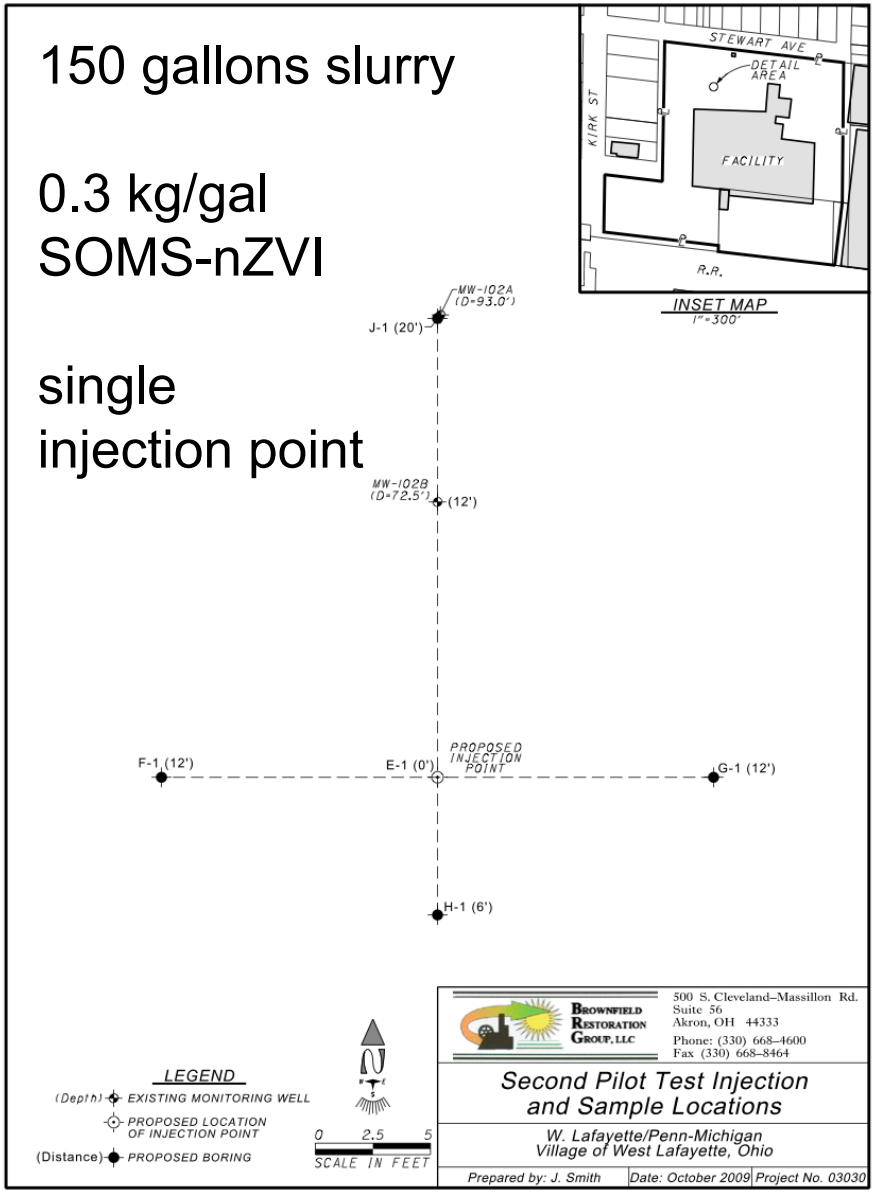
** Historical data provided from Ohio EPA records Aug 2003-June 2009

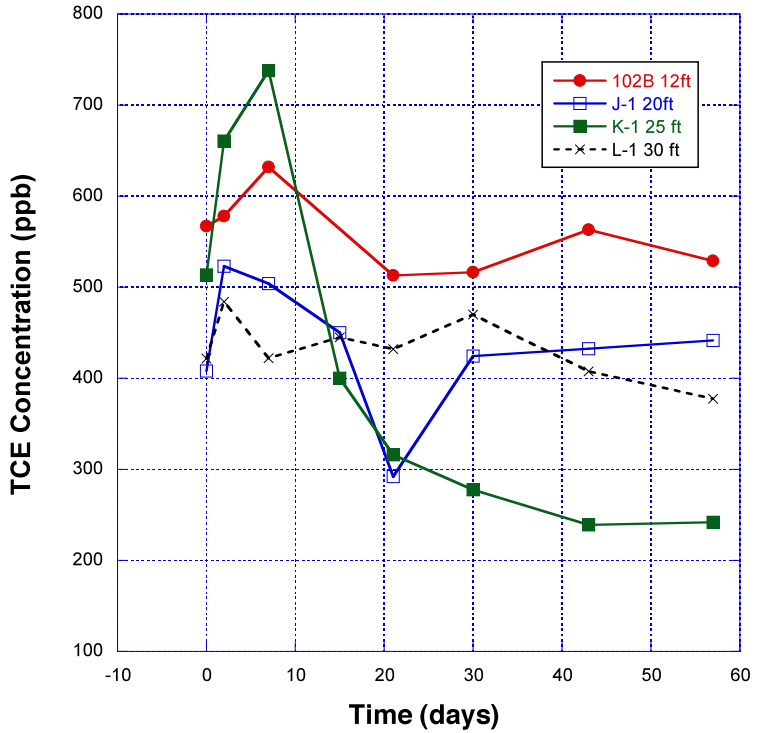
Phase II: Central Ohio

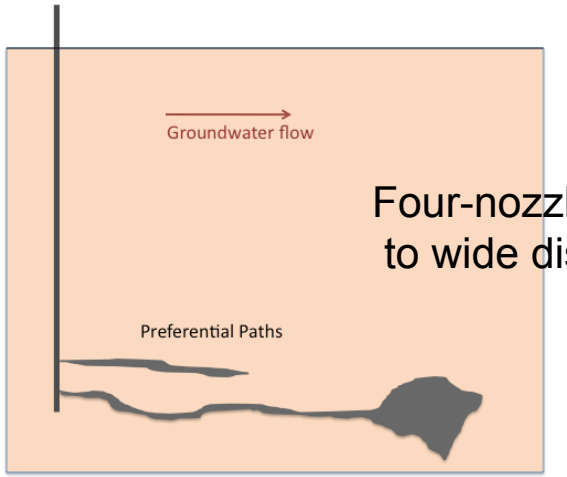
150 gallons slurry

0.3 kg/gal
SOMS-nZVI

single
injection point







Four-nozzle tool led to wide distribution

Ohio River Pilot

-Ironton, Ohio: complex hydrogeology near Ohio River
-120 ppb TCE, 20’ at factory site
-Three injections of SOMS-nZVI with tracer
-Extensive soil testing

Conclusions

(120ppb->70 ppb->?)
Tracer showed material traveled in preferred paths
seams within the soil system

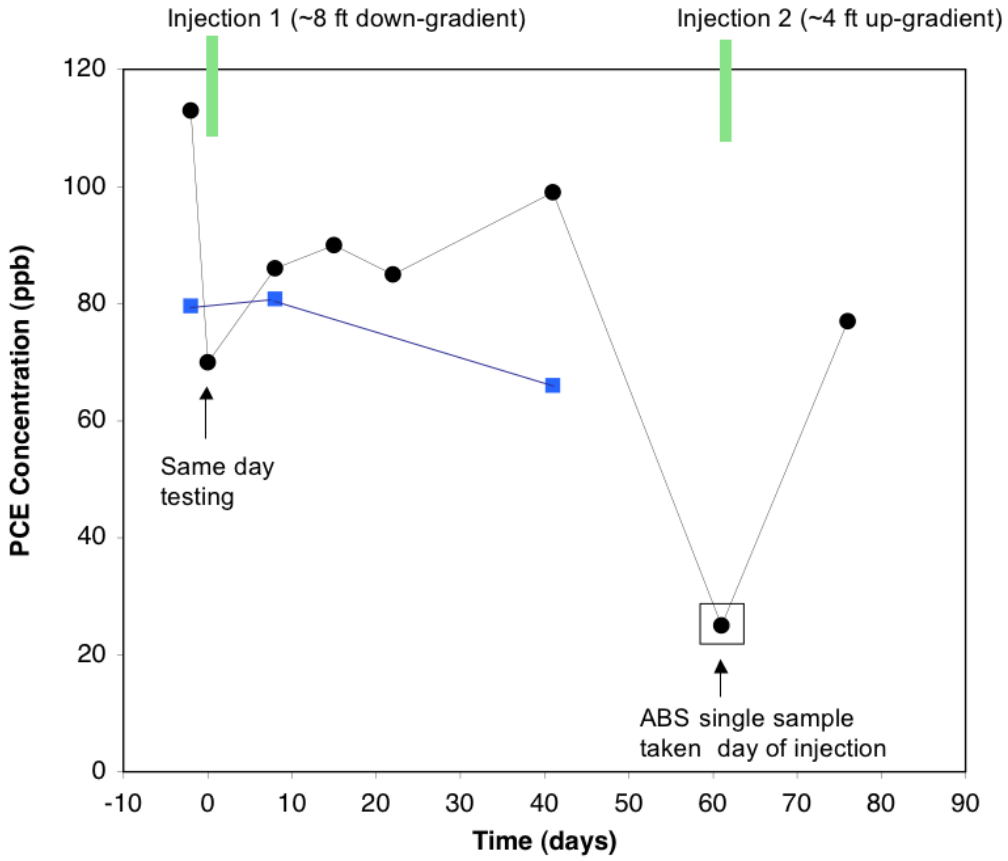
Dayton Pilot

Site: 120 ppb PCE, 7 ppb TCE from leaky tank
High perc, low flow, sand and gravel with clay

3 injections Iron-Osorb (15 kg each) up-gradient of a MW (~7ft)

Used multi-hole Injection tool

Soil sampled to count particles

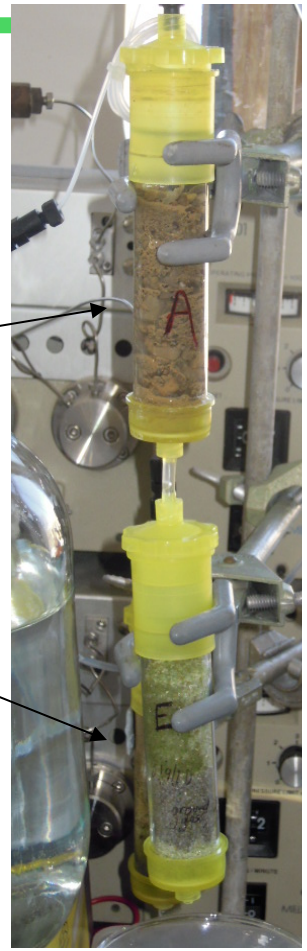


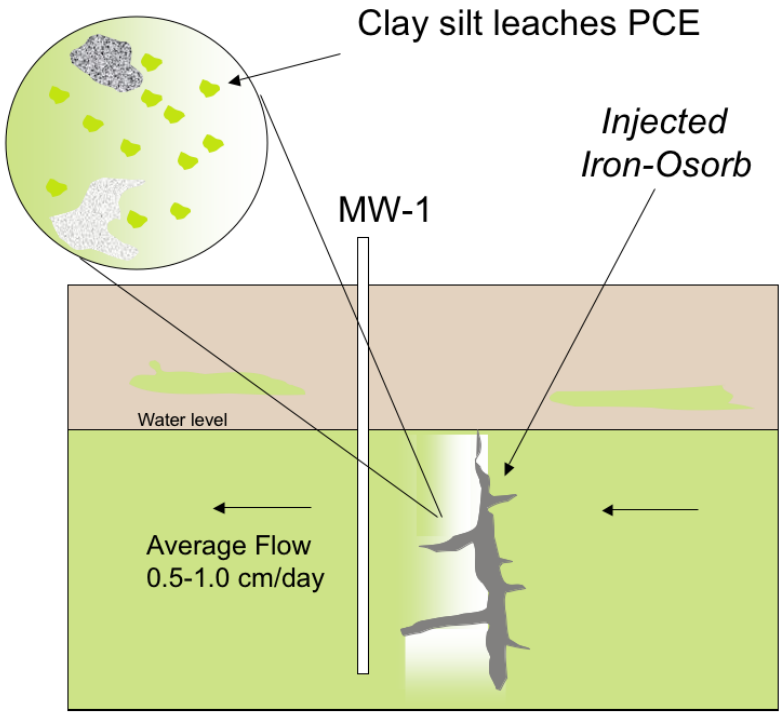
Dayton Pilot

-PCE contamination is controlled by clay fines

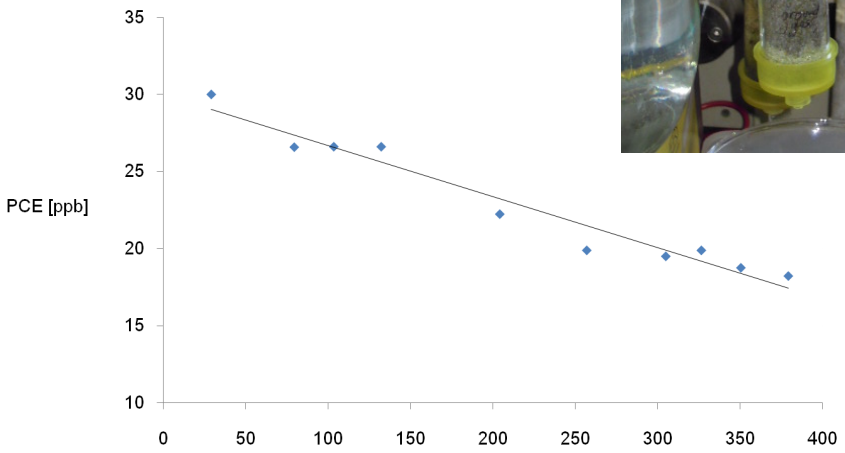
-Will require 10 years to extract PCE from soil at natural flow rate

Contaminated soil from pilot test site





SOMS-nZVI PRB
250 mg SOMS material
600 column volumes
12 mL/hr – 40 ppb PCE



Pilot Testing: Conclusions to Date

What we have learned

- When properly placed steep declines in TCE/PCE are seen
- A basic understanding of what types of injections work
- Material can be dispersed a long distance
- Must treat clay in addition to water

Future directions with upcoming projects

- Blends of high reactivity and low reactivity SOMS-nZVI
- Use of custom designed injection tools
- Hit <5ppb targets.
- Develop systems that are both work over short and long timescales.

Ex situ Remediation

Pump and treat

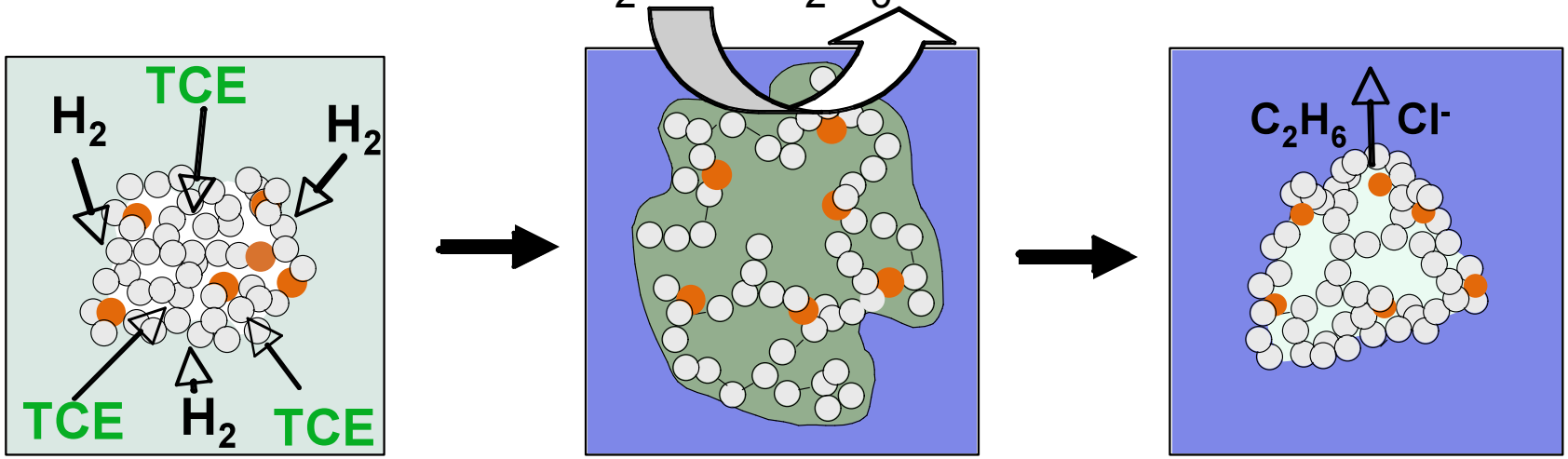
Air Sparging

Disadvantages:

- High energy input
- Maintenance cost
- Transfers contaminants water to air

SOMS-Pd *ex situ* Remediation

$$TCE + 4H_2 \rightarrow C_2H_6 + 3H^+ + 3Cl^-$$

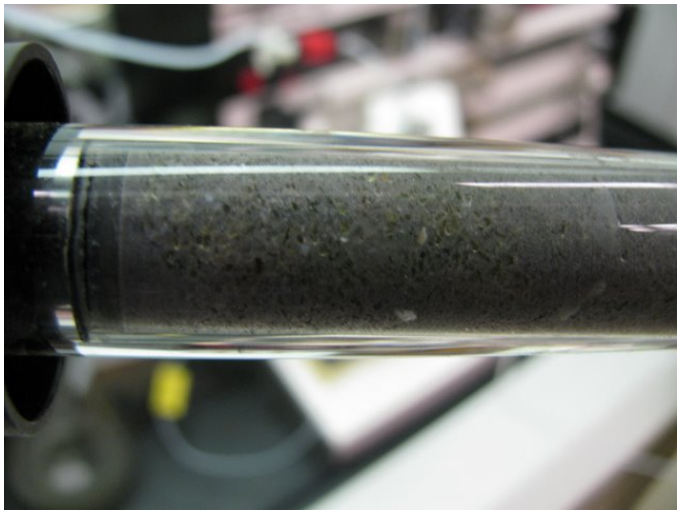


○ = Osorb crosslinked organosilica particle

● = Palladium catalyst

TCE contaminated water

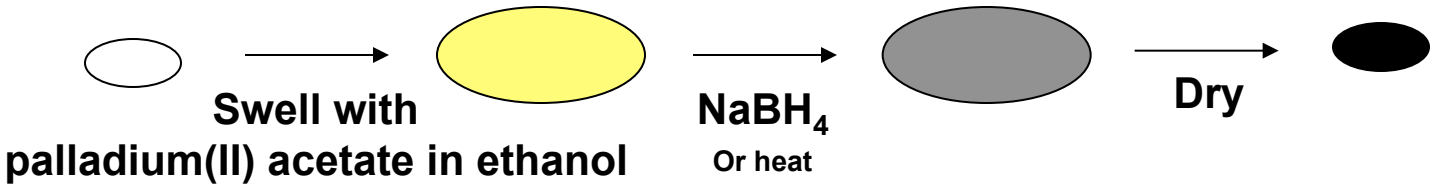
hydrogen



ethane

HCl (NaCl out)

SOMS-Pd *ex situ* Remediation

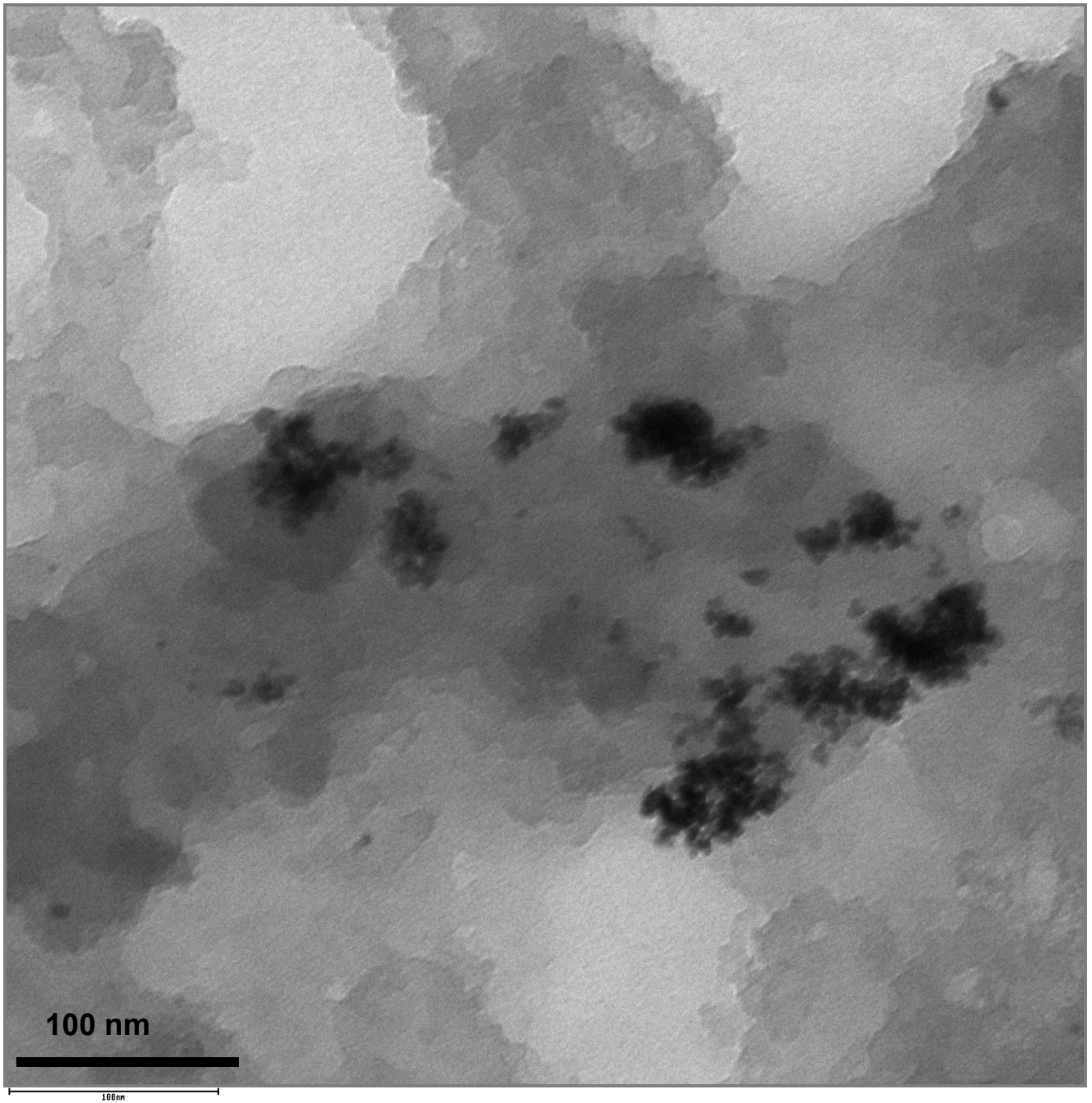


- Loading 1% Pd *w*/*w* to SOMS glass matrix

- TEM indicates particles size is ~5nm

-Swelling behavior is not impacted by addition of metal

-Metal particles do not leach from the glass matrix



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19-04-2010 09:56:51
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Mag (k) = 75.0
Mean = 379.8
Devi = 101.07

SOMS-Pd *ex situ* Remediation

40 bench scale columns tested to date

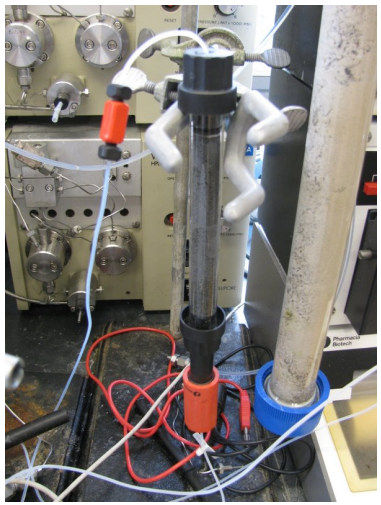
1. Effective to reduce TCE to no detect up to 24,000 ppb input

2. Not affected by 1 mM carbonate or 1 mM sulfate.
   Effectiveness decreases by 25% with sulfide laced water.

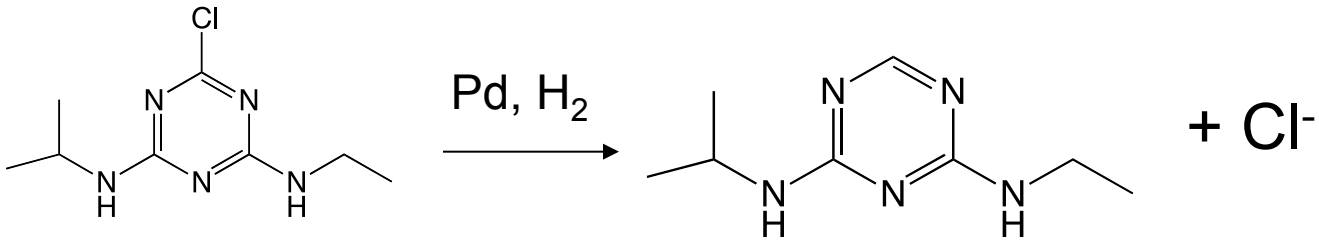
3. No fouling with precipitates (reducing environment).

4. 10 days continuous, 6,000 ppb water from pilot site to no detect

5. Good understanding of how much material for flow rate.



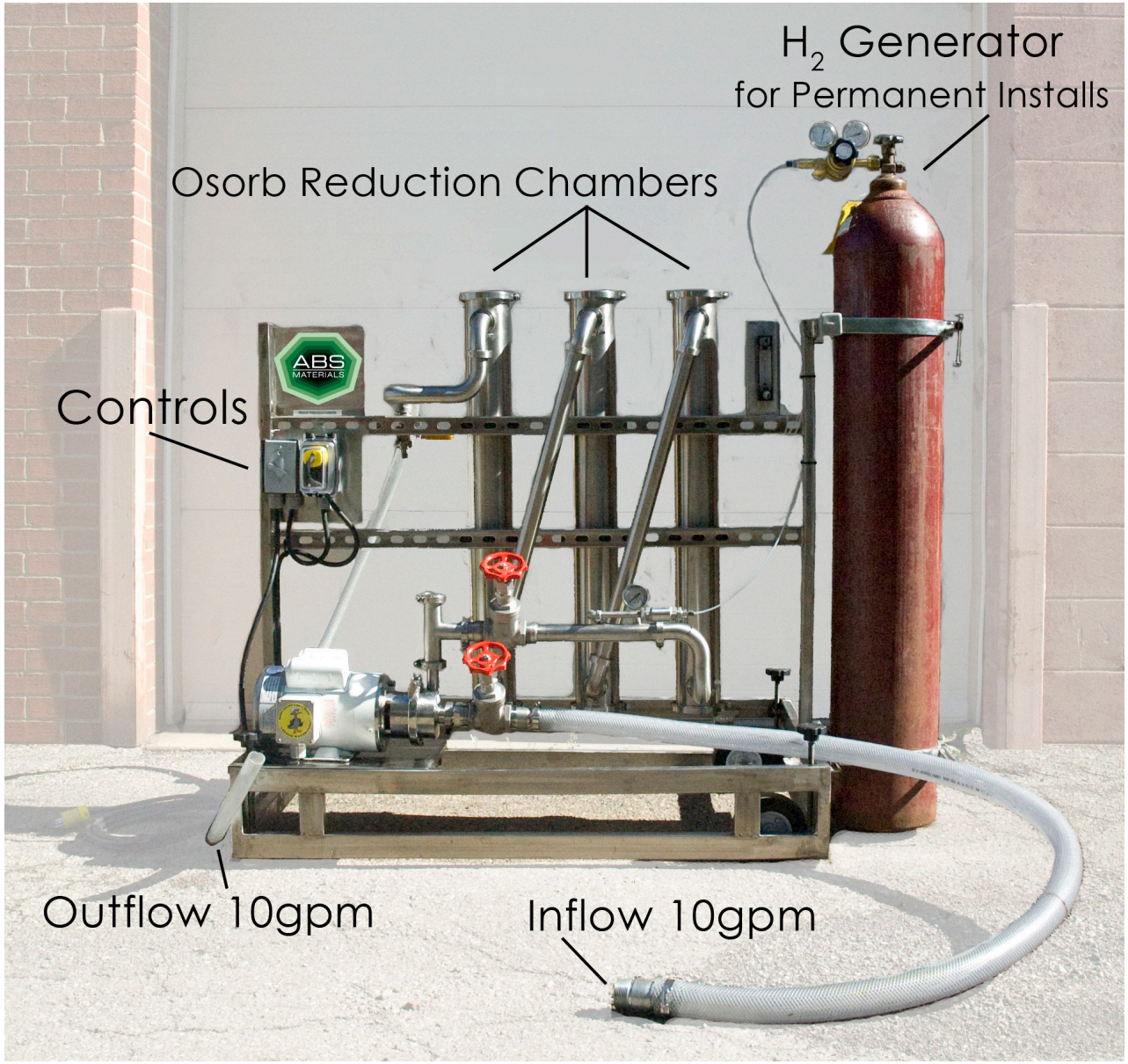
SOMS-Pd *ex situ* Remediation



Species Remediated by SOMS-Pd

Compound	Input	Outlet	Product species
TCE	6,000 ppb	no detect	ethane, H^+, Cl^-
PCE	6,000 ppb	no detect	ethane, H^+, Cl^-
atrazine	50 ppm	1 ppb	2,4-bis(ethylamine)-6-methyl-s-triazine
triclosan	10 ppm	no detect	2-phenoylphenol
trinitrotoluene	100 ppm	no detect	triaminotoluene
benzophenone	40 ppm	no detect	diphenylmethanol, diphenylmethane

SOMS-Pd "Osorb-Pd" *ex situ* Remediation



Columns filled with
2 kg total SOMS-Pd

SOMS-Pd *ex situ* Remediation Pilots

In house:
600 gal/hr, 1000 ppb -> no detect

Wooster well field:
600 gal/hr, 40 ppb TCE, 5 ppb DCE -> no detect

SW Ohio:
500 gal/hr, 5,500 ppb TCE (2 week pilot in progress)

Future pilots scheduled for: NY, KS, and WY.

Conclusions

- SOMS acts as a expandable high affinity, high capacity nano-sized beaker to capture organics from water.

- Nanoscale reactive metals and catalysts can be added

- Materials are produced at kg-ton scale

- Attractive mechanism to use nanoscale materials while encapsulating them in an animated, yet chemically inert matrix

- Pilot testing has done to prove usefulness at scale.

- Research into new composites and contaminants.

Acknowledgements

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Laura Underwood
Deanna Pickett
Laura West
Matthew Varga

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330-234-7999

Absorption of TCE

Concentration (ppm)	Mass SOMS/ Volume H_2O (%)	Percent Extraction§	Partition Coefficient /10^3	μg TCE abs/ mg SOMS
0.1	0.0025%	66 ± 1	78 ± 4	2.6
2.5	0.5%	82 ± 8*	1.1 ± 0.6	0.39
10	0.5%	82 ± 2	1.7 ± 1.1	1.8
25	0.5%	58 ± 8	0.3 ± 0.08	2.7
30	0.5%	87 ± 2	1.3 ± 0.2	5.7
50	0.5%	82 ± 4	0.7 ± 0.2	8.3
120	0.5%	92 ± 1	2.2 ± 0.2	24
200	0.5%	89 ± 3	1.8 ± 0.9	36
300	0.5%	87 ± 1	1.3 ± 0.2	51
650	0.5%	84 ± 1	1.3 ± 0.2	115
1200	0.5%	89 ± 5	1.7 ± 0.7	210
1200	0.1%	84 ± 3	5.8 ± 1.7	1010
1200	0.04%	74 ± 7	7.3 ± 2.3	2200

*Temperature= 25°C.

§ n=3 for all measurements