Objective: Use of Controlled Slow-Release Encapsulated Substrates to Enhance In-Situ Reductive Dechlorination Processes

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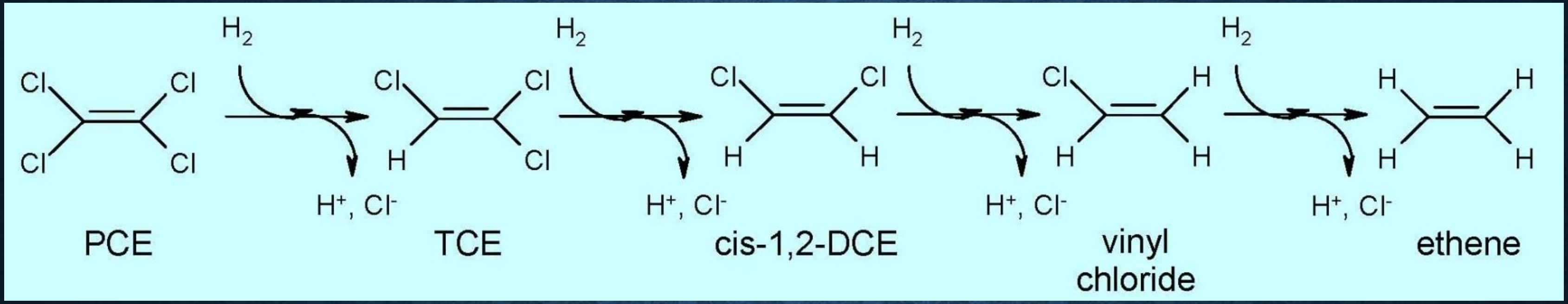
Anaerobic Reductive Dechlorination

- Occurs in the absence of oxygen
- The chlorinated solvent substitutes for oxygen in the physiology of the microorganisms carrying out the process
- The chlorinated compound is used as a terminal electron acceptor and one or more chlorine atoms are removed and replaced by hydrogen
- Dissolved hydrogen serves as an electron donor
- Common substrates that trigger dissolved hydrogen generation via fermentation include acetate, propionate, butyrate, glucose, lactate, formate, methanol, molasses, hydrogenated cottonseed oil beads, corn oil, coconut oil, soybean oil, and hydrogenated soybean

Anaerobic Reductive Dechlorination



- Sequential dechlorination mechanism
  - PCE > TCE > cis-1,2-DCE > Vinyl Chloride

Organic Hydrogen Donors

- Organic and carbonyl salts have been effectively used as organic hydrogen donors during anaerobic dechlorination process
- Calcium propionate has been found to be more effective than other electron donors that produce hydrogen necessary for dehalogenation
- The reason is that various groups of microorganisms compete for hydrogen, and that dehalogenating microorganisms can survive better than others at very low hydrogen concentrations.

Organic Hydrogen Donors

- Slug addition of compounds such as formate, ethanol, or glucose is not as effective for dehalogenation as propionate, due to the fact that they convert rapidly to hydrogen and acetate, and the latter is not

- The rapid conversion is a result of more favorable thermodynamics with respect to hydrogen formation

- The rapid conversion places hydrogen in a concentration range where methanogens and sulfate reducers can compete effectively with dehalogenators

Lipid Bilayer

- A lipid bilayer is the effective encapsulating mechanism
- A lipid bilayer is a thin polar membrane composed of two layers of fatty acids organized in two sheets
- It is typically 5-10 nm thick and surrounds all cells providing the cell membrane structure
- The lipid layer forms a continuous barrier around cells and provides a semipermeable interface between the interior and exterior of a cell and between compartments within the cell
- Although lipid bilayers are only a few nanometers in width, they are impermeable to most water-soluble (hydrophilic) molecules.

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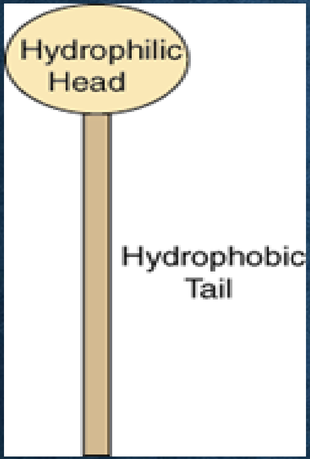
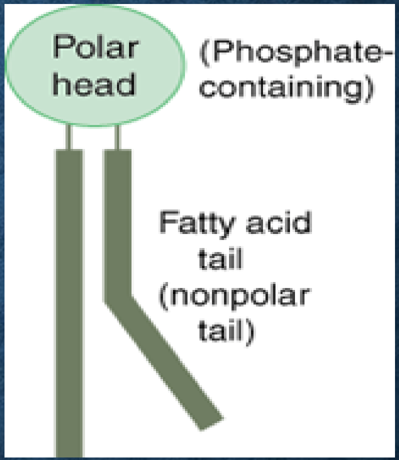
Lipid Bilayer



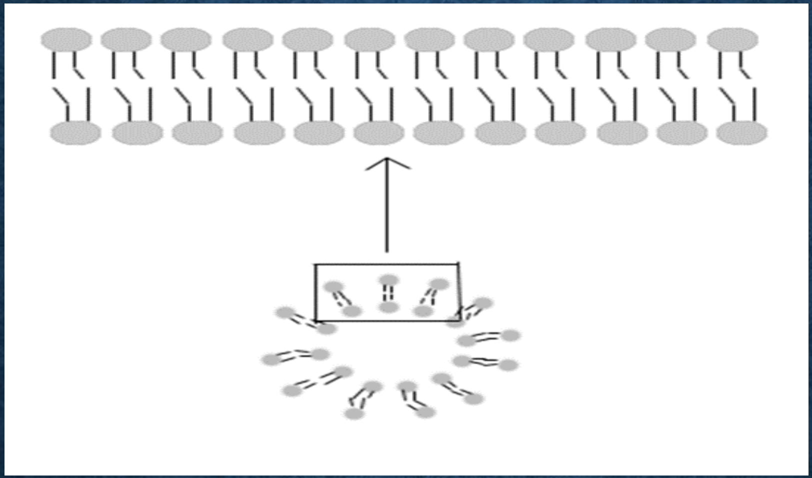
Basic Lipid Structure



Phospholipid Structure

- There are two important regions of a lipid that provide the structure of the lipid bilayer
- Each lipid molecule contains a hydrophilic region, also called a polar head region, and a hydrophobic, or nonpolar tail region
- The phospholipid molecule's polar head group contains a phosphate group and has two nonpolar fatty acid chain groups as its tail

Lipid Bilayer



Lipid Bilayer Structure

- Natural bilayers are usually composed of phospholipids
- The phospholipid bilayer is the two-layer membrane made up of molecules called phospholipids
- Phospholipids arrange themselves in two parallel layers, forming a membrane that can only be penetrated by certain substances.

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Encapsulated Hydrogen Donor

- Goal: Effective encapsulation of organic hydrogen donors at certain concentrations, and controllable releases of their content at the target site over a specific period of time
- Advantages
  - Encapsulation prevents the species from direct biological interactions and exposure to the environmental conditions
  - Encapsulating organic hydrogen donors can help control their efficiency by controlling their bio-distribution and kinetics of release.
  - Lipid-based substrates are biocompatible, biodegradable and can easily be produced by versatile processes

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Encapsulated Hydrogen Donor

- Lipid-based systems have been used for the encapsulation of a wide variety of various agents, while controlling their kinetics of release
- The internal physical state of the lipid core nanoparticles dramatically affects the encapsulation, while maintaining significant prolonged release rates.
- Due to the existence of the complicated structure of a potential lipid bi/multilayer electron donor, the release rates for the cations and anions in the solution is significantly enhanced and is much slower compared to single layer electron donors.

Encapsulated Hydrogen Donor

- During in-situ reductive dechlorination the lipid multilayer compound is present for a longer period of time in the environmental media
- The encapsulated material controls the amount of hydrogen provided during the process
- Experimental procedures were performed using encapsulated calcium propionate 80% in a distilled monoglyceride matrix.
- Monoglycerides are among the most promising polar lipid compounds since they form self-assembly structures in both lipid and aqueous phases

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Encapsulated & Regular Calcium Propionate Experiments

Table 1. Calcium release of ECP and RCP during a 2-day and a 14-day experiment

2 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	0	0.0
RCP	0.5	107	40	37.4
ECP	1	171	20	11.7
RCP	1	214	120	56.1
14 DAYS - CAPPED				
Material	Dosage (g/L)	Available calcium (mg/L)	Calcium in Solution (mg/L)	% release in solution
ECP	0.5	86	5	5.8
RCP	0.5	107	60	56.1
ECP	1	171	30	17.5
RCP	1	214	140	65.4

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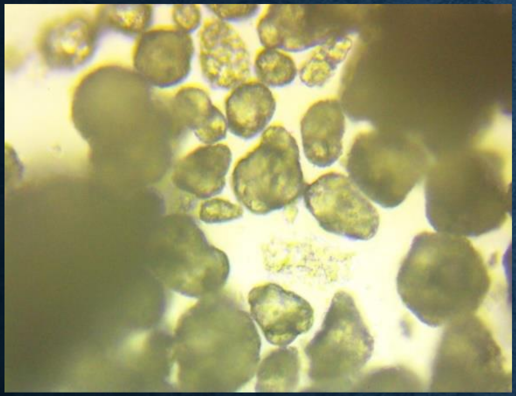
Encapsulated Calcium Propionate Microscope Pictures

DAY 1



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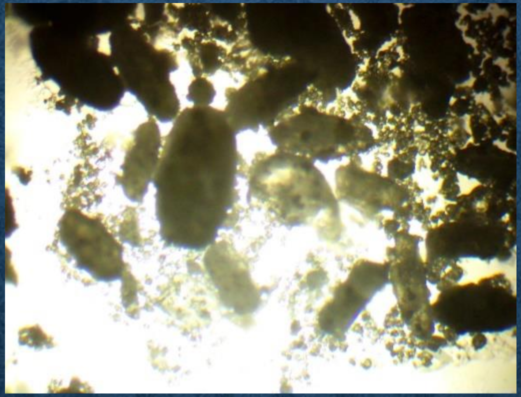

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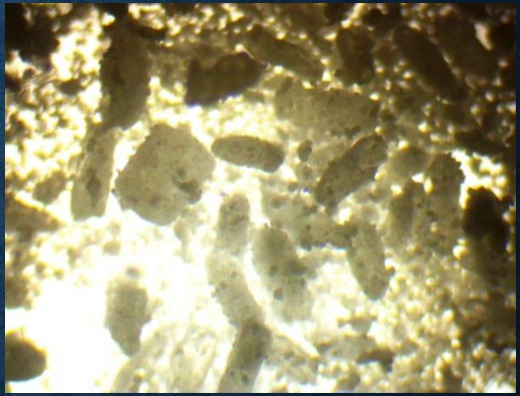

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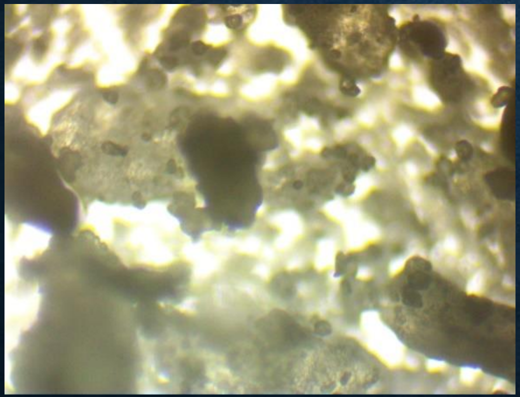

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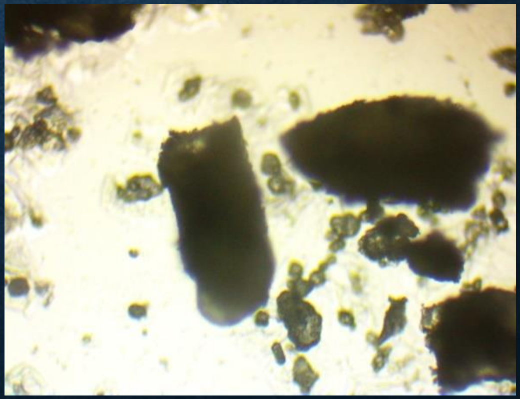

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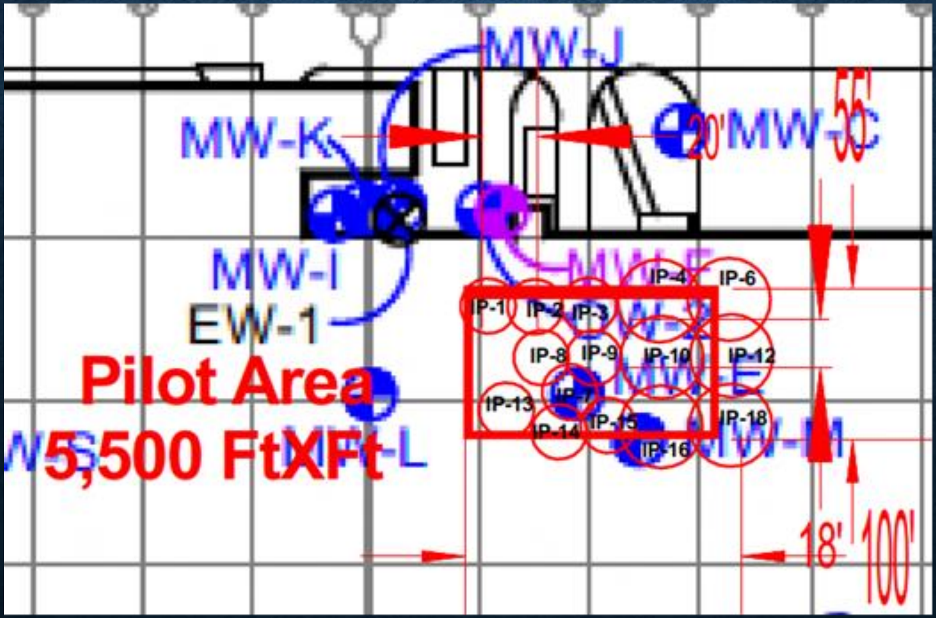
Remedial Event: 75% Regular Propionate – 25% Encapsulated Propionate

- In situ reductive dechlorination remedial event at a facility in Sydney, OH, in June 2016.
- Targeted contaminants PCE and daughter chlorinated products.
- Total treatment area of 5,500 square foot area, treating between 9 and 20 feet below ground surface.



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Remedial Design

Amendment Selection Considerations

- Longevity
- pH Control
- Minimization of Daughter Compound Formation
- Deliverability
- Speed of Reaction
- Initial Concentrations

IET 20' MOBILE INJECTION SYSTEM

Injection Feed Tank – Configuration

Feed Systems, Safety Systems, Compressed Gas Systems
All piping Welded Stainless Steel
Floors Coated in Chemical Resistant RinoLining

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Remedial Components

<u>The injection program consisted of a suspension/solution of</u>:

Calcium Propionate – Readily Soluble VFA source (propionic acid)

Sodium Sulfite – Reducing Agent/Oxygen Scavenger

Carbonyl ZVI – Abiotic Remedial Surface/pH control/Hydrogen Source

Hydrolyized Yeast and Kelps - Contains iron porphyrins, which in the presence of a reducing agent, catalyze the reductive dehalogenation of several chlorinated **methanes** and **ethanes**. Iron porphyrins are present in almost all living organisms, bound in complex molecules such as hemoglobin, cytochromes and catalases.

Vitamin B-2 - vitamin B2 (riboflavin) plays the critical role of a hydrogen mover in the mitochondrial energy equation. As fuel in the form of VFAs is broken down via oxidation, hydrogen atoms are metabolized or "broken off" and "picked up" by vitamin B2, which is reduced to form $NADH^+$.

Vitamin B-12 - Mediates the reductive dechlorination of carbon tetrachloride and tetrachloroethene. In these biological systems the rate-limiting step to complete dechlorination to ethylene is the last stage conversion of vinyl chloride. The rate of that process has been found to be significantly enhanced by the presence of vitamin B12, which acts as an electron carrier

Provect-IR® - Long term organic hydrogen source – limited iron contribution

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“Use of Controlled Slow-Release Encapsulated Substrates to Enhance In-Situ Reductive Dechlorination Processes”

Field and Geochemical Parameters Historic Data

Table 2. CVOC Data for MW-E (µg/L).

MW-E				
Sampling Date	**02/26/2016**	**06/17/2016**	**09/13/2016**	**01/18/2017**
Depth to Groundwater (ft)	10.82	11.15	11.81	11.21
D.O. (mg/L)	0.21	0.32	1.80	1.59
ORP (mV)	-72	-146.8	-119.0	-128.5
Conductance (mS/cm)	1.83	3.28	3.51	2.52
pH	6.66	6.29	6.46	6.55
Sulfate (m/L)	<5.0	<5.0	<5.0	<5.0
Total Iron (µg/L)	4.14	38.6	67.9	15.7
Dissolved Iron (µg/L)	<0.10	0.839	NA	0.228
Methane (µg/L)	0.116	0.068	0.174	2.38
Ethane (µg/L)	<0.013	0.0151	0.0155	0.0253
Ethene (µg/L)	<0.013	0.013	<0.013	0.0365
Acetic Acid (mg/L)	<1.0	32.0	82.0	22.0
Propionic Acid (mg/L)	<1.0	65.0	190	13.0
Butyric Acid (mg/L)	<1.0	27.0	85.0	7.2

CVOC Analytical Historic Data

Table 3. CVOC Data for MW-E (µg/L).

MW-E				
Sampling Date	**02/26/2016**	**06/17/2016**	**09/13/2016**	**01/18/2017**
PCE (µg/L)	26.1	<10	<50	<10
TCE (µg/L)	14,200	2,780	243	110
cis-1,2-DCE (µg/L)	30,400	31,300	25,300	12,550
trans-1,2-DCE (µg/L)	1,180	1,100	963	770
1,1-DCE (µg/L)	724	633	626	472
Vinyl Chloride	133	113	94.6	89.0
1,1,1-TCA (µg/L)	14,900	12,000	6,730	3,550
1,1,2-TCA (µg/L)	168	147	87.6	42.3
1,1-DCA (µg/L)	26,100	19,000	16,900	8,800
1,2-DCA (µg/L)	117	127	107	42.7

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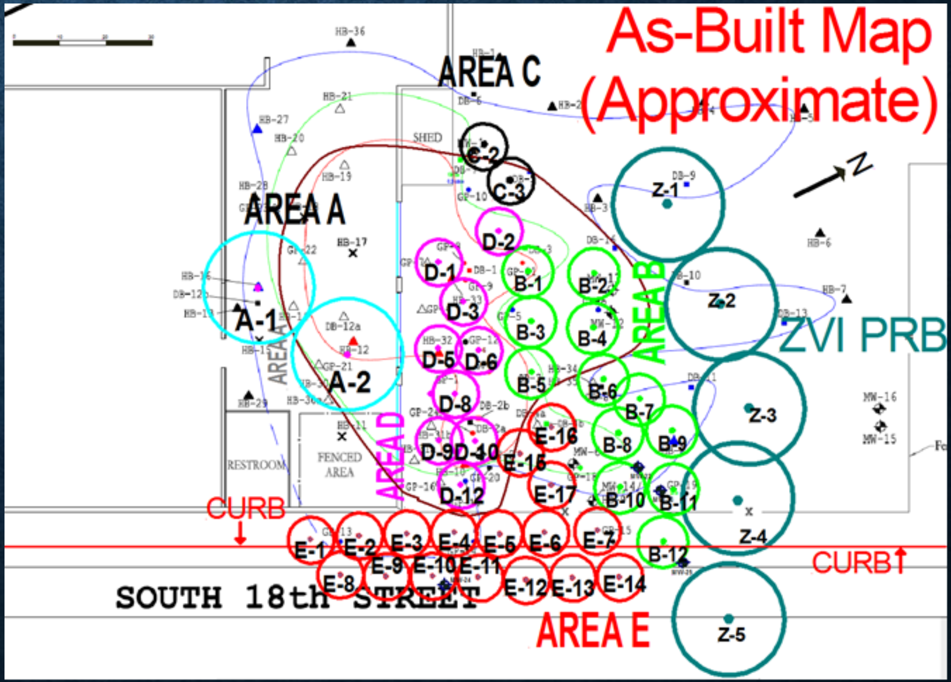
Remedial Event: 50% Regular Propionate – 50% Encapsulated Propionate

- In situ reductive dechlorination remedial event at a facility in East Orange, NJ, in November 2015.
- Targeted contaminants PCE and daughter chlorinated products.
- Total treatment area of 10,224 square foot area, treating between 11 and 28 feet below ground surface.



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Provect-IR® - Long term organic hydrogen source – limited iron contribution

EZVI – Emulsified Zero-Valent Iron

Field and Geochemical Parameters Historic Data

Table 4. CVOC Data for MW-1 (µg/L).

MW-1				
Sampling Date	05/13/2015	12/11/2015	02/29/2016	05/26/2016
Depth to Groundwater (ft)	20.52	23.33	24.00	23.01
D.O. (mg/L)	0.23	<0.01	<0.01	0.60
ORP (mV)	-71	-123	-210	-155
Conductivity (uohms/Con)	773	2,040	1,010	3,370
pH	5.87	8.69	7.50	7.20
Sulfate (mg/L)	ND	10.1	<10	<10
Total Iron (µg/L)	3,050	3,110	16,300	11,900
Methane (µg/L)	2,500	21.5	14.7	5,730
Ethane (µg/L)	13.1	1.6	1.2	178
Ethene (µg/L)	18.9	3.0	1.4	150
Acetic Acid (mg/L)	ND	164	203	148
Propionic Acid (mg/L)	ND	677	716	435

CVOC Analytical Historic Data

Table 5. CVOC Data for MW-1 (µg/L).

MW-1				
Sampling Date	05/13/2015	12/11/2015	02/29/2016	05/26/2016
TCE (µg/L)	259	3.7 J	31.2	<0.26
cis-1,2-DCE (µg/L)	5,480	1,430	54.6	51.6
Vinyl Chloride	1,750	1,530	197	149

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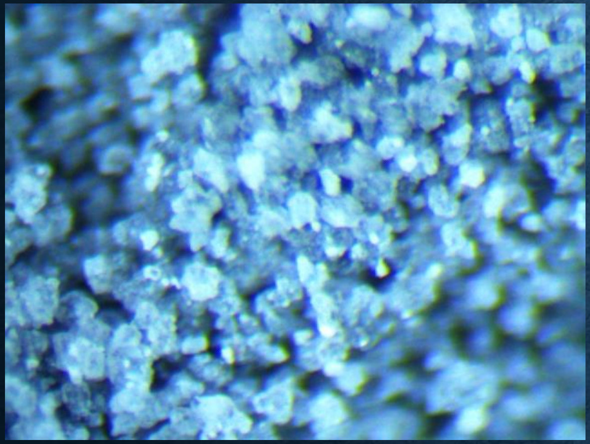
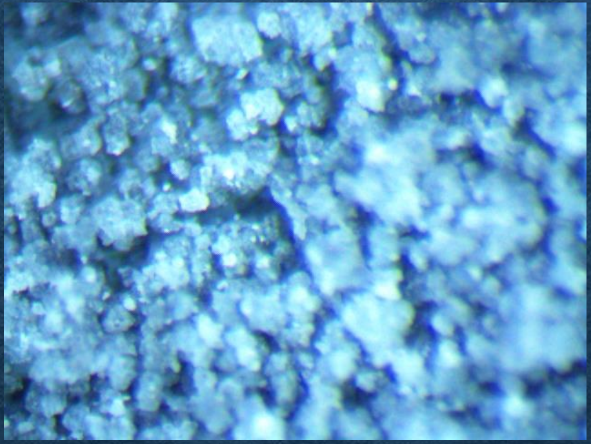
Encapsulated Iron (Dry) Microscope Pictures

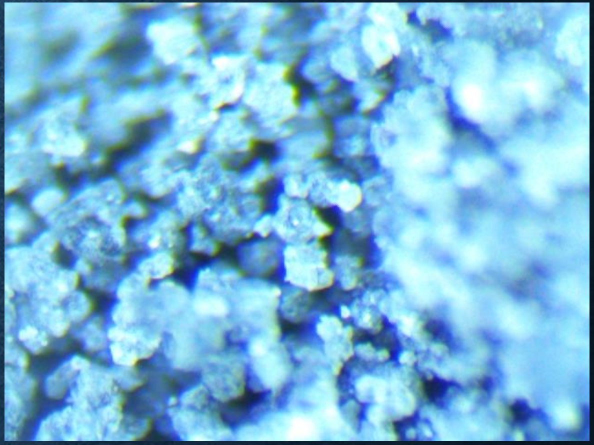
PICTURE 1



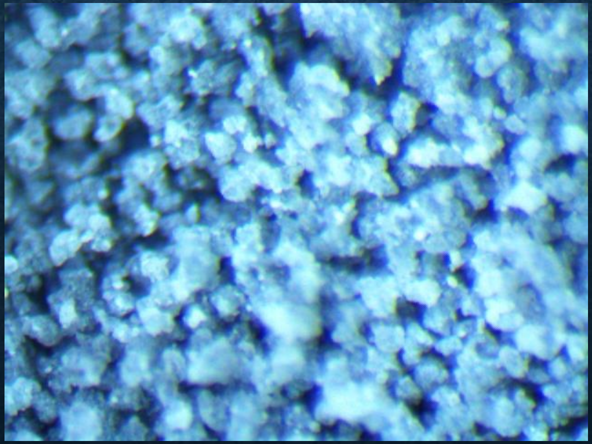
PICTURE 2



PICTURE 3



PICTURE 4



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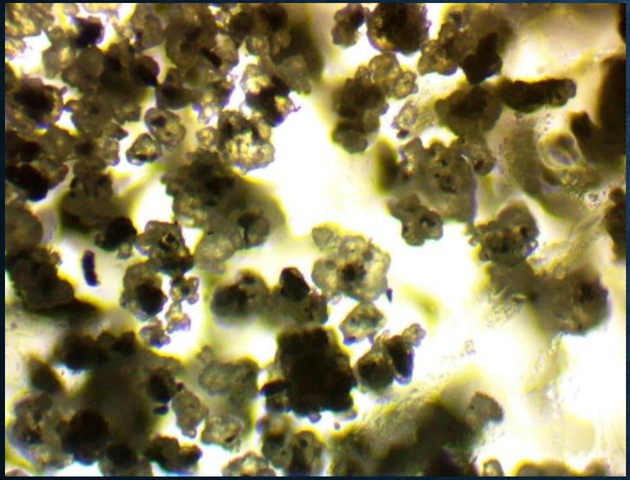
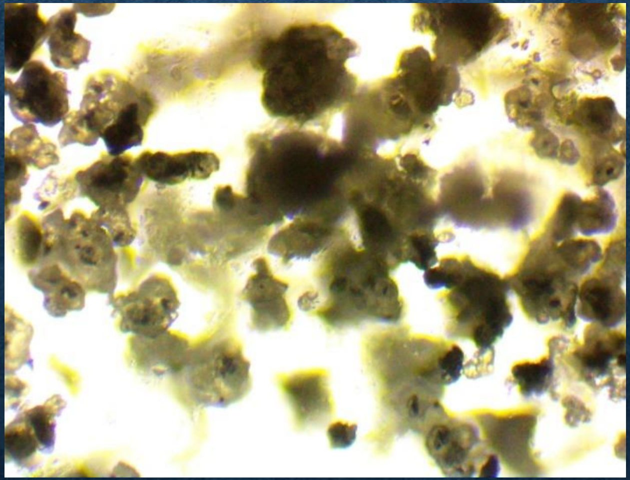
Encapsulated Iron (Water Solution) Microscope Pictures

DAY 1

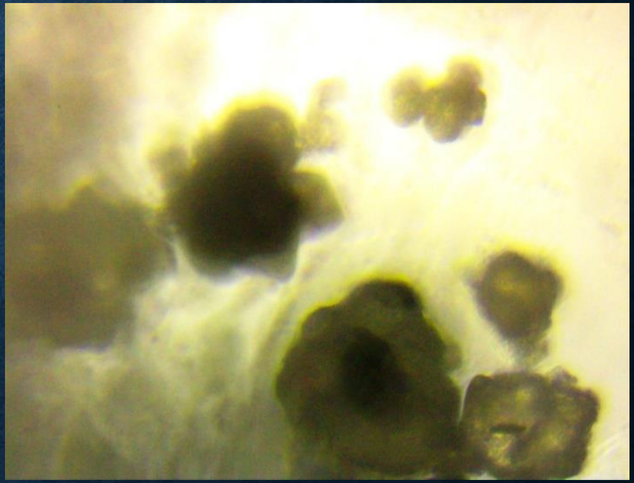
PICTURE 1



PICTURE 2



PICTURE 3



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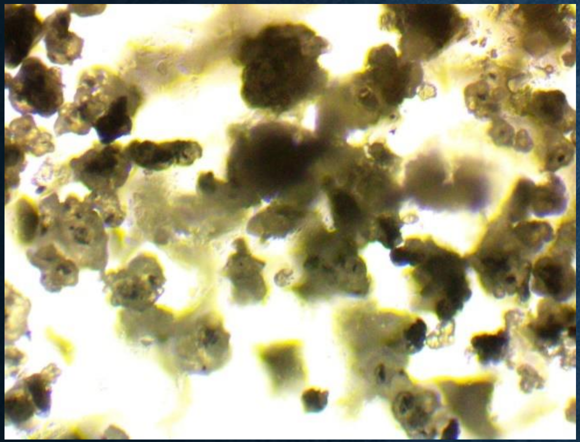
Encapsulated Iron (Water Solution) Microscope Pictures

DAY 1



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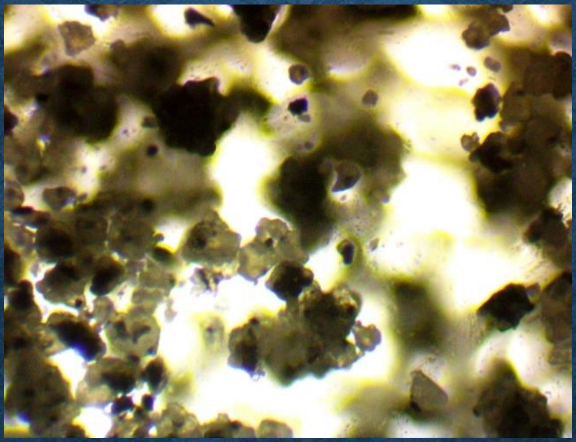

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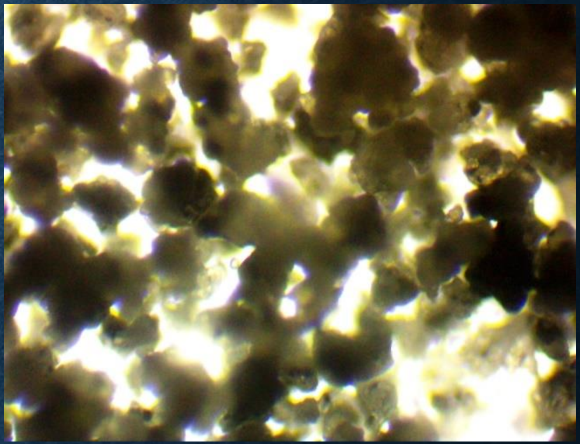

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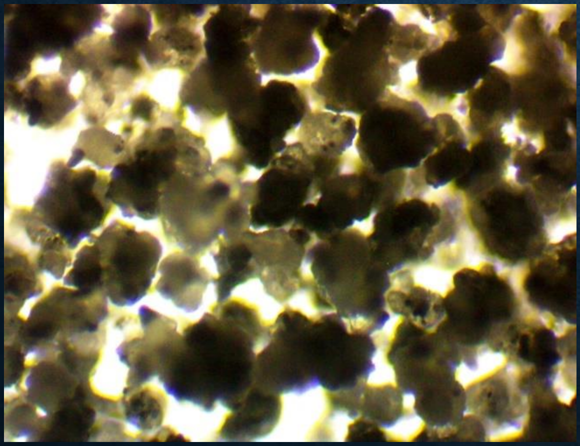
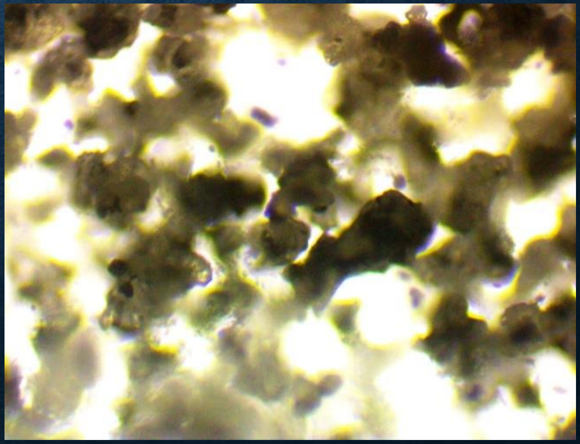


DAY 5



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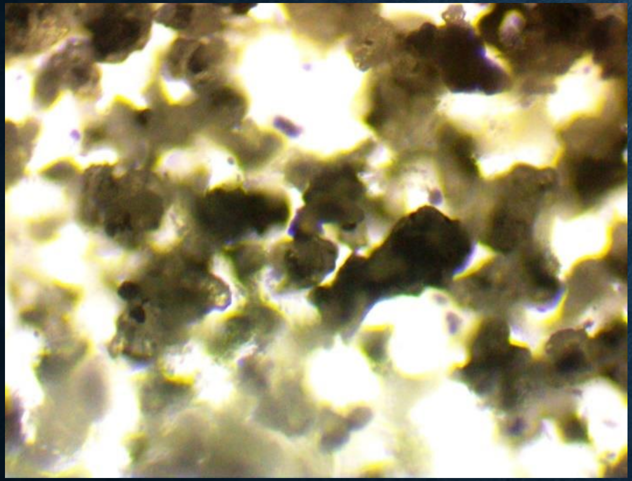
Encapsulated Iron (Water Solution) Microscope Pictures

DAY 5

PICTURE 1



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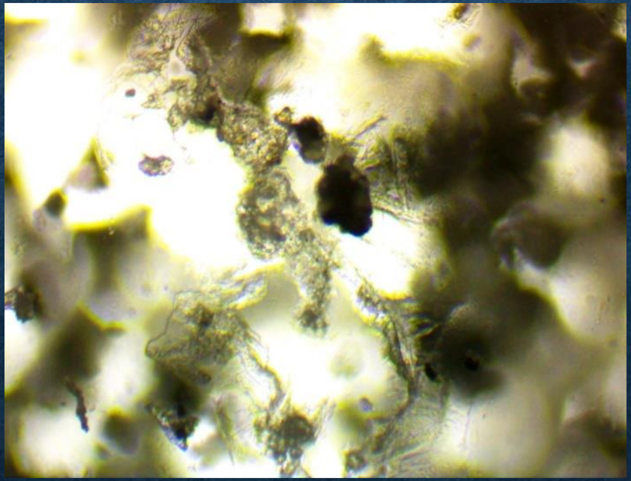

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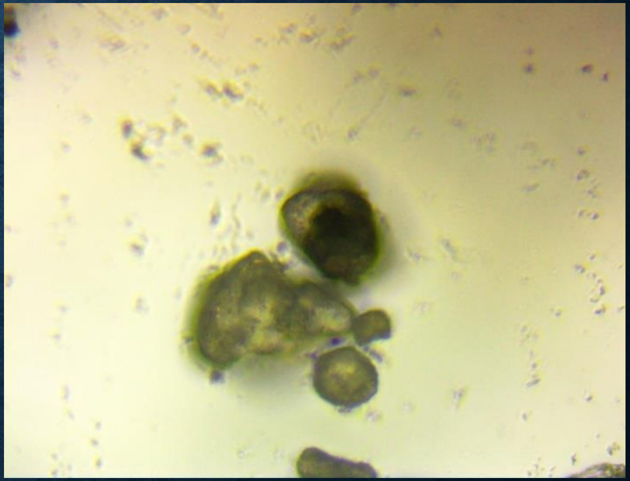

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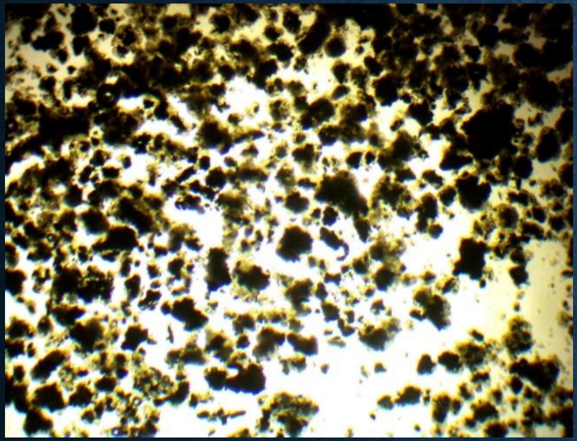
Encapsulated Iron (Vegetable Oil) Microscope Pictures

DAY 1



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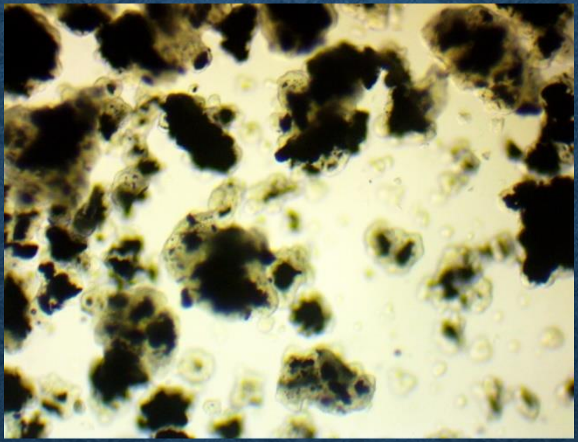
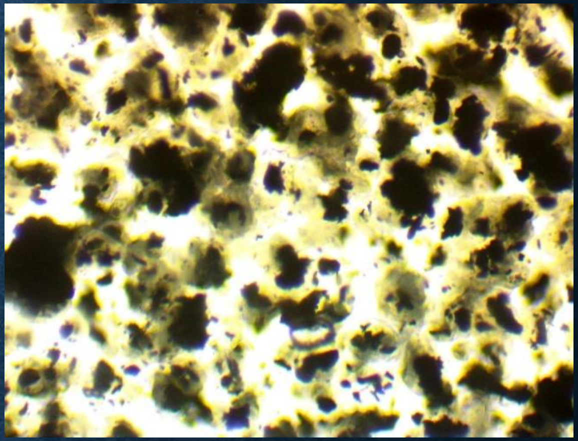
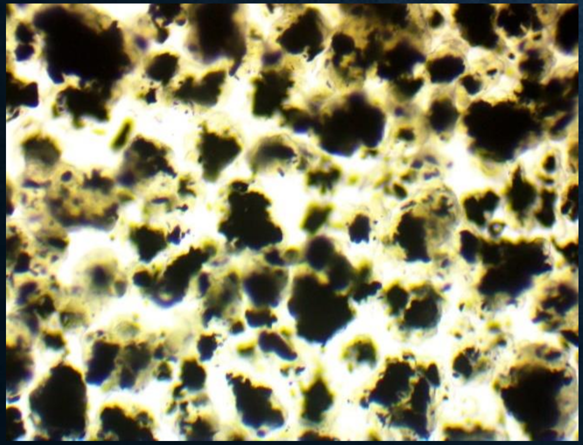


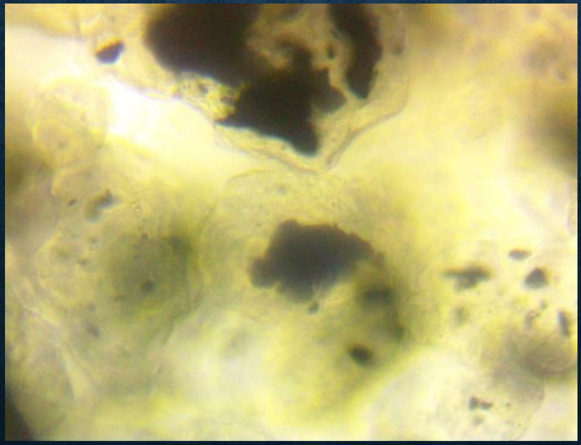
DAY 3



DAY 4 – Pic A



DAY 4 – Pic B



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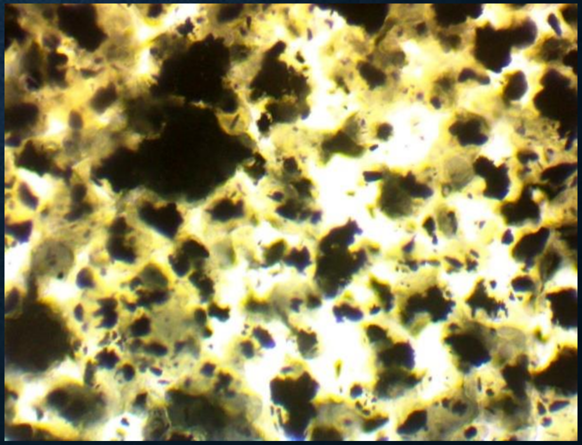

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Questions

Offices: Pipersville, PA; Forked River, NJ; Columbus, OH; Concord, NC