



# SUSTAINABLE REMEDIATION WITH GREEN CHEMISTRY

John Collins, Ph.D., George E. Hoag, Ph.D., Catherine R. Miceli, VeruTEK™ Technologies, Inc., Bloomfield, CT, USA

www.VeruTEK.com

## Sustainable Remediation Processes

**Sustainability** is a characteristic of a process or state that can be maintained at a certain level indefinitely

### Sustainable Remediation Goals

- Reduce CO<sub>2</sub> Emissions
- Reduce Energy Consumption
- Permanent *In Situ* Remedies
- Utilize Green Processes
- Maximize Use of Recycled Materials
- Minimize Secondary Impacts
  - Air Emissions
  - Transport & Landfilling
  - Community Impacts
- Restore Natural Resources
- Reclaim Land Resources

## VeruTEK Case Studies

- VeruTEK Technologies Treats NAPL Source Areas, Soils and Groundwater
- Developed New, Green Technologies to Clean Up the Environment
- Cheaper, Faster, Cleaner
- Lower CO<sub>2</sub> Footprint than Traditional Technologies

## Green Surfactants

- Biodegradable, Safe, Low Toxicity
- From Citrus Waste Products and Plant Oils
- Renewable Plant-Based
- Uses U.S. FDA Generally Recognized as Safe Compounds
- Solubilizes NAPLs in a Controlled Way

## Surfactant Enhanced In Situ Chemical Oxidation (S-ISCO™)

Developed to Overcome the Limitations of ISCO in Treating LNAPL and DNAPL Contaminated Sites

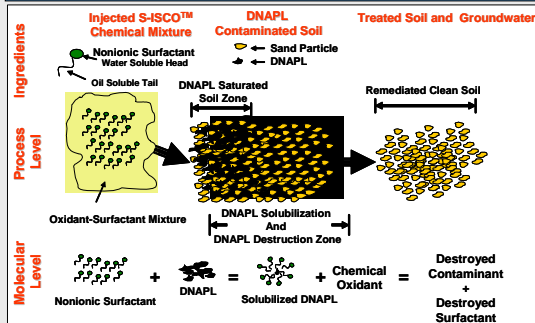
### Conceptual Model for S-ISCO™ of NAPLs

- Increase NAPL COC Solubility with either Cosolvent/Surfactant Mixtures or Surfactants Alone
- Apply Chemical Oxidation to Destroy Dissolved COCs *In Situ*
- As Rate of Solubilization Increases, then Rate of COC Destruction Increases – when oxidant is present



- "If You are Washing Oil-Stained Clothes, Would You Use Bleach Alone or Detergent and Bleach?"

## S-ISCO™ Technology



## Sustainable S-ISCO™

Reduce CO <sub>2</sub> Emissions	Alkaline Persulfate Sequesters CO <sub>2</sub> Generated from Mineralization
Reduce Energy Consumption	FMC's Persulfate Made Using Hydroelectric Power – Renewal Energy Source
Permanent <i>In Situ</i> Remedies	Permanent and <i>In Situ</i>
Utilize Green Processes	Uses Citrus and Plant Extracts as Surfactants
Maximize Use of Recycled Materials	Citrus Extract from a Fruit Juice Waste – Plant Materials are Renewal Resources
Minimize Secondary Impacts	- Air Emissions Incomparably Lower than Excavation, Thermal or Stabilization - Transport & Landfilling – No Waste Transport or Landfilling - Community Impacts – No Disruption to Community
Restore Natural Resources	Yes
Reclaim Land Resources	Yes

## S-ISCO™ with DNAPLs

### MGP DNAPL



Dissolved DNAPL

DNAPL

MGP DNAPL Dyed with Sudan IV and Near Complete Dissolution in VeruSOL-3™

DNAPL is from a Former Manufactured Gas Plant Site

### Chlorinated Solvent DNAPL

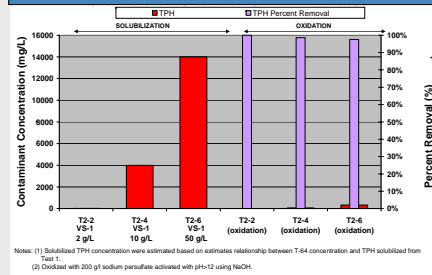


Dissolved DNAPL

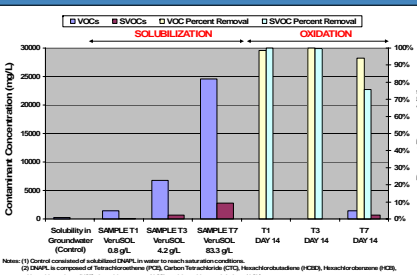
DNAPL

Chlorinated Solvent DNAPL dyed with Sudan IV and Complete Dissolution in VeruSOL-3™

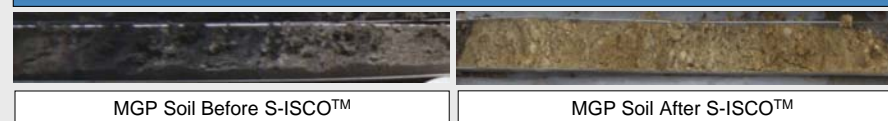
### Solubilization and Oxidation of MGP DNAPL



### Solubilization and Oxidation of Cl- DNAPL



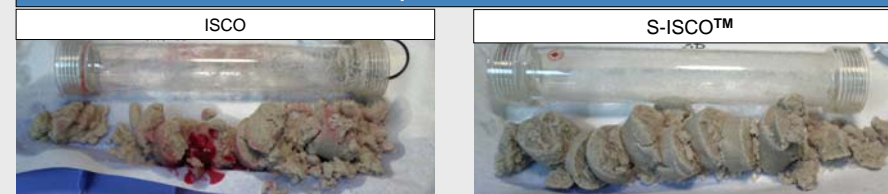
### S-ISCO™ Before and After



MGP Soil Before S-ISCO™

MGP Soil After S-ISCO™

### TCE Column Experiments ISCO vs. S-ISCO™



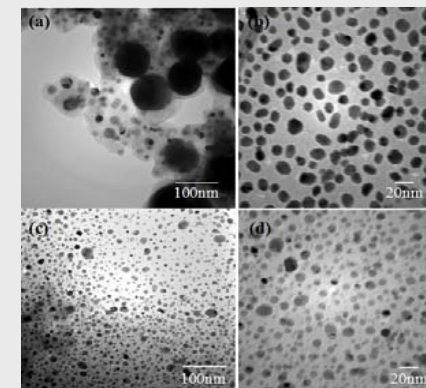
## Summary S-ISCO™ Remedy

- USFDA Generally Recognized as Safe Cosolvents and Surfactants Can Readily Dissolve NAPLs in a Controlled Manner
- Surfactant – Cosolvent Dissolved or Emulsified NAPL COCs Can Be Readily Oxidized
- With Proper Lab Tests and Design Surfactant - Oxidant Mixtures Coelute with: Conductivity > Persulfate > IFT
- Coupling Enhanced Solubilization With ISCO is a Powerful Tool in Remediation of NAPL Sites

## Green Synthesized Nanomaterials

- Cooperative Research and Development Agreement with USEPA Green Chemistry Program and VeruTEK to Develop Remediation and Treatment Applications
- For Biotic and Abiotic Reduction Processes and Use as Oxidation Catalysts
- Designer Solutions Using Natural Renewable Products and Recycled Natural Products
- Focus on In Situ, Wastewater and Disinfection Processes Including Biological Agents
- USEPA Collaborators –Rajender S. Varma, Ph.D and Mallikarjuna N. Nadagouda, Ph.D. - National Risk Management Research Laboratory Sustainable Technology Division, Green Chemistry and Engineering Group

## Green Synthesis of Nanometal Particles TEM Images of Ag and Pd Nanoparticles\*



(a-b) Ag nanoparticles made from coffee (a) and tea (b) extracts (c-d) Pd nanoparticles made from coffee (c) and tea (d) extracts

Notes: \* Patent Pending by U.S. EPA and VeruTEK. 400 mg of coffee powder was dissolved in 15 mL of water. 2 mL of 0.1 N AgNO<sub>3</sub> (AgNO<sub>3</sub>, Aldrich, 99%) was mixed with 10 mL of coffee extract and shaken to ensure thorough mixing. 1 gm of tea powder (was boiled in 50 mL of water and filtered through a 25µ Teflon filter). A similar procedure was repeated for Ag and Pd nanoparticles (using 0.1 N PdCl<sub>2</sub>, Aldrich, 99%).

## Green Tea Manufacture of Nanoscale Zero Valent Iron Particles with Ferric Chloride and Ferric Nitrate

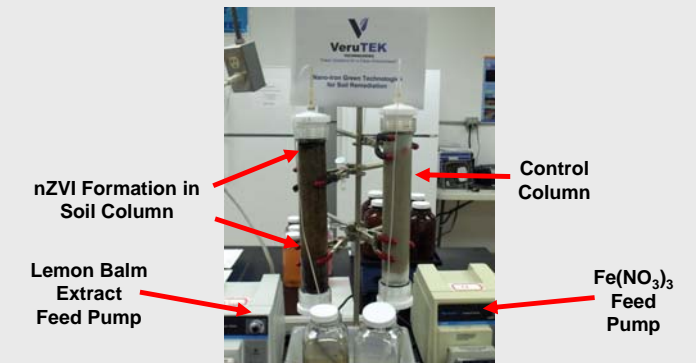


Formation of Nanoscale Zero Valent Iron Green Tea Extract with Ferric Chloride

Formation of Nanoscale Zero Valent Iron Green Tea Extract with Ferric Nitrate

Notes: Green Tea extract made by heating a 20 g/L solution of Dry Chumnee Tea for 20 minutes at 90°C then filtering with paper filter. Green Tea extract added to 0.1 M Ferric solutions on a 1:2 (v/v) basis.

## In Situ Formation of Nanoparticle Zero Valent Iron in Soils with Lemon Balm Extract with Fe(NO<sub>3</sub>)<sub>3</sub>



nZVI Formation in Soil Column  
Lemon Balm Extract Feed Pump

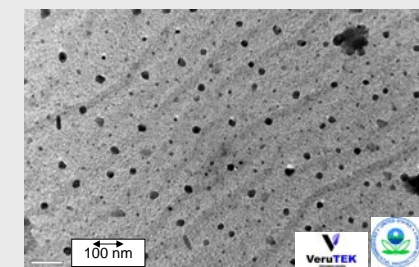
Control Column

Fe(NO<sub>3</sub>)<sub>3</sub> Feed Pump

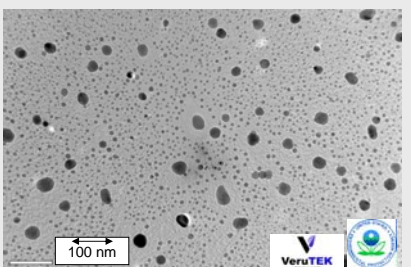
## In Situ Generated Nanoparticle Zero Valent Iron in Effluent of Soil Column



## Green Tea Synthesized Zero Valent Iron Nanoparticles with 0.1 M Ferric Chloride with 0 g/L VeruSOL™.3



## Green Tea Synthesized Zero Valent Iron Nanoparticles with 0.1 M Fe(III)-EDTA with 5 g/L VeruSOL™.3



## Summary Green Synthesis of Nanometal Particles\*

- Nanoparticle Metal Structures can be Generated with Polyphenolic and Other Plant Extract Compounds Using Metal Salts
  - Does Not Use Toxic Ingredients or Generate of Toxic or Hazardous Wastes
  - Plant Extracts can Include Coffee, Tea, Selected Herbs, Tree Leaves and Grains
  - Metal Chelates can be Used as Dissolved Metal Source – Enables Use of Indigenous Metal Sources
  - Nanometals can be Made in the Presence of VeruSOL™ – VeruTEK's USFDA GRAS Cosolvent Surfactant Mixture
  - Disinfection and Chemical Destruction Applications Include Use of Silver and Gold Nanoparticles
  - Zero Valent Iron Nanoparticles and Bimetallic Additions have Widespread Use in Various Environmental Applications
- \* Patent Pending – VeruTEK™ and USEPA