**Direct Sensing Subsurface Investigation with** 





#### Matt Ednie ZEBRA Environmental

#### 

#### We're Not Your Typical Driller...We Carry a Different Tool Box

ZEBRA provides the widest range of Geoprobe<sup>®</sup>/ DPT services available anywhere, including a tool box full of **Injection** and **Direct Sensing** systems. For the past 20 years, ZEBRA has given you the best tools to investigate subsurface conditions at your site. Now we offer more options with the addition of the

**NEW** combined MIP & HPT probe = **MiHPT and the UVOST**<sup>®</sup> system.



ZEBRA is now offering UVOST<sup>®</sup> services along with **MIP**, **HPT**, **MiHPT**, **EC**, **CPT**, **MIP/CPT** ZEBRA offers the most complete array of **Direct Sensing** and **Optical Screening Tool** systems available on the **East Coast**.



High Resolution Site Characterization Applying Next Generation Tools

#### **Strategies for Cost Effective Site Characterization**

- Multiple lines of evidence (data) Geologic Hydrogeologic Contaminant
- High density data sets plan view and vertical
- Adaptive, flexible, dynamic..... sampling plan with clear DQOs
- On-site, real-time analysis
- On-site, real-time decisions
- Evolving conceptual site model

### ZEBRA ZEBRA 7822 UNIT



### ZEBRA Real Time Benefits

- Make decisions in the field.
- Collect higher density of data.
- Use of screening data to select laboratory samples.
- Accelerate project schedules
- Reduce overall project costs
- Improve project outcomes



# ZEBRA ENVIRONMENTAL UVOST

- Laser Induced Fluorescence (LIF) investigation allows for rapid and highly adaptable assessment of NAPL impacts.
- Technology is based on fluorescent properties of polyaromatic hydrocarbon (PAH) compounds that are commonly found in gasoline and fuel oil.
- Can be used to delineate/define the extent of a wide range of petroleum products.
- Allows for very accurate vertical and horizontal characterization of NAPL impacts.



### 

LIF Detects PAH-containing NAPLs (Source Material)

Using UV excitation

- Gasoline
- Diesel fuel
- Jet fuel
- Hydraulic fluids
- Motor Oil
- Cutting Fluids
- Crude Oil

Never or Rarely used for

- PCBs
- Chlorinated Solvents
- Dissolved Phase PAHs

The fluorescence signal scales proportionally with NAPL concentration.

### Fortunately all PAH non-aqueous phase liquids or NAPLs Fluoresce

PAH fluorescence is a way to detect them by their "glow"





### ZEBRA MUNICIPALITY Potential LIF Characterization Sites

Leaking Underground Storage Tanks

Pipelines

Refineries

**Fueling Areas** 

**Automobile Service Locations** 

Lagoons and Waste Ponds

### ZEBRA The UVOST System



### ZEBRA JUVOST/LIF





### ZEBRA JUVOST/LIF















### ZEBRA Conductivity Di-Pole



Shock-resistant and water-tight SPOC is advanced with direct-push equipment

Changes in soil conductivity are indicative of:

- Changes in soil particle size
- Changes in the mineralogy
- Changes in the pore fluid
- Presence of ionic contaminants





### ZEBRA Laser Induced Fluorescence (LIF) Concepts

#### Each Aliphatic Solvent yield a fairly unique wavelength/time matrix (WTM)



### ZEBRA Fluorescence



crude oil diesel



### 



### ZEBRA SHAREPOINT WEBSITE FOR LIF DATA SHARING

**ZEBRA SharePoint Site** A custom web site for your Technical Documents ) Home - Regenesis - Earth Tech - Microsoft Interpat Fanlarar . . . Quel + () - 🖹 🖹 🟠 Danh 👷 taores 🕹 🔂 + 🔜 🛍 🥥 🤹 -C Sand · B M O O to to Ø Processor T Des · C Anture · Charles O · O Come Your Logo Regenesis MIP HOME BDS can provide a functionage of Direct Sensing Services including MIP/EC, CP7/MIP and EC. In addition ZEBRA sessiv incorporate the functional of Mobile Lab Services from KB Labs and the widest range of DPT Services. EBRA 2/3/2006 2:05 PM Post Events and announcements. 2/3/2006 10:56 44 REGENESIS Boston, Na 1/23/2006 8:00 AM 1/23/2006 5:00 PM Restort Ma 1/24/2006 7-00 444 a 1 Charad Documents - Microsoft Internet Europe - 0 × • 🖸 - 🖻 🖻 🐔 🔎 Sanch 👷 Faroriss 🤣 🙆 - 🍶 🔯 - 🧾 🎇 🥥 🤹 0 63 🖳 🖸 Sand 🔹 🖬 🧑 🥱 00 40 🖆 🖓 Paras say 🍏 Data 🔍 Antala • 🖓 Antala 🖓 • 📢 Ottora d Shared vocuments with the team by adding it to this do 150Fed 2/3/2006 11:58 AM 2/3/2006 11:58 44 2/3/2006 11:58 AM 2/3/2004 11:58 44 2/3/2006 11:58.4 2/3/2004 11/58 AM 2/3/2004 12-17 PM 2/3/2006 12:17 # Internet Access to all MIP/EC Documents Anytime any place with access to computer and the internet.

#### ZEBRA SharePoint Site

A custom web site for your Technical Documents





#### **NAPL Pre-SAMPLE**



















HRSC Solid Model with Surface Objects

#### For more information Contact Matt Ednie

#### 1-800-PROBE-IT or 518 355 2201

#### matt@zebraenv.com

#### www.TeamZEBRA.com



**ZEBRA Environmental Corporation 2013** 

### 

**Potential LIF Characterization Sites** 

### **Consulting Engineers and Scientists**

### LSPA LNAPL Laboratory Techniques for Evaluating Mobility Brandon J. Fagan LSP, PG December 2013

Presentation Acknowledgments:

PTS Laboratories Dakota Technologies





**Overview:** A brief discussion of various laboratory analyses that are used to determine the mobility of light non-aqueous phase liquid (LNAPL) in soil. The analysis includes methods to test LNAPL capillary pressure drainage, relative permeability in soil in the saturated zone (wetting fluid), and unsteady state conditions and water flood pore volume exchange. These methods are used to develop remedial strategies to recover LNAPL, reduce dissolve phase concentrations, and support risk characterization assessments.



### LNAPL Mobility Evaluation

- LNAPL Screening & Analytical Methods
  - Property Index Tests for Models
  - Photography
  - Laser Induced Fluorescence
  - LNAPL Saturation Analysis
- Laboratory Test Methods
  - Residual Saturation Analysis
  - Capillary Pressure Test
  - Unsteady State Relative Permeability Test
  - Pore Volume Analysis



LNAPL Properties	ASTM D445, ASTM D971, ASTM D1331, ASTM D1298, ASTM D 2983	LNAPL Porosity, Interfacial tension, Surface Tension, and Specific gravity are a key mobility parameter performed at a specific temperature (field conditions) Source: STL Laboratories, Inc.	

Inputs	Porosity	0.26 (gravel)	
	Specific Gravity	0.883	
	LNAPL/Water Interfacial Tension	26.3	
	Air/LNAPL Surface Tension	36	
	<b>Residual LNAPL Saturation</b>	10.9 %	
	LNAPL Saturation	7%	



#### CORE White Light & UVL Photography







#### LIF Fluorescence Relationship to PAH Saturation



Profile of LIF collected from PAH absorption to Poly-di-methyl-siloxane tubing



Profile of LIF collected using Geoprobe LIF Tool (UVOST/ROST/TarGOST)





# Mobility & Residual Saturation Analysis





### LNAPL Mobility Testing Laboratory Information (Direct Tests)

Comparison of Methods for Mobility / Residual Saturations						
Test Description	Residual Saturation Method	Cost (1)	Duration (2)	Advantage	Limitation	
Steady-State Relative Permeability	CT Scanning	High	8-10 wks	Direct saturation and permeability measurements	Cost, duration, non- native fluids	
Unsteady-State Relative Permeability	Dynamic displacement	High	4-6 wks	Native site fluids, well established method. Can use field gradients.	Large volumes of field fluids required. Indirect saturations	
Capillary Pressure	Curve Fitting	Moderate	3-4 wks	Rapid; multiple samples per run	Residual saturation dependant on curve fit routine	
Nuclear Magnetic Resonance	Magnetic Field	Moderate	2-3 wks	Multiple parameter generation	Specific soil type; new method and may be difficult to defend	
ASTM D-425M (Centrifuge)	Dean-Stark Extraction	Low	1-2 wks	Rapid, low cost screening. Multiple samples per run	Sample preservation is critical.	
Literature Values	Look-up Tables	Low	Varies	Low cost	Non-Site Specific data. Difficult to defend	

Table 1Comparison of Methods for Mobility / Residual Saturations

(1) Low: \$200-300/sample; Moderate: \$500-750/sample; High: \$950-3000/sample.

(2) Typically multiple samples are run in series.



### LNAPL Soil Saturation Analysis

Test	Reference	Purpose and Description	Cost
Dean-Stark Extraction	ASTM D95 API RP 40	Percentage of LNAPL and water by volume, i.e. Fluid Saturation A method for the measurement of fluid saturations in a core sample by distillation extraction. The water in the sample is vaporized by boiling solvent, then condensed and collected in a calibrated trap. This gives the volume of water in the sample. The solvent is also condensed, then flows back over the sample and extracts the oil. Extraction continues for a minimum of two days until the extracted solvent is clean or the sample shows no more fluorescence. The weight of the sample is measured before and after extraction. Then the volume of oil is calculated from the loss in weight of the sample minus the weight of the water removed from it. Saturations are calculated from the volumes. Information includes fluid saturations (LNAPL, water, air), total porosity, air- filled porosity, grain density, dry bulk density, and moisture content. Source: Schlumberger Oilfield Glossary www.glossary.oilfield.slb.com	\$90 to \$150


## **Residual Saturation Analysis**

Test	Reference	Purpose and Description	Cost
Screening Method for Determining Free Product Mobility - Capillary Pressure Drainage Test (Centrifuge Method)	ASTM D425M API RP 40	Single point quantification of residual saturation and LNAPL drainage. Provides a conservative estimate of residual saturation under gravity drainage by applying centrifugal force at 1000 times gravity for one hour to demonstrate product mobility equal to 1G for 1000 hours. Includes initial and residual pore fluid saturations, total porosity, dry bulk density and LNAPL Drainage observations (greater/less than residual where product mobilizes or does not mobilize from the sample) Source: PTS Laboratories <u>www.ptslabs.com</u>	\$345



Test	Reference	Purpose and Description	Cost
Water/LNAPL Imbibition Capillary Pressure Test (Centrifugal Method)	ASTM D6836 API RP 40 EPA 9110	Develop curve of capillary pressure vs. LNAPL saturation/production/loss by initially saturating a sample in the laboratory with LNAPL,, then introducing water as the permeant. increasing pressure incrementally. Measure fluid drainage out of the sample as LNAPL drainage changes to water and LNAPL production stops. Plot saturation vs. capillary pressure. Includes initial fluid saturations, LNAPL imbibition saturation, saturation change & drainage endpoints, hydraulic conductivity, specific permeability (relative permeability) to LNAPL	\$450 to \$700



### Capillary Pressure Test: Centrifugal Method

- Capillary Pressure tests demonstrate that at 2 psig or ~4.5-ft of head, LNAPL has little potential mobility based on saturation relationships to existing conditions.
  - Very low gradient across site, approx.
    0.001 ft/ft
  - Under maximum LNAPL thickness scenario and average seasonal head, product in the source area is relatively immobile.



Capillary Pressure Centrifugal Method

Test	Reference	Purpose and Description	Cost
Unsteady State Relative Permeability Test Dynamic Displacement	Triaxial Shear Cell Or Core Holder	Using changing gradients, develop curves of water saturation vs. LNAPL saturation/production/ loss by saturating a soil sample in a core holder or cell. with water as the wetting fluid Then, either imbibe LNAPL or a ratio of LNAPL to the water through one end of the soil core at a constant ratio of LNAPL and water . The pressure gradient across the core is measured, and the fluids leaving the soil core are collected with changing gradients and LNAPL to water ratios to develop relative permeability curves. Results include initial fluid saturations, LNAPL imbibition saturation, saturation change & drainage endpoints, hydraulic conductivity, specific permeability (relative permeability) to LNAPL RTDF "The Basics : Presentation 2005"	\$650 to \$1500



## **Relative Permeability Analysis**





# Average Water-LNAPL Relative Permeability Curves



## Pore Water Volume Drainage Analysis





### Model Calibration with Laboratory Results

Well ID	Maximum Apparent LNAPL Thickness bo <sub>max</sub>	Average Apparent LNAPL Thickness bo <sub>avg</sub>	Maximum LNAPL Relative Permeability K <sub>ro</sub>	Maximum Effective LNAPL Saturation S₀	Laboratory Results (So)
B-501	0.71	0.32	0.000	0.105	
B-502	1.44	0.77	0.005	0.164	A So = 12.7-15.5%
B-503	0.82	0.57	0.000	0.112	
B-305	0.03	0.03	0.000	0.082	
MW-13	1.04	0.29	0.001	0.129	
BF-15	2.07	0.69	0.022	0.215	B So = 1.3-7.1%
BF-16	1.40	0.65	0.004	0.161	0 00 - 1.0-7.1/0

### **Residual Saturation Sors Relationship to So**

	A	В
S <sub>ors</sub>	10.9%	20.5%
	So > Sors	So < Sors





### **Questions?**

# CAN ANYONE TELL WHY THE SATURATION ANALYSIS OF THE MODEL DID NOT REFLECT THE **So** LABORATORY ANALYTICAL RESULT FOR SAMPLE B .....?

The answer was in the White Light Photograph.





In Situ Geochemical Stabilization (ISGS) for NAPL Management LSP Association LNAPL- Assessment and Extraction Technologies Westborough, MA Dec 12, 2013

> Fayaz Lakhwala, Ph.D. FMC Corporation Fayaz.Lakhwala@fmc.com

Ravi Srirangam, Ph.D. FMC Corporation Ravi.Srirangam@fmc.com



# **Presentation Overview**

- What is ISGS Technology?
- History of ISGS Technology
- Bench Test / Proof of Concept
- Field Applications
  - Denver, CO
  - Gainesville, FL
  - Boston, MA
- Geochemical Modeling and Longevity
- Costs





# The NAPL Challenge – "Secondary Sources"







# Contaminant Flux Definition (Enfield, 2001)





# **ISGS™** Chemistry

# ISGS solution is a proprietary blend of permanganate and mineral salts that form a stable mineral precipitate



In the presence of an organic compound (R),  $MnO_4$  reactions yield an oxidized intermediate (Rox) or  $CO_2$ ,... plus  $MnO_2$ 

 $R + MnO_4 - \rightarrow MnO_2 + CO_2 \text{ or Rox}$ 



# **A New NAPL Management Tool**



### ISGS Effects

- Creates a stable "crust"
- Reduces permeability
- Immobilizes NAPL



### ISGS Addresses NAPL Challenges

- Reduces measurable NAPL
- Reduces dissolution of NAPL constituents
- Reduces flux of NAPL into groundwater
- Enhances natural attenuation of NAPL constituents







# **ISGS for NAPL Challenges - Advantages**

- Liquid amendment easy to inject and target source areas.
- 2. Rapid reactions (days) yield reduced aquifer permeability and COI flux
- 3. Applicable to wide range of organic and inorganic COIs
- 4. Only treat a fraction of TOD
- Long term (crust analyses & geochemical modeling suggest > 100 yr, supported by over 10 yr field data)
- 6. Relatively low cost for localized source areas
- 7. Logical alternative to mass removal and mass destruction





# **Technology Development**

- ✓ 1997 Conceptualization / Proof of Concept
- ✓ 1998 1999 TCE R&D at UW and Adventus
- ✓ 1999 2001 Camp Borden (pilot)
- ✓ 2002 2003 PAHs, PCP Denver, CO (pilot)
- ✓ 2004 PAHs Denver, CO (full scale)
- ✓ 2004 PAHs, PCP Gainesville, FL (bench).
- ✓ 2005 PAHs, PCP Gainesville, FL (pilot)
- ✓ 2007 PAHs MGP NE Utilities (bench)
- ✓ 2008 PAHs, PCP Gainesville, FL (pilot)
- ✓ 2008 PAHs Creosote works, LA (bench)
- ✓ 2009 solvents, benzene plastics manufacturer (bench)
- ✓ 2010 PAHs Montgomery, AL (full scale)
- ✓ 2010 LNAPL South Boston, MA (bench test)
- ✓ 2013 LNAPL Fanwood, NJ (full-scale)
- ✓ 2013 LNAPL and DNAPL, Frankford, PA (pilot test)
- ✓ 2013 Creosote and PAHs Gainesville (full scale)





# **Proof of Concept** – **Bench Testing**



- •Saturate w/ISGS reagents
- •20 days reaction time
- •Drain
- •Run Up-flow Column (DI)
- •Compare with Control



# Typical Bench Test Results – COIs in Leachate (ca. 7 days treatment time)





# First Full-Scale Application - Denver, CO





# **Pre Injection – NAPL Thickness (ft)**











## Non-Treated Soil 14 ft bgs

## ISGS Treated Soil 14 ft bgs





# **Flux Reduction**



The HMW COI were removed at a proportionally higher rate than the LMW compounds.

COI (mg/L)	Average Background	Average Treated	% Reduction
LMW PAHS	34.41	12.75	73
HMW PAHs	6.05	0.11	99
TOTAL PAHs	40.46	12.86	79
* PENTA	18.91	9.66	49
* TOTAL CPs	23.38	10.41	56

\* Excludes sample IB05A-14 to 14.5 ft bgs (80 v. 8 ppm dissolved phase penta + 296 ppm total penta)



# Phase II ISGS Application (2004)





# **South Boston Site – Bench Test**





2009 LNAPL THICKNESS DATA WE-27 – 0.07' AVG (MAX 0.19') MW13 – 0.04' AVG (MAX 0.07') WE-33 – 0.02' AVG (MAX 0.07')



# **South Boston Bench Test Results**

- Objectives:
  - Validate ISGS treatment applicability to TPH
  - Identify most cost-effective treatment regime (based on site soil)
- Method:
  - batch & column studies
- Results:
  - TOD 5 to 8 g/kg (B-Header), 30 to 42 g/kg (WE-27)
  - 60 to 80% reduction in EPH leachate concentrations in 14 days
  - 13 to 30% reduction in EPH soil concentrations in 14 days
  - 44 to 67% reduction in permeability to NAPL and 17% reduction in NAPL fluid saturation
  - ISGS was effective for NAPL stabilization for soils and constituents at this site
  - 4.5% ISGS solution was recommended for full-scale



# Cabot Carbon / Koppers Superfund Site, Gainesville, FL





- 90 acre site
- Pump & treat in place
- Secondary NAPL issues





# **Results - NAPL Monitoring Wells**





1 week Post ISGS treatment = no measurable free-phase NAPL in any of the monitoring wells.

Monitoring Well	Pre-Injection	Post-Injection
NISBS- 1	NAPL	stain
NISBS-2	NAPL	stain
TIP-3	ND	ND
TIP-4	ND	ND
UGH Recovery	NAPL	No NAPL



# **Results - Total PAH Concentrations in Soil and in Leachate**





- 6 cores (3 sections) before treatment
- 6 cores (2 depths) after treatment

Best matched cores (SOIL): dropped from 7,250 mg/kg to 3,600 mg/kg

Best matched cores (LEACHATE): dropped from 11,700 mg/L to 560 mg/L

PAH concentrations in soil reduced by up to 50% within 3 months.

PAH leachate concentrations reduced by up to 98% within 3 months.



# ISGS Field Data – Decrease in K<sub>h</sub> Values Woodward Coke Site – Dolomite, AL





# Treated Soil Core Close-up Showing ISGS "Crust" or Coating and NAPL Ganglia







Likely NAPL

**ISGS** coating

Soil Grain

Epoxy (open pore space)

# Conclusion: Soil grains and NAPL blobs coated with ISGS crust



# **Birnessite** is an oxide of Mn and Mg along with Na, Ca and K with the composition: $(Na,Ca,K)(Mg,Mn)Mn_6O_{14}.5H_2O$







# cale

# **Regulatory Issues for Full-Scale Applications**

- Crust Longevity
  - Crust weathering is dependent on changes in Eh and pH
  - Conduct mineralogy assay
  - Validate using geochemical modeling
- Performance Monitoring
  - Eh, pH for crust stability
  - Permeability tests for flux reduction
  - NAPL fluid saturation





# **Geochemical Modeling of the Crust**





# **Crust Longevity**

- Back of the envelope calculations suggest crust life  $\sim$  400 years.
- This may be overestimated because it assumes Eh (-400 mV) and pH (6) at which birnessite is sparingly soluble



Water oxidized

1.40

Figure 16. Fields of stability of manganese solids and equilibrium dissolved manganese activity as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as  $SO_1^2$ , and carbon dioxide species 61 mg/L as HCO<sub>3</sub>.

ьH

Eh-pH diagram from Hem (1985)

# Representative Experience ISGS – Creosote and Related Sites



	i	İ
Site	COI / Environmental Setting	ISGS Approach / Status
Active Wood Treating Site Superfund Site Denver, CO	Phase separated creosote (PAHs) and pentachlorophenol (penta). Consolidated shallow alluvium.	KMnO₄ (no catalysts; no buffer) successful bench and pilot studies completed; full-scale application completed 2004.
(Active) Wood Treating Site Superfund Site Gainesville, FL	Phase separated creosote (PAHs). Sand silt environment, 5 to 22 ft bgs.	NaMnO <sub>4</sub> (catalyzed, buffered) completed bench-scale engineering optimization tests; Pilot-scale technology validation performed in January 2008. 2012 Full- scale application recommended as part of the ROD – installation 2013 to 2015.
Former Wood Treating Site Montgomery, AL	Phase separated creosote (PAHs)	Field Scale application completed 2009. One to two orders of magnitude reduction in permeability.
Former Wood Treating Site Cape Fear, NC	Phase separated creosote (PAHs)	Conceptual design completed.
Former American Creosote Works Winnfield, LA	Phase separated creosote (PAHs)	Engineering optimization bench work completed.
Former Wood Treating Site Sand Point, ID	Phase separated creosote (PAHs)	Engineering optimization bench work completed; Field Pilot Completed Q3 2010.
Former Wood Treating Site Netherlands	Phase separated creosote (PAHs)	Engineering optimization bench work completed. Field Pilot pending





# **ISGS Material Cost – Field Applications**

Denver, CO	Dolomite, AL	Gainesville, FL
TOD = 18 g/kg	TOD = 1 g/kg	TOD = 122 g/kg
Dense Alluvium KMnO <sub>4</sub> @ 4.5 g/kg Injection Wells	Fractured Karst RemOx EC Push-Pull	Sand/Silt RemOx EC Direct Push and Injection wells
1,273 m <sup>3</sup> soil 3% solutions 1,850 USG/IP 2-5 gpm (20 psi)	1,500 m <sup>3</sup> soil 1% solutions 20,000 USG 13 gpm (20-50 psi)	1,415 m <sup>3</sup> soil 4.5 % solutions 620 USG/DIP 2-5 gpm (<50 psi)
Cost = \$40 - 50/m <sup>3</sup> \$31 - 38/yd <sup>3</sup>	Cost = \$45 - 50/m <sup>3</sup> \$34 -38/yd <sup>3</sup>	Cost = \$60 - 75/m <sup>3</sup> \$50 -60/yd <sup>3</sup>

The amount of ISGS reagent required for a given site has a significant influence on project cost. Typical **material costs** range from \$13/yd<sup>3</sup> to \$53/yd<sup>3</sup>.





## **Questions?**

