Surfactant Enhanced Bioremediation (SEB) of F2, F3, and F4 Hydrocarbons
Technical Overview & Case Studies

REMTECH 2008
October 15 – 17, 2008
Banff, Alberta
Surfactant Enhanced Bioremediation (SEB)
Environmental Remediation Market Value
In USA Estimated at **23 Billion** Annually

Bioremediation Market Is Estimated At
**Between 5 to 7 Billion** Annually And Growing!

*Ref: John Sankey, True Blue Technologies*

Considerable effort and resources (Millions $) are being poured into research and development for innovative Bioremediation Technologies to meet the growing Bio Market Demands.
In North America

We Have Been Undertaking In-situ and Ex-situ Bioremediation Since The Early 1980’s.

From This Success and Failure Have Lined The Path

Lessons Learned have prevailed...we now better understand what affect success and failure when conducting Bioremediation.

I will share from this to reveal the #1 limiting factor for successful Bioremedaition...
In North America
The Typical Cost For Bioremediation
Ranges From $30 to $100 US /m³
($20 to $80 US per cubic yard)
For Petroleum Hydrocarbons
The Rate /m³ Is Much Higher For
Hazardous Materials Like
PCB, PAH, DDT, DCB, TCE, PCE, Etc…
SEB of F2, F3 and F4 Contamination
Presentation Overview

i) Overview of Bioremediation;
ii) Factors affecting Bioremediation;
iii) False Assumption On F3-F4 Bioremediation;
iv) Contaminant Sorption Overview;
v) Overview of Surfactants;
vi) SEB Mechanism;
vii) Case Studies;
viii) Q&A
Bioremediation can be defined as any process that uses microorganisms or their enzymes to remove and or neutralize contaminants within the environment (i.e., within soil and water) to their original condition.

Bioremediation can be employed to remediate specific types of contaminants such as: petroleum hydrocarbons (F1, F2, F3, F4), PAH, PCB, chlorinated solvents, pesticides - all of which can be bio-degraded by microorganisms given proper treatment conditions.
**Aerobic**
In the presence of sufficient oxygen (aerobic conditions), and other nutrient elements, microorganisms will ultimately convert many organic contaminants to carbon dioxide, water, and microbial cell mass. *F2, F3 and F4 Bioremediation is an aerobic biodegradation process.*

**Anaerobic**
In the absence of oxygen (anaerobic conditions), the organic contaminants will be ultimately metabolized to methane, limited amounts of carbon dioxide, and trace amounts of hydrogen gas. *eg. Reductive dechlorination.*
BIOSTIMULATION
Where you stimulate existing microorganisms in the soil through addition of amendments to degrade the contaminants present. This assumes the bacteria are capable of breaking down the contaminants present.

BIOAUGMENTATION
Where you add microorganism as part of the amendment process to achieve bioremediation of the subject soils.

ENHANCED BIODEGRADATION
The use of special chemical additives, such as Surfactants (SEB-Surfactant Enhanced Bioremediation) to help with the desorption of contaminants and nutrients making them more Bio-Available to the bacteria during Biostimulation or Bioaugmentation.

‘SEB Newest Innovative Form of Bioremediation’
Advantages of Bioremediation

- Bioremediation is a ‘natural process’ and is therefore perceived by the public as an acceptable waste treatment process for contaminated material. The residues for the treatment are harmless products, including carbon dioxide, water, and cell biomass.

- Bioremediation is useful for the ‘complete destruction’ of a wide variety of contaminants. Many compounds that are legally considered to be hazardous can be transformed to harmless products after treatment.
In-situ & Ex-situ
SEB Application Options
Ex-Situ (SEB) Surfactant Enhanced Bioremediation of F2, F3 and F4 Petroleum Hydrocarbons

EX-SITU BIOREMEDIATION

- Agricultural silage plastic cover sheet
- 150 CFM blower on interval timer
- 100mm PVC perforated pipe
- 6 mil vapour barrier liner
Advantages of Bioremediation

- Bioremediation can often be ‘carried out on site’, often without causing a major disruption of normal activities. This also eliminates the need to transport quantities of waste off site, and the potential threats to human health and the environment that can arise during transportation.

- Bioremediation can prove ‘less expensive’ than other technologies that are used for clean-up of hazardous wastes.

- *Sustainable* and Natural
Factors Affecting Bioremediation

- Contaminant Type & Concentration
- Moisture Content
- Soil Type (Clay, Silt, Sand and Gravel)
- Oxygen (Concentration & Availability)
- Nutrient C:N:P (Ratio and Availability)
- Salinity (NaCl)
- pH
- Temperature
- Red-Ox Potential
- Contaminant Sorption (i.e., absorption and adsorption)
- Bacterial & Microbial Consortium (Presence & Availability)
- Soil Science (i.e., Compaction, Charged Surfaces, etc.)
- Sorption of Contamination (Absorption & Adsorption)
- Any toxic compounds to microorganisms (If Present)

When Other Factors Are Fair to Good, Sorption Is The #1 Limiting Factor Affecting Successful F2, F3 & F4 Bioremediation
Question: Is F3 and F4 Petroleum Hydrocarbon Bioremediation Possible???

Industry Quotes Collected In 2006 & 2007

► ’Bacteria do not like F3 and F4 hydrocarbons’
► ’F3 and F4 petroleum hydrocarbons are toxic to the soil bacteria’
► ’F3 and F4 bioremediation takes too long to be considered cost effective…’
► ’The salinity in F3 and F4 contaminated soils is what limits their biodegradability…’
► ‘Bioremediation of silt and clay soils with F3 & F4 is not possible…’
F3 and F4 hydrocarbons are among the most biodegradable organic chemical structures. They are generally ‘not’ toxic to bacteria.

Slow F3 and F4 biodegradation is due to not addressing contaminant ‘SORPTION’ and associated reduced ‘bio-availability’ of the contaminants to the bacteria present.

Salinity may inhibit bacteria, but is less significant compared to contaminant sorption. Recall bacteria thrive in the oceans.

Fine grain soils (silt/clay) can affect bioremediation, but mostly due to contaminant sorption given the greater surface areas for absorbing and adsorbing of the contaminants.
Bio-Availability - Sorption Factor

‘...During the past decade, much discussion has centered on the unavailability of absorbed and adsorbed compounds to soil microorganisms. It is generally now assumed that desorption and diffusion of bound contaminants to the aqueous phase is required for microbial degradation...’

F2 - F3 - F4 Compounds

Generally speaking, the higher the molecular weight of a petroleum compound, the more likely it is to sorb onto the soil matrix verses being free and more bio-available

Sorption For F1 to F4 Fractions:

\[ F4 > F3 > F2 > F1 \]
Sorption (i.e., Absorption and Adsorption) of Contamination in Soil Matrix Limits The Bio-Availability of Contaminants

Soil Bioremediation Must Address This Factor To Be Successful For F2, F3, & F4.
FACTS

90 to 95% of All Contaminants Are Sorbed To Particles In Soil, Bed Rock and Groundwater

● Contaminant Sorption Limits Availability of Contaminants For Bioremediation

● Sorption #1 Reason Why Many In-situ and Ex-situ Remediation Project are Slow, Costly or Fail.
Soil From AB
See Clay, Silt
and Sand
Seams
Lots of
Surfaces for
F2, F3 & F4
Sorption
For Effectively Bioremediation of F3 and F4 Contaminated Soil

YOU MUST ADDRESS SORPTION

Sorption = Limited Bio-Availability

Contaminant Sorption Is the #1 Limiting Factor Negatively Affecting All In-situ & Ex-situ Remediation of F2, F#, and F4 Contaminants.
SURFACTANT ENHANCED BIOREMEDIATION (SEB)

New Innovative Process to Desorb F2, F3, and F4 Contaminants Making Them Bio-Available For Bioremediation

Overview of Surfactants & Case Studies
Surface Active Agent (SAA), i.e., Hydrophilic (water loving) and Hydrophobic (oil-liking) Groupings Shown.
**Classes Of Surfactants**

**Anionic**: They have one or more negatively charged groupings. They have very good detergent ability and are commonly used as *laundry detergent*.

**Cationic**: They have one or more positively charged groupings. They typically have poor detergency, but are well suited for use as *germicides, fabric softeners, and emulsifiers*.

**Non-ionic**: As their name implies, they have no ionic constituents or groupings. They are the largest single group of SAA and have a correspondingly wide range of chemical characteristics and application. Some (Ivey-sol, SPT, SPTT) have the unique ability to selectively dissolve LNAPL, DNAPL, polycyclic aromatic hydrocarbons (PAH’s), dichloroethane (DCE), trichloroethane (TCE), perchloroethylene (PCE) and other similar petroleum products.

**Amphoteric**: They contain both anionic and cationic groupings and have the characteristics of both anionic and cationic SAA. They work well at neutral pH and are found in products such as *hair shampoo, skin cleaners, and carpet shampoo*. 
Surfactants are used in cleaners and detergents to:
► Improve wetting / spreading
► Provide detergency by solubilizing & suspending soil (particulate, oily)
► Produce, modify or control foam
► Emulsify / disperse (e.g., silicone, wax)
► Couple or compatibilize formulation components
► Modify viscosity

Other commercial and environmental uses include:
● Vapour and odour suppression;
● Storage tank and parts cleaning;
● Off-shore dispersants, and shoreline spill clean-up;
● In-situ Surfactant Enhanced Aquifer Remediation (SEAR);
● In-situ and Ex-situ Surfactant Enhanced Bioremediation (SEB);
● In-situ and Ex-situ Surfactant Enhanced Oxidation (SEO);
● Oil recovery form oil sand and oil-shale;
● Treating drilling mud and drilling cuttings; and
● Improving oil recovery form oil production fields.
Surfactants Lower The Surface Tension of Water From 72 Dynes to <50 dynes with some capable of < 30 dynes.

This increases the wetting ability of the water when present, makes surfactant application possible in fine grain soils improving Water Permeability (K).

Helps Improve Desorption In Finer Grain Soil Aiding Bioremediation By Increasing Bio-Availability
Surfactant Enhanced Bioremediation (SEB)
Mechanism of Surfactant Desorption
To Increase Bio-Availability
Surfactant Interaction With Organic (NAPL) On A Surface With Partial Micelle of F2, f3, or F4 (Surfactant Effective Below CMC – No Emulsification)
SEB Mechanism For PAH

A) bacterial cell
uptake from micelle
micelle
surfactant-solubilized PAH
PAHs

B) bacterial cell
uptake of dissolved PAH
micelle
solubilized PAH
PAHs

C) bacterial cell
direct uptake of PAH
PAHs

D) bacterial cell
direct uptake of surfactant-associated PAH
non-micellar biosurfactant
biosurfactant-solubilized PAH
PAHs
In-situ & Ex-situ SEB Applications

Overview & Case Studies
In-Situ SEB
Surfactant Enhanced Bioremediation (Aerobic)

In-Situ SEB Zone

Hydraulic Conductivity
\[ K = 1 \times 10^3 \text{ TO } 1 \times 10^5 \text{ cm/s} \]
In-situ Bioremediation.

Injection of amendments to stimulate Bioremediation of contamination

Injection at an Injection Well (IW).
Ex-Situ SEB
Surfactant Enhanced Bioremediation (F3 & F4)
Ivey International Inc. was retained to apply their SEB technology to treat >2000 tons of F2, F3, and F4 fine grained contaminated soil at a remote site in Northern, Alberta, Canada.

The project was commenced in late August 2006, just prior to the on-set of colder northern weather in an area known for minus 30 °C to minus 40°C winter temperatures.

The soils had some Salinity and EC levels issues.
Ex-situ Surfactant Enhanced Bioremediation (SEB) of F2, F3, F4 Soil Contamination

RESULTS
### CONCLUSIONS

- The SEB process was effective in achieving the soil remediation goals in <11 months, commencing with average baseline hydrocarbon concentration of **F1 441 ppm, F2 1,189 ppm, F3 2,064 and F4 965**.

- The total % reduction in each hydrocarbon fractions were: **F1 (100%), F2 (92%), F3 (83%), and F4 (81%)**, achieving the applicable Alberta Environment Soil Remediation Guidelines (ABENV, June 2007).
CASE STUDY #2
Quebec, Canada

► 6,000 ton Soil Bioremediation treated in May 2006 using Ivey-sol SEB Process.

► Client was having difficulty lowering their PAH concentration in soils at their soil bioremediation facility.

► Surfactant Enhanced Bioremediation treatment was undertaken and within four months significant reductions in total PAH levels were realized.

► The subject company had a good ex-situ bioremediation system design application in place, their main problem was not being able to overcome the strong sorption of the PAH compounds to the soils.
SEB Ex-situ Soil Remediation Project
Quebec, Canada

Andain A-1

Date:
- July 3
- August 9
- September 18
- November 14

C10-C30, mg/kg:
- July 3: 2400
- July 3: 2200
- August 9: 1000
- September 18: 1200
- November 14: 650
CASE STUDY #3
Mine Site
Western Canada


► Silty, clay and sandy soil impacted with Fuel oil and Diesel >5000ppm to 10,000 ppm.

► Surfactant Enhanced Bioremediation treatment was undertaken and within 12 to 14 weeks the soil was remediated to the BC Ministry of Environment Soil Clean Up Commercial Standard.
Ex-Situ SEB
Surfactant Enhanced Bioremediation (F3 & F4)
“After excavating and bio-piling the soil, the surfactant enhanced bioremediation (SEB) treatment was applied and the bio-pile was then covered. Daily aeration was done during the treatment period. After only 12 weeks samples taken from the pile showed that the remediation of the Fuel-oil/Diesel and PAH contamination was completed to the applicable BC Environmental Standards and the soils were safe to re-use on-site.”

Reference: Tony Robson, Director, Mining Plant & Equipment-Quinsam Coal Corp.
Tel: (250) 286 3224 (ext 224); E-mail: tonyr@oberon.ark.com

Environmental Science & Engineering Magazine Ca. 2005
CASE STUDY #4
Research Project (SER-SEB)
Madrid Spain

► In 2007 Ivey international Inc. conducted a joint Research and Development project with CIEMAT in Madrid Spain.

► Purpose was to evaluate the ability of Surfactant (Ivey-sol) to Desorb Sorbed PAH compounds in column tests. If effective; to evaluate potential for increasing the Bio-Availability of PAH for biodegradation using the SEB process.

► Results were that the Ivey-sol Surfactants were very effective at desorbing the PAH compounds making them more Available for remediation; including increased Bio-Availability for Bioremediation.
Free desorption  Induced desorption
RESULTS

Free desorption

PAHs desorption (%)

HAP

PAHs desorption in free desorption test

Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene
PAHs desorption in induced desorption test
RESULTS

PAHs desorption in surfactant aided desorption test

Surfactant desorption (Ivey sol 106)
RESULTS

Comparative PAHs desorption (%) for all tests
Waste Water Treatment
Surfactant Enhanced Bioremediation

Multi-Stage Bioreactor
TPH Treatment
Packing Material (Growth Substrate)

Bacterial Growth on substrate to treat the water
Pre & Post (24 Hour) Ivey-sol Addition
Outperforming Other Surfactant
Duration of Bioremediation Treatment

Ex-situ: Typically 3 to 4 months or less.

In-situ: Typically 12-18 months or less.

Duration of bioremediation is a function of contaminant type, its concentration, and the soil geology.
For Additional Information

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