

Surfactant Enhanced Aquifer Remediation (SEAR) Using Ivey-sol® Surfactant Technology

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Executive Summary

This paper will focus on the application of Ivey-sol® non-ionic surfactant technology to improve the in-situ remediation of petroleum hydrocarbon contamination in soil and bedrock aquifers.

Normally hydrophobic organic chemicals (HOC) exhibit limited solubility in groundwater as the contaminants tend to partition onto the soil and bedrock matrix. This partitioning can account for as much as 90-95% or more of the total contaminant mass. As a consequence, the hydrocarbon contaminants exhibit moderate to poor recovery during pump and treatment; limited bioavailability to microorganisms; and limited availability to oxidative and reductive chemicals when applied to in-situ and or ex-situ applications. Hence certain HOC's can persist in the soil and or bedrock matrix for long periods of time.

The sorption (i.e., adsorption and desorption) of contamination onto solids is often considered the principal limiting factor affecting the effectiveness of the many remediation technologies. This coupled with complex site geology; including sands and gravels, to fine grained silts and clays and fractured bedrock; only further complicate their application.

Ivey-sol® is a non-ionic surfactant technology, comprised of several proprietary formulations, are capable of selectively desorbing and dissolving contaminants as microscopic 'surfactant-hydrocarbon-water' partial encapsulations, called partial micelles, well below their critical micelle concentration (CMC). In addition, Ivey-sol can lower the surface tension of water from 72 dynes to less than 30 dynes increasing the wetting and permeability properties of water in fine grain soils and fractured bedrock.

Ivey-sol® surfactants affect the sorption of HOC and surfactants at the solid-liquid interface (i.e., the surface-H₂O-NAPL interface). As a result, they increase the solubility of the contaminants in the groundwater for the improved removal by P&T, or treatment by bioremediation, and or chemical oxidative or reductive treatment processes.

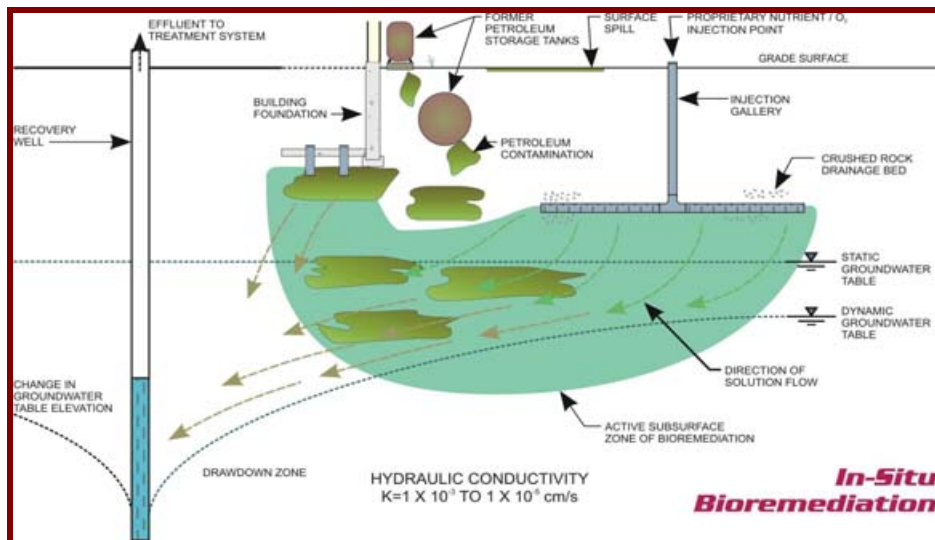
Through desorbing contamination and lowering the surface tension, Ivey-sol formulations address two principal factors affecting the successful application of remediation technology. They overcome the contaminant absorption limitations, and improve the transitivity of the water by reducing the surface tension allowing greater effective water penetration into and through finer grained less permeable, soil substrate.

1.0 SURFACTANT ENHANCES AQUIFER REMEDIATION (SEAR)

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, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyl's (PCB), chlorinated solvents, and chlorinated pesticides, all of which can be degraded by bacteria.

Generally, bioremediation technologies can be classified as In-situ or Ex-situ approaches. In-situ techniques are defined as those that are applied to soil and groundwater at the site with minimal disturbance. Ex-situ techniques are those that are applied to soil and groundwater at the site which has been removed from the site via excavation (soil) or pumping (water). In-situ bioremediation involves treating the contaminated material in-place at the site while Ex-situ bioremediation involves the removal of the contaminated material to be treated elsewhere. This paper will focus of in-situ Aquifer (Groundwater) surfactant remediation applications only.

Enhanced Bioremediation can be defined as the application and regulation of certain biochemical and physicochemical properties to enhance the conditions within the aquifer to aid the mineralization of contaminants by the microbial population present. This includes adjusting biochemical parameters such as: oxygen, phosphorus, nitrogen, pH, Eh, moisture, temperature and their associated application rates.



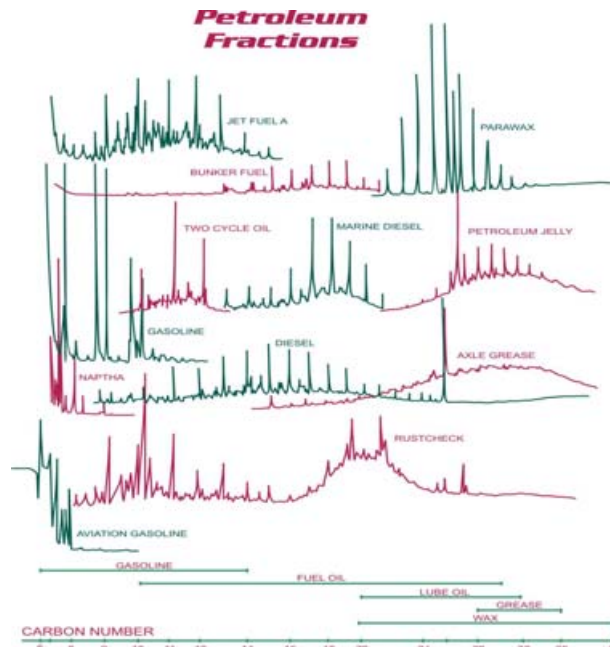
In-situ Bioremediation: Subsurface bioremediation of target aquifer contamination. This may or may not include a dynamic pump and treatment system.

Typically 90 to 95% of most hydrocarbon contaminants are absorbed onto surfaces (i.e. soil and bedrock) within the aquifer matrix (Ivey, G.A. et al., 2005). The surface sorption and low solubility of the certain hydrocarbons, such as the PAH benzo[a]pyrene), exhibit low bioavailability as a result.

Changing the physicochemical properties of the aquifer contaminants can be achieved through the addition of Ivey-sol® surfactants which are non-ionic surfactants formulations which can selectively desorb and dissolve a broad range of petroleum hydrocarbons including PAH, PCB's. The addition of Ivey-sol® to improve the physicochemical properties and biodegradation of contamination in groundwater is known as Surfactant Enhance Aquifer Remediation (SEAR).

1.1 Composition of hydrocarbon contaminants

Gasoline and fuel oil are complex mixtures of hydrocarbons that include n-alkanes, branched alkanes, cycloalkanes and aromatic compounds. The approximate composition of gasoline and fuel oil is 60% aliphatic - 40% aromatic and 80% aliphatic-20% aromatic respectively.



This GCMS Scan illustrates the complex range of petroleum hydrocarbon compound in commercial use.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of compounds exhibiting similar characteristics: they are large, high-molecular-weight compounds with low water solubility, and two to five condensed aromatic rings. Common PAH's include: anthracene, benzo-(a) pyrene, chrysene, naphthalene and pyrene. Most PAH's exhibit moderate to good biodegradation with SEAR. Some PAH compounds are present in gasoline and fuel oils.

1.2 Bioremediation Mechanisms

1.2.1 Hydrocarbon Structure and Biodegradation

Hydrocarbon compound structure is important in bio-degradability. The n-alkanes (straight chain) and n-alkyl- aromatics (substituted aromatic) in the C10 to C22 range are considered to be of low toxicity and the most biodegradable (Bossert and Bartha, 1984). Hydrocarbons above C22 have lower toxicity and are generally considered less biodegradable due to their physical characteristics, which include low water solubility, sorption onto surfaces, and a solid to semi-solid state at 35°C.

Compounds in the C1 to C4 range are gaseous and considered to be biodegradable, but this is not the typical mechanism employed to remove these. Counterparts in the C5 to C9 range have high solvent-membrane toxicity to microorganisms, but in low concentration they are considered to be easily biodegradable.

Branched n-alkanes and cyclo-alkanes are less biodegradable as their tertiary and quaternary carbon atoms inhibit the β -oxidation step required for degradation. Aromatic hydro-carbons are biodegradable, but the bioavailability of high molecular weight

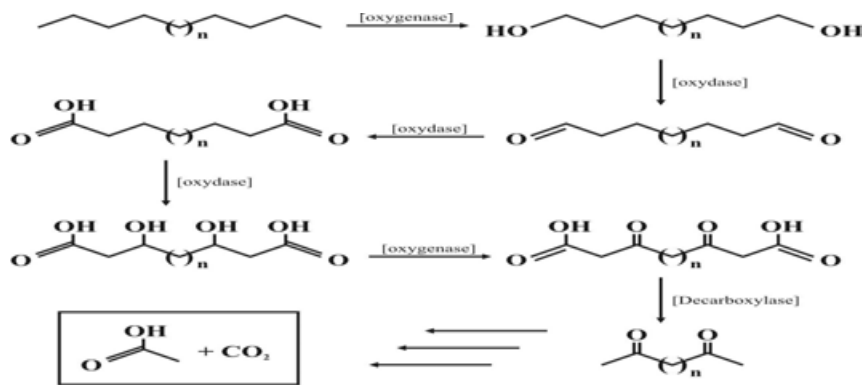
compounds such as PAH's decreases dramatically as the number of condensed rings increases. These compounds exhibiting lower biodegradability due to surface absorption and low solubility are commonly referred to as recalcitrant or xenobiotic.

1.2.2 N-Alkane

The biological degradation pathway for n-alkane (straight chain) and branched alkanes has been well established and reported extensively in literature. The biodegradation pathway for n-alkane is shown below (Grubbs and Molnaa, 1987)

Typically, the degradation pathway consists of the following steps:

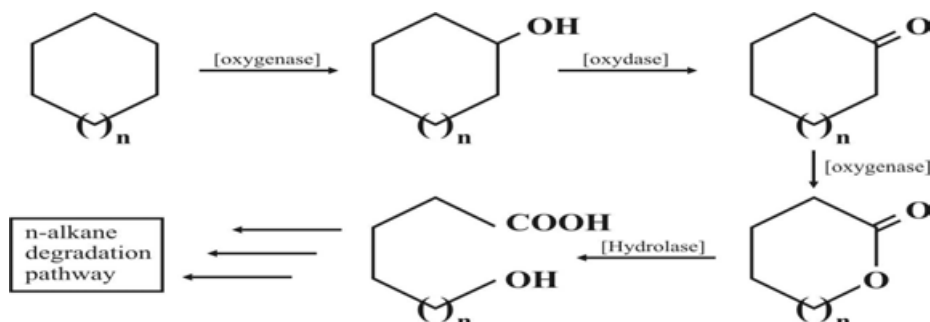
- Initial enzyme catalyzed oxidation to produce primary fatty alcohol.
- Sequential oxidation of the alcohol to fatty acid.
- Oxidation of the β -carbon to produce a β -keto acid.
- Decarboxylation to produce a degraded alkane.



Clearly all resultant intermediates in this mineralization process should possess a low to very low toxicity since only naturally occurring fatty acids are being produced.

1.2.3 Cyclic Alkanes

Even though cyclic alkanes are very similar in structure to n-alkanes, their biodegradation pathway appears to be fundamentally different.



Biodegradation pathway for cyclic alkanes (adapted from Bartha, 1986)

Although not fully characterized, it has been reported (Bartha, 1986) that the following Steps are required:

- Sequential enzyme mediated oxidation of the ring to form a cycloalkanone
- Baeyer-Villiger type oxidation of the cyclic ketone by an as yet uncharacteristic second oxygenase enzyme to produce a lactone

- Hydrolysis, resulting in ring fission, to generate what amounts to an oxidized n-alkyl fatty acid that can be further degraded by the mechanism outlined in the n-alkane pathway.

1.2.4 Aromatics

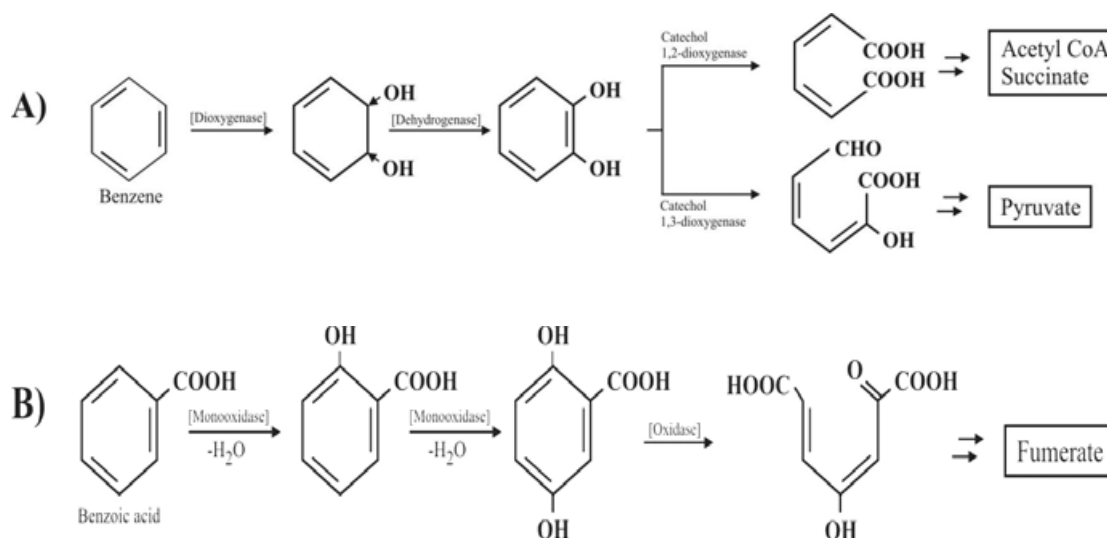
Simple aromatic or "benzenoid type" compounds generally pose no resistance to microbial degradation for a large variety of microorganisms (Fewson, 1981).

The key factor in the degradation of aromatic compounds by these ring fission enzymes is their ability to destroy the resonance contained within the ring. This can be accomplished, however, only by the initial positioning of at least two hydroxyl groups, either ortho or para, relative to each other.

The biodegradation of aromatic compounds proceeds via two well-established pathways: a) catechol and b) gentisate (illustrated below, Leisinger and Burner, 1987).

In both pathways, ring activation is followed by ring cleavage and the subsequent transformation of the fission products.

The degradation of substituted aromatics, such as ethyl- benzene and toluene, would also proceed via an analogous pathway. These products, once generated, would then follow a similar microbial mineralization as outlined in the n-alkane pathway.

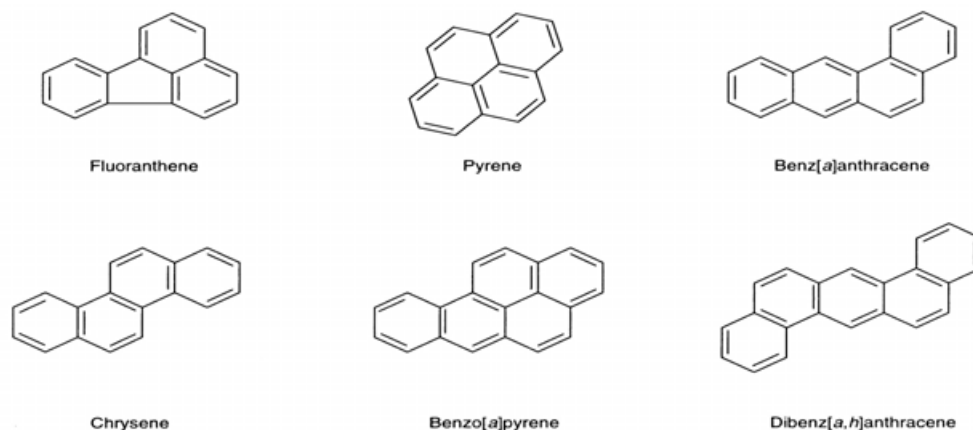


Biodegradation of simple aromatics, (A) the catechol pathway, and (B) the gentisate pathway (adapted from Leisinger and Burner, 1987)

1.2.5 Polycyclic Aromatic Hydrocarbons (PAH)

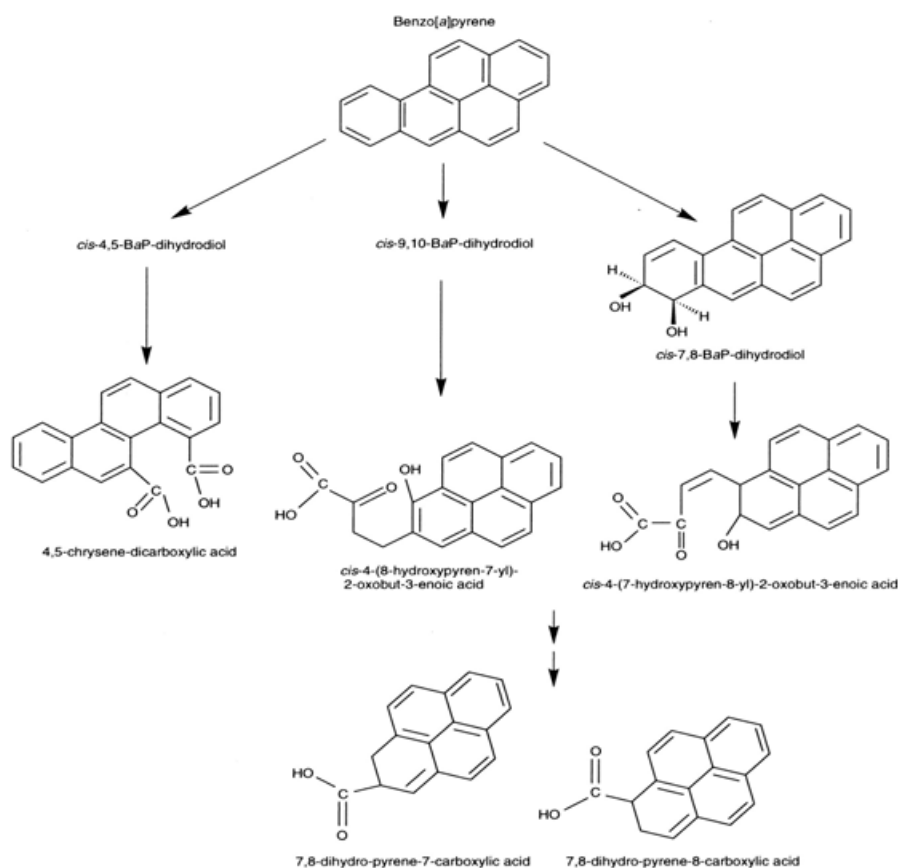
Polycyclic Aromatic Hydrocarbons (PAHs) are hydrocarbon compounds with multiple benzene rings. PAHs are typical components of asphalts, fuels, oils, and greases. They are also called polynuclear aromatic hydrocarbons. The bacterial degradation of PAHs with more than three rings, often referred to as high molecular weight (HMW) PAHs, are often challenging to mineralize by microorganisms. This is related to their low solubility and high affinity to solid surfaces and organic liquids, which generally limits their bioavailability to microorganisms present in soils (J.J Ortega-Calvo, 2004). Surfactant-

enhanced bioremediation of soils containing low soluble hydrocarbons is a promising biodegradation technique (P.R. Jaffe, 2000)



Typical High Molecular Weight PAH Compounds

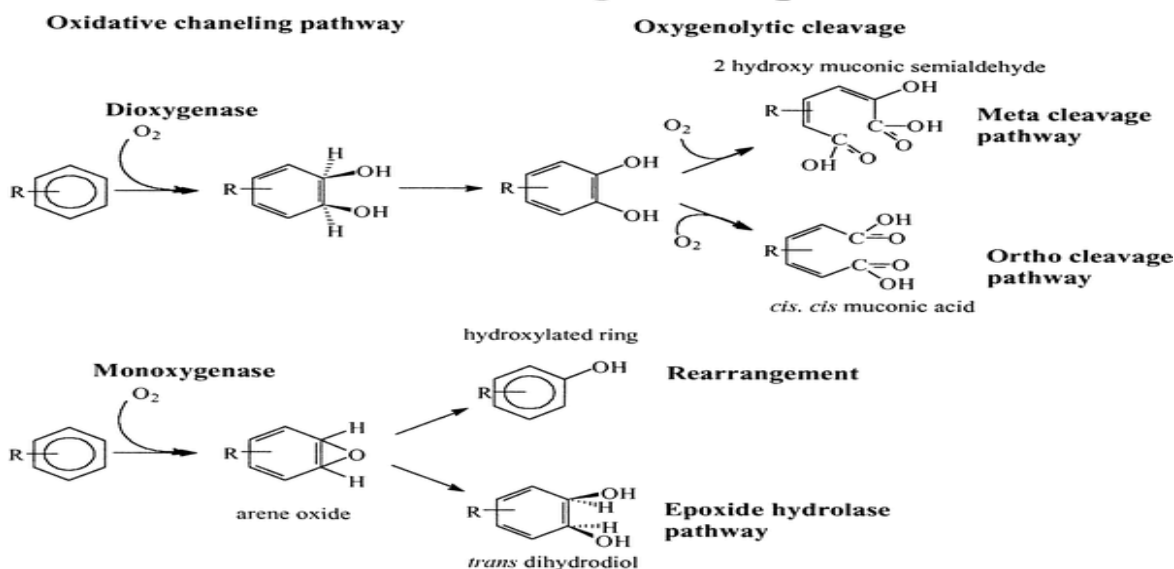
The biodegradation of high molecular weight PAH aromatic compounds has been well described (Gibson, D.T., and V. Subramanian, 1984). The initial step in the aerobic catabolism of a PAH molecule occurs via oxidation of the PAH to a dihydrodiol by a multi-component enzyme system. The dihydrodiol intermediates may then proceed through either an ortho cleavage type pathway or a meta cleavage pathway, leading to central intermediates such as protocatechuates and catechols, which are further converted to tricarboxylic acid cyclic intermediates (J.A. an der Meer et al, 1992).



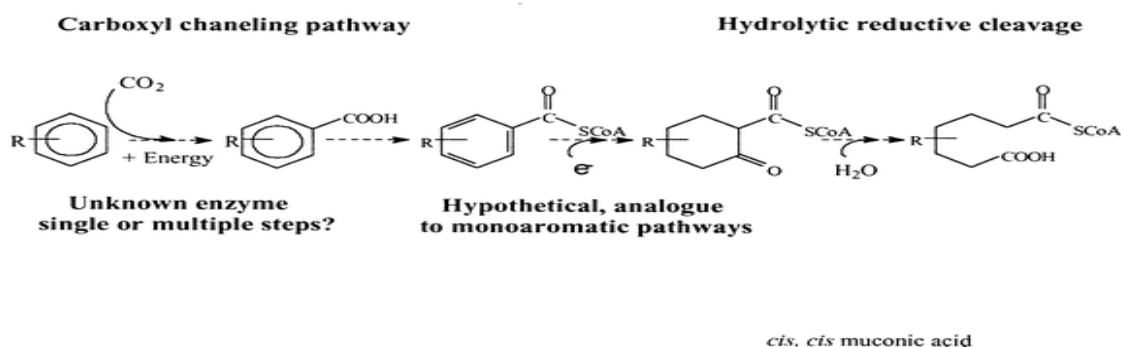
Biodegradation pathway for Benzo[a] pyrene.

The mechanism for PAH ring cleavage under aerobic conditions and anaerobic conditions is described below.

Aerobic Ring Cleavage



Anaerobic Ring Cleavage



2.0 SURFACTANT ENHANCE AQUIFER REMEDIATION (SEAR) OF HYDROPHOBIC ORGANIC CHEMICALS (HOC)

Surfactant Enhanced Aquifer Remediation (SEAR) using Ivey-sol[®] involves the use of Ivey-sol[®] surfactant formulations which are non-ionic surfactant mixtures used in the in-situ and ex-situ treatment of petroleum hydrocarbons, heavy metals, and more recently radioactive type contaminated waste. These surfactant formulations have the ability to enhance aquifer biodegradation. During In-situ aquifer bioremediation, the effectiveness of the bioremediation process is a function of balancing several physical and chemical parameters to achieve effective bio-mineralization and reclamation of the target contaminants. The addition of Ivey-sol[®] to the substrate can aid in the controlled desorption of the contaminants from the soil and or bedrock making them more bioavailable to the bacteria. As a result, the duration for of hydrophobic organic chemicals (HOC) bioremediation can be reduced by as much as 40 to 60%, or more.

Normally hydrophobic organic chemicals (HOC) exhibit limited bioavailability to microorganisms as the contaminants tend to partition onto the soil matrix. This partitioning can account for as much as 95% or more of the total contaminant mass. Thus this limits the concentration of HOC available to the microbial population. Hence certain HOC's such a Polycyclic Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyl's (PCB's) can persist in the aquifer soils and bedrock for extended periods of time. The use of Ivey-sol[®] surfactant formulations, as part of a well designed bioremediation process, will provide a mechanism to mobilize the target contaminants

from the soil and bedrock surfaces to make them more available to the microbial population.

Ivey-sol surfactants enhance key factors that influence the effectiveness of HOC bioremediation in aquifers. In particular, they increase the HOC's desorption rate and available solubility within the aquifer matrix. Thus as the HOC become more bioavailable, as the Ivey-sol surfacants improving the accessibility of the HOC substrate for the microorganisms present.

Bioavailability is governed by the substrate concentration that the cell membrane comes in contact with (i.e., what the microorganisms 'see') as well as the rate of mass transfer from potentially bioavailable (e.g., non-aqueous HOC's) phase to the directly bioavailability (e.g., surfactant-aqueous HOC) phase. SEAR affects the sorption of HOC and surfactants at the solid-liquid interface (i.e., the surface-H₂O-NAPL interface). This mechanism is in-part responsible for the increased bioavailability of the HOC and surface-bound nutrients. SEAR using Ivey-sol[®] is effective at low surfactant concentrations. It expedites bioremediation of the sorbed contamination and positively affects the surfactant-soil-NAPL systems (e.g., mass transfer of HOCs, cell hydrophobicity, and cell attachment at interfaces) while averting the inhibiting and/or microbial toxic effects associated with some surfactants (i.e., cationic and anionic) which are only effective at much higher concentrations. The SEAR mechanisms, by which Ivey-sol surfactants influence these processes is illustrated below.

2.1 Ivey-sol[®] Surfactant Technology (How It Works)

An illustration of how the SEAR - Ivey-sol technology works, (i.e., the mechanism) has been illustrated below. This should be used to augment one's present knowledge of bioremediation to appreciate the Ivey-sol surfactants effects on a microscopic scale in improving the controlled liberation of hydrocarbons and nutrients (i.e., surfactant-aqueous HOC's and nutrients-aqueous) and their controlled availability for mineralization by the microorganisms present.

This illustration demonstrates how the Ivey-sol Technology desorbs the contaminants off the soil and or bedrock surfaces, dissolves them, making them more Bio-Available and as a result and expedite the biodegradation process.

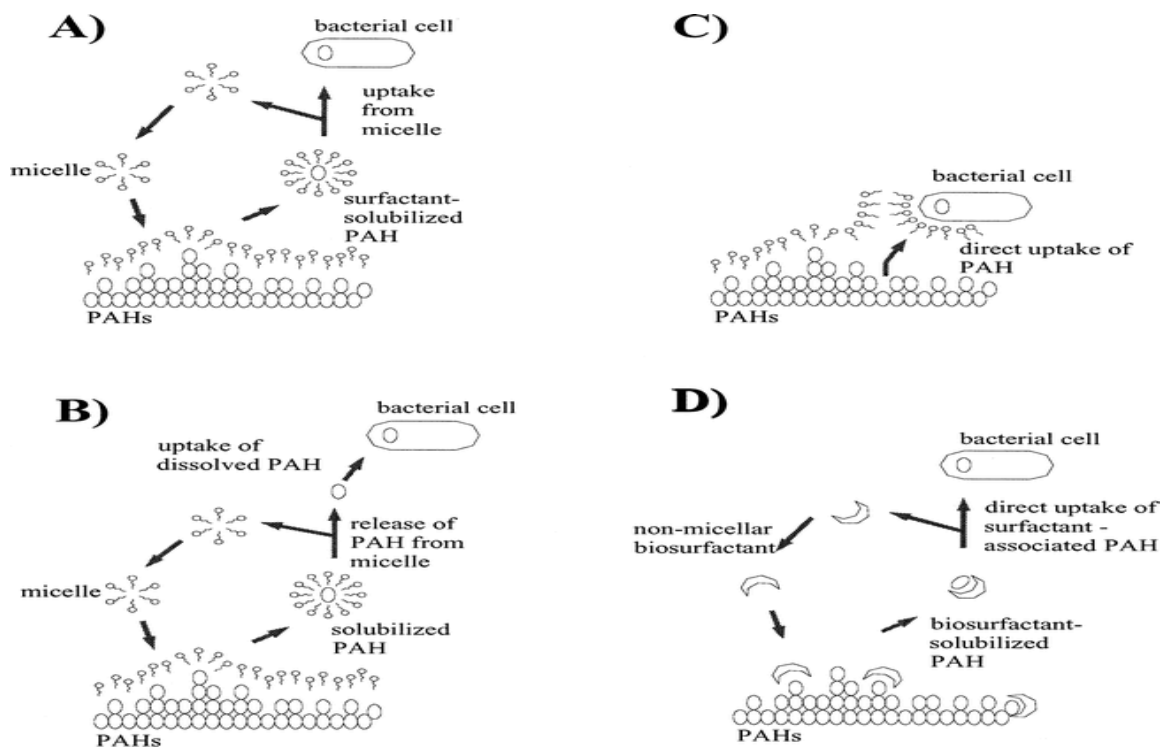
This mechanism can be described as follows:

- i) When HOC (i.e., petroleum product) is absorbed on a soil grain or bedrock surface, water alone will not remove it from the surface. This is a function of the hydrophobic characteristics of the HOC, which repels the water at its surface and its inherent low water solubility.
- ii) With the addition of Ivey-sol surfactants, the Ivey-sol hydrophobic grouping is repelled by the water but attracted to the HOC on the surface. At the same time, the Ivey-sol hydrophilic grouping is attracted to the water molecules.

- iii) These opposing forces loosen the HOC from the surface matrix and suspends it in the aquifer (groundwater) phase. Once dissolved, the suspended HOC is more visible to the microbial population present.
- iv) Once liberated in low concentration in a 'surfactant-aqueous HOC' microscopic outward appearance, it is more bioavailable to the microbial population.

2.1 Ivey-sol[®] Bioavailability Enhancement Mechanism

The mechanism for PAH bioavailability enhancement using Ivey-sol surfactants are as follows. (A) Direct uptake of the PAH from partial micelle, (B) uptake for PAH from aqueous phase after release from partial micelle, (C) facilitated direct uptake of PAH via cell-surfactant-PAH contact, and (D) hypothesized non-micellar biosurfactant enhancement of PAH solubilization (A & C adapted from Schippers et al, 2000).



2.2 SEAR Improving Pump and Treatment, and SEO (Surfactant Enhanced Oxidation) Using Ivey-sol[®] Surfactants

As the HOC are desorbed and their concentration in the groundwater increased, they are more hydraulically available for removal by pump and treatment systems. Increases in rates of contaminant recovery of greater than 400% have been reported using the Ivey-sol SEAR process (D. Smith, Handex of CT, Monro Case Study, 2002). Ivey-sol has been effectively employed to improve the performance of chemical oxidation of HOC's such as PCB's. Ivey-sol desorbed the PCB's permitting greater contact and improved reaction kinetics and corresponding oxidation of the PCB's to well within regulatory limits.

Ivey-sol, have proven to enhance the effectiveness of In-situ aquifer bioremediation by increasing the HOC's hydraulic availability for pump and treatment, it's bioavailability for bioremediation, and it's chemical availability for oxidative or reductive chemical treatment.

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