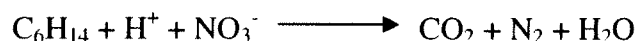


APPENDIX D

NITRATE AMENDMENT

The use of nitrate to enhance in-situ bioremediation of petroleum hydrocarbons is a developing remediation technique. Nitrate (NO_3^-) serves as a terminal electron acceptor for anaerobic and facultative anaerobic bacteria indigenous to the soil and groundwater at the site. Nitrate is added to the subsurface by percolation from the surface in an area where hydrocarbons have impacted the soil and groundwater. Nitrate and hydrocarbons are depleted as the nitrate molecule is utilized as the terminal electron acceptor by microbes during the anaerobic metabolization of hydrocarbons. The general stoichiometry of this process is shown below. The precise stoichiometry is sufficiently uncertain due to field conditions (e.g., microbial requirements, range of hydrocarbons present in the subsurface, groundwater environment) that additional field testing would be required to ascertain the true stoichiometry of the nitrate utilization process at this site.



The stoichiometric balance of the chemical reaction depends on several variables. However, an approximation of the theoretical nitrate mass requirements for the degradation of various petroleum hydrocarbons can be calculated. Stoichiometrically, approximately 6 pounds of nitrate are required to degrade 1 pound of hydrocarbons. The pilot study will establish more accurately the nitrate mass requirements for full-scale applications.

The application of nitrate is followed by consistent groundwater monitoring to determine changes in concentrations of dissolved nitrate. The oxidation/reduction potential of groundwater will also be monitored as an indicator of anaerobic bacterial activity. This monitoring will determine the rate of nitrate utilization in each location. Phosphate and sulfate may also be introduced as nutrients to the subsurface during the pilot test to further enhance bioactivity.

CHEMICAL OXIDATION PRINCIPLES

A chemical oxidation reaction involves the breaking of chemical bonds and the removal of electrons. The electrons are transferred from the contaminant to the oxidant. The contaminant is in turn oxidized and the oxidant, the electron acceptor, is reduced. All reactions are always paired in this way – hence the term oxidation-reduction reaction. We use the term “direct oxidation” for this simplest of mechanisms. With RegenOx™ however, there are other more complex mechanisms including catalyzed direct oxidation and free radical mechanisms that mediate contaminant degradation by both oxidation and reduction.

Direct Chemical Oxidation

A molecule of sodium percarbonate ($\text{C}_2\text{H}_6\text{Na}_4\text{O}_{12}$ or $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$) dissolved in water yields sodium carbonate and hydrogen peroxide creating an alkaline, oxidative

environment. As illustrated in the formula, sodium peroxide “carries” hydrogen peroxide in the same way as a molecule carries a “water of hydration”. This is a big advantage in that it makes it less immediately reactive.

RegenOx™, using sodium percarbonate can directly oxidize a wide range of contaminants including:

- Fuel hydrocarbons from gasoline through the higher molecular weight compounds.
- Aromatic hydrocarbons such as the BTEX compounds and the heavier PAH compounds
- Gasoline oxygenates such as MTBE, TAME and their derivatives (TBA)
- Petrochemically derived reagents such as phenols, aldehydes and ketones
- Chlorinated solvents with emphasis on the common chlorinated ethenes (PCE, TCE), chlorinated ethanes (TCA, DCA) and chlorinated methanes (CT, chloroform)

Surface-Mediated Chemical Oxidation

This is a variant of direct oxidation involving catalytic complexes. The RegenOx™ system, employs a complex which includes a proprietary catalytic surface that provides a unique surface (activator complex) for both the contaminant and the RegenOx™ oxidizer complex to interface. Once the contaminant, oxidizer complex and activator complex come together oxidation reactions take place more frequently. Reactions can still take place without the catalytic surface via direct oxidation, however, surface-mediated oxidation is more efficient. The advantages of surface-mediated reactions include:

The RegenOx™ system, employs a complex which includes a proprietary catalytic surface that provides a unique surface (activator complex) for both the contaminant and the RegenOx™ oxidizer complex to interface.

- Increased efficiency- brings oxidant and contaminant together isolating the oxidation reaction from soil matrix effects
- Adjustable reaction rates -- accomplished by varying oxidant to activator ratios
- Positional longevity- activator mobility in the subsurface can be adjusted by injection design

Free Radical Mediated Oxidation and Reduction

In order to completely oxidize (mineralize) contaminants to carbon dioxide and water all chemical oxidants must either supply oxygen from the oxidant itself or from reactions involving water. In addition to the oxygen provided by its oxidant, RegenOx™ is capable of promoting the propagation reactions that yield a mixture of free radicals. This free radical formation will react with water to produce oxygen.

A free radical is a highly reactive molecule having an unpaired electron. Free radicals are generated by the decomposition of peroxide in the presence of metal salts such as a ferrous salt.

Chemical Addition at Harbor Island

The Harbor Island Pug mill operates at 100 lbs/hr and the oxidation chemical will be injected to pug mill using a feed pump.

- to make a desired oxidant solution for every 5 lbs of oxidant(Part A) and 5 lbs of activator(Part B) (10 lbs total RegenOx™), use 10 gallons of water.

Mixing

- 1) Pour the pre-measured quantity of RegenOx™ Oxidizer to make the desired target % oxidant in solution mixture into the mixing drum or tank. Mix the water and oxidant with a power drill paint stirrer to ensure that the Oxidizer has dissolved in the water.
- 2) Pour the applicable amount of the pre-mixed RegenOx™ Activator into the oxidant mixing tank or pump hopper. Mix the Oxidant and Activator using a power drill paint stirrer or hand paddle mixer for at least 5 minutes until a homogenous mixture is formed. After mixing the RegenOx™ mixture should be injected into the subsurface as soon as possible.
- 3) Transfer the contents of the mixing tank using a pump to the Pug Mill.