BIOSOLIDS ENHANCED REMEDIATION

PROCESS DESCRIPTION

OVERVIEW

Innovative Remediation Technologies Inc. uses a bioremediation process that is unique to the industry. The Biosolids Enhanced Remediation (BER) approach takes advantage of aerobic and facultative metabolic pathways utilized by specifically cultured microorganisms and inoculation levels which far exceed the numbers of bacteria which can be typically attained by stimulating the natural population of selected petroleum hydrocarbon degraders. Moreover, the mechanical processing and subsequent injection of the appropriate nutrients and microbial cultures are the result of years of experience with soil handling equipment and bioremediation projects by INNRT personnel. Additionally, the BER process easily lends itself to compatibility with other remedial methods such as biological venting and cometabolic technologies utilizing gases such as methane and propane for the treatment of chlorinated solvents.

DESIGN PARAMETERS

Bacterial Production

Bacterial inoculum is produced on-site for addition to the petroleum-contaminated soil. Inoculum supplied by INNRT is added to appropriately sized reactor tanks (generally 2500 gallons) with macro- and micro-nutrients. The macro-nutrients (nitrogen, phosphorus, and carbon source) are supplied by adding diammonium phosphate and petroleum product (500 mg/L), respectively. The micro-nutrients are vitamin Bs, magnesium, calcium, manganese, iron and others. The mixture is aerated until the bacterial population reaches the maximum (generally 8-10 hours). A one time application of concentrated bacteria typically represents $>1 \times 10^8$ *petroleum degrading bacteria* per gram of soil. Due to the immediate availability of nutrients, food (petroleum in the soil) and petroleum degrading bacteria, the soil cleansing process begins immediately without the lag time associated with other such processes. Repeated additions of concentrated bacteria can be performed to enhance treatment time. This is typically done in cases where moisture levels have fallen below acceptable levels. The dominant bacteria used for remedial process have been identified as common, non-pathogenic soil bacteria and are given below. It should be noted that these organisms will typically be present within the target contaminated soil but in low numbers. These existing organisms will also begin to increase their numbers as nutritional requirements are met. The addition of bacteria to the soil is necessary primarily to decrease lag time as previously mentioned.

Pseudomonas putida	*Alcaligenes xylosoxydans*
Corynebacterium aquaticum	*Agrobacterium tumefaciens*
Arthrobacter crystallopoietes	*Ochrobactrum anthropi*
Pseudomonas aeruginosa	*Pseudomonas alcaligenes*

Nutrient Addition

In order for the bacteria to successfully metabolize petroleum contaminants, it is critical that the soil contain all of the necessary nutrients to accommodate growth. Nutrients added to the soil are in the form of ammonia nitrogen, nitrate nitrogen and ortho-phosphate. Ammonia nitrogen and ortho-phosphate are essential for efficient cell growth and maintenance. Nitrate nitrogen is added to allow metabolism to continue in the absence of oxygen when necessary as given below. Biomass is represented as $C_5H_7O_2N$. Petroleum is represented as $C_{13}H_{28}$. Similar equations can be solved for other petroleum products with fewer or greater numbers of carbons such as gasoline, kerosene, motor oil, or heavy oils. Innovative Remediation Technologies Inc. manages the nutrient requirements stoichiometrically as follows.

The equations that demonstrate the chemical requirements for biological treatment are derived from the combination of the half reactions associated with bacterial systems. A balanced chemical reaction for a given biological conversion is useful in obtaining a mass balance. This equation is generally written as follows.

$$\mathbf{R = f_sR_c + f_eR_e - R_d}$$

$\mathbf{R_c}$ = the half reaction for synthesis of bacterial cells ($C_5H_7O_2N$)
$\mathbf{R_e}$ = the half reaction for the electron acceptor
$\mathbf{R_d}$ = the half reaction for the electron donor
$\mathbf{f_s}$ = the portion of the electron donor used for cell synthesis
$\mathbf{f_e}$ = the portion of the electron donor used for cell energy, i.e., maintenance

Aerobic Mass Balance:

$\mathbf{f_s}$ = 0.7 using oxygen as the electron acceptor
$\mathbf{f_e}$ = 0.3

$\mathbf{f_sR_c}$: $0.14\ CO_2 + 0.035\ HCO_3 + 0.035\ NH_4^+ + 0.7\ H^+ + 0.7\ e^- = 0.035\ C_5H_7O_2N + 0.315\ H_2O$
$\mathbf{f_eR_e}$: $0.075\ O_2 + 0.3\ H^+ + 0.3\ e^- = 0.15\ H_2O$
$\mathbf{-R_d}$: $0.01236\ C_{13}H_{28} + 0.3267\ H_2O = 0.1609\ CO_2 + H^+ + e^-$

$\mathbf{R}$ = $0.01236\ C_{13}H_{28} + 0.075\ O_2 + 0.035\ NH_4^+ + 0.035\ HCO_3^- = 0.0209\ CO_2 + 0.1383\ H_2O + 0.035\ C_5H_7O_2N$

Facultative Mass Balance:

$\mathbf{f_s}$ = 0.6 using nitrate as the electron acceptor
$\mathbf{f_e}$ = 0.4

$\mathbf{f_sR_c}$: $0.12\ CO_2 + 0.03\ HCO_3^- + 0.03\ NH_4^+ + 0.6\ H^+ + 0.6\ e^- = 0.03\ C_5H_7O_2N + 0.27\ H_2O$

$\mathbf{f_eR_e}$: $0.08\ NO_3^- + 0.48\ H^+ + 0.4\ e^- = 0.04\ N_2 + 0.24\ H_2O$
$\mathbf{-R_d}$: $0.01236\ C_{13}H_{28} + 0.3267\ H_2O = 0.1609\ CO_2 + H^+ + e^-$

R: $0.01236\ C_{13}H_{28} + 0.08\ NO_3^- + 0.03\ HCO_3^- + 0.03\ NH_4^+ + 0.08\ H^+ = 0.0409\ CO_2 + 0.1833H_2O + 0.04\ N_2 + 0.03C_5H_7O_2N$

Inorganic nutrient salts are generally dissolved in large tanks of water (500 gallons). A single application of full strength nutrients will degrade approximately 3000 ppm of diesel fuel as calculated using the previous equations. The nutrient addition to the soil may be modified based upon soil analytical data for nitrogen and phosphorus. Repeated applications of nutrients and inoculum to treat higher concentrations are carried out as required to keep the process moving forward at a steady rate.

Certain knowledge of the fate of nitrogen and phosphorus within the soil matrix is essential to understanding the control of such nutrients when used during the remedial processes. Ammonia nitrogen is added at an initial concentration sufficient to satisfy the aerobic biodegradation equation as given for 3000 mg/kg TPH. However, ammonia nitrogen is taken up by microorganisms during the process of cell synthesis (growth). This newly formed organic nitrogen may be recycled within the soil during cell growth and death, but will not be expressed as ammonia nitrogen in nutrient analyses since it has taken an organic form.

Nitrate nitrogen may be consumed by bacteria in two ways, assimilation and dissimilation. Certain soil microbes have the ability to utilize nitrate nitrogen in the same manner as ammonia nitrogen. However, in most cases nitrate nitrogen serves as the final electron acceptor (replacing oxygen) as shown in the equation for the facultative destruction of petroleum. Nitrate nitrogen is not recycled within the soil in this process, but converted to nitrogen gas and released to the atmosphere. Therefore, nitrate is consumed during the remedial process and may be controlled based upon petroleum concentration and appropriate addition rates. This requires an efficient monitoring and control process. However, nitrate concentrations can be reduced or eliminated from the treatment in situations where this is a concern. The aerobic pathway would then become the primary remedial technique and regular soil mixing would become a requirement.

Ortho-phosphate is the most essential nutrient, although required in the least amounts. It is critical to cell metabolic functions due to its role in ATP and ADP energy transformations. Ortho-phosphate is used rather than other forms of inorganic or organic phosphorus due to its ability to be rapidly taken up by microbial cells. Other forms most always require transformation in the soil matrix before utilization can occur. However, it is important to note that most forms of phosphorus are quickly bound to the soil and are not available for leaching. This is why it is critical to insure that the nutrients, the specific organisms and food (petroleum) are in contact instantaneously.

OPERATING PARAMETERS

Biological

Certain operating conditions are required to insure that biodegradation takes place effectively. Proper nutrients, bacterial culture, moisture, temperature and pH are most important. The proper nutrients and bacterial culture addition have been previously described. Moisture is critical to maintaining viable bacterial cultures. A total of *two percent* moisture is added to the soil during the addition of the inoculum and nutrient solutions. This in addition to existing soil moisture (typically 15-20%) is sufficient to maintain biological activity. Temperature dictates the level of biological activity, that is, the higher the temperature the greater the biodegradation rate. The cultures used as inoculum have enzyme systems that are active between 35 F and 120 F with an optimum around 80 F. Bioremediation activities for all practical purposes should be conducted outdoors only as temperatures rise above 40 F. Likewise, pH is important for efficient biodegradation. The enzyme systems of most petroleum degrading bacteria operate at their optimum between pH 6.0-8.0. The nutrients that are added to the soil during normal processing are generally sufficient to buffer against any pH drop that may occur as a result of biological activity and results no free liquids. When moisture levels fall below acceptable levels, additional moisture is added along with bacteria as described. The average time of treatment under these conditions ranges from five to six weeks for diesel range organics.

Soil Handling

Petroleum contaminated soil is fed through a soil screen with a hammermill which effectively reduces the soil particle size to approximately one inch. The soil falls out of the screen onto a conveyor belt where it is spray injected first with a nutrient solution and secondly with the appropriate bacterial culture. The nutrient and bacterial sprays are supplied from an on-site production facility. The process is designed to exceed by orders of magnitude, the numbers of petroleum degrading bacteria that could be grown naturally in the soil under optimum conditions. The premise of this strategy follows the concepts developed for activated sludge wastewater treatment**.** As with the activated sludge wastewater concept, it can be demonstrated that the time of treatment correlates predictably with the number of bacteria consuming the contaminant. Innovative Remediation Technologies, Inc. is not aware of any other bioremediation company that has implemented this strategy. Once the food source (petroleum contaminant) has been metabolized by the bacteria, the population of organisms begins to die off until a normal background level of organisms remains which would be supported by available food sources.

Soil Pile Design

Once the soil has been excavated and treated by the BER process, it is placed in conical piles. Each cone is approximately 40 feet in diameter and will contain somewhere between 1200 and 1500 tons each. The soil is placed on a plastic base liner and covered with plastic for protection against inclement weather. As the conical piles are built, oxygen is provided by 1) turning the soil with end loaders and/or 2) actively blowing air into the piles via reciprocating blowers through a manifold system built into the piles as they are constructed. During times when oxygen becomes in short supply the bacteria with facultative capabilities will continue to degrade the petroleum at approximately 60 percent of the rate of the aerobic process.

BIOLOGICAL DEGRADATION PRODUCTS

As previously presented, the end-products of biological degradation are carbon dioxide, nitrogen gas and water. None of these end-products will interfere with the bioremediation process. The soil is sufficiently buffered by the added nutrients to handle the amounts of carbon dioxide produced.

AIR EMMISIONS

Recent studies of air quality within an indoor soil treatment facility substantiated that volatile organic compound emissions are negligible as would have been expected. Two water sprays are applied to the soil immediately as it exits the soil screen (nutrients and bacterial inoculum). Water sprays are an effective VOC and dust control measure as recognized by the U.S.E.P.A.. Subsequently, the soils are placed in windrows and covered with plastic to further minimize the loss of any volatiles. More importantly, volatiles are the most readily degraded compounds and are generally removed within 3 days after treatment with an average DRE of >98%.

An independent air monitoring study was performed on an indoor facility. The dimensions of the building are 160 feet wide by 400 feet long and 25 feet high. The soil receiving and BER processing areas are at one end and the side of the building with a footprint of about 25 feet by 80 feet. The remainder of the building is used for windrow treatment. The facility contained 5200 tons of gasoline and diesel contaminated soil that was already processed and standing in windrows. Additionally, approximately 700 tons of gasoline contaminated soil (average concentration of 3400 mg/kg) were stockpiled in the building and were being treated by the BER process during air monitoring. NIOSH Methods 1500 and 1501 were used for determining total hydrocarbons and aromatic hydrocarbons, respectively. Six air samples were taken. Three were in the immediate area of the soil processing area and three were from the area of the building holding the previously treated soils. Specifically, one sample was collected from inside the soil screen. The air samples are identified below.

Sample Number	Identification
1	Incoming soil truck unloading area
2	Inside soil shredder
3	Treated soil area next to processing area
4	Center of building
5	End of building most distant from processing area
6	Over incoming stockpiled soil pile

The results of the air monitoring were as follows.

Sample	Sample	Sample	Air Concentration (mg/m^3)*				
Number	Time(min)	Vol(L)	Benz	Tol	Eth Benz	Xyl	Tot. VOCs

1	310	15.2	0.2	0.8	0.3	2.6	33.4
2	293	14.4	2.5	9.4	3.0	30.5	421.2
3	290	14.6	0.2	1.2	0.5	3.9	42.1
4	279	14.3	0.2	0.8	0.3	2.4	29.2
5	254	13.0	0.2	1.0	0.3	3.1	36.4
6	249	12.4	0.3	1.4	0.6	4.4	48.6
ACGIH TWAs (mg/m^3)			32	188	434	434	

*ppm = (mg/m^3) (24.45)/gram molecular weight of compound