A NEW TECHNOLOGY FOR IN SITU PASSIVE INJECTION OF OXYGEN TO ENHANCE BIOREMEDIATION

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Abstract

Golder Associates Ltd. has developed a low cost technology for the stimulation of in situ aerobic biodegradation of petroleum hydrocarbons by injection of dissolved oxygen in groundwater. Although natural attenuation has been used for a number of years as a recognized management approach for groundwater remediation, natural attenuation is always limited to natural processes. In situ biodegradation however, is not subject to this limitation. The biodegradation process can simply speed up the natural biodegradation that is already occurring or can actually stimulate new reactions that destroy recalcitrant organic compounds. Oxygen is used by micro-organisms to degrade petroleum hydrocarbons into harmless end products. Golder has developed a passive oxygen injection system needing minimal maintenance, having low construction costs and a very high transfer coefficient of gaseous oxygen into the groundwater. The system produces a dissolved oxygen concentration around 30 ppm which is 5 times greater than the natural oxygen concentration in a non-impacted groundwater. This technology was first designed to be used in different situations:

- After an active treatment at the source in a polishing phase to destroy a residual mass of hydrocarbons;
- Where biodegradation is occurring but where natural attenuation only is not able to decrease contaminant concentrations to acceptable levels; and
- Where other technologies are inefficient, particularly in fractured rock aquifers.

Oxygen injection is done via injection wells or injection trenches. The injection of oxygen will create a reactive zone around the injection point and in time, this zone will increase in size. The plume migrating in groundwater will flow through these reactive zones and contaminants will be degraded. Groundwater is then used as the oxygen carrier. Laboratory and pilot tests on three sites have shown that high levels of oxygen concentrations in the injection wells can be maintain using this system to stimulate biodegradation. The resulting radius of influence for oxygen injection is increased compared to passive injection systems using polymeric tubes. This system is highly versatile and could be merged with a nutrient injection system if needed. This system could also be used in fractured rock aquifers and in low permeable aquifers systems.

Introduction

Aerobic biodegradation has been shown to be the most effective in reducing the concentration of aromatic hydrocarbon compounds such as BTEX. Although it has been shown that natural biodegradation by indigenous bacteria is sometimes sufficient to make it a viable remediation option, the enhancement of the biodegradation process can speed significantly the time for remediation. The traditional methods to enhance aerobic biodegradation are either active and consist of injecting air directly into the groundwater ("sparging") or pumping and re-injecting aerated groundwater. These methods have shown some limitations such as a non uniform distribution of oxygen, limited transfer rates, and significant operation and maintenance requirements. In recent years new approaches have been developed to overcome these limitations by limiting the extent of the mechanical processes and allowing at the same time a uniform distribution of oxygen. These methods are categorized as "passive" injection methods and can consist of using slow oxygen release materials or gas diffusion devices. The oxygen release materials are made of a solid metal oxide such as magnesium oxide or calcium oxide that are inserted into the ground in the form of a slurry. It will release oxygen in contact with water when groundwater will flow through it. The amount of oxygen that can be released is fixed and decreases with time until another injection is performed. Another recent method for oxygen delivery consists of using plastic tubing as semipermeable membrane to transfer oxygen in a gaseous form to a dissolved form into groundwater by molecular diffusion in the tubing. The Waterloo Emitter™ is a commercial version of such an application. Oxygen concentrations of up to 25 mg/l can be maintained in wells and transfer rates depends on the type of tubing used. Low density polyethylene (LDPE) offers a good chemical resistance for hydrocarbons and a reasonable transfer rate while silicone tubing is more efficient but will degrade more rapidly (Wilson and Mackay, 2002). Oxygen is delivered with oxygen cylinders. Although these passive emitters are efficient in terms of oxygen transfer, the mass flux of oxygen delivery in the aquifer is often not sufficient if the mass of hydrocarbons to be degraded is important. Hence, if the oxygen transfer rates are increased, the remediation of groundwater and furthermore of the soils in the saturated zone will be accelerated. Therefore, laboratory experiments were performed to investigate other configurations and types of tubing to increase oxygen transfer rates by polymeric membrane diffusion. The use of a "semi-passive" system using injection of oxygenated water was also tested.

Laboratory tests

Laboratory experiments were performed to determine and compare diffusion transfer coefficients for different types of tubing. The experimental set up for the experiments was based on the set up used by Wilson and Mackay (Wilson and

Mackay, 1995 and 2002). The layout of the experimental set up is presented on figure 1.

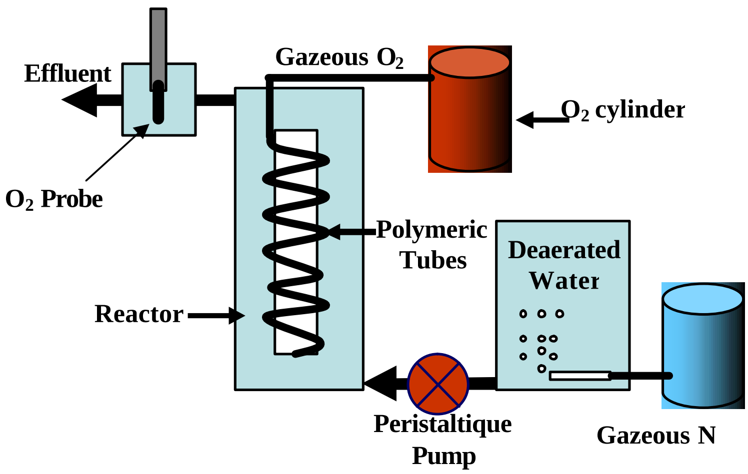

Figure 1. Schematic of the experimental set-up for the polymeric tube experiments

The tubes tested were four types of silicone and one LDPE tubing. Different configurations were also tested such as vertical and horizontal installation in relation to the flow direction.

In order to increase the amount of oxygen that could be delivered in a well, a different approach for oxygen transfer was also tested. A pressurized container, where water is placed in contact with pure oxygen gas was tested. The idea is to obtain the same oxygen concentrations in water as with the polymeric tubes but inside a container above ground. The oxygenated water can then be injected inside the wells. In this matter, the mass flux of oxygen is increase by increasing the injection flow rate. A water level gradient can be established in the well to favor the dispersion of the oxygen around the well.

Volumetric flow rate of oxygenated water was evaluated with different contact time in the cylinder and under different pressures to obtain the desired oxygen concentrations. Figure 2 illustrate the experimental set-up for the container experiment

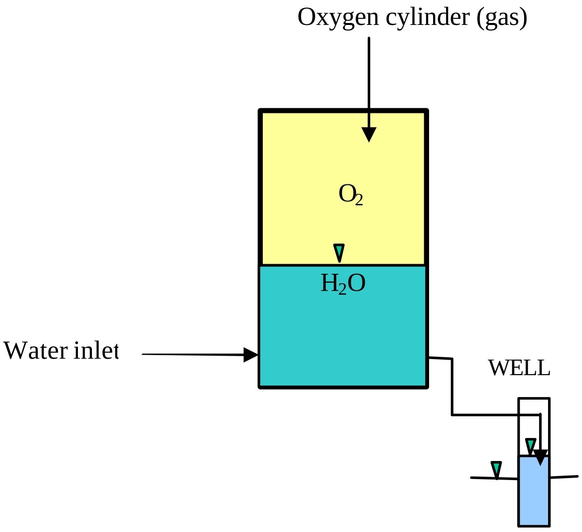

Figure 2. Experimental set-up for the container experiment

Results of the laboratory studies

The results of the polymeric tubing experiments revealed that oxygen diffusion coefficients obtained were not significantly different from the ones obtained in previous studies as illustrated on table 1. Therefore, oxygen transfer rates could not be increased significantly.

Table 1. Diffusion coefficient results compared to other studies

Studies	Tubing material	*D* (cm^2/s)
Golder (2003)	Silicone	$(0.8–6.6) \times 10^{-5}$
	LDPE	0.4×10^{-5}
Kjeldsen (1993)	Teflon	1.36×10^{-6}
	Nylon 6	4.72×10^{-9}
	PEL	1.12×10^{-6}
	PMMA	2.48×10^{-8}
	Polypropylene	3.76×10^{-7}
	PVC, flexible	7.92×10^{-7}
	Silicone	1.00×10^{-4}
Wilson et Mackay (2002)	3350 Tygon (silicone)	6.67×10^{-7}
	2275 Tygon	5.11×10^{-8}
	2075 Tygon	1.59×10^{-7}
	LDPE	1.73×10^{-8}
Patterson et coll. (2002)	Silicone	$(1.0-2.1) \times 10^{-5}$

Using these results it was calculated that for a typical bio-barrier of 50 m length where the incoming groundwater flow rate is 2.9 m³/day with a total hydrocarbon concentration of 100 mg/l, the required total length of LDPE tubing to transfer enough oxygen for complete biodegradation of the hydrocarbons would be 25 km. Considering that a 4 inch well can contain approximately 50 m of tubing, it would require 500 wells to complete the barrier. The use of such amount of tubes was considered not technically and economically feasible.

The container experiments revealed that high oxygen transfer rates could be obtained with a small installation at a fairly low flow and pressure. The final design of the pressurized oxygen container consisted of a cylinder of less than 50 liters. With this system it was demonstrated that with a pressure of 25 psig, a continuous flow rate of more than 2 liters per minute could be obtained at 30 ppm oxygen concentration.

Using the same typical bio-barrier mentioned above, it was calculated that only 6 pressurized oxygen containers would be required to deliver the same mass flow rate of oxygen in the groundwater barrier than the 500 wells equipped with LDPE tubing.

Pilot tests

Three sites were selected to perform pilot tests on the application of the oxygen injection system to increase oxygen transfer rates into the aquifer to eventually increase microbial population and biodegradation rates. The objectives of the pilot tests were primarily to demonstrate that the injection methodology using the pressurized oxygen container could increase significantly the oxygen transfer rate into the groundwater in order to stimulate indigenous biodegradation at a rate that would allow the remediation of the sites in a reasonable time frame. For the three sites, evaluation of the hydrogeological conditions and mechanisms of natural occurring degradation were performed. Limiting conditions for degradation were determined followed by the design of an engineered bioremediation system specific for each site. In summary, the characteristics of the three sites selected for the pilot tests are the following:

- Site no.1: A gas station still in operation. Site geology is characterized by a dense and impermeable till (10^{-6}cm/sec). Soils and groundwater are impacted by BTEX from gasoline. A high vacuum remediation system (VER) has been operated for a number of years to remove the free phase and decommissioned (technology limitations for soil and groundwater treatment). Residual hydrocarbons remain in the soils (above criteria) and the contaminated groundwater plume is extending offsite but stabilized. Site characterization has revealed that indigenous bacteria degrading BTEX was present but limited by the absence of oxygen and lack of nutrients. A bioremediation system including 11 injection wells was designed to remediate the site within a 5 years time frame at a cost of 215 000$.

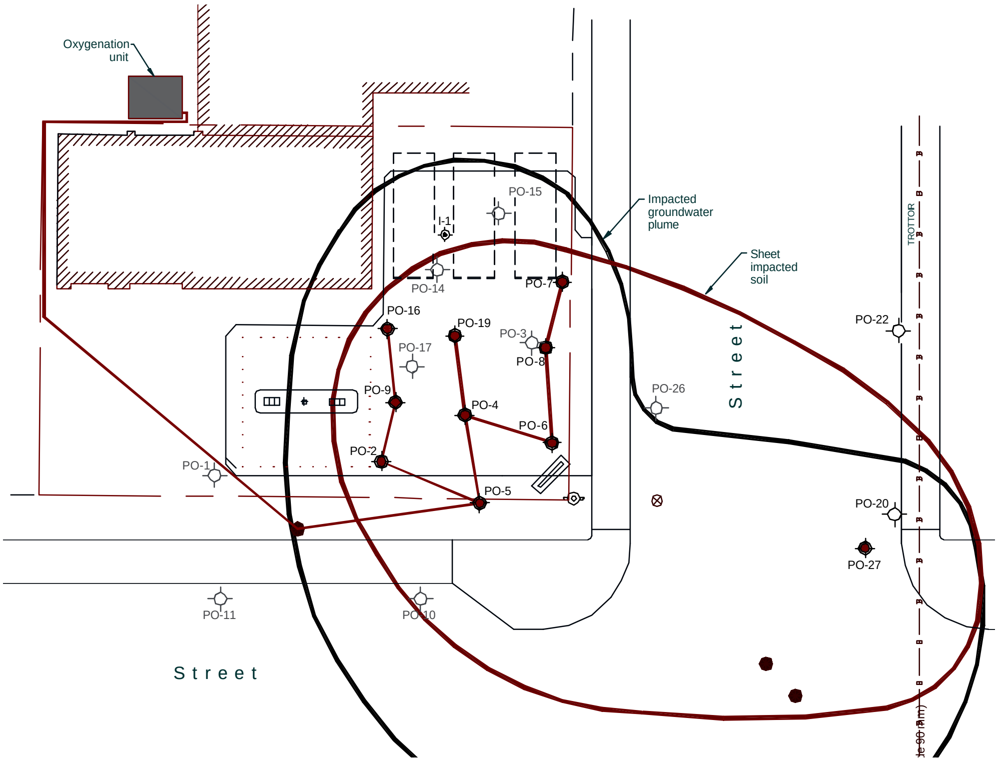

Figure 3. Layout of site no.1 with oxygen injection system

- Site no. 2: Former gas station where most of the contaminated soils were removed by excavation after closure of the site. The soils were impacted by gasoline (BTEX). The geology of the site is characterized by a sandy aquifer (k= 10^{-3} m/sec). Following the remediation impacted soils remained at locations where excavation was impossible, underneath a building and under a wooden area off site. The groundwater fluctuations are high in the area (>1,5 m) resulting in a large smearing zone and soils are impacted below and above the groundwater level located at 5 m below grade. There is a dissolved hydrocarbon plume also impacted by BTEX an extending off site but stable. A bioremediation system including 9 oxygen injection wells was designed to remediate the groundwater and the soils in the saturated zone. The system is coupled with a bioventing system including 10 vapor extraction wells to remediate the soils in the unsaturated zone above the water table. The site is to be remediated within a 5 years time frame at a cost of 215 000$.

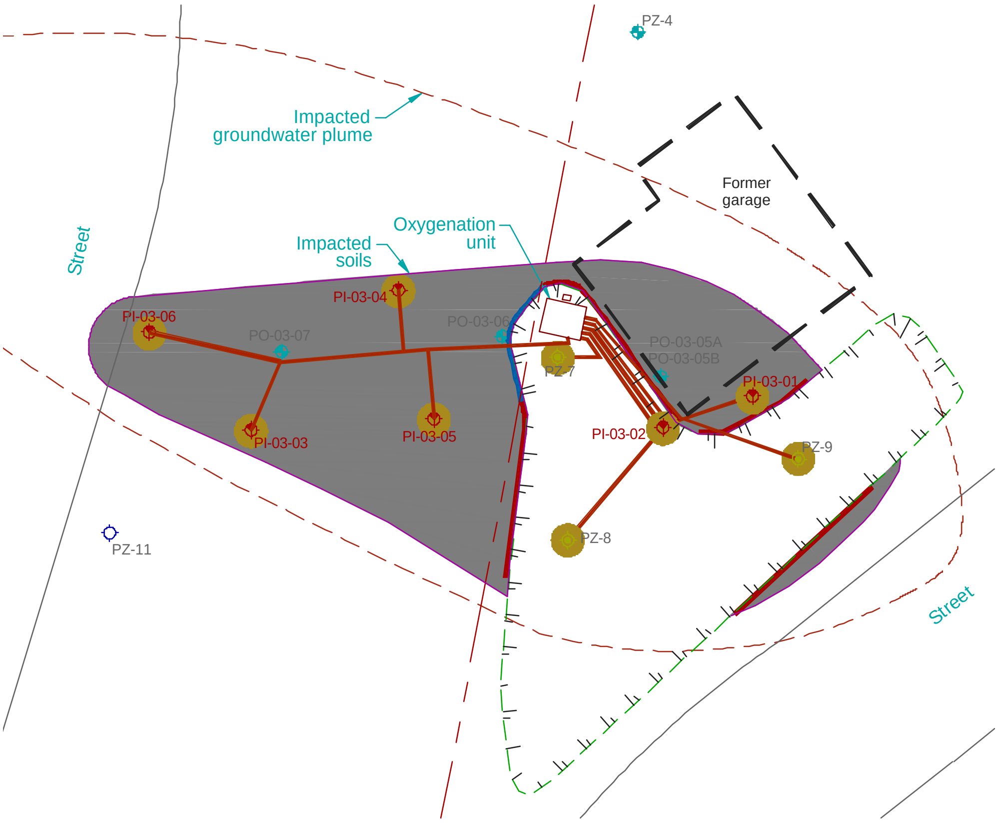

Figure 4. Layout of site no.2 with oxygen injection system

Site no. 3: Former petroleum depot where all the impacted soils have been excavated and treated offsite. However, impacted groundwater by diesel range organics is present at soil-bedrock interface and the plume has migrated off-site but is stable. At some locations there is free phase hydrocarbons in wells (film to <5cm). The geology is characterized by a fill on top of fractured bedrock. The hydraulic conductivity is 10^{-5} m/s. The objective of the remediation project is to limit off-site migration and also remediate the entire plume. A bioremediation system including three bio-barriers have been design to remediate the site within 2,5 years at a cost of 175 000$.

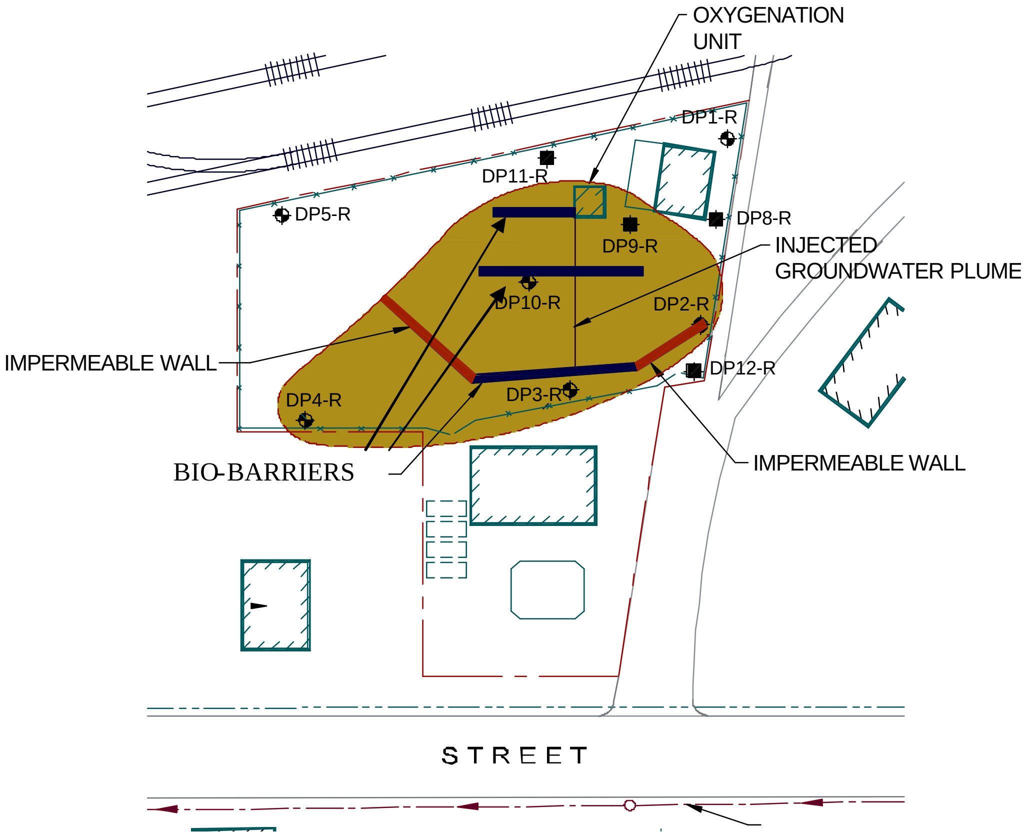

Figure 5. Layout of site no.3 with oxygen injection system

The pilot tests consisted of injecting oxygen in a limited number of wells using the developed system for each site. For site no. 1 the injection was performed in two wells at a rate of 4,5 liters per hour per well. For site no.2 injection was performed in 3 wells at 60 liters per hour per well and for site no. 3, a small scale barrier of 5 m in length was constructed where five injection points were installed and the injection rate is 80 liters per hour per injection point.

The injection system was fully automated allowing monitoring and controlling the water injection from Golder office using PLC control system and a telephone line installed on site. Two oxygen cylinders were installed for each site which was sufficient for the duration of the pilot tests that lasted for 6 months.

Modeling of the injection

Simulations of the injection of oxygen for each of the pilot test sites were performed using a numerical model. At this point biodegradation was not incorporated in the simulations in order to evaluate the theoretical mass transfer of oxygenated water into the subsurface. The simulations were used also to compare passive injection using polymeric tubes in comparison to the pressurized oxygen container. The following figures illustrate a simulation of oxygen concentrations in groundwater with time for site no.1 with injection in two wells. Both simulations were with a fixed concentration of oxygen inside the wells maintained at 30 ppm.

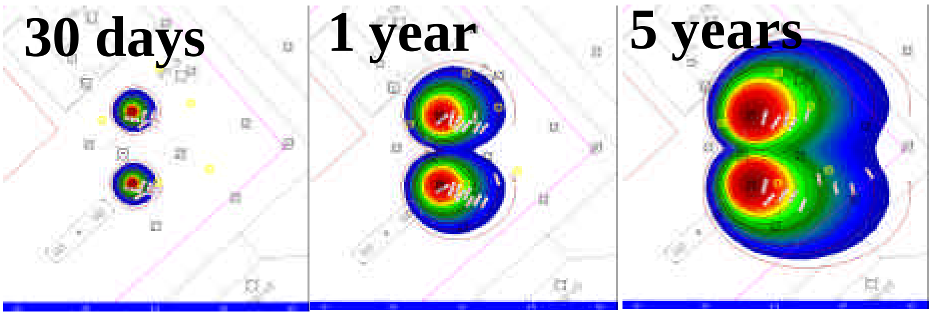

Figure 6. Simulation of oxygen concentrations in groundwater for site no.1 with injection in two wells using the pressurized oxygen container

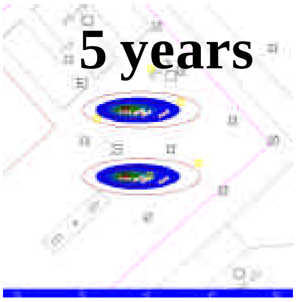

Figure 7. Simulation of oxygen concentrations in groundwater for site no.1 with injection in two wells with passive injection using polymeric tubes (LDPE)

These figures demonstrate that the radius of influence of increased oxygen concentrations around the wells is significantly greater with the pressurized container system. This is caused by the continuous injection of oxygen saturated water inside the wells creating a hydraulic gradient between the wells and the surrounding groundwater which is the driving force of this process. The dispersion of oxygen saturated water with the passive tubing system is limited by the natural groundwater flow rate which the limiting factor with this system.

Results of the pilot tests

For Site no. 1, the results can be summarized as follow:

- During the 6 months of injection, the oxygen concentrations in both injection wells were maintained at all times above 25 ppm;
- The microbial population increased by a factor of 1000 during the injection and decreased to its initial values three weeks after shutdown of the pilot tests; and
- The total BTEX concentrations in the injection wells before the pilot tests were
  43 ppm and 75 ppm and three weeks after the tests were stopped, the BTEX concentrations were non detected (after purging of the wells).

For site no.2, oxygen concentrations in injection wells were also maintained above
30 ppm during the entire test period. However, there was no significant decrease in BTEX concentrations and no increase in bacterial population in the wells sampled after shut down of the pilot test. These results could be explained by the high permeability of the aquifer and the small scale of the test compared to the size of the plume. Therefore it is suspected that the equilibrium state with the surrounding groundwater was re-established when sampling was performed.

Finally, for site no.3, the oxygen concentrations in the barrier were maintained above
20 ppm during the entire test period. After shutdown of the test the oxygen concentrations decreased to less than 4 ppm. The microbial population in the barrier increased by a factor of 400 during the tests and decreased to its initial state after the test. Total hydrocarbon concentrations were between 100 and 300 ppm before the tests and decreased after the test to non detected in the barrier and to 7,6 ppm in a well 3 m down gradient.

Conclusion

These results demonstrated that the use of an oxygen injection system using an above ground pressurized container can increase delivery rates of oxygen in the subsurface to accelerate biodegradation rates of hydrocarbons. Laboratory and pilot tests on three sites have shown that high levels of oxygen concentrations in the injection wells. The resulting radius of influence for oxygen injection is increased compared to passive injection systems using polymeric tubes. The limiting factor of polymeric tubes systems is the groundwater flow rate which is the mechanism by which the oxygen is dispersed in the surrounding subsurface. With the “semi-passive” injection using a pressurized container and a water injection flow rate, a gradient is created in the injection well and creates the driving force for the dispersion of the oxygen. However, groundwater flow modeling must be incorporated in the design of the injection system in order to make sure that the water injection will not cause the spreading of the plume and that biodegradation will be the principal mechanism of hydrocarbon mass reduction. The full-scale treatment of the sites no 1, 2 and 3 is planned for 2005.

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