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COST IMPLICATIONS OF HYDROGEN DONOR SELECTION FOR IN SITU BIOREMEDIATION OF CHLORINATED SOLVENTS

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ABSTRACT: The use of enhanced anaerobic bioremediation for treatment of chlorinated solvents in groundwater has increased at a rapid rate within the past three years. Since there are a number of different hydrogen donors that can potentially be used, it is important that practitioners understand the cost implications of the hydrogen donor(s) selected for the project.

A comparative economic analysis is presented which indicates that the donor source cost can be misleading unless converted to a cost per pound of hydrogen equivalents. Although we have not attempted to determine the minimum hydrogen donor dose that is necessary to achieve complete dechlorination, we have based the hydrogen requirements on stoichiometric demand. In addition to the donor cost, practitioners must also be cognizant of the cost associated with the required delivery system.

A template site approach is used to compare remediation net present value costs for the following in situ bioremediation processes to treat chlorinated solvents: anaerobic bioremediation with a recirculation system using lactate, methanol, ethanol, and sodium benzoate; anaerobic bioremediation with periodic feeding of soluble substrates such as molasses or lactate; anaerobic bioremediation with long-lasting substrates such as Hydrogen Release Compound (HRCTM) or edible oil emulsions; and natural attenuation. The analysis shows that the cost of hydrogen donors can vary significantly in addition to having a significant effect on the substrate delivery system cost.

INTRODUCTION

Now that the reductive dechlorination process is being moved from pilot scale to full scale projects, it is imperative that practitioners understand the cost implications of the hydrogen donor(s) selected for the project. There are a number of different hydrogen donors that can potentially be used. Each of the donors yields different amounts of hydrogen per pound of substrate. In addition to the hydrogen donor yield, the practitioner must also consider the dosage required to achieve dechlorination (DiStefano, et al. 2000). It should be noted that we have not considered the dosage variability in this economic analysis.

Anaerobic biodegradation takes advantage of natural biological processes. Sites with co-contaminants such as petroleum fuels, other biodegradable hydrocarbon solvents, or natural organic matter often have developed microbial populations capable of complete dechlorination. If the microbial population is not present, bioaugmentation with a dechlorinating enrichment culture has been shown to be effective (Ellis, et. al. 2000). If a source of organic carbon is not

present in sufficient quantities to promote reductive dechlorination, there are a number of anaerobic substrates available as a supplement.

Hydrogen is the source of electron donors that drives the reductive dechlorination of chlorinated hydrocarbons. Therefore, one measure of the cost effectiveness of anaerobic substrates is the number of hydrogen units generated per dollar cost. In Table 1, an average molecular formula was calculated for each compound and the amount of hydrogen generated from its biodegradation according to the stoichiometry presented in He et al (2002). However, acetate was assumed not to yield hydrogen.

Various types of in situ biological systems are available for addressing halogenated solvents in a groundwater flow field. A recirculation system is one type of system, which may add significantly to the project cost for installation of the extraction and injection wells as well as the operation and maintenance requirements including rehabilitation of biofouled injection wells (Ellis, et al 2000). However, better distribution of the soluble substrate can be achieved with the recirculation system than non-recirculation systems and the process is likely to be more rapid. Alternatively, soluble substrates can be added without a recirculation system. However, large volumes of diluent are added, radial distribution may be limited and frequent reapplication may be necessary. Soluble substrates include lactate, benzoate, molasses, citrate, acetate, methanol, and ethanol.

An alternative to the recirculation system with soluble substrates has been developing over the past several years with the use of slow release substrates such as HRCTM and, more recently, edible oil emulsions (Borden and Lee, 2002) that are directly injected into the flow field. These substrates are typically injected using the direct-push method (Geoprobe® or similar). At some sites, temporary injection wells have been used for injection of the slow-release substrates when multiple applications or significant amounts of substrate per well are required.

Another approach is the use of a barrier system to prevent contaminants from migrating offsite. Typically slow-release substrates are used in this application to minimize the cost associated with reapplication.

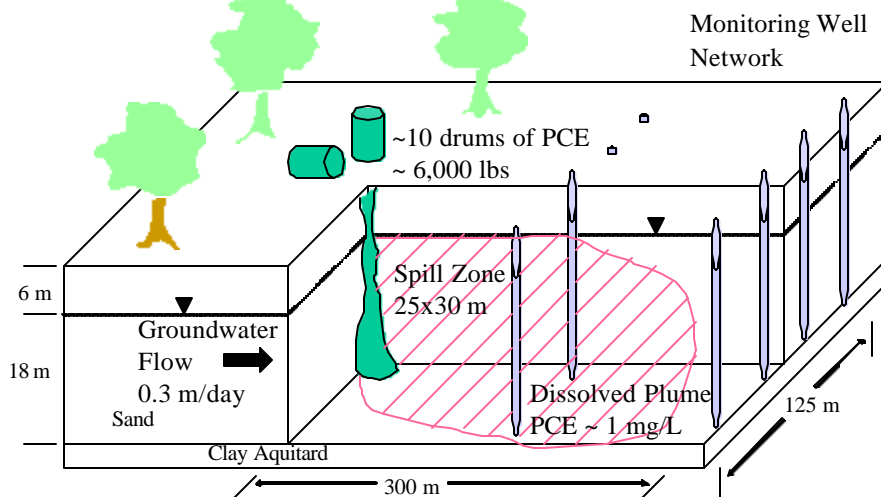
A template site approach is used to compare remediation net present value costs for the following in situ bioremediation processes to treat chlorinated solvents: anaerobic bioremediation with a recirculation system using soluble substrates (active treatment system); anaerobic bioremediation with periodic feeding of slow-release substrates in a grid configuration for source area treatment (passive treatment system); anaerobic bioremediation with slow-release substrates in a barrier configuration to prevent the off-site migration of contaminants; and natural attenuation.

As in all remedial systems, the four major general cost categories are site characterization, design, construction, and operations and maintenance (including monitoring costs). For the purposes of this analysis, it is assumed that the cost of a proper site characterization will remain relatively constant for each of the substrate delivery systems.

Substrate cost is driven by the hydrogen donor demand, base donor cost, donor preparation cost and donor delivery cost. The primary goal is to provide bioavailable carbon to the dehalorespirers whether in the source area or in a downgradient barrier. If a barrier system is used, the contaminated groundwater must come in contact with the substrate enhanced area in

the subsurface. Although regulatory requirements can impact monitoring costs, the typical cost driver is the length of time that the system must operate. It should be noted that a recirculation system will usually require a more intense monitoring (process control) program than the use of a direct-injection slow-release system.

Figure 1
Template Site



The cost model assumes the presence of dehalorespirers within the entire impacted area. It should be noted that there is evidence that dehalorespirers are not present at all sites with chlorinated contaminants (Hendrickson, et al. 2002).

MATERIALS AND METHODS

The economic analysis that is described in this paper is based upon a method developed by DuPont Company that was used to compare in situ remediation technologies on a consistent economic basis (Quinton et al, 1997) and utilized by GE Research & Development to evaluate costs for enhanced anaerobic biodegradation systems (Harkness, 2000). The methodology utilizes a template site impacted by 2,727 kg (6,000 lbs) of perchloroethene (PCE) which is equivalent to ten 55-gallon (208 L) drums of PCE (Figure 1). The spill area is 22.9 X 30.5 meters (75 X 100 ft.) in the saturated zone with a saturated thickness of 18.3 meters (60 ft.) beneath a 6.1 meter (20 ft.) unsaturated zone. The dissolved plume is 305 meters long X 122 meters wide X 18.3 meters deep (1,000 X 400 X 60 feet) with an average PCE concentration of 1 mg/L. The soil porosity is 0.25 and the average linear groundwater velocity is 0.3 meter/day (1.0 foot/day).

The DuPont method included costs associated with engineering, including design and modeling, operation, maintenance, and labor, substrate, monitoring, and project duration. It was assumed that a microbial population capable of reductive dechlorination is present. The monitoring network at the site consists of 20 monitoring wells and the installation costs are the same for all cases considered. Monitoring costs include labor, equipment, analytical, and

reporting costs. Monitoring frequency is assumed to be quarterly for the first year and semi-annually thereafter.

Harkness (2000) expanded on DuPont's original analysis (Quinton et al., 1997) by comparing three configurations of enhanced anaerobic bioremediation systems. Both analyses used net present cost to keep all of the cases on a consistent economic basis. In the case of containment, a remediation time of 30 years was used because the net present cost method is minimally affected by costs beyond 30 years. We have also remained consistent with the combined discount rate of 8.7% for annual costs. However, we updated costs for the various elements of the cost structure (substrate and substrate direct injection) as appropriate.

The efficiency of donor utilization for reductive dechlorination has not been explored for the purposes of this evaluation. The hydrogen will be consumed to reduce oxygen, nitrate, sulfate, iron and generate methane. DiStefano and Baral (2000) reported donor dosages ranging from 5 to 50 times the stoichiometric amount for various soluble substrates including methanol to achieve complete PCE removal. Harkness (2000) used a ratio of 35 to 1 for sodium benzoate to PCE. We assumed that 20 times the stoichiometric demand of electron donor processes for reductive dechlorination was provided to meet this demand.

Passive System. Two passive substrate delivery systems were evaluated for the template site: a barrier system that intersects the plume 305 meters (1,000 ft.) from the spill zone which acts as a containment strategy and a grid pattern that is focused on remediating the spill zone. In the case of the grid pattern, it is assumed that any parent and daughter compounds leaving the spill zone will naturally attenuate prior to crossing the property boundary.

- **Barrier** – The model utilizes two rows of temporary injection points on 3 meter (10 ft.) centers installed 305 meters (1,000 ft) downgradient of the spill zone and will be operational for a period of 30 years because the spill zone will act as a continuing source of contaminant. A variation of this approach is the installation of 80 injection wells that can be reused during the operational period. Reusable injection wells are estimated to cost \$240,000. Substrates that require two or more injection events per year have a minimum net present cost of \$400,000 for injection. Substrate injection events are based on estimated length of time the substrate will continue to generate hydrogen. Unfortunately, there is very little information in the literature regarding substrate life. For the purposes of this model, molasses is estimated to last 6 months, HRC for 24 months, and edible oil emulsion for 36 months.
- **Grid System** – The model utilizes 80 temporary injection points within a 22.9 X 30.5 meter (75 ft X 100 ft.) area to a depth of 24.4 meters (80 ft.) below ground surface within the spill zone. Substrate utilization is assumed to be consumed over a 5 year period with injection events based on the estimated length of time the substrate will continue to generate hydrogen.

Natural Attenuation. The original DuPont model (Quinton et al., 1997) assumed costs for 20 monitoring wells placed on the template site and groundwater monitoring events on a semi-

annual basis for intrinsic and groundwater quality parameters throughout the plume for a period of 30 years. It also included the investment necessary to generate enough data to support a technical argument that natural attenuation is occurring on the template site.

Active System (Groundwater Recirculation System). The model is based on a batch feed system that requires two substrate/nutrient additions per month. The substrate comparison is limited to the soluble substrates excluding molasses and includes a standard nutrient package such as ammonium phosphate. The mixture is injected into a recirculation system that consists of 4 extraction and 4 injection wells constructed down gradient and up gradient of the spill zone. We have used the same conservative assumption as contained in the DuPont model that the system will operate for 5 years.

RESULTS AND DISCUSSION

A key element in the evaluation of the total anaerobic bioremediation system cost is the amount of hydrogen generated by the various available substrates. As shown in Table 1, the volume (grams) of hydrogen donor per dollar cost ranges from 4.1 to 276.5. It should be noted that hydrogen donor cost is only one element of the analysis. The net present cost details of various substrates as applied in a passive system are presented in Table 2 and an active system are presented in Table 3. The cost categories include design costs (modeling and tracer studies), capital costs (injection wells and monitoring wells), operation and maintenance costs, monitoring costs, and substrate costs. As shown in Tables 2 and 3, there are three key points that the analysis makes to highlight the effect of the various cost elements:

- Depending on the hydrogen donor selected, the analysis indicates that a passive grid (source area treatment) system is lower in cost than an active (source area treatment) system.
- There is a significant difference between the cost of a barrier and a grid system. It appears that a barrier system will generally be twice as expensive as a grid system.
- The barrier system cost is similar to that of an active system.

A comparison of the costs for injection points and injection wells was done. Except for substrate used in the barrier configuration that requires semi-annual injection events, it is less expensive to use temporary injection points instead of injection wells. The installation of an injection well network was estimated to have a net present cost of \$240,000 as compared to \$156,000 for bi-annual injection events using the direct-push method for 30 years. The net present cost of semi-annual injection events using the direct push method for 30 years was estimated to be \$400,000. This makes the assumption that the injection wells will not have to be replaced during their 30 year life. Costs incurred after 30 years are not material because the net present cost method is minimally affected by costs beyond 30 years.

TABLE 1. Hydrogen yields for different electron donors.

Name	Formula	Mol weight (g/mol)	Mole H ₂ /mole substrate	g H ₂ /g substrate	US\$/Kg	Purchased Concentration	Price/Kg for 100% Solution	g H ₂ /US\$
Sodium lactate	C ₃ H ₅ O ₃ Na	112	2	0.036	\$ 1.52	60%	2.53	14.2
Sodium benzoate	C ₇ H ₅ O ₇ Na	144	3	0.042	\$ 1.76	100%	1.76	23.9
Ethanol	C ₂ H ₆ O	46	2	0.087	\$ 1.19	95%	1.25	69.6
Methanol	CH ₄ O	32	3	0.188	\$ 0.68	100%	0.68	276.5
Molasses								
35% Sucrose	C ₁₂ H ₂₂ O ₁₁	342	8	0.047	\$ 0.14	35%	0.40	117.5
7% Glucose	C ₆ H ₁₂ O ₆	180	4	0.044	\$ 0.14	7%	2.00	22.0
9% Fructose	C ₆ H ₁₂ O ₆	180	4	0.044	\$ 0.14	9%	1.56	28.2
Total Molasses			3.4	0.023	\$ 0.14	51%	0.27	85.2
Emulsified Veg. Oil	C _{17.9} H _{32.9} O ₂	265.6	16	0.120	\$ 1.76	20%	8.80	13.6
Hydrogen Release Compound (HRC™)	C ₃₉ H ₅₆ O ₃₉	956	26	0.054	\$ 13.20	100%	13.20	4.1

Note:

Costs assume bulk quantities, but does not include shipping

Calculation of hydrogen yield: e.g. Lactate: $C_3H_5O_3^- + 2H_2O \Rightarrow C_2H_3O_2^- + 2H_2 + H^+ + HCO_3^-$. Therefore lactate has 2H₂/mole

As shown in Tables 2 and 3, the hydrogen donor cost ranges from 2% to 51% of the total project cost for the above bioremediation systems. The primary cost for the active systems is for the hydrogen donor delivery system operation and maintenance which is a result of the level of labor required to keep the system operational.

TABLE 2. Passive anaerobic bioremediation system costs.

Cost Category	Capital	Design	O&M	Monitoring	Substrate	Total
Barrier System – 30 Yr. Operation						
Molasses	320	120	106	560	54	1160
Cost % of Total	28%	10%	9%	48%	5%	
HRC™	80	120	156	560	299	1215
Cost % of Total	7%	10%	13%	46%	25%	
Emulsified Veg Oil	80	120	124	560	76	960
Cost % of Total	8%	12%	13%	58%	8%	
Grid System – 5 Yr. Operation						
Molasses	80	120	149	130	121	600
Cost % of Total	13%	20%	25%	22%	20%	
HRC™	80	120	98	130	446	874
Cost % of Total	9%	14%	11%	15%	51%	
Emulsified Veg Oil	80	120	72	130	104	506
Cost % of Total	16%	24%	14%	26%	21%	
Natural Attenuation – 30 Yr. Operation	80	250	0	560	0	890
Cost % of Total	9%	28%	0%	63%	0%	

TABLE 3: Active anaerobic bioremediation system cost.

Cost Category	Capital	Design	O&M	Substrate	Monitoring	Total
Sodium Lactate	155	120	542	122	130	1069
Cost % of Total	15%	11%	51%	11%	12%	
Methanol	155	120	542	15	130	962
Cost % of Total	16%	12%	56%	2%	13%	
Ethanol	155	120	542	18	130	965
Cost % of Total	16%	12%	56%	2%	13%	
Sodium Benzoate	155	120	542	43	130	990
Cost % of Total	16%	12%	55%	4%	13%	

The O&M costs in Table 2 primarily reflect the cost of direct push equipment and labor used to deliver the substrate to the subsurface. The number of injection events is dictated by the amount of time substrate supply can yield hydrogen in the subsurface. As shown in the table, this category can range from 11% to 25% of total project cost.

In evaluating the various alternatives, the project engineer should also consider the opportunity costs associated with extending the project beyond the time required for an active remediation system to remediate the site.

The original DuPont economic study calculated the net present cost for monitored natural attenuation for this site to be \$890,000. The passive anaerobic grid system cost are calculated to be lower and therefore, offer potential cost savings in addition to a shorter remediation period.

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