Evaluation of Groundwater Management/Remediation Technologies For Application to the Paducah Gaseous Diffusion Plant

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EXECUTIVE SUMMARY

The Paducah Gaseous Diffusion Plant (PGDP) began uranium enrichment operations in 1952 and became fully operational by 1955. Three large apparent plumes of contaminated groundwater have migrated outside the plant boundaries. Of most concern are two northern plumes oriented roughly north-northeast from the plant toward the Ohio River. The primary contaminants in all three plumes are trichloroethylene, TCE, an industrial degreasing solvent, and technetium 99, Tc-99, a fission byproduct of uranium enrichment.

The objective of the present study was to evaluate remediation technologies for the contaminated groundwater at PGDP by updating the recommendations of the Technical Advisory Group (TAG) of the Innovative Treatment Remediation Demonstration Program (ITRD) made in the Paducah Project Innovative Technology Review final report (ITRD 2000). The TAG identified and reviewed thirty *in situ* remediation technologies for general maturity, cost, and quality of performance as the technologies would apply to PGDP. Their ranking of technologies recommended for *in situ* treatment of contaminated slowly permeable soils was:

- Rotary treatment
- Chemical oxidation-ozone/fracturing
- Direct heating
- Soil Vapor Extraction (SVE)/fracturing

The ranking of technologies recommended for *in situ* treatment of a contaminated highly permeable sand and gravel aquifer was:

- Chemical oxidation (C-Sparge)
- Direct heating
- Steam/ Dynamic Underground Stripping/Hydrous Pyrolysis Oxidation (DUS/HPO)
- Chemical oxidation (permanganate)

The TAG endorsed an elemental iron reactive wall pilot study and ranked the pilot studies needed for further study. Priority 1 consisted of C-Sparge with ion exchange for Tc-99 in the highly permeable sand and gravel aquifer and fracturing with ozone in the slowly permeable soils. Priority 2 consisted of direct heating (six-phase heating) and chemical oxidation using permanganate.

The present study updated the work of the TAG by:
1. Presenting results and economic evaluation of more recent case studies (reported since 1999) using technologies endorsed by the TAG;
2. Updating the economic analyses of the TAG when no recent studies were reported using specific technologies; and
3. Analyzing case studies of newer technologies not available during the time of the TAG study. These technologies included various bioremediation applications, applications of nanotechnology, and newer developments in permeable reactive barrier (PRB) techniques.
   Conclusions from the present study are summarized as follows:

1. Six-phase heating is a very effective treatment at high contaminant concentration levels but has the highest overall cost, approximately twenty times more expensive per cubic yard of

treatment zone than rotary treatment which has been shown to be just as effective at similar contaminant concentration levels.

2. SVE may not be as difficult to implement as six-phase heating or rotary treatment but is the second most expensive treatment method particularly at higher contaminant concentration levels.

3. Steam (DUS/HPO) did not perform well in reducing contamination levels during trial durations comparable to other technologies.

4. PRBs can be very cost-effective for preventing contaminant source or plume migration.

5. *In situ* chemical oxidation (ISCO) showed significantly lower cost per cubic yard of treatment zone than 6-phase heating or SVE, and could be very effective in treatment of VOCs. Of the ISCO technologies reviewed, C-Sparge with ozone, and peroxide-activated sodium persulfate, showed the most promise in remediating dissolved phase, DNAPL, and adsorbed, chlorinated hydrocarbons, within relatively short treatment periods. ISCO remediation with potassium permanganate and Fenton's reagent showed contaminant concentration rebound in the groundwater when chemical addition ceased, indicating an inability of these techniques to deal with DNAPL or adsorbed contaminants.

6. The bioremediation case studies showed that under certain site conditions microbes can be utilized to remediate groundwater contaminated with VOCs at a very low cost compared to other technologies.

7. Soil fracturing may enhance *in situ* chemical oxidation using permanganate more than it enhances the other remediation technologies considered.

8. While several technologies (mentioned above) appear to be feasible for TCE remediation, the only existing remediation method for Tc-99 is immobilization, using either microbes (extremophiles) to transform Tc-99 to its insoluble reduced state, or PRBs with reducing treatment media to prevent Tc-99 movement beyond the PRB.

9. Humic products have the potential to be cost effective for TCE remediation but, more importantly, humic products can immobilize Tc-99. Humic material provides a substrate and nutrient for microbes, and fosters a diversity of microbes, which allows remediation at higher contaminant concentrations possibly permitting bioremediation in the high TCE concentration source areas of PGDP.

In summary, review of case studies indicated that the use of microbes with cometabolites, application of ISCO methods, and use of PRBs became very popular for remediation in the period 2000-2005. In contrast, there were few or no case studies involving the other, older, technologies reported in the literature during this period.

Recommendations from the study are as follows:

1. The site assessment parameters outlined in Section III-K of this report should be used to determine the feasibility of using bioremediation. It is believed that while bioremediation may not be most suitable for source areas, it may be the most practical remediation technology for TCE in the three plume zones. Another advantage of bioremediation is that anaerobic reduction may immobilize Tc-99.

2. If evaluation of conditions in the plume zones indicates that bioremediation would not be cost-effective, the ISCO methods should be investigated. Despite the contaminant rebound problems with permanganate and Fenton's reagent, those techniques could still be implemented successfully in the plume areas where undissolved and adsorbed contaminant

mass is not a concern. In DNAPL zones where large amounts of undissolved and adsorbed contaminant mass could exist, ozone and persulfate ISCO methods should be investigated.

3. Small-scale tests could be conducted in the UCRS using the selected ISCO or bioremediation methods with and without fracturing to determine if soil fracturing would improve remediation.

4. Table 1, below, ranks this study's recommended technologies, together with six-phase heating which has been applied previously at PGDP, using a typical grading system (A = best, B, C, D, and F = worst) in the context of various application factors.

Table 1. Technology Ranking

Technology	Percent Reduction of Contaminant	Relative Ease of Implemen-tation	Applicable in Source Zones?	Cost-Effective for Plume Treatment?	Time to Treat	Cost for use at Source	Cost for use in Plume
Bioremedi-ation	A	A	C	A	C	A	A
Bioremed. w/Humics	A	A	B	A	C	A	A
ISCO [typical]	B	A	B	B	C	A	B
ISCO-Persulfate	A	A	A	B	A	A	B
Six-Phase Heating	A	C	A	D	A	D	F

I. INTRODUCTION

    A. <u>Groundwater Contamination</u>

The Paducah Gaseous Diffusion Plant (PGDP) is located on approximately 3,600 acres in western Kentucky near the Ohio River, with 750 acres located inside a security fence area. The plant area is situated 10 miles west of Paducah and about 3.5 miles south of the Ohio River. The map in Figure A-1 shows the PGDP location.

The PGDP began uranium enrichment operations in 1952 and became fully operational by 1955. Initially, the plant produced materials used in the U.S. nuclear weapons industry. Operations gradually expanded to include nuclear weapons disassembly and disposal, recovery of trans-uranics, exotic metals recovery, and uranium milling and recovery. Eventually, the plant produced fuel for commercial nuclear power plants. Radioactive and hazardous wastes have been generated and deposited at the site from previous waste disposal and plant operations. Improper disposal practices, accidental or deliberate releases, spills and leaching from buried waste materials have contributed to contamination of the soil and groundwater at the PGDP site. (ANA 2004 p 145-147)

Three large apparent plumes of contaminated groundwater have migrated outside the plant boundaries. These plumes are referred to as the Northwest Plume, the Northeast Plume and the Southwest Plume. The two northern plumes are oriented roughly north-northeast from the plant toward the Ohio River. The primary contaminants in all three plumes are TCE, an industrial degreasing solvent, and Tc-99, a fission byproduct of uranium enrichment. (ITRD 2000 p 7) The maps in Figures A-2 and A-3 (pages 105 and 106) show the TCE and Tc-99 plumes, respectively.

B. Categories of Groundwater Remedial Problems

The objective of the present 2005 study was to evaluate remediation technologies for the contaminated groundwater at the Department of Energy (DOE) Paducah Gaseous Diffusion Plant (PGDP). The primary contaminants of concern were the chlorinated solvent trichloroethylene (TCE) and the radionuclide technetium-99 (Tc-99). The Technical Advisory Group (TAG) of the Innovative Treatment Remediation Demonstration Program (ITRD) made technology recommendations in the Paducah Project Innovative Technology Review final report (ITRD 2000).

Information on ITRD activities was obtained from the ftp site maintained by the KRCEE at the University of Kentucky. Under listing ITRD I, a draft report was found giving preliminary findings as of October 16, 1999. On p. 9 of that draft, indications were given that it may have been appropriate to arrange field tests for Huma-Sorb for remediation of TCE and Tc-99 because of success claimed in laboratory experiments and in work at other sites where aerobic bioremediation has been done. On p. 62 of the draft report, the use of humic acid products was mentioned again and developed more fully. The product was described as an adsorbent designed to remove metals, radionuclides, oxoanions, and/or organics from contaminated water. Removal capability was attributed to the high cation exchange capacity of the product, it ability to chelate metals, and ability to adsorb organics. The material was suitable for injection in solid phase in a reactive zone trench, or liquid phase by conventional injection techniques. Any secondary wastes produced from the process were considered to be combustible. The primary issues related to use of humic acid products included the ability of a vendor to produce significant amounts of product for large-scale field operations, and the unproven effectiveness of the product in treating the contaminants at PGDP. However, humic

acid products were considered to possess high potential for use at PGDP. The TAG recommended that an independent treatability study be done at the EPA research laboratory using PGDP groundwater to verify vendor claims and assess applicability.

On p. 16 of that same draft report, the lack of cost data on full-scale bioremediation operations was noted. However, several pages farther into the report, the use of *in situ* bioremediation was mentioned as being more frequently considered because of the increased understanding of the factors that control microbial degradation of VOCs. The potential low cost of this technology was cited, as was the potential to decompose chlorinated organics and fix toxic metals. For these reasons, the TAG worked with EPA to evaluate the applicability of bioremediation at PGDP. The ground water system at PGDP was characterized as highly aerobic, and it was considered necessary to use aerobes to degrade TCE. Low levels of TCE [up to tens of ppm] can be degraded aerobically by injecting cometabo-lites such as methane, propane or toluene. No toxic by-products are generated; toxic by-products are produced in anaerobic degradation of chlorinated solvents. A second advantage cited in the draft report was the ability of some microbes to "reduce Tc99 concentrations." The sensitivity of aerobic degradation methods to the types and kinds of indigenous bacteria was mentioned, and the EPA recommendation for column studies to investigate the interactions of treatment microbes with indigenous microbes was referenced. The fact that aerobic bioremediation costs were similar to or somewhat lower than costs for equivalent air sparging systems was noted. Several companies were looking at the use of microbes in a biosparging curtain as a way to reduce degradation costs. The key to using bioremediation at PGDP was thought to be the identification of an appropriate cometabolite. Before bioremediation column studies were

undertaken, it was recommended that a cost comparison be made between this method and other technologies.

Cost data as of April 22, 1999 were given in the draft report. Other potentially limiting factors cited in the ITRD draft report (pages 47, 60 and 72), in addition to the need for column studies of interactions with indigenous microbes, included the fact that the treatment rate in a reactive zone depends on the groundwater flow rate, contaminant concentrations and volume of the desired treatment zone. The lack of evidence of natural bioattenuation at PGDP within the Regional Gravel Aquifer obviously indicated that induced aerobic stimulation would be required, but the technology was considered potentially applicable to the RGA.

On page 218 of the draft report, reference was made to information on aerobic bioremediation presented by a representative of Waste Microbes, Inc. That information included data from operations in Calvert City, Kentucky where DCE/TCE was remediated. The Waste Microbes, Inc., process required waster circulation in the treatment zone and use of injection and recovery wells to cause such flow. Although it was proposed that Tc-99 could be precipitated in process sludge, the possibility of future mobilization of the radionuclide was noted. Waste Microbes, Inc., personnel had proposed that the Regional Gravel Aquifer and the Upper Continental Recharge System be remediated concurrently, at the C-400 building. The feasibility of adding microbes and nutrients to large dissolved-phase zones was questioned by members of the TAG.

On p. 530 of the draft report, the TAG members questioned the use of bioremediation to degrade contaminants where they occur in sufficiently high concentrations to be considered nonaqueous-phase liquids (NAPL). Uncertainty about the final end-product of the bioremediation process was cited as an inherent disadvantage of bioremediation. The

feasibility of adding cometabolites in sufficient volumes to promote degradation of NAPL zones was questioned, also. The microbes that are used for bioremediation were not considered capable of survival in NAPL zones because osmotic pressures in such zones were considered so high that cell walls of the microbes would burst. If the microbes could be used only when and as contaminants dissolved from NAPL zones, then the bioremediation process was considered no more advantageous than pump-and-treat methods. Natural attenuation by indigenous microbes at the site also was considered to be too slow to meet treatment schedules for the groundwater contaminants at PGDP.

At the second ITRD location on the ftp site, several files were reviewed; those files contained information on *in situ* chemical oxidation techniques developed by IT Corporation. At the ITRD III location, one file contained information about physical plant, utility lines, boring locations, etc. A second file contained slides of a vendor presentation on six-phase heating. A third file contained PDF files comprising pages from an EPA document on NAPL assessment and remediation from 1991. The fourth file on the location was a set of pdf files that comprised the same document given at the ITRD I site.

Review of the data contained in the ITRD files on the ftp site indicated that the most current version of the ITRD report was the Final Draft from April 7, 2000; however, that draft was not included on the ftp site.

The 1999 data used in the ITRD report were considered to be obsolete as of the year 2004. The cost and performance estimates of the recommended technologies were deemed in need of updating, and technologies favored in the 2000 report were to be compared to newer innovative technologies not considered in the ITRD review.

The TAG identified and reviewed thirty *in situ* remediation technologies that could be applied to the TCE and Tc-99 contamination at PGDP. The technology categories considered in the TAG study included *in situ* treatment of contaminated slowly permeable soils in both the saturated and vadose zones; and *in situ* treatment of a contaminated highly permeable sand and gravel aquifer. The identified technologies were evaluated for general maturity, cost, and quality of performance as the technologies would apply to PGDP. The most promising technologies were reviewed further through engineering evaluations with several vendors. The results of the TAG review can be found in Table A-1 in Appendix A.

The TAG made recommendations on treatment technologies to be implemented at PGDP based on their review. The ranking of technologies recommended for *in situ* treatment of contaminated slowly permeable soils in both the saturated and vadose zones was: rotary treatment; chemical oxidation-ozone/fracturing; direct heating; and SVE/fracturing. The ranking of technologies recommended for *in situ* treatment of a contaminated highly permeable sand and gravel aquifer was: chemical oxidation (C-Sparge); direct heating; Steam/ Dynamic Underground Stripping/Hydrous Pyrolysis Oxidation (DUS/HPO); and chemical oxidation (permanganate). Descriptions of these technologies are given in Chapter III.

In addition to the recommendations listed above, the TAG evaluated the results of characterization and pilot studies. The TAG suggested that a range of characterization technologies suitable for wide areas of contamination should be considered in order to optimize the overall remedial design in such areas. Deeper characterization and better characterization under buildings can help minimize remediation cost associated with difficulty of implementation.

The TAG endorsed an elemental iron reactive wall pilot study that was planned for the PGDP site. The TAG also ranked the pilot studies needed for further study. Priority 1 consisted of C-Sparge with ion exchange for Tc-99 in the highly permeable sand and gravel aquifer and fracturing with ozone in the slowly permeable soils. Priority 2 consisted of direct heating (six-phase heating) and chemical oxidation using permanganate. These pilot studies were recommended to determine the feasibility of these technologies under specific site conditions at PGDP.

II. PROJECT APPROACH

The complexity of the hydrologic and infrastructure issues at the PGDP site led the TAG to separate the summary of the technology review into two categories: technologies for treatment or containment of contaminants in low permeability vadose soils; and technologies for treatment of saturated low permeability and high permeability soils and groundwater. The TAG also considered the different contaminant concentration levels to be treated; these included higher concentrations near the source and lower concentrations in the plumes. Table A-2 in Appendix A shows the technologies considered in these categories.

The TAG did not consider treatment of Tc-99 in the vadose zone because they believed that after the TCE source was removed, Tc-99 would not be mobile. They also believed that Tc-99 in the groundwater was of more concern than Tc-99 in the vadose zone. According to the TAG, regulators had indicated that removal of TCE from the vadose zone would be adequate remediation without addressing Tc-99 in the vadose zone. (ITRD 2000 p 13)

In order to develop the context for the work conducted in the present 2005 study, it is necessary to describe, albeit very concisely, the remediation technologies that were considered

by the TAG, and technologies that have been developed since the TAG report was submitted. Chapter III describes the remediation technologies, how they work physically and how they can be applied to the appropriate location. That chapter also describes how the technologies were evaluated. The factors considered by the TAG included: implementation cost and ease of implementation; technology maturity and appropriateness; life-cycle costs and overall cost-effectiveness; ability to reduce the contaminant concentrations to regulatory levels of compliance; compatibility with existing site constraints and treatment systems; stakeholder considerations; and regulatory permits.

Chapter IV describes full-scale and pilot studies utilizing the technologies being considered for PGDP, as documented through September 2005. The characterization factor values for each technology were determined from the full-scale and pilot studies investigated.

Chapter V summarizes the results from the review and evaluation of the technologies considered by the TAG and those described in Chapter IV. Site assessment investigations necessary for technology selection at PGDP also are described in Chapter V. Chapter VI presents conclusions and recommendations based on the Chapter V summary and assessment.

III. REMEDIAL TECHNOLOGIES

In the previous chapter, the objective, background, and parameters for the present 2005 study were presented. In this chapter, descriptions of the relevant technologies are presented, illustrating how they can be applied to the PGDP site. The TAG ranking of technologies recommended for *in situ* treatment of contaminated low permeability soils in both the saturated and vadose zones were rotary treatment; chemical oxidation-ozone with fracturing; direct heating (six phase heating); and soil vapor extraction (SVE) with fracturing. The ranking of

technologies recommended for *in situ* treatment of a contaminated highly permeability sand and gravel aquifer was chemical oxidation (C-Sparge); direct heating; Steam Treatment by Dynamic Underground Stripping (DUS) or Hydrous Pyrolysis Oxidation (HPO); and chemical oxidation (permanganate).

In addition to revisiting the TAG recommended technologies, this study compares use of peroxide activated sodium persulfate and Fenton's process to other *in* situ chemical oxidation (ISCO) methods using permanganate and ozone. Bioremediation, use of humic materials, applications of nanotechnology, and permeable reactive barriers (PRBs) are considered as other newer developing technologies.

A. <u>Rotary Treatment</u>

In this method, augers are used to mix soil with a reactive agent or medium such as steam, ozone, permanganate, or iron filings. (ITRD 2000 p 15) In rotary steam stripping, steam is used to volatilize organic contaminants (VOCs) such as TCE and force them to the surface. When steam is condensed near the surface, the VOCs are collected and transferred to a stripping column where they are absorbed using activated carbon. Rotary treatment also can be used with an oxidizing agent such as permanganate or ozone to treat the VOCs *in situ*. Reactive media, such as zero-valent iron, can be used with rotary treatment to immobilize Tc-99.

Rotary treatment can be applied to contaminated low permeability soils in both the saturated and vadose zones with high levels of contaminant concentration (up to 300,000 ppm VOCs). Treatment depths up to 70 feet have been attained with effective treatment areas of 40 to 75 square feet per bore hole. Treatment rates range from 20 to 40 cubic yards per hour with contaminant removal efficiencies of 80 to 90 percent. (ITRD 2000 p 15)

B. Soil Fracturing

Pneumatic and hydraulic fracturing of slowly permeable soils can enhance the performance of extraction or injection wells. (US DOE 2000 p 1) Pneumatic fracturing involves the injection of highly pressurized gas (nitrogen or air) into the soil via borings to extend existing fractures and create a secondary network of subsurface channels. Hydraulic fracturing uses water or slurry instead of gas. Soil fracturing can extend the range of treatment when combined with other technologies such as bioremediation, chemical oxidation/reduction or soil vapor extraction. (US DOE 2000 p 6-1)

C. Chemical Oxidation with Ozone

Ozone (O_3) is a strong oxidizing agent having an oxidation potential about 1.2 times that of hydrogen peroxide. Because of its instability, ozone typically is generated on site and delivered to the contaminated zone through sparge wells. Air containing up to 5 percent ozone is injected through strategically placed sparge wells. Ozone dissolves in the groundwater and oxidizes the contaminant while decomposing to oxygen (O_2). Pneumatic fracturing can be used to enhance ozone effectiveness in low permeability soils. (US EPA May 2004 pp. XIII-11 and 12)

Ozone is ten times more soluble in water than is oxygen; therefore, the groundwater becomes replete with dissolved oxygen as the unstable ozone molecules decompose into oxygen. Approximately half of the ozone introduced into the subsurface decomposes into oxygen within 20 minutes of injection. Rapid decomposition into oxygen can aid in bioremediation by creating an oxygen-rich environment for aerobic bacteria.

C-Sparge is an ozone oxidation technology developed by Kerfoot Technologies, Inc. (AEHS 2001 p 1) C-Sparge is a patented ozone microsparging technology for *in situ* treatment of VOCs. In this process, ozone and air are injected into the groundwater through specially designed spargers to create nano-size to micro-size bubbles of air-encapsulated ozone. The VOCs are extracted from the aqueous solution into small bubbles where they are oxidized by the encapsulated ozone, producing carbon dioxide (CO_2), oxygen (O_2) and water (H_2O). The system can be applied to soil with hydraulic conductivities ranging from 1000 to 0.01 ft/day. (Kerfoot 2005) Kerfoot Technologies claim that sites can be cleaned in one- quarter to one-third of the time required for typical pump-and-treat systems, at a cost reduction of 20 to 50 percent over the costs of pump-and-treat methods.

D. Chemical Oxidation with Permanganate

Potassium permanganate ($KMnO_4$) is the preferred chemical form of permanganate for oxidation because it is more widely available and less costly than sodium permanganate and is available in a solid form, which permits safer handling. A liquid form of sodium permanganate ($NaMnO_4$) is also available, but is more expensive than potassium permanganate. Permanganate can be delivered to the contaminated zone by injection probes, soil fracturing, soil mixing and ground water recirculation. (US EPA May 2004 p XIII-10)

Despite having less oxidation potential than hydrogen peroxide, potassium permanganate can react in environments with higher pH and can exist longer (hours to days longer) in these environments than hydrogen peroxide. For field application, potassium permanganate is shipped as a gray powder and is dissolved in water, creating a purple liquid. The purple color can be used as an indicator of unreacted potassium permanganate. The reacted permanganate is dark brown to black, indicating the presence of manganese dioxide

(MnO_2), and a compound that is commonly found in soils. (Jacobs 2001 p 7) Temperature influences the solubility of potassium permanganate, and at 30°C, $KMnO_4$ can be present at a concentration slightly over 8 percent. (ITRC Jan. 2005 p 5) The following equation represents the chemical oxidation of TCE using potassium permanganate:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2MnO_2 + 2CO_2 + 3Cl^- + H^+ + 2K^+ \quad \text{(III-1)}$$
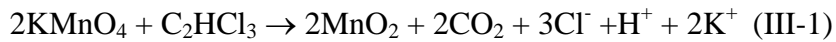
Three considerations that could cause concern to the owner, operators or regulators monitoring remediation operations should be evaluated before potassium permanganate is selected for application at a site: (US EPA May 2004 p XIII-10)

1. The potassium ores from which potassium permanganate is derived typically contain salt and metal impurities such as arsenic, chromium, and lead. These impurities may be a concern depending on the water quality criteria and the amount of potassium permanganate being used at the site (This limitation is also pertinent for sodium permanganate since it is mined and processed in a similar fashion.);

2. Since potassium permanganate is used to manufacture pharmaceuticals, its use should be monitored carefully, to preclude theft and misuse;

3. The flowable form of potassium permanganate contains silica, which can accumulate in wells and plug well screens.

Despite those concerns, permanganate has three advantages over other oxidants (US EPA May 2004 p XIII-10):

1. It oxidizes organics over a wider pH range than do other oxidants;

2. It reacts over a longer period in the subsurface, which allows the oxidant to permeate the soil and contact adsorbed contaminants more effectively; and

3. It does not typically produce heat, steam and vapors that may cause health and safety concerns.
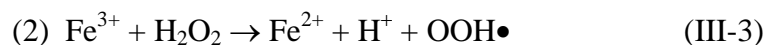
E. Chemical Oxidation with Fenton's Process

Hydrogen peroxide (H_2O_2), discovered in the late 1700s, was one of the first chemical oxidants to be used in industry and was commercialized in the early 1800s. Hydrogen peroxide works as a remedial chemical oxidant in two ways: direct chemical oxidation as hydrogen peroxide; and production of free radicals.

The exothermic and violent reaction of hydrogen peroxide with iron salts (ferrous sulfate) was described by a British professor, H. J. H. Fenton, in 1894. This process, known as Fenton's chemistry (or Fenton's reagent), utilizes a transition metal catalyst or an acid to enhance the chemical oxidation of hydrogen peroxide by producing the hydroxyl radical. (Jacobs and Testa 2003 p 4)

The most common field applications in chemical oxidation have been based on Fenton's Reagent, where hydrogen peroxide (H_2O_2) is applied with an iron catalyst (Fe^{2+}), creating a hydroxyl free radical (OH•). When peroxide is injected at concentrations of 10 percent to 35 percent into the subsurface, the hydroxyl free radical oxidizes the VOCs to carbon dioxide (CO_2) and water. Iron can occur naturally in some soil types in different forms. (Hem p114) The iron that is occurring naturally in the soil and groundwater, or added during the injection of remediation media, catalyzes this reaction. The residual hydrogen peroxide decomposes into oxygen and water, and the remaining iron precipitates. (Jacobs and Testa 2003 p 5) The following reaction sequence represents the role of the iron catalyst with hydrogen peroxide in Fenton's process:

$$(1) \quad Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \qquad\qquad (III\text{-}2)$$

$$\text{(2)} \quad Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + OOH\bullet \qquad\qquad \text{(III-3)}$$

$$\text{(3)} \quad OH\bullet + H_2O_2 \rightarrow H_2O + OOH\bullet \qquad\qquad \text{(III-4)}$$

$$\text{(4)} \quad OH\bullet + Fe^{3+} \rightarrow Fe^{2+} + OH^- \qquad\qquad \text{(III-5)}$$

Appendix B gives a more detailed version of this reaction process.

This process is capable of producing self-generating oxidants (primarily OH radical, OOH radical and oxygen species) when catalyzed by ferrous iron. In the first reaction, hydrogen peroxide oxidizes the iron to yield the OH radical. In the second reaction, hydrogen peroxide reduces the iron, regenerating the iron catalyst. (US DOE 1999 p 9)

The oxidation reaction for TCE forms several unstable daughter products such as epoxides, which break down to aldehydes and ketones, which then finally decompose to carbon dioxide, chloride ions and water. The following reaction shows the results of this oxidation: (Jacobs and Testa 2003 p5)

$$4OH\bullet + C_2HCl_3 \rightarrow 2CO_2^{\ -} + 3Cl + 5H^+ \qquad\qquad \text{(III-6)}$$
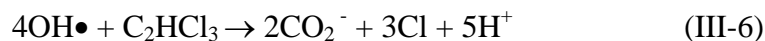
The pH of the surrounding medium increases as the reaction process continues; therefore, it is necessary to lower the pH with acids. Organic acids should be avoided since they have a tendency to increase side reactions. The optimal pH range is from 3.5 to 5.0.

The exothermic nature of the oxidation process causes a rise in subsurface temperature. A rise in temperature above 60°C decomposes the peroxide. Conditions can become explosive and unsafe if temperatures rise above 82°C. Field research has determined the optimal reaction temperature to be in the range of 35 to 41°C. (Jacobs and Testa 2003 p6) The temperature of subsurface reactions can be monitored and controlled by adding water, adjusting catalyst or oxidant concentrations, and reducing injection pressures.

Despite pH, temperature and other safety concerns, production of the hydroxyl radical through Fenton's process is very advantageous since the radical is one of the most potent oxidative species known. The reaction time for remediation is very fast and the process is relatively inexpensive. As for any chemical oxidation process, careful evaluation of the site conditions, including the physical and chemical properties of the soil and groundwater, is required prior to implementation of Fenton's process as a remediation technology.

F. Chemical Oxidation with Peroxide Activated Sodium Persulfate

Chemical oxidation of chlorinated organics such as TCE using persulfate is one of the newer emerging remediation technologies. (Block et al 2004 p 1) Persulfates have been used in many applications such as initiating emulsion polymerization reactions, clarifying swimming pools, bleaching hair, micro-etching copper printed circuit boards, and total organic carbon (TOC) analysis. Persulfate salts dissociate in water to produce persulfate anions ($S_2O_8^{-2}$). Persulfates are usually available as sodium, potassium and ammonium salts. For groundwater remediation, potassium persulfate is not a good choice because of its low solubility in water. Use of ammonium persulfate can lead to generation of ammonia, which is regulated in groundwater. Therefore, sodium persulfate is the best choice as a chemical oxidant in the treatment of soil and groundwater contamination. (ITRC Jan. 2005 p 7)

The persulfate anion is one of the strongest oxidants used in remediation. The following reaction has an oxidation-reduction potential of 2.1 V:

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad \text{(III-7)}$$

This redox potential is slightly lower than that of ozone at 2.2 V, but greater than that of the permanganate ion at 1.7 V and that of hydrogen peroxide at 1.4 V.

As in the hydroxyl radical reactions produced by Fenton's process, sodium persulfate can be activated to form sulfate radicals ($SO_4^-\bullet$). The sulfate radical formation can be activated using various initiators such as heat in the presence of transition metal catalysts. The following reaction shows how the sulfate radical is formed:

$$S_2O_8^{-2} + initiator \rightarrow SO_4^-\bullet + (SO_4^-\bullet \text{ or } SO_4^{-2}) \qquad \text{(III-8)}$$
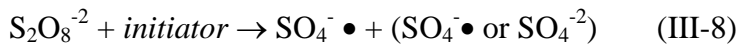
The sulfate radical and the hydroxyl radical are very strong aqueous oxidizing agents, having redox potentials of 2.6 V and 2.7 V, respectively. In addition to oxidation strength, use of persulfate (and sulfate radical) oxidation has several other advantages over the other chemical oxidation technologies: (Block et al 2004 p 1)

1. Faster reaction time when compared to other oxidants;

2. The sulfate radical is more stable than the hydroxyl radical and therefore able to be transported over longer distances in the subsurface; and

3. Compared to the permanganate ion, persulfate has less affinity for organics in soil and therefore is more efficient in highly organic soils.

The sulfate radical initiation methods have been shown to be effective in lab-scale studies but have displayed limitations in field applications. Heat activation requires installation of a system to heat the aquifer to a desired temperature. Therefore, heat initiation is not practical in many situations because of high capital expenditures and additional operating costs. In general, heating is used for source treatment where the target area is smaller. Also, iron transport capabilities are limited because iron II is oxidized to iron III by the persulfate, and at pH above 4, iron III is insoluble in water.

Because of the problems of heating and use of iron catalysis to initiate sulfate radical formation, alternative activation systems were developed. The criteria for the improved persulfate activation systems included:

1. The initiator must be transportable in a groundwater system.

2. The initiator should increase the reactivity of persulfate in a wide range of organic contaminants.

3. The system should be easy to apply in a variety of subsurface conditions.

One of the alternative activation systems has proven to be very effective in TCE removal. (Block et al 2004 p 4) A dual oxidation system using hydrogen peroxide and sodium persulfate was developed by FMC-Orin in 2003. This system combines the reactivity of peroxide in the reduction of the contaminant with the enhanced stability of persulfate. The hypothesis is that hydrogen peroxide and persulfate have synergistic effects. The hydroxyl radicals from hydrogen peroxide can initiate the development of persulfate radicals, while the sulfate radicals can promote the development of the hydroxyl radicals. Hydrogen peroxide can break down the more reactive contaminants quickly, allowing the sulfate radicals to degrade the more recalcitrant contaminants. The multi-radical attack mechanism of peroxide and sulfate radicals provides a higher efficiency in destroying contaminants and permits the more recalcitrant contaminants to be more readily degraded. (Block et al 2004 p 4)

G. Soil Vapor Extraction (SVE)

Soil vapor extraction (SVE) is a remediation technology that uses a vacuum applied to an extraction well to remove vapor-phase VOCs from the vadose zone. (ITRD 2000 p13) The extracted vapor typically is removed through carbon adsorption although other treatments such as chemical oxidation can be used. The three types of SVE systems that are available

commercially consist of Passive SVE, Standard SVE (5-10 inches Hg vacuum) and High

Vacuum SVE (15-29 inches Hg vacuum). High Vacuum SVE typically is used in tight vadose

zone soils having hydraulic conductivities less than one foot per day. Soil fracturing can

enhance SVE for soils with lower hydraulic conductivities. High Vacuum SVE has been

applied successfully to soils with permeability as low as those in the UCRS at the PGDP.

The SVE technology by itself is used only above the water table, although when

combined with other technologies that volatilize the contaminants below the water table, SVE

can remove VOCs from greater depths. Figure III-1 shows a cross-section of a typical SVE set

up.

Figure III-1. Typical Soil Vapor Extraction (Suthersan 1999)
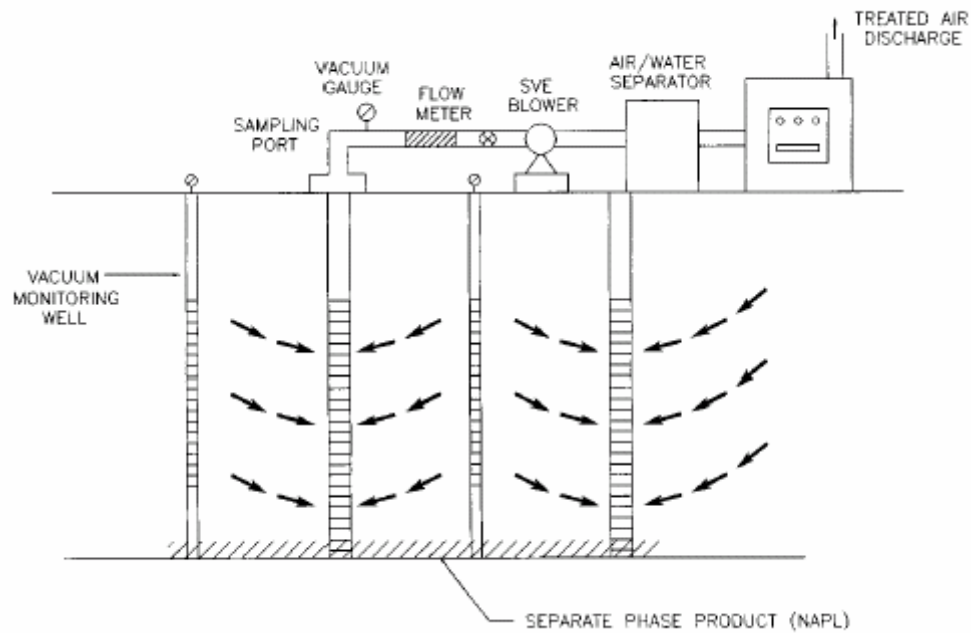
H. <u>Six-Phase Heating</u>

Six-phase heating is a patented direct heating remediation technology available through Current Environmental Solutions (CES 2005). This method is used to increase the efficiency of SVE. (ITRD 2000 p 14) In this technique, the soil in the subsurface is heated uniformly, volatilizing the VOCs to be removed by SVE. The CES technology features six electrodes positioned in a hexagonal array with a SVE well in the center of the hexagon. The array of electrodes typically has a diameter of 25 to 35 feet with the diameter of the heated zone being about 40 percent larger than the array diameter. Electrical current from the electrodes passes through the soil. The soil matrix is used as a resistive element in the system and emits heat. The factors that govern the resistance between electrodes include: soil type; moisture content; and distance between electrodes. With soil type and distance between electrodes fixed, regulating moisture content and applied voltage can control current flow. (CES 2005)
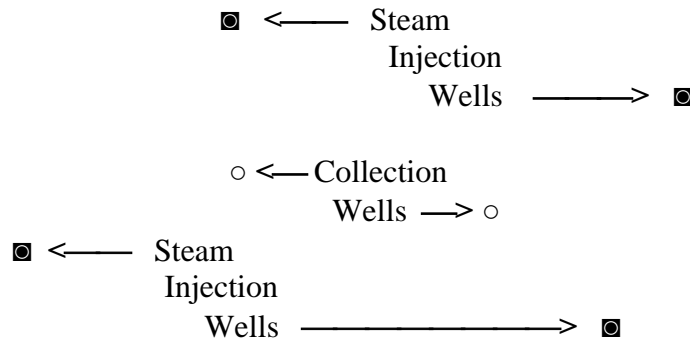
When voltage is applied to the electrodes, current flows through the path of least electrical resistance, but the soil is heated to some degree wherever the current flows. As the subsurface soil temperature approaches the boiling point of water, the VOCs with boiling points lower than 100°C volatilize. The soil moisture is removed as steam by SVE. The resistance increases as the soil dries, causing the current to flow through other more preferential pathways. This effect redirects the heat to the remaining contaminated locations. This automatic redirection allows for uniform heating over time even with heterogeneous soil. (CES 2005)

The SVE technology can be applied to highly contaminated locations in low permeability soils. A pilot study was conducted at the PGDP with electrodes installed to a depth of 99 feet below ground surface. The results of this study are described in Chapter IV.

I. Steam: Dynamic Underground Stripping (DUS) and Hydrous Pyrolysis Oxidation

(HPO)

Steam flushing technology was developed originally for increasing the productivity of

oil wells and oil fields. (WSRC 2001 p 11) Oil or DNAPL removal involves concentrating the

liquid phase along the expanding steam front and retrieving it from collection wells. Steam

delivers heat and sweeps residual DNAPL from the subsurface as the system is altered to cause

flow from a set of delivery wells to a set of collection wells. To minimize the potential for the

plume to spread, the collection wells typically are located on the interior in the plan view of the

well layout. Figure III-2 shows a plan view for the well layout of a steam remediation project.

Figure III-2. Plan View of a Well Layout for Steam Remediation

◉ ←—— Steam
                Injection
                        Wells ——→ ◉

        ○ ←—Collection
                Wells —→ ○
    ◉ ←—— Steam
              Injection
                  Wells ——————→ ◉

Steam raises the temperature of the soil and groundwater and increases the DNAPL

component solubility and vapor pressure, as well as providing the heat energy to increase the

rate of mass transfer of contaminants from fine-grained soils. A benefit of steam heating and of

other *in situ* heating methods is that part of the organic phase breaks down in the subsurface in

the presence of oxygen and heat.

In this technology, operators alternately inject oxygen and low-pressure steam into the

contaminated location. This injection produces a thermal destruction zone for the contaminated

groundwater flowing into this zone. Use of low pressures during steam injection encourages the steam to move horizontally rather than vertically upward.

The most successful and widely used of the commercially available steam technologies are: Dynamic Underground Stripping (DUS) for the steam sweep phase and Hydrous Pyrolysis Oxidation (HPO) for the abiotic action phase. (WSRC 2001 p 12) These processes were developed with the support of the DOE Office of Technology Development (OTD) and Subsurface Contaminant Focus Area (SUBCON) and are licensed by the Lawrence Livermore National Laboratory (LLNL).

Compared to other thermal technologies, steam heating reduces the required number of access points because of the rapid expansion of steam. Steam works best in highly permeable soils such as those in the RGA. Horizontal drilling can be used to install injection and collection wells for remediation under buildings and other obstacles. (ITRD 2000 p 27)
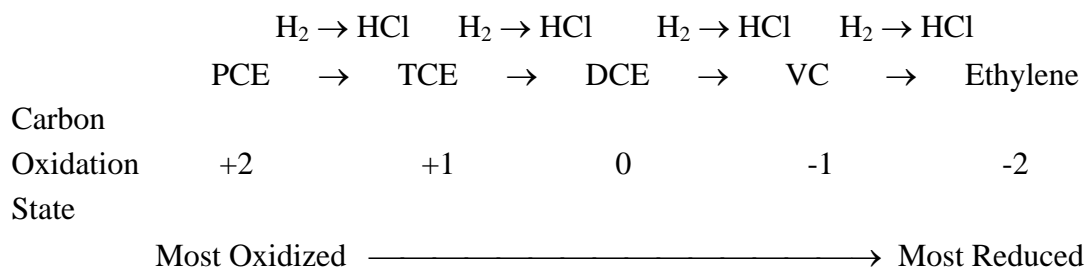
Limitations on using this technology near the surface include elevated temperature and pressure, and the need for proper overburden characterization to prevent steam breakthrough.

J. Bioremediation

Under anaerobic conditions, microbes use the chlorinated aliphatic hydrocarbons (CAHs) such as TCE as electron acceptors in energy-producing redox reactions. The microbes gain energy and grow as one or more chlorine atoms are replaced with hydrogen. The hydrogen typically is supplied indirectly as the result of the fermentation of organic substrates. Figure III-3 shows the step by step reduction of tetrachloroethylene (PCE) to ethylene in the presence of hydrogen.

Figure III-3. Anaerobic Reductive Dechlorination of PCE to Ethylene

(US EPA 2000 p 2-15)

$$H_2 \rightarrow HCl \quad H_2 \rightarrow HCl \quad H_2 \rightarrow HCl \quad H_2 \rightarrow HCl$$

$$PCE \quad \rightarrow \quad TCE \quad \rightarrow \quad DCE \quad \rightarrow \quad VC \quad \rightarrow \quad Ethylene$$

Carbon
Oxidation   +2   +1   0   -1   -2
State

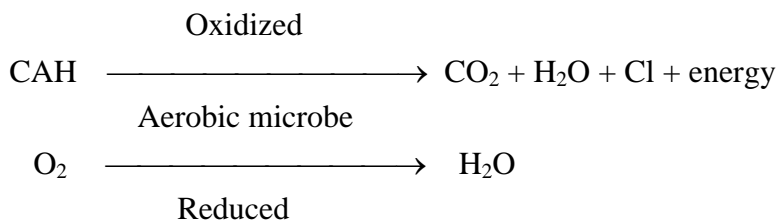Most Oxidized   ——————————————————→ Most Reduced

Dechlorination of the more highly chlorinated CAHs such as PCE and TCE occurs more readily than dechlorination of the more reduced CAHs such as dichloroethylene (DCE) and vinyl chloride (VC). In anaerobic environments, DCE and VC can accumulate when PCE and TCE are being directly reduced by anaerobic microbes. According to the National Institute for Occupational Safety and Health (NIOSH), there are no allowable exposure limits for VC and 1,1-DCE. Even though 1,2-DCE has an allowable exposure limit twice that of PCE and TCE, it is still a concern due to the fact that it could degrade to VC. To overcome the problem of possible degradation to vinyl chloride, a cometabolite can be used. (US EPA 2000 p 2-15)

Cometabolic anaerobic reductive dechlorination is a biodegradation reaction in which a CAH is degraded by an enzyme or cofactor produced during microbial metabolism of another compound. Several anaerobic microbe species can dechlorinate compounds reductively through cometabolic reactions, by transfer of electrons from the reduced cofactors. This enzymatic breakdown of the CAHs does not provide energy to the microbes for life processes and therefore is not as efficient as the actions of another type of anaerobic microbe group called dehalorespiring or chloro-respiring microbes. (Major et al 2001 p 27) The chloro-respiring microbes use chlorinated solvents as terminal electron acceptors and gain energy

from reductive dechlorination to support their life processes. Of the chloro-respiring microbes, *Dehalococcoides ethenogenes* is able to dechlorinate chlorinated ethenes completely.

Aerobic oxidation is the process of microbial breakdown of a compound in which the compound serves as an electron donor and as a growth substrate for the microbe. The oxygen in the aerobic environment acts as the electron acceptor. Figure III-4 illustrates the reaction process for the aerobic oxidation of a CAH. (US EPA 2000 p 2-13)

Figure III-4. Aerobic Oxidation of a CAH

$$CAH \xrightarrow[\text{Aerobic microbe}]{\text{Oxidized}} CO_2 + H_2O + Cl + energy$$
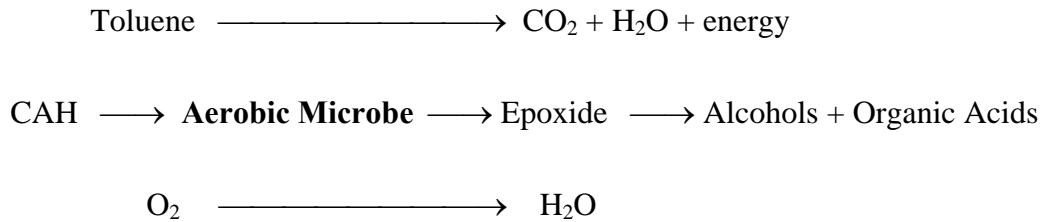
$$O_2 \xrightarrow[\text{Reduced}]{} H_2O$$

In general, only the less fully chlorinated CAHs such as DCE and VC can be oxidized under aerobic conditions. This circumstance presents a limit to the use of this type of microbe since aerobic oxidation has no effect on the more chlorinated CAHs such PCE and TCE.

To solve the problem of the recalcitrant DCE and VC, a cometabolite can be used. (US EPA 2000 p 2-14) Cometabolic aerobic oxidation is microbial breakdown of a compound in which the compound is oxidized incidentally by a cofactor or enzyme produced during the microbial metabolism of another compound. Figure III-5 illustrates the reaction process for cometabolic aerobic oxidation of a CAH using toluene as the cometabolite.

Several studies (US EPA 2000 p 2-17) have suggested that the most efficient remediation of CAHs using microbes occurs where the aquifer is anaerobic in the upgradient

27

zone and aerobic in the downgradient zone. Cometabolites are not necessary in this situation since anaerobic

Figure III-5. Cometabolic Aerobic Oxidation of a CAH

$$Toluene \longrightarrow CO_2 + H_2O + energy$$

$$CAH \longrightarrow \textbf{Aerobic Microbe} \longrightarrow Epoxide \longrightarrow Alcohols + Organic\ Acids$$

$$O_2 \longrightarrow H_2O$$

microbes from the upgradient zone reduce PCE and TCE to DCE and VC. Then the DCE and VC are resulting from the anaerobic reduction move with the groundwater flow to the aerobic zone where they are oxidized to carbon dioxide, chlorine and water.

In general, the substrate requirement for cometabolism is much greater than that required for direct metabolism. Typically, for the cometabolic process, the amount of primary substrate required is 100 to 1000 times the amount of CAH. (US EPA 2000 p 2-17)

K. <u>Bioremediation Technology Selection and Implementation</u>

The steps followed in selecting and implementing an *in situ* microbial remediation system at a site contaminated with CAHs are basically the same as for other remediation technologies except that special attention is given to identifying degradation mechanisms that exist at the site and enhancement technologies that could be applied.

Typical steps in selection and implementation are:

1. Evaluate site characteristics

2. Identify general site conditions

3. Identify primary reactants and possible

    additives

4. Perform treatability (laboratory scale)

    testing

5. Perform field design, field testing and

    implementation

Steps 1, 2 and 3 determine the preliminary selection of the technology but the selection must be confirmed by lab tests. Steps 4 and 5 determine the feasibility of implementation of the technology.

Site Characteristics

The physical, chemical and biological parameters of the site must be determined in order to select and design the appropriate technology. (US EPA 2000 p 4-1)

The physical parameters determine how and at what rates gases and liquids move through the soils, aquifers and other geologic units. Physical parameters include porosity, hydraulic conductivity and hydraulic gradient of the various geologic units, and the organic and moisture contents of the soil.

The chemical and biological parameters determine what type of degradation mechanism is possible and the rate of degradation.

The chemical parameters include: concentrations of CAHs and daughter products; oxygen content; pH; redox potential; concentrations of electron donors and acceptors; and nutrient concentrations. These parameters determine if the site is aerobic or anaerobic, whether sufficient electron acceptors or donors are present to support biodegradation and how much intrinsic biodegradation is already occurring at the site.

The CAH concentrations can affect the degradation mechanisms that may be occurring, as well as substrate levels for direct degradation. The presence of contaminants such as toluene, methane or phenol may augment performance by providing a substrate for depleting oxygen or a substrate for cometabolic degradation. High levels of toxic compounds or metals could inhibit microbial activity. Daughter product concentrations and distributions can indicate whether or not microbial degradation is taking place already.

The dissolved hydrogen concentration can indicate what type of terminal electron acceptance process is occurring. Table III-1 shows the relationship between hydrogen concentration and terminal electron acceptance process. The terminal electron acceptance process is used in determining what types of microbes are present at the site.

Table III-1. Terminal Electron Acceptance Process Related to Hydrogen Concentration (US EPA 2000 p 4-5)

Terminal Electron Accepting Process	Hydrogen Concentration (nanomoles/L)
Denitrification	< 0.1
Iron (III) reduction	0.2 to 0.8
Sulfate reduction	1 to 4
Reductive dechlorination	>1
Methanogenisis	5 to 20

The redox potential is used to determine if the site conditions will promote oxidation or reduction.

The biological parameters include the presence of specific and non-specific microbes and microbial activity. The presence and concentration of non-specific microbes is measured as total organic carbon and is used to estimate the quantity of microbes at the site. The presence and concentration of specific microbes can be used to determine the concentration of the target microbe at the site. Microbial activity is measured by oxygen uptake rate or dehydrogenate activity. The uptake rate is used to quantify the rate of activity of the target microbe. (US EPA 2000 p 4-1, 2 and 5)

Site Conditions

Data on hydrogeologic conditions and aquifer chemistry can determine if the site conditions are favorable for microbial remediation. Table III-2 lists the favorable and unfavorable hydrogeologic conditions and aquifer chemistry conditions. (US EPA 2000 p 4-6) Possible engineered solutions for the unfavorable conditions are also listed.

Primary Reactants and Possible Additives

The type of reactants and additives typically used in microbial remediation vary by mechanism (such as direct or cometabolic aerobic oxidation, and anaerobic reductive dechlorination) and also vary by targeted CAHs. (US EPA 2000 p 4-7) Table III-3 shows the different combinations of these variations (only includes CAHs mentioned in this report).

Table III-2. Favorable and Unfavorable Site Conditions for Microbial Remediation of CAHs and Engineered Solutions for Unfavorable Conditions
(US EPA 2000 p 4-6)

Conditions		Engineered Solution for Unfavorable Conditions
Favorable	**Unfavorable**	
Hydrogeologic Conditions		
Granular porous media	Fractured rock	N/A
High permeability (K > 10^{-4} cm/s)	Low permeability (K < 10^{-4} cm/s)	Hydro and pneumatic fracturing
Saturated media	Unsaturated media	Water application
Minimal heterogeneity	Highly stratified deposits	N/A
Aquifer Chemistry		
Minimal NAPL in target area	Significant NAPL in target area	Source contaminant treatment, or removal
pH between 6 and 8	pH extremes	Chemical additives (NaHCO$_3$ as a buffer)
Nontoxic contaminant concentrations	Toxic contaminant concentrations	Dilution by injection of water or bioremediation additives
Simple contaminant mixtures	Complex contaminant mixtures	N/A
Moderate to high microbial activity of appropriate microbes	Little microbial activity or inappropriate microbes	Bioaugmentation
Sufficient nutrients present	Insufficient nutrients present	Addition of nutrients
Sufficient primary reactants	Insufficient primary reactants	Add reactants needed to employ specific mechanism

Table III-3. Primary Reactants and Additives for Microbial Engineered Systems (US EPA 2000 p 4-7)

Engineered Bioremediation Mechanism	Targeted CAHs	Primary Reactants and Additives for Microbial Engineered Systems	
		Primary Reactants	**Additives (primary reactant supplemented)**
Aerobic oxidation (direct)	DCE, VC	Oxygen, CAH	Air, oxygen, hydrogen peroxide, magnesium peroxide (oxygen)
Aerobic oxidation (co metabolic)	TCE, DCE, VC	Oxygen	Air, oxygen, hydrogen peroxide, magnesium peroxide (oxygen)
Anaerobic reductive dechlorination	PCE, TCE, DCE, VC	Hydrogen, organic carbon, or carbon from contaminant source	Lactate, methanol, hydrogen, molasses (electron donor)

Treatability (Laboratory Scale) Testing

Treatability (laboratory scale) testing can proceed after site characteristics, degradation mechanisms, and potential enhancements are identified. Lab tests are conducted to evaluate the effectiveness of the degradation mechanisms and enhancements that are being considered for implementation at the site. Tests are conducted utilizing samples from several areas of the site because microbe populations are usually heterogeneous and conditions in a plume may vary across the site. It should be noted that degradation rates observed in the lab are typically higher than those found in the field. (US EPA 2000 p 4-7)

System Design, Field Testing and Implementation

The information derived from the first four steps in selecting and implementing an *in situ* microbial remediation system is used in designing the system, testing the system in the field and implementing the technology on a full-scale cleanup.

In previous sections, the potential for using microbes as a remediation technology for TCE has been described. Microbes also can be utilized for treatment of other contaminants.

Heavy metals such as Tc-99 can be immobilized by a special group of microbes termed extremophiles.

Extremophiles

Extremophiles are microbes that can survive in the most inhospitable environments. Some of these microbes can withstand large doses of radiation; that fact led to research on using them for radioactive waste cleanup. (Fialka Nov. 16, 2004)

The mobility of the radionuclides technetium (Tc-99) and uranium (U) in groundwater depends on site-specific biogeochemical conditions. In oxidizing environments, Tc-99 occurs as Tc(VII) in the form of a highly soluble and mobile pertechnetate anion (TcO_4^-) and U occurs as U(VI) which forms highly soluble and mobile complexes with carbonate at pH > 5. In reducing environments, Tc occurs as Tc(IV and V) and U occurs as U(IV), which has much lower solubility and much less mobility than their oxidized forms.

The concept of bio-immobilization has been proposed as a strategy for reducing Tc and U concentrations in groundwater. (Istok et al 2004 p 468) Bio-immobilization is the addition of nutrients to stimulate indigenous microbes (extremophiles) to reduce Tc(VII) and U(VI) to produce and precipitate Tc(IV and V) and U(IV) solid phases.

For aerobic conditions, the addition of an electron donor is necessary to produce the anaerobic and reducing conditions required for the growth of these extremophile metal-reducing microbes. The use of extremophiles may be complicated because of the presence of high concentrations of nitrate (NO_3^-) from ore processing and isotope separation processes that took place at contaminated sites such as PGDP. NO_3^- serves as a competing and more favorable electron acceptor, and must be removed to maintain reducing conditions.

Other concerns with reducing Tc and U to their precipitate forms is the restriction of flow in the aquifer caused by the deposition of immobile precipitates, and the possibility for the precipitates to reoxidize and become mobile again from changes in the aquifer environment. (Luo April 25, 2004)

L. Humic Products

In this report, the term "humic" refers to a type of decomposed organic matter such as compost, to be used in contaminated soil and groundwater remediation. Scientists of the Newly Independent States (NIS) of the former Soviet Union developed a humic product called Humosorb to be used as a soil amendment to immobilize heavy metals and prevent their uptake into plants. (CRADA 1998 p 2)
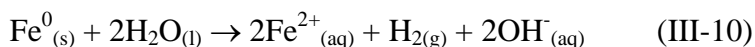
Another humic product called HMA has been covered by an application for a patent (personal communication, Dave McEwan 2005). Lab studies have shown that HMA is capable of reducing polychlorinated biphenyls (PCBs) in soil. Field studies show HMA is capable of immobilizing a variety of heavy metals. The results of these studies are described in Appendix C.

In a personal communication (Shulgin, July 1, 2005), Dr. Alexander Shulgin, a NIS scientist, described the benefits of HMA. According to Shulgin, TCE remediation can be accomplished by mechanisms similar to those featured in PCB remediation using HMA. HMA can be used as a substrate and nutrient to enhance bioremediation of TCE. HMA as a nutrient can foster diversity in microbe species to allow remediation of a variety of contaminants.

M. Nanotechnology

Researchers at Lehigh University have reported that nanoscale (1 to 100nm) iron particles can play a large role in remediation of contaminated groundwater. (Zhang 2003 p 323) The advantage of the small size of such particles is that the specific surface of the iron is increased greatly so that the iron is more effective, and the iron can be transported more easily through the groundwater. Slurries of nanoparticles of iron in water can be injected into contaminated plumes by gravity flow or under pressure. Once in a plume, the nanoparticles will stay in suspension for long periods of time to create an *in situ* treatment zone. The nanoscale iron will react with chlorinated organic compounds such as TCE by reductive dechlorination. By the same process, nanoscale iron particles have the potential to immobilize heavy metals and radionuclides such as Tc-99. (Zhang 2003 p 324)

Zero-valent iron (Fe^0) can react with dissolved oxygen and, to some extent, with water. The following reactions represent electrochemical corrosion where iron is oxidized from exposure to water and oxygen.

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad \text{(III-9)}$$

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad \text{(III-10)}$$

Chlorinated solvents such as tetrachloroethylene (C_2Cl_4) can readily accept electrons from the iron oxidation and be reduced to ethylene as shown in the following reaction: (Zhang 2003 p 325)

$$C_2Cl_4 + 4Fe^0 + 4H^+ \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl^- \qquad \text{(III-11)}$$
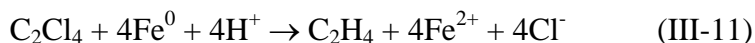
Environmental applications of zero-valent iron have been accepted by users and regulators because costs are low and no toxic effects have been induced by the process. Zero-

valent iron has been used in the form of packed bed reactors and in permeable reactive barriers. (Zhang 2003 p 325)

The pertinent water chemistry in the iron-mediated reactions produces 1) an increase in pH, and 2) a decrease in redox potential. A highly reducing environment is developed from the consumption of oxygen and the production of hydrogen. This effect should favor the growth of anaerobic microbes that could be beneficial to biodegradation.

N. Permeable Reactive Barriers

Permeable reactive barriers (PRBs), also known as *in situ* reactive wall groundwater treatment systems, or passive reactive barrier systems, are feasible when an existing hydraulic gradient can be used to cause ground-water to pass through a treatment medium, yielding a passive treatment system. The advantage of PRBs is the reduced operating and maintenance cost since there are no pumps and processing equipment to operate and maintain. Expense for monitoring is typically the only operating cost encountered with PRBs. (Andromalos 2005)

The term "barrier" in the PRB name refers to a barrier for the contaminants, but not for the groundwater. The PRB should be designed to be more permeable than the surrounding aquifer so the water can flow through the barrier freely, leaving the contaminants in the barrier. Figure III-5 illustrates the basic dimensions used to describe a PRB.

PRBs typically are used as on-site containments or as a contaminant-source management remedy. Different site- specific objectives determine the PRB design. A PRB

Figure III-6 Dimensions of a Permeable Reactive Barrier (ITRC Feb 2005 p 3)
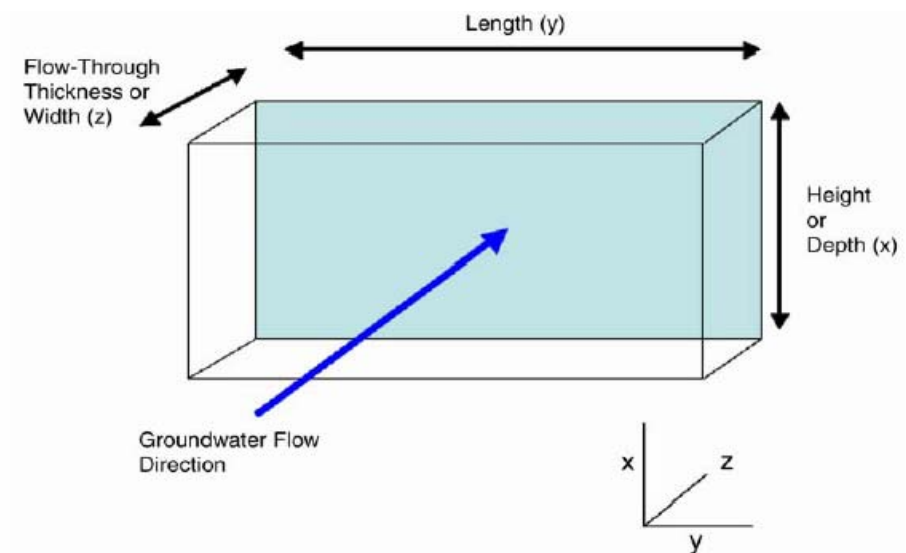

could be installed near a downgradient site boundary to prevent further migration of a contaminant plume. A PRB installed near the downgradient side of the source could be used to reduce high contaminant levels to a lower concentration that can be treated by natural attenuation or some other remedy, to address the residual contamination downgradient from the PRB. (ITRC Feb 2005 p 2)

Alternative Systems

PRB systems can be separated into four general categories: continuous wall; funnel and gate; passive collection with treatment reactor cells; and injection well barriers. Examples of the various types of PRBs are shown in Figure III-7.

Figure III-7 Examples of various types of PRBs (ITRC Feb 2005 p 3)
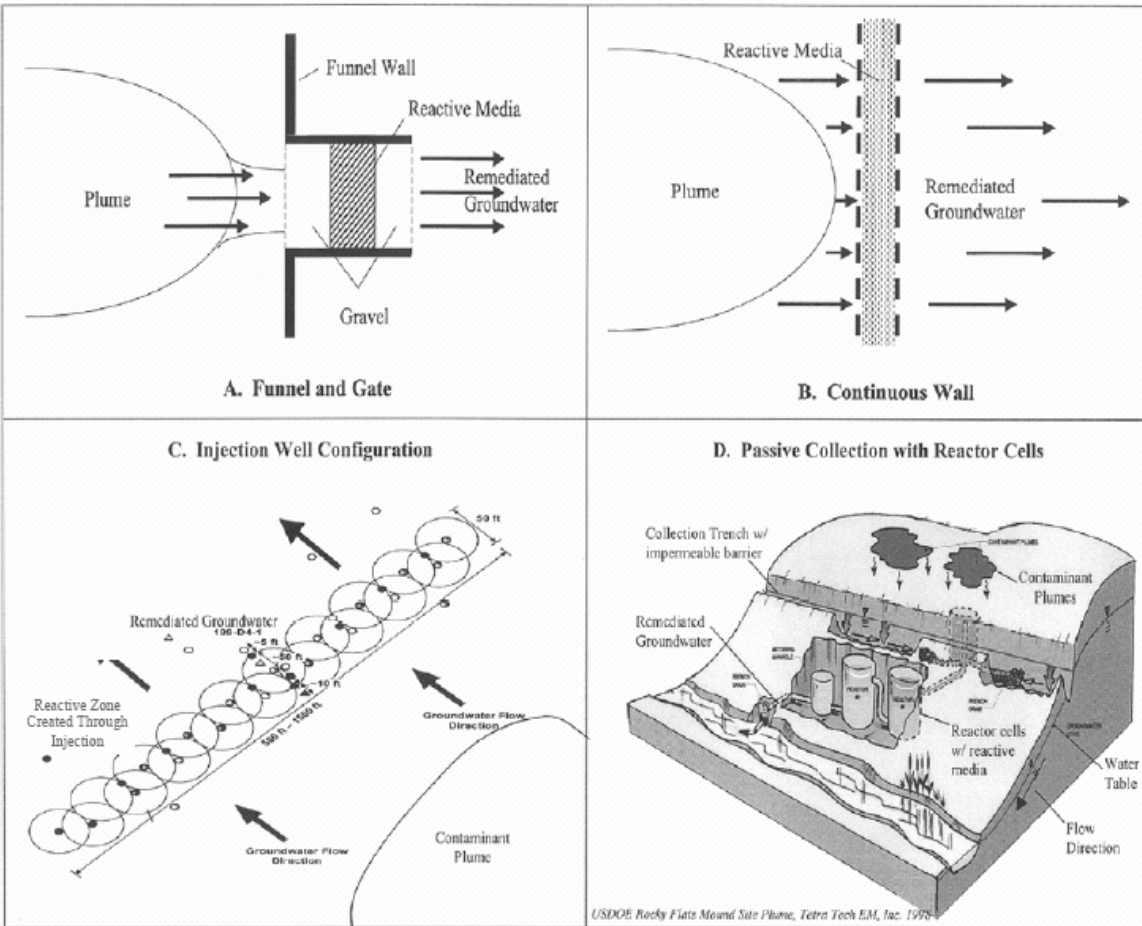
The funnel and gate system consists of vertical groundwater barriers arranged as a "funnel" to direct groundwater flow through a PRB section or "gate" for treatment. The funnel portion can be constructed in a variety of configurations such as slurry walls, steel sheet pilings with grouted interlocks, and high-density polyethylene (HDPE) composite walls. The slurry walls used for the barrier sides or funnel walls typically are constructed using soil-bentonite and soil-cement-bentonite combinations.

Continuous-wall PRBs consist of treatment media installed as continuous walls perpendicular to the groundwater flow direction. The treatment media can be installed by a variety of methods such as traditional excavation and backfill techniques, caisson drilling, one-

pass trenching with specialized machines, biopolymer slurry trenching techniques, deep soil mixing, high-pressure jetting and hydraulic fracturing techniques.

Injection well barrier PRB systems include a line of injection wells from which treatment media are released to make a reactive zone. The treatment media typically used with this system would be nutrients to create a biofilm barrier, or oxygen-releasing and hydrogen-releasing compounds to promote biodegradation of the contaminants.

Passive collection with treatment reactors is a PRB system that incorporates a series of underground treatment reactors instead of the reactive gates used in the funnel and gate system. The reactors can be arranged in series or in parallel to permit changing the treatment media while the system is active.

Treatment Media

The treatment media successfully used in PRB systems as of 2005 include zero-valent iron, limestone, activated carbon, a variety of biological nutrients, and various hydrogen-releasing and oxygen-releasing compounds. Zero-valent iron has been used most widely in full-scale PRBs through 2005. (ITRC Feb 2005 p 1) The prevalent use of zero-valent iron has occurred because of its ability to degrade a variety of contaminants, the most common of which are chlorinated solvents such as PCE and TCE. Zero-valent iron degrades PCE and TCE by the abiotic reductive dehalogenation process described in the nanotechnology section of this chapter.

For PRB systems that include passive collection with treatment reactors, activated carbon typically is used as the treatment medium. Activated carbon can remove a variety of contaminants but must be replenished after extended use.

Limestone gravel is used as the treatment medium when an increase in pH is needed. An increase in pH can help immobilize metals that are dissolved in the groundwater or make the appropriate pH adjustment in an acidic environment. Solubility of many metals is dependent on pH.

The key elements involved in oxidation-reduction reactions used to degrade contaminants include carbon, nitrogen, sulfur, iron, and manganese. The proper balance of these elements in an aqueous system can ensure that the oxidation-reduction reactions control the fate of the contaminant. Modification of the redox-sensitive elements combined with pH adjustment can be effective in improving PRB-based remediation. Based on the ability to manipulate the redox condition of an aquifer, a new class of redox enhanced PRBs evolved. (ITRC Feb 2005 p 12) The use of these PRBs appropriately has been called an "in situ redox manipulation" process. Treatment media applied to PRBs in order to promote remediation through oxidation-reduction control include iron, compost, sodium dithionate, hydrogen sulfide, acetate, and a variety of carbohydrates.

Materials used in the groundwater remediation industry to promote sorption reactions typically have not been associated with PRBs. These materials have been used in groundwater remediation to limit the migration or removal of contaminants but increasingly are being applied to PRB systems. For effective sorption in PRBs, the materials must be relatively hydrophobic, insoluble and easy to apply. (ITRC Feb 2005 p 13) Treatment media applied to PRBs in order to promote remediation through sorption include granular activated carbon, bone char, phosphatic compounds (including apatite and enhanced apatite), zeolites, coal, peat, synthetic resins, solid carbon sources (compost, peat, sawdust, wood chips, wheat straw and

cheese whey), recycled carbon-rich materials (foundry byproducts, tire chips, and paper sludges) and green waste sands. (ITRC Feb 2005 p 13)

Biological enhancements have been developed to improve treatment media applied to PRBs. Biological processes, despite involving multiple steps to reduce or destroy a contaminant, can be used effectively in a remediation strategy in a PRB environment. The benefits of biological PRBs are that the treatment process can extend beyond the installed treatment zone, and a single system can treat multiple contaminants having different chemical characteristics. Treatment media applied to PRBs in order to promote remediation through a biological process include solid oxygen-releasing and hydrogen-releasing compounds, oxygen and hydrogen sources in gas emitters, solid and liquid carbon sources (saw dust, wheat straw, cheese whey, vanilla, sucrose, and other carbohydrates), different compositions of compost, pecan shells and granular activated carbon. (ITRC Feb 2005 p14) A partial list of treatment media that can be used in PRBs is given in Table III-4 on the next page.

Table III-4 PRB treatment media for different treatment methods

(ITRC Feb 2005 p 14)

PRB Treatment	Treatment Media	Contaminants Treated
Metal enhanced reductive dechlorination of organic compounds	Zero-valent metals (iron)	Chlorinated ethenes, ethanes, methanes, propanes, chlorinated pesticides, freons, nitrobenzene
Sorption and ion exchange	Zero-valent iron, granular activated carbon, apatite, bone char, zeolites, peat, humate	Some chlorinated solvents, BTX, Sr-90, Tc-99, U, Mo
pH control	Limestone, zero-valent iron	Cr, Mo, U, acidic water
In situ redox manipulation	Sodium dithionite, calcium polysulfide	Cr, chlorinated ethenes
Enhancement for bioremediation	Oxygen release compounds, hydrogen release compounds, carbohydrates, lactate, zero-valent iron, compost, peat, sawdust, acetate, humate	Chlorinated ethenes and ethanes, nitrate, sulfate, perchlorate, Cr, MTBE, polyaromatic hydrocarbons (PAHs)

IV. TECHNOLOGY COSTS AND PERFORMANCE

The previous chapter provided a detailed description of the remediation technologies being considered for use at the PGDP and indicated the site conditions to assess in order to evaluate the feasibility of implementing each technology. This chapter summarizes recent full-scale and pilot studies of the technologies under consideration. Vendor information is given for newer technologies and technologies without current case studies. Site conditions and contamination scenarios similar to those at the PGDP site were the primary criteria for selection in the search for case studies. The purpose of the case studies is to allow comparison of values of critical factors for each technology as given in the case documentation. The factors considered by the TAG included: implementation cost and ease of implementation; technology maturity and appropriateness; life-cycle costs and overall cost-effectiveness; ability to reduce the contaminant concentrations to regulatory levels of compliance; compatibility with existing site constraints and treatment systems; stakeholder considerations; and regulatory permits. The costs represented in the following case studies are the costs at the time when the technology was implemented for each study. A summary of values for these factors, based on these case studies, is given in Chapter VI for the relevant technologies. The cost data in the Chapter VI summary are estimated at current worth for the year 2005.

A. Rotary Treatment

Rotary treatment case studies of more recent date than those contained in the ITRD 1999 data were not available. The vendor used in the cost and performance estimates for rotary treatment was In-situ Fixation. A personal communication on June 22, 2005 with Collin Murdoch, the representative for In-situ Fixation, provided useful data. Mr. Murdoch confirmed

that the 1999 ITRD data on performance could be used in lieu of updated performance data, and costs could be increased in proportion to inflation.

B. Soil Fracturing

A field demonstration of hydraulic fracturing was conducted at the Portsmouth Gaseous Diffusion Plant in Piketon, Ohio. The demonstration compared the effects of fracturing on four different remediation technologies in the same soil conditions. The technologies compared were: steam injection; hot air injection; iron metal PRB; and chemical oxidation using potassium permanganate. The tests were conducted in silty clay soil where the depth to groundwater was typically 11.5 feet below ground surface. The soil water content was near saturation levels almost to the ground surface.

The dimensions of the four test cells were 45 feet by 45 feet in plan to a depth of 16 feet. The four test cells were categorized as: Cell A – Steam injection; Cell B – Hot air injection; Cell C – iron metal PRB; and Cell D – permanganate. The contaminant was TCE at a concentration of 100 mg/kg. Four to five fractures were produced in each cell at depths 4 to 18 feet below the ground surface and spaced two to three feet apart. Cells A and B were operated 60 days in fall 1996 and 45 days in summer 1997. Cells C and D were operated passively during a two-year period.

The results from Cell A showed no significant improvement in steam injection remediation when combined with fracturing. Cell B showed that fracturing with hot air injection increased the rate of contaminant removal by volatilization. Cell C showed that the iron remained active (30 to 40 percent initial degradation of TCE) for up to 27 months after placement. Cell D showed that the permanganate was more active than in the situation without

fractures, degrading more than 99 percent of the TCE in two hours. The costs for sand-propped fractures generally ranged from $850 to $1,500 per fracture. (US EPA 2001 p 18)

C. Chemical Oxidation with Ozone

C-Sparge with ozone injection was implemented June 1, 2002 at the former Market Place Shopping Center in Hilton Head, South Carolina. At the former location of the facility, Dryclean USA, in the shopping center, perchloroethene (PCE) was used in the cleaning operation. The contaminants present and the highest amount detected in the groundwater, in ppb, were: 13,000 PCE; 5,600 TCE; 6,300 DCE; and 44 VC. The size of the contaminant plume was 250 feet by 200 feet in plan with a depth of 45 feet.

As of October 21, 2004, almost 28 months after injection, the contaminant concentrations were reduced to (ppb): 146 PCE; 33.6 TCE; and 77.1 DCE; with VC not detected. The cost for site assessment was $160,000. The cost to design and implement the project was $311,000. The cost for operation and maintenance for the 28-month period was $50,000. (SCRD 2005 p 33)

D. Chemical Oxidation with Permanganate

Butler Cleaners, located in Jacksonville, Florida has been an active PCE dry-cleaning site since 1972. The contaminants present at this site, and the highest amounts detected in the groundwater, in ppb, were: 17,000 PCE; 830 TCE; 120 DCE; and 1,170 VC. The size of the treatment area was 10 feet by 40 feet in plan with a depth of 30 feet.

The treatment consisted of three initial injections of 5,000 gallons per injection of a 7.7 g/L aqueous solution of potassium permanganate ($KMnO_4$). Periodic injections are ongoing.

Post-pilot test monitoring indicated that after permanganate injection, contaminant concentrations decreased in the treatment areas. Periodic monitoring indicates that rebound of

elevated PCE concentrations occurs with the reduction of permanganate concentrations. The rebound of PCE concentrations likely occurs because of the residual DNAPL PCE that acts as a source of dissolved phase PCE.

The cost to design and implement the pilot test system was approximately $230,000. The cost for quarterly monitoring and permanganate injection (not including reporting cost) was approximately $30,000 per event. No time frame was given for the periodic injections. The last profile update was reported for December 8, 2003. (SCRD 2005 p 9)

E. Chemical Oxidation with Fenton's Process

Swift Cleaners formerly was located in Jacksonville Beach, Florida but was demolished and replaced by a parking lot for a Walgreen store. The contaminants present and the highest amounts detected in the groundwater, in ppb, were: 21.5 PCE; 440 TCE; 1,400 DCE; and 21 VC. The amounts detected in the soil in μg/kg were: 530 PCE; 73 TCE; and 35 DCE. The size of the contaminant plume was given as an area of 1.6 acres at a depth of 40 feet.

Lab tests and a treatability study for chemical oxidation using Fenton's process were conducted in February 2002. Two chemical oxidation injections were implemented using Fenton's reagents on March 19-22, 2002 and April 23-24, 2002. A total of 40 injection points (20 clustered dual-zone) were used. The reagents were injected in one zone 3 to 11 feet below ground surface and in a second zone 11 to 17 feet below ground surface. Approximately 240 gallons of 12 percent hydrogen peroxide (H_2O_2) and 120 gallons of catalyst were injected at each injection point.

The contaminant concentrations decreased considerably following the two injections. After two years of post-injection monitoring, the contaminant concentrations returned to levels found in the baseline sampling. The contaminant rebound is thought to have occurred because

of the residual contaminant source that remained in the unsaturated zone. In June 2004, approximately 57 cubic yards of soil were removed from the source area in the unsaturated zone.

The cost for site assessment was $72,000. The costs to design and implement the project were $9,300 (remedial action plan), $10,000 (lab test and treatability study), $117,000 (two chemical oxidation injections) and $39,506 (soil excavation). The cost for operation and maintenance was $7,700 (annual monitoring). (SCRD 2005 p 12)

F. Chemical Oxidation with Peroxide Activated Sodium Persulfate

The peroxide-activated sodium persulfate chemical oxidation process is referred to as CleanOX. The company that owns the patent on CleanOX is MECX. Owners of a chlorinated solvent manufacturing facility in St. Marys, Pennsylvania contracted with MECX to conduct a series of two applications of CleanOX in order to remediate contamination under the floor of an existing production area. The first ten-day cycle of injections took place in December 2002 and the second ten-day cycle in April 2003. The purpose of the two application cycles was to obtain a preliminary site characterization including a preliminary estimation of the total contaminant mass, and an evaluation of the apparent lithology. The first application indicated that the actual site contaminant mass was approximately five times larger than the mass in the original estimate and that the non-homogeneous contaminant variance was higher than anticipated.

The average contaminant concentration in the soil prior to the first application was 106,300 ppb. After the first application, the contaminant level dropped to about 51,000 ppb and after the second application the contaminant level dropped to approximately 7,200 ppb. The average contaminant concentration in the groundwater prior to the first application was about

40,000 ppb. After the first application, the contaminant level dropped to just over 14,000 ppb and after the second application the contaminant level dropped to about 6,600 ppb.

The data show a 52 percent decrease in contaminant concentration in the soil and a 72 percent decrease in contaminant concentration in the groundwater after the first application. After the second application, the data show a 93 percent decrease in contaminant concentration in the soil and an 83 percent decrease in contaminant concentration in the groundwater. Cost data were not available. (MECX 2005)

G. Soil Vapor Extraction

Dollar Cleaners operated as a drycleaner in Lake Worth, Florida for some time, using PCE for 19 months (1986-1987). Below the site of the cleaning plant, the contaminants present and the highest amount detected in the groundwater, in ppb, were: 19.9 PCE; 27.4 TCE; and 66.3 DCE. The only information given on soil contamination was that the highest contaminant concentration detected in the soil was 190 µg/kg, PCE. The size of the contaminant plume was 70 feet by 120 feet in plan with a depth of 12 feet.

On December 13, 2001 six horizontal SVE wells were installed at the site under the floor slabs of the plant buildings. Four vertical and one horizontal passive vapor inlet wells were installed beneath the slabs. Three horizontal passive vapor inlet wells were located outside the facility. Two 500-pound granular activated carbon vessels in series were used for emissions treatment.

The system operated until April 2002 (four months). Soil sampling showed that PCE in the soil had been reduced below cleanup target levels (less than 30 µg/kg). No contaminants were detected in the groundwater at levels exceeding cleanup goals (less than 3ppb). The cost for site assessment was $70,831. The cost to design and implement the project was $134,598.

The cost for operation and maintenance was $29,910. The cost for groundwater monitoring was $4,574. The cost for closure and site restoration was $4,983. The total cost for cleanup was $244,806. (SCRD 2005 p 30)

H. <u>Six-Phase Heating</u>

A pilot study using Six-phase heating was conducted at the PGDP near the southeast corner of the C-400 building. The activities associated with the C-400 building were: cleaning machinery parts; disassembling and testing components; and laundering clothes from plant workers. The two most significant sources of leaks and spills of VOCs have been identified at the southeast corner of the C-400 building. (US DOE 2003 p 1-3)

The six-phase heating array was 30 feet in diameter, heating a subsurface treatment area with a diameter of about 43 feet. The electrodes reached a depth of 99 feet below ground surface. The SVE system maintained a slight vacuum and the vapor was drawn into vessels containing granular activated carbon. (US DOE 2003 p 1-7)

The demonstration to allow evaluation of the feasibility of treatment by this method study began on February 14, 2003 and was scheduled to continue for 130 days. Because of positive TCE extraction results and desire to increase the temperature at the base of the RGA, a 45-day extension was implemented. The heating was discontinued on September 6, 2003. The SVE system was used for three more days to purge the treatment area of steam. (US DOE 2003 p ix)

The baseline soil sampling results indicated an average TCE concentration of about 125,500 ppb, with a maximum concentration of 2,900,000 ppb. The average reduction of TCE in the soil was 98 percent. The average baseline groundwater concentration was 645,000 ppb. The average reduction of TCE in the groundwater was 99 percent. (US DOE 2003 p 2-1)

The estimated cost for the study was $6.3 million. This cost included expense for installation of the system for which construction began in June 2002 and was completed in January 2003. (US DOE 2003 p 4-18) It is pertinent to note that the costs for implementing six-phase heating remediation at the PGDP undoubtedly were increased vis-à-vis what such costs would have been at an industrial contamination site because of the added expenses associated with working at an active Department of Energy secure facility. It was impossible, however, to estimate exactly how much the costs of remediation by six-phase heating were increased simply because the method was implemented at a secure facility. The relatively high use of electrical power necessary to this method would entail relatively large expenditures in operating funds even if the method were implemented at a facility not subject to security restrictions such as those in place at PGDP.

I. Steam: Dynamic Underground Stripping (DUS) and Hydrous Pyrolysis Oxidation (HPO)

Steam (DUS/HPO) was used as a remediation technology in a field demonstration at the Savannah River Site 321-M Solvent Storage Tank Area in Aiken, South Carolina from September 9, 2000 to September 28, 2001. The contaminants were PCE and TCE, introduced into the environment by leaks and spills from storage areas.

Three steam-injection well clusters were installed around the perimeter of the 100-foot by 100-foot treatment area. Each well cluster consisted of three injection wells with screened intervals at 50 to 70 feet, 110 to 130 feet, and 150 to 160 feet below ground surface. A dual-phase groundwater and vapor extraction well was installed in the center of the target zone with a screened interval from 20 to 160 feet below ground surface. The dual-phase well operated using an electric submersible pump, resistant to high temperatures, located at 143 feet below

ground surface. Three vadose zone SVE wells were installed along the perimeter of the target zone. The steam for the system was supplied from other operations at the site. The extracted vapors were sent through a heat exchanger and a DNAPL-water separator. Air was injected into the deep saturated zone to enhance the HPO process. Groundwater was heated to approximately 100 °C; the soil in the source zone reached the same temperature.

The operation began September 9, 2000 and performance objectives were met by March 8, 2001. The system was operated until September 26, 2001 for additional contaminant removal. Specific values for treatment goals were not provided in the literature; however, by March 2001 it was reported that TCE levels were reduced by 62 percent and PCE levels were reduced by 26 percent.

The cost for the pilot project was $29 per cubic yard not including cost of steam generation and cost of treatment of dissolved and vapor phase contaminants. The total volume of the treatment zone was approximately 59,000 cubic yards. (US EPA July 2003 p 28)

J. Bioremediation

Anaerobic Microbes

A natural microbial combination containing *Dehalococcoides ethenogenes* was used by the Remediation Technologies Development Forum (RTDF) in a field study at Dover Air Force Base in Delaware. Anaerobic microbe dechlorination had been attempted but the process had stalled after production of DCE, leaving an accumulation of DCE and VC despite continued electron donor addition. After bioaugmentation using the *Dehalococcoides ethenogenes* combination, complete dechlorination of DCE and VC to ethylene was observed. This excellent result led to a full-scale demonstration study at Kelly Air Force Base in Texas. (Major et al 2001 p 27)

The study at Kelly Air Force Base utilized an indigenous anaerobic microbe with a natural non-pathogenic microbial combination referred to as KB-1. Geosyntec worked with the University of Toronto to isolate KB-1 to be used for bioaugmentation. The KB-1 combination utilizes strains of the *Dehalococcoides ethenogenes* microbe. A key component to this demonstration was the ability to assess the absence of *Dehalococcoides ethenogenes* at the site before the remediation began and to track the spread of the KB-1 strains of *Dehalococcoides ethenogenes* during the remediation. As in the field study in Delaware, the use of indigenous anaerobic microbes for dechlorination had stalled at the production of DCE, leaving an accumulation of DCE and VC. (Major et al 2001 p 28)

The field demonstration setup consisted of a closed loop recirculation system, with three extraction wells, one injection well, and five biomonitoring wells. Figure IV-1 shows a plan view of the system. The horizontal distance from the injection well to the extraction wells was 30 feet.

Figure IV-1. Plan View of Test Area at Kelly Air Force Base (Major et al 2001 p 29)

Injection Well •

• BW-1

• BW-4   • BW-2   • BW-5

groundwater
gradient
↓   • BW-3

•   •   •
E-1   E-2   E-3
Extraction Wells
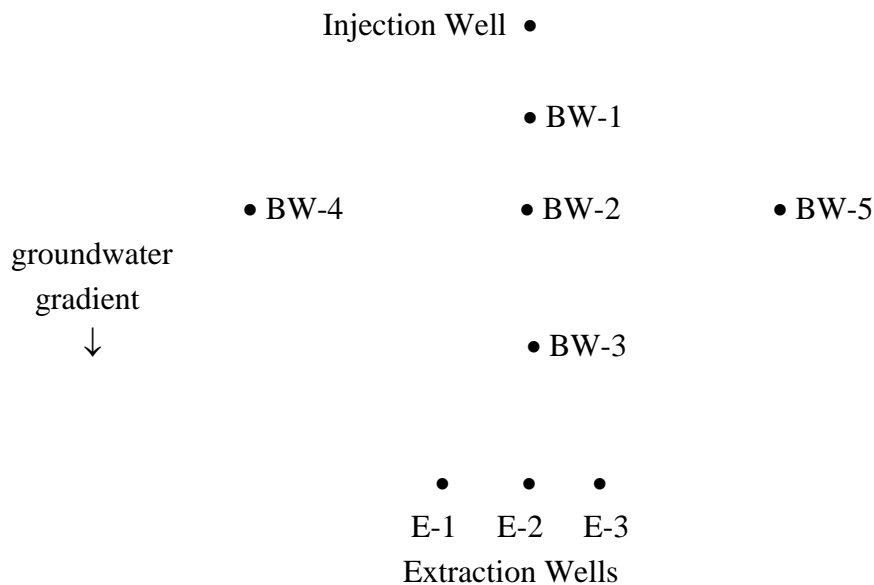
Electron donors (methanol/acetate) were injected into the groundwater at a rate to achieve desired concentrations based on the groundwater flow rate. After 87 days, all monitoring wells showed that PCE levels had decreased by more than 90 percent from original concentrations, with the dominant degradation product being DCE. Before adding KB-1, soil and groundwater samples showed that *Dehalococcoides ethenogenes* was not detected. After 142 days of bioaugmentation with KB-1, ethylene was the dominant product in the test area. (Major et al 2001 p 31)

This field study demonstrated that indigenous microbes in the presence of electron donors could dechlorinate PCE reductively to DCE. Complete dechlorination was observed only after KB-1 was added to the aquifer. No cost data were provided with this study. (Major et al 2001 p 32)

Anaerobic Microbes

The Remediation Technologies Development Forum (RTDF) sponsored a field demonstration from May 1996 to March 1998 at the Dover Air Force Base, Area 6 in Dover, Delaware using *in situ bioremediation* conducted in two phases. The first phase was stimulation of indigenous microbes for reductive dechlorination of TCE. In the second phase, a culture of microbes was imported from Largo, Florida to bioaugment the dechlorination process. The contaminants and concentrations in the groundwater were 3 μg/L PCE, 4,800 μg/L TCE and 1,200 μg/L DCE.

Three injection wells and three extraction wells were aligned perpendicular to the groundwater flow with injection wells spaced 60 feet from extraction wells to create a recirculation area. During the first phase, sodium lactate was added on a seven-day cycle and nutrients (ammonium phosphate and yeast extract) were injected in discrete pulses. No

reduction beyond DCE was observed during the first phase. During the second phase, after a lag period of 90 days, the imported culture began reducing DCE to VC and ethylene. Complete reduction of the chlorinated solvents to ethylene occurred by the end of the demonstration.

The estimated net 2005 value of the cost of the demonstration was $596,000. (US EPA June 2002 p 42)

Anaerobic Microbes

The King of Cleaners plant in Orlando, Florida has been an active PCE dry-cleaning facility since 1987. Under the plant, the contaminants present and the highest concentrations, in ppb, detected in the groundwater were: PCE 390; TCE 43.3; DCE 73.8; and VC 7.8. Only PCE was found in the soil, in a maximum concentration of 170 μg/kg. The size of the contaminant plume was 300 feet by 140 feet in plan at a depth of 40 feet.

Site assessment information led to the decision to use biostimulation to accelerate reductive dechlorination of the contaminants. On October 15, 2003, phase one was begun by injecting five gallons of 60 percent potassium lactate solution mixed with 1000 gallons of native water from one of the monitoring wells. Performance monitoring was conducted from November 2003 to January 2004, during which time little change in contaminant levels occurred. Phase two began on February 27, 2004, when an additional 50 gallons of 60 percent potassium lactate solution mixed with 2000 gallons of water were injected. Monitoring on March 26, 2004 failed to detect PCE, and showed concentrations of TCE at 3.9 ppb and DCE at 51.1 ppb. Later post-remedial monitoring failed to detect PCE, TCE and VC, and DCE levels had dropped to a range of 40.8 to 20.6 ppb.

The cost for site assessment was $81,100. The cost to design and implement the project was $37,800. The cost for operation and maintenance was $45,400 (six years of groundwater

monitoring). The cost for site restoration was $4,200. The total cost for cleanup was $168,500. (SCRD 2005 p 158)

Aerobic Microbes

The groundwater beneath the Savannah River Site Sanitary Landfill (SLF) in Aiken, South Carolina was found to be contaminated primarily with TCE, DCE and VC. The SLF occupies a total area of 71 acres. A low-permeability geosynthetic cap was installed over 55 acres of the landfill to minimize infiltration and produce anaerobic conditions to facilitate reductive dechlorination of TCE. For the remaining uncapped 16 acres of the landfill, the site assessment warranted the use of a methanotropic (methane oxidizing) aerobic microbe using nitrous oxide and triethyl phosphate as nutrients.

The depth to groundwater ranged from 30 to 60 feet below ground surface in an unconfined aquifer consisting of interbedded clean sands and clayey/silty sands.

The biosparging system consisted of two horizontal wells, each with an injection pad, compressor and header; a nitrous oxide supply cylinder; a triethyl phosphate supply drum and methane vents that discharged directly into the atmosphere. The horizontal wells were installed 60 feet below ground surface, screened to lengths of 800 feet and 900 feet, respectively. The system was operated on a pulsed injection schedule. The groundwater monitoring network included 90 monitoring wells.

Initially, one well was used to inject methane, air and nutrients (nitrous oxide and triethyl phosphate) to stimulate the growth of the methanotropic microbes in order to degrade TCE. A second well was used to inject air and nutrients to promote degradation of DCE and VC aerobically.

Operations began in October 1999 and by January 2001 the extent of the TCE plume had diminished and methane injection was stopped. By February 2003, TCE levels were within compliance levels upgradient of the landfill and not detected at wells in the interior and downgradient of the landfill. VC concentrations continued to decrease from concentrations in the previous year and by February 2003 VC levels were reduced by 99 percent and TCE levels were reduced by 75 percent at wells in the interior and upgradient of the landfill, and contaminants were not detected at wells downgradient of the landfill.

The cost for installation of two horizontal injection wells was $1 million. The cost for construction of injection pad and well piping was $750,000. The cost for the operation of the biosparging system was $225,000. The cost for groundwater monitoring was $215,000 per year. (US EPA June 2004 p 44)

Extremophiles

A field study at a Department of Energy site in Oak Ridge, Tennessee showed a difficult situation: a site with a groundwater flow system with combination of low pH, and high and variable concentrations of NO_3^-, Tc(VII), and U(VI) in an aerobic environment. These conditions are typical of DOE uranium mill tailings reclamation areas, and ore processing and isotope separation facilities. (Istok et al 2004 p 469)

To monitor the response of indigenous microbes to electron donor additions, single well push-pull tests and down-well microbial samplers were used to obtain representative samples of groundwater. A series of injections of ethanol, acetate, or glucose was able to stimulate the growth and activity of the metal-reducing microbes. The results from this study showed that these microbes could reduce Tc(VII) and U(VI) successfully in the aquifer

conditions encountered when an appropriate electron donor is added in appropriate concentrations. (Istok et al 2004 p 472)

K. <u>Nanotechnology</u>

A field demonstration of the use of nanoparticles of iron and palladinized iron, with diameters in the range of 1 to 100 nm, as reductants and catalysts was done by researchers from Lehigh University at an industrial site in Trenton, New Jersey. Laboratory tests had shown that nanoparticles of iron were very effective in reducing a wide range of chlorinated hydrocarbons. (Glazier et al. 2003) Bimetallic (Fe/Pd) nanoscale particles were used to treat groundwater contaminated with trichloroethene (TCE), carbon tetrachloride, and other chlorinated organic solvents. Nanoparticles were injected from a well into the aquifer; 1.7 kg of reactant was injected. Removal efficiencies from 35 to 96 percent were observed for TCE within a radius of 4.5 m from the injection well within four weeks after the injection.

On the basis of the trial described in the previous paragraph, a field demonstration of groundwater treatment was performed in fractured sedimentary bedrock strata at a facility in Research Triangle Park, North Carolina. (Glazier et al. 2003) Bimetallic Nanoscale Particle (BNP) technology was used to remove VOCs in a zone downgradient from a former waste disposal area. A single well was used to inject BNP slurry into shallow bedrock about 38 m from the former waste disposal area. Three wells downgradient from the injection well were used to monitor performance of the treatment. The hydraulic conductivity of the fractured bedrock was about 0.001 cm/s.

Baseline sampling was done before BNP injection, and all samples were analyzed for the VOCs included in appendix IX of the RCRA regulations, other redox-sensitive biogeochemical parameters, and metals on the EPA target analyte list. Samples also were

analyzed for polymerase chain reactions (PCR) to determine if *Dehalococcoides ethenogenes* (DHE), a dechlorinating microorganism, was present and, if so, in what concentrations. Assays also were made to detect phospholipids fatty acid (PLFA) profiles to evaluate the biomass and structure of the microbial population present at the site.

On September 13-15, 2002 6,056 L of BNP slurry were injected, at a BNP concentration of 1.9 g/L and an average injection rate of 2.27 L per minute. Post-injection sampling was done after one day, and after one, two, four, six and eight weeks. The preinjection baseline concentration of total chlorinated VOCs was about 14,000 μg/L and that concentration was reduced more than 90 percent within several days. TCE concentrations were reduced more than 95 percent within 50 days after injection. Concentrations of PCE and DCE were reduced to levels near or below groundwater quality standards within six weeks, without any increase in VC concentrations. Those levels corresponded to a reduction of more than 99.9 percent. Preinjection baseline redox potentials in the test area indicated iron-reducing conditions and those potentials were lowered to methanogenic conditions after BNP injection. (Glazier et al. 2003) The lower redox potentials persisted for more than ninety days within a 12.2 m radius of the injection well, but they rebounded in the downgradient zone. The radius of influence of the injection was roughly 12 m, as shown by reductions in VOC concentrations. Microbiological testing of groundwater samples indicated that the microbial community near the injection well was changed significantly, with increase in the overall biomass and in the relative proportion of gram-positive bacteria at the injection well. No cost data were provided for this demonstration.

Another pilot study was conducted at the Naval Air Engineering Station (NAES) Site (Area 1) in Lakehurst, New Jersey using *In Situ* BNP treatment to remediate groundwater

contaminated with volatile organic compounds. The treatment zone encompassed an area approximately 300 square feet at a depth from 30 to 50 feet "below the water table". (US EPA June 2004 p 48) The contaminants consisted of PCE, TCE, DCE and VC having a total VOC concentration of approximately 900 µg/L. The BNP material consisted of nanoscale particles of zero-valent iron, with a trace coating of palladium (0.1 percent by weight) that acts as a catalyst.

Groundwater pumping was initiated one day prior to BNP injection to enhance *in situ* mixing and gain hydraulic control of the aquifer in the test area. BNP pressure injection was performed February 5 to 7, 2002 using three injection points. Groundwater monitoring was conducted on days 1, 7, 14, and 28 following injection, and at later times, and samples were analyzed for VOCs, chloride, iron and geochemical parameters.

The results of the test were evaluated on the basis of data collected from February 6 to May 6 of 2002. The total VOC reduction during this period was approximately 74 percent. Specific wells showed reductions as high as 100 percent for PCE, 74 percent for TCE, 89 percent for DCE and 88 percent for total VOCs. Reducing conditions were observed for two months after the pilot test. Based on the results, a larger scale pilot test was recommended. No cost data were provided in the report on this study. (US EPA June 2004 p 48)

L. Permeable Reactive Barriers

At a former dry-cleaning site in an urban area in Westphalia, Germany a continuous-wall PRB was used for groundwater remediation. The contaminants present and the highest concentrations detected in the groundwater, in ppb, were: PCE 5,000; and DCE 500. The contaminant plume was 1,640 feet long and 820 feet wide in a loamy sand layer at 16 to 33 feet

below ground surface. The measured hydraulic conductivity varied from 0.3 to 2.8 ft/day and the water table was 10 feet below ground surface.

The continuous wall PRB was 74 feet long and approximately two-and-a-half feet wide. The PRB was constructed by drilling a line of overlapping three foot-diameter boreholes, filled with reactive media up to the water table. The reactive media used in the wall were 69 tons of granular zero-valent iron mixed with gravel at a one-to-two volume ratio in 33 feet of the wall and 85 tons of iron sponge in the remaining 41 feet of wall. The iron sponge consisted of wood chips permeated with iron oxide.

The effluent concentration of PCE was reduced to 500 ppb from the granular iron section and reduced to 10 ppb in the iron sponge section of the wall. No VC was observed. After four years of use, the sponge section was still increasing in degradation efficiency with the effluent PCE concentration less than 10 ppb. The degradation efficiency of the granular iron section was decreasing with the effluent PCE concentration increasing from 33 ppb to 500 ppb over time. DCE and TCE were detected in the effluent from the granular iron section but no VC was detected. The research and development project was terminated in March 2004 after four years of monitoring.

The cost to design and implement the project was $30,000 for design and $93,000 for reactive material and construction. The cost for operation and maintenance was $13,000 for monitoring. (SCRD 2005 p 31)

V. TECHNOLOGY SUMMARY

This chapter includes an evaluation of the case study information given in Chapter IV, for performance and cost. Table V-1 lists the approximate size of the treatment zone, contaminants, treatment period, percent contaminant reduction at the end of the treatment period, design and implementation cost, operation and maintenance cost, total cost and cost per cubic yard for each technology. The 1999 ITRD data were used for rotary treatment with a 17 percent increase in cost. This cost increase was based on the US Department of Labor Bureau of Labor Statistics CPI Inflation Calculator. This method of adjusting costs was used to change actual costs to 2005 dollars for all of the technologies. Table D-1 in Appendix D gives the percent increase used for the years 1996 through 2004. Soil fracturing was not included in Table V-1 because soil fracturing is used to enhance the effects of other technologies. Recommendations on soil fracturing are given in Chapter VI based on the case study information given in Chapter IV. Remediation methods using humic products were not listed in Table V-1 since there were no case studies on the use of humic products for remediation, in the published literature reviewed. The recommendations on evaluation of the use of humic products are given in Chapter VI.

Table V- 1 Performance and Cost for Technology Case Studies

Technology	Size of Treatment Zone	Contaminant and Concentration in ppb	Percent Contaminant Reduction	Treatment Period	Design and Implementation Cost	Operation and Maintenance Cost	Total Cost	Cost per cubic yard
Rotary Treatment	10,000 yd^3	100,000 TCE	99.9 TCE	2 months 250 yd^3/day			$643,500	$64.00
C-Sparge with Ozone	83,000 yd^3	13,000 PCE 5,600 TCE 6,300 DCE 44 VC	98.9 PCE 99.4 TCE 98.8 DCE 100 VC	2 years and 4.67months	$335,880	$54,000	$389,880	$4.50
Potassium Permanganate	450 yd^3	17,000 PCE 830 TCE 120 DCE 1,170 VC	Rebound of contaminant levels	Not provided	$243,800	$31,800 every 3 months	No time provided for O & M cost	
Fenton's Process	103,000 yd^3	gw 21.5 PCE 440 TCE 1,400 DCE 21 VC soil 530 PCE 73 TCE 35 DCE	Rebound of contaminant levels	2 years	$224,964 did not include soil excavation	$8,316 annual monitoring	$241,596	$2.50
Peroxide Activated Sodium Persulfate		gw 39,772 Chlorinated solvent soil 106,283 Chlorinated solvent	gw 83 soil 93	4 months			Cost not provided	
SVE	310 yd^3	gw 19.9 PCE 27.4 TCE 66.3 DCE soil 190 PCE	All contaminants reduced to: gw less than 3 ppb soil less 30 ppb	4 months	$221,863	$32,303	$254,166	$815
Six-Phase Heating	5300 yd^3	gw 645,000 TCE soil 125,459TCE	gw 99 soil 98	7 months			$6,678,000	$1,250

Table V-1 (cont.) Performance and Cost for Technology Case Studies

Technology	Size of Treatment Zone	Contaminant and Concentration in ppb	Percent Contaminant Reduction	Treatment Period	Design and Implementation Cost	Operation and Maintenance Cost	Total Cost	Cost per cubic yard
Steam (DUS/HPO)	59,000 yd^3		26 PCE 62 TCE	5 months			$1,890,362	$32.00
Anaerobic Microbes (Bioaugment with imported microbes)		3 PCE 4,800 TCE 1,200 DCE	100	1 year and 10 months			$596,000	
Anaerobic Microbes (Potassium Lactate)	62,000 yd^3	gw 390 PCE 43.3 TCE 73.8 DCE soil 170 PCE	100 PCE 100 TCE 73 DCE	5 months	$122,467	$51,088	$173,555	$3.00
Aerobic Microbes (Methane)	1,549,000 yd^3	TCE DCE VC	downgradient 100 all contaminants, interior treatment zone 75 TCE 99 VC	2 years and 3 months	$1,977,500	$254,250	$2,231,750	$1.50
Nanotechnology	220 yd^3	900 VOC (PCE, TCE, DCE and VC)	100 PCE 74 TCE 89 DCE				Cost not provided	
PRB	847,000 yd^3	5000 PCE 500 DCE	granular iron 90 PCE sponge 99 PCE	4 years	$138,990	$14,690	$153,680	$0.20

The anaerobic bioremediation case study from Dover Air Force Base and extremophile case studies were not listed in Table V-1, because of the lack of information regarding those studies, although they are addressed in Chapter VI.

The information for every case study on the use of potassium permanganate found in EPA Abstracts of Remediation Case Studies and SCRD reports was incomplete. The case study presented in Chapter IV was the most complete case study on potassium permanganate found from those sources. The case study lacked the time of the study, the time of the treatment period and percent contaminant reduction. The cost per cubic yard would have been $ 834 per year if the treatment were conducted for one year. The cost would be more if the treatment period were longer.

All reports from case studies in which potassium permanganate were used for remediation contained references to contaminant rebound after the treatment process was stopped. Some of the reports on case studies for the other ISCO methods (use of ozone and use of Fenton's reagent) also contained references to contaminant rebound after the treatment period. The rebound of contaminant levels in the groundwater could be caused by the residual DNAPL dissolving after the dissolved phase contaminants were oxidized or when the contaminants adsorbed in and on the soil migrated into the groundwater.

In addition to the review of case studies, an attempt was made to secure information from vendors in order to obtain cost data for remediation technologies that were considered to show potential for use at PGDP. Contact was made by email with Doug Carvel, PE, president of MECX, on July 14, 2005 for cost information on ISCO. The following four paragraphs were contained in his reply, received on July 16, 2005.

"I am an approved supplier and applicator for Carus Chemical Corp. I can provide you with an accurate cost comparison between activated sodium persulfate using various

activation methodologies, and permanganate. Unfortunately cubic yard estimates are meaningless. What I need is surface area and depths throughout the treatment zone. The reason for this is that for these technologies, the chemical costs will vary linearly with thickness of the treatment zone but the labor and equipment will remain constant up to a certain point. With Perozone or just ozone, the labor is a minute portion of the project and the equipment and O &M is the major costs. With the other ISCO technologies the labor can be as high as 60 % of the total cost or as low as 30%. Another difference is ozone delivers very little oxidant per day and therefore operates for a much longer time and can be used as little or as great as needed just by extending the time. With other technologies, in order to get sufficient contact, the minimum in situ concentration is pretty much the same for 1000 ppb as it is for 2 ppb. Roughly the solubility limit of potassium permanganate is 4- 5% and it is 1 – 2 % for activated sodium persulfate.

Regarding the labor cost, the vendors that inject the chemicals under pressure, waste chemical, displace the contaminants, and do not get effective mixing and contact. To estimate the labor we need to estimate the time in the field. This is based on the infiltration rate which is related to the screened interval as well as the permeability and the ability to set up a network of extraction and injection points to get optimum distribution without displacement.

The size of the plume appears to control which technology is the most efficient for a given site as well as the nature of contamination. If large amounts of the contaminant mass are sorbed, only the peroxide based treatments are truly effective. This is due to peroxide's ability to desorb and dissolve mass. No other technology even gets close. Using peroxide with permanganate is an option if used first in addition to peroxide activated persulfate or perozone.

Sorry, you quest has too many variables to be simplified. The fact is if you have a large sorbed mass, the technologies are limited to peroxide combinations. If you have no sorbed mass, distribution is the key, not the oxidant, for the target contaminants and if labor controls the cost there is virtually no difference between permanganate and persulfate. If the chemical controls the cost for larger plumes, then you have to look more closely at the chemical and as a side, you have to look at if the chemical is from the USA or China. There is a large variation in these costs and it can affect the outcome of the evaluation."

The contact for information on bioremediation was Dick Raymond of Terra Systems Incorporated. Mr. Raymond gave a presentation on *in situ* bioremediation of TCE at the University of Louisville on June 2, 2005. He stated that, with certain site conditions, bioremediation can be the most cost-effective remediation technology for TCE and if site conditions do not favor bioremediation, *in situ* chemical oxidation (ISCO) and the use of PRBs should investigated. This statement does seem to be in agreement with the data on cost per cubic yard of treatment zone given in Table V-1.

The vendor contacts made for PRBs were Robbie Laird of C3 Environmental and John Vogan of EnviroMetal Technologies. C3 Environment installs the patented sheet pile Waterloo Barrier for funnel and gate PRBs. EnviroMetal has a patented iron treatment medium used in PRBs, that is very effective for remediation of TCE and that can immobilize Tc-99. Information from these sources has been included in the data presented.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. <u>Conclusions</u>

The performance and cost evaluations of the relevant remediation technologies given in Chapters IV and V are not meant to be used directly for choosing a remediation technology and estimating a cost for remediation at PGDP. The purpose of the evaluation was to determine which technologies are the most practicable and determine what site conditions at PGDP must be evaluated further to facilitate the most efficient use of the most practicable technologies. Once site assessment indicates which technology (or technologies) should be selected, then cost and treatment time can be estimated.

1. Six-phase heating proved to be a very effective treatment at high contaminant concentration levels but has the highest overall cost, twenty times more expensive per cubic yard of treatment zone than rotary treatment which has been shown to be just as effective at similar contaminant concentration levels. Both of these methods would have implementation difficulty if their application is near buildings, buried utilities or any other obstructions.

2. SVE may not be as difficult to implement as six-phase heating or rotary treatment but is the second most expensive treatment method. At higher contaminant concentration levels similar to those encountered in the six-phase heating and rotary treatment cases, SVE would cost more than $ 815 per cubic yard because of the increase in operation and maintenance costs.

3. Steam (DUS/HPO) did not perform well in reducing contamination levels, although if the system ran longer, more contaminants would be reduced; longer operations would have generated higher operation and maintenance costs.

4. The low cost per cubic yard given in the PRB case study may be misleading since the percent contaminant reduction refers to the effluent from the PRB during the life of the PRB and not the reduction in contaminant concentration in the entire treatment zone. PRBs can be very cost-effective for preventing contaminant source or plume migration.

5. The ISCO and bioremediation methods as described in the case studies, showed significantly lower cost per cubic yard of treatment zone and the case studies showed how some of these methods can be very effective in treatment of VOCs.

ISCO Methods

Permanganate seems to be a questionable choice as chemical oxidant because of the lack of a successful case study proving its effectiveness in reducing contamination levels. In the reported cases, rebound in contaminant concentration took place after permanganate concentrations decreased. The operation and maintenance cost for use of permanganate was much higher than for the other ISCO methods.

The Fenton's process case study showed the lowest overall cost of the ISCO methods but exhibited contaminant rebound problems similar to those cited in the permanganate case study.

The C-Sparge with ozone case study had complete information showing 99 percent reduction in contaminant levels at a cost of $4.68 per cubic yard. The contamination level of the C-Sparge study was about 25,000 ppb total VOCs, about 26 times lower than the TCE concentration encountered at PGDP in the six-phase heating study. If the total cost of the C-Sparge study is calculated by multiplying the operation and maintenance cost by 26 and adding the design and implementation cost, the cost per cubic yard is less than $ 21, and, thus, less than two percent of the cost for six-phase heating at PGDP. Implementing C-Sparge at PGDP

would be more costly than at the site reported in the literature because of expenses incurred in complying with security issues, but, even so, C-Sparge would probably be much less expensive that six-phase heating.

The peroxide-activated sodium persulfate case study did not provide cost data but the method performed impressively in significantly reducing high VOC concentrations in a very short treatment period (four months). The 93 percent reduction in soil contamination confirmed what Carvel said about persulfate's ability to desorb and dissolve contaminant mass. (as cited herein, pp 81-2)

Bioremediation

The bioremediation case studies showed that under certain site conditions microbes can be utilized to remediate groundwater contaminated with VOCs at a very low cost compared to other technologies.

Qualitative Observations

Review of case studies indicated that the use of microbes with cometabolites, application of ISCO methods, and use of PRBs became very popular for remediation in the period 2000-2005. In contrast, case studies involving the other technologies listed in Chapter II essentially disappeared during the same time period.

B. Recommendations

The site assessment parameters outlined in Section III-K should be used to determine the feasibility of using bioremediation. It is unlikely that bioremediation would be feasible in the source zones identified at PGDP because of the high concentrations of contamination in those zones. If the plume area conditions are conducive to using microbes for treatment of TCE, then bioremediation would be the most practical technology for remediation of the three

TCE plumes at PGDP. Another advantage of bioremediation is that anaerobic reduction will immobilize the Tc-99.

If evaluation of conditions in the plume zones indicates that bioremediation would not be cost-effective, the ISCO methods should be investigated. Despite the contaminant rebound problems with use of permanganate and Fenton's process, those techniques could still be implemented successfully in the plume area where undissolved and sorbed contaminant mass is not a concern. In DNAPL zones where large amounts of undissolved and sorbed contaminant mass could exist, ozone and persulfate ISCO methods should be investigated.

The soil fracturing case study cited in Section IV-B showed that fracturing can improve remediation depending on which technology is the primary method. The study concluded that soil fracturing would enhance *in situ* chemical oxidation using permanganate more than the other remediation technologies considered in that study. Small-scale tests could be conducted in the UCRS using the selected ISCO or bioremediation methods with and without fracturing to determine if soil fracturing should be used.

Several technologies appeared to be feasible for TCE remediation, but for Tc-99, the only existing remediation method is to immobilize Tc-99, either using microbes (extremophiles) to transform Tc-99 to its insoluble reduced state, or using PRBs with reducing treatment media to prevent Tc-99 movement beyond the PRB.

The methods of using humic products described herein have the potential to be cost effective for TCE remediation but, more importantly, use of humic products can immobilize Tc-99 more effectively. Shulgin (personal communication, August 1, 2005) described how humic material can bind to both anion and cation forms of heavy metals. This ability of humic materials potentially could solve the problems encountered using microbes to immobilize Tc-

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99. The particular problems encountered when microbes are used to transform Tc-99 to an insoluble reduced state include: 1) restricting flow in the aquifer because of the precipitate; and 2) the possibility of changes in the aquifer environment that would re-oxidize the Tc-99 causing it to become mobile again.

The humic material not only provides a substrate and nutrient for microbes used in bioremediation, but it also fosters a diversity of microbes and allows the microbes to remediate at higher contaminant concentrations. This combined method application possibly could allow bioremediation in the source zones at PGDP even where contaminant concentrations are high.

Technology Ranking

Table VI-1 ranks the recommended technologies and six-phase heating using a typical grading system (A = best, B, C, D, and F = worst) in the context of various application factors.

Table VI-1. Technology Ranking

Technology	Percent Reduction of Contaminant	Relative Ease of Implementation	Applicable in Source Zones?	Cost-Effective for Plume Treatment?	Time to Treat	Cost for use at Source	Cost for use in Plume
Bioremedi-ation	A	A	C	A	C	A	A
Bioremed. w/Humics	A	A	B	A	C	A	A
ISCO [typical]	B	A	B	B	C	A	B
ISCO-Persulfate	A	A	A	B	A	A	B
Six-Phase Heating	A	C	A	D	A	D	F

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APPENDIX A

ITRD COST AND PERFORMANCE ESTIMATES

Table A-1 ITRD Cost and Performance Estimates for Application at Paducah UCRS Part A

Technology	TCE in Soil, ppm	Volume, Cubic yd cy	Capital* Cost, $	Treatment Cost, $	Treatment Period/Rate
Rotary steam (*In-situ* Fixation	> 100	10,000	0.2 M		2 mos or 250 cy/day
	> 100	40,000	0.2 M	1.2 M	7 mos or 250 cy/day
	> 1,000	10,000	0.2 M	0.8 M	4 mos or 100 cy/day
Ozone Sparge (IT Corp)	> 100	10,000	ND	40/yd	1 year
	> 100	40,000	ND	35/yd	1 year
	> 1,000	10,000	ND	55/yd	1 year
C-Sparge (KV Assoc)	> 100	10,000	0.15 M	0.05 M/y	1 year
	> 100	40,000	0.25 M	0.09 M/y	1 year
	> 1,000	10,000	0.15 M	0.06 M/y	2 years
Bio (WMI)	> 100	40,000	0.35 M	0.5 M	1 year
Steam Enhanced Extraction & Destruction SEED [Steam Tech]	> 100	10,000	ND	137/yd	2-3 years (6-8 mos [steam] w/ 1.5 years [HPO]
	> 1,000	10,000	ND	113/yd	"
ECGO (Elec-Chem GeoOxida-Tion [Weiss]	> 100	10,000	0.37 M	0.54 M	1 year
	> 100	40,000	1.3 M	1.6 M	1 year
	> 1,000	10,000	0.35 M	0.6 M	1 year
LASAGNA (electro-Kinetics)	> 100	10,000	ND	140/yd	14 years
	> 100	40,000	ND	140/yd	62 years
	> 1,000	10,000	ND	115/yd	12 years
ChemOx/ Permanganate (IT Corp)	> 100	10,000	Did not estimate – Vendor suggests Ozone oxidation would be more Cost-effective in the vadose zone		
	> 100	40,000			
	> 1,000	10,000			
SVE w/Frac (McLaren/ Hart)	> 100	10,000	0.606 M	0.091 M 0.077 M 0.070 M	1 year 2 years 3 years
	> 100	40,000	1.1 M	0.099 M 0.091 M 0.081 M	1 year 2 years 3 years
	> 1,000	10,000	0.614 M	0.053 M 0.050 M 0.047 M	1 year 2 years 3 years
Six Phase Heating (Current Environ. Solutions)	> 100	10,000	0.315 M	0.120 M	6-12 mos
	> 1,000 (UCRS and RGA)	40,000	0.95 M	0.900 M	8 mos
Surfactant Flush(Duke Eng. Svcs.)	NA				

Table A-1 ITRD Cost and Performance Estimates for Application at Paducah UCRS Part B

Technology	Res. TCE in soil, ppm	Implementation Difficulty	Waste* Generation	Tc-99 Treatment	Total Costs[3], $
Rotary steam (*In-situ* Fixation	~5-10	Low (in easy access)	PPE and NaCl solution	Partial Recov if cond. sub to IX	0.55 M
	~5-10	High (util. Problems)	"	"	1.6 M
	~50	"	"	"	1 M
Ozone Sparge (IT Corp)	~5-10	Med (effect. in clays)	Drill Cuttings	No	0.4 M
	~5-10	"	"	No	1.4 M
	~20-30	"	"	No	0.55 M
C-Sparge (KV Assoc)	~1-5	"	Drill Cuttings; GAC	Possible W/ resin in Well	0.2 M
	~5	"	"	"	0.34 M
	< 50	"	"	"	0.27 M
Bio (WMI)	~1-5	High(effect. In clays?) fouling	Trenching Waste	No	0.85 M
Steam Enh. Extrac. & Destruction SEED [Steam Tech]	< 0.1	Med-high (effect-tiveness in clays?)	Drillcuttings; oper. filter cake; PPE; contam. Equip.	Yes, entr water will have Tc-99	1.4 M wo/ion Exch for Tc-99
	< 10	High (util. Problems)	"	"	1.1 M
ECGO (Electro Chemical GeoOxida-Tion [Weiss Assoc]	0.010	Medium (tren-ching & drill for cables & electrodes)	Electrodes Plated w/Tc-99; drill cuttings	Yes	0.91 M
	0.1	"	"	Yes	2.9 M
	0.1	"	"	Yes	0.95 M
LASAGNA (electro-Kinetics)	~1-50	Med-high (access problems	Groundwater Treatment, Iron? GAC ?	Yes	1.4 M
	~1-50	"	"	Yes	5.6 M
	~10-500	"	"	Yes	1.2 M
SVE w/Frac (McLaren/ Hart)	30 10 5	ND	Water from steam regen.of GAC; drill cuttings	No	0.697 M 0.774 M 0.844 M
	30 10 5	ND	"	No	1.2 M 1.3 M 1.4 M
	30 10 5	ND	"	No	0.667 M 0.717 M 0.764 M
Six Phase Heating	~ 1	Low	Vapor/steam cond. drill cuttings	No	0.435 M
	~ 1	Med	"	No	1.9 M

Table A-1 ITRD Cost and Performance Estimates for Application at Paducah RGA Part A

Technology	TCE in Water, ppm	Volume, Cubic yd cy	Capital* Cost, $	Treatment Cost, $	Treatment Period/Rate
C-Sparge (KV Assoc)	> 1	50,000	0.193 M	0.032 M/y	2 years
	> 100	5,000	0.212 M	0.059 M/y	1 year
Ozone Sparge (IT Corp)	> 1	50,000	Did not estimate; Vendor suggests Permanganate more efficient		
	> 100	5,000			
Rotary Steam (In-situ Fixation	Depth generally limited to 40'; not applicable to RGA				
Aerobic Bio (WMI)	> 1	50,000	0.3 M	0.450 M	1 year
	> 100	ND			
	> 100	5,000	0.100 M	0.225 M	1.5 years
Steam Enhan. Extrac. & Destruc. [steam strip Steam tech]	> 1	50,000	Not Applicable		
	> 100	5,000	ND	113/yd	2-3 years (6-8 mos [steam] w/ 1.5 years [HPO]
ECGO (Electro-Chemical GeoOxida-tion [Weiss Associates]	> 1 (saturated UCRS and RGA)	2.4 million	52 M	19.2 M	10 mos
	> 100 (saturated UCRS and RGA)	3.0 million	60 M	24 M	10 mos
ChemOx/ Permanganate (IT Corp)	> 100	18.1 M (NW plume)	ND	1.50-2.50 per yd	-
	> 100	8.8 M (NE plume)	ND	1.00-2.00 per yd	-
	> 100	1.5 M (SW plume)	ND	3.00-6.00 per yd	-
SVE w/Frac (McLaren/ Hart)	> 1	50,000	Not Applicable		
	> 100	5,000	Not Applicable		
Six Phase Heating	> 100	20,000 (UCRS) + 20,000 (RGA)	0.95 M	0.900 M	1 year
Surfactant Flush(Duke Eng. Svcs.)	>1	50,000	ND		
	> 100	5,000	0.317 M	1.202 M	1 mo/35 gpm

Table A-1 ITRD Cost and Performance Estimates for Application at Paducah RGA Part B

Technology	Res. TCE in soil, mg/L	Implementation Difficulty	Waste* Generation	Tc-99 Treatment	Total Costs[3], $
C-Sparge (KV Assoc)	< 0.005	Low	Spent IX resin, well cuttings, GAC	Yes	0.257 M
	< 0.005	Low	"	Yes	0.271 M
Aerobic Bio (WMI)	< 0.002	Medium	Drill cuttings	No	0.750 M
	ND				
	10	Medium	Drill cuttings	No	0.325 M
Steam Enhan. Extrac. & Destruc. [steam strip Steam tech]	Not Applicable				
	~ 1	High (utilities problems)	Drill cuttings; oper. Filter cake; PPE; Contamin. equipment	No	0.565 M
ECGO (Electro-Chemical GeoOxida-tion [Weiss Associates]	~ 0.005	Medium (trenching & drill for Conduits, cables & electrodes	Liquid waste from GAC regen. Electrodes Plated w/ Tc-99; drill cuttings	Yes	71 M
	"	"	"	"	84 M
ChemOx/ Permanganate (IT Corp)	< 0.1	Medium (geology causes preferential flow paths)	Drill cuttings	No	27-45 M
	< 0.1	"	"	"	9-17 M
	< 0.1	"	"	"	4-9 M
Six Phase Heating	~ 0.01	Low	Vapor/steam Condensate, Drill cuttings	No	1.9 M
Surfactant Flush(Duke Eng. Svcs.)	ND				
	< 2	-	Waste water trmt $ 4.2M Incl. GAC And IX. Drill cuttings	No	6 M

Table A-1 ITRD Cost and Performance Estimates for Application at Paducah Reactive Walls
Part A

Technology	TCE con-centration in water, mg/L	Area	Capital* Cost, $	Maint Costs, $	Useful Life, Years
Fe (jet grout) [Foremost Solutions]	1-10	4000' x 50'	3 M ($15/sq ft)	0.100 M per year	10 yr/ wall;2 walls needed
	1-10	1000' x 50'	0.500 M ($15/sq ft)	0.050 M per year	10 yr/ wall; 2 walls needed
C-Sparge (KV Assoc)	1-10	4000' x 50'	0.850 M	0.285 M per year	20
ECGO [Weiss & Assoc.]	< 10	900,000 cubic yards	25 M	1 M per year	20
Pneumatic Injection of Fe (McLaren/ Hart	1-10	1000' x 60'	8.5 M	0.300 M	20

Reactive Walls Part B

Technology	Contaminant Reduction	Implementation Difficulty	Waste* Generation	Tc-99 Treatment	Total Cost, $
Fe (jet grout) [Foremost Solutions]	TCE 99 % Tc-99 99%	Medium; depth and continuity concerns	Spent iron Removal or encap.; drill cuttings	Yes	8 M (2 Walls)
	TCE 99 % Tc-99 99%	"	"	yes	2.5 M
C-Sparge (KV Assoc)	TCE 99.5 % Tc-99 97%	Low	Spent IX Resin	Yes	6.6 M
ECGO [Weiss & Assoc.]	TCE 99.5 % Tc-99 99.95 %	Medium	Liquid waste from GAC regen. Electrodes Plated w/ Tc-99; drill cuttings	Yes	45 M
Pneumatic Injection of Fe (McLaren/ Hart	TCE >90 % Tc-99 >909%	Medium	Spent iron Removal or encap.; drill cuttings	Yes	8.8 M

Notes for Table A-1

     1. Resin use costs $0.14/cu yd of treated volume and resin disposal costs $ 0.22/cu yd of treated volume assuming 40,000 pCi/L water, soil porosity of 0.3, resin ion exchange capacity of 0.0133 Ci/cu ft and resin cost of $ 200/cu ft. Resin transportation cost is negligible. Decontamination water for drilling is less than 20 gallons per hole drilled.

     2. Assuming cuttings into RGA is mixed waste, cuttings disposal cost is $0.90/cu yd of treated volume and transportation is $0.54/cu yd of treated volume.

     3. Cost excludes horizontal drilling for access under buildings where applicable.

     * Abbreviations: PPE = Personal Protection Equipment

                                ND = Not Determined

                                NA = Not Applicable

                                GAC = Granulated Activated Carbon

                                IX = Ion Exchange

Table A-2 ITRD Preliminary Technology Applications by Geologic Unit

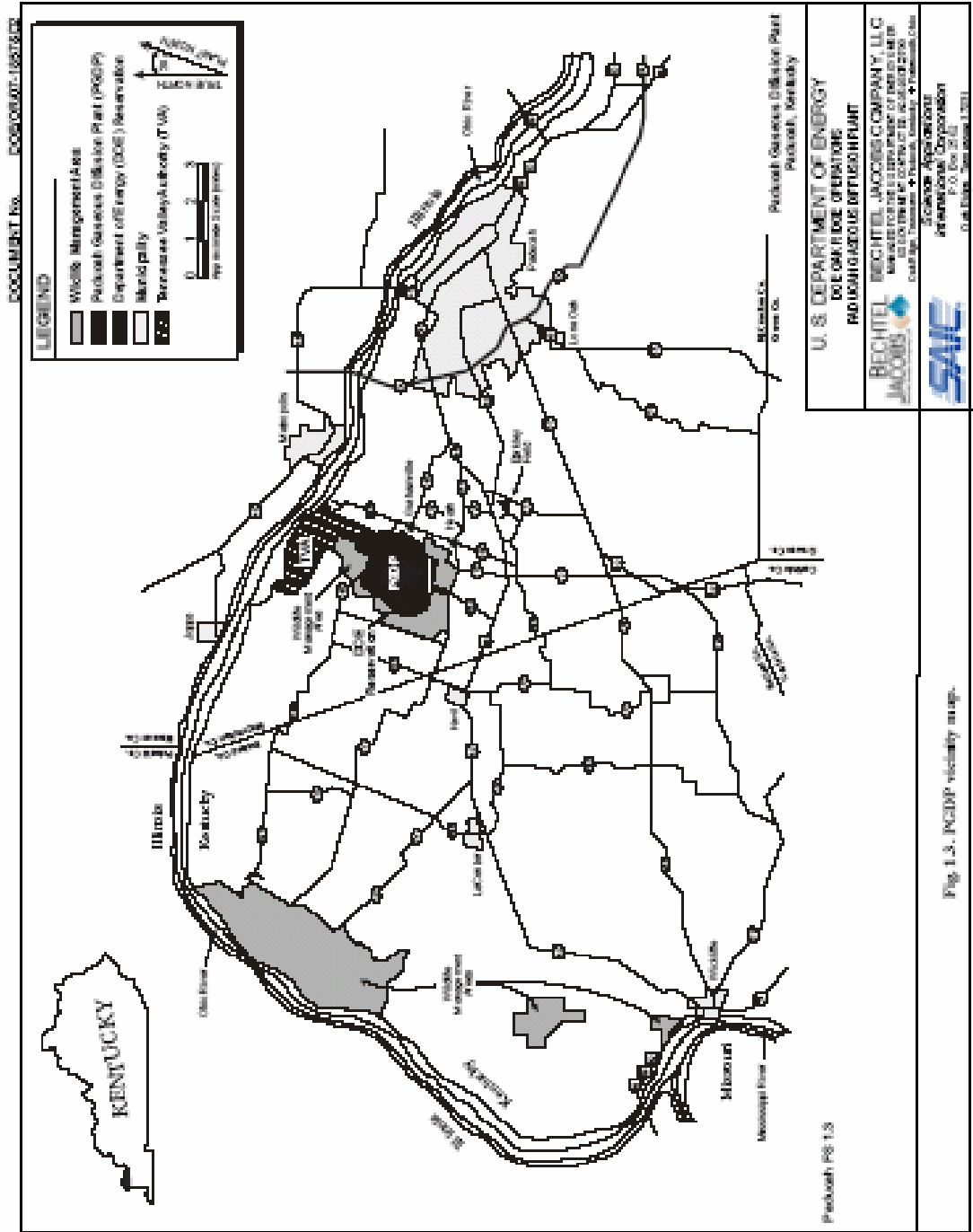| Formation	Source (Easy Access)	Source (Hard Access)	Low Concentrations
UCRS Vadose Zone K = 0.01 to 0.00001 cm/s Depth 0-40 ft bgs	• Direct Heating • Rotary Steam Stripping • Electrokinetics • Horizontal Reactive Barriers • HVSVE • Gaseous Chemical Oxidation Natural Attenuation & Containment	• HVSVE (with enhancements) • Gaseous Chemical Oxidation • Horizontal Reactive Barriers • Direct Heating • Electrokinetics Natural Attenuation & Containment	• Rotary Steam Stripping • Electrokinetics • HVSVE • Gaseous Chemical Oxidation • Direct Heating • Natural Attenuation & Containment • Horizontal Reactive Barriers
UCRS/Saturated Depth 30-60 ft bgs	• Two Phase Vapor Extraction • Direct Heating • Rotary Steam Stripping • Electrokinetics • Horizontal Reactive Barriers		• Rotary Steam Stripping • Electrokinetics • Multi-Phase HVSVE • Horizontal Reactive Barriers
RGA K = 1 to 0.01 cm/s Depth 60-130 ft bgs	• Dynamic Underground Stripping/Hydrous Pyrolysis-Oxidation • Chemical Oxidation • Soil Flushing • Direct Heating • Air Sparging (w/o ozone) • Pump and Treat		• Aerobic Bio; Bio-venting • Chemical Oxidation • Steam Stripping • Reactive Walls • Pump and Treat • Natural Attenuation

Figure A-1 Map of PGDP Location (US DOE 2001 p 1-10)
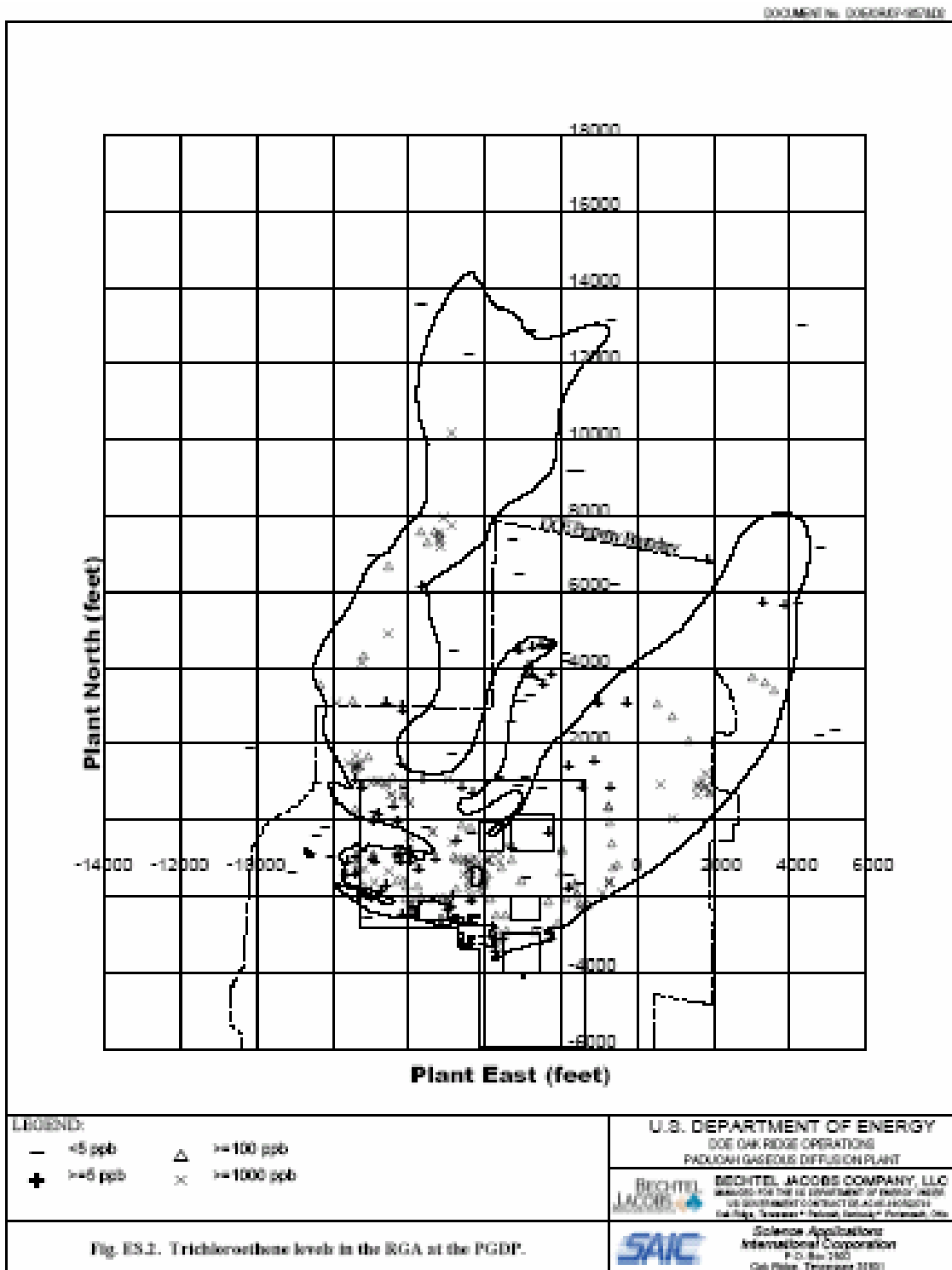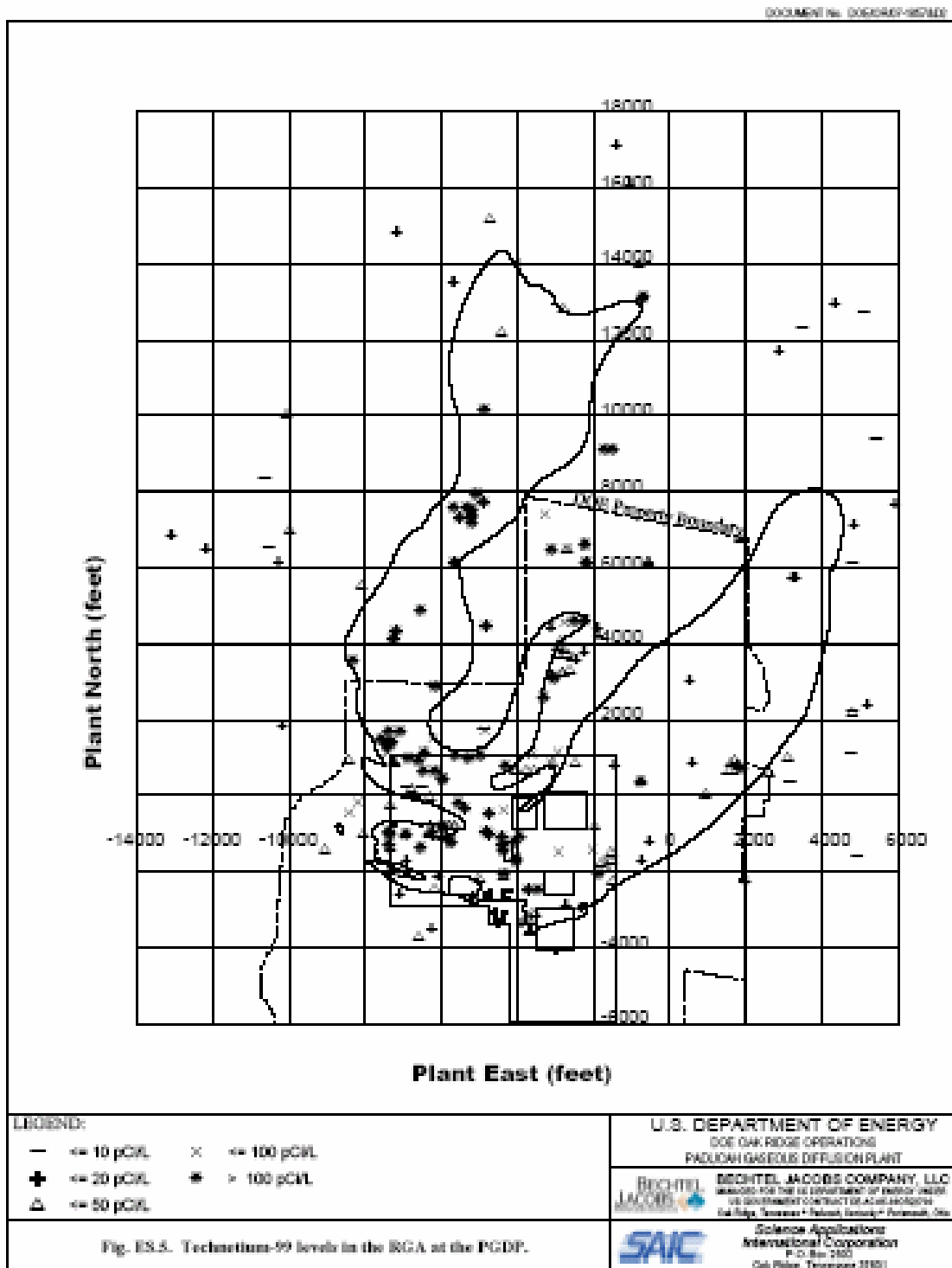
Figure A-2 TCE Plume Map (US DOE 2001 p ES-8)

Fig. ES.2. Trichloroethene levels in the RGA at the PGDP.

Figure A-3 Tc-99 Plume Map (US DOE 2001 p ES-11)
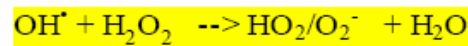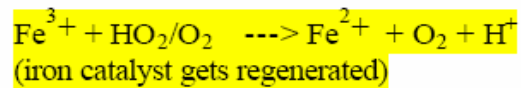

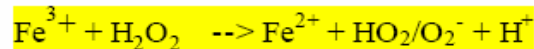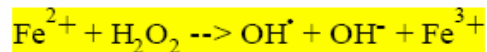Fig. ES.5. Technetium-99 levels in the RGA at the PGDP.

APPENDIX B

FENTON'S PROCESS
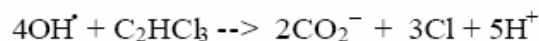
Fenton's Process (Jacobs and Testa 2003)

When chemical oxidant H_2O_2 is injected at concentrations of 10 to 35% into the subsurface, it decomposes readily into reactive hydroxyl radicals (OH˙) and water. The hydroxyl radical (OH˙) in the subsurface can be used to rapidly mineralize hydrocarbon, solvent and other contaminants to water and carbon dioxide. This reaction is enhanced i the presence of iron. Iron is naturally occurring in soil and groundwater or can be added during the injection process, if needed. The reaction is based on the principle of Fenton': Chemistry where iron and hydrogen peroxide react to form hydroxyl radicals and other by-products as shown in Equation 1.

The double bonds, C=C, that characterize chlorinated ethenes are more reactive than the single C-C bonds of chlorinated ethanes. Therefore, PCE and TCE are more susceptibl to chemical oxidation than TCA. Although all these chemicals are susceptible to chemical oxidation, relative resistance to oxidation from highest to lowest: PCE, TCE, vinyl chloride, phenanthrene, benzene and hexane. The oxidation reaction for a common solvent, trichloroethene (TCE), forms several unstable daughter products (epoxides), the breaks down to ketones and aldehydes, finally yielding carbon dioxide, water and chloride ions (Suthersan, 2002). The oxidation of TCE is shown in Equation 2:

Equation 1:

$$Fe^{2+} + H_2O_2 \longrightarrow OH^{\cdot} + OH^{-} + Fe^{3+}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2/O_2^{-} + H^{+}$$

$$Fe^{3+} + HO_2/O_2 \longrightarrow Fe^{2+} + O_2 + H^{+}$$
(iron catalyst gets regenerated)

$$OH^{\cdot} + H_2O_2 \longrightarrow HO_2/O_2^{-} + H_2O$$

$$OH^{\cdot} + Fe^{2+} \longrightarrow Fe^{3+} + OH^{-}$$

$$HO_2/O_2^{-} + Fe^{2+} + H^{+} \longrightarrow Fe^{3+} + H_2O_2$$

$$OH^{\cdot} = \text{hydroxyl radical}$$

Equation 2: $$4OH^{\cdot} + C_2HCl_3 \longrightarrow 2CO_2^{-} + 3Cl + 5H^{+}$$
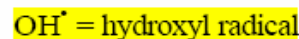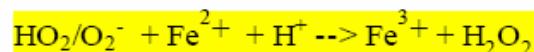
The hydroxyl radical that attacks the carbon-hydrogen bonds is capable of degrading many chlorinated solvents, chloroalkenes, esters, aromatics, pesticides and other recalcitrant compounds such as MTBE, PCP and PCB. The Fenton's chemistry reaction is highly complex, The iron cycles between the Fe(II) and Fe(III) oxidation states yields the hydroxyl radical and other by products (Suthersan, 2002).

APPENDIX C

INFORMATION ON SHULGIN'S HMA EXPERIMENTS

Example 6

There was carried out detoxication of soil samples taken in the vicinity of the condenser manufacturing works in the city of Serpukhov (Moscow region), said samples being polluted with polychlorinated biphenyl (PCB). Soil sample were taken from plowing areas 100x100 m using the "envelope" technique.

Then put in a hothouse to be held there for 60 days at a constant temperature (14^oC) and humidity (70% of total soil moisture capacity). The HMA dose applied was from 0.1 to 10% in terms of dry matter of total soil dry weight. Used as the control were soil samples free from the HMA. The HMA application procedure was repeated four times in succession. The starting PCB content was from 0.12 to 300 mg/kg.

It was found that the soil samples featuring low PCB content (0.12 mg/kg on the average) displayed a reduction in said content by 40-50% on the average for 60 days following the treatment with HMA, the most effective reduction of said content was observed in the range of the HMA doses applied from 0.3 to 5%. With the HMA dose above 5% no perceptible difference was noted (except for the effect of "diluting" the soil samples).

It was also found that PCB content (300 mg/kg on the average) said content was found to have dropped by 30-34% for 60 days.

It was noted that with the temperature elevation to 24^oC the soil samples featuring a low PCB content (0.12 mg/kg on the average) after having been held for 60 days at that temperature, displayed a 60-70% reduction in said content, while the soil featuring a high PCB content (300 mg/kg on the average) exhibited a 40\50% reduction in the PCB content for the same period of time.

Example 7

As a result of industrial-economical activities, as well as warehousing and burial of domestic and industrial waste, an unfavorable ecological situation has arisen on some land areas consisting mainly in high levels of soil pollution and ground with heavy metals.

Decontamination and detoxication procedures of one such area were carried out in Moscow.

To select optimum HMA doses a number of experimental plots were laid on the area subject to decontamination, each plot being equal to 1x1 m. Plot No 1 was given one percent of HMA (in terms of dry matter) of a total soil weight, applied for a depth of 20 cm; plot No2, 1.5% of HMA; plot No 3, 3% of HMA; plot No 4 was the control.

Once HMA had been applied, the plots were dug over again for a depth of 20 cm so that HMA was spread uniformly over the profile of the polluted soil. Each of the plots was irrigated with water (8-10 L/m^2), whereupon samples were withdrawn for chemical analysis.

In view of the fact that during soil tillage humic acids strongly bind the ions of toxic heavy metals by transforming them into stationary (water-insoluble) forms, the concentrations of metals in a mobile form were assigned for assessing the efficiency of the detoxication procedure performed. The results of the sample analysis are presented in Table C-1.

Element	Buffer type	Form of element	MAC	Heavy metals content, mg/kg			
				1%	1.5%	3%	control
Zinc	Ammonium-acetate buffer, pH=4.8	Mobile	23,0	14,50	10,75	7,5	18,0
Manganese	-"-	Mobile	1500	7,05	6,59	5,90	7,14
Strontium	-"-	Mobile		27,5	19,1	3,3	33,3
Nickel	-"-	Mobile	4,0	8,0	3,6	2,2	10,0
Cobalt	Ammonium-sodium buffer, pH=3.5	Mobile	5,0	8,2	4,0	2,1	8,3
Chromium	Ammonium-acetate buffer, pH=4.8	Mobile	6,0	16,0	5,0	3,5	21,0
Copper	-"-	Mobile	3,0	4,0	2,5	2,0	5,0
Lead	-"-	Bulk	30,0	33,0	22,5	10,3	35,0
Arsenic	-"-	Bulk	2,0	10,0	1,6	0,5	14,0
Vanadium	-"-	Bulk	150,0	6,6	5,0	3,9	7,6
Antimony	-"-	Bulk	4,5	0,50	0,42	0,33	0,52
Silver	-"-	Bulk		0,42	0,30	0,24	0,47
Tin	-"-	Bulk		12,0	8,0	6,5	15,0
Cadmium	-"-	Bulk		1,01	0,83	0,48	1,02

Table C-1

As is evident from Table C-1, the MAC (maximum acceptable concentration) values assigned for soil are attainable with a HMA application dose of about 1.5%. As a result, the content of heavy metals capable of migrating into water medium and plants drastically diminishes. For an optimum HMA dose equal to 1.5%, a land area of 1.8 hectare was subjected to detoxication. Soil samples were taken before and after the detoxication procedure using the HMA. Efficiency of the detoxication procedure is presented in Table C-2.

Element	Mean concentration before detoxication, mg/kg	Mean concentration after detoxication, mg/kg	Reduction Efficiency, percent
Zinc	25	10,1	60%
Manganese	7,7	6,24	19%
Strontium	45,6	5,78	87%
Nickel	9,6	2,7	72%
Cobalt	9,3	3,66	61%
Chromium	23,7	5,38	77%
Copper	4,3	2,46	43%
Lead	34,8	9,32	73%
Arsenic	12	1,76	85%
Vanadium	8,4	6,18	26%
Antimony	0,7	0,268	62%
Tin	12,2	5,28	57%
Cadmium	0,99	0,338	66%

Table C-2, Efficiency of the detoxication procedure

Analysis of the experimental evidence obtained from detoxication treatment of the polluted area enables one to conclude about a good efficiency of the soil detoxication procedure performed:
- Concentrations of mobile forms of cadmium, nickel and arsenic are reduced by up to a factor of 5 or 6;
- Concentrations of mobile forms of chromium and strontium are reduced by a factor of 4 or more;
- Concentrations of mobile forms of lead, tin and cobalt are reduced to about one third of original values;
- Concentrations of mobile forms of zinc and copper are approximately halved while those of vanadium and antimony are reduced by about one third.

In addition, content of manganese, strontium, zinc, copper, lead, cadmium, nickel, chromium, arsenic, silver, vanadium, antimony and tin in all soil samples taken after detoxication procedure are much below the MAC level.

Example 8
There was performed detoxication of samples of copper ore dressing rejects available from "Asarel-Medet" integrated ore-dressing plant (Bulgaria), said samples being taken from the "oxide" dump (samples No10) and from the "eastern" bank (samples No2).

An average copper content of sample No1 was 500 mg/kg with the pH value of 3.7; that of sample No 2 was 700 mg/kg, with a pH value of 3.5.

Acid reaction of the samples was neutralized by adding hydrated lime. An increase in pH value of the samples from 3.5-3,7 to virtually neutral pH values of 7.8-8.5 were achieved with a

lime dose of approximately 0.4% in terms of dry matter of a total dry weight of samples. However, as times went by, the pH of the lime-treated samples dropped drastically. Thus, for instance, the pH value of lime-treated sample No1 was found to have dropped from 8.5 to 6.2 after 21 days and that of sample No 2 from 8.2 to 4.2 during the same period of time.

It is also found that when neutralizing the acid reaction of the samples by adding hydrated lime thereto in an amount of 0.4% (in terms of dry matter) and bringing the pH value of said samples to 7.5-8.5 is followed by adding HMA thereto in an amount of from 0.15 to 12%, much lower reduction in the pH values is observed. Moreover, with the HMA content within 10%, the higher the HMA content of the samples the lower the pH reduction therein. Thus, for instance, with the HMA content of 0.15% in terms of dry matter of a total dry weight of samples #1 the pH value is found to have dropped from 8.5 to 6.2 for 21 days; with the HMA content of 1.5% the pH value decreased from 8.5 to 7.6, and with the HMA content of 3% the pH value decreased from 8.9 to 7.8. However, with the HMA content of 10% and over no further changes in the pH value were observed.

The efficiency of detoxication of the waste products represented by samples No 1 and No 2 was studied upon adding hydrated lime thereto (0.4% of the sample weight), as well as hydrated lime (~0.4%) and the HMA in an amount of from 0.15 to 10%. A toxic effect of the waste products on the growth and development of plants before and after adding hydrated lime and lime along with the HMA thereto was conducted in keeping with ISO Standard 11269-2. It was determined also a change in the species composition of microorganisms following adding lime and the HMA. The results of said studies including plant germination percentage (exemplified by barley), average plant height and biomass are given in Table C-3.

Table C-3

Nos	Test variants	Seed germinating capacity, percent of total amount of seeds sowed	Percent of control	Average height of plant, percent of control	Average dry biomass, percent of control
Original sample No1 (control)	32,6	100	100	100	2
Sample No 1 + 0.4% of lime	68,5	210	186	260	3
Sample No1 + 0.4% of lime + 0.75% of GM	100	306	339	395	4
Sample No 1 + 0.4% of lime + 1.5% of GM	100	306	390	450	5
Sample No1 + 0.4% of lime + 3% of HMA	100	306	410	563	6
Original sample No2	0	0	0	0	7
Sample No2 + 0.4% of lime (control)	21,4	100	100	100	8
Sample No 2 + 0.4% of lime + 0.75% of HMA	75,0	350	171	160	9
Sample No 2 + 0.4% of lime + 1.5% of HMA	85,4	399	163	180	10
Sample No 2 + 0.4% of lime + 3% of HMA	100	467	211	220	

Note. Table C-3 contains data for a HMA application dose of 0.75, 1.5 and 3%. With said dose ranging from 0.15 to 1.5% there is observed a gradual increase in waste detoxication efficiency which reaches maximum values with HMA doses from 0.75 to 10%. The exposure time is 21 days (till the stage of second leaf).

As is can be seen from Table C-3, it is the waste of sample #2 that proves to be most toxic so that seeds fail to germinate thereon. Lime application reduces toxicity but partially. By that reason the seventh test variant involving lime application is adopted for samples #2 as the control.

Active microflora of the samples were studied both before and after lime and HMA application. Preliminarily, a 1 g dose of a soddy-podzolic soil suspension was applied to all samples as a carrier of typical soil microorganisms. A great many sulfur bacteria of Thiobacillus ferooxidans and Leptospirillum ferooxidans genera were detected in the original (untreated) samples. No active forms of said sulfur bacteria are found after treatment thereof.

APPENDIX D

COST INFLATION

TABLE D-1 Cost Inflation Adjusted to the Year 2005

Year	Percent Increase
1996	24
1997	21
1998	19
1999	17
2000	13
2001	10
2002	8
2003	6
2004	3