Predecisional Draft

***In Situ* Treatment of Mixed Contaminants in Groundwater:
Review of Candidate Processes**

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ACRONYMS, ABBREVIATIONS, AND INITIALISMS

AFB	--	Air Force Base
AOP	--	advanced oxidation processes
Bq/L	--	becquerel per liter
cfm	--	cubic feet per minute
cm	--	centimeter
CMC	--	critical micelle concentration
CRADA	--	cooperative research and development agreement
1,2-DCE	--	1,2-dichloroethene
DOC	--	dissolved organic compounds
DOE	--	Department of Energy
DOT	--	Department of Transportation
ECD	--	electron capture detector
EPA	--	Environmental Protection Agency
eV	--	electron volts
ft	--	feet
gal	--	gallons
h	--	hours
ISR IP	--	<i>In Situ</i> Remediation Integrated Program
ITEP	--	International Technology Exchange Program
KCP	--	Kansas City Plant
kW	--	kilowatt
L	--	liters
m	--	meter
M	--	molar
MMES	--	Martin Marietta Energy Systems
$\mu\text{g/L}$	--	microgram per liter
μm	--	micrometer or micron
μM	--	micromolar
mg/g	--	milligram per gram
mg/kg	--	milligram per kilogram
mg/L	--	milligram per liter
min	--	minutes
mL/g	--	milliliter per gram
mV	--	millivolts
ng/L	--	nanogram per liter
nm	--	nanometers
NREL	--	National Renewable Energy Laboratory
O&M	--	operation and maintenance
ORNL	--	Oak Ridge National Laboratory
OTD	--	Office of Technology Development
PGDP	--	Paducah Gaseous Diffusion Plant
PIXE	--	particle-induced x-ray emission
ppb	--	part per billion
ppm	--	part per million

psi	--	pounds per square inch
RFP	--	Rocky Flats Plant
SRL	--	Savannah River Laboratory
SRS	--	Savannah River Site
1,1,1-TCA	--	1,1,1-trichloroethane
TCE	--	trichloroethylene
TVA	--	Tennessee Valley Authority
UV	--	ultraviolet light
UVB	--	Unterdruck Verdampfer Brunnen
V	--	volts
VOCs	--	volatile organic compounds

PREFACE

In October 1993, a research and development project was initiated to study *in situ* treatment of groundwater using recirculation-well networks coupled with *in situ* treatment modules. This project, entitled "*In Situ* Treatment of Mixed Contaminants in Groundwater," is funded by the *In Situ* Remediation Integrated Program (ISR IP) within the U.S. Department of Energy's (DOE) Office of Technology Development (OTD). Conceived as a three-year effort, the project involves several key research elements, including treatment-process evaluation and screening, hydrodynamic flow and transport modeling, bench- and pilot-scale experimentation, and full-scale field demonstration at a DOE site.

This document describes the methods and results of the initial evaluation and screening phase of the project. In this work, candidate treatment processes were identified that appeared to have potential for adaptation and incorporation into an *in situ* groundwater treatment system wherein treatment modules are coupled with recirculation wells. To guide the evaluation and screening effort, major groundwater plumes at the DOE Portsmouth, Ohio, and Paducah, Kentucky, sites were chosen as primary candidates for an eventual field demonstration. The key groundwater contaminants, trichloroethylene (TCE) and technetium-99, are the primary targets used in evaluating the treatment potential of various candidate processes.

This evaluation and screening effort led to selection of a set of promising treatment processes for initial study. These processes were selected from those that were commercially available or emerging, appeared compatible with an *in situ* treatment module system, and offered a high probability of successful performance in that application. However, it is envisioned that as the project evolves, there will be opportunities for testing additional processes, including some that appeared promising but were not sufficiently developed to include in any project planning at this time. In addition, it is recognized that physical settings and contamination scenarios different from those at the Portsmouth and Paducah sites are important to DOE (e.g., Hanford), and it is intended that the results of this project will have at least some application to those conditions as well.

The work described herein could not have been accomplished without the sponsorship of DOE's ISR IP or the valuable contributions of many individuals. DOE and these project contributors are gratefully acknowledged for their support and participation.

1. INTRODUCTION

This document describes the screening and preliminary evaluation of candidate treatment processes for use in treating mixed contaminants [volatile organic compounds (VOCs) and radionuclides] in groundwater. The project, initiated in October 1993, is funded by the Department of Energy's (DOE) Office of Technology Development (OTD) and is an extension of prior work with the DOE International Technology Exchange Program (ITEP). Prior work identified vertical recirculation technologies as potentially applicable to groundwater contamination problems at DOE sites (Siegrist et al. 1993).

In recirculation systems, extraction and injection wells recirculate groundwater and soil air through the well structure, where treatment occurs. Historical use of this general process has typically been limited to air stripping within vertical wells (Herrling et al. 1991; Philip and Walter 1992). The use of vertical recirculation wells limits the technology to locations where the saturated zone is both permeable and relatively thick (20 to 30 ft or more). In contrast, this project will extend the use of recirculation technology to both less permeable and thinner formations (< 10 ft) by using horizontal recirculation wells, an emerging technology. In addition, this project will employ coupled treatment processes (Fig. 1.1) that will remove radionuclides and remove or destroy VOCs. Treatment of mixed contaminants is a significant issue for DOE because the coexistence of chlorinated hydrocarbons and radionuclides has been identified as the predominant groundwater contamination problem in the DOE complex (Riley et al. 1992).

Treating mixed contaminants presents unusual difficulties. Typically, VOCs are the most abundant contaminants, but the presence of radionuclides results in additional health concerns that must be addressed, usually by a treatment approach different from that used for VOCs. Furthermore, the presence of radionuclides may yield mixed solid wastes if the VOCs are treated by conventional means (e.g., pump-and-treat with aboveground carbon adsorption). These issues were specifically addressed in the evaluation of candidate treatment processes for testing in this program. Moreover, because no research or early development of a particular process would be performed, the technology review also focused on technologies that could be readily adapted and integrated for use with mixed contaminants. The objective is to couple emerging or available processes into treatment modules for use *in situ*.

The three year project, to be completed in September 1996, includes a full-scale field demonstration. The entire project structure is shown in Fig. 1.2. The findings reported in this document encompass all activities through the treatment process evaluations. An overview of the project has been provided previously in a project description document (Siegrist et al. 1994).

Fig. 1.1 Process train for groundwater treatment by *in situ* modules coupled with vertical and/or horizontal recirculation wells.

PRM020

Fig. 1.2. Project structure.

PRM019

2. METHODS

The initial activity in this project was to identify candidate technologies for the *in situ* treatment of groundwater. Table 2.1 summarizes the project objectives that encompass achievement of a safe, effective, and efficient process. The order of objectives does not imply importance. Efficient removal and destruction processes are desirable in order to limit the treatment time (objectives 1 and 2). Successful completion of the project includes general-public and site-worker protection (objective 3). Objective 4 reflects project cost and resource effectiveness. Processes that destroy and/or concentrate contaminants may achieve desired minimization of secondary waste streams (objectives 5 through 7). Most processes target single contaminants or classes of compounds. This project seeks to develop processes that are able to work effectively in the presence of multiple contaminants (objective 8). Generation of mixed waste is undesirable (objective 9). Obviously, an effective design for general DOE use is desirable (objective 10).

This identification of treatment technologies was accomplished through a group meeting that included technology experts, additional follow-on, small-group meetings, and literature searches. Once technologies were selected, individual experts were requested to provide evaluations (see Appendix B). Although the responsible personnel are all affiliated with Martin Marietta Energy Systems (MMES), the evaluations included consultations with numerous other experts to ensure that the review contained the latest available information. In addition, representatives from DOE's Paducah, Kentucky, and Portsmouth, Ohio, sites were consulted to ensure applicability of the processes to actual site problems. Paducah and Portsmouth are the primary candidate sites for performing the field demonstration. Both sites have several groundwater plumes containing mixed contaminants and have an urgent need for alternatives to conventional pump-and-treat and the handling of mixed waste that would be generated. Management from both sites have indicated a strong interest in hosting a demonstration with the intention of full-scale implementation, following promising laboratory and bench-scale results.

The technology reviewers were provided with a format (Table 2.2, Appendix A) and with ranges of contaminant concentrations and treatment-unit flow rates (Tables 2.3 and 2.4) representative of the potential field sites. The dimensions and conditions presented in Table 2.4 take into account the technical and economic viability of implementation. Larger treatment modules were considered too expensive for consideration. Finally, based on the selection of the Paducah and Portsmouth facilities as probable field-test sites, chlorinated hydrocarbons and ^{99}Tc are the target contaminants.

Table 2.5 lists the processes that were evaluated and the scientists and engineers who were responsible. As noted previously, these processes were identified by attendees at an initial scoping meeting. The candidate processes were selected based on known treatment rates and efficiencies of various processes and compatibility of these processes with *in situ* treatment of the target analytes. The planned approach is to package the technologies as modular components for use with horizontal or vertical recirculation wells. The modules will be located *in situ* and may be used independently or in combination to treat the mixed contaminants.

Table 2.1. Objectives for the project

Desired features of an <i>in situ</i> treatment module train

---

1. Remove/destroy VOC (e.g., TCE) by 90% in one pass.   2. Reduce radionuclide (e.g., ⁹⁹Tc) concentration by 90% in one pass.   3. Minimize occupational exposure of site workers and potential exposure of general public.   4. Demonstrate that the reliability/operability/maintainability of the processing system is high.   5. Minimize secondary waste streams.   6. Destroy VOC in preference to removal.   7. Concentrate radionuclides.   8. Processes must retain operability in the presence of multiple classes of mixed waste.   9. No mixed waste produced.   10. Demonstrate a process that has general application to DOE sites.

Table 2.2. Elements included in the technology reviews

-
1. Process name and type
  2. Process description
  3. Mechanisms of VOC treatment
  4. Mechanisms of radionuclide treatment
  5. Treatment efficiencies expected and reliability
  6. Limiting conditions and interferences
  7. Stage of development
  8. Processing capacities and rate
  9. Chemicals or treatment agents required
  10. Secondary waste streams produced
  11. Utility requirements
  12. Monitoring requirements
  13. Operation and maintenance requirements
  14. Potential environmental impact risks
  15. Potential safety risks
  16. Process capital and operating costs
  17. Case histories
  18. Potential vendors/providers
  19. References and contacts

Conclusion

Note: Appendix A presents the detailed format and technical constraints considered in preparing the reviews.

Table 2.3. Representative concentrations of groundwater species and contaminants

Constituent	Units	Range	Typical
Chloride	mg/L	20 to 30	25
Sulfate	mg/L	10 to 30	15
Nitrate	mg/L	2 to 10	5
Phosphate	mg/L		< 2
Fluoride	mg/L	< 0 to 0.2	0.1
Calcium	mg/L	20 to 40	30
Sodium	mg/L	15 to 25	20
Magnesium	mg/L	5 to 15	10
Total iron	mg/L	0 to 2	0.02
Total nickel	mg/L	0 to 0.2	0.1
Total zinc	mg/L	0 to 0.1	0.05
pH	not reported	6 to 7	6.5
Oxygen	mg/L	0 to 0.2	0.1
TCE ^a	mg/L	0 - neat liquid	300
⁹⁹ Tc ^a	ng/L	not reported	≈25
Uranium ^a	μg/L	not reported	≈50

^a Key contaminant.

Source: Adapted from Cul, G. D. D., W. D. Bostick, D. R. Trotter, and P. E. Osborne. 1993. *Separation Science and Technology*, 28:551. Davenport, D., and T. Houk. 1993. *Project Identification and Screening*. POEF-ER-4564, p. 5, Environmental Restoration and Waste Management Program, U.S. Department of Energy.

Table 2.4. Ranges of dimensions and yields for recirculation wells and *in situ* modules

Depth ^a , m	Yield ^b , m ³ /min	Treatment module diameter ^c , m	Treatment module cross-sectional area ^d , m ²
10	0.02 (5 gal/min)	0.5	0.2
10	0.02 (5 gal/min)	2.0	3.1
10	0.10 (25 gal/min)	0.5	0.2
10	0.10 (25 gal/min)	2.0	3.1
75	0.02 (5 gal/min)	0.1	0.008
75	0.02 (5 gal/min)	0.3	0.07
75	0.10 (25 gal/min)	0.1	0.008
75	0.10 (25 gal/min)	0.3	0.07

^a Depth is based on the Portsmouth (10 m) and Hanford (75 m) sites.

^b Indicates the amount of groundwater withdrawn from the aquifer by a set of horizontal recirculation wells. Estimates reflect conditions in a low to moderately conductive aquifer (e.g., approximately 25 ft/d) and are based on experience at the Portsmouth site.

^c Indicates the available internal diameter of the treatment module. Values selected are based on readily achievable diameters with conventional drilling equipment.

^d Indicates the available cross-sectional area of the module. Values selected are based on readily achievable diameters with conventional drilling equipment.

Table 2.5. Candidate processes for VOC and radionuclide removal or destruction

Candidate processes	Primary reviewer^a	Target
Stripping, with aboveground treatment of the gas stream	M. Ally, Chemical Technology Division	VOCs
Advanced oxidation processes, UV/peroxide	N. Korte, Environmental Sciences Division	VOCs
Photocatalytic destruction (TiO ₂), liquid-phase destruction	N. Korte, Environmental Sciences Division	VOCs
Reductive dechlorination using zero-valence metal	N. Korte, Environmental Sciences Division	VOCs
Radionuclide precipitation	D. Marsh, Environmental Sciences Division	Radionuclides
Reduction and sorption using zero-valence metal	W. Bostick, K-25 Technical Division	Radionuclides
Selective ion exchange	W. Bostick, K-25 Technical Division	Radionuclides
Selective sorption (ion exchange and adsorption)	P. Taylor, Chemical Technology Division	Radionuclides
Organic sorbent mixtures	L. Liang, Environmental Sciences Division	VOCs, radionuclides
Biodegradation <i>in situ</i> with injection of treatment agents	A. Palumbo, Environmental Sciences Division	VOCs
Surfactant-enhanced bioremediation	J. M. Strong-Gunderson, Environmental Sciences Division	VOCs, radionuclides (?)
Reduction/sorption by Al and Fe ₂ O ₃	A. Mattus, Chemical Technology Division	Radionuclides
Photocatalytic membrane	B. Bischoff, J. Stockdale, K-25 Technical Division	VOCs, radionuclides

^a Addresses and phone numbers are provided in Appendix B.

3. RESULTS

The individual technology reviews are assembled in Appendix B and the results are summarized in Tables 3.1 through 3.10.

3.1 TREATMENT PROCESSES FOR VOCs

Tables 3.1 through 3.4 summarize the information obtained on eight candidate processes for treating VOCs.

3.1.1 Features of VOC Treatment Processes

Table 3.1 presents the mechanisms and potential interferences of candidate processes for VOC treatment. The photocatalytic membrane process, biological degradation process, and reductive dechlorination using zero-valence metals process all destroy VOCs, while the other methods represent a transfer of VOCs from the groundwater to another medium.

Table 3.1 presents a comparison of design factors. Air stripping stands out as a rapid process. Indeed, the slow or uncertain kinetics of reductive dechlorination with zero-valence metals may preclude use of that technique in this application. Both the ultraviolet light (UV)/peroxide and biological degradation methods require the addition of treatment agents downhole, complicating their use.

Table 3.2 outlines the stage of development of each process. Again, air stripping is clearly the most mature technology, while most of the others are at the demonstration or bench stage.

Table 3.3 describes operating features of the processes. None of the technologies present particular problems with secondary waste streams. Utility and monitoring requirements are also relatively modest. Capital and operating costs are extremely variable, however. The use of zero-valence metals for reductive dechlorination or the use of organic sorbents appear attractive based on low cost.

Finally, Table 3.4 demonstrates that none of the candidate processes present any significant issues with respect to environmental impact or safety risks.

3.1.2 VOC Treatment Process Screening

The VOC candidate processes are screened in Table 3.5. The screening resulted in the selection of air stripping as the process for use in the initial treatment program. The UV/peroxide process was eliminated because a downhole unit was judged too cumbersome and because of the expense of the process. Photocatalytic decomposition with TiO_2 was eliminated because success of the process was judged as uncertain at the present time. Reductive

dechlorination with zero-valence metals and organic sorbent mixtures are retained for further evaluation. Further developments with the photocatalytic membrane will also be evaluated. The latter technology and the zero-valence metal and organic sorbent processes are attractive because all offer the possibility of simultaneous treatment and removal of VOCs and radionuclides. Finally, the surfactant-enhanced mobilization processes are retained because it may be possible to inject these agents in latter stages of the field demonstration if time and funding are available.

3.2 TREATMENT PROCESSES FOR RADIONUCLIDES

Tables 3.6 through 3.9 summarize the information obtained on seven candidate processes for removing radionuclides.

3.2.1 Features of Treatment Processes for Radionuclides

Table 3.6 presents the mechanisms, treatment agents and conditions required, reaction rates, and potential interferences of the candidate processes for removing radionuclides. Sorption processes are applicable over a wide range of conditions and are not subject to the interferences that are significant in natural groundwaters. Processes that require the injection of other chemicals for pH control are considered less desirable because of the greater difficulty in engineering, monitoring, and controlling a downhole system. The photocatalytic membrane, reduction and sorption using zero-valence metals, and the use of organic sorbent mixtures are all of greater interest because they hold the promise of treating both VOCs and radionuclides.

Reaction rates for all of the candidate processes are favorable; however, the precipitation and reduction/sorption with $\text{Al/Fe}_2\text{O}_3$ processes are hampered by the need to inject treatment agents. In contrast, the ion exchange/sorption processes are all simple to design, and some are commercially available.

Table 3.7 outlines the stage of development of each process. Selective ion exchange stands out as the most mature process, with all of the other processes at the bench or demonstration phase.

Table 3.8 describes operating features of the processes. There is little difference with respect to secondary waste streams because there is spent resin or some type of contaminated substrate in each case. Utility and monitoring requirements are also straightforward. Costs are generally moderate, but again the selective ion exchange appears most favorable.

Finally, Table 3.9 demonstrates that none of the candidate processes present any significant issues with respect to environmental impact or safety risks.

Table 3.1. VOC candidate process treatment features

Process	Primary mechanism	Required conditions	Required treatment agents	Approximate reaction rate ^a	Potential interferences
Stripping, with aboveground treatment of the gas stream	Phase distribution	Large distribution coefficient. Volatilization requires energy	None	Fast	None
UV/peroxide destruction	Hydroxyl free radicals, direct photodecomposition	Peroxide or acid addition downhole	Hydrogen peroxide addition, pH adjustment if necessary	Medium	Carbonates
Photocatalytic destruction (TiO ₂), liquid phase	Hydroxyl free radicals	Acid addition downhole	Hydrogen peroxide; acid if necessary	Medium	Nitrate and carbonate
Dechlorination using zero-valence metals	Reductive dechlorination	Contact times are long	Iron filings	Slow	Unknown
Photocatalytic membrane	Hydroxy-free radicals, direct photodecomposition	Fiber optic cable downhole	None	Medium	Colloids and membrane fouling
Organic sorbent mixtures	Selective adsorption	None	None	Medium	None
Biodegradation <i>in situ</i> with injection of treatment agents	Biological degradation	TCE concentration > 10 mg/kg is limiting for aerobic degradation	Nutrient additions	Slow	Cu concentration > 4 μ M is limiting
Surfactant-enhanced bioremediation	Biological degradation, enhanced contaminant mobility	Applicable in a wide range of conditions	Nutrient additions	Slow	Potential clogging of aquifer pores

^a Ratings are based on the following scale: fast = seconds, medium = minutes, slow = hours or days. These ratings are based on the mix of contaminants often found at DOE sites. Certain specific compounds may react faster or slower than the specified rate.

Note: See Appendix B for detailed descriptions.

Table 3.2. VOC candidate process development history and commercial availability

Process	Stage of development	Case histories available	Potential vendors
Stripping, with aboveground treatment of the gas stream	Commercial	Common process	Many vendors available
UV/peroxide destruction	Commercial	None for downhole use but many for aboveground use	Peroxidation Systems Inc., Tucson, Ariz. Purus, Inc., Newport Beach, Calif. Solarchem Environmental Systems, Las Vegas, Nev. and Toronto, Canada
Photocatalytic destruction (TiO ₂), liquid phase	Commercial	None for downhole use but a few for aboveground use	Matrix photocatalytic, Toronto, Ontario
Reductive dechlorination using zero-valence metals	Demonstration	Successful bench and pilot studies	Envirometal Technologies, Inc., Guelph, Ontario
Photocatalytic membrane	Bench	None	None
Organic sorbent mixtures	Bench	Successful bench and pilot studies	None
Biodegradation <i>in situ</i> with injection of treatment agents	Demonstration	Savannah River Site	Envirogen, Ecova, others
Surfactant-enhanced bioremediation	Bench	None	None

Note: See Appendix B for detailed descriptions.

Table 3.3. VOC candidate process operating features

Process	Secondary waste streams	Utility requirements	Monitoring requirements	Capital and operating costs, \$K
Stripping, with aboveground treatment	Depends on the vapor treatment system	Nominal	Routine ^a	150 capital, 65/year O&M
UV/peroxide destruction	None	Substantial	pH, off-gas	75 capital, O&M unknown
Photocatalytic destruction (TiO ₂), liquid phase	Wet scrubber will need periodic replacement	Nominal (3 kW)	off-gas	Unknown, expected to be low
Reductive dechlorination using zero-valence metals	Spent Fe	Nominal	Routine	Unknown, expected to be low
Photocatalytic membrane	Spent membrane	Nominal (several kW)	Routine	Unknown, expected to be moderate
Organic sorbent mixtures	Spent sorbent	Nominal	Routine	Unknown, expected to be low
Biodegradation <i>in situ</i> with injection of treatment agents	None	Nominal	Routine	Low
Surfactant-enhanced bioremediation	None	Nominal	Routine	Low

^a Routine is influent/effluent monitoring at the treatment unit in conjunction with combined monitoring of groundwater wells.

Note: See Appendix B for detailed descriptions.

Table 3.4. VOC candidate process environment and safety features

Process	Environmental impact	Safety risks
Stripping, with aboveground treatment of the gas stream	None	Limited
UV/peroxide destruction	None	Limited: high voltage, pH adjustment, UV
Photocatalytic destruction (TiO ₂), liquid phase	None	Limited: high voltage
Reductive dechlorination using zero-valence metals	None	Limited
Photocatalytic membrane	None	Limited: high voltage, UV
Organic sorbent mixtures	None	Limited
Biodegradation <i>in situ</i> with injection of treatment agents	Alteration of site geochemistry	Limited: methane production
Surfactant-enhanced bioremediation	None	Limited

Note: See Appendix B for detailed descriptions.

Table 3.5. Rating of VOC candidate processes

Process	Maturity	Implementability	Simultaneous radionuclide treatment	Cost	Cumulative score
Stripping, with aboveground treatment of the gas stream	5	4	0	5	14
UV/peroxide destruction	5	2	0	2	9
Photocatalytic destruction (TiO ₂), liquid phase	3	3	0	3	9
Reductive dechlorination using zero-valence metals	2	4	2 ^a	5	13
Photocatalytic membrane	2	3	4	3	12
Organic sorbent mixtures	3	4	2 ^a	4	13
Biodegradation <i>in situ</i> with injection of treatment agents	3	3	0	4	10
Surfactant-enhanced bioremediation	2	2	0	3	7

^a Rating is reduced because mixed waste is produced.

Note: Ratings are based on the following scale: 0 = very poor, 1 = poor, 2 = fair, 3 = good, 4 = very good, 5 = excellent.

This screening of candidate processes considered only their potential application as *in situ* treatment modules for mixed contaminants. No general conclusions should be drawn regarding overall process performance or viability.

See Appendix B for detailed descriptions.

Table 3.6. Radionuclide candidate process treatment features

Process	Primary mechanism	Required conditions, treatment agents	Approximate reaction rate^a	Potential interferences
Precipitation	Solubility control	Reducing conditions are required, acid or base adjustments	Medium	Organic matter, carbonate, phosphate, reduced iron
Reduction and sorption using zero-valence metal	Reduction, sorption	Applicable in a wide range of conditions; Fe filings required	Fast	No environmental interferences expected, fresh-water environment
Selective ion exchange	Sorption to anion exchange resin	Applicable in a wide range of conditions	Fast	No environmental interferences expected
Selective sorption (ion exchange and adsorption)	Selective adsorption with a cage-type molecule	Applicable in a wide range of conditions	Fast	No environmental interferences expected
Reduction/sorption by Al and Fe ₂ O ₃	Reduction, sorption	Most efficient at high pH (> 11.5); addition of base	Fast	No environmental interferences expected
Photocatalytic membrane	Reduction, precipitation on a photocatalytic membrane	Applicable in a wide range of conditions	Fast	No environmental interferences expected
Organic sorbent mixtures	Reduction, sorption	Applicable in a wide range of conditions	Medium	No environmental interferences expected

^a Ratings are based on the following scale: fast = seconds, medium = minutes, slow = hours or days. These ratings are based on the mix of contaminants often found at DOE sites. Certain specific compounds may react faster or slower than the specified rate.

Note: See Appendix B for detailed descriptions.

**Table 3.7. Radionuclide candidate process development history
and commercial availability**

Process	Stage of development	Case histories available	Potential vendors
Precipitation	Demonstration	None	None
Reduction and sorption using zero-valence metal	Bench	None	Envirometal Technologies, Inc., Guelph, Ontario
Selective ion exchange	Commercial	Paducah, Portsmouth Gaseous Diffusion Plants	Dow Chemical, Midland, Mich. Reilly Industries
Selective sorption (ion exchange and sorption)	Demonstration	None	IBC Advanced Technologies
Reduction/sorption by Al and Fe ₂ O ₃	Bench	None	None
Photocatalytic membrane	Bench	None	None
Organic sorbent mixtures	Bench	None	None

Note: See Appendix B for detailed descriptions.

Table 3.8. Radionuclide candidate process operating features

Process	Secondary waste streams	Utility requirements	Monitoring requirements	Capital and operating costs, \$K
Precipitation	Sludge	Nominal	pH	Moderate
Reduction and sorption using zero-valence metal	Spent Fe	Nominal	Routine ^a	Unknown, expected to be low
Selective ion exchange	Spent resin	Nominal	Routine	Moderate to low
Selective sorption (ion exchange and adsorption)	Spent sorbent	Nominal	Routine	Moderate to low
Reduction/sorption by Al and Fe ₂ O ₃	Spent sorbent	Nominal	pH	Unknown, expected to be moderate
Photocatalytic membrane	Spent membrane and treatment unit	Nominal (several kW)	Routine	Unknown, expected to be moderate
Organic sorbent mixtures	Spent sorbent	Nominal	Routine	Unknown, expected to be low

^a Routine is influent/effluent monitoring at the treatment unit in conjunction with combined monitoring of groundwater wells.

Note: See Appendix B for detailed descriptions.

Table 3.9. Radionuclide candidate process environment and safety features

Process	Environmental impact	Safety risks
Precipitation	None	Limited: pH adjustment
Reduction and sorption using zero-valence metal	None	Limited
Selective ion exchange	None	Limited
Selective sorption (ion exchange and adsorption)	None	Limited
Reduction/sorption by Al and Fe ₂ O ₃	None	Limited
Photocatalytic membrane	None	Limited: high voltage, UV
Organic sorbent mixtures	None	Limited

Note: See Appendix B for detailed descriptions.

3.2.2 Radionuclide Treatment Process Screening

The radionuclide candidate processes are screened in Table 3.10. The screening resulted in the selection of selective ion exchange as the appropriate process to use for the initial treatment program. The reduction/sorption by Al and Fe_2O_3 and precipitation processes were eliminated because of the need to inject, monitor, and control treatment agents downhole. Sorption with zero-valence metals and sorption with organic sorbents are retained for further evaluation. Further developments with the photocatalytic membrane will also be evaluated. The latter technology and the zero-valence metal and organic sorbent processes are attractive because all offer the possibility of simultaneous treatment and removal of VOCs and radionuclides.

Table 3.10. Rating of radionuclide candidate processes

Process	Maturity	Implementability	Simultaneous VOC treatment	Cost	Cumulative rating
Precipitation	4	2	0	2	8
Reduction and sorption using zero-valence metals	3	4	2 ^a	5	14
Selective ion exchange	5	5	1	4	15
Selective sorption (ion exchange and adsorption)	3	4	1	3	11
Reduction/sorption by Al and Fe ₂ O ₃	3	3	0	2	8
Photocatalytic membrane	3	3	4	2	12
Organic sorbent mixtures	3	4	2 ^a	3	12

^a Rating is reduced because mixed waste is produced.

Note: Ratings are based on the following scale: 0 = very poor, 1 = poor, 2 = fair, 3 = good, 4 = very good, 5 = excellent.

This screening of candidate processes considered only their potential application as *in situ* treatment modules for mixed contaminants. No general conclusions should be drawn regarding overall process performance or viability.

See Appendix B for detailed descriptions.

4. SUMMARY AND CONCLUSION

A research and development project was initiated in October 1993 to study *in situ* treatment of groundwater using recirculation well networks coupled with *in situ* treatment modules. This project, entitled "*In Situ* Treatment of Mixed Contaminants in Groundwater," was initiated with funding provided by the ISR IP within the DOE OTD. This three-year effort involves several key research elements, including treatment-process evaluation and screening, hydrodynamic flow and transport modeling, bench- and pilot-scale experimentation, and field-scale demonstration and testing at a contaminated DOE site.

This document describes the methods and results of the initial evaluation and screening phase of the project. In this work, candidate treatment processes were identified that appeared to have potential for adaptation and incorporation into coupled treatment modules for use *in situ* as part of a groundwater recirculation treatment system. Groundwater plumes at the DOE Portsmouth, Ohio, and Paducah, Kentucky, sites were chosen as primary candidates for an eventual field demonstration due to their need for an *in situ* technology and a keen interest to co-sponsor research and field testing. The key contaminants in these groundwater plumes, TCE and ^{99}Tc , were the primary targets used in evaluating the treatment potential of various candidate processes.

This evaluation and screening effort necessarily led to selection of a set of treatment processes for initial study: gas stripping of TCE coupled with selective ion exchange of ^{99}Tc . These processes were judged to have reaction kinetics and treatment efficiencies compatible with the performance objectives of an *in situ* treatment module system. Moreover, they were judged to be sufficiently well developed that limited research and development in this project could rapidly lead to field-scale demonstration and testing at a DOE contaminated site.

It is envisioned that as the project evolves, experimental protocols are developed, and a field test site is established, there will be opportunities to test additional processes, including some that appeared promising but were not sufficiently developed to include in any firm project planning at this time. These processes included photocatalytic membranes, zero-valence metals, and organic sorbent mixtures. In addition, it is recognized that physical settings and contamination scenarios different from those at the Portsmouth and Paducah sites are important to DOE (e.g., Hanford), and it is intended that, as far as possible, the results of this project will have application to those situations as well.

Based on the results of this scoping phase, experiments have been designed and implemented at ORNL at the bench and pilot scale to verify treatment process performance characteristics under the operating conditions anticipated within an *in situ* recirculation system. Other elements of the project are also proceeding, including hydrodynamic modeling and field-scale testing of horizontal well recirculation networks at a clean test area at the DOE Portsmouth site.

5. REFERENCES

- Herrling, B., J. Stamm, and W. Buermann. 1991. Hydraulic circulation system for *in situ* bioreclamation and/or *in situ* remediation of strippable contamination. Published in *In Situ and On-Site Bioreclamation*, R. E. Hinchee and R. F. Olfenbuttel, eds., 173. International Symposium, March 19 - 21, 1991, San Diego, California.
- Philip, R. D., and G. R. Walter. 1992. Prediction of flow and hydraulic head fields for vertical circulation wells. *Ground Water*, 30(5):765.
- Riley, R. G., J. M. Zachara, and F. J. Wobber. 1992. *Chemical Contaminants on DOE Lands and Selection of Containment Mixtures for Subsurface Science Research*. DOE/ER-0547T. U. S. Department of Energy.
- Siegrist, R. L., O. F. Webb, M. O. Ally, P. M. Kearl, J. Zutman, and W. Sanford. 1993. *In Situ Treatment of VOCs by Recirculation Technologies*. ORNL/TM-12317. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Siegrist, R. L., P. M. Kearl, N. E. Korte, and O. F. Webb. 1994. *In Situ Treatment of Mixed Contaminants in Groundwater: Project Description* (draft). Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Note: Additional references and contacts for each of the treatment processes reviewed may be found in Appendix B.

6. APPENDICES

APPENDIX A
FORMAT FOR TREATMENT-TECHNOLOGY REVIEWS

EXHIBIT 1
FORMAT FOR TREATMENT-TECHNOLOGY REVIEWS

1. **Process Name and Type:** What type of process described is it, e.g., adsorption, precipitation, biodegradation.

2. **Process Description:** Describe in detail the process and its potential for packaging in a downhole treatment module as part of an *in situ* recirculation system. Please enter your estimates of required treatment contact times to effect 90% removal or destruction of your target compound in the fifth column of A.1. Also, enter the corresponding required module heights in column 6. Required module heights can be calculated by multiplying volumetric flow rate by contact time and dividing by cross-sectional area. Please base your estimates on the conditions listed in Tables 2.4 and 2.5. Operational requirements (electricity, etc.) may greatly depend upon module dimensions. For example, a long module will have a large head pressure associated with it and may require a significant power load. Compounded by the depth of the aquifer, these factors may greatly reduce the attractiveness of a treatment process.

3. **Mechanism(s) of VOC Treatment:** What is the mechanism(s), if any, for treatment of VOCs like TCE?

4. **Mechanism(s) of Radionuclide Treatment:** What is the mechanism(s), if any, for treatment of radionuclides like ^{99}Tc ?

5. **Treatment Efficiencies Expected and Reliability:** What are the expected treatment efficiencies, and how robust is the process? Should the groundwater be modified to improve operation of your process? For example, stripping VOCs using nitrogen decreases groundwater Eh. Would this process improve the operation of a reductive destruction process for TCE using base iron metal? How reliable is the process?

6. **Limiting Conditions and Interferences:** Will your process add agents to the groundwater or affect groundwater chemistry or biology in an adverse manner? Will your process adversely affect the well-aquifer interface (e.g., process produces precipitates which plug the interface). Porbaix plots are available if you would like to consider the effects of pH, Eh, and specific ions on precipitation processes.

7. **Stage of Development:** Please describe the present level of development of the technology: at-bench, pilot, demonstration, or commercial. Please explain.

8. **Processing Capacities and Rates:** What is the capacity and rate of reaction for the process?

9. Chemicals or Other Treatment Agents Required: What chemicals or treatment agents might be released to the aquifer as a result of the treatment process?

10. Secondary Waste Streams Produced: Are there any secondary wastes produced, e.g., spent sorbent cartridges, etc.?

11. Utility Requirements: What utilities are required, e.g., electricity, compressed gases, etc.?

12. Monitoring Requirements: Does your process require on-line or frequent monitoring? Does your process require any special equipment for monitoring? Assume that periodic samples are taken from the well for measurement of influent and effluent contaminant concentrations.

13. Operation and Maintenance Requirements: Overall, how much technician time would be required for monitoring and operating your module? Assume that the well is operated 24 h/d and that the well is attended by three 8-h shifts of technicians each day, e.g., changing adsorbent every 24 h, etc.

14. Potential Environmental Impact Risks: Are there any potential environmental risks associated with the process, e.g., fugitive air emissions, release of hazardous agents into the groundwater, etc.?

15. Potential Safety Risks: Are there any safety hazards such as risk of explosion?

16. Process Capital And Operating Costs: What are the order-of-magnitude costs for the process of both capital equipment and operation (dollars/L of groundwater treated)?

17. Case Histories: Are there any case histories providing relevant information regarding the process for application to *in situ* groundwater treatment?

18. Potential Vendors/Providers: Are there any commercial vendors for the process?

19. References and Contacts: Please list any key references or contacts.

Prepared By:

Date:

Table A.1. Estimated treatment residence times and module dimensions

Depth, m	Yield, m³/min	Diameter, m	Cross- sectional area, m²	Estimate of required residence time, min	Estimate of required module height, m
10	0.02 (5 gal/min)	0.5	0.2		
10	0.02 (5 gal/min)	2.0	3.1		
10	0.10 (25 gal/min)	0.5	0.2		
10	0.10 (25 gal/min)	2.0	3.1		
75	0.02 (5 gal/min)	0.1	0.008		
75	0.02 (5 gal/min)	0.3	0.07		
75	0.10 (25 gal/min)	0.1	0.008		
75	0.10 (25 gal/min)	0.3	0.07		

Note: Please enter your estimates of treatment contact times and module heights based on the conditions listed here and in Tables 2.3 and 2.4. Depth indicates the average depth of the aquifer. Yield indicates the amount of groundwater withdrawn from the aquifer by a set of horizontal wells (Fig. 1.1). Diameter and cross-sectional area indicate the available internal dimension of the treatment module.

APPENDIX B EVALUATIONS OF CANDIDATE PROCESSES

This appendix contains the technology reviews prepared for this project and used in the selection process outlined in the main text. Each reviewer was requested to follow the format in Exhibit 1 (Appendix A) and to consider the technical constraints presented in Table A.1 (Appendix A).

APPENDIX B CONTENTS EVALUATIONS OF CANDIDATE PROCESSES

Stripping, with Aboveground Gas-Phase Treatment, Moonis Ally

Advanced Oxidation Processes, UV/Peroxide, Nic Korte

Photocatalytic Oxidation with Titanium Dioxide, Nic Korte

Reductive Dechlorination and Precipitation Using Zero-Valence Metals (Fe), Nic Korte

Radionuclide Precipitation, Dan Marsh

Zero-Valence Metal Reduction, Sorption, W. D. Bostick

Ion Exchange, W. D. Bostick

Selective Sorption, Paul Taylor

Organic Sorbent Mixtures, Liyuan Liang

Biodegradation of VOCs, A. V. Palumbo

Surfactant-Enhanced Bioremediation, J. M Strong-Gunderson

Reduction/Sorption of Technetium-99 and Uranium VI by Aluminum and Magnetite, A. J. Mattus

Photocatalytic Membrane, J. A. Stockdale and B. L. Bischoff

Stripping, With Aboveground Gas-Phase Treatment

Moonis Ally
Oak Ridge National Laboratory
Chemical Technology Division
615-576-8003

1. Process Name and Type: Stripping of volatile organic compounds (VOCs) from contaminated water, with aboveground gas-phase treatment.

2. Process Description: The removal of dissolved gases and VOCs from water by air stripping is a proven and reliable method, widely practiced by industry and in municipal water treatment plants. The EPA has identified air stripping as one of the best available technologies for the removal of VOCs from water. The time and extent of VOC removal by air stripping depends on the contacting pattern, interfacial mass-transfer area, and solute partitioning between aqueous and vapor phases.

The design of the sparger and the pressure drop in the air-supply pipe require specific attention, especially if the pipe is very long, as in some scenarios described in Table A.1. Long pipes can develop large pressure drops, which must be overcome either externally or by increasing the diameter of the air-supply pipe. The conditions of air and contaminated water flow eventually dictate the interfacial area for transfer of VOCs from the aqueous to the air phase, the interfacial mass-transfer resistance, the residence time, the extent of removal, etc. These have been taken into account in completing Table A.1.

3. Mechanism of VOC Treatment: The VOCs that are stripped out can be adsorbed onto activated carbon beds or condensed out. The former is a well-developed process. The latter is simple in principle, but needs to be proven through bench-scale experiments. The spent carbon can easily be steam-stripped to reactivate the carbon for reuse.

4. Mechanism of Radionuclide Treatment: Not applicable.

5. Treatment Efficiencies Expected and Reliability: The degree of VOC removal that can be reasonably obtained depends upon the level of contamination. For example, it is easier to remove 99% of contamination at the 300-ppm level than it is at the 5-ppm level. The proposed process is capable of removing 99.9% of TCE from contaminated water containing 5 ppm TCE. This has been documented in Siegrist et. al. (1993). No special treatment of the aquifer water is required.

6. Limiting Conditions and Interferences: Only atmospheric air will be pumped through the contaminated water. This is not expected to adversely affect groundwater chemistry or biology.

7. Stage of Development: The technology is in demonstration phase. It utilizes off-the-shelf items. Air stripping is a well-established technology practiced in the chemical process industries.

8. Processing Capacity and Rates: The parameters outlined in Table A.1 are particularly applicable to the capacity and rates for this process. It is noteworthy that 25 gal/min of waste water can be treated with 90% TCE recovery in a volume of 0.38 m³ within 0.28 min. The capacity and rates are influenced by the value of the Henry's constant (measure of volatility) for that particular VOC.

9. Chemicals or Other Treatment Agents Required: The only chemicals that can be released into the aquifer are in air as dissolved gases due to sparging.

10. Secondary Waste Streams Produced: The exiting air will carry the VOCs that are stripped from the aquifer. Traditionally, the VOCs are removed with activated carbon. In that case, the carbon will need to be regenerated by steam-stripping and the spent carbon replaced. Following steam-stripping, a condensed solution/emulsion of TCE in water will need to be disposed of as a hazardous waste. After cleanup is completed, the residual spent carbon is likely to be incinerated.

11. Utility Requirements: Electricity is needed to blow air into the aquifer, and a partial vacuum needs to be maintained over the well head because of the slightly reduced pressure (approximately 12 psi). The energy requirements for this depend upon the volume of air needed for sparging, but are not significant.

12. Monitoring Requirements: Frequency of monitoring would be determined by regulatory needs. Aliquots of water can be sampled by gas chromatography with an electron capture detector (ECD). Air samples also need to be taken and sent for analysis.

13. Operation and Maintenance Requirements: Two technicians per shift are estimated to be required. The equipment and process require minimum maintenance. Frequency of changing absorbent beds depends upon the breakthrough characteristics, the initial size of the equipment, the extent of TCE removal, the ambient temperature, etc.

14. Potential Environmental Impact Risks: Fugitive air emissions would contain about 3000 ppm of TCE and would result in the release of hazardous substances into the air. Release of hazardous substances into the groundwater is not germane to the process.

15. Potential Safety Risks: The Guidebook for Response to Hazardous Materials Incidents published by the U. S. Department of Transportation lists TCE under Guide #74. TCE vapors may cause dizziness or suffocation. Exposure in an enclosed area may be very harmful. Contact may irritate or burn skin and eyes. Fire may produce irritating or poisonous gases. Runoff from fire control or dilution may cause pollution TCE burns, but may not ignite readily (I have not checked the flash point for this material). For large fires, water spray, fog, or standard foam is recommended.

16. Process Capital and Operating Costs: An independent assessment has not been made to my knowledge.

17. Case Histories: *In situ* treatment of VOC recovery has been demonstrated in Germany and has also been evaluated by the DOE under the ITEP.

18. Potential Vendors/Providers: There is at least one commercial vendor for the *in situ* process. HYDRODATA GmbH, Germany, and an affiliate organization, IEG in the USA, offer this technology. There are many other vendors that can provide the equipment needed to assemble a customized system.

19. References and Contacts

R. L. Siegrist, ORNL.

Advanced Oxidation Processes, UV/Peroxide
Nic Korte
Oak Ridge National Laboratory
Environmental Sciences Division
303-248-6210

1. Process Name and Type: Advanced oxidation processes (AOPs), UV/peroxide
(Note: UV/peroxide/ozone systems are also available, but are too costly and complex to be considered for this application.)

2. Process Description: UV light can break molecular bonds in organic molecules directly, or in conjunction with hydrogen peroxide, can produce hydroxyl free radicals to break the bonds. In a typical system, contaminated water is pumped into a tank where it is mixed with hydrogen peroxide (and with acid if neutralization of carbonates is required). The tank contains a bank of UV lights that produce reactions within the organic contaminants and hydrogen peroxide. The tank is sized appropriately for flow rate and contaminant concentrations to ensure adequate treatment.

3. Mechanism of VOC Treatment: Either adsorption of energy directly from UV light or reaction with hydroxyl radicals breaks the molecular bonds in the organic compounds.

4. Mechanism of Radionuclide Treatment: None.

5. Treatment Efficiencies Expected and Reliability: Virtually 100% efficiency is routinely obtained in field installations. Treatment time and reactor size are adjusted to the particular waste stream. This technology is sufficiently mature that reliability is not an issue.

6. Limiting Conditions and Interferences: The extent of pH adjustment required (possibly none is required), the concentrations of iron and manganese and resulting scaling, and the turbidity of the water all affect the cost effectiveness and amount of O&M required. For example, if the pH is high, hydroxyl free radicals that are formed are consumed by carbonates. This is prevented by adding acid. The system is highly oxidizing; consequently, dissolved iron and manganese will precipitate and cause scaling on the lamps, requiring additional O&M. Likewise, if the water is highly turbid, then the throughput of UV energy is reduced. One contact did not recommend using peroxide in a downhole recirculation system, stating that bubble formation, increased microbial biomass, and precipitation of iron oxides would greatly reduce permeability.

Portsmouth, Ohio

Some waters at the Portsmouth site contain several ppm iron and nitrate. Water at these locations would be much more difficult to treat.

Paducah, Kentucky

Groundwater at Paducah is generally sufficiently free of carbonate and nitrate to treat effectively.

7. Stage of Development: Although advancements are still being made in lamp life, lamp energy, and lamp wipers, this technology is relatively mature and available from a number of commercial vendors. Variations of AOP treatment systems are installed and operating routinely at the Kansas City Plant (KCP), the Rocky Flats Plant (RFP), and at Lawrence Livermore Laboratory.

8. Processing Capacities and Rate: Kinetics are site-specific because of variations in pH, turbidity, carbonate content, and concentrations of Fe and Mn. The size of units needed to treat more than 50 to 100 gal/min, however, is unlikely to be appropriate for a downhole operation.

9. Chemicals or Other Treatment Agents Required: Depending on the characteristics of the water, acid and hydrogen peroxide addition may be required. It is possible that neither is required. However, to obtain the highest efficiencies, hydrogen peroxide is typically used in aboveground systems.

10. Secondary Waste Streams Produced: None.

11. Utility Requirements: The high-power lamps require substantial energy and constitute much of the \$64K/year O&M costs specified below.

12. Monitoring Requirements: If acid adjustments are required, on-line pH monitoring and metering pumps are necessary. The only other requirements are influent/effluent monitoring.

13. Operation and Maintenance Requirements: O&M depends on the rate at which scale builds up on the lamps and on lamp life. Vendors use different types of wiper systems to remove scale, and some state that these eliminate the scale problem. Lamp life ranges from one to three or four months.

14. Potential Environmental Impact Risks: None.

15. Potential Safety Risks: None, other than those normally associated with electrical equipment.

16. Process Capital and Operating Costs: Capital costs for a 75 gal/min unit are estimated to be \$144K. Yearly O&M costs are estimated to be \$64K/year. Therefore, treatment cost per 1000 gal is \$1.62.

17. Case Histories: There are no downhole case histories. There are numerous case histories throughout the country and several at DOE facilities for aboveground units. The UV/peroxide system works as advertised. However, there is a "prove-in" period in which the balance of acid and peroxide additions must be optimized to obtain the necessary efficiency. Once those operating parameters are resolved, the process is efficient and reliable.

18. Potential Vendors/Providers: Peroxidation Systems, Inc, Tucson, Arizona; Purus, Inc., Newport Beach, California; Solarchem Environmental Systems, Las Vegas, Nevada, and Toronto, Canada

19. References and Contacts:

Garland, S. R., and G. R. Peyton. 1990. *An Evaluation of the Use of an Advanced Oxidation Process to Remove Chlorinated Hydrocarbons from Groundwater at the U.S. Department of Energy Kansas City Plant.* ORNL/TM-11337. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Payton G. R. 1989. *Feasibility of Adding TCE Still Area and Northeast Area Plumes to Ultraviolet Radiation, Ozone, Hydrogen Peroxide Groundwater Treatment Plant, Department of Energy Kansas City Plant.* ORNL/Sub/89-SD212V/1. Prepared for Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Payton, G. R., and W. H. Glaze. 1988. Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone. *Environmental Science and Technology*, 22:761-767.

Conclusion: This technology may be considered for a low flow rate (20 gal/min), relatively low-concentration (a few ppm) VOC plume where UV light alone can provide sufficient treatment. Moreover, the plume should not require acid addition. A downhole application where acid and hydrogen peroxide addition are required is not recommended. Such circumstances would require extensive aboveground batch tests and an extensive control-panel installation and would result in a system difficult to troubleshoot from the surface.

Considerations with adding hydrogen peroxide to the aquifer (e.g., clogging with bubbles, precipitates, and excess microbial biomass) are also a concern.

Table A.1 Estimated Treatment Times and Module Dimensions

Treatment occurs in a matter of one or two min in a treatment tank that holds 25 to 30 gal. The vendors contacted (see No. 18) stated that a module with sufficient capacity to treat 25 gal/min could be constructed to fit in a 6-ft diameter caisson at a depth of 10 to 12 ft. The precise treatment module size depends on site-specific factors that cannot be quantitatively assessed without a treatability study.

Photocatalytic Oxidation with Titanium Dioxide

Nic Korte

Oak Ridge National Laboratory

Environmental Sciences Division

303-248-6210

1. Process Name and Type: Photocatalytic oxidation with titanium dioxide
(There are two versions, aqueous and gas-phase treatment)

2. Process Description

Organic Compounds

Aqueous Phase

The treatment process consists of the production of free radicals that destroy the molecular bonds of organic molecules. TiO_2 is irradiated with light of the proper wavelength. Photoexcited electrons (e^-) and holes (h^+) are produced. These can migrate to the oxide surface and participate in half-cell reactions that are part of a closed, catalytic cycle. In the aqueous phase, the illuminated surface is believed to produce hydroxyl radicals (e.g., $h^+ + \text{OH}^- = \text{OH}^\cdot$). The hydroxyl radicals, and other highly oxidizing initial products of this indirect photochemistry, attack oxidizable contaminants such as organic compounds. Hydrogen peroxide can be added to increase the production of hydroxyl radicals. There are several approaches for performing aqueous treatment: use of TiO_2 slurries (e.g., Sandia), use of immobilized TiO_2 (Matrix Photocatalytic, TVA), and pre-extraction of TCE into fluorocarbons (Gilbert Brown, Chemical Technology Division, ORNL, Oak Ridge, Tennessee, personal communication with Nic Korte, ORNL, Grand Junction, Colorado, November 1993).

Gas Phase

The gas-phase treatment process utilizes the same basic theory except that in this case the contaminants are vapor stripped *in situ*, as in the Unterdruck Verdampfer Brunner (UVB) process. The vapor is then conducted to the aboveground catalytic treatment unit. However, in the vapor phase, poisoning and erosion of the TiO_2 surface is significantly reduced, and most interferences are eliminated. The destruction process is rapid, virtually 100% efficient for TCE, and is reportedly inexpensive to operate.

Inorganic Components

Many metals are subject to photodeposition, involving the reduction of ions by conduction band electrons and oxidation of water to molecular oxygen by valence-band holes. Research is very active in this area, with various groups applying the technique to a variety of complex waste streams, including mine wastes. Several people have successfully immobilized uranyl

ions with this technique, and at least one researcher said that the technique would also be applicable to Tc. Another approach is to apply a potential across the immobilized TiO_2 . In this way, electrodeposition could be induced as well.

3. Mechanisms of VOC Treatment: As noted above, the principal mechanism involves the creation of free radicals that can break molecular bonds in organic compounds. For TCE, this process is believed to be highly efficient, resulting in the formation of HCl , H_2O , and CO_2 .

4. Mechanisms of Radionuclide Treatment: No work was identified that was specific to Tc. However, uranyl has been successfully photoreduced, and the same process may work with Tc. The radionuclide would be photodeposited or electrodeposited, depending upon the approach chosen. The TiO_2 substrate would have to be removed from the system and regenerated periodically.

5. Treatment Efficiencies Expected and Reliability

Organic Compounds

Aqueous Phase

Treatment efficiency is based on mass action: that is, the geometry of the system, flow rate, and interferences (color, turbidity, competing reactants) all affect treatment time. Routinely, however, these systems are more than 99% efficient. Process reliability depends on two factors: the nature of the water being treated and variations in system operation. For example, free radicals are rapidly consumed by nitrate and carbonate. Groundwater with carbonates must be neutralized with acid to promote efficient operation. When acid treatment is needed, system variations may be very important. For example, if several wells are on the treatment system, the balance among the wells may affect the amount of acid needed, requiring a complex optimization and maintenance process.

Gas Phase

Employing gas-phase treatment (e.g., following vapor stripping) removes virtually all of the variables listed under the aqueous-phase operation. Efficiency is more than 99%, and the expected lifetime of the TiO_2 catalyst is believed to be months. This type of system has been tested a number of places [e.g., March Air Force Base (AFB), Savannah River Laboratory].

Inorganic Components

Efficiency and reliability are defined by contact time and the characteristics of the system under study. Research has shown that photocatalytic systems can be highly efficient. No research was identified, however, that quantified how such systems would be scaled up for the treatment of inorganic components.

6. Limiting Conditions and Interferences: Color, turbidity, and competing reactants affect aqueous-phase processes for both organic and inorganic components. There are no significant limiting conditions for gas-phase applications.

7. Stage of Development

Organic Compounds

Aqueous Phase

This technology is at the demonstration and commercial phases. Several demonstrations are in progress or have recently been completed. There are vendors, however, who will sell a full-size commercial system.

Gas Phase

This technology is also at the demonstration and commercial phases. At least one company (Matrix Photocatalytic) markets, and has sold, full-size commercial units. IT has a cooperative research and development agreement (CRADA) with National Renewable Energy Laboratory (NREL) that is to lead to a commercial product.

Inorganic Components

This technology is presently at the bench scale but is clearly ready for the pilot or demonstration phase. Funding for scale-up has not been available to the researchers, or else health and safety concerns for the study of radionuclides have been so cumbersome that such research was not pursued.

8. Processing Capacities and Rates

Organic Compounds

Aqueous Phase

The capacity of the process is limited only by the size of the system required. Presently, however, waste streams on the order of 50 to 100 gal/min seem most amenable.

Gas Phase

Treatment systems that have been installed routinely handle 100 to 200 cfm.

Inorganic Components

No data are available, but again this process would depend on the size of the membrane and the characteristics of the waste stream.

9. Chemicals or Other Treatment Agents Required

Organic Compounds

Aqueous Phase

Hydrogen peroxide or a proprietary reagent (sold by one vendor) may be needed to increase the yield of free radicals. Depending upon the characteristics of the water, it may also be necessary to inject acid to remove carbonates.

Gas Phase

None

Inorganic Components

None

10. Secondary Waste Streams Produced

Organic Compounds

Aqueous Phase

The quantities of by-products produced are not believed to present a significant factor.

Gas Phase

The gas stream must be scrubbed. HCl is produced if chlorinated hydrocarbons are destroyed, and traces of phosgene have been reported. A wet scrubber will reportedly last for many weeks without need for adjustment or replacement.

Inorganic Components

The TiO_2 catalyst would have to be regenerated periodically. The deposited metals would be stripped into an aqueous phase that would have to be disposed of.

11. Utility Requirements: These processes use UV light to excite the electrons on the TiO_2 surface. Typical power requirements for a nominally sized system are 3 kW.

12. Monitoring Requirements

Organic Compounds

Aqueous Phase

None are required other than influent/effluent monitoring.

Gas Phase

The scrubber output requires on-line monitoring to ensure the absence of leaks and proper operation of the scrubber. These systems can be set up to operate unattended with an alarm.

Inorganic Components

None are required other than the influent/effluent monitoring.

13. Operation and Maintenance Requirements

Organic Compounds

Aqueous Phase

The O&M requirements are assumed to be modest because the system design would be based on a treatability study. That treatability study would assess the effects of interferences (e.g., poisoning of the TiO_2 with Fe and Mn). Presumably, routine inspections would be required on a daily basis, and regeneration or cleaning of the system would be required on a weekly or less frequent basis.

Gas Phase

O&M requirements are greatly reduced in the gas phase relative to the water phase. Poisoning of the TiO_2 surface is greatly reduced, and there are no aqueous additions (acid or hydrogen peroxide) required wherein pumps would have to be monitored. Vendors believe that cleaning or replacement of the TiO_2 would be necessary only every few months. Maintenance of the scrubber would be a design factor based on the flow rate and contamination level that is treated.

Inorganic Components

No information is available, but overall, the circumstances are presumed to be as described for the aqueous treatment of organics.

14. Potential Environmental Impact Risks: There are no identified environmental impact risks associated with this technology.

15. Potential Safety Risks: The only safety risks would be those normally associated with the use of electrically operated equipment. Failure of the scrubber could expose employees to hazardous air pollutants. That risk, however, would be eliminated by using an alarm or emergency shut-off system on the scrubber.

16. Process Capital and Operating Costs

Organic Compounds

Aqueous Phase

The capital cost is nominally \$75K, including pumping systems for adding acid and hydrogen peroxide for a 30 to 50-gal/min system.

Gas Phase

The capital cost is nominally \$50K for a 100 to 200-cfm system.

Inorganic Components

Configuring the system for treatment of inorganics would increase the cost. The size of the system may not be affected, but additional design and construction costs would be involved.

17. Case Histories

Organic Compounds

Aqueous Phase

A field test was being conducted mid-November 1993 at the Savannah River Plant. The test was successful, but some phosgene was produced. Other field tests have been conducted at the Savannah River Plant and other sites. These tests were all aboveground. No one contacted had heard of a belowground system.

Gas Phase

IT, in conjunction with NREL, is currently conducting a pilot test at March AFB in California. Likewise, Matrix Photocatalytic has conducted pilot tests at the Savannah River Laboratory and maintains that units have been delivered for routine use.

18. Potential Vendors/Providers: Matrix Photocatalytic is the most mature potential vendor. IT expects to have commercial units by the end of 1994. (Patent battles are occurring with the process.)

19. Reference and Contacts

Mike Prairie, Sandia, 505-844-7823

Kathy Pugh, TVA, 205-844-7823

Gilbert Brown, ORNL, 615-576-2756

John Ireland or Norma Lewis, Environmental Protection Agency, Cincinnati and Rich Miller, IT Corp, 615-690-3211

Craig Turchi, NREL, 303-231-1351

Hussein Al-Ekabi or Bob Henderson, Matrix Photocatalytic, 519-457-2963 (in Canada)

Conclusion: This technology is very promising and is certain to see increasing use in the next few years.

Organic Compounds

Aqueous Phase

This technology, for organic compounds alone, will work well for groundwater contaminated with TCE. However, it is clear that if only organics are being treated, air stripping with vapor-phase destruction would be less expensive and more reliable. This technology, in conjunction with metal and radionuclide removal, should be considered further.

Gas Phase

Using photocatalysis of the off-gas from downhole air stripping would be a very favorable process and should be considered for an organics-only treatment method.

Inorganic Components

Marc Anderson from the University of Wisconsin asserts that his biased membrane method will be ready for a full-scale field test in fiscal year 95 or 96. This is one of the few technologies that promises both organic and inorganic treatment. Substantial laboratory experiments and treatability studies are needed before deployment in the field. These should be pursued if time and funding permit.

Table A.1 Estimated treatment residence times and module dimensions

Organic Compounds

Aqueous Phase

Design information from Matrix Photocatalytic and discussions with Marc Anderson of the University of Wisconsin indicated a great deal of confidence that units with sufficient treatment capacity could be designed to fit inside of a 6-ft diameter caisson with a depth of 10 ft. There is a great deal of site-specific information that is required to design the system.

Gas Phase

Commercially available and pilot-scale units now in use could handle the expected air flow. These could be skid-mounted units because they would be installed aboveground.

Inorganic Components

There is no specific design information available. However, the size of treatment cell would be similar to that used for the treatment of organics.

**Reductive Dechlorination and Precipitation Using
Zero-Valence Metals (Fe)**

Nic Korte

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Environmental Sciences Division
303-248-6210

1. Process Name and Type: Reductive dechlorination and precipitation using zero-valence metals (Fe)

Target: VOCs (reductive dechlorination), ^{99}Tc (precipitation)

Advantages: Inexpensive and common materials

Disadvantages: Slow kinetics for some compounds, controversy regarding the reaction mechanism

2. Process Description: Reacting zero-valence base metals such as iron with chlorinated hydrocarbons results in reductive dechlorination of the hydrocarbon. This technique was originally proposed by Gillham and co-workers at the University of Waterloo (Gillham and O'Hannesin 1992). Though the exact mechanism has not been reported, the process appears to be abiotic, reductive dechlorination, requiring the presence of highly reducing conditions and metallic surfaces. In batch tests reported by Gillham and co-workers, there was a notable absence of significant accumulations of breakdown products, suggesting that the technique provides complete destruction of the chlorinated hydrocarbon. More recent information from Gillham's group suggests that 1,2-dichloroethene (1,2-DCE) and chloroethene are formed but that they do breakdown subsequently within the flow path (J. Baker, AlliedSignal Inc., personal communication with N. Korte, ORNL, March 1994). Complete destruction of TCE has also been reported by other researchers [J. Salvo, General Electric Corp., personal communication with J. L. Clausen, MMES-Paducah Gaseous Diffusion Plant (PGDP), November 1993]. The principal reaction product is reportedly ethene.

As the potential for this technique has become more widely noted, a number of controversies and contradictions have surfaced. These are discussed below.

Nature of the Porous Medium

The initial work by Gillham used 100-mesh, electrolytically pure iron filings obtained from Fisher Scientific (R. Gillham, University of Waterloo, personal communication with N. Korte, ORNL, January 1993). Later reports from this group were less descriptive of the material. For example, a March 1993 report stated that an "iron-based catalyst" was used (O'Hannesin and Gillham 1993). Later in the report, the medium was described as 22% by weight iron grindings and 78% by weight concrete sand. The sand was used to ensure that the reactive area was more permeable than the surrounding material. The article further stated that once in place, the catalyst "remains in place, unattended, continuing to purify water year after year." Traces of 1,2-DCE but no chloroethene were found downgradient of the iron gate.

Work performed by General Electric indicates that very large excesses of Fe are needed (D. Olsen, General Electric, personal communication with T. Early, ORNL, 1993). Work performed by Fernando indicated that iron from laboratory supply houses and the grindings used in later experiments by Gillham and co-workers had very different properties with respect to impurities and surface area (Q. Fernando, University of Arizona, personal communication with N. Korte, ORNL, October 1993).

Effect of Varying Hydrogeochemical Environments

Gillham stated that research was needed to determine the most effective means of pH control (personal communication with N. Korte, ORNL, January 1993). Eh decreases and pH increases as the reaction occurs. At a pH of approximately 9, the reaction stops. General Electric researchers stated that there was an optimum pH but provided no details (J. Salvo, General Electric Corp., personal communication with J. L. Clausen, MMES-PGDP, November 1993).

Very little has been done to evaluate the effect of the redox environment. The field system employed at the University of Waterloo is in an oxidizing environment. Experiments at the EPA, Athens, were also conducted in oxidizing systems, but preliminary experiments suggested that the reaction rate was halved in an anoxic environment (L. Wolfe, EPA, Athens, Georgia, personal communication with N. Korte, ORNL, November 1993). Experiments performed at the Oregon Graduate Center were performed in closed systems, but preliminary observations indicated no difference when an open system was used (P. Tratnyek, Oregon Graduate Center, personal communication with N. Korte, ORNL, November 1993).

Mechanistic Questions

The initial reports on this technique either did not mention mechanisms or noted that the mechanism was unknown.

The surface area available appears to be proportional to the rate and completion of reaction. This was reported both by Fernando (Q. Fernando, University of Arizona, personal communication with N. Korte, ORNL, November 1993) and by General Electric (J. Salvo, General Electric Corp., personal communication with J. L. Clausen, MMES-PGDP, November 1993).

Work conducted by the EPA has suggested that sulfide may be involved in the reaction (Cipollone et al. 1993, Hassan et al. 1993). Indeed, in the latter study the authors noted that sulfur, usually present as an impurity in metallic iron, plays an important role in the reduction process. The authors have also reportedly developed a reaction mechanism based on the formation of a matrix of iron sulfide and metallic iron. In contrast, Fernando stated that

sulfur is definitely not involved in the reaction and based this statement on surface analysis with proton-induced X-ray (PIXE)(Q. Fernando, University of Arizona, personal communication with N. Korte, ORNL).

Matheson and Tratnyek (1993) have also been studying the mechanism and stated that iron participates in the reductive dechlorination reaction primarily as a direct, electrolytic reduction. Reduction by hydrogen produced during the corrosion process is not believed to be a major contributor.

Completeness of the Reaction

Matheson reported that dichloromethane accumulated when the reaction was performed with carbon tetrachloride (L. Matheson, Oregon Graduate Institute, personal communication with N. Korte, ORNL, April 1993). Gillham has reported that dichloromethane is the only chlorinated compound that has been tried that does not degrade (R. Gillham, University of Waterloo, personal communication with N. Korte, ORNL, January 1993). At this stage of development, not all chlorinated compounds have been comprehensively studied. More work with the TCE by-products *cis*-1,2-dichloroethene and chloroethene is particularly needed.

Kinetics

There has been little published on kinetics, but the reaction appears to be relatively slow in some instances. For example, batch experiments performed by Gillham showed that complete removal of 1,1,1-trichloroethane (1,1,1-TCA) occurred in less than a day while similar concentrations of TCE required 100 h (R. Gillham, University of Waterloo, personal communication with N. Korte, ORNL, January 1993). Indeed, the half-life of TCE was stated to be 13.6 h and that of 1,2-DCE 432 h. These values suggest significant issues with respect to the nature of the reactant and the reaction mechanism. The reaction obviously occurs more favorably with the more oxidized compound. If the reaction occurs on the metallic surface as some believe, then it may be that once TCE sorbs onto the surface, complete reduction occurs. However, if the reaction occurs on the surface, dichloromethane may never adequately sorb onto the surface to fully react.

Life of the System

When pH increases to 9 and Eh decreases significantly, the reaction stops. Precipitates of iron hydroxide at such a high pH may occur, and calcite may also precipitate at that pH and cause clogging.

3. Mechanism of VOC Treatment: Generally speaking, the reaction is reductive dechlorination. It has been reported that compounds such as tetrachloroethene and TCE are reduced to ethene. When the starting reactant is carbon tetrachloride, the reaction stops at dichloromethane. As noted above, there is controversy regarding the exact mechanism at the molecular level.

4. Mechanism of Radionuclide Treatment: The propensity of iron oxide surfaces to sorb metals is well known. In particular, from the standpoint of soils, anions are much more efficiently sorbed by iron oxide surfaces than by other exchange sites in soils. Consequently, Tc and other radionuclides would most likely be sorbed by an iron filings reaction module. Preliminary experiments indicate that iron has a significant capacity for the sorption of Tc (W. D. Bostick, Martin Marietta Energy Systems, personal communication with N. Korte, ORNL, February 1994).

Adsorption of uranyl ions by ferric oxyhydroxides has been studied and is a favorable process. Treatability studies would be needed to evaluate both the efficiency and the reliability of this process because the nature of the adsorbent will change with time. Another issue is whether the system would foster growth of microorganisms. Recent research has revealed that dissimilatory metal reduction does occur with respect to both Tc and U. The iron filings produce a highly reducing environment. Consequently, the possibility of utilizing this environment for the growth of the appropriate bacteria could result in additional removal of radionuclides in insoluble, reduced forms.

5. Treatment Efficiencies Expected and Reliability: Treatment efficiency is variable and will depend on site-specific factors. For example, as noted previously, Gillham reported that the half-life for TCE in contact with the iron filings was 13.6 h, while it was 432 h for 1,2-DCE. It is also known that the reaction stops when the pH reaches 9. Hence, the buffering capacity of the water will be a factor. All researchers contacted expressed concerns about clogging with iron and manganese and with soil particles.

6. Limiting Conditions and Interferences: The small quantities of reaction by-products from TCE degradation will not adversely affect water quality. As noted under Process Description, however, there is considerable uncertainty with regard to the reaction mechanism and the effect of other constituents in the groundwater. Some of these may cause clogging. Some contaminants may not be treated efficiently. Hence, additional research is required to identify and quantify limiting conditions and interferences.

7. Stage of Development: This process has been proposed for field-scale testing at a site in California. All of the researchers are uncomfortable with the mechanistic unknowns, but feel that the potential is so significant that field tests should be performed.

8. Processing Capacities and Rates: There has not been a controlled set of kinetic measurements reported. It is clear that experimental conditions (Fe-contaminant ratio, Fe surface area) significantly affect the apparent reaction rate. Contaminant half-lives of minutes to days have been reported.

Lee Wolfe of EPA's laboratory in Athens, Georgia, noted that preliminary experiments showed that the reaction rate in anaerobic systems was half that of aerobic systems (L. Wolfe, EPA, Athens, Georgia, personal communication with N. Korte, ORNL, November 1993).

9. Chemicals or Other Treatment Agents Required: The small quantities of reaction by-products will not adversely affect water quality.

10. Secondary Waste Streams Produced: The iron filings would be applied in some type of cartridge. Some Tc would undoubtedly sorb onto the iron. Hence, the iron would certainly be considered a radioactive waste and may be considered a mixed waste. Washing the iron to remove any residual solvent and the Tc is believed to be relatively easy. Again, however, the process has not been evaluated.

11. Utility Requirements: The base metal process represents a system with no moving parts. Thus, there are no special utility requirements.

12. Monitoring Requirements: Periodic sampling of the influent and the effluent for the contaminants of interest and pH is all that is necessary from a chemical analysis standpoint. Monitoring of flow rates and system back-pressure would also be needed to evaluate whether the system is clogging.

13. Operation and Maintenance Requirements: The amount of O&M cannot be safely predicted because of the question of scale. However, it is believed that replacement and/or regeneration of the iron will not be required more often than every few months or possibly years.

14. Potential Environmental Impact Risks: None identified.

15. Potential Safety Risks: None identified beyond those inherent in handling the contaminants already present at the site.

16. Process Capital and Operating Costs: There is no data available. The cost of the iron filings, however, is very low.

17. Case Histories: None identified.

18. Potential Vendors/Providers: The only commercial vendors are believed to be EnviroMetal of Guelph, Ontario, who has filed for a patent on the process.

19. References and Contacts

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Gillham, R. W., and S. F. O'Hannesin. 1992. Metal-catalyzed abiotic degradation of halogenated organic compounds. Paper presented at the 1992 IAH conference Modern Trends in Hydrogeology, May 10-13, 1992, Hamilton, Ontario, Canada.

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Contacts:

R. Gillham, University of Waterloo
 P. Tratnyek, Oregon Graduate Center
 L. Wolfe, EPA, Athens, Georgia
 J. Salvo, General Electric Corp., Schenectady, New York
 T. Sirarec, General Electric Corp., Schenectady, New York
 Q. Fernando, University of Arizona, Tucson, Arizona

Conclusion: Site-specific treatability studies and pilot tests are needed to determine the efficiency and lifetime of an Fe filings reactive cartridge. The technique has the potential for such favorable characteristics, especially in a low-flow rate regime, that these tests are recommended.

Table A.1 Estimated Treatment Times and Module Dimensions

The table cannot be completed because the information available is inadequate. The mechanism of this process has not been reported. Thus, the effects of site-specific factors cannot be quantitatively described. The only organic compound half-lives reported were on the order of hours. Based on that information, the use of this technique in a recirculation module would seem to be precluded based on the desire to achieve 90% treatment in one-pass. However, there is so little information regarding this aspect of the reaction that the primary conclusion must be that additional research is required.

Radionuclide Precipitation
Dan Marsh
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1. **Process Name and Type:** Radionuclide precipitation
2. **Process Description:** This treatment would require changing the pH and/or redox chemistry of the waste plume and adding the appropriate precipitating agents. This could be accomplished *in situ* by diverting the waste plume through a reaction zone or aboveground by typical pump-and-treat methods.
3. **Mechanism of VOC Treatment:** Not applicable.
4. **Mechanism of Radionuclide Treatment:** The mechanism involved here is simple chemical solubility. The theory is well known, but its application to uncontrolled environmental systems can be tricky. For the co-contaminants Tc and U, the oxidized forms, TcO_4^- and UO_2^{+2} , are the most soluble and the most likely to occur in aqueous systems. Therefore, diverting the waste plume through a reducing zone can convert these species to their reduced, insoluble forms, TcO_2 and U(IV) , and remove them by precipitation. However, there are many complicating factors.
5. **Treatment Efficiencies Expected and Reliability:** Treatment efficiencies could be as high as 90% but more typically 70%-80% may be expected, depending on the groundwater conditions and the reaction-path length. The treatment system would be quite reliable, incorporating off-the-shelf, proven technology.
6. **Limiting Conditions and Interferences:** Naturally occurring organic material and certain organic contaminants can form stable organic complexes with radionuclides and prevent reduction and precipitation. If this is a problem, this method may not work. Alternatively, this method may be used in conjunction with processes to remove organics, such as a UV/peroxide system as long as the groundwater is deoxygenated prior to running through the reducing zone. Some inorganic complexes such as carbonates and phosphates can prevent uranium from precipitating. This is especially true in limestone aquifers. An additional interference for uranium is the presence of reduced iron. The insoluble forms of uranium and iron are inversely related. The reduced form of iron, Fe^{+2} , and the oxidized form of uranium, UO_2^{+2} , are the soluble forms, while the oxidized form of iron, Fe^{+3} , and the reduced form of uranium, U(IV) , are the most insoluble. Therefore, concentrations of iron and uranium in groundwater are usually inversely related. Geochemical modeling of representative data from Portsmouth (Davenport and Houk 1993) and Paducah (Cul et al.

1993) show the groundwater to be supersaturated with respect to the iron minerals: goethite, hematite, and others. This would imply oxidizing conditions. Although no alkalinity data were given, it is safe to assume that carbonate is present, and at pH=6.5, uranium would be most soluble as UO_2CO_3^0 or $\text{UO}_2(\text{CO}_3)_2^{-2}$ (see Fig. 1). Indeed the geochemical modeling shows all uranium minerals to be undersaturated; thus, the uranium would be soluble and able to migrate through the aquifer. Under these same conditions, ^{99}Tc would also be soluble as the pertechnetate ion, TcO_4^- (see Fig. 2). Only by reducing the pH and/or the redox conditions can both uranium and technetium be made insoluble. However, this may cause dissolution of other minerals, such as iron, which may cause water-quality problems off site. This could also be an important consideration for other iron-utilizing methods.

7. Stage of Development: Technology is currently available.

8. Processing Capacities and Rates: The processing capacity will depend on the size of the system required and on site-specific parameters such as pH, Eh, alkalinity, buffering capacity, and mineral composition of the aquifer. For solubility reactions, the rate of reaction would be fast. Redox reactions would be slower, requiring more control of the reaction parameters.

9. Chemicals or Other Treatment Agents Required: The same chemicals would be required as those for pump-and-treat methods. However, the water could be neutralized, and harmful by-products could be removed by ion-exchange and/or filtration prior to returning the water to the aquifer.

Acids or bases used to adjust the pH of the waste plume in a downhole treatment would, however, produce chemical changes in the aquifer. Depending on the conditions, certain minerals could dissolve or precipitate. This could produce scaling and clogging of well screens and also reduce the porosity of the aquifer itself. Depending on the scale of the treatment, the acid anions, such as chloride and nitrate, could produce adverse changes in water quality off site. Precipitating and reducing agents such as H_2S would create an anoxic environment that may be harmful to organisms living underground and could also affect water quality.

10. Secondary Waste Streams Produced: No secondary waste stream for *in situ* treatment would be produced. For a pump-and-treat method, filter cartridges and pH-adjusted groundwater would need disposal. The treated groundwater could possibly be neutralized and returned to the aquifer.

11. Utility Requirements: Electric generators will be required to power the pumps for a pump-and-treat process or for injecting acid/base or precipitating agents for an *in situ* process.

12. Monitoring Requirements: Routine monitoring of groundwater conditions for pH, Eh, precipitating agents, if any, and concentrations of Tc and U are required to assess performance.

13. Operation and Maintenance Requirements: O&M requirements would be standard for any pump-and-treat or downhole process, but the magnitude would depend on the size of the waste plume being treated.

14. Potential Environmental Impact Risks: The only potential risks that might have environmental impact would be in the handling of large quantities of acid, base, and/or H₂S for adjusting the pH and redox conditions of the aquifer to the appropriate range for precipitation to occur.

15. Potential Safety Risks: No additional safety risks other than those normally found associated with field work and handling of contaminants.

16. Process Capital and Operating Costs: Assuming pumps, generators, and chemicals are already available, there would be no capital costs, and operating costs would be only for chemicals, replacement pumps and generators, groundwater monitoring, and analytical costs. The actual dollars would depend on whether a pump-and-treat or *in situ* method was selected and the extent of sampling (and analytical data) needed to monitor the method's performance.

17. Case Histories: None identified.

18. Potential Vendors/Providers: No commercial vendors for this process are known.

19. References and Contacts:

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Conclusions: Radionuclide precipitation may be a viable method for removing ^{99}Tc and possibly uranium, depending on conditions, but not for VOCs such as TCE. TCE would require additional treatment technologies.

Table A.1. Estimated treatment residence times and module dimensions.

The residence time and module height cannot be estimated based on the information available. However, residence time is probably on the order of hours, not minutes.

Zero-Valence Metal Reduction, Sorption

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1. **Process Name and Type:** Zero-valence metal reduction, sorption.
2. **Process Description:** Use of inorganic material (e.g., iron powder or ferrous sulfide) to reduce Tc(VII) to Tc(IV), with sorption of the Tc(IV) species.
3. **Mechanism(s) of VOC Treatment:** Not applicable. Investigators at the Waterloo Centre for Groundwater Research have proposed the use of similar material (granulated iron) for degradation of halogenated aliphatic compounds (Gillham and O'Hannesin 1992), but operational conditions may be significantly different from the *ex situ* treatment of ^{99}Tc .
4. **Mechanism(s) of Radionuclide Treatment:** The most stable chemical species of Tc in aqueous solution is the pertechnetate anion, TcO_4^- . As the pertechnetate ion, Tc(VII) is highly soluble in water, but reduced forms [e.g., the tetravalent oxide ($\text{TcO}_2 \cdot n\text{H}_2\text{O}$) and the sulfide] have limited solubility (Meyer et al. 1987; Wildung et al. 1979; Lieser and Bauscher 1987). Elemental iron, ferrous sulfide, and select other solid reducing agents are capable of chemically reducing and sorbing ^{99}Tc under oxic or anoxic conditions (Bostick and Evans-Brown 1988; Bostick et al. 1990). Other ferrous or mixed-valence iron minerals (e.g., magnetite, Fe_3O_4) may reduce Tc(VII) under anoxic conditions (Vandergraaf et al. 1984; Walton et al. 1986; Palmer and Meyer 1981; Ito and Kanno 1988); in addition, magnetite is said to be a sensitive and selective sorbent for tetravalent Tc (Rinshaw 1961).
5. **Treatment Efficiencies Expected and Reliability:** Effectiveness has been demonstrated at a laboratory-scale: >90% removal of ^{99}Tc from brine solutions with initial ^{99}Tc concentrations of 0.1 to 10 mg/L (Bostick and Evans-Brown 1988; Bostick et al. 1990). Performance was variable with different preparations of ferrous sulfide (correlated with reducing potential) and with different grades of reagent iron [best results for common steel; less reactivity for highly purified, reduced iron (Bostick and Evans-Brown 1988)]. Development needs include specifying a consistent source for reactive reagent. Long-term effectiveness of iron in oxic aqueous medium needs to be demonstrated (e.g., formation of rust, which may deactivate reactive surface, slough-off to clog filters, etc. needs to be evaluated).

6. **Limiting Conditions and Interferences:** Other redox-active metals were affected by iron or FeS [removal of Cr(VI) and complexed Hg (Bostick and Evans-Brown 1988)].
7. **Stage of Development:** This treatment has been demonstrated on a laboratory scale (Bostick and Evans-Brown 1988; Bostick et al. 1990).
8. **Processing Capacities and Rates:** Iron metal was demonstrated on a laboratory scale to achieve a high waste loading for a given volume of spent sorbent (Bostick and Evans-Brown 1988). To date, no large-scale demonstrations have been performed.
9. **Chemicals or Other Treatment Agents Required:** No chemicals in addition to the sorbent material will be required.
10. **Secondary Waste Streams Produced:** Spent sorbent can be immobilized in grout or be imbedded in a resin matrix, such as vinyl ester styrene (Morgan and Bostick 1992).
11. **Utility Requirements:** Minimal utilities are required (pump through packed-bed column).
12. **Monitoring Requirements:** When used in a packed-bed reactor configuration, the back-pressure (indicative of column plugging) will be an important operational parameter. Determination of the breakthrough of ^{99}Tc will be valuable. For the latter, occasional effluent samples could be drawn for laboratory analysis. Recently, Hoffmann and Ledford have proposed an *in situ* aqueous-phase Tc sensor, combining conductimetric and optical responses, to allow real-time, *in situ* measurements (Hoffman and Ledford 1993). If this device is capable of demonstrating sufficient sensitivity, it could be used to monitor Tc in-well and in the post-reactor effluent to determine reactor performance.
13. **Operation and Maintenance Requirements:** Column backpressure must be monitored for possible column plugging.
14. **Potential Environmental Impact Risks:** If ferrous sulfide reagent is used, very small quantities of soluble sulfide will leach into the water system; the Eh of the system may be shifted to reductive values, with possible reduction of dissolved oxygen (as trace sulfide slowly converts to sulfate ion).

15. **Potential Safety Risks:** If ferrous sulfide reagent is used, influent water pH values should be near-neutral to avoid possible formation of hydrogen sulfide gas.
16. **Process Capital and Operating Costs:** Development costs were very roughly estimated to be approximately \$1.25M for a three-year development plan for advanced inorganic sorbents and other contaminants and transfer of technology to private industry (Beck 1993; Bostick 1993).
17. **Case Histories:** In batch experiments, the kinetics for reduction and sorption of ^{99}Tc by iron metal may be relatively slow, but recent packed bed column flow experiments have been successful (the volume of wastewater treated for a given volume of sorbent was significantly higher than for organic polymers, including ion-exchange resins)(Bostick 1993).
18. **Potential Vendors/Providers:** Reagent-grade iron and ferrous sulfide are available from several sources; however, suppliers have not yet been identified for bulk quantities of suitably reactive material.

19. **References and Contacts:**

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Ion Exchange
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615-574-6827

1. **Process Name and Type:** Ion Exchange.
2. **Process Description:** Organic Resin: Sorption and Ion Exchange.
3. **Mechanism(s) of VOC Treatment:** Removal of VOCs is somewhat incidental. Polyvinylpyridine resin (Reillex™-402) has a moderate sorptive affinity for TCE ($K_d \sim 40$) (Morgan 1989). Significant reduction in the concentration of TCE was reported in a treatability study for the removal of ^{99}Tc in Paducah purge well water, using strongly basic anion exchange resin in a packed column, although the possibility of fugitive emissions during the operation could not be eliminated (Story 1989). Use of supported liquid membranes for the removal of ^{99}Tc will likely remove VOCs by solvent extraction into the organic-carrier medium.
4. **Mechanism(s) of Radionuclide Treatment:** The most stable chemical species of Tc in aqueous solution is the pertechnetate anion, TcO_4^- . Pertechnetate is tightly bound to strongly basic (quaternary amine) anion exchange resin (e.g., Dowex™-1) (Hoffman et al. 1956; Roberts et al. 1962; Kiseleva et al. 1971; Saraceno 1981; Deacon and Greiner 1982; Acox 1983; Bostick and Evans-Brown 1988; Del Cul et al. 1993)). Polyvinylpyridine-based resins (e.g., Reillex™ resins, Reilly Industries) act as a weak-base anion-exchange medium in strongly acidic solutions, but appear to be effective solid-phase sorbents for Tc in near-neutral solutions (Bostick and Evans-Brown 1988; Del Cul et al. 1993). Reillex™-HPQ resin is a mixed strong- and weak-base exchange resin, with a large affinity for pertechnetate in strongly acidic solution (Ashley et al. 1993). Quaternary amine strongly basic anion exchange resin is relatively more effective in groundwater, whereas polyvinylpyridine resin is relatively more efficient in acid or high-ionic-strength solution (i.e., solutions containing high concentrations of ions that may compete for binding sites on conventional ion-exchange media) (Bostick and Evans-Brown 1988; Del Cul et al. 1993). An alternative to use of beaded ion-exchange resin is the use of supported liquid membranes (Beck 1993). Chiarizia reported on the use of tertiary amine (trilaurylamine) in n-dodecane carrier to remove pertechnetate from acidified ($\text{pH} \leq 2$), synthetic, Hanford site groundwater (Chiarizia 1991).
5. **Treatment Efficiencies Expected and Reliability:** Removal of ^{99}Tc from real (Story 1989) and simulated (Del Cul et al. 1993) Paducah site groundwater has been demonstrated at bench scale.

6. **Limiting Conditions and Interferences:** Strongly basic anion-exchange resin will bind many strong anions, including nitrate; however, pertechnetate can displace most other anions that may have sorbed on the resin. Polyvinylpyridine resins show less tendency to bind anions at near-neutral solution values (Bostick and Evans-Brown 1988).
7. **Stage of Development:** Ion-exchange technology is a standard industrial practice for numerous other applications. The PGDP has utilized strongly basic anion-exchange resin to remove ^{99}Tc from their neutralized, filtered decontamination brines (Saraceno 1981; Deacon and Greiner 1982; Acox 1983).
8. **Processing Capacities and Rates:** Capacities and rates are similar to other full-scale applications of ion-exchange technology.
9. **Chemicals or Other Treatment Agents Required:** Solid resins require no waste stream preconditioning other than coarse filtration. Supported liquid membranes may require acidification of the wastewater before treatment, with pH readjustment prior to reinjection into the aquifer (Chiarizia 1991).
10. **Secondary Waste Streams Produced:** Regeneration of the spent, strongly basic anion-exchange resin (displacement of pertechnetate) does not appear practical (Bostick and Evans-Brown 1988; Del Cul et al. 1993). Spent resin beads may be disposed of in cement-based matrices, with waste loadings of typically < 40% (Morgan and Bostick 1992; Del Cul et al. 1991; Dyer and McGinnes 1988), although careful grout formulation and quality control is required to ensure wasteform durability. Resin beads may be imbedded in a polymer matrix (e.g., vinyl ester styrene) with minimal volume increase (Morgan and Bostick 1992). The resin matrix may be destroyed by thermal treatment; the ChemChar process has shown to destroy anion-exchange resin loaded with Tc-99m, with 99.9% retention of Tc retained on the char/ash residue (Kinner et al. 1993). Spent organic ion-exchange resin is a good candidate for destruction by the molten salt process; the relatively low operating temperature and the ionic molten salt should enhance retention of pertechnetate in the melt (Del Cul et al. 1993).
11. **Utility Requirements:** Electrical utilities are needed for pumps, etc.
12. **Monitoring Requirements:** When used in a packed-bed reactor configuration, the back-pressure (indicative of column plugging) will be an important operational parameter. Determination of the breakthrough of ^{99}Tc will be valuable. For the latter, occasional effluent samples could be drawn for laboratory analysis. Recently, Hoffmann and Ledford have proposed an *in situ* aqueous-phase Tc sensor, combining conductimetric and optical

responses, to allow real-time, *in situ* measurements (Hoffmann and Ledford 1993). If this device is capable of demonstrating sufficient sensitivity, it could be used to monitor Tc in-well and in the post-reactor effluent to determine reactor performance (e.g., column breakthrough).

13. **Operation and Maintenance Requirements:** These are similar to other full-scale applications of ion-exchange technology.
14. **Potential Environmental Impact Risks:** Supported liquid membranes may require acidification of the wastewater (before treatment), with pH readjustment prior to reinjection into the aquifer (Chiarizia 1991); this may effect aquifer pH and salinity.
15. **Potential Safety Risks:** Risks are similar to other full-scale applications of ion-exchange technology. It is not recommended that strongly basic anion-exchange resin be used in concentrated nitric acid solution due to potential instability of the spent resin (Bostick and Evans-Brown 1988; BeCraft and Holland 1979). This will not be a problem for use in near-neutral groundwater applications.
16. **Process Capital and Operating Costs:** These are similar to other full-scale applications of ion-exchange technology.
17. **Case Histories:** The PGDP has utilized strongly basic anion-exchange resin to remove ⁹⁹Tc from their neutralized, filtered decontamination brines (Saraceno 1981; Deacon and Greiner 1982; Acox 1983).
18. **Potential Vendors/Providers:** Many vendors supply strongly basic anion-exchange resin (e.g., Dow Chemical, Bio-Rad, etc.). Reilly Industries supplies various grades of Reillex™ polyvinylpyridine resin. Numerous vendors can provide turn-key packed ion-exchange column systems.

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Selective Sorption
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615-574-1965

1. **Process Name and Type:** Selective sorption; type: adsorption

2. **Process Description:** Selective adsorbents are being developed for a wide range of contaminants. A few of these adsorbents are commercially available (e.g., for removing trace contaminants from metal solutions), while others are currently being tested on a laboratory scale (e.g., for removing ^{137}Cs and ^{90}Sr from liquid low-level-waste solutions). Selective adsorbents are currently being developed for ^{99}Tc . These adsorbents use multiple properties of the target molecule, such as size, charge, and chemical interactions, to provide very high selectivities over potential competing molecules. Selectivities over 106 have been demonstrated for some applications. Because selective adsorbents for ^{99}Tc are in a very early stage of development, the information needed to design a treatment module is not yet available.

3. **Mechanism of VOC Treatment:** Not applicable.

4. **Mechanism of Radionuclide Treatment:** The mechanism entails selective adsorption within a cage-type molecule.

5. **Treatment Efficiencies Expected and Reliability:** Vendor tests indicate a selectivity of 106 for the target contaminant (^{90}Sr or ^{137}Cs) over many other competing compounds.

6. **Limiting Conditions and Interferences:** A successful selective adsorbent would essentially remove only ^{90}Sr or ^{137}Cs , so water chemistry would not be altered significantly.

7. **Stage of Development:** Adsorbents are currently being developed. Applications data are in the process of being measured, but are not yet available.

8. **Processing Capacities and Rates:** Vendor tests indicate capacities of about 10 mg/g.

9. **Chemicals or Other Treatment Agents Required:** These are probably insignificant.

10. Secondary Waste Streams Produced: Since the adsorbents are likely to be very expensive, it would be desirable to regenerate them. Vendor information suggests regeneration with 5 mL/g of 5 M HNO₃.

11. Utility Requirements: Unknown.

12. Monitoring Requirements: Unknown.

13. Operation and Maintenance Requirements: Unknown.

14. Potential Environmental Impact Risks: Unknown.

15. Potential Safety Risks: The adsorbents would presumably yield ⁹⁰Sr or ¹³⁷Cs at very high concentrations. Handling of the spent adsorbent or regeneration solutions would require careful planning.

16. Process Capital and Operating Costs: Unknown.

17. Case Histories: None.

18. Potential Vendors/Providers: Adsorbents are being developed at IBC Advanced Technologies.

19. References and Contacts:

Steve Izatt, IBC.

Organic Sorbent Mixtures
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1. Process Name and Type: Reduction and sorption of VOCs and Tc by organic sorbents and sorbent mixtures.

2. Process Description: Organic sorbents such as peat moss and a combination of peat moss, elemental iron, and clay soil are found to be effective in removal of metals and organic compounds (Viraraghavan 1993). In a recent study, up to 10 mg/g of benzene was removed by several types of peats (Stack et al., 1993). Fixation of U(VI) onto sphagnum peat has been shown to be attributed to ligand exchange and sorption processes with carboxylic and possibly phenolic functional groups (Zielinski and Meier 1988; Szalay 1964; Idiz et al. 1986; Borovec et al. 1979; Halback et al. 1980; Longmire et al. 1991). Our on-going research indicates that peat has high capacity (about 5 mg/g) for heavy metals (such as Cr, Cd, Pb, and Ni). We also found that ^{90}Sr was reduced from 18,000 Bq/L to 960 Bq/L in the presence of 10 g of garden peat.

Natural peat suspension has a pH between 3 to 5, averaged at pH 4. Adsorption varies with pH of the peat suspension and depends on the specific sorbates. For PCP, the maximum adsorption occurs at pH 2 to 6, with decreasing adsorption capacity at pH >7 (Viraraghavan 1993). Batch kinetic studies show that the sorption process is fast. Column studies are on-going, and these studies will yield information on residence time, etc. The kinetic information from a column study will help in designing a treatment module. It is estimated that the height of a treatment module does not need to be very long, based on the fast kinetics.

3. Mechanism of VOC Treatment: Most studies indicate that removal of VOCs from peat suspension results from adsorption and absorption. When using a mixture of peat and elemental iron, chemical reduction can also be involved. The reductive dechlorination of halogen compounds by elemental iron is being studied at several universities and private and federal laboratories (N. Korte, ORNL, and J. Clausen, MMES PGDP, personal communication with L. Liang, ORNL).

4. Mechanism of Radionuclide Treatment: Analogous to other heavy-metal removal, adsorption and absorption of Tc are the major mechanisms. In oxygenated environments, Tc is present as TcO_4^- , which does not adsorb well on soils. Studies are needed to evaluate sorption of Tc by peat. When using a mixture of peat and elemental iron, Tc(VII) is reduced to Tc(IV), which precipitates out as TcO_2 and may be adsorbed by the iron/peat mixture.

5. Treatment Efficiencies Expected and Reliability: The high capacity of peat indicates that the treatment will be efficient. There is not much information on desorption of organic compounds and heavy metals. We are planning to test the reversibility of desorption and desorption kinetics and evaluate the longevity of the treatment process.

6. Limiting Conditions and Interferences: Peat in water will produce dissolved organic compounds (DOC). How these DOC interact with metals and VOCs needs to be evaluated. The by-products of iron filings in peat/iron mixture has yet to be evaluated.

7. Stage of Development: The technology is presently at bench scale. A pilot demonstration is being conducted at WAG5 seeps.

8. Processing Capacities and Rates: The capacity is discussed above in No. 2. Peat can be packaged in any dimension. For the WAG5 demonstration, we have packaged peat into a 6 in. x 4 in. cylindrical column. Resistance through peat is high when peat is tightly packed. For a 20-in. water head, a 2 L/h flow rate is maintained. Another column was filled with 1-in.-diameter peat balls to increase the permeability of the treatment column. For the same water head, the flow rate in this column was increased by 5 orders of magnitude.

9. Chemicals or Other Treatment Agents Required: pH-buffering chemicals may be needed depending on the optimal treatment pH, the groundwater pH, and alkalinity.

10. Secondary Waste Streams Produced: Spent sorbent cartridges are produced. If both Tc and VOCs are adsorbed onto the cartridges, the spent cartridges will be considered mixed waste. Since the bulk material of peat is combustible, it is possible to incinerate these, and a small residue of concentrated Tc can be collected for disposal. This type of research is needed for the eventual application.

11. Utility Requirements: The peat or peat/iron mixture will be packaged as cartridges; the process represents a system with no moving parts. Thus, there are no special utility requirements.

12. Monitoring Requirements: Based on current knowledge, no additional monitoring is required if periodic samples are taken from wells for measurement of influent and effluent concentrations. Monitoring of flow rates and system back pressure will be helpful to evaluate the performance of the system (detection of clogging).

13. Operation and Maintenance Requirements: Further pilot-scale testing is needed to assess the capacity of peat and peat mixtures. Operation and maintenance requirements can then be determined. The bench-scale study indicates that peat has high capacity and that the absorbent does not need frequent changing.

14. Potential Environmental Impact Risks: Peat produces dissolved organic matter in water. However, these organic compounds are naturally occurring.

15. Potential Safety Risks: Peat is flammable, but not explosive.

16. Process Capital and Operating Costs: There are no data available. The peat material itself is very cheap, and iron filings are relatively cheap. The overall cost is expected to be low.

17. Case Histories: Not identified.

18. Potential Vendors/Providers: There are commercial vendors for peat and packages for sorbing oil spill (Harmon, AL). We are working on packaging of peat for *in situ* remediation. We have tried several geotextiles, as well as nylon screen materials.

19. References and Contacts:

Contacts:

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Guidry, SphagSorb, Wilson Associates, Oak Ridge, Tennessee

D. B. Steele, Harmon Bio-natural Corporation, LaFayette, Alabama

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Biodegradation of VOCs
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1. Process Name and Type: Cometabolic and anaerobic biodegradation of VOCs

2. Process Description: There are several applications for biological degradation in the proposed downhole treatment module, including surface treatment of the off-gas, *in situ* treatment of the aquifer surrounding the treatment module, and biotreatment within the module. The biological processes would be fundamentally similar, but with the present state of the art, much more control and, thus, confidence in the results could be expected with the surface-treatment units. Logistically, there are some problems with the *in situ* method, but engineering problems should be minor. Problems with the *in situ* method relate to control of the biological process, particularly the achievement and maintenance of high levels of activity. Biological treatment of TCE must be by cometabolic processes (Little et al. 1988; Palumbo et al. 1991) or by anaerobic degradation (Vargas and Ahlert 1987; Vogel et al. 1987). These problems are much more tractable with a surface unit that is treating only the off-gas since groundwater does not contact the populations. Also, monitoring is easier, and cultures can be maintained on site to rapidly re-inoculate the reactor if necessary.

The utilization of aromatic degraders (Folsom and Chapman 1991; Roy 1991) for the cometabolic processes would result in better control of degradation activity than use of the methanotrophs (e.g., due to effects of copper on activity of the methanotrophs). However, use of the aromatic degraders may require addition of a potential hazardous substrate for induction of the enzyme activity. On the other hand, some of the other treatment processes (e.g., use of peat) may result in addition of substrates that could induce TCE degradation. Thus, biotreatment should be evaluated in combination with these to determine if additional attention to biotreatment could result in more efficient or more rapid remediation.

The potential for generation of vinyl chloride and the potential slow rates of dechlorination are disadvantages of the anaerobic process. The advantage is the much higher concentrations of VOC that could be treated. It should be possible to add one of the cometabolic processes as a low-cost first step, probably in conjunction with other technologies for the removal of TCE, with polishing of the off-gas occurring at the surface as either a biological or non-biological process.

3. Mechanisms of VOC Treatment: Three mechanisms are possible for biodegradation of TCE. The first two are aerobic, cometabolic processes (with methanotrophs or with aromatic degraders), and the third is anaerobic dechlorination. The aerobic processes depend on the production of an oxygenase enzyme by bacteria utilizing a substrate other than TCE for growth and induction of the enzyme. The anaerobic process would require addition of a carbon and energy source, such as a simple organic compound (formate, methanol, acetate). The potential exists for using a relatively impure, lower-cost product, but some development work would be needed. Maximum control of the process *in situ* would require constant addition of highly active cells grown at the surface. However, this approach is likely to result in plugging of the aquifer. All the *in situ* approaches would also likely require addition of inorganic nutrients. Nutrient additions could be manipulated to minimize the competitive inhibition that could occur with the use of ammonia as a nitrogen source. Lack of nitrogen in the nutrient addition could result in selection for type two methanotrophs that fix nitrogen and also degrade TCE effectively. Nutrients could be added as part of an air stripping procedure by use of volatile compounds such as triethyl phosphate and nitrous oxide. Use of peat as an adsorbent for the radionuclides would provide a prime environment for promotion of TCE degradation. Bioremediation can be an effective process, but there are significant concerns associated with this technology (Hoyle 1993; Thayer 1991; Thomas and Ward 1989).

4. Mechanisms of Radionuclide Treatment: Adsorption to biomass may be possible, but is speculative and not necessarily a significant improvement over adsorption by non-living (e.g., peat) or non-biological products.

5. Treatment Efficiencies Expected and Reliability: Concentrations of TCE can be reduced in the laboratory to less than 2 ppb. This has not been proven in the field, but may have been achieved in off-gas units and has been achieved in localized wells at the SRS demonstration using a combination of air stripping and biological treatment. This is an experimental technology and should be backed up by a polishing system. This would be an effective test of bioremediation in the field under conditions most likely to result in data that can be evaluated for effectiveness.

6. Limiting Conditions and Interferences: For aerobic degradation, concentrations of TCE significantly above 10 ppm will become toxic and, thus, will be limiting. Copper concentrations above 4 μM will decrease TCE degradation by methanotrophs by 100x by shifting production of the oxygenase from the soluble to the less-active particulate form. For optimal maintenance of the methane monooxygenase enzyme, concentrations of oxygen should be less than atmospheric (> 10% O_2 would be a good starting point).

7. Stage of Development: Pilot-scale surface-treatment units have been demonstrated. The most robust units are probably units that could be used to treat the off-gas. *In situ* treatment has been demonstrated via injection of methane as part of the SRS integrated demonstration. The effectiveness of TCE degradation in this demonstration is still being evaluated, but preliminary evidence (e.g., increases in chloride concentration) indicates that biodegradation was occurring. According to preliminary evaluations, biotreatment costs are small, incremental add-on to the costs associated with air stripping using horizontal wells, and even small amounts of biodegradation (e.g., 5% of total TCE) are cost-effective.

8. Processing Capacities and Rates: Rapid degradation (less than 1 h) of 5 to 10 ppm of TCE has been demonstrated in cometabolic processes at the laboratory. However, this is with optimized cultures and is probably not applicable to cultures grown *in situ*. Rates are usually significantly slower with anaerobic processes.

9. Chemicals or Other Treatment Agents Required: A growth substrate and inducer (may be the same compound) must be added for the cometabolic processes. For methanotrophs, this would be methane. For the aromatic degraders, this would be either an aromatic inducer (e.g., phenol) or possibly a "natural inducer" that could be present in the groundwater, in the soil, or in a component of another treatment process (e.g., peat). Additional nutrients, primarily nitrogen and phosphorous, may be needed.

10. Secondary Waste Streams Produced: There could be a small quantity of sludge produced by surface bioreactors.

11. Utility Requirements: There are minimal requirements for pumps and electricity to add nutrients and inducers.

12. Monitoring Requirements: Monitoring requirements would depend on the technology applied. Requirements would be minimal with surface-treatment units or with treatment within a module. Requirements for monitoring would be more substantial if the effort is focused on increasing rates of degradation in the surrounding aquifer material.

13. Operation and Maintenance Requirements: Requirements vary depending on the type of biological treatment examined. Methanotrophs would require a constant supply of methane at levels of 3% of the incoming air. Use of aromatic degraders would require addition of a growth substrate that could act as an inducer. This would likely have to be an aromatic such as toluene or phenol. Addition of these compounds should present no real risk since they would be rapidly consumed by the bacteria. However, permission to add these compounds may be difficult to obtain. Thus, natural inducers should be investigated.

14. Potential Environmental Impact Risks: If anaerobic methods are chosen, there may be significant alterations in groundwater chemistry. Metals may be mobilized. Also, incomplete degradation of the VOC could result in production of vinyl chloride. Complete dechlorination would result in production of ethylene at concentrations equal to the original TCE concentration. Potential exists for loss of the inducer (toluene or phenol) to the aquifer. This risk should be minimal, but concentrations would have to be monitored to guard against a catastrophic event (e.g., a toxic slug of TCE) that eliminated the bacteria utilizing the inducer. With uncontrolled growth of the bacterial population, there is potential for plugging of the well.

15. Potential Safety Risks: Presence of methane at the site is a potential safety risk. Risks could be minimized by using only premixed gas at less than 3% methane. Use of aromatic inducers could also represent a safety risk.

16. Process Capital and Operating Costs: No specifics are available. These will depend on the process chosen. Minimal costs would be associated with the cometabolic aromatic degraders. Higher costs would be associated with the methanotrophs due to requirements for handling of methane gas. Higher costs for anaerobic option would result from added costs for growth substrates and monitoring (due to potential production of undersized by-products). As an add-on to another process, the biotreatment option could have very low incremental costs.

17. Case Histories: There are no good data on *in situ* application. Data at SRL are being evaluated, but the open nature of the system makes data interpretation difficult. Preliminary evidence indicates that biodegradation was promoted in the subsurface and that most of the TCE removal was by air stripping. The biocomponent appeared to add a benefit that was higher than the incremental costs associated with the addition of methane and nutrients to promote the *in situ* TCE degradation. There is much anecdotal evidence for surface treatment units that could be used to treat the off-gas.

18. Potential Vendors/Providers: Environgen, Ecova, and a host of other potential vendors.

19. References and Contacts:

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Contacts:

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Surfactant-Enhanced Bioremediation

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1. Process Name and Type: Surfactant- and biosurfactant-enhanced contaminant desorption for *in situ* mineralization.

2. Process Description: This process involves the addition of surfactant compounds into the groundwater region for contaminant solubilization from the soil matrix. In doing so, the contaminant is more available for either removal from the aquifer, i.e., soil washing, or for enhanced *in situ* degradation. Surfactant-enhanced desorption is not a stand-alone technology; however, it can potentially enhance the effectiveness of other treatment technologies.

Surfactant addition can follow one or two methods. First, a synthetic surfactant or microbially produced biosurfactant would be introduced into the aquifer to enhance solubilization of the contaminants. The second method would be selective stimulation of the indigenous microorganisms to produce biosurfactants. Regardless of the method, this process could increase contaminant solubilization for either *in situ* remediation or removal for above-ground treatment.

The necessary surfactant concentration will depend upon the contaminant concentration and the goal of either soil washing/soil venting or *in situ* remediation. It will be necessary to use higher concentration of surfactant should recovery of the contaminants aboveground be preferred. If *in situ* TCE degradation is the primary goal, then a lower concentration of surfactant would be needed, and it is likely that additional nutrients will be needed to support microbial metabolism.

Limited work has examined the interaction between biosurfactants and radionuclides. However, microbial-produced exopolymers that function as chelators may alter the mobility of metals and radionuclides and facilitate soil washing techniques (Rudd et al. 1984).

3. Mechanisms of VOC Treatment: A primary problem with contaminant biological treatment is low solubility or sorption to the soil matrix. Since biodegradation takes place in the liquid phase, insoluble contaminants are usually not available for microbial degradation. Thus, even if all other parameters are optimized, the rates of degradation are often limited by mass-transfer problems.

Synthetic surfactants, although quite expensive, can increase solubilization rates and render organics more amenable to pump-and-treat technologies. The addition of surfactants and biosurfactants into contaminated soils is known to increase desorption rates. Synthetic surfactants have been used in soil washing technologies at concentrations greater than the critical micelle concentration (CMC) (Abdul et al. 1992). The contaminants are associated with the surfactants or locked within a micelle and are thus transported to the surface for remediation. However, surfactants at these concentrations, can reduce microbial degradation rates. Recent reports have discussed using surfactants at concentrations below the CMC to obtain increased degradation rates (Aronstein and Alexander 1992). The surfactant concentration is critical to maintaining contaminant bioavailability. We have determined that both surfactants and biosurfactants can increase the degradation of toluene and naphthalene in both the aqueous phase and soil slurries if added below the CMC (Strong-Gunderson et al. 1993).

Biosurfactants and some synthetic surfactants are biodegradable, which could be a concern for *in situ* remediation if these compounds were preferred as a carbon source over the contaminant material. However, this is also an attractive feature since once their job is done, i.e., contaminant desorption, they are not persistent within the aquifer.

In situ bioremediation techniques provide several substantial advantages for removal of organics. When bioremediation proceeds to complete mineralization, contaminants are permanently removed rather than transferred from the subsurface to another medium. *In situ* bioremediation processes can effectively treat the unsaturated soil zone, as well as the groundwater, and minimize disruption to aboveground operations.

4. Mechanisms of Radionuclide Treatment: The effects of surfactant addition to systems containing radionuclides is currently unknown.

5. Treatment Efficiencies Expected and Reliability: Bench-scale experiments of toluene and naphthalene degradation show a significantly enhanced rate of degradation following the addition of biosurfactants (Strong-Gunderson et al. 1993). These experiments have not been tested at a pilot-scale level; however, it is anticipated that degradation rates would be enhanced.

6. Limiting Conditions and Interferences: The addition of surfactants can stimulate the microbiological community by increasing the rates of TCE degradation. This increase in community activity has a potential to affect pore spaces and plugging. However, since surfactants can temporarily (hours) make the contaminant unavailable for degradation, it may be possible to "transport" the surfactant-contaminant complex away from the injection port (meters) for degradation in a "remote" site. This increased transport would increase the treatment zone and decrease well-head plugging.

7. Stage of Development: Some literature is available for the successful use of surfactants in soil washing technologies. In these cases surfactants are used at high concentrations (>CMC). Recent reports suggest enhanced contaminant degradation with low concentration of surfactant addition. To date, this work has primarily been at the bench scale.

8. Processing Capacities and Rates: The desorption rates will be dependent on the surfactant concentrations used. Concentrations at the CMC will facilitate the fastest solubilization rates, but will inversely affect the degradation rates. Utilizing surfactants and/or biosurfactants for remediation will shorten the required treatment time by significantly attenuating the "time-release" source of contamination from the soil matrix while remediating the groundwater.

9. Chemicals or Other Treatment Agents Required: This type of treatment will stimulate the microbiological community, thereby adding metabolic by-products to the subsurface. This technology will require the addition of inorganic nutrients (NPK) for *in situ* remediation.

10. Secondary Waste Streams Produced: None are known or anticipated. Once in operation, all organic degradation will be below the surface. No secondary treatments, adsorbent regeneration, or landfill disposals will be required. Furthermore, none of the materials required for operation is expected to cause equipment deterioration.

11. Utility Requirements: Standard utilities of operational field sites, such as electricity and water, will be required. Surfactant compounds will be added and samples obtained and analyzed on site.

12. Monitoring Requirements (other than routine sampling): During surfactant delivery, the surface tension of the groundwater will need to be periodically monitored to determine the surfactant feed rates. This process is very simple and requires little training and minimal equipment. If biosurfactants are to be used, they will be prepared off site and shipped to the injection facilities.

13. Operation and Maintenance Requirements: Site technicians will be used to add surfactant compounds and monitor the groundwater surface tension. The operating system for these methods will be of simple design, consisting of storage tanks and pumps and associated instrumentation. Implementation of the system will require the standard drilling of multiple delivery wells; outside of general site operation, there should be no unique technical support demands.

14. Potential Environmental Impact Risks: None are known or anticipated. Synthetic surfactants will be chosen for their low toxicity and finite environmental persistence. The benefits of *in situ* remediation via the selective stimulation of indigenous biosurfactant-producing microorganisms will eliminate the concern over using genetically engineered bacteria. These biosurfactants will not persist once stimulation conditions are terminated and the aquifer is permitted to return to "normal" conditions.

15. Potential Safety Risks: None are known or anticipated. The environmental advantage of an *in situ* approach for treating contaminated aquifers is general site containment. Contaminated material is not pumped aboveground, thus minimizing cleanup and personnel exposure and avoiding the transfer of contaminated materials to landfills.

16. Process Capital and Operating Costs: The costs of commercially available synthetic surfactants will vary depending on the type and concentrations used. One of the more common surfactants, Tween 80, costs about \$200 for 3 L. This is generally used at a concentration of less than 1%. Biosurfactants, if used as pure compound, would be too expensive; therefore, they would be used as cell free supernatant, a process that is becoming increasingly popular. The primary costs involved in producing biosurfactant are media nutrient requirements and fermentors.

17. Case Histories: Surfactants have been used in soil washing technologies with varying degrees of success. Large-scale demonstration of biosurfactants *in situ* has not been reported.

18. Potential Vendors/Providers: Materials are available from numerous vendors.

19. References and Contacts:

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Reduction/Sorption of Technetium-99 and Uranium VI by Aluminum and Magnetite

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1. Process Name and Type: Aluminum and magnetite reduction of technetium-99 and uranium VI in modular cells.

Reaction Type: Reduction/adsorption

2. Process Description: In this proposed process, Tc(VII) is reduced to insoluble Tc(IV) using aluminum metal and/or magnetite, which function as chemical reductants. The reduced products are trapped in a porous magnetite that maintains reducing conditions. The insoluble technetium is adsorbed on the magnetite surfaces until removed from the well. Any uranyl carbonate in the groundwater would also be reduced from the hexavalent soluble to the tetravalent insoluble state and precipitate due to hydrolysis, reporting to the magnetite module for removal also.

3. Mechanism(s) of VOC Treatment: Not applicable.

4. Mechanisms of Radionuclide Treatment: Technetium-99 is known to be a very mobile species, due partly to its ability to retain a negative charge as the weak oxidant, pertechnetate anion, TcO_4^- (Paquette et al. 1990). This species is analogous to permanganate, which is readily reduced to insoluble manganese dioxide in neutral to alkaline pH regimes and the manganous form in low pH environments. Likewise, the pertechnetate anion can be readily reduced to an insoluble, hydrated oxide such as $\text{TcO}(\text{OH})_2$, which may exist in equilibrium with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$.

The drinking water limit concentration for this radioelement is $2 \times 10^{-7} \text{ M}$ (10 CFR 60, Appendix B) and at a pH of 7 and below an oxidation potential of +0.2 volts, the concentration of technetium will be below this limit (Isherwood 1985; Rard 1983). Otherwise, the pertechnetate anion is not prone to hydrolysis, is very soluble, and is calculated to have a sodium form solubility of 11.30 M (Boyd 1978).

In underground water, it is the couple between Fe(III) and Fe(II) that is believed responsible for controlling redox conditions, due to the presence of minerals such as biotite, chlorite, and hornblende. In reducing water with low O_2 partial pressures, the hematite-magnetite redox

buffer is thought to be controlling and may be present by reaction 1:

with the potential in mV versus the SHE given by

$$E = 0.214 - 0.059 \text{ pH @ } 25^\circ\text{C} \quad (2)$$

At a pH of 6.5, we can expect a potential of approximately -0.2 mv, which is sufficiently reducing to be able to reduce Tc(VII) to Tc(IV) in groundwater. Under anaerobic conditions, magnetite has been shown to reduce and irreversibly adsorb Tc from solution at room temperature (Haines et al. 1987).

Maintaining a localized pocket of anaerobic conditions is the most important controlling parameter. The maintenance of a localized reducing environment is aided by the presence of the aluminum bed module located below the magnetite module. Because aluminum is not stable in water, it will slowly react, releasing three moles of electrons per mole of aluminum, and also produce small amounts of hydrogen gas, depending upon the pH and surface area. Any U (IV) in the groundwater, likely present as uranyl carbonate, will also be reduced, will hydrolyze, and then will report to the magnetite module for collection with the Tc.

The aluminum will also reduce some portion of the Tc as it passes through the aluminum bed; however, the magnetite module will be able to reduce and adsorb this radioelement without the need for the aluminum. Technetium (VII) reaching the magnetite module will be reduced at the surface by oxidation of ferrous iron to ferric, forming a Fe_2O_3 (hematite) coating on the magnetite until its utility is diminished and replacement is required. Experimental work would be performed with and without the aluminum pellet module shown in Fig. 1.

5. Treatment Efficiencies Expected and Reliability: The process is expected to be very reliable since it does not employ any moving parts. We do not believe that we will be able to lower the ^{99}Tc activity to below $2.0 \text{ E-}7 \text{ M}$. Aluminum metal has been used to reduce ^{99}Tc in ORNL pond waters to a level at which it could be counted only using very long count times (Taylor/Mattus) in the presence of oxygenated water. Since the groundwaters contain as much as 0.2 ppm dissolved oxygen, an inert sparging gas such as nitrogen would aid in lowering the amount of dissolved oxygen and as a result, improve efficiency as long as gas-pocket blinding of metal and oxide surfaces does not occur.

Uranium and Technetium-99 Recovery Modules

Fig. 1. Schematic representation of the uranium and technetium recovery module.

RMODULE

6. Limiting Conditions and Interferences: The only species added to the groundwater may be small amounts of hydrated aluminum (gibbsite), which, if able to pass through the magnetite bed before its useful life is expended, could enter the aquifer. It is, therefore, a dual purpose of the magnetite bed to offer chemically reducing conditions and surfaces and pores to remove this hydrate. Initially, amorphous gibbsite will age to crystalline products that will no longer cause a problem in an aquifer, such as reaction with alkaline earth cations.

7. Stage of Development: The technology is presently at bench-top status (Mattus et al. 1993).

8. Processing Capacities and Rates: At higher pH (> 11.5), the reaction is nearly instantaneous; however, at pH 6.5, it is unknown and will be a function of the specific surface area of both the aluminum and magnetite particles. Water and gas bypass tubes pass through the proposed modules to enable 1) higher flow rates with little pressure drop and 2) the removal of hydrogen gas, which could otherwise blind pores from having contact with water, as shown in Fig. 1.

9. Chemicals or Other Treatment Agents Required: No chemicals would be released to the aquifer.

10. Secondary Waste Streams Produced: The only secondary waste produced is the magnetite bed module, which would be periodically removed with its Tc and U contents.

11. Utility Requirements: No utilities are required except for a blower aboveground to vent low concentrations of hydrogen gas and pumps to move aquifer water through the modules.

12. Monitoring Requirements: The actual field-use equipment will require only periodic analysis of aquifer recharge water for uranium, soluble aluminum, pH, and ^{99}Tc in order to predict magnetite saturation or plugging.

13. Operation and Maintenance Requirements: These will depend upon the aquifer flow rate and module size; they are presently unknown.

14. Potential Environmental Impact Risks: Only nonhazardous metals and oxides of iron and aluminum are used or formed in the process. These are natural components of the earth's biosphere and are nontoxic to both flora and fauna.

15. Potential Safety Risks: There are no known safety risks. It is expected that the rate of hydrogen production from aluminum reaction with water will be slow enough to be well below hydrogen's explosive limit in air, which ranges between 18.3 to 59%, and well below its flammability limit of 4% by volume.

16. Process Capital and Operating Costs: The materials and simplicity of the process mean that both capital and operating costs will be very low. No cost per liter of groundwater treated can be assigned presently, but is likely to be very low.

17. Case Histories: The author has a patent pending on the use of aluminum metal to reduce nitrate and nitrite to ammonia gas at greater than 90% efficiency and understands the chemistry and interaction with these species and water. Limited tests have already been performed by Paul Taylor (1991) at the author's direction using ^{99}Tc contained in ORNL pond water, with better results than with any other removal techniques employed. In this work, water containing 38 Bq/L of ^{99}Tc was reduced to 3 Bq/L for a 92% reduction under less-than-favorable conditions. Applicability to *in situ* use in aquifer water is simply a matter of laboratory and field testing specific to groundwater chemistry and flow rates.

18. Potential Vendors/Providers: None are known.

19. References and Contacts:

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Note that the above may contain potentially patentable concepts or ideas and should not be disseminated to non-Martin Marietta Energy Systems (MMES) personnel without first checking with MMES legal council and the author.

Photocatalytic Membrane
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1. Process Name and Type: Photocatalytic membrane

2. Process Description: Circulating groundwater is passed through a cylindrical inorganic membrane, or bundle of membranes, whose photocatalytic properties are associated with the use of titanium dioxide in the anatase form. The interior of each membrane cylinder is illuminated with near-UV (350-380 nm) fed by an optical fiber from a mercury arc lamp or other source located at the well head. Individual membrane tubes are approximately 0.5 in. in diameter and approximately one ft in length. The porosity of these tubes is controlled in manufacture to achieve an optimum combination of flow rate through the membrane wall and exposure of VOC molecules to the illuminated photocatalytic surface, with the design aim of 90% VOC destruction on a single flow pass. For a flow rate of 0.02 m³/min (5 gal/min), as listed in Table A.1, we try to achieve a module configuration of approximately 20-cm diameter and 40-cm length containing 40 to 50 individual membrane tubes in parallel at an input pressure of approx 10 psi. Light is transmitted to the module by either 1) a single fiber that is optically coupled by a splitter arrangement at the module head to individual fibers feeding each tube or 2) a fiber bundle split at the module. The entire inorganic membrane structure is mechanically rugged and cleanable by backflow.

The same or similar module can be located above the water table, where it can be used to remove and destroy VOC molecules in the return air stream (water-vapor saturated). Ollis et al. (1991) provide a recent overview of destruction of water contaminants by heterogeneous photocatalysis.

3. Mechanism of VOC Treatment: UV photons of wavelength less than 380 nm pump electrons from the ground state to the valence band when they strike the photocatalytic surface of the membrane tube. This creates electron-hole pairs that have a certain lifetime against recombination. Many VOC molecules, such as TCE, forced to pass through the photocatalytic surface react with OH radicals produced by the holes and are completely mineralized to H₂O, CO₂, and HCl. The efficiency of the process is enhanced by the presence of oxidizers such as dissolved O₂ or certain metal species that scavenge the initial electrons and prevent electron-hole recombination. The circulatory wells proposed appear to be favorable configurations for the photocatalytic process since adequate dissolved oxygen will be present due to the circulation of surface air through the system.

4. Mechanism of Radionuclide Treatment: The photocatalytic membrane is specifically designed for removal and mineralization of VOC molecules; however, it is known that the process can effectively remove certain dissolved metal species (e.g., noble metals). These are normally plated onto the membrane surface, which may eventually result in a decrease in photocatalytic efficiency. At present the effectiveness of such a membrane in removing species such as Sr, Cs, and Tc does not appear to be known. The criterion for photocatalytic removal has been given as a half-reaction standard reduction potential more positive than 0.3 eV (Prairie et al. 1993). If the value for Tc can be taken to be 0.738 eV (Meyer et al. 1987), the photocatalytic process should work well for Tc removal in the presence of VOCs or other reducing agents. The simultaneous removal of dissolved ^{99}Tc and mineralization of TCE is a very attractive potential feature of the photocatalytic process.

Very recently experiments have been carried out on TiO_2 suspensions in the laboratories of the Technical Division at the K-25 site. ^{99}Tc solutions simulating those to be found in aquifers at the Portsmouth, Ohio, site were used. The results showed rapid removal of ^{99}Tc from solution and deposition onto the anatase particles when both UV and TCE were present. In the absence of either TCE or UV, no deposition was observed. Under the conditions used, the ^{99}Tc rapidly redissolved and returned to solution once the UV was turned off. It is probable that the rate of redissolution can be controlled by solution pH or by other factors. Additional funding and further experimentation will be required to investigate this. However, it does now appear that the photocatalytic process as embodied in the membrane reactor described above should be capable of simultaneous *in situ* removal of VOCs and ^{99}Tc .

The fact that the VOC mineralization products are returned to the aquifer while the ^{99}Tc is transiently bound may be an advantage. The reactor could be periodically lifted up the borehole while maintaining UV illumination and then be placed in a receptacle at the surface. This container would receive the accumulated ^{99}Tc , which would redissolve once the UV illumination was turned off. The radioactively clean membrane reactor could then be lowered again into the aquifer for further *in situ* VOC destruction.

In addition to the photocatalytic action, it is possible that the filtering action of the membrane, and other surface interactions, may be effective in removing certain species. To maintain the efficiency of the module it may be necessary to remove particulate matter from the input stream by a filter. This pre-filter similarly could be an inorganic membrane, possibly fabricated of stainless steel or ceramic material. It would afford additional opportunities through chemical treatment or other means for removal of radioactive species.

5. Treatment Efficiencies Expected and Reliability: Efficiencies greater than 90% on a single pass are the design aim for photocatalytic complete mineralization of TCE at concentrations in water on the order of 300 mg/L or 300 ppm. Similar efficiencies are expected for most other common VOCs, although not for CCl_4 . The literature on the subject of photocatalysis using titanium dioxide in the anatase form is large, and many processes are

well documented (Ollis et al. 1991). The photocatalytic membrane itself is a new concept, presently being investigated in the Membrane Technology Department of the Technical Division at K-25. Patent applications are being considered by the DOE Patent Office at the present time.

The module should be reliable. The materials are inorganic and corrosion-resistant. The UV involved in the photocatalysis process should make the interior of the membrane tubes self-sterilizing for bacterial contamination and growth. Eventual blockage of membrane pores or the pre-filter could occur, depending on the clarity of the aquifer. It may be possible to design a reverse-flow cleaning system into the module to prolong down-hole life.

6. Limiting Conditions and Interferences: Photocatalytic mineralization of TCE produces HCl; however, at the expected TCE concentrations of ~300 ppm, groundwater chemistry or biology is not likely to be affected adversely. The well-aquifer interface will not be affected.

7. Stage of Development: A bench-scale photocatalysis test flow loop was built in FY93 and is in operation in building 1004L at K-25 (Membrane Technology Department, Technical Division). UV from a short-arc mercury vapor discharge is conveyed by an optical fiber to illuminate the interior of a photocatalytic membrane tube. The system permits independent control of cross flow and flow through the membrane. Photocatalytic destruction of TCE has been observed, and experiments are proceeding to optimize flow and membrane surface conditions. Scintillation equipment and qualified radiation laboratories are available in building K1006 at K-25 site for tests of Tc removal. Recent tests on TiO_2 suspensions have shown that the photocatalytic process will simultaneously remove both VOCs and ^{99}Tc , as described above. Flow loop tests of Tc removal by photocatalytic membrane designs will require additional funds.

Numerous experiments have been performed by others in which UV-illuminated TiO_2 (anatase) in slurry form or coated on surfaces has been used to mineralize TCE in aqueous solution. These experiments have extended to the demonstration scale in some cases. The slurry process suffers from the drawback that the photocatalytic particles must be subsequently recovered from the process stream, while in surface-coated reactor systems, the difficulty lies in ensuring efficient surface contact between the active photocatalytic surface sites and dissolved TCE molecules. The present system seeks to solve these problems by forcing the contaminated fluid through a membrane, which itself is photocatalytic.

The use of fiber optics to convey UV to the photocatalytic surface permits use of remote light sources. To our knowledge, no previous studies have employed fiber optics illumination. We have performed calculations and have made measurements of illumination distributions inside membrane cylinders illuminated by UV conveyed by a single fiber from a short-arc mercury discharge.

8. Processing Capacities and Rates: The photocatalytic membrane system may be scaled up and manufactured. The Membrane Department has expertise extending over 40 years in the design and manufacture of special inorganic membranes on pilot and industrial scales. Reaction rates for the photocatalytic membrane are presently being established using the test loop mentioned above; however, as stated in item 2, the design aim is for a bundle of tubes approximately 10 cm in total diameter and 40 cm in total length capable of complete mineralization of more than 90% of TCE molecules dissolved in water at 300 ppm in a single pass. This module would require fiber feed from two to three 1-kW (electrical) mercury arc lamps located at the surface.

9. Chemicals or Other Treatment Agents Required: None required.

10. Secondary Waste Streams Produced: Input filters may require replacement depending on their composition. The photocatalytic membrane structures are cleanable by reverse flow and unaffected by VOC mineralization. ⁹⁹Tc plated on the interior membrane surfaces can be redissolved at the surface and concentrated for disposal or storage. Waste volume would be minimized compared to, for example, sorption techniques.

11. Utility Requirements: Several kilowatts of electrical power (110 V ac) will be needed to power UV sources located at the surface and a submersible lamp.

12. Monitoring Requirements: The process does not require on-line or frequent monitoring. Periodic input and output samples from the well should be adequate.

13. Operation and Maintenance Requirements: Provided the aquifer is clear of particulate matter, or a pre-filter is used and does not block, maintenance requirements should be minimal. If the aquifer contains metals that are photocatalytically plated onto the reactive membrane surface, decreasing its efficiency for mineralization of TCE, eventual replacement of the unit may be necessary.

14. Potential Environmental Impact Risks: Complete photocatalytic mineralization of TCE in an aqueous environment produces three molecules of HCl per molecule of TCE destroyed. Depending on the aquifer chemistry, these chloride ions may be quickly neutralized or may migrate from the treatment point. The concentration produced is likely to be low and not of environmental significance.

15. Potential Safety Risks: Precautions are necessary with the high voltage and high temperatures associated with UV generation at the surface. Mercury arc lamps produce ozone that must be vented. Exposure of skin and eyes to high-intensity UV that may be present during setup must be prevented. ⁹⁹Tc removed by redissolution at the surface would require contamination-control precautions.

16. Process Capital and Operating Costs: These are dependant upon ongoing laboratory-scale tests. Note that technology is driving down fiber optics costs and that diode-pumped solid state laser costs are rapidly dropping and may become economic as power sources for this application (*Laser Focus World*, November 1993, p. 105). Such sources would have advantages in longevity and in fiber injection efficiency.

17. Case Histories: This is an original process; there are no available case histories.

18. Potential Vendors/Providers: No commercial vendors are known for complete systems. Commercial suppliers are available for all components except the photocatalytic membranes.

19. References and Contacts:

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- 327. D. D. Wodrich, H0-30, Westinghouse Hanford Company, PO Box 1970, Richland, WA 99352.
- 328. J. Bibler, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 329. T. Coleman, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 330. T. C. Hazen, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 331. K. Jerome, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 332. B. Looney, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 333. J. Steele, Westinghouse Savannah River Co., Savannah River Site, Aiken, SC 29808.
- 334. L. W. McClure, WINCO, Inc., PO Box 4000, MS 3211, Idaho Falls, ID 83415-3211.