Overview of Non-Thermal Mixed Waste Treatment Technologies

- **Treatment of Mixed Waste (*Ex Situ*)**
- **Technologies and Short Descriptions**

July 1995

**U.S. Department of Energy
Assistant Secretary for Environmental Management
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FOREWORD

This compendium contains brief summaries of new and developing non-thermal treatment technologies that are candidates for treating hazardous or mixed (hazardous plus low-level radioactive) wastes. It is written to be all-encompassing, sometimes including concepts that presently constitute little more than informed "ideas". It bounds the universe of existing technologies being thought about or considered for application on the treatment of such wastes. This compendium is intended to be the very first step in a winnowing process to identify non-thermal treatment systems that can be fashioned into complete "cradle-to-grave" systems for study. The purpose of the subsequent systems paper studies is to investigate the cost and likely performance of such systems treating a representative sample of U.S. Department of Energy (DOE) mixed low level wastes (MLLW). The studies are called Integrated Non-thermal Treatment Systems (INTS) Studies and are being conducted by the Office of Science and Technology (OST) of the Office of Environmental Management (EM) of the U.S. Department of Energy. Similar studies on Integrated Thermal Treatment Systems have recently been published. These are not designed nor intended to be a "downselection" of such technologies; rather, they are simply a systems evaluation of the likely costs and performance of various non-thermal technologies that have been arranged into systems to treat the sludges, organics, metals, soils, and debris prevalent in DOE MLLW.

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LIST OF ACRONYMS

ABS	aqueous biphasic separation
AECL	Atomic Energy of Canada Ltd.
AETS	acid extraction treatment system
ANL	Argonne National Laboratory
ARPA	Advanced Research Projects Agency
ART	alternative remedial technologies
As	arsenic
ASH	air-sparged hydroclone
Ba	barium
BCD	base-catalyzed decomposition
BIDU	bioisotope disposal unit
BNFL	British Nuclear Fuels Ltd.
BNL	Brookhaven National Laboratory
BTEX	benzene toluene ethylene xylene
Btu	British thermal unit
Ca	calcium
CBPC	chemically bonded phosphate ceramics
CCS	chromated copper arsenate
Cd	cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CIP	carbon-in-pulp
cm ²	centimeters squared
Co	cobalt
CO	carbon monoxide
CO ₂	carbon dioxide
CRADA	Cooperative Research and Development Agreement
Cs	cesium
CSS	coal sorbent system
CST	crystalline silicotitanates
Cu	copper
D ₂ O	heavy water
DDT	dichlorodiphenyl/trichloroethane
DETOX	Catalytical Chemical Oxidation (Delphi Process)
DNA	Defense Nuclear Agency
DoD	Department of Defense
DTPA	diethylnetriamine pentaatic acid
EDTA	ethylenediamine tetra acetate
EM	Environmental Management
EMR	electromembrane reactor
EPA	Environmental Protection Agency
FFCA	Federal Facilities Compliance Act
FCTAC	Freeze Crystallization Technologies Acquisition
Fe	iron
ft ³	cubic feet
g	gram or gallon
GAC	granulated activated carbon
gpm	gallons per minute

LIST OF ACRONYMS (continued)

SVOC	semivolatile organic compound
T ₂ O	tritium oxide
Tc	technetium
TCA	tetrachloroethane
TCDD	tetrachlorobibenzofurans
TCE	trichloroethylene
TCLP	Total Concentrate Leachate Procedure
TEA	triethylamine
TNT	trinitrotoluol
TRU	transuranic
TRUEX	transuranic extraction
TSD	treatment, storage, and disposal
TSG	technical support group
TSWG	tribal and stakeholder working group
UK	United Kingdom
UV	ultraviolet
VISITT	Vendor Information System on Innovative Treatment Technologies
VOC	volatile organic compounds
WHC	Westinghouse Hanford Corporation
WRF	white rot fungus
yd ³	cubic yards
Zn	zinc
Zr	zirconium
ZrO _x	zirconium oxides
°C	degrees Celsius
°F	degrees Fahrenheit

INTRODUCTION

This document is the result of initial investigations to identify currently available and developing non-thermal technologies that may be applicable to the treatment of mixed low-level wastes.

Non-thermal technologies are those processes where the primary chemical reaction proceeds at a temperature of less than 350° Centigrade.

Furthermore, technologies have been identified that fall into one of six broad categories: Destruction, Separation, Stabilization, Decontamination, Treatment Train and Air Pollution; each of which has several subcategories. Technologies are listed alphabetically in each category. The listing does not indicate any type of prioritization. Data included have not been verified and were taken from the promotor/developer/vendor at face value.

It is recognized that an identified technology may overlap or fall into more than one category, but for purposes of this study, it has been placed in one category or another. The intent was not to determine the appropriateness of the category in which it was placed, but rather to simply account for the candidate technology. Moreover, this is not meant to be a compendium of every fact about such technologies (often, data were extremely scarce, if existent) but merely an attempt to list all non-thermal technologies that could be obtained over a very short period of time.

In this document, an attempt has been made to identify all developing non-thermal treatment technologies that could possibly be applied to DOE mixed low-level waste; however, it is recognized that it is virtually impossible to include every single one in existence. If you feel strongly that an omitted technology should be included, please so indicate to Gary Knight of the Waste Policy Institute at (301) 990-3016.

Note: (1) *Mention of trade names or commercial products does not constitute endorsement or recommendation for use at any particular hazardous waste site.*

(2) *For costs provided, the basis of the cost estimates has not been evaluated nor validated. For each application, cost factors for type of waste form, process, and cost elements such as capital costs, operation and maintenance, life-cycle, administrative, and cost of money should be considered.*

BACKGROUND

In July 1994, the Idaho National Engineering Laboratory (INEL), under a contract from U.S. Department of Energy's Office of Science and Technology (OST, EM-50) within the Office of Environmental Management (EM), published a report entitled "Integrated Thermal Treatment System Study - Phase I Results" (EGG-MS-11211). This report was the culmination of over a year of analysis involving scientists and engineers from around the DOE complex. The stated purpose of that study was "to conduct a systematic engineering evaluation of a variety of DOE mixed low level waste (MLLW) treatment system alternatives." The study also "identified the research and development, demonstrations, and testing and evaluation needed to assure performance of the unit operations in the most promising alternative systems." This study evaluated ten primary thermal treatment technologies, that had been organized into complete "cradle-to-grave" systems (including complete engineering flow sheets) to treat DOE MLLW, and calculated mass balances and 20-year total life cycle costs for all systems. The waste input used was a representative heterogeneous mix of typical DOE MLLW.

The INEL has now published a Phase II (INEL-95/0129) to what has come to be known as the Integrated Thermal Treatment System (ITTS) study. This study conducted the same evaluations for an additional nine primary thermal treatment technologies, including some of the more advanced technologies presently being considered for funding by OST. Both Phase I and the Phase II reports were the subject of an internal DOE peer review panel conducted in November, 1994 (DOE/EM-0268). This Panel found that such systems analyses were extremely useful in helping DOE headquarters program managers, as well as field personnel, in evaluating costs and performances for candidate treatment systems. Two nonthermal technologies were included in the Phase II study. However, the panel "strongly" recommended:

...inclusion of other non-thermal organic destruction and thermal technologies not yet studied in order to put EM in the position of having carefully considered an appropriate range of treatment technologies on a comparable basis. *Additional non-thermal studies would be helpful for stakeholder considerations and could form the basis for later selection of specific technologies* (Italics supplied; p. 5 of "Integrated Thermal Treatment Systems Study", U.S. DOE, Internal Review Panel Report, April 1995, DOE/EM-0268).

Moreover, in its 1994 Annual Report, the Mixed Waste Working Group of the Western Governors Association gave the following advice:

D. STAKEHOLDER CONCERNS ABOUT THERMAL TECHNOLOGIES NEED TO BE ADDRESSED.

Thermal technologies, important treatment options for mixed waste, are controversial among many tribal representatives, public interest groups, and other stakeholders. The concerns about DOE's consideration of "thermal" technologies, including alternatives, should be addressed. A diverse group of stakeholders should be involved in a study of available and/or developing thermal and non-thermal technologies, including closed-loop systems, that address mixed waste treatment, reduction, remediation and disposal. A workshop should be convened to provide education and a forum for the productive discussion of barriers to thermal technologies posed by regulatory issues, laws, and standards and related stakeholder concerns. A forum would provide an opportunity for stakeholders to express concerns and clarify issues related to thermal versus non-thermal technologies. Data needs, technology modifications and other issues could be identified to address tribal and stakeholder concerns to enhance the potential for deployment of such technologies (p. 26 of "Annual Report 1994", Mixed Waste Working Group of the Western Governors Association).

A summary of nonthermal technologies is the first step in responding to that strong recommendation. The document summarizes over 200 nonthermal treatment technologies, including technologies for destruction, separation, stabilization, and decontamination -- and lists available air pollution control technologies which have been amply described in other OST-sponsored work. The next step will be for a group of technical experts from around the DOE complex to recommend which technologies should be included into a series of draft flowsheets based on a set of draft selection criteria, such as the Federal Facilities Compliance Act criteria. This technical group will be known as the Technical Support Group (TSG) and will be made up of representatives from the DOE and EPA, as well as a couple of technically-trained members of public and environmental interest groups.

The draft selection criteria and technology recommendations of the TSG will then be reviewed by a diversely representative tribal and stakeholder working group (known as the Tribal and Stakeholders Working Group or TSWG) to provide their recommendations, followed by a full-spectrum technical analysis to be performed by Morrison Knudsen Environmental Services, Inc. (MK), a firm used by both private and public sectors to do engineering analysis and design/costing work. MK will perform the same analyses (using substantially the same assumptions) on the formulated nonthermal treatment systems as it did on the thermal systems in the ITTS study. Both the technical and stakeholders working groups will then review MK's work and make recommendations concerning such systems. Finally, a DOE sponsored review group may "peer review" the work of both the TSG and the TSWG. The committee of the National Academy of Sciences looking at the OST program will also review the INTS draft.

After the reviews, a report will be issued providing comparative information on non-thermal and thermal systems for DOE mixed waste.

While risk is clearly a matter that receives consideration throughout the DOE complex when technology selections are made, the issue must first be fully discussed with stakeholders before detailed studies on risk are performed. Nevertheless, future plans have been laid for a comprehensive process risk study to evaluate risks for both thermal and non-thermal systems.

INTEGRATED NON-THERMAL TREATMENT SYSTEM (INTS) STUDY

PROBLEM

Existing mixed low-level waste and future DOE MLLW generated from remediation and waste treatment operations at DOE require treatment and stabilization for disposal by a method acceptable technically, economically, socially, and from a risk reduction and regulatory standpoint. While thermal technologies have either proven effective or shown promise in treating MLLW, there has been public concern over the possible environmental impacts of such thermal systems. Accordingly, there is a need for DOE to examine the performance of non-thermal systems on the same waste streams as were treated in the ITTS study and to compare performance and costs.

MISSION STATEMENT

Non-thermal systems are sought and evaluated in the INTS study that have the capability to process all types of MLLW as stored or arising from remediation and treatment of contaminated sites. Hazardous chemical content, radioactive content, and reusable or disposable content are converted into forms suitable for release to the environment, for reuse, or for disposal in sites typical of those required for commercial hazardous and nuclear disposal.

OBJECTIVES

1. Identify known candidate technologies and provide brief descriptions.
2. Screen the technologies against criteria (e.g., technical, public, and Federal Facilities Compliance Act) and document the rationale for application of the technology.
3. Conceptually, incorporate non-thermal technologies into a treatment system as was done in the OST ITTS studies and evaluate mass and volume balances as a measure of complexity, versatility, disposal volumes, safety, and costs.
4. Conceptually, explore specific attractive applications where the technologies could reduce costs and risks.
5. Identify research and development requirements for the most promising technologies used in the non-thermal systems.

PRODUCT

The INTS study will develop conceptual designs of systems using non-thermal technologies. The study will document the non-thermal technologies in a way that both technical promoters and stakeholders can recognize the application or lack of application to mixed waste treatment. The document will identify which technologies EM should or should not support with further development. As such, it will match problems with technical solutions as a system.

BASIS

INTS technologies must process the same wastes as identified by the ITTS at same rate (2900#/hr) with processes that operate at or below 350° C with total life cycle costs to include development, construction, operation and maintenance, D&D (of the processing and treatment facility), and residue disposal based on a 20-year operating period.

ORGANIZATION

Technical support contributors (TSCs) include scientists and engineers from Idaho National Engineering Laboratory, Waste Policy Institute, BDM, Inc., and Morrison Knudsen (MK) Environmental Services, Inc.

- Prepare proposed bases, draft criteria, technology summaries, cost estimates, etc.
- Prepare analyses and report based on recommendations and guidance

Technical Support Group (TSG) consists of members representative of DOE EM-30, 40, 60 and 50 views, EPA, and technical stakeholder representatives. The TSG will:

- Develop and use a recommended screening criteria and methodology for screening technologies and systems of technologies.
- Evaluate functional flowsheets, organize technologies according to their function, and screen and recommend technologies and systems of technologies that should be included in the INTS study. The rationale for selecting or rejecting a technology or system for further analysis must be documented.
- Develop guidelines by which systems of technologies can be evaluated. Guidelines may include costs, performances, risks, maturity, etc.
- Develop evaluation strategies for the systems to be analyzed in the INTS study that allow comparison with thermal treatment systems including definitions of waste stream compositions that are treatable by a technology, disposal strategies, application of versatile technologies or systems, and processing of special wastes.
- Serve as the technical resource for meetings with stakeholders.
- Assist in resolving stakeholder concerns and issues that must be addressed in the INTS study.
- Serve as the technical resource for a "peer review" meeting.
- Develop technical positions on the systems of technologies for tribal and stakeholder consideration.
- Review and comment on the draft iterations of the report on the INTS study.

- For those technologies that are supported by the TSG and TSWG for further development, recommend the most likely applications and the associated development work.
- Identify the wastes and percentages of DOE wastes that can be treated by the non-thermal technologies selected for further consideration.

Tribal and Stakeholder Working Group (TSWG) consists of volunteers from across the U.S.

- Reviews TSG recommendations on criteria, technologies, and systems and raises concerns, issues, etc. to be answered by the study. Recommends TSWG preference for systems of technologies to be included in the INTS study.

INTS Independent Peer Review Panel (To be determined)

- If created, reviews recommendations of TSG, TSWG, and INTS study document prepared by the TSCs. Recommends to OST and Mixed Waste Focus Area (MWFA) significant findings and development work needed to support favored system or systems and the component technologies.

1.0 DESTRUCTION TECHNOLOGIES

1.1 Biological Destruction

1.1.1 General

Biological treatment refers to the degradation and detoxification of organic wastes using microorganisms like bacteria and fungi. The end result of biological treatment is the conversion of the contaminant into biomass (more microorganisms) and byproducts (water and carbon dioxide, in the case of complete mineralization). Inorganic contaminants, such as radionuclides and heavy metals, will reside in the water effluent or the biomass.

Aqueous or organic liquid waste streams and soils have the most promise for biological treatment. For treatment of liquid wastes, two types of reactors are commonly used: the suspended growth systems and the fixed film systems. In suspended growth systems the aqueous waste stream is mixed in a reactor with the biologically active sludge mass of microorganisms for the requisite period of time to achieve destruction. In fixed film systems the microbial growth occurs on the surface of an inert, solid support matrix and the aqueous waste flows through the reactor in such a manner as to achieve good contact with the microorganisms attached to the solid surfaces.

Various organisms are available for treatment depending on the contaminants, the waste matrix, and other physical and chemical characteristics of the waste stream. Biological processes have been shown to have application to treatment of compounds such as chlorinated solvents, PCBs, and other aromatic and aliphatic hydrocarbons. However, biological systems may be sensitive to variations in the input stream and to toxic chemicals. The lack of successful full-scale systems and the inability to translate results from controlled laboratory conditions to field conditions have limited the use of biological systems for the treatment of hazardous and mixed waste.

Following are descriptions of general biological treatment processes; specific reactor design and use of specific organisms will depend on the waste characteristics. To our knowledge, biological systems that can be used in "any" application are not commercially available. Each system must be designed for the specific application.

1.1.2 Aerobic Reactors

Description Biological activity in the presence of oxygen is referred to as aerobic degradation and is carried out by microorganisms classified as aerobes. These organisms require the presence of oxygen for growth and substrate utilization. Stirred batch reactors contain either specially selected aerobic microorganisms or methanotrophic bacteria. The input stream must be treated to provide materials to support the growth and metabolism of the cells; often this involves adding micronutrients or a compound to promote the expression of an appropriate enzyme. The Zimpro Wastewater Treatment system combines biological treatment and powdered activated carbon. The Biotrol system reduced pentachlorophenol in water from 45 to 1 ppm, and achieved 96-99% removal of PCP. The Ecova system degraded 96% of the total soil-bound PAHs in 14 days. (Schwinkendorf, W.E., "Alternatives to Incineration Technical

Area Status Report," DOE/MWIP-26, April 1995, and EPA SITE Technology Profiles, 6th Edition, November 1993)

Waste Treated Aqueous streams containing low levels ($< 10,000$ ppm) of petroleum hydrocarbons and derivatives (aliphatic and polycyclic aromatic hydrocarbons, alcohols, ketones, and BTEX compounds); PCBs, halogenated aliphatics, and halogenated aromatics with limited chlorination; and nitroaromatics.

Residue Typically 40-50% of the aerobically degraded waste is converted to biomass; the remainder is converted to carbon dioxide and water. Metals, radionuclides and other inorganics remain with the aqueous effluent or are sorbed onto the biomass.

State of Development Typical municipal and industrial waste water systems use aerobic systems. Vendors of systems for specific applications are available such as Biotrol, Inc. for waste waters; and Ecova Corp. and Remediation Technologies, Inc. for soils and sludges. Allied Signal is developing a dual bioreactor. None provide systems for mixed waste or uncharacterized streams.

Cost Data Operating costs for the Biotrol system per 1,000 gallons were \$3.45 for a 5-gpm unit, and \$2.43 for a 30-gpm unit.

Issues Aerobic reactions are considerably faster than anaerobic systems, and are less likely to produce toxic intermediates which might accidentally be discharged. However, they cannot degrade very complex compounds, or waste streams with high contaminant levels, and are best used as a follow-up technology to anaerobic digestion. Effluent may not meet discharge requirements because of insufficient nutrients with decreased organic concentration. Culture viability may be a problem in a radioactive environment.

1.1.3 Anaerobic Reactors

Description Biological activity in the absence of oxygen is referred to as anaerobic degradation. One type of system is the fluidized bed reactor, employing bacteria immobilized on particulate matter such as alumina or coal, which permits the residence time and other contact parameters to be controlled very closely. The anaerobic reactions can be considered a valuable pretreatment to begin the destruction of especially resistant compounds. Soil contaminated with 2% TNT was treated to below detection limits by the J.R. Simplot process, and Dinoseb was reduced by $> 99.8\%$. (Schwinkendorf, W.E., "Alternatives to Incineration Technical Area Status Report," DOE/MWIP-26, April 1995, and EPA SITE Technology Profiles, 6th Edition, November 1993)

Waste Treated Aqueous streams containing low to moderate concentrations of polynuclear aromatics and highly chlorinated PCBs, halogenated aliphatics, and halogenated aromatics which are reduced in chlorine level. Facultative anaerobes can be used to denitrify aqueous streams, degrade cyanide, dehalogenate carbon tetrachloride, and reduce metals such as chromium and mercury.

Residue Typically 5-10% of the anaerobically degraded waste is converted to biomass; the remainder is converted to carbon dioxide, methane and water. Metals, radionuclides and other inorganics remain with the aqueous effluent or are sorbed onto the biomass. Typically some

toxic materials that have been incompletely degraded, such as less chlorinated organic species, remain in the effluent.

State of Development Several proprietary engineered processes are commercially available. All components, including bacteria, are readily available and there are many research efforts and pilot projects using some form of anaerobic digestion. The Biotrol, Inc. system can run under aerobic and anaerobic conditions and over 20 full-scale systems are installed. J.R. Simplot Company has a pilot-scale system for the degradation of dinoseb and TNT in soil.

Cost Data A 12 m³ mobile soil slurry reactor has been estimated to cost \$228,000 with an average operating cost of \$90/ton of soil.

Issues Effluent may not meet discharge requirements because of insufficient nutrients with decreased organic concentration. Large-scale systems are rare due in part to the sensitivity of the cultures to some toxic contaminants and changes in the input stream. Culture viability may be a problem in a radioactive environment.

1.1.3.1 EIMCO Biolift™ Slurry Reactor (Aerobic)

Description IT Corporation has used the EIMCO Biolift™ Slurry Reactor to successfully treat polynuclear aromatic hydrocarbons (PAH) in soil. During this project, IT will operate two 60-liter EIMCO Biolift™ Reactors and a 10-liter fermentation unit in semi-continuous, plug-flow mode. (IT Corporation/EPA SITE Technology Profile, 7th Edition, 11/94 EPA/540/R-94/526, pp. 350, 351)

Waste Treated This technology is applicable to PAH contaminated soils and sludges that can be readily excavated for slurry reactor treatment.

Residue The test objective is to achieve a less than 20% residue carcinogenic PAH.

State of Development IT's slurry reactor was accepted into the SITE Emerging Technology Program in 1993. Pilot scale investigation was planned in the Summer of 1994.

Cost Data Not available at this time.

Issues None identified at this time.

1.1.4 Biodechlorination

Description Most of the environmental contamination by PCBs is in the form of complex commercial mixtures containing > 60 different congeners with varying degrees of chlorination. Two classes of bacteria have been identified that biodegrade PCBs by different mechanisms including aerobic oxidative biodegradation and microbial reductive dechlorination under anaerobic conditions. Anaerobes, in general, leave the biphenyl rings intact while removing chlorines and leave less chlorinated derivatives. Aerobes, on the other hand, attack and destroy less chlorinated compounds including the ring structure. These two processes are complementary, and a two-step treatment process may permit the biological destruction of nearly all the PCB mixtures commonly used. (Schwinkendorf, W.E., "Alternatives to

Incineration Technical Area Status Report," DOE/MWIP-26, April 1995, and EPA SITE Technology Profiles, 6th Edition, November 1993)

Waste Treated Aqueous waste and soils contaminated with PCBs and chlorinated hydrocarbons.

Residue A two step process may produce carbon dioxide, methane, water, and an effluent containing chlorobenzoic acids, as well as chlorinated biomass described above for aerobic and anaerobic processes.

State of Development Allied Signal, Inc. has developed and demonstrated an ICB Biotreatment system that can be operated in an aerobic, anaerobic, or combined aerobic/anaerobic mode. It has been applied commercially to waste water containing a range of contaminants including PAHs, phenols, gasoline, chlorinated solvents and chlorobenzene. Pilot-scale tests demonstrated reduction of TCE from 100 ppm to low ppb levels.

Cost Data Not available at this time.

Issues Effluent may not meet discharge requirements because of insufficient nutrients with decreased organic concentration. Large-scale systems are rare due in part to the sensitivity of the anaerobic cultures to some toxic contaminants and changes in the input stream. Culture viability may be a problem in a radioactive environment.

1.1.5 Biotreatment

Description Nitrite and nitrate ions can be bacterially reduced to gaseous nitrogen by a variety of microorganisms in an anaerobic environment. An organic carbon source, such as acetic acid or calcium acetate, is needed to act as a hydrogen donor and to supply carbon for biological synthesis. (Brown, C.H. and W.E. Schwinkendorf, "Technical Area Status Report for Chemical/Physical Treatment, Vol. II," DOE/MWIP-8, August 1993)

Waste Treated Nitrated aqueous wastes streams. Wastes high in sodium content require dilution, and alkali wastes require neutralization.

Residue The products of Biotreatment are nitrogen gas, carbon dioxide, water, and a sludge containing calcium carbonate, aluminum hydroxide, and biomass.

State of Development Biological denitrification has been used at the Oak Ridge Y-12 Plant since 1976 to treat highly concentrated nitrate wastes. More dilute waste streams are being treated in fluidized-bed bioreactors at the Portsmouth Gaseous Diffusion Plant and the Fernald Feed Materials Plant. Biotreatment systems are often used in waste water treatment plants treating millions of gallons per day. All necessary equipment for these processes is currently available through commercial industry. Suppliers include BioGenesis, Inc. and Bio-Rem, Inc.

Cost Data Operating cost for the Y-12 plant bioreactor is about \$4/kg of NO_3^- ; capital cost was not specified.

Issues Sudden changes in the process chemistry will shock the bacteria and disrupt the process. Large amounts of acid may be required to neutralize alkali waste.

1.1.6 Biofiltration

Description Biofilters are a type of bioreactor specifically designed for the efficient biotreatment of gas and vapor streams. In a biofilter, the gas stream is passed over a medium on which microorganisms are growing; when the microbes come in contact with the gas or vapor, they degrade the contaminants. Biofiltration provides an advantage over more common liquid phase bioreactors in that contact between the microorganisms and the contaminants is not dependent on solubilization of the contaminated gas or vapor in water. Biofiltration offers an alternative to incineration or activated carbon sorption for the treatment of vapor vacuum extraction (VVE) off-gases. EG&G Rotron has developed a biofilter for the treatment of hydrocarbon off-gases, whereby the off-gas stream is passed through a bed of compost, soil, or peat, and microorganisms growing as a thin biofilm on the bed degrade the organic constituents of the gas stream.

Waste Treated Hydrocarbons such as BTEX compounds. Gasoline off-gas has been successfully treated using this system.

Residue None; contaminants are completely degraded to carbon dioxide and water.

State of Development EG&G Rotron's "Biocube™" has been demonstrated and commercialized. This aerobic biofilter received the R&D 100 Award in 1993. Removal efficiencies for a properly functioning unit are reported to approach 95%-99% depending on the particular application in question.

Cost Data Cost drivers for this system are large front and back end costs due to shipping of the unit to and from the site, installation, and decommissioning. Long use at a single site, for high concentrations of contaminants, dramatically improves the economics of the system. According to one preliminary cost analysis, treatment of BTEX compounds using the EG&G Rotron biofilter was estimated to cost approximately \$11/pound of BTEX destroyed, assuming multiple cycles of use of the filter at the same site.

Issues Biofilters for the treatment of halogenated hydrocarbons are still under development.

1.1.7 Bioscrubber

Description The bioscrubber technology digests hazardous organic emissions generated by soil, water, and air decontamination processes. The bioscrubber consists of a filter with an activated carbon medium that supports microbial growth. The filter removes biomass, supplies nutrients, and adds moisture.

Waste Treated Organic contaminants in airstreams from soil, water, or air decontamination processes.

Residue Carbon dioxide, water, and trace amounts of the original contaminants.

State of Development The technology was accepted into the SITE Emerging Technology Program in July 1990. Bench-scale bioscrubbers operated continuously for more than eleven months to treat an air stream with trace concentrations of toluene at about 10 to 20 ppm. The scrubbers accomplished a removal efficiency of greater than 95%. The project was completed in June 1993.

Cost Data Not available at this time.

Issues Pilot unit testing was accomplished at two standard cubic feet per minute. Additional tests are underway to confirm results at higher flow rates.

1.1.8 Composting

Description Composting is a controlled biological process by which biodegradable hazardous materials are converted by micro-organisms to innocuous byproducts. Soils are excavated and mixed with bulking agents and organic additives such as wood chips, animal and vegetative wastes to enhance the porosity of the mixture to be decomposed. Moisture content, pH, oxygenation, temperature, and carbon-to-nitrogen ratio must be maintained. Three process designs are used aerated static pile composting (compost is formed into piles and aerated with blowers or vacuum pumps), mechanically agitated in-vessel composting (compost is placed in a reactor vessel where it is mixed and aerated), and windrow composting (compost is placed in long piles and periodically mixed with mobile equipment). (Remediation Technologies Matrix and Guide, Fed Remediation Tech Roundtable, DOD/EPA/DOE 2nd Edition - 10/94)

Waste Treated Composting is relatively insensitive to toxicants but has not been widely used for hazardous waste applications; however, it is potentially applicable to soils, and sludges containing high levels of organic contaminants. Tests have demonstrated the ability to reduce concentrations and toxicity of explosives (TNT, RDX, and HMX), propellant, coal tar, and ethylene glycol. Specific contaminants amenable to treatment depend on the micro-organisms present, either naturally or added, and the ability to maintain the required environment.

Residue Potentially uncontrolled release of VOCs; and leachate containing heavy metals, radionuclides and unreacted organic material. The total volume of material is increased because of the addition of amendment material.

State of Development Demonstrated for specific applications involving contaminated soil. All materials and equipment are commercially available.

Cost Data Costs of composting soils using bioreactors has been estimated at \$200 to \$250 per ton. Estimated costs for windrow composting of 20,000 yd³ explosives contaminated soil is about \$190 per yd³. Capital costs were not identified.

Issues Leachate must be collected, substantial space is required, and VOC containment or treatment may be required. This is a slow process requiring weeks to months depending on the contaminant and concentration.

1.1.9 Enhanced Hydroponic Bioreactor

Description The Enhanced Hydroponic reactor is a completely enclosed bioreactor containing a subset of plants and much of the decontamination ability found in a natural wetland. The root system of the plants and the complex consortia they contain, in which most of the metabolism of toxins and immobilization of metals occurs, are mounted in a framework that facilitates the robotic harvesting of plant material. The reactor is enhanced by several additional technologies. The most notable of these are electrically driven biocatalysts to begin dechlorination of intractable compounds in the inlet stream, and an electrochemical immobilization of trace metals before discharge. (ANL Fact Sheet)

Waste Treated This process is applicable to dilute aqueous wastes. Metals, complex aromatic compounds, and volatile solvents are absorbed or degraded. Natural systems have demonstrated degradation of oils, dehalogenation of solvents, mineralization of aromatics, and removal of metals such as zinc, cadmium, copper, and uranium. Specific contaminants amenable to treatment depend on the micro-organisms present, either naturally or added, and the ability to maintain the required environment.

Residue Plant material containing heavy metals and radionuclides.

State of Development To date a complete system has not been deployed. Lower technology units are in commercial use to treat food waste and sewage.

Cost Data Not available at this time.

Issues Plant material must be harvested and treated. Metal and radionuclide uptake, organic mineralization, and long term performance need to be determined.

1.1.10 White Rot Fungus

Description Because of its lignin degrading and wood rotting enzymes, and secretion of chemicals such as hydrogen peroxide, white rot fungus (WRF) has been reported to degrade a wide variety of organic contaminants. Two treatment configurations have been tested, both of which require wood chip additives: aeration in an enclosed bioreactor, and an open system similar to composting. (Remediation Technologies Matrix and Guide, Fed Remediation Tech Roundtable, DOD/EPA/DOE 2nd Edition - 10/94)

Waste Treated Tests at the laboratory scale using pure cultures have demonstrated degradation of TNT, and low concentrations (<250 ppb) of PCBs have been degraded. Laboratory tests have shown degradation of lindane, benzo(a)pyrene, DDT and TCDD. High concentrations of TNT and PCP in soil have killed or limited the growth of WRF. However, information from a developer (Intech One-Eighty Corp. provided by the Mixed Waste Working Group of the Western Governors Association) indicates that the WRF are generally indifferent to the concentration of the contaminants.

Residue Biomass, adsorbed metals and radionuclides, and unreacted organics.

State of Development This technology is patented by Utah State University Foundation and licensed by Intech One-Eighty Corp. who is developing and marketing the technology. Tests by EPA and DOD under field conditions appear to be unfavorable. However, an application at

a 10,000 m³ site in Finland reduced pentachlorophenol from 700 ppm to < 10 ppm, and bench scale testing reduced TNT in soil from 2000 ppm to non-detectable levels in a few weeks.

Cost Data Costs are estimated at \$98 per m³ (\$75 per yd³).

Issues The process may be limited by contaminant concentrations and toxicity, competition from bacterial populations, and insufficient degradation of contaminants to meet cleanup standards. For the process to be viable, specific environmental conditions must be established and maintained. No data exists regarding the effect of radionuclides on the organisms.

1.2 Dehalogenation

1.2.1 General

Dehalogenation technologies are of generally two classes chemical dehalogenation, and photo-dehalogenation.

Chemical dehalogenation systems typically mix wastes with a dehalogenation reagent (typically an alkaline polyethylene glycolate, of which potassium ethylene glycolate is the most common) and heats them in a reactor vessel. The dehalogenation reaction replaces halogens with polyethylene glycol, rendering the compound non-hazardous and generating a chlorinated-liquid secondary waste stream. Destruction efficiencies were found to be greater than or equal to 99.9%.

Photo-dehalogenation systems use ultra-violet light in combination with a reducing environment to dehalogenate chlorinated, brominated, or iodinated organics. Dehalogenation reactions can occur in a solvent (e.g., water or alcohol), or mixed with a reducing gas (e.g., methane). The photochemical process is initiated by the absorption of ultra-violet light. When used in conjunction with the reducing environment, the halogen-organic bonds break thus forming non-volatile residue.

1.2.2 Chemical Dechlorination

1.2.2.1 Base-Catalyzed Decomposition Process

Description The base-catalyzed decomposition (BCD) process is a chemical dehalogenation technology that is initiated in a medium temperature thermal desorber. Materials contaminated with chlorinated organics are detoxified by the addition of chemicals which remove chlorine from the contaminant and replace it with hydrogen. Because the chlorinated organics have some volatility, there is a degree of volatilization that takes place in parallel with chemical dechlorination. (Risk Reduction Engineering Laboratory).

Waste Treated The process can treat soils, sediments, and sludges contaminated halogenated volatile organic compounds, halogenated semi-volatile organics, PCBs, pentachlorophenol, and dioxins and furans.

Residues Off-gases from the solids reactor are sent to a vapor recovery system where collected oils and dusts are treated with dechlorination reagents in a base-catalyzed liquid

reactor. Solids from the solids reactor are containerized for on/off-site disposal. Destruction efficiencies exceeding 99.99% have been achieved.

State of Development The process was successfully demonstrated at a Superfund site in 1993.

Cost Data The cost for full-scale operation is estimated to be \$270 per metric ton and does not include excavation, refilling, residue disposal, or analytical costs.

Issues High clay and moisture content will increase treatment costs.

1.2.2.2 Birch Process

Description In this process, soil contaminated with PCBs is slurried with excess liquid ammonia at ambient temperatures. A solution of calcium-ammonia is added to the slurry and agitated until the reaction is completed. Upon completion, the ammonia is flashed off and condensed. (A.L. Sandpiper).

Waste Treated Sandy, organic, and clay soils contaminated with PCBs have been successfully tested using this technology.

Residue The products of reaction are calcium chloride, calcium hydroxide, and the organic basis of the chlorinated waste (e.g. biphenyl). Destruction efficiencies exceeding 99.7% have been achieved.

State of Development A.L. Sandpiper, a small R&D company in Columbus, Ohio, has a patent on the process and has performed treatability studies for various clients using a bench-scale system.

Cost Data Not available at this time.

Issues Decontaminated soil may require some post-treatment such as washing the reaction products before disposal.

1.2.2.3 Dehalogenation (Glycolate)

Description In this technology an alkaline polyethylene glycol (APEG) reagent is used to dehalogenate halogenated aromatic compounds in a batch reactor. Potassium polyethylene glycol (KPEG) is the most common APEG reagent. In the APEG process the reaction causes the polyethylene glycol to replace halogen molecules and render the compound non-hazardous or less toxic. (EPA).

Waste Treated The target contaminant groups for glycolate dehalogenation are halogenated semi-volatile organic compounds and pesticides. It has also been successfully tested on PCBs.

Residues The APEG reagent dehalogenates the pollutant to form a glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble byproducts. Destruction efficiencies of 99.9% have been achieved.

State of Development The technology is in full scale production at several PCB contaminated sites.

Cost Data Costs to use APEG treatment are expected to be in a range of \$220 to \$550 per metric ton.

Issues

- The technology is generally not cost-effective for large waste volumes.
- Concentrations of chlorinated organics greater than 5% require large volumes of reagent.
- Media water content above 20% requires excessive reagent volume.

1.2.2.4 PCB- and Organochlorine-Contaminated Soil Detoxification

Description of Technology This technology uses an aprotic solvent, other reagents, and heat to dehalogenate polychlorinated biphenyls (PCB) to inert biphenyl and chloride salts. The reagent, consisting of a solvent and an inorganic alkali material, completely strips chlorine from the PCB molecule. (Trinity Environmental Technologies, Inc.)

Wastes Treated The process has treated PCB Arclor mixtures, specific PCB congeners, pentachlorophenols and individual chlorinated hydrocarbons.

After Treatment Residues Process produces no toxic or hazardous products. PCBs are completely dehalogenated.

State of Development Bench-scale with a modular pilot-scale processor planned.

Cost Data Not available at this time.

Issues None identified at this time.

1.2.3 Photo-Dehalogenation

1.2.3.1 Light Activated Reduction of Chemicals (LARC)

Description The LARC process uses UV light combined in a reducing environment to dehalogenate chlorinated, brominated, or iodated organics. LARC dehalogenation reactions are normally conducted in a basic water, alcohol, or hydrocarbon solvent. The solvent is used to extract the halogenated organics from the contaminated media (e.g., soil). The extract is then subjected to the LARC process and the solvent recycled to the extractor. (Arctech, Inc.)

Waste Treated Soils contaminated with halogenated organics.

Residue Typical reaction products include biphenyl and sodium chloride as the final products. No oxygenated derivatives such as dioxins or furans are formed.

State of Development Several bench- and pilot-scale demonstrations have been completed, and a mobile unit for soil decontamination is in development. This technology is being commercialized by Arctech, Inc.

Cost Data Cost estimates in a 1984 report for treatment of soils contaminated with 1,500 ppm PCBs were \$84.60 per ton including extraction costs.

Issues None identified at this time.

1.2.3.2 Reductive Photo-Dechlorination

Description This technology uses ultraviolet light in a reducing atmosphere to remove chlorine from chlorinated organic wastes. The chlorinated wastes are vaporized, mixed with a reducing gas such as hydrogen or methane, and passed into a photothermal chamber where the mixture is heated to a temperature that will sustain a chemical reaction that produces radicals that break the carbon-chlorine bonds. After a suitable residence time, HCl is scrubbed from the mixture, and the hydrocarbons can be recycled as an energy source to heat the reaction chamber. (M.L. Energia, Inc.)

Waste Treated The process is designed specifically to treat volatile chlorinated wastes in the gaseous state. Field applications include treatment of organic wastes produced from soil venting operations and from regeneration of activated carbon. The process can also be used to pretreat gas streams entering catalytic oxidation systems to reduce the chlorine content and thereby protect the catalyst against poisoning.

Residue Because chlorinated organics are destroyed in a reducing environment, process byproducts include hydrocarbons and HCl. Hydrocarbons produced from the dechlorination process include ethane, acetylene, ethylene, and methane.

State of Development The technology was accepted in to the EPA SITE program in 1992 with the objective to test the effectiveness of a pilot-scale system in treating wastes streams containing various chlorocarbons. A pilot-scale prototype unit is under construction.

Cost Data The estimated cost is less than \$1 per pound of treated chlorocarbon.

Issues None identified at this time.

1.3 Direct Chemical Oxidation of Organics

1.3.1 Acid Digestion

Description Acid-digestion systems are capable of treating a wide variety of waste streams containing hazardous organics. There are two basic acid-digestion processes; the sulfuric-acid digestion process developed by Westinghouse Hanford Company, and the phosphoric-acid process being developed by Westinghouse Savannah River Company. The sulfuric acid process is no longer receiving much attention as a candidate for organic waste treatment. Acid-digestion technology is an oxidation process carried out in a concentrated acid medium which functions to break carbon-hydrogen bonds in organic waste, and also acts as a corrosive on

metallic and non-metallic inorganic wastes. The phosphoric acid technology involves a wet-chemical process using nitric acid or nitric/phosphoric acid combination for the complete oxidation of organic and inorganic materials. SRTC is conducting research on a closed-loop wet chemical process for the complete oxidation of combustible solid waste and the decontamination of non-combustible solids. (Westinghouse Hanford and Savannah River)

Waste Treated Organic solids and liquids such as cellulose, rubber, plastic, resins, and sludges, and inorganic solids contaminated with organics.

Residue In the sulfuric acid digestion process, organics are converted to carbon dioxide, water, and other gaseous products, and the non-volatile inorganics form insoluble oxides and/or sulfate salts. The composition of the offgas consists of CO₂, CO, water, and HCl from the oxidation of the waste; entrained acid solution; and SO₂, NO₂, NO, N₂, and water from decomposition of the acids. Offgas from the phosphoric acid process will consist of large amounts of NO, NO_x, nitric acid mist, phosphoric acid mist, and halogen acids if halogens are present in the waste feed. Destruction efficiencies have been measured at 99.99%.

State of Development Westinghouse Hanford cold tested an acid-digestion pilot plant in the 1970s. Bench-scale testing has been conducted at the Savannah River Site.

Cost Data Not available at this time.

Issues

- The process may exhibit limitations when treating high-ash waste because of the large volume of residual wastes generated.
- Direct oxidation of most organic compounds by nitric acid is energetically favorable but very slow due to its inability to break the carbon-hydrogen bond.
- High levels of acids and NO_x in the offgas must be recycled or disposed.
- Safety and operational concerns are more complex with such high concentrations and quantities of acids.

1.3.2 DETOX - Catalytic Chemical Oxidation (Delphi Process)

Description This process involves the use of a chemical catalyst system to destroy wastes. The catalyst system consists of an oxidizing agent, Fe (III), and co-catalysts. Catalysts break down the waste in the presence of a concentrated iron chloride/hydrochloric acid solution at temperatures of 150° to 200°C and moderate pressure. The catalyst is regenerated chemically. The process is composed of a stirred reaction vessel that may be operated in batch or continuously, a waste feed assembly, a system for oxygen injection, and an off gas treatment train. In the continuous mode, a predetermined volume of catalyst solution is loaded into the reaction vessel and sealed. Oxygen is then introduced and the system stabilized with respect to temperature and pressure before the waste is injected. The reaction gases composed of carbon dioxide, water vapor, and trace volatile organics are passed through a condenser, and the condensate is recycled to the reaction vessel. (Delphi Research, Inc.).

Waste Treated The technology is applicable to mixed waste oils, PCBs, and a variety of solid combustibles contaminated with metals and halogenated and non-halogenated organic compounds, volatiles, semi-volatiles, and organic solids, including paper and plastic, and inorganic solids contaminated with organics.

Residue Secondary waste streams from the process include heavy metal and radionuclide hydroxides or oxides, and the hydrated oxide of iron precipitated from solution upon neutralization; and salts resulting from the destruction of organic compounds. Potentially corrosive and mixed waste in the form of the spent catalyst solution. Further treatment may be required if the pH is low and/or if heavy metals and radionuclides co-exist in the solution. The organic destruction efficiencies in bench-scale testing range from 99.0 to 99.9997%.

State of Development Bench-scale. Delphi Research is testing, under contract with Los Alamos National Laboratory, a continuous bench system incorporating a 4-liter reactor to develop scale-up data for a 100-gal. reactor system.

Cost Data Capital costs for a 10 kg/hr mixed waste transportable treatment unit are estimated to be between \$800,000 and \$1,000,000. Treatment of 10 kg/hr for a total of 1,500 hrs/yr over 10 (with two operators) results in an estimated operating cost of \$15 /kg. For a 100 kg/hr system the capital cost is between \$2,100,100 and \$2,800,000 and the operating cost is estimated to be \$2.50 /kg.

Issues Post-treatment of wastes may be required.

1.3.3 Direct Chemical Oxidation

Description This process uses peroxydisulfate as the oxidizer to completely destroy organic wastes at ambient pressure and near 100°C. After oxidizing the organic compounds, the oxidizer is reduced to sulfate. The persulfate can be regenerated by electrochemical oxidation of sulfate in a sulfuric acid solution. For the waste treatment process, the persulfate/sulfuric acid solution and organic waste are added to a digester that is maintained at approximately 100°C. After the waste is destroyed and the oxidizer is reduced, the mixture is returned to the persulfate generator. (Lawrence Livermore National Laboratory).

Waste Treated This technology is applicable to mixed wastes containing water soluble/miscible organic and water insoluble organic solids that are porous or finely shredded; also to halogenated and non-halogenated liquids, dilute and concentrated, and chemical warfare agents.

Residue Aqueous low pH solutions and sludges containing carbon dioxide, water, and trace organics.

State of Development The technology has been tested on a bench-scale and batch mode at the Lawrence Livermore National Laboratory to destroy a Dowex anion exchange resin.

Cost Data Not available at this time.

Issues

- Secondary waste streams containing sulfates and sulfuric acid need to be recycled to regenerate peroxydisulfate.
- Methods to remove by-products of phosphorus and halogens need to be developed.

1.3.4 Electrochemical Destruction

Description A highly caustic electrochemical flow reactor is used to treat liquid waste solutions containing nitrates, nitrites, and organics. By-product gases have low solubilities in alkaline solutions, and therefore, can be effectively separated from wastes. Metal ions can be reduced, producing solid phases and deposits on the cathode that can also be separated from the liquid waste. In addition, anodic electrochemical reactions can be effected to oxidize organic compounds to carbon dioxide and water. (Westinghouse Savannah River).

Waste Treated Liquid waste streams containing nitrates/nitrites and organics.

Residue For nitrate waste by-product waste gas contains nitrogen, ammonia and NO_x . For organic wastes, the gas by-products are carbon dioxide and water. By-product organics will also be contained in aqueous secondary waste solutions.

State of Development Two engineering-scale electrochemical flow reactors have been constructed at Savannah River Site to study the destruction of nitrates/nitrites and organic wastes. Electrolytic destruction of nitrates and nitrites was demonstrated in a flow reactor using actual waste from the Savannah River Site.

Cost Data Not available at this time.

Issues An off-gas treatment system will be required for NO_x and ammonia recovery.

1.3.5 Mediated Electrochemical Oxidation (MEO) for Treatment of Mixed Wastes

Description This is an aqueous process for treating mixed wastes containing organics. The process involves the electrochemical oxidation of a mediator in an acidic medium. The mediator consists of metallic ions such as silver, cobalt, cerium or iron, which are oxidized to their higher valence state at the anode. The mediator in turn oxidizes and destroys the organics and dissolves the radioactive components of mixed wastes which are introduced directly into the electrolyte. A wide variety of organic liquids including halogenated and aromatic compounds have been destroyed in laboratory-scale apparatus. The process is suited for surface cleaning of metallic parts and equipment, and to destroy organics and dissolve radionuclides in sludges, soils, and ash. The primary (electrochemical) process requires secondary processes to regenerate and recycle the reagents, and to remove inorganics, including radionuclides from the system. Information provided by the Mixed Waste Working Group of the Western Governors Association indicate that ECOSYSTEMS, Inc. is commercializing this technology as part of a CRADA with LLNL, and has signed a licensing agreement with PNL for their variation of the MEO process. (Lawrence Livermore National Laboratory).

Waste Treated The process is ideally suited to treat organic liquids and aqueous/organic streams, and inorganic solids contaminated with organics. It is also suitable for surface cleaning of metallic parts and equipment contaminated with organics and for destroying organics contained in sludges, soils, ash, and fine debris.

Residue Aqueous low pH solutions, solids and sludges containing metal and radionuclide salts, and trace organics.

State of Development The technology has been tested for organic destruction on the bench-scale facility at Lawrence Livermore National Laboratory. A wide variety of organic liquids have been destroyed using bench-scale apparatus. A bench-scale unit was used to destroy the organic component of typical mixed waste from Rocky Flats. The destruction efficiency was greater than 99%.

Cost Data Not available at this time.

Issues The primary process requires secondary processes to regenerate and recycle the reagents, and to remove organics, including radionuclides from the system.

1.3.6 MIOX Process

Description The Mixed Oxidants (MIOX) process generates a mixed oxidant solution electrolytically from a sodium chloride brine. The uniqueness of this system is the patented method of separating the solutions generated at the anode (oxidants) and at the cathode (reductants) before substantial recombination can occur. The anode solution contains a mix of oxidants (chlorine, hypochlorite, and ozone) rather than solely hypochlorite, which would be the case if the flows were allowed to recombine. The anode solution containing the mixed oxidants is then injected into raw water for the purpose of organic destruction or disinfection. (Company literature provided by the Mixed Waste Working Group of the Western Governors Association)

Waste Treated Aqueous waste containing pathogenic organisms, and a wide range of industrial wastes such as VOCs, aromatic hydrocarbons in fuel, and cyanides. The process is also being suggested for the passivation of uranium metal and uranium hydride in spent nuclear fuel or metal shavings. The concept is to react the surface of the uranium or UH_3 particles with the mixed oxidant solution to produce a safe oxide and prevent pyrophoric reactions with the air.

Residue Hydrogen and sodium hydroxide from the electrolysis of NaCl . The mixed-oxidant solution produces from 20% to 50% of the total trihalomethanes produced by hypochlorite on an equal chlorine basis. Passivation process water containing radionuclides.

State of Development This process has been patented, commercialized and demonstrated by Los Alamos Technical Associates, Inc. (LATA) for treatment of wastewaters. The passivation application has been tested at LANL on uranium chips/shavings, and requires further testing and demonstration.

Cost Data Not available at this time.

Issues Organic destruction efficiencies and reaction by-products need to be determined for DOE wastes.

1.3.7 Wet Air Oxidation

Description In this technology oxidizable materials, usually organic materials, are oxidized in a dilute, aqueous, liquid matrix at temperature of 200° to 300°C at pressures in the range of 230 to 1250 psi or greater. The process is applicable to material in solution or to finely divided suspended solids in water. Air and an aqueous waste stream are compressed to the required pressure and heat is added as the mixture flows to the reactor. Oxidation of the material in the feed raises the reactor temperature thus increasing the destruction rate. The degree of oxidation of organic and inorganic is a function of the reaction temperature, residence time, and the contaminant. High destruction efficiency will require the reactor to be operated in plug rather than continuous flow. (ITTS Internal Review).

Waste Treated Wet air oxidation has application to a variety of dilute aqueous waste streams containing organic and oxidizable inorganic wastes including halogenated organic, inorganic/organic cyanide, and phenols.

Residue Most organic compounds are oxidized, the carbon going to carbon dioxide, the hydrogen to water, any halogens to halides, sulfur to sulfate, phosphorous to phosphate, and nitrogen to nitrogen gas or ammonia. The oxidation products from treating organic compounds may consist of low-molecular weight compounds such as acetaldehyde, acetone, acetic acid, and methanol distributed between the off-gas and liquid phases. Most organic compounds are destroyed with a destruction efficiency of 95 to 99% in 15 to 60 minutes at temperatures in the range of 200°C to 280°C.

State of Development Wet air oxidation is a commercialized process and has been applied on a bench-, pilot- and full-scale basis to several industrial wastewater and sludges containing hazardous organic and inorganic compounds. Systems are available from Zimpro Passavant Environmental Systems, Inc., Rothschild, Wisconsin.

Cost Data The average costs are approximately \$1.25 million for a 10 gpm system, and \$3.25 million for a 50 gpm system. Operating costs may be as low as 3 to 6 cents per gallon.

Issues

- Oxidized effluent from this process generally requires further treatment to meet effluent COD discharge limitations, and to meet EPA treatment standards of 99.99% destruction efficiency for toxic organics.
- Wet air oxidation is used primarily for pretreatment.
- The process is not effective on halogenated aromatic compounds such as Hexachlorobenzene, dichlorobenzene, and PCBs.
- A high pressure system in a radioactive environment may be a safety/risk issue.

1.3.8 Wet Oxidation Process

Description In this process organic waste is decomposed by hydrogen peroxide into carbon dioxide and water. This process takes place in a reaction vessel at 100°C and atmospheric pressure. Waste is supplied to the reactor, and a iron sulfate or copper sulfate catalyst is added along with sulfuric acid to adjust the pH of the mixture. The oxidation reaction proceeds by continuously supplying hydrogen peroxide. (JGC/ADTECH and AEA).

Waste Treated The primary application of this process is the volume reduction of radioactive and mixed organic solid wastes such as spent ion-exchange beads, powdered resins, filter sludges, and organic liquid wastes. The process has also been demonstrated as highly effective for decomposing water-soluble organic acids used as radioactive decontamination agents.

Residue After decomposition of the organic wastes, the pH of the mixture is neutralized by adding sodium hydroxide. The reaction mixture is then concentrated by evaporation until the sodium sulfate concentration is approximately 25% by weight. The concentrate is then drained, dried or solidified, and packaged for storage or disposal. Typical degrees of decomposition are 90% in 4 to 6 hours for bead resins; 90% in 5 to 6 hours for powdered resins; and 98% in 2 to 4 hours for filter sludges.

State of Development A full-scale system is being installed at the F-1 treatment facility at Hanford to process 150 gpm of aqueous waste by JGC Corp. AEA has built and tested a pilot-scale mobile facility. This technology has also been applied at the Virginia Power Company's Surry Radwaste Treatment Facility. The facility processes multiple wastewater streams from this two-unit nuclear plant. Liquid steam generator cleaning solution wastes containing copper and iron are treated using this process. The insoluble inorganic wet oxidation residue is solidified and the evaporated soluble residue is bitumen (asphalt) solidified.

Cost Data Not available at this time.

Issues

- Because this is a low temperature and pressure process, destruction efficiencies for many of the hazardous organic compounds do not reach the 99.99% level.
- The system has not been demonstrated on mixed waste.

1.4 Gas Phase Destruction

1.4.1 Electron Beam

1.4.1.1 Electron Beam Dry Scrubbing Technology

Description An electron beam dry scrubbing technology is being considered by the Defense Nuclear Agency (DNA) as a process for the removal of sulfur dioxide and nitrous oxide generated by the combustion of high sulfur coal. Water and ammonia are injected into the smokestack and processed with an electron beam. In a one-step process, and without stack gas reheat, both pollutants are removed. (DNA).

Waste Treated The technology treats off-gases from the combustion of high sulfur coal.

Residues Chemical reactions convert sulfur dioxide and nitrous oxide to ammonium sulfate, nitrate, and ammonium nitrate, which are commercially valuable fertilizers.

State of Development The Defense Nuclear Agency has begun a three-phase program to build, operate and demonstrate this technology. In the first phase DNA will design and build a half-megawatt electron beam gun and a one-megawatt power conditioning system. In the next phase, DNA will build another one-megawatt pulsed power module and continuously operate it at one-megawatt. Phase III will involve an 18 month demonstration of the system.

Cost Data Phase I consists of about \$6 million in construction and demonstration costs.

Issues None identified at this time.

1.4.1.2 Tunable Hybrid Plasma

Description In this technology a 100 to 300 keV electron beam is directed into a flow of air containing organic contaminants to produce a plasma. The electron beam produces a plasma with electron densities in the range of 10^9 to 10^{10} /cm³ and creates reactive radicals such as OH·, O·, and O₃. The electron density of the plasma, and thus the chemical reaction rates, can be controlled by the electron-beam current, and the electron temperature can be controlled by a superimposed electric field. The combination of the electron beam and electric field give rise to the term tunable hybrid plasma reactor. (MIT/DOE).

Waste Treated The technology can be applied to a wide variation of chlorinated volatile organic compounds (from 10 to 2,000 ppm) in dry air. It has been demonstrated to destroy carbon tetrachloride, chloroform, and trichloroethylene.

Residues The main byproducts from carbon tetrachloride decomposition are carbon dioxide, carbon monoxide, chlorine, and hydrochloric acid with trace amounts of phosgene. The byproducts from the decomposition of TCE were dissolved in an aqueous solution of sodium hydroxide to produce sodium acetate. The field tested unit demonstrated the reduction of carbon tetrachloride from 1,100 ppm to less than 1 ppm, with a 99.7% removal efficiency. The destruction of TCE required less than 10% of the energy needed to destroy the carbon tetrachloride. The primary variable that governs the destruction level for any set of inlet conditions is the absorbed dose. The system parameters that contribute to the absorbed dose include the beam acceleration voltage, the beam current, and the mass flow rate of the contaminated air stream.

State of Development Field-scale. The field-scale unit is capable of processing 0.3 to 0.6 cubic meters per minute of contaminated air. Full-scale units will be capable of processing 50 cubic meters per minute.

Cost Data A full-scale system is projected to cost about \$1 million including the accelerator and support equipment. The estimated cost of destroying carbon tetrachloride for a full-scale system is between \$3 and \$4 per pound; the cost for TCE is less than \$0.40 per pound.

Issues

- There is a potential need for post-processing to achieve required destruction efficiencies.
- The technology may also require post-processing acid gas scrubbers.
- The technology is applicable to only vapor-phase waste streams.

1.4.1.3 Zapit Technology

Description This low-power (200 kW), skid-mounted, portable electron-beam technology system was developed for application to organic vapors. This technology is currently being marketed and commercialized for on-site groundwater treatment and air pollution control applications. The unit has a single power source and electron beam head and can treat up to 1,000 cfm with contaminant concentrations of up to 250 ppm in a one foot reaction chamber. More heavily contaminated vapor streams can be treated by adding a second power source and e-beam head. The technology involves irradiating vapor-phase waste streams to produce sizable quantities of free radicals, aqueous electron, H^+ , and OH^- . These species react with organic contaminants to break the chemical bonds and produce water, carbon dioxide, and salts. (Zapit Technology, Inc.)

Waste Treated The technology has been tested at a TCE contaminated site at Lawrence Livermore National Laboratory (LLNL), and at McClellan Air Force Base at a site containing a mixture of organic contaminants.

Residue Zapit claims reduction of TCE to non-detectable levels, and other toxic contaminants by 99.99% or more in some applications. Field tests performed at LLNL reduced TCE concentrations by several orders of magnitude. Tests performed at McClellan Air Force Base indicated that most of the hazardous organics were reduced to non-detectable levels. Treatability tests on a variety of organics, including PCBs, halogenated aromatics, and other halogenated hydrocarbons indicate complete destruction with the production of carbon dioxide, water, and salts.

State of Development Field-scale.

Cost Data The technology using a dc power supply has daily power costs of \$10 to \$15, and the treatment costs are estimated to be \$6 to \$10 per pound of volatile organic compound treated. A one-time system cost is about \$100,000.

Issues

- There is a potential need for post-processing to achieve required destruction efficiencies.
- The technology may also require post-processing acid gas scrubbers.

- The technology has been limited to a concentration of 500 ppm of volatile organic compounds but is expected to be able to treat up to 3,000 ppm.

1.4.2 Non-Thermal Plasma

1.4.2.1 High Energy Corona

Description The High Energy Corona process uses high-voltage electricity to destroy volatile organics at room temperature. The objective of the technology is to provide a portable means of treating soil off-gases produced during soil treatment operations. The technology consists of a cylindrical ceramic or glass reactor with an inner electrode along the centerline of the cylinder, and a grounded metal screen attached to the outer surface of glass cylinder. The annular region between the coaxial electrode and the glass tube is filled with dielectric pellets or beads with a void fraction of approximately 40%. When a high-voltage alternating electric field is established across the gap between electrodes, corona discharges occur among the dielectric beads creating plasma. The primary function of the dielectric beads is to provide a surface to catalyze the reactions, and to amplify the electric fields that occur at the contact points between the beads. When the gas to be treated is pulled through the dielectric material, the plasma destroys the contaminants. The technology is packaged in a self-contained mobile trailer that includes gas handling equipment and on-line analytical capabilities. (Pacific Northwest Laboratory).

Waste Treated Contaminants that can be treated include most or all volatile organics and semi-volatile organics. The potential also exists for the treating of inorganic compounds, such as oxides of nitrogen and oxides of sulfur. The technology is specifically useful for destroying organics and chlorinated solvents such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, diesel fuel, and gasoline. Gas phase contaminants are treatable.

Residue The technology appears to destroy more than 99.9% trichloroethylene and 90 to 95% tetrachloroethylene. When chlorinated volatile organics are treated, water containing either sodium hydroxide or baking soda is recirculated in a scrubber to remove acid gases, hydrochloric acid, and chlorine from the reactor effluent.

State of Development Bench-scale.

Cost Data Estimate cost is about \$10 per pound of waste treated, including a 25% contingency to account for any unknown additional costs. Although maintenance costs are minimal, the total cost figure assumes 8% downtime and a capital payback period of 6 months.

Issues Continued research is needed to fully characterize reactor emissions and complete mass balances, develop larger reactors, better understand the process, and optimize the hardware and packaging associated with the process.

1.4.2.2 Microwave Plasma Destruction of Organic Compounds

Description This technology allows for the destruction of organic compounds, especially chlorinated compounds using the highly reactive environment of a low-temperature plasma.

The plasma is generated and sustained by coupling microwave radiation (2450 MHZ) with either an air or argon plasma at atmospheric pressure. (Argonne National Laboratory).

Waste Treated Although the process involves a gas-solid reaction, the technology is applicable to organic liquid wastes only after vaporization. It can be applied to solid and non-combustible wastes if a method of separating the organic contamination from the solid, such as thermal desorption, is employed.

Residue Under conditions of wet oxidation, chlorinated compounds, such as trichloroethylene and trichloroethane, are converted to simple compounds such as carbon dioxide, halide acids, and water. Destruction removal efficiencies of greater than 99.99% are typical.

State of Development Bench scale. Ability to scale the process a major hurdle. Currently discussing with private industry a novel reactor concept that will allow construction of a larger capacity plasma reactor with capability to treat large volumes that could potentially make this a viable technology.

Cost Data None available at this time.

Issues The ability to scale the process up for large capacity is a major hurdle.

1.4.2.3 Silent Discharge Plasma

Description The Silent Discharge Plasma system is being developed and demonstrated at Los Alamos National Laboratory in conjunction with a packed bed reactor. The silent discharge plasma unit is an offshoot of industrial units for generating ozone. Cold plasmas, such as those created by electrical discharges in gases, involve the efficient generation of large quantities of reactive free radicals in a gaseous stream from the dissociation of molecular oxygen by energetic electrons in the discharge. The free radicals have been demonstrated as effective in destroying organic compounds in a gaseous waste stream containing up to a few thousand ppm of contaminants. The silent discharge plasma is produced by electrical discharges in gases, where one or both of the electrodes are covered by a dielectric layer. The geometry is usually planar, using metal electrodes and glass dielectric plates. The power supply is a series inverter that switches charged capacitors through a pulse transformer by high-power thyristors. The present unit supplies 4kW of power at voltage pulse repetition frequencies up to 4.5 kHz. The gaseous waste is destroyed as it passes through the electrical discharge field between the two dielectric barriers. (Savannah River Site).

Waste Treated This technology is applicable to destruction of vapor-phase organics.

Residue Destruction products include trace amounts of dioxins and furans, carbon dioxide, water, hydrochloric acid, and low levels of carbonyl halides when chlorinated hydrocarbons are involved. Tests with the prototype cell were performed on TCE. Approximately 600 to 1,000 ppm TCE at a feed rate of 10 liter per minute was reduced to 1 ppm in the effluent. TCE removals ranged from 90% to >99% for energy densities from 0.02 joules per cubic centimeter to 0.09 joules per cubic centimeter for dry feeds (wet feeds required about 1 joule per cubic centimeter for removals >99%). The best removal efficiency for carbon tetrachloride was >99% with dry feed and an energy density of 3 joules per cubic centimeter.

State of Development Prototype tests have been performed at Los Alamos National Laboratory, and tests in conjunction with a packed bed reactor have been performed on simulated waste from the Rocky Flats Plant and from the Mound Plant. A pilot-scale demonstration of the process was performed at the Savannah River Site on volatile organic compounds liberated from the soil using a vacuum extraction process.

Cost Data Not available at this time.

Issues

- Survivability and maintainability are key to the development of the process's reactor. Its working environment is characterized by an oxidizing and corrosive atmosphere, thus dual dielectric barriers are required to prevent contact between the corrosive gas mixture and the metal electrodes.
- An off-gas treatment system will likely be required.

1.4.3 Photolytic Destruction

1.4.3.1 Photocatalytic Oxidation with Air Stripping

Description In gas-solid photocatalytic oxidation of volatile organics, a titania catalyst and near ultraviolet light simultaneously contact a contaminated air stream in a continuous flow, completely destroying the volatile organics. Arizona State University is investigating an integrated pilot-scale pump and treat system in which chlorinated volatile organics are transferred to a gas carrier stream using air stripping, with photocatalytic oxidation reactors installed downstream to treat the contaminated air stream. The system also incorporates a closed-loop caustic scrubber for hydrochloric acid removal. (Arizona State University/IT Corporation).

Waste Treated This technology can treat vapor streams from thermal desorbers and volatile organic contaminated air streams produced by air stripping contaminated groundwater. Laboratory studies indicated rapid, non-detectable destruction (98 to 99%) of various concentrations of TCE and TCA in humid air streams.

Residue Destruction products include carbon dioxide, water, hydrochloric acid and low levels of carbonyl halides when chlorinated hydrocarbons are involved.

State of Development Bench-scale.

Cost Data Not available at this time.

Issues None identified at this time.

1.4.3.2 Photolytic Destruction for Soil Vapor Extraction Off-Gases

Description This technology photolyzes vapor-phase halogens contained in off-gases from a soil vapor extraction system. The technology operates using low pressure mercury lamps.

High intensity ultraviolet light at 185 and 254 nanometers generated by the mercury lamps destabilizes and facilitates the breakdown of volatile organic contamination in the soil vapor extraction exhaust gas stream. A proprietary liner material present in the light zone captures and neutralizes the resulting process byproducts. (Process Technologies, Inc.)

Waste Treated The technology treats air and gases contaminated with volatile organics including chlorinated volatile organics, and chlorofluorocarbons.

Residue The gaseous products exiting the system include air, water vapor, carbon dioxide, and HCl.

State of Development Field-scale testing at McClellan Air Force Base conducted in September 1994.

Cost Data Not available at this time.

Issues None identified at this time.

1.4.3.3 Photolytic Oxidation Process (Purus Process)

Description The photolytic oxidation process indirectly destroys volatile organic compounds in soil and groundwater. The process uses a xenon pulsed-plasma flash-lamp that emits short wavelength ultraviolet light at very high intensities. The plasma is produced by pulse discharge of electrical energy across two electrodes in the lamp. Contaminants are directly photolyzed when they absorb sufficient UV light energy, transforming electron to higher energy states and breaking molecular bonds thus converting the volatile organics into less hazardous compounds. (Purus, Inc.)

Waste Treated The process is designed to destroy volatile organics, including dichloroethene, tetrachloroethene, trichloroethene, and vinyl chloride volatilized from soil and groundwater.

Residue The gaseous products exiting the system include air, water vapor, and carbon dioxide. TCE destruction efficiencies obtained during the field-scale demonstration exceeded 99.9%.

State of Development Field-scale.

Cost Data Not available at this time.

Issues

- To be rapidly photolyzed, some volatile organics require photosensitization or an even lower-wavelength light source.
- TCE removal yielded undesirable intermediates during the field-scale demonstration.

1.4.3.4 Photo-Thermal Detoxification Unit

Description The Photo-Thermal Detoxification Unit uses Photothermal photolysis reactions conducted in a reaction chamber at higher temperatures (200° C to 500° C) than conventional photochemical processes, but lower than combustion temperatures (typically greater than 1000° C). The Photo-Thermal Detoxification Unit consists of an insulated reactor vessel illuminated with high-intensity UV lamps. Technologies that generate high-temperature gas streams may supply the Photo-Thermal Detoxification Unit directly with the contaminated air stream. The initial destruction of VOC's are due to direct photolysis of the organic molecule. This technology can be equipped with a preheater for use with low-temperature extraction technologies and standard air pollution control devices for removal of acids and suspended particulates. (DOE Alternatives to Incineration, Technical Area Status Report 11/94)

Waste Treated The Photo-Thermal Detoxification Unit has proven effective in destroying PCBs, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, aromatic and aliphatic ketones, and aromatic and chlorinated solvents, as well as brominated and nitrous wastes found in soils, sludges and aqueous streams.

Residue A significant number of products of incomplete combustion (PICs) have been observed. CCl_4 is produced at 18% of the input Trichloroethylene concentration.

State of Development Testing is currently underway by the EPA and the University of Dayton Research Institute.

Cost Data None available at this time.

Issues Temperatures for purely thermal destruction, of around 700°C, are required for complete photothermal destruction at current exposure times, radiation sources, and radiation levels. The high temperatures at under current exposure conditions are inappropriate for a field operational system.

1.5 Inorganic Decomposition

1.5.1 General

The following technologies provide for the decomposition of various inorganic compounds which are toxic or hazardous to the environment in high concentrations. Nitrates in wastes common to many Department of Energy facilities will generally increase the volume and/or reduce the integrity of all final waste forms that have been proposed. The nitrate anion is very mobile and difficult to immobilize, especially in the relatively porous, cement-based grout that is currently used. Destruction or removal of nitrates may also be required to meet environmental discharge limits for aqueous waste water or to reduce the hazard of vigorous exothermic reactions.

1.5.2 Bio-Catalytic Nitrate Destruction

Description Reductase enzymes, immobilized on a solid support, may be used to reduce nitrates and nitrites in mixed waste to N_2 and water. The most effective reduction of nitrate is achieved when the matrix, containing the enzymes is entrapped in a thin layer over a large cathode surface, and the water is first flowed past the anode. A low-voltage electrical current

transfers electrons from the cathode to the enzymes via an electron transfer dye. To protect the enzymes from denaturing by excessive concentrations of electrolytes, they are maintained in the polyethylene glycol (PEG) or polypropylene glycol (PPG) phase of an aqueous biphasic system of waste water and immiscible liquid. Nitrate and nitrite selectively partition from the salt rich aqueous phase into the PEG or PPG leaving behind the H^+ and OH^- in the aqueous phase. The use of enzymes eliminates the need for additional chemical reagents or the production of secondary waste streams. (ANL Fact Sheet)

Waste Treated Aqueous waste with high nitrate or nitrite salt concentration.

Residue Sodium hydroxide and nitrogen.

State of Development Nitrate reductase enzymes are commercially available from plant or bacterial sources. The technology is at the bench-scale development stage and research is being conducted at Argonne National Laboratory.

Cost Data Not available at this time.

Issues At the development stage; testing is being performed to optimize the enzyme activity for nitrate/nitrite destruction.

1.5.3 Cyanide Destruction by Electrochemical Chlorination

Description A circulation pump passes the waste solution through an electrochemical cell where strong oxidizing agents are generated to convert cyanide to carbon dioxide and nitrogen. Salt and sodium hydroxide are added to maintain a pH greater than ten. Metal chlorides are precipitated in the process and are collected for a separate immobilization treatment. (EPA)

Waste Treated Aqueous solutions of cyanide compounds.

Residue Carbon dioxide, nitrogen, precipitated metal chlorides, metals and/or radionuclides plated out on electrodes, depleted electrodes, and membrane material depending on the system design.

State of Development Commercialized systems exist for recovery of metals from plating solutions. Development and demonstration is being conducted under EPA's SITE program. No vendor is known that deals with radioactive or mixed waste. Tests required to determine effects of organics and radionuclides in the waste streams. The technology was demonstrated at the pilot scale, and will be demonstrated at Rocky Flats in FY95.

Cost Data Depending on the application and the scale of the technology, pilot plant costs may be as much as one million dollars.

Issues None identified at this time.

1.5.4 Electrochemical Destruction of Nitrates and Organics in HLW and LLW

Description In an electrochemical cell, nitrate and nitrite ions in alkaline HLW can be reduced at the cathode to nitrogen, ammonia, and nitrous oxide. These gases have low solubility in alkaline HLW and can be separated from the waste. Easily reduced metal ions can also deposit on the cathode and thereby be separated from the liquid waste. At the anode, organic compounds can be oxidized to carbon dioxide and water.

Waste Treated Alkaline high-level waste and low-level waste containing high concentrations of nitrate/nitrite and/or organic materials such as EDTA that significantly impact radionuclide separation processes and the safe storage of high-level wastes.

Residue Gases discharged may be recovered (e.g., hydrogen, ammonia) or treated for ultimate release to the atmosphere. Recovered solid metals can be recycled or disposed as a low-volume waste form. Waste volume requiring disposal could be reduced by as much as 75% as a result of electrochemical treatment.

State of Development Electrolytic destruction of nitrate and nitrite was demonstrated in an engineering-scale flow reactor using actual waste from the Savannah River Site. Parametric studies for oxidation of organics present in Hanford high-level waste have been conducted at engineering scale. Development work continues at Savannah River Technology Center, Pacific Northwest Laboratory, and the University of South Carolina.

Cost Data Not available, but will be highly dependent on the composition of the waste stream and the degree of waste volume reduction. The process is energy-intensive.

Issues Recovery and recycle of the sodium hydroxide produced by this process would significantly decrease the volume of waste requiring disposal. Electrolysis does not require the use of additional chemical reagents, and produces little secondary waste.

1.5.5 Electrochemical Ion Exchange

Description This process involves the destruction of nitrate and nitrite salts by first isolating the anions using an ion exchange resin, migrating them to the anode of an electrolytic cell, and then reducing them to nitrogen gas at a cathode. The nitrate can be recovered as nitric acid from the anode compartment and distilled for reuse, or the anolyte containing the nitrate can be pumped through an electrochemical destruction cell to destroy the nitrate at a series of cathodes to produce nitrogen and other products, such as oxygen gases and sodium hydroxide. All of the equipment for this process is commercially available and it has been tested on simulants for radioactive waste streams expected at the Rocky Flats Plant and the Savannah River Plant. Decontamination factors (ratio of influent concentration to effluent concentration) of over 100 have been achieved. (Selentec, Inc., "Electrochemical Ion Exchange Treatment for Plutonium-Bearing Nitrate Waste Demonstration Study," August 1992 and AEA Industrial Technology, Company Literature)

Waste Treated Aqueous waste containing concentrated nitrate salts.

Residue Aqueous waste containing sodium hydroxide and other initial contaminants, and gaseous emissions of oxygen and nitrogen or ammonia, with measurable quantities of N_2O and hydrogen. Heavy metals plated onto electrodes.

State of Development The process is under development at Savannah River Plant and has been tested at the laboratory-scale at the Rocky Flats Plant on simulated DOE mixed waste. It is also being developed by Selentec Corp. and AEA Technology, and is available commercially from these sources.

Cost Data Capital cost for a system to treat 0.1 gpm of a high nitrate concentration (1M) feed was estimated to be \$150,000. Operating costs for DOE wastes have not been estimated; however, electrical costs are approximately \$1.53/kg NO_3^- assuming electric power costs \$0.10/kWh.

Issues Chromium must be removed from the waste stream for efficient operation. Resulting aqueous effluent containing NaOH and other contaminants (heavy metals and radionuclides) must be treated. Plating of metals on electrodes may reduce efficiency.

1.5.6 Nitrate to Ammonia and Ceramic (NAC) Process

Description The NAC process is a low temperature process (50°C to 60°C) that uses aluminum metal to reduce alkaline, nitrate-based aqueous waste to ammonia and an aluminum oxide-sodium aluminate-based solid. The aluminum is converted to sodium aluminate and aluminum hydroxide which irreversibly dehydrates to Gibbsite which is quite insoluble. Silica is added to the product from the reactor and the material is calcined, pressed, and sintered to form a ceramic which may be an acceptable high level waste form. Most cations, metallic and non-metallic, precipitate from solution as highly insoluble aluminum spinels. Ammonia off-gas from the reactor is passed over a heated, catalytic bed where it is converted to nitrogen and water prior to discharge to the atmosphere. Between 85 to 99% of the nitrate is converted to ammonia in the process, and volume reduction from batch processing is 50-55%. (Brown, C.H. and W.E. Schwinkendorf, "Technical Area Status Report for Chemical/Physical Treatment, Vol. II," DOE/MWIP-8, August 1993)

Waste Treated Alkaline, nitrate-based aqueous waste.

Residue Dehydrated aluminum oxide-sodium aluminate-based ceramic which may be an acceptable high level waste form. The aluminum hydroxide will co-precipitate and/or absorb many inorganic contaminants from the waste solution, such as heavy metals and Sr-90, which will be incorporated into the final waste form. Most cations, metallic and non-metallic, precipitate from solution as highly insoluble aluminum spinels. Nitrogen and water vapor offgas.

State of Development This technology is being developed at Oak Ridge National Laboratory at the bench- scale, so there are no commercial suppliers at present. Bench-scale tests have been performed on DOE waste simulants.

Cost Data Preliminary estimates are \$20M in capital costs for a batch plant to process 1200 kg NO_3^- /hr over 20 years, with an operating cost of about \$2.50/kg NO_3^- destroyed.

Issues If oxygen is present, the off-gas will be flammable so an inert gas blanket will be required for the reactor.

1.6 Radiation Induced Oxidation

1.6.1 Electron Beam

1.6.1.1 High-Voltage Environmental Applications, Inc.

Description The Florida International University Electron Beam Research Facility consists of an electron beam pilot plant capable of treating an aqueous waste stream at a flow rate of 170,000 gallons per day. In this process, electrons are accelerated by high-voltage to approximately 95 % the speed of light and are then shot into a thin stream of water or sludge as it falls through the beam. Reactions are completed in less than one-tenth of a second. Information provided by the Mixed Waste Working Group of the Western Governors Association indicate that Denver Research Institute has teamed with HVEA, Titan Environmental Corp. and Titan Beams who manufacture and install LINAC electron accelerators, to propose a mobile treatment system for Rocky Flats to treat VOC, TCE and PCE contaminated groundwater and soil. (High Voltage Environmental Applications, Inc.(HVEA) Florida International /University of Miami, SITE Technology Profiles Seventh Edition, Nov 1994, EPA/540/R-94/526, p.264,265.)

Waste Treated The system has been found effective in treating in excess of 50 common organic compounds. The treatment process is appropriate for removing various hazardous organic compounds from aqueous waste streams and sludge containing up to 8% solids.

Residue Carbon dioxide, water, reaction byproducts, and a trace of the original contaminants.

State of Development A full-scale facility can treat 170,000 gallons per day. The high-energy electron irradiation process was accepted into the SITE Emerging Technology Program in June 1990. Studies have been completed for six organic compounds (TCE, PCE, chloroform, benzene, toluene, and phenol. Additional studies are underway to determine destruction efficiencies and to characterize reaction by-products of carbon tetrachloride and methylene chloride. HVEA now has a mobile electron beam treatment system that has been demonstrated to the EPA.

Cost Data "Depends on many factors..such as dose rate required for destruction, volume of waste to be treated, size of treatment facility, time utilization of facility, and manner capital is recovered."

Issues Reaction by-products have been determined for all studied compounds. None of the compounds were toxic at the levels determined. Additional studies are underway to characterize reaction by-products of carbon tetrachloride and methylene chloride.

1.6.1.2 Science Research Laboratory

Description This experimental study is to examine the effectiveness of direct electron beam radiolysis on destruction of water borne organic contaminants. The research will explore destruction, and in some cases, products formation as a function of initial concentration, dosage, and dose rate. It will explore the enhancing effects of the addition of an oxidizing, hydrogen peroxide. (DoD ARPA SBIR)

Waste Treated Aqueous wastes containing organic contaminants, benzene, methylene chloride, and pentachlorophenol

Residue Carbon dioxide, water, and traces of original contaminants.

State of Development Bench test Science Research Laboratory

Cost Data Not available at this time

Issues None identified at this time

1.6.1.3 TETRA Corporation

Description TETRA Corporation is investigating an innovative treatment process for the combined removal of metallic ions and the destruction of volatile organic chemicals (VOCs) in waste water using high-energy electrons directly injected in a water stream along with titanium dioxide as a catalyst. (DoD ARPA SBIR)

Waste Treated Organic contaminants and metals in the same waste water stream

Residue Carbon dioxide, water, reaction byproducts, traces of original contaminants and TiO_2 particulates containing radionuclides and heavy metals. traces of original contaminants

State of Development Bench test at Tetra Laboratory

Cost Data Not available at this time

Issues None identified at this time

1.6.2 Photochemical Oxidation

1.6.2.1 General

Photochemical oxidation processes require the UV light source to emit wavelengths in the regions absorbed by either the contaminant to be destroyed or an oxidant to produce free radicals. Photochemical oxidation systems share a common method of operation. Typically, they destroy the waste compounds through an indirect photochemical process that uses UV energy provided by a small number of high-energy lamps, or large numbers of low-energy lamps, to photolyze either hydrogen peroxide or ozone to generate hydroxyl radicals in the bulk fluid. These radicals react with the organic species in the water. (DOE Alternatives to Incineration, Technical Area Status Report, 11/94)

The ultraviolet (UV)/oxidation process is an innovative groundwater treatment technology that has been used in full-scale treatment applications for more than ten years. A majority of these applications are for groundwater contaminated with petroleum products or a variety of industrial solvents. Limitations of the UV/oxidation include the amount of aqueous stream turbidity, free radical scavengers, heavy metals, and pretreatment activities. A wide range of sizes of UV/oxidation systems are commercially available from single-lamp benchtop reactors

to full-scale systems to handle throughput of 1,000 to 1,000,000 gallons per day. (Remediation Technologies Matrix and Guide, Fed Remediation Tech Roundtable, DoD/EPA/DOE 2nd Edition- 10/94)

1.6.2.2 Peroxidation Systems, Inc.

Description The Peroxidation ultraviolet oxidation process utilizes a reactor that is annular in configuration with the lamp in the center and the waste stream circulated through the annular region around the lamp. The lamp is a medium high pressure, broadband, mercury-arc lamp and several may be used in series. Hydrogen peroxide may be injected at multiple points to make it available throughout the reactor. Most contaminants are rapidly destroyed by hydroxyl radicals with oxidation rates 10^6 to 10^9 faster than for ozone and removal efficiency of 82-99%. However there are some compounds that are not readily attacked by the OH radicals. (DOE Alternatives to Incineration Technical Status Area Status Report, November 1994)

Waste Treated Clear aqueous waste stream with organic contaminants

Residue Carbon dioxide, water, and trace amounts of contaminants

State of Development This technology has been commercialized by several companies (Peroxidation Systems, Purus, Ultrox, Solarchem, UV Technologies, etc.) and several DOE laboratories have used commercial systems to perform tests and evaluations. A new proprietary surface-discharged UV light source with improved destruction efficiency has been tested at ORAL.

Cost Data Not available at this time

Issues Ability of UV light to penetrate and destroy pollutants requires removal of suspended solids and turbidity. At the current state of development most systems are only useful for treatment of aqueous streams contaminated with less than 1% organics, although work is continuing to increase the acceptable contamination level.

1.6.2.3 Photocatalytic Degradation of PCB-Contaminated Sediments and Waters

Description This system includes a reactor that consists of three chambers connected in series. Each of the chambers is covered with a transparent material that allows sunlight and artificial light penetration. In Chamber A, sediment is continuously agitated to allow separation of the suspended and bottom sediment fractions, and a titanium dioxide catalyst is added. The suspended fraction is irradiated at the slurry-air surface to promote photocatalysis. The suspended sediment fraction is then slowly discharged to Chamber B, exposing the bottom sediments in Chamber A to light sources. A tank baffle in Chamber A agitates the bottom sediment to maximize contact with the catalyst. Following continued treatment in Chamber B, the suspended sediment fraction is gravity-discharged to Chamber C, where additional catalyst is added for continued treatment and eventual discharge. The sediment can be recirculated through Chamber B if additional treatment is needed. (State University of New York at Oswego).

Waste Treated The technology is designed to treat sediment contaminated with PCBs and other chlorinated organic contaminants, including volatile and semi-volatile organic compounds on site.

Residue Trace levels of PCBs in treated soil residues.

State of Development Pilot-scale testing at New York State Superfund Sites. Field testing resulted in reductions of 68% and 90% during two separate tests.

Cost Data Not available at this time.

Issues None identified at this time.

1.6.2.4 Photocatalytic Water Treatment

Description The Matrix Photocatalytic Inc. photocatalytic oxidation system removes and destroys dissolved organic contaminants from water in a continuous flow process at ambient temperatures. When excited by light, the titanium dioxide semiconductor catalyst generates hydroxyl radicals that oxidatively break the carbon bonds of organic compounds. The catalyst also generates electron holes, which are powerful reducing species. (Matrix Photocatalytic Inc.)

Waste Treated The system was initially designed to destroy organic pollutants or to remove total organic carbon in drinking water, groundwater, and plant process water. The system also destroys organic pollutants such as PCBs, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, chlorinated alkenes, chlorinated phenols, chlorinated benzenes, alcohols, ketones, aldehydes, and amines.

Residue The system converts organics to carbon dioxide and water and trace organics. Typically, efficient destruction occurs between 30 seconds and 2 minutes of exposure time.

State of Development Pilot-scale field tests have been conducted at numerous sites on raw effluent contaminated with a variety of organics, mainly BTEX, trichloroethene, and methyl tertiary butyl ether.

Cost Data For an average treatment time of 60 seconds, direct operating costs have been estimated at \$1 to \$2 per 1,000 gallons.

Issues None identified at this time.

1.6.2.5 Photochemical Oxidation (PhotoCAT™)

Description The PhotoCAT™ process technology photochemically oxidizes compounds in waste water using a chemical oxidant, ultraviolet radiation, and a photocatalyst. (Energy and Environmental, Inc/ SITE Technology Profile, 7th Edition EPA/540/R-94/526)

Description The ultrasonic-aided leachate process involves enhanced chemical treatment of acidic soil leachate solutions (acid mine drainage). This process uses an ultrasonic field to improve contaminant removal. The process is followed by a solid-liquid separation by filtration equipment. The major difference between this technology and conventional processes is the use of ultrasonic mixing instead of mechanical agitation in large tanks. Research indicates that an ultrasonic field significantly increases the conversion rate of dissolved contaminants to precipitates and the rate of oxidation and ion exchange. (Atomic Energy of Canada Limited, SITE Technology Profiles Seventh Edition, EPA/540/R-94/526, 11/94, P. 320, 321.)

Waste Treated Acid mine drainage contaminated with heavy metals and radionuclides

Residue "The process generates minimal fugitive emissions and produces a treated effluent that meets applicable discharge limits."

State of Development The ultrasonic-aided leachate treatment process was accepted into the SITE Emerging Technology Program in 1993. Under this program Atomic Energy of Canada Limited (AECL) plans to develop and test a pilot-scale unit to treat acidic soil leachate solutions containing low levels of metals and radionuclides. AECL plans to use waste from Nordic Mine near Ontario, Canada and the Berkeley Pit near Butte, Montana.

Cost Data Not available at this time

Issues None identified at this time

1.6.4 X-Ray Treatments

1.6.4.1 X-Ray Treatment of Aqueous Solutions

Description The Pulse, Inc. process for x-ray treatment of organically contaminated aqueous solutions is based on the in-depth deposition of *ionizing* radiation. Secondary electrons break-up the complex contaminant molecules, and form radicals. These radicals react with volatile and semi-volatile compounds to form non-toxic by-products such as water, carbon, dioxide, and oxygen. A high-power linear induction accelerator (LIA) plus an x-ray converter generates the x-rays used. (Pulse Science, Inc. SITE Technology Profiles Seventh Edition, EPA/540/R-94/526, p.296,297)

Waste Treated X-ray's deep penetration and high flux allow waste to be treated in containers, flowing systems, or in situ.

Residue Water, carbon dioxide, oxygen, and reaction byproducts

State of Development The technology was accepted into the SITE Program in 1991. Two sets of experiments were completed on a Superfund site at LLNL.

Cost Data Not available at this time.

Issues Based on results to date, estimates for dose level to destroy mixtures of contaminants should be applied judiciously.

1.6.4.2 X-Ray Treatment of Soils

Description X-ray technology treatment of organically contaminated soils is based on the in-depth deposition of ionizing radiation. A high power linear induction accelerator (LIA) plus X-ray converter generates X-rays that can penetrate about 20 centimeters into the soil. Secondary electrons ionize and excite the atomic electrons, break up the complex contaminant molecules, and form radicals that react with contaminants. (Pulse Science, Inc. SITE Technology Profiles Seventh Edition, EPA/540/R-94/526, 11/94, p.362,363)

Waste Treated X-ray treatment of organically contaminated soils

Residue Water, carbon dioxide, and oxygen

State of Development The X-ray treatment of organically contaminated soils technology was accepted into the SITE Emerging Technology Program in 1993. The program's primary objective is to demonstrate that X-ray treatment can reduce VOC and SVOC levels in soils to acceptable levels and determine any hazardous by-product that may be produced.

Cost Data Pulse Science, Inc. estimates that the cost of high throughput X-ray processing is competitive with alternative processes. The program will develop a conceptual design and cost estimate for a high throughput X-ray treatment system.

Issues None identified at this time.

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