1 of 5

**TECHNICAL AREA STATUS REPORT
FOR
CHEMICAL/PHYSICAL TREATMENT**

**VOLUME II
APPENDICES**

**Clifton H. Brown, Jr.
Martin Marietta Energy Systems, Inc.
Oak Ridge National Laboratory**

**William E. Schwinkendorf
BDM Federal, Inc.**

**and the
Chemical/Physical Treatment Technical Support Group
Mixed Waste Integrated Program
Office of Technology Development**

**Prepared for the
U.S. DEPARTMENT OF ENERGY
OFFICE OF TECHNOLOGY DEVELOPMENT
Washington, D.C. 20585**

August 1993

**Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 83731-6285
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC01-EW30030**

MASTER

als
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	PAGE
ACRONYMS.....	iii
INTRODUCTION.....	iv
APPENDIX A. BIOLOGICAL PROCESSES.....	A-1
A-1. Anaerobic Fluidized Bed Reactor.....	A-1.1
A-2. Hydroponic Reactor.....	A-2.1
A-3. Stirred Batch Bioreactor.....	A-3.1
APPENDIX B. ELECTROCHEMICAL SEPARATION TECHNOLOGIES.....	B-1
B-1. Capacitive Deionization.....	B-1.1
B-2. CEPOD, MEO, and Persulfate Processes.....	B-2.1
B-3. Electrokinetic Technology.....	B-3.1
B-4. Electrolytic Technology.....	B-4.1
APPENDIX C. ELECTROMAGNETIC SEPARATION TECHNOLOGIES.....	C-1
C-1. Magnetic Separation.....	C-1.1
C-2. High Field Gradient Magnetic Separation.....	C-2.1
APPENDIX D. FREEZE CRYSTALLIZATION.....	D-1
APPENDIX E. PHASE SEPARATORS.....	E-1
APPENDIX F. MECHANICAL SOLID/LIQUID SEPARATION.....	F-1
F-1. Traditional Coagulation and Flocculation.....	F-1.1
F-2. Flotation.....	F-2.1
F-3. Foam Fractionation.....	F-3.1
F-4. Sedimentation/Decantation.....	F-4.1
F-5. Centrifugal Sedimentation.....	F-5.1
F-6. Hydrocyclones.....	F-6.1
F-7. Filtration.....	F-7.1
APPENDIX G. MEDIA BEDS.....	G-1
G-1. Granulated Activated Carbon Adsorption.....	G-1.1
G-2. Powered Activated Carbon Adsorption.....	G-2.1
G-3. Alternative Rohm and Haas Process.....	G-3.1
G-4. Activated Alumina Adsorption.....	G-4.1
G-5. Ferrite Adsorption.....	G-5.1
G-6. Silica Gel Adsorption.....	G-6.1
G-7. Ion Exchange.....	G-7.1
G-8. Chromatography.....	G-8.1
G-9. Ion Specific Chromatography.....	G-9.1
G-10. Bioadsorption.....	G-10.1

TABLE OF CONTENTS (Concluded)

	PAGE
APPENDIX H. MEMBRANES	H-1
H-1. Reverse Osmosis	H-1.1
H-2. Ultrafiltration.....	H-2.1
H-3. Microfiltration.....	H-3.1
H-4. Electrodialysis.....	H-4.1
H-5. Supported Liquid Membranes.....	H-5.1
H-6. Pervaporation	H-6.1
APPENDIX I. NITRATE DESTRUCTION/SEPARATION	I-1
I-1. Nitrate to Ammonia and Ceramic (NAC) Process	I-1.1
I-2. Electrochemical Ion Exchange.....	I-2.1
I-3. Biodentrification	I-3.1
I-4. Chemical Reduction	I-4.1
I-5. Hydrothermal Process	I-5.1
I-6. Calcination.....	I-6.1
I-7. High Temperature Processes.....	I-7.1
I-8. Salt Splitting.....	I-8.1
APPENDIX J. PRECIPITATION.....	J-1
J-1. Standard Precipitation Methods.....	J-1.1
J-2. TRU/CLEAR®	J-2.1
J-3. Sequestering Agents	J-3.1
APPENDIX K. PYROCHEMICAL PROCESSING.....	K-1
APPENDIX L. SOLVENT EXTRACTION.....	L-1
L-1. Conventional Solvent Extraction.....	L-1.1
L-2. Supercritical Fluid Extraction.....	L-2.1
L-3. TRUEX Actinide Segregation.....	L-3.1
L-4. Cloud Point Extraction.....	L-4.1
APPENDIX M. THERMAL TECHNIQUES.....	M-1
M-1. Conventional Evaporators.....	M-1.1
M-2. Thin Film Evaporators.....	M-2.1
M-3. Drying.....	M-3.1
M-4. Distillation	M-4.1
M-5. Air Stripping	M-5.1
M-6. Stream Stripping	M-6.1
APPENDIX N. MERCURY SEPARATION PROCESSES.....	N-1
APPENDIX O. DECONTAMINATION	O-1

ACRONYMS

ASME	American Society of Mechanical Engineers
BRC	Below Regulatory Concern
BWR	Boiling Water Reactor
CPTS	Chemical/Physical Treatment System
DF	Decontamination Factor
DOE	Department of Energy
EM	Office of Environmental Restoration and Waste Management
EPA	Environmental Protection Agency
ES&H	Environmental Safety and Health
F&OR	Functional and Operational Requirements
FEH	Front-end Handling
FFCA	Federal Facility Compliance Agreement
FWF	Final Waste Forms
HEPA	High-Efficiency Particulate Air
IGR	Institute of Gas Research
LDR	Land Disposal Restrictions
LLMW	Low-level Mixed Wastes
LLW	Low-level Waste
MVR	Mechanical Vapor Recompression
MW	Mixed Waste
MWIP	Mixed Waste Integrated Program
MWTP	Mixed Waste Treatment Plant
MWTP	Mixed Waste Treatment Project
NPDES	National Pollution Discharge Elimination System
OGT	Offgas Treatment
OTD	Office of Technology Development
PCB	Polychlorinated biphenyl
PCE	Perchloroethylene
PWR	Pressurized Water Reactor
RCRA	Resource Conservation and Recovery Act
RDDT&E	Research, Development, Demonstration Test and Evaluation
RF	Radio Frequency
RO	Reverse Osmosis
SF	Separation factor
TASR	Technology Area Status Report
TCE	Trichloroethylene
TDS	Total Dissolved Solids
TSG	Technical Support Group
TTP	Technical Task Plan
UHPW	Ultra High Pressure Water
UV	Ultraviolet
VOC	Volatile Organic Compound
VR	Volume Reduction
WDS	Waste Destruction and Stabilization

INTRODUCTION

These Appendices describe various technologies that may be applicable to the Mixed Waste Treatment Plant (MWTP) Chemical/Physical Treatment System (CPTS). These technologies were identified by the CPTS Technical Support Group (TSG) as potentially applicable to a variety of separation, volume reduction, and decontamination requirements. The purpose was to identify all available and developing technologies, and their characteristics, for subsequent evaluation for specific requirements identified for the CPTS. However, the technologies described herein are not necessarily all inclusive, nor are they necessarily all applicable. Subsequent investigations will assuredly uncover additional technologies for evaluation, and will provide additional information for the technologies described in these Appendices to allow a more comprehensive and accurate technology evaluation.

APPENDIX A BIOLOGICAL PROCESSES

The biological processes described in this appendix are as follows:

- A-1 Anaerobic Fluidized Bed Reactor
- A-2 Hydroponic Reactor
- A-3 Stirred Batch Bioreactor

APPENDIX A-1 ANAEROBIC FLUIDIZED BED REACTOR

1.0 TECHNOLOGY DESIGNATION

This technology involves an anaerobic fluidized bed reactor containing bacterial cells immobilized on either alumina or finely ground particles of coal. Depending upon the exact nature of the input stream, the bacteria can be facultative anaerobes, or consortia of strict anaerobes and methanogens.

2.0 NEED FOR THE TECHNOLOGY

Many compounds commonly found in waste streams, compounds such as perchloroethylene, chlorinated biphenyl, and nitrated polyaromatics, are resistant to aerobic degradation by microbes. However, most can be degraded under proper anaerobic conditions. Anaerobic digestion is a process that can begin the degradation of resistant forms so that oxidative or methanotrophic bacteria can be used in subsequent procedures.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Fluidized bed reactors, employing bacteria immobilized on particulate matter such as alumina or coal, permit the residence time and other contact parameters to be controlled very closely. Facultative anaerobes, such as nitrate and sulfate reducing bacteria, can be used to denitrify aqueous streams, degrade cyanide, dehalogenate carbon tetrachloride, and reduce metals such as chromium and mercury. Methanogenic bacteria, and the consortia that are often used with them, can mineralize perchloroethylene, chlorinated biphenyls, chlorobenzene, and a variety of polynuclear aromatics. Surprisingly, strict anaerobes are capable of direct reduction of aromatic rings.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The support requirements for facultative organisms are minimal. Methanogens, however, have more specific requirements which may include the addition of appropriate one and two carbon compounds to support their growth and metabolism. Also, the presence of hydrogen scavengers may inhibit many of the important reactions, so some adjustment of the contents of the reactor may be necessary. No matter which anaerobes are used, the output stream may contain toxic compounds such as vinyl chloride that may not have been present in the input

stream. Therefore, it may be necessary to follow anaerobic digestion with a subsequent step that promotes oxidation.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

All components, including bacteria, are readily available. However, no vendors of complete systems have been identified at this time, and it is likely that the systems would have to be maintained by on-site staff.

There are many research efforts and pilot projects using some form of anaerobic digestion. Fluidized bed applications include efforts to degrade cyanide, dimethyl phenol, chloroethylene, carbon tetrachloride, and naphthylene. Some of these projects are using the same biological materials to recover metals such as uranium.

3.3.2 Reliability and Maintenance Requirements

Without data from pilot plant studies, it is difficult to determine how reliable and easily maintained a continuous flow anaerobic reactor would be. Much would depend upon the strictness of the system. Methanogenic systems are more easily poisoned than others.

3.3.3 Secondary Waste Streams

In general, waste streams from anaerobic biological processes contain some toxic materials that have been incompletely degraded. However, virtually all of these can be completely degraded by subsequent oxidative steps. The anaerobic reactions can be considered a valuable pretreatment to begin the destruction of especially resistant compounds.

3.3.4 Separation Efficiency

Most of the troublesome organics in MW aqueous streams, such as benzene, degreasing solvents, and chloroform, are susceptible to degradation by anaerobic organisms. Residence times in existing experimental systems range between one-half day and two days. That, of course, is a function of cell density, concentration, and reactor design.

3.3.5 Safety and Health

Anaerobic reactors require the same intensive process control as do other bioreactors, and should these controls fail, the operators might possibly be exposed to the contents of the reactor. These contents, however, might be only slightly more toxic than the input stream and could, in fact, be considerably less toxic.

3.3.6 Operational Complexity

It is conceivable that small continuous-flow reactors might be operated in a controlled atmosphere environment. Obviously, the most important requirement for that atmosphere is that it be as low in oxygen as possible. Typically, it is possible to operate such boxes at 2 ppm oxygen or below for extended periods of time.

3.3.7 Glovebox Capability

The need for, and ability, to apply this technology in a glovebox has not been determined.

3.3.8 Environmental Impact

It is important to note that the effluent from an anaerobic reactor is not necessarily innocuous. Anaerobic processes are useful for reducing large, complex molecules, breaking rings, and dechlorinating recalcitrant solvents. The reactor may actually increase the biological toxicity of its contents under certain circumstances. Therefore, the effluent must be transferred to an aerobic or microaerobic facility, not into the environment.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

It is not possible, at this time, to perform a realistic cost analysis.

3.5 TECHNOLOGY COMPARISON

It has been assumed that, for very dilute aqueous streams in which the concentration of toxic wastes is low but unacceptable, anaerobic digestion is less expensive than chemical treatment. This is especially true for perchloroethylene, benzene, and many polyaromatic compounds.

4.0 DEMONSTRATION REQUIREMENTS

Although preliminary work has been done in Germany, Argentina, and Canada, fluidized bed anaerobic reactors are still in an early stage of the development cycle.

An alternative, which could be explored at this time, is the CBT technique, developed by the Institute of Gas Research (IGR) in Chicago, and co-funded by the Department of Energy and the EPA. In this process, hydroxyl radicals are produced from metal salts and peroxide, and used in an initial oxidation step. Then, the material is treated with alternating cycles of anaerobic and aerobic digestion to promote further degradation. Although the anaerobic step is currently not as stringent as the mixed waste stream probably requires, it is possible that a

collaboration between IGR and fluidized bed engineers at a national laboratory could develop a more suitable process using this very promising technology.

5.0 VENDOR LIST

At this time there is no known vendor of a complete system.

6.0 REFERENCES

None

APPENDIX A-2 HYDROPONIC REACTOR

1.0 TECHNOLOGY DESIGNATION

This section describes an enclosed hydroponic reactor, containing many of the plants and much of the biochemical capability of a natural wetland. The device is a special example of a baffled reactor, containing compartments in which a variety of degradation and remediation reactions can occur. A majority of the biological activity occurs in complex consortia associated with the root systems of higher plants.

2.0 NEED FOR THE TECHNOLOGY

This type of reactor is appropriate for the treatment of mixed aqueous waste, containing moderate amounts of organic solvents and metals. Due to the low operating cost and wide variety of decontamination activities it can perform, it is suitable for low to medium throughput streams that are variable in composition. With the possible addition of polishing steps to remove traces of certain metals, the output stream will generally meet most environmental standards.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The collection of organisms that associate with the roots of characteristic wetland flora is capable of a wide variety of decontamination activities. Among these are sedimentation, coagulation, filtration, volatilization, adsorption, chelation, oxidation, and chemical reduction.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

These plant and microbial systems have been used in natural wetlands to purify municipal waste, denitrify groundwaters, and remove metals from heap leachates and other surface waters associated with mining. They are capable of removing better than 99% of metals such as zinc, cadmium, and copper, and have been used to concentrate uranium and thorium. Since both aerobic and anaerobic degradation activities exist within the system, reductive dehalogenation followed by oxidative mineralization has been observed for a number of volatile solvents. The systems are sensitive to high salt concentrations, so dilution of the input stream may occasionally be necessary. In addition, performance may be enhanced by adjusting the pH of the input stream, as well as by the addition of micronutrients not present in the liquid.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Since neither the equipment nor plant material are commercially available, there are presently no vendors who provide and maintain systems. Although there are no absolute requirements for the kind of equipment that must be used, the system functions best as a baffled reactor, and may require custom construction. One disadvantage is that the system must be maintained by on-site staff, since it is necessary that the treatment modules remain alive and in reasonable health. It is also, of course, necessary that the system be exposed (through a transparent or translucent cover) to the light, since that is the source of energy for most of the remediation activities.

There are experimental units being used as water purification systems for agricultural and dairy waste streams. In addition, there is some development work being done in the area of metal reclaiming. However, these units are neither completely enclosed nor under process control.

3.3.2 Reliability and Maintenance Requirements

Until a "wetland" hydroponic bioreactor can be built, estimates of maintenance requirements remain somewhat theoretical. However, once the consortia are established, they tend to be quite stable when the input stream remains reasonably constant. This is, of course, exactly the opposite of what is expected in this case. Therefore, the extent to which the system might adapt to large changes in the types and concentrations of contaminants is unknown.

3.3.3 Secondary Waste Streams

The waste stream is water containing small amounts of metals. However, some of the biomass within the system must occasionally be removed, and it may contain high levels of metals as well as unreacted toxins that were adsorbed or incorporated within the organisms of the rhizosphere.

3.3.4 Separation Efficiency

Most organic compounds will be degraded by the wetland system. Actively transpiring plants can accomplish a significant volume reduction in aqueous streams. Virtually all toxic metals will be precipitated, adsorbed, or otherwise retained within the reactor.

3.3.5 Safety and Health

The detoxifying powers of microbial-vascular plant consortia are considerable, implying that this should be one of the safest bioreactors from an operator's point of view. However, when maintenance is required, some contact with the plant materials, and adherent metals, etc., cannot be avoided. It is expected that most biomass harvesting, etc., can be robotized.

3.3.6 Operational Complexity

The same diversity that provides this system with its broad range of remediation abilities, should make it easier to operate. Process control will be necessary to regulate flow, fluid levels, temperature and light. Most of the complexity will be due to the need to monitor concentrations of contaminants, and environmental conditions, at several places within the system.

3.3.7 Glovebox Capability

The system is, in a sense, a glovebox.

3.3.8 Environmental Impact

As a large volume, low concentration, final step in the decontamination process, the effluent from a wetland bioreactor can be expected to meet all environmental requirements for discharge.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Because the design of the system is so straightforward, most of the cost is expected to be in the process control and monitoring component. The reactor itself is little more than an array of hydroponic compartments contained within a transparent enclosure.

3.5 TECHNOLOGY COMPARISON

Even though this technology is completely untried, the phenomenal success of natural wetlands to detoxify everything from mine drainage to municipal waste would highly recommend hydroponic systems for this application. Wetland organisms are very hardy, and resistant to most environmental toxins. However, the primary advantage of wetland consortia is their biochemical diversity, and their ability to deal with a very broad slate of chemical contaminants and metals present in low but unacceptable concentrations. In addition, a hydroponic reactor represents a source of, and use for, recycled process water. Volume reduction can also occur through controlled transpiration.

4.0 DEMONSTRATION REQUIREMENTS

It is considered unlikely that this technology will be developed by commercial interests. It is rare that commercial facilities need to completely contain their processes, because natural wetlands are plentiful. A facility in which to treat mixed waste would have to be developed within the federal laboratory system, and transferred to private business at a later date.

5.0 VENDOR LIST

There is no known vendor of complete hydroponic systems.

6.0 REFERENCES

None

APPENDIX A-3 STIRRED BATCH BIOREACTORS

1.0 TECHNOLOGY DESIGNATION

Stirred batch reactors contain either specially selected aerobic microorganisms or methanotrophic bacteria. These systems are especially suited to the degradation of chlorinated solvents and may be used for hydrochlorofluorocarbon compounds as well.

2.0 NEED FOR THE TECHNOLOGY

As much as one percent of aqueous liquids may be composed of organic compounds, including degreasing solvents and formaldehyde. Some of these, such as trichloroethylene, have appreciable solubility in water. Between cycles of growth, selected aerobic bacteria are capable of degrading some of these organics, especially in the presence of compounds that induce certain specific catalytic activities. In addition, methanotrophic bacteria are capable of co-metabolizing chlorinated aliphatics and related compounds as a consequence of their vigorous oxidation of methane.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Although no bacteria rely on solvents as a natural food source, a few are capable of oxidizing them with enzymes designed for other purposes. A dioxygenase designed to modify toluene, for example, can oxidize trichloroethylene and a variety of less chlorinated aliphatic compounds. Similarly, a monooxygenase used by methanotrophic bacteria to oxidize methane can also attack volatile organic compounds as a minor, but significant, activity. These reactions may be useful in remediating aqueous waste streams containing only low levels of solvents. Alternately, they may be important to complete a more extensive and general remediation process that was begun in an anaerobic digester.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The input stream must be treated to provide materials to support the growth and metabolism of the cells. Often this involves adding a sugar such as lactate, and some micronutrients. In addition, an inducing compound, such as toluene, must occasionally be present to promote the expression of the appropriate enzyme. Methanotrophs, obviously, must be provided with methane, usually in the form of a gas uplift. Also, sufficient oxygen must be

present to support the oxygenase activity, as well as other normal metabolic activities in the bacterial cells.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Vendors of systems for specific degradative needs have been identified. However, there are presently none who provide systems for mixed waste or uncharacterized streams.

Research into oxygenase-producing bacteria is very active. Most efforts are focused on ways to increase the activity, have it expressed throughout the growth cycle, and eliminate the need for inducers or co-metabolites.

3.3.2 Reliability and Maintenance Requirements

Successful tests have generally employed dispersed-growth systems, in which bacteria and soluble enzymes are not immobilized. Thus, maintenance of such continuous-flow devices is related to keeping the flow rate within acceptable limits and removing from the input stream those compounds which are capable of interfering with the degradation process.

3.3.3 Secondary Waste Streams

To the extent that the oxidation of the substrate is complete, the secondary waste stream meets most environmental requirements.

3.3.4 Separation Efficiency

At present, the upper limit of degradation of compounds such as *Pseudomonas* bacteria is approximately one gram of material per day per gram of cellular mass. Methanotrophs may be capable of higher rates of degradation due to advances in soluble enzyme production. Some *Methylosinus* species may be capable of degrading more than one gram per hour, per gram of cellular mass. In addition, methanotrophs may be more likely to degrade chlorinated single carbon compounds.

3.3.5 Safety and Health

It is generally understood that the contents of batch reactors are considered hazardous until the degradation reaction has reduced the concentration of contaminants to acceptable levels. However, bioreactors are no more hazardous than their input streams, and do not constitute additional health considerations for operators.

3.3.6 Operational Complexity

Biological reactors are inherently complex due to the constant need for monitoring and process control. Under normal circumstances, these are the responsibilities of the computerized control system, that is capable of determining concentrations of contaminants, nutrients, cells, and even degradation enzymes.

3.3.7 Glovebox Capability

It is unlikely that this technology would be operated within a glovebox.

3.3.8 Environmental Impact

Tests involving water containing TCE, DCE, vinyl chloride, and chloroform have indicated that the effluent generally meets the requirements for discharge into a sanitary sewer system.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Cost estimates have been requested.

3.5 TECHNOLOGY COMPARISON

Biological reactors are most competitive when volumes are high and concentrations of organic contaminants are too low to be effectively treated by chemical processes. Among biological reactor systems, those which use aerobic or microaerobic conditions enjoy a slight superiority because they 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 and are best used as a follow-up technology to anaerobic digestion.

4.0 DEMONSTRATION REQUIREMENTS

Since this technology is used near end-stream, the input stream must be conditioned to remove toxic metals (bioadsorption) and reduce complex aromatics (anaerobic digestion). For testing and demonstration purposes, the input must still retain the organic complexity of the actual waste stream, since unknown organics might have profound effects of the process.

4.1 DATA REQUIREMENTS

At this time, only one vendor has been identified that may be able to provide a full-scale system in a realistic time frame. However, the data on pilot scale tests are apparently being compiled for submission and are not immediately available.

4.2 TESTING REQUIREMENTS

A methanotrophic bioreactor system is being developed by Biotrol, Inc., 11 Peavey Road, Chaska MN 55318. Their contact person is Durell Dobbins, (612) 448-6050. Biotrol has tested their system with a variety of halogenated aliphatic hydrocarbons, and has applied for patents on methods to increase enzyme production and to colorimetrically detect enzyme concentrations in-process.

5.0 VENDOR LIST

There is no known vendor that can provide systems for mixed waste or uncharacterized waste streams.

6.0 REFERENCES

None

APPENDIX B ELECTROCHEMICAL SEPARATION TECHNOLOGIES

The electrochemical separation technologies described in this appendix are as follows:

- B-1 Capacitive Deionization**
- B-2 CEPD, MEO, and Persulfate Processes**
- B-3 Electrokinetic Technology**
- B-4 Electrolytic Technology**

APPENDIX B-1 CAPACITIVE DEIONIZATION

1.0 TECHNOLOGY DESIGNATION

Capacitive Deionization is a type of deionization that is done without ion exchange resins or chemical regeneration.

2.0 NEED FOR THE TECHNOLOGY

This technology would be used as a secondary or tertiary treatment (Process 190 and 195) on the Mixed Waste process flow sheet for the Aqueous Liquids Treatment Line. Prior to discharge as clean water, the waste water must be substantially free of dissolved salts, acids, and bases. This technology could take the place of a mixed bed ion exchange column, which produces waste from chemical regeneration. The stream must be clean except for dissolved species. Only the ionized (i.e., charged) species will be removed. Charged colloidal material is probably too large to migrate within the solid. The output stream could be described as deionized water.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Although the technology was described more than 20 years ago, it has not been commercialized due to lack of suitable materials. The needed materials are now available and are produced by the aerogel process, which produces monolithic blocks with many micropores. These aerogel electrodes, with insulating porous separators between, are stacked vertically touching each other. Brine flows in at the bottom of the stack and through the pores of the electrodes and spacers, exiting the top. Once wetted, the stack must be prevented from drying, but this is a typical operating situation. Alternating electrodes would be either slightly anodic or slightly cathodic. Voltage is kept low to avoid electrolysis. Regeneration is accomplished by switching polarities. When a field is applied, the solid acts as a large surface capacitor, trapping ions in the Stern and to a lesser extent the Guoy parts of the electric double layer in the liquid.

The aerogel traps the ions on its extensive internal surface. Separators are insulators that prevent electrical shorting of adjacent electrodes of different polarity. The concentrated solution is within the electrodes. After treating a dilute electrolyte for a while, the effluent is routed to a waste tank and the polarity of the stack is reversed which causes all the

accumulated ions to desorb and exit the stack. The outlet end of the stack will start adsorbing just before the regeneration is over.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The usual pretreatments of suspended solids removal is appropriate. Also, any dissolved material that could destroy the aerogel must be absent. There are no known limits on feed concentration or outlet purity. However, residence time may become too long to be practical if the performance requirements are too demanding.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The technology and equipment are not available, and commercialization possibilities will depend on the outcome of the research. To date, both carbon and semiconducting oxide-based aerogels have been made, and the carbon ones have found application in electrical capacitors. Also, carbon aerogel is known to allow water to flow through its structure, although the relationship between flow rate and pressure drop has not been established. Application to deionization is in the research stage. Research on this technology has been proposed by LLNL to EM-50 as an off-shoot of their rather large aerogel program.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintenance issues are unknown at this time.

3.3.3 Secondary Waste Streams

There is no secondary waste, but only concentrated primary waste. Macroporous separators should have essentially an unlimited life. The aerogel electrode has an unknown useful life, but soaking it in water for a long time does not seem to degrade it.

3.3.4 Separation Efficiency

Based on the theoretical description, the separation can be made very efficient and the output stream could be regarded as deionized water. Volume reduction of water contaminated with ions is thought to be approximately 99%. Volume reduction of chemicals used for regeneration is approximately 100%.

3.3.5 Safety and Health

There are no known safety issues.

3.3.6 Operational Complexity

Operation is very simple. The physical size is not known and will depend on the flow rate of solution that can be achieved at reasonable pressure differentials.

3.3.7 Glovebox Capability

The technology has not been demonstrated in a glovebox, but no special requirements are anticipated.

3.3.8 Environmental Impact

No environmental impact has been identified, except that it can result in a cleaner water effluent.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

The cost to complete development is not known, because actual development has not started and unforeseen problems could be encountered. Capital cost is not known, but if aerogels find the market anticipated, which would require their mass production, the technology should be remarkably inexpensive. Considerations are that the process can be automated, requires no chemicals, and uses DC current at about 2 V. The amount of current will depend on the concentration of ions to be removed, approximately 10^5 coulombs per equivalent.

3.5 COMPETITIVE TECHNOLOGIES

The most obvious competitive technology is ion exchange using chemicals to regenerate the resin when it becomes loaded with the ions being removed. This new process would clearly be superior because no secondary waste is generated. The lifetime of the resin may be a year or more but the lifetime of the aerogel is unknown in this application.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data on the nature of flow through the solid are needed, and how it can be influenced by choice of material and aerogel structure manipulation. In addition, data are needed on the steady state and transient behavior of the material when an ionic solution is in the solid and the

power is turned on. The capacity of the solid to trap ions and then reversibly release them must be determined. The capacity is expected to be much higher than an ion exchange resin that depends on the presence of functional groups being attached to the polymer. Since there are no vendors with the data needed, the necessary data will be obtained through tests.

4.2 TESTING REQUIREMENTS

The testing requirement would be to obtain the data described in Section 4.1 as functions of temperature, applied voltage, and electrode thickness. This data will be obtained at a federal laboratory using existing equipment. If the technology is well funded, testing with surrogate material is probably not required, so pilot-scale equipment need not be in a glovebox. Testing will be completed in about one year. At that point it should be possible to judge the merits of the process and decide if it deserves to move from the research stage to development. Research will cost between \$0.5M and \$1M. Development will cost about the same and should include a pilot-scale facility.

5.0 VENDOR LIST

There are no vendors of this technology.

6.0 REFERENCES

1. Johnson, A. M., and John Newman. *J. Electrochemical Soc.* Electrochemical Tech., 118, 510, 1971.
2. Conference on Aerogels. *J. Noncrystalline Solids*, 145, 1, 1992.
3. Slater, M. *Principles of Ion Exchange Technology*, Butterworth and Heinemann: Boston, 1991.
4. Cotts, P. and R. Pekala. *Polymer Preprints*, 32 451, 1991.
5. Hrubesh, L., *Chem & Industry*, 24 824, 1990.
6. Pahl, R., et al. *J. Applied Crystallography* 24 771, 1991.
7. Lu, X., et al. *Science*, 255 971, 1992.

APPENDIX B-2 CEPOD, MEO, AND PERSULFATE PROCESSES

1.0 TECHNOLOGY DESIGNATION

This is nominally a one-step aqueous electrochemical process or a two-step process with one aqueous electrochemical step. CEPOD is an acronym for catalyzed electrochemical plutonium oxide dissolution, whereas MEO is an acronym for mediated electrochemical oxidation. Persulfate is a process in which the strong oxidizer peroxydisulfate ion is generated in an electrochemical cell and is then added to a solution that may or may not contain a metal capable of performing as a mediator (catalyst).

2.0 NEED FOR THE TECHNOLOGY

This process will remove mixed waste from the surface of homogeneous or heterogeneous dry solids just prior to the mechanical separations process. The remaining waste treatment processes can then be conducted outside gloveboxes. Gloveboxes cost about a million dollars each and are much harder to work in for maintenance, etc.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The process depends on the ability of strong oxidizers, when used with a redox couple in acid solution, to remove both hazardous and radioactive species from the surfaces of many solids. After treatment the solids can normally be handled or further processed outside of gloveboxes. An electrochemical cell is used to generate the oxidizer at the anode, which then moves into the bulk electrolyte. Commercial designs are quite satisfactory. A microporous membrane is usually placed between the electrodes to prevent the oxidizer produced at the anode from being reduced at the cathode. The separator may be a microporous ceramic or glass or a nanoporous polymeric membrane that may be ion-selective. The oxidizer will produce hydroxyl free radicals from water; and the oxidizer and free radicals both attack organic compounds converting most of them to CO₂, water, and inorganic ions. The oxidizer along with the acid dissolves compounds of radionuclides, including PuO₂, which is not soluble in nitric acid alone. The oxidizers destroy hazardous organic compounds and dissolve inorganic compounds containing radionuclides. To keep waste generation to a minimum, chemicals added should all be recycled. Recovery/recycle processes have been developed or are under development for the materials used in MEO and CEPOD processes. The process can be

applied inappropriately and result in dissolving the bulk solid rather than separating it from the surface waste.

Setting the current and flow rate for a fixed time will minimize dissolution of the substrate. Leaded glovebox gloves, Teflon, high density polypropylene, glass and ceramics, and metals that form a stable oxide in nitric acid (stainless steels, titanium, etc.) are very easy to decontaminate. The key to success is in the front-end sorting operation to remove unsuitable materials from the waste stream.

The system volume will depend on the size of parts to be cleaned and the required throughput. The biggest volume in the system is likely to be the tank in which the parts are cleaned and that will be influenced by a front-end size reduction process. Frequency of waste acid treatment will be determined by substrate attack.

3.2 INPUT AND OUTPUT SPECIAL CHARACTERISTICS

The pretreatment requirement includes sorting so that potentially dissolvable bulk solids are not fed to the process. An example of this unwanted dissolution would be to put a copper piece into a nitric acid electrolyte. Also, some size reduction may be required because the treatment tank size has some practical limit based on the inventory of electrolyte the plant operator is willing to store. In addition, the electrolyte must be able to contact all the solid surfaces to be treated. Internal surfaces must be accessible to be treated.

The process works on virtually all hazardous organics. It is not recommended for metals that dissolve (as mentioned), or highly oxygenated bulk organics such as cellulose, which also are destroyed. Output streams are carbon dioxide, water, inorganic anions if heteroatoms are in the organic hazardous waste, cations from radionuclides that were in inorganic form such as oxide, and the electrolyte which could contain a redox metal ion (mediator/catalyst). All process chemicals are expected to be regenerated and recycled. Therefore, the output streams will be gaseous, liquid (usually a strong acid), and decontaminated solid (the treated input).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Vendors that supply cells, plastic pipe, pumps, and tanks are numerous. Their performance is not uniformly excellent and the equipment should be evaluated for ease of use in a glovebox, particularly with respect to reliability and maintainability. The most comprehensive listing is in the Thomas Register, but other suppliers can be found in the monthly issues of Chemical Equipment and Pollution Equipment.

This separation method has been demonstrated and is under development at PNL and LLNL. A coordinated pair of TTPs were prepared and submitted to MWIP. The process for making peroxydisulfate ion is commercially available and using it to raise the valence of a mediator ion or destroy organics has been demonstrated on a laboratory scale. Recovery and recycle of some process chemicals has also been demonstrated on a laboratory scale. Details of pre- and post-treatment solids handling needs more work.

The availability of this technology is within reach, but not from commercial vendors. All the development has been done at DOE sites. As mentioned earlier, components are readily available for most parts of a system. The technology could be ready within a year, but would require a major thrust in development. Time to procure components will be vendor-dependent, but 90 days ARO is sufficient for everything other than custom-fabricated items.

3.3.2 Reliability and Maintenance Requirements

Reliability of system operation has not been demonstrated. Scheduled annual shut-down for cell refurbishment is expected and would require a week.

3.3.3 Secondary Waste Streams

Secondary waste will be primarily ion permeable membranes and possibly deteriorated gaskets, depending on choice of gasket material. The amount will depend on the size of the system.

3.3.4 Separation Efficiency

The separation accomplished should range between 99% and 99.99%.

3.3.5 Safety and Health

The major health issue is working with about 100 L of strong acid. Most of the operations will be done in a glovebox, however, and the technology is already automated. Some hydrogen could be produced, so a constant slow purge with another gas would be a good precaution.

3.3.6 Operational Complexity

The size is equal to or smaller than competing technologies. The competing technology is a lengthy series of washings alternating between various solvents or other cleaners to remove organics and acid solutions to remove radionuclides.

3.3.7 Glovebox Capability

The bulk of the process has been demonstrated in a glovebox flushed with air.

3.3.8 Environmental Impact

Environmental impact will be small. The best impact is that the environment will be saved from small quantities of hazardous materials. The worst is that a spill could occur and would have to be cleaned up and disposed of properly.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

Development costs are about a million dollars. Assuming the facility is fully equipped, up and running, and the gloveboxes are installed, plumbed, and instrumented, capital costs will be approximately one million dollars. Energy costs for operating the facility will be higher than many other processes, such as sedimentation. Trade-offs can be made between maintenance and replacement. Secondary materials may be negligible if everything is recycled. (This is another trade-off study that needs to be performed.) Disposal costs are expected to be small, but the same caveat applies to recycling. With no recycling, disposal costs would be higher.

3.5 TECHNOLOGY COMPARISON

See Section 3.3.6. Further details will be provided at a later date.

4.0 DEMONSTRATION REQUIREMENTS

4.1 Data Requirements

The types of mixed waste that must be removed from solid surfaces must be identified. In addition, methods are needed to show whether treated solids are clean and secondary treatment methods are needed for solids requiring further treatment. At the present time, there are no relevant vendor data for a system like this. Testing is needed to determine the degree of cleaning obtained for various wastes, cost of process chemical recycle versus disposal, and reliability in long-term operation.

4.2 TESTING REQUIREMENTS

As discussed in Section 4.1, testing is required to determine the degree of cleaning obtained for various wastes, cost of process chemical recycle versus disposal, and reliability in long-term operation. Full-scale test support of the pilot plant is anticipated to be provided by

federal laboratories. Initial testing should be conducted using surrogate materials since the labor needed is usually less if changes are made or spills occur.

Depending on the system configuration, testing may cost about \$500K, and the pilot plant may cost about one million dollars if existing facilities are used. A schedule for testing is unknown at the present time.

5.0 VENDOR LIST

There are no vendors for such a system, but there are for most of the components. See previous remarks in Section 3.3.1.

6.0 REFERENCES

1. Glasstone, S. *Sourcebook on Atomic Energy*. 3rd ed. Van Nostrand Reinhold: New York, 1967.
2. Froment, G. and K. Bischoff. *Chemical Reactor Analysis and Design*. 2nd ed. John Wiley & Sons: New York, 1990.
3. Kurath, D., et al. "Engineering of the CEPOD II Dissolver System." Pacific Northwest Laboratory, Report No. PNL-7275, 1990.
4. Farmer, J. "Electrochemical Treatment of Mixed and Hazardous Wastes." in *Environmental Oriented Electrochemistry*. C. Sequeira, ed. Elsevier: New York, 1992.
5. Hickman, R. "Mediated Electrochemical Hazardous Waste Destruction." in *Emerging Technologies for Hazardous Waste Management*. D. Tedder, ed. ACS Symposium Series, American Chemical Society, Washington, 1992.

APPENDIX B-3 ELECTROKINETIC TECHNOLOGY

1.0 TECHNOLOGY DESIGNATION

Electrokinetic technology pertains to migration, and therefore separation of water and/or charged ions and colloids in an electric field. Other related names are electro-osmosis, electromigration, electrophoresis, and electrofiltration.

2.0 NEED FOR THE TECHNOLOGY

This set of technologies may find use as an alternative to pressure-driven filtration, filtration aid (plugging prevention), or in the treatment of sludges by removing unwanted colloids or dissolved ions when used in conjunction with electrodeposition. This technology may be used in the Wet Solids Treatment Line prior to the dryers or as a filtration step in the aqueous treatment line to remove very fine suspended particles.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

In a medium that allows migration to occur, such as a liquid or a porous solid, application of a dc electric field will cause motion of charged species relative to the medium or to species of opposite charge, or of the solvent relative to a fixed charge. Electro-osmosis can be used for water purification using the fixed charge on a permeable membrane structure. Deposition of colloidal latex on to metal substrates is accomplished in tanks on a commercial basis, and soils can be dried in-situ by causing water to migrate in clays until the water that was in a region is no longer present.

A particle in contact with water will typically acquire a net excess charge at its surface that produces an electrical potential difference between the solid and aqueous phases. Since the overall system must retain electrical neutrality, the excess surface charge is balanced by an equal and opposite charge in solution. This charge in solution is distributed over a finite distance from the solid surface and is known as the electrical double layer.

The presence of the double layer gives rise to the electrokinetic transport phenomena in solid/liquid systems. These phenomena include electro-osmosis, which involves movement of water in response to an electric field, predominantly to the cathode; electrophoresis, which refers to the migration of charged particles or colloids in suspension (generally dilute) and their deposition on an oppositely charged electrode, usually the anode; and electromigration, which

involves movement of solute ions in the electric field to oppositely charged electrodes. These phenomena can be used to separate solids from an aqueous suspension. For more concentrated suspensions, the particles can be regarded as immobile and only electro-osmosis and electromigration take place.

Because electro-osmosis directs the water toward the cathode, cathodes require some means to mechanically collect the water. That is, cathodes need to be electrically conducting and porous to water, but not to the particles of the suspension. In practice such cathodes comprise metal mesh covered with fabric in the form of a reservoir. Anodes must also be protected to prevent particles from the suspension from being deposited directly on the anode, and to maintain a relatively constant electrolyte composition around the anode.

Current flow is accompanied by reactions at the electrodes: hydrogen is released at the cathode and oxygen is released at the anode. One of the major problems in developing electrofiltration equipment is the availability of an anode material that is technically and economically acceptable. Most metals when used as anodes corrode electrochemically, due to the severe oxidizing conditions, producing metal ions and excess electrons. Cathodes do not corrode electrochemically. The normal situation at the cathode is production of hydrogen and the hydroxyl radical causing the water around the cathode to be alkaline. Therefore, there are fewer problems in selecting cathode materials in terms of corrosion resistance, and stainless steel mesh is usually adequate.

Consumable electrodes may be used when contamination of the deposited product by the anode is not an issue, dimensional instability can be tolerated, and the cost of replacing the anodes is acceptable. Consumable electrodes include retort carbon, graphite, copper, and zinc. However, carbon and graphite electrodes are seldom used in electrofiltration because the particles contaminating the electrolyte can create stray currents and plug membranes.

New, dimensionally stable anodes (DSA) have been developed using a titanium substrate coated with a mixture of noble metal catalysts. These electrodes fall into two main categories: platinum iridium over titanium, and mixed oxide semiconductors over titanium. These electrodes require control of the contacting electrolyte for long life, a minimum conductivity to prevent electrical stress from blowing off the coating, and some of these coatings can be poisoned by specific ions such as calcium and magnesium. The chemistry of the electrolytes bathing the electrodes can be controlled by isolating the electrodes using ion selective membranes. Their major drawback is cost.

Unprotected electrodes, particularly the anode, lead to the cake being deposited directly on the electrode surface causing DSA coatings to become deactivated after a relatively short period. Also, the considerable pH changes that occur in the immediate vicinity of the electrodes (the electrolyte solution becomes alkaline near the cathode and acidic near the anode) cause the

electrodes to operate in a continuously changing environment. The advantage of isolating or protecting the electrodes is to extend the electrode life and prevent the electrode reaction products from entering the separation chamber.

Protected electrodes and, in particular, protected anodes can be achieved by means of a solid electrolyte polymeric membrane or a selective ion exchange membrane that allows passage of ionic current between the slurry and the anolyte (the electrolyte surrounding the anode), while preventing intermixing of the anolyte and the fluid of the slurry. A suitable choice of anode membrane and anolyte composition allows accurate control of the chemical environment of the product cake, thus enabling a higher quality final product to be obtained and to maintain a homogeneous composition of the electrolyte around the anode.

Dewatering and filtering rate and efficiency are easily controlled by regulating the electric current and/or the applied voltage. Operation at constant current can enable a larger volume to be filtered compared with that at constant voltage. However, electric power consumption increases considerably in the last stages of the process because the electric resistance of the sludge bed increases with decreasing water content. The flow rate of water for a given suspension at a particular solid's content is proportional to current, although the proportionality factor (liters/Ampere-hour) varies with solids content, conductivity, nature of the suspension, etc. Since the ionic strength of the electrolyte effectively shrinks the solution double layer, the solution pH also becomes a controllable parameter. Electro-dewatering/filtering can also be controlled through the surface area used and separation of electrodes, which directly affect the current draw at a given voltage. Thus, the time to dewater a given sample is decreased, or the amount of water removed in a given time is increased, at large surface area/separation ratios of the electrodes.

Vertical positioning of protected electrodes offers the possibility to perform semicontinuous removal of the cake from the anodes by lifting them and mechanically removing the solid product with a doctor blade. Enhancement of performance for both rate of separation and ultimate purity or concentration has led to development of combined separation techniques in which the effect of the electric field is combined synergistically with the influence of other methods such as gravitation, mechanical pressure, vacuum, acoustic energy, and centrifugation.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Pretreatments, stream treatability, and both input and output streams will depend on feed stream content and to a lesser extent, volume. One can imagine that pH adjustment and control would be required. If the input stream is wet sludge, the output could be a damp cake possibly with an undesirable ion or organic colloid removed.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The presence of electrically charged solids in a polar solvent such as water leads to electrokinetic effects upon application of an electric field. Electro-osmotic dewatering was applied on a practical scale in 1939. The US Bureau of Mines pioneered research and development on electro-osmotic dewatering for fine suspensions from mineral processing in the early 1970s. Research in England began in 1976 on the electrical characteristics and electro-dewatering of clay suspensions with particle sizes in the micron to sub-micron range. Semicontinuous dewatering in reusable tanks developed to the stage of large-scale field tests in England as of 1986.

One of the applications of electrokinetics is to reduce the particulate blinding of dewatering or filtering membranes by electrophoretically driving the particles away from the membrane while hydraulically drawing fluid through the membrane. The electrophoretic deposition of particles and their subsequent removal from the system is another application of electrokinetics.

Although the MWIP charter does not include site remediation, several electrokinetic technologies being developed for the remediation of soils may be modified to remove contaminant ions from thick sludges in the CPTS. In addition to development of equipment for electrokinetic soil remediation, research is being performed to enhance the electrokinetic effects for certain contaminants in waste waters and sludges. This includes development of chelating agents that will bind with actinides and hazardous metal ions and optimize the electrokinetic effects. These studies are described below and the results should be evaluated for potential modification and application to removing selected species from wet solid waste streams.

Commercial electrofilters have been developed in the United States, Japan, and Germany. Other electrokinetic processes are being developed by industry and by DOE, primarily for soil remediation. Some of the applications of electrokinetic phenomena are well established, whereas others are very much in the developmental or even research stage. Much equipment is commercially available but may require adaptation for handling mixed waste. Some equipment is available off-the-shelf and probably no further development is necessary.

3.3.1.1 Electro-dewatering/Electro-filtration

The Dorr-Oliver Electrofilter is an industrial electrokinetic separator (Figure B-3.1) that combines vacuum filtration with electrophoresis and electro-osmosis. It uses DSAs, structural oxidation resistant plastics, ion selective membranes, and sophisticated process controls. The

THE ELECTROFILTRATION PROCESS

ELECTROPHORESIS: Particles migrating toward the anode element.

ELECTROOSMOSIS: Filtrate pumped out at the cathode element.
Product cake densified at the anode element.

Figure B-3.1. Schematic of Dorr-Oliver Unit

(From "Scale-Up Aspects in Electro-Osmotic Dewatering," Advances in Solid-Liquid Separation. H.S. Muralidhara, editor, page 288; 1986; Battelle Press, Columbus, Ohio.)

Electrofilter consists of a series of parallel plate-like electrode assemblies suspended in a tank containing the slurry to be separated. The anode assembly consists of an ion selective membrane surrounding an electrolyte solution which bathes a DSA element. The cathode assembly consists of a filter media surrounding a filtrate collection chamber. When electric current is applied, a cake is formed on each anode surface due to electrophoretic migration of particles. The cake is further dewatered electro-osmotically, typically yielding a cake moisture of 10% to 25%. Simultaneously, filtrate is continuously withdrawn from the cathode due to the combined effects of vacuum filtration and electro-osmosis. When the anode cake builds to a sufficient thickness, the anode is withdrawn from the bath, and the cake is discharged mechanically onto a conveyor belt. This system is a fully automated operation with microprocessor control. The Electrofilter is best suited to dewatering ultrafine (less than 10 micron) slurries, thereby competing with thermal dewatering. The number of anode (protected) and cathode elements determines the size of the machine which uses only 3% to 10% of the energy needed for thermal drying (Ref. 6).

Another machine on the market is from Fuji Electric (Figure B-3.2). The combined effect of the electric field and mechanical pressure is exploited. The machine has a revolving anode and a moving belt sliding above the cathode. Operating pressure is 3.5 kg/cm² and applied voltage is 90 volts (Ref. 6).

3.3.1.2 Electrochemical Migration

Chemical Waste Management and Bradtec are developing an electrochemical migration process for soil cleanup that selectively migrates contaminant ions while leaving the non-hazardous soil chemistry unchanged (Figure B-3.3). In the treatment of soils, a cathode and anode are placed in the soil. The collector electrode (cathode for cations, or anode for anions) may be surrounded by a porous material to provide a liquid reservoir that is separated from the soil. The driving electrode (anode for cations, cathode for anions) is surrounded by a permeable membrane which passes only the ion of the same charge as the contaminant to be collected. The driver electrode compartment contains a solution which provides free driver ions (i.e., cations for cation collection, or anions for anion collection). The driver ions migrate through the permeable membrane carrying the electric current. The driver ions are selected such that as they enter the contaminated soil, they will displace the contaminant ions in the soil with the contaminant ion migration carrying the electric current. The contaminant ions then interact at the collector electrode to form a precipitate, amalgam, or to plate out on the electrode; or are selectively recovered from the collector electrolyte solution. Contaminant recovery is either by recirculation of the electrolyte solution (in the case of a precipitate formation or selective

Figure B-3.2. Revolving Anode and Moving Belt in Fugl Electric Unit

(From "Scale-Up Aspects in Electro-Osmotic Dewatering," Advances in Solid-Liquid Separation, H.S. Muralidhara, editor, page 289; 1986; Battelle Press, Columbus, Ohio.)

Figure B-3.3. Schematic Diagram of the Electrochemical Migration Removal Process

(Reproduced with permission of Rust Remedial Services, Inc.)

recovery of a dissolved solid), or by periodically removing and replacing the electrode (in the case that an amalgam forms or the contaminants plate out on the electrode).

Applications include the recovery of contaminant ions (e.g., Hg^{+2}) or ionic compounds (e.g., CrO_4^{-2}) from soil. This process has been demonstrated in laboratory-scale tests. No pilot-scale or full-scale applications have been fielded.

3.3.1.3 Electrokinetics In Unsaturated Soil: Electrokinetic remediation of anionic heavy metal contamination from unsaturated soil

This work is being performed at Sandia National Laboratories under Technical Task Plan AL2311Q6 for the In-Situ Remediation IP to remediate unsaturated soil. The objective is to develop an in situ electrokinetic process for removing chromate contamination from unsaturated soil in support of the Mixed Waste Landfill ID. This work builds on results of previous efforts (TTP AL221122 "Electrokinetic Remediation"). Previous work focused on migration of anionic dyes as a chromate analog; this work will use chromate ions and will study the removal of contaminants at the electrode. If successful, the process will be tested on uranyl carbonate contaminated unsaturated soil.

3.3.1.4 Electrokinetic Process Development: Process development related to electrokinetic removal of chromium contamination from saturated soil

This work is being performed at Sandia National Laboratories under Technical Task Plan AL2311Q7 for the In-Situ Remediation IP to remediate unsaturated soil. The objective is to develop an in situ electrokinetic process for removing chromate contamination from unsaturated and saturated soil. The work is directed toward soils and water chemistry conditions like those at the Mixed Waste Landfill. This work builds on results of previous efforts (TTP AL221122 "Electrokinetic Remediation"). A multidisciplinary team is proposed to fully evaluate the electrokinetic remediation process. The product will be a multidimensional macroscale model that incorporates the appropriate chemistry, physics, and electrochemistry that can be used to extrapolate electrokinetic remediation to new sites and conditions.

3.3.1.5 Electrochemical Decontamination by Electromigration and Capture

This work is being performed at Los Alamos National Laboratories under Technical Task Plan AL1311Q3 for the In-Situ Remediation IP to remediate saturated soil. The focus is to develop an electrochemical decontamination technique to remove actinides (U and Pu) and other radionuclides (Cs-137 and Sr-90) from saturated soils. The proposed work will concentrate on the electrochemical removal of U from Fernald soils, Pu from NTS soils, and Sr and Cs from soils with a high content of cation exchangers. Laboratory experiments will be

used to assess the feasibility of mobilizing these radionuclides under the influence of an electric field. Two methods of contamination capture will be tested: capture of the contaminants into chemical solutions in the electrode housings and capture of contaminants into host polymer receptor matrices surrounding the electrodes (ELECTROSORB). Contaminant capture into solutions will be followed by a purification step where the contaminants will be removed from solution by flocculation, filtration, electrically enhanced filtration, ion exchange, or electrochemical ion exchange.

3.3.1.6 Metal Complex Design for ElectrokINETICS

This work has been proposed by Los Alamos National Laboratories for the In-Situ Remediation IP to remediate saturated soil. Its purpose is to develop a method to selectively mobilize and remove contaminants of concern during electrokinetic remediation of actinide contaminated soils. The metal must be mobilized in a manner that minimizes interferences with sorbing soil components and optimizes the mobilized complex with respect to charge. The mobilized complex must be robust due to varying chemical conditions and soil characteristics over the migration path. The goals of this project are to:

- * Develop mobilization technologies based on synthetic chelators or natural biochelators that are optimized for electrokinetic remediation of actinide contaminated soils with emphasis on U, Th, and Pu.
- * Develop optimized methods for recovery of the actinides at the target electrodes.
- * Transfer the technology to other participants in the DOE ElectrokINETICS Integrated Program.

3.3.2 Reliability and Maintenance Requirements

Commercial equipment is usually reasonably reliable.

3.3.3 Secondary Waste Streams

In general, there are few if any secondary waste streams. They consist mostly of membranes and electrodes.

3.3.4 Separation Efficiency

It is anticipated that any electrokinetic process alone in a single stage cannot achieve 100% separation, but may achieve about 80%. This is only an assessment and should be compared with the theoretical maximum as well as what is experienced in practice. Regardless, 80% per stage for a single process (or physical phenomenon) is acceptable. What might be unacceptable is that the process cannot be staged or combined with a complementary process.

3.3.5 Safety and Health

Safety of these processes is generally not of great concern. This process operates at ambient conditions of temperature and pressure and does not require the use of noxious chemicals. Voltages seldom exceed a couple hundred volts and are often less. The industrial processes are already automated.

3.3.6 Operational Complexity

For the applications that fall under Chemical and Physical separations, where these technologies are mostly a substitute for filtration, they are more complex than filtration in terms of both equipment and control. Physical size is probably on the same order.

3.3.7 Glovebox Capability

There is no evidence that the technology has been demonstrated on a useful scale inside a glovebox.

3.3.8 Environmental Impact

Since no chemicals are added and no reactions occur, environmental impact is considered insignificant.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

Development is done for most applications of this technology. If a facility is running and equipped to accept commercial apparatus, demonstration will cost half a million dollars. Capital cost will depend on the stream to be treated. The technology is more sophisticated and costly than simple filtration or drying, but it is also more capable. It might handle a stream that filtration cannot. The decision awaits stream definition. Operating costs for energy are moderate if dealing with colloids and higher if dealing with ions. Maintenance and replacement costs can range from near zero for the simplest of applications to higher-than-average for the most advanced. Secondary materials and disposal should be low.

3.5 TECHNOLOGY COMPARISON

Conventional methods of dewatering or filtering concentrated suspensions to a low moisture content are inefficient because they rely on hydraulic flow that falls off drastically with decreasing particle and pore size. This is particularly true for fine particles in suspension. However, the electro-osmotic flux is independent of particle size and is therefore more effective for dewatering fine particle sludges or slimes. Also, electro-osmotic filtration is independent of

the cross-sectional areas of the pores of the filter, which eliminates the inherent limitations of conventional filtration resulting from pore clogging or filter cake compression. However, as the particle size increases, the advantage of electro-osmotic flow rapidly falls off. The hydraulic flux that is achievable at modest pressure differentials becomes much greater than the electro-osmotic flux above a particle size of 100 microns.

The high cost of electricity over fossil fuel, process development costs, uncertainty of unproven technology, and capital cost of electrokinetic equipment has combined to present a potential risk which has limited applications of electrokinetic technologies to specialty markets. These include dewatering clays, and certain polymers, and deposition of latex colloids. Therefore, we have no extensive background of experience.

The waste stream has not been defined yet except that it is probably a sludge. It is assumed to be predominantly inorganic, but there is the possibility of a minor organic component. This is presumed to be in the wet solids waste line, but things can be wet from other materials than water. Based upon the Mixed Waste process flow sheets, the competitive technologies seem to be filtration and drying(thermal). These technologies are so simple and effective they are hard to beat unless there is something unwanted in the feed stream.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data requirements are to show the efficiency of these technologies in a nuclear environment. If reliability is high, capital cost can be shown to be of minor importance due to lower worker dose and maintenance cost. Also, absence of secondary waste generation can result in considerable savings. Test data requirements are about the same as data requirements. All data needs operating (experimental) confirmation before committing to a plant-scale installation.

4.2 TESTING REQUIREMENTS

Testing requirements are that the technology chosen be tested first on a representative cold surrogate and if successful, tested on hot material. Equipment longevity should be confirmed in a glovebox that will probably have a damp atmosphere. Preliminary testing can be completed at a vendor site (if one exists) in 4 months. Testing in a glovebox will take a year longer. If the technology is fully developed, the cost for verification testing is approximately one million dollars. Surrogate will depend on feed stream.

5.0 VENDOR LIST

Dorr-Oliver, Inc.
P. O. Box 3819
Milford, CT 06450
(800) 243-8160

Fuji Electric Corporation of America
G-A Frassetto Way
Lincoln Park, NJ 07035
(201) 633-9004

6.0 REFERENCES

1. Pletcher, D. and F. Walsh. *Industrial Electrochemistry*. 2nd Ed. Chapman and Hall: New York, 1990.
2. Rautenbach, R. and R. Albrecht. *Membrane Processes*. John Wiley: New York, 1989.
3. Williams, R., ed. *Colloid and Surface Engineering: Applications in the Process Industries*. Butterworth and Heinemann, Boston: 1992.
4. Newman, J. *Electrochemical Systems*. 2nd ed, Prentice Hall: Englewood Cliffs, NJ, 1991.
5. Lockhart, N.C. "Electro-Dewatering of Fine Suspensions." in *Advances in Solid-Liquid Separation*. H. S. Muralidhara, ed. Battelle Press: Columbus, OH, 1986.
6. Porta, A. "Scale-Up Aspects in Electro-Osmotic Dewatering." in *Advances in Solid-Liquid Separation*. H. S. Muralidhara, ed. Battelle Press: Columbus, OH, 1986.
7. Krishnaswamy, P. and P. Klinkowski, "Electrokinetics and Electrofiltration." in *Advances in Solid-Liquid Separation*. H. S. Muralidhara, ed. Battelle Press: Columbus, OH, 1986.

APPENDIX B-4 ELECTROLYTIC TECHNOLOGY

1.0 TECHNOLOGY DESIGNATION

Electrolytic technology includes electroreduction (or electrodeposition), electro-oxidation (as contrasted with CEPD/MEO addressed elsewhere), electrodialysis, and salt splitting.

2.0 NEED FOR THE TECHNOLOGY

A general need for the technologies results from the desire to minimize waste. In these processes, electrons at controlled energy levels are used to drive reactions that otherwise would require the addition of more chemicals. In addition, these processes almost always operate at ambient pressure and only slightly above ambient temperature. They are often described as environmentally friendly. For example, electroreduction might be used to recover nonvolatile inorganic soluble Hg compounds. Finally, in some cases, the processes can make chemical reactions "run backwards," which can be a substantial benefit.

Their location in the Mixed Waste treatment process would probably be in the Special Treatment process for the aqueous treatment line. Dissolved chloride (or mercury), for example, might be removed there. The aqueous treatment line follows current practice, producing pure water without regard to the amount of solids produced. In municipal treatment plants, solids are disposed of relatively inexpensively and may even be sold as byproducts. This will not be the case if the solids are chemically toxic or radioactive.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Electrolytic recovery techniques are based on the oxidation-reduction reactions that take place at the surface of conducting electrodes (cathode and anode). The electrodes are immersed in a chemical medium under the influence of an applied voltage. At the cathode, the metal ion is reduced to its elemental form and hydrogen may be evolved. At the same time, gaseous products such as oxygen or nitrogen may evolve at the anode. The gases produced at the anode depend on the chemical composition of the medium.

The conventional electrochemical reactor consists of the electrodes, associated equipment (such as recirculating pumps), and a power supply. The conventional recovery system is very efficient at high concentrations but not at low concentration due to mass-transfer-limiting conditions caused by cathodic polarization. In such systems, as the metal is plated at the

electrode, the layer of solution next to the electrode that is depleted of metals forms a polarized layer that offers high resistance to metal migration to the electrode. For example, in a conventional copper plating cell the electrical efficiency is approximately 16% with a copper concentration of 200 ppm, whereas the efficiency was 90% to 95% in a fluidized bed cell with the same copper concentration. The problem with conventional cells can be solved by agitating the solution; by using low-current-density, high-surface-area flow-through electrodes; or, as in fluidized beds, by bringing the electrodes in contact with fresh influent streams.

As a result, advanced electrolytic recovery systems, such as the system illustrated in Figure B-4.1, have been fully developed and are commercially available. Unlike conventional systems, these advanced systems recover metal better at low concentrations making recovery from dilute streams economically attractive. These systems may be in the form of a packed bed or fluidized bed, cells with spiral-wound electrodes, or cells with rotating cylindrical electrodes. Commercially available advanced electrolytic recovery devices include the extended-surface electrolysis recovery system, the high-surface-area reactor, and the fluidized-bed electrochemical reactors.

Figure B-4.1. Application of Extended-Surface Electrolysis

(From H. Freeman, editor. *Standard Handbook of Hazardous Waste Treatment and Disposal*, 1989, McGraw-Hill Book Co. Reproduced with permission of McGraw-Hill.)

In general, the processes all use a pair of electrodes that have an aqueous electrolyte between them. The electrolyte can be either acidic, which is the more typical, or basic,

particularly if cyanides are present. In addition, sometimes thin ion selective polymeric membranes are located in the electrolyte between the electrodes. This helps provide selectivity for the process when a current is passed between the electrodes. Cell voltages are a few to several volts. As a matter of convenience, electrolytic cells are usually connected in series so as to use conveniently available line voltages and to avoid excessively high currents. Typical currents are 100-500 mA/cm².

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Input ranges run from about 10 g/day to 1000 tonne/day in industrial settings. Usually sludges cannot be handled, although slurries containing up to 10% solids can be. Concentration ranges of salts in the input stream may range from the solubility limit (several molar) down to tens of ppm. Depending on the application, inputs and outputs can range from strong acid to strong base. Gases can be produced at the electrodes which can include hydrogen, ammonia, nitrogen oxides, oxygen, chlorine, and carbon dioxide. It really is necessary to know what is desired before a suitable process selection can be made. As evidenced from the ranges of inputs and outputs, the technologies are very versatile. Contrary to Figure B-4.1, deionized water is not an output; the goal is to produce water that can be discharged to a sewer.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Electrolytic recovery techniques have been used for many years in the mining industry for refining ores and are finding wide application in the electroplating, rolling mill, and electronics industries. Applications are primarily to recover metals from process streams or rinsewaters. These processes have been demonstrated for the recovery of gold, silver, cadmium, copper, zinc, and other metals. Tin and silver have been electrolytically recovered from their respective wastewaters using conventional methods. The recovery rate for tin was reported as 97% to 99%, and a 99.8% recovery was reported for silver. A high-surface-area (HSA) reactor was used to recover cadmium and destroy cyanide with a reported 99.9% metals recovery. Using a flow-through cathode, 99.999+% metal recovery was achieved (Ref. 7).

This technology is mature and available through dozens of vendors. However, this technology may require some modification to be used in the mixed waste treatment process. Delivery of this technology is probably 90 days ARO, depending on the supplier.

3.3.2 Reliability and Maintenance Requirements

Reliability is high enough that private companies invest hundreds of millions of dollars and make a profit.

3.3.3 Secondary Waste Streams

Secondary waste streams are produced due to change-out of membranes semiannually and electrodes less frequently.

3.3.4 Separation Efficiency

Separation capability is good. Silver and cobalt have been removed from acid feed to levels below the California EPA discharge limits. Mixed sodium nitrate and sulfate solution has been separated into nominally pure sodium hydroxide and a pure mixed acid stream. Oxalic acid has been converted completely to carbon dioxide and water in HCl.

3.3.5 Safety and Health

Electrolytes can be corrosive. People should not touch energized equipment if electrical shock is possible. The equipment is already automated.

3.3.6 Operational Complexity

An ion exchange column can remove metals from an aqueous stream, but it cannot split a salt into its corresponding acid and base. It cannot destroy nitrate or oxalate, etc. When it does remove ions from a stream, secondary waste is produced during regeneration. The size of electrochemical cells can be fairly large, depending on the application, but they are simple enough.

3.3.7 Glovebox Capability

The technology has been demonstrated in a gloved enclosure. Fresh air ventilation is needed.

3.3.8 Environmental Impact

Environmental impact should be favorable since electrons are used to replace chemicals and output streams suitable for recycle can be produced. However, gases such as hydrogen and chlorine may be produced at the electrodes requiring an offgas treatment system.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

Development costs are about one million dollars, depending on the process and scale required. Assuming the facility exists and the needed gloveboxes are in place and fully operational, the cost of the processing equipment will be less than that already spent on the glovebox(es). In operating costs, energy and maintenance will dominate.

3.5 TECHNOLOGY COMPARISON

The advantages of electrolytic technology are:

- * Valuable metals can be recovered, re-used, or sold
- * Toxic heavy metals can be removed from an aqueous waste stream
- * Initial investment is low
- * Operating expenses are low
- * Equipment maintenance is minimal.

A limitation of this technology is that it appears to be applicable only to aqueous waste streams. Complexing of the targeted metal in solution may also cause a problem, as with nickel, which forms a highly stable cyanide complex. Failure of electrolytic techniques in removing nickel is also due to nickel's low standard potential. Use of electrolytic systems may require an offgas control system resulting from formation of gases such as chlorine at the electrodes. Other disadvantages, if any, do not appear to have any practical consequences.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data are needed on the input stream definition, pretreatments that might be required, and conversion or separation achieved as functions of relevant process parameters.

4.2 TESTING REQUIREMENTS

Testing is needed for life testing and maintenance under operating conditions in addition to obtaining data identified in Section 4.1. Testing needs depend on the application: metal ion removal, cyanide or nitrate destruction, etc. Depending on the application and scale of this technology, pilot plant costs could be approximately one million dollars a piece.

5.0 VENDOR LIST

Many vendors provide equipment for cleaning electroplating bath electrolytes, where the motivation is metal recovery for resale. However, no vendor is known that deals with

radioactive components or mixed waste. Further discussions with vendors are required and process flowsheets require further definition.

6.0 REFERENCES

1. Mitchell, P. ed. *Electrochemical Engineering and the Environment*. Taylor and Francis: Bristol, PA, 1992.
2. Murray, R. *Molecular Design of Electrode Surfaces*. John Wiley: New York, 1992.
3. Newman, J. *Electrochemical Systems*. 2nd ed. Prentice Hall: Englewood Cliffs, NJ, 1991.
4. Scott, K. *Electrochemical Reaction Engineering*. Academic Press: New York, 1991.
5. Rautenbach, R. and R. Albrecht. *Membrane Processes*. John Wiley: New York, 1989.
6. Pletcher, D. and F. Walsh. *Industrial Electrochemistry*. 2nd ed. Chapman and Hall: New York, 1990.
7. Freeman, H. M., ed. *Standard Handbook of Hazardous Waste Treatment and Disposal*. McGraw-Hill Book Co.: New York, 1989.

APPENDIX C ELECTROMAGNETIC SEPARATION TECHNOLOGIES

Electromagnetic separation techniques involve passing a liquid or solid waste stream through an electromagnetic field to separate metals from nonmetals. Other technologies, such as eddy current, electrostatic and magnetic fluid separation are applicable to dry solid/solid separation and are discussed in the Front End Handling TASR. The technologies described in this appendix are as follows:

- C-1 Magnetic Separation**
- C-2 High Field Gradient Magnetic Separation**

APPENDIX C-1 MAGNETIC SEPARATION

1.0 TECHNOLOGY DESIGNATION

Magnetic Separation removes magnetic or recovers nonmagnetic materials from wet or dry waste streams.

2.0 NEED FOR TECHNOLOGY

In the Mixed Waste process, the magnetic separator may be used to remove ferrous metals from the homogeneous dry solids stream as shown in Process Number 434, or from the aqueous, liquid organic or wet solid waste streams. The ferrous metals are routed to the Ferrous metal induction melter, Process Number 770, in the thermal treatment line of the facility.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Magnetic separation is a physical separation process that can be used to concentrate ferrous materials from a mixture. The method can be applied to either a dry particle or a wet particle slurry using either open or high gradient magnetic separation equipment. As the waste materials enters the magnetic separator, the ferrous materials encounter the magnetic field which separates it from the nonferrous materials. The force of the magnetic field is supplied by either electromagnets or permanent magnets. Utilizing a pretreatment, nonmagnetic materials can be bound to a magnetite-containing polymer to produce magnetic materials. A V-shaped pole opposite a flat bar is the preferred method for producing a converging field. There are several types of separators that operate at various intensities, including drum, induced-roll, and belt.

Drum separators are used for low-intensity magnetic separation. There are three types of drum separators: cocurrent, counter-rotation, and counter-current. Cocurrent drum separators (Figure C-1.1) extract an extremely clean magnetic concentrate from relatively coarse materials. It is usually used in heavy medium recovery systems. The counter-rotation drum separator (Figure C-1.2) is often utilized in roughing operations because it can handle occasional surges, minimizes magnetic material losses, and can handle high solids loading. The counter-current drum separator (Figure C-1.3 and C-1.4) is utilized in the belt separators and are used on dry materials for low-intensity magnetic separation. This separator is used to concentrate moderately magnetic ores. A disc separator (Figure C-1.5) is a modified cross-belt separator that provides even greater selectivity.

Figure C-1.1. Drum Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 605, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Figure C-1.2. Counter-Rotation Drum Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 605, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Figure C-1.3. Counter-Current Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 606, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Figure C-1.4. Cross-Belt Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 607, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Figure C-1.5. Disc Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 608, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Induced-roll separators (Figure C-1.6) are high-intensity separators. They are primarily used to separate magnetic materials from beach sand, wolframite, tin ores, glass sands phosphate rock, and iron ores. One specific type of roll separator is the Permroll.

Figure C-1.6. Induced Roll Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 610, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Wet magnetic separators for high-intensity fields include induced roll machines and Jones. One type of induced roll machine is the Gill (Figure C-1.7), which has been effective for separating highly magnetic ilmenite from heavy mineral concentrates. The Jones separator (Figure C-1.8) is effective in separating fine hematite ores. Other applications of wet, high-intensity separators include separating magnetic particles from cassiterite concentrates, asbestos, scheelite concentrates, talc, flotation tailings, beach sand, and cyanidation residues.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Magnetic separation will work with any waste containing magnetic particles that can be separated. The process can be used on water, slurries, soils, sludges, and sediments. It removes particles with diameters as small as 1 micron with flow rates 100 times greater than ordinary filtration. For particle sizes less than 0.5 cm, dry separation tends to be replaced by wet methods which produce less dust loss and usually a cleaner product. Since magnetic separation is a physical separation process, there is essentially no waste stream generated.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Magnetic separation equipment is available through many commercial sources. The off-the-shelf magnetic separation equipment would need to be modified to be integrated into the Mixed Waste treatment process.

Bradtec has developed a process for the selective binding of contaminant materials to magnetite to allow removal of specific contaminants from wastewater and groundwater. The magnetite/contaminant particle is removed from the waste stream by magnetic filtration. Linkages have been developed for removal of heavy metals and radionuclides. Dissolved metals can be removed to the parts per billion level at flow rates up to 2400 gpm using commercially available equipment.

The particle consists of magnetite and an organic polymer coating which may be designed for selective binding to specific contaminants. The contaminated particles are removed from the stream by a magnetic filter that is periodically backflushed into a recovery tank. The magnetite/contaminant bond is broken chemically and the magnetite recovered and reused. The contaminant is recovered as a slurry for further treatment or disposal.

To date, several specialized particle types have been tested. The process equipment (magnetic filter) is standard, commercial equipment. A treatment system, or pilot plant, has yet to be operated to obtain process data and establish commercial feasibility.

Figure C-1.7. Side View of Four-Pole Gill Wet Magnetic Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 611, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

Figure C-1.8. Operating Principle of the Jones High-Intensity Wet Magnetic Separator

(Reprinted from B.A. Wills: Mineral Processing Technology, An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, 4th Ed., Copyright 1979, page 612, with permission from Pergamon Pres Ltd, Headington Hill Hall, Oxford, OX30BW, UK)

A Cooperative Research And Development Agreement (CRADA) was signed between AWC/Lockheed and Los Alamos National Laboratory (LANL) in 1992 under TTP #AL124102. Other TTPs submitted to the DOE's Office of Technology Development for magnetic separation technology development include:

- * TTP # AL121121 - Selective Extraction/Leaching
- * TTP # AL121203 - Magnetic Separation of Process Residues from UST

3.3.2 Reliability and Maintainability Requirements

The magnets need periodic cleaning to remove buildup of ferrous contaminants and to assure maximum separation efficiency. A magnet loaded with collected iron or other ferrous contamination will lose efficiency as its field is "keepereed" or shunted by the contaminants. The frequency of cleaning is dependent upon the amount of ferrous contamination in the feed. To prevent costly shutdowns associated by removing, cleaning and reinstalling magnetic elements, self-cleaning magnets can be used.

3.3.3 Secondary Waste Streams

Since magnetic separation is a physical separation process, not a chemical separation process, there is minimal secondary waste generated from this process.

3.3.4 Separation Efficiency

Off-the-shelf magnetic separation equipment is very efficient in separating waste stream components, but the equipment would need to be modified to be integrated into the Mixed Waste process.

3.3.5 Safety and Health

Magnetic separation technology can be automated, thus reducing operator exposure. For dry waste streams, safety and health concerns would be associated with dust containment as discussed in Section 3.3.7.

3.3.6 Operational Complexity

Considering the high throughput rates and separation efficiencies for particle sizes in the micron range, magnetic separation equipment is relatively compact and has low power requirements for generating the magnetic field. For example, high-intensity wet magnetic separators ranging from 1 to 120 tons per hour for processing feed would have power requirements which range from 3.2 to 90 Kw and dimensions ranging from 78" L by 58" W by 56" H to 228" L by 136" W by 150" H.

3.3.7 Environmental Impact

Magnetic Separation of dry mixed waste streams may generate hazardous and/or radioactive dust. Containment of this dust would be a factor in the magnetic separator design for dry waste streams.

3.4 COSTS OF TECHNOLOGY OR EQUIPMENT

Capital equipment costs for a 20 ton per hour high intensity magnetic separator are in the range of \$260,000. Operating costs would be primarily based upon the cost of power which can range from 1 to 90 Kw needed to generate the magnetic field.

3.5 TECHNOLOGY COMPARISON

In general, magnetic separation can process diluted contaminants at higher separation efficiencies and faster processing rates using smaller equipment than current methods such as soil washing, gravity separation, inertial separation, electrostatic precipitation, froth flotation and filtration. These other methods are either limited by slow processing rates or a large equipment volume requirement. In addition, some of these current methods may produce secondary waste streams.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

While a variety of magnetic separation systems are readily available commercially, data are required to select and tailor the system to meet specific waste separation needs. Some of these data requirements include the feed characteristics, separation efficiency, and processing rates. Feed characteristics include magnetic susceptibility, liberation, percentage of magnetic particles and particle size. For wet waste streams, additional data requirement may include slurry density, viscosity and dispersion.

4.2 TESTING REQUIREMENTS

Laboratory and pilot scale testing using wet surrogates would be required to properly tailor the magnetic separation system to a particular waste processing need. Tests would be required to optimize feed rate, separation efficiency, magnetic field configuration and magnetic field intensity.

5.0 VENDOR LIST

Carpco
4120 Haines Street
Jacksonville, FL 32206
(904) 353-3681

Eriez Magnetics
P.O. Box 10608-M
Erie, PA 16514
(800) 345-4946

Bradtec
1010 Huntcliff Tr.
Suite 1350
Atlanta, GA 30350
(404) 640-7059

S.G. Frantz
E. Darrah Lane
P.O. Box 1138
Trenton, NJ 08606
(609) 882-7100

Engineered Magnetics
55 Stevens Street
Belleville, NJ 07109
(201) 759-0818

6.0 REFERENCES

1. Wills, B. A. *"An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery."* Mineral Processing Technology, 4th Edition, Pergamon Press: New York, NY, 1979.
2. Norrgran, D. A. and J.N. Orlich. *"Fundamentals of High-Intensity Magnetic Separation as Applied to Industrial Minerals."* Minerals and Metallurgical Processing, February 1988.
3. Norrgran, D.A. and J.A. Selvaggi. *"Superconducting High Gradient Magnetic Separator System and Its Application to Industrial Minerals."* International Congress, undated.
4. Twichell, E.S. *"Industrial Use of Magnets."* Quality, August 1987.
5. *"Wet High Intensity Magnetic Separators (WHIMS)."* OTB-480, Eriez Magnetics, 1992.
6. *"Magnetic Separation of Process Residues from UST."* TTP# AL121203, December 19, 1991.
7. *"Magnetic Separation CRADA."* TTP# AL124102, April 20, 1992.

APPENDIX C-2 HIGH GRADIENT MAGNETIC SEPARATION (HGMS)

1.0 TECHNOLOGY DESIGNATION

High gradient magnetic separation (HGMS) is a physical separation process that segregates materials on the basis of magnetic susceptibility.

2.0 NEED FOR TECHNOLOGY

HGMS, a physical separation process based on magnetic susceptibility (Refs. 1 and 2), produces minimum secondary waste and is suitable for the separation of iron, chromium, rare earths, plutonium, uranium, americium compounds, and certain radioactive contaminants existing in particulate form in wet homogeneous solids and soils as encountered in units 340 and 345 of the wet solids stream. It may also be a useful secondary treatment for colloid to micron size particles that are not filtered out of the aqueous stream by the grit filters (e.g., down stream of units 130 & 155). This process would reduce the amount of radioactive and toxic metal waste volume requiring special disposal, as in the case of contaminated waste streams or soils, without creating additional waste streams.

Biomagnetic separation processes (microorganisms combined with HGMS) can be used on ionic solutions to form precipitates of paramagnetic materials on the cellular surface of microorganisms that are then scavenged by HGMS (Ref. 3). This technology could be used in the aqueous or organic streams to remove plutonium, uranium, and fission products in solution and as a replacement or in conjunction with the units down stream of unit 595 (mercury removal).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

High gradient magnetic separation is a process in which magnetizable particles are extracted onto the surface of a fine ferromagnetic wire matrix, that is magnetized by an externally applied magnetic field. Electromagnets, in conjunction with an iron circuit, are used to generate a magnetic field in an air gap. Field gradients are produced by shaping the poles or by using secondary poles consisting of shaped ferromagnetic material introduced into the air gap. The magnetizable particles are separated by being deflected by the magnetic field configuration or they are captured and held by the secondary poles. A combination of the magnetic field and field gradient generates a force on the particles such that paramagnetic and

ferromagnetic particles move toward the higher magnetic field regions, and the diamagnetic particles move toward the lower field regions. Paramagnetic and ferromagnetic species have a positive magnetic susceptibility while diamagnetic species have a negative magnetic susceptibility. When a paramagnetic or a ferromagnetic particle encounters a non-uniform magnetic field, the particle is deflected in the direction in which the field gradient increases. All plutonium and uranium compounds, and many fission products are paramagnetic. Many inert waste components are diamagnetic and are deflected in the direction of decreasing field gradient. When the field gradient is of sufficiently high intensity, paramagnetic particles, as small as colloids, can be physically captured and separated from extraneous material with high speed and efficiency. The particles are released from the secondary poles either by switching off the magnetic field or by mechanically removing the secondary poles from the field.

High gradient magnetic separation uses very high intensity magnetic fields at or exceeding 20,000 gauss. Magnetic fields of 200,000 gauss can be reached with today's commercial superconducting magnet technology (Ref. 1). With these high field strengths, paramagnetic particles as small as 0.1 micron diameter and smaller have been removed. A diagram of the method is shown in Figure C-2.1. Usually, the feed is slurried with water and passed through a magnetized volume. Field gradients are produced in the magnetized volume by a ferromagnetic matrix material. The matrix material can be steel wool, steel balls, nickel foam, or other ferromagnetic material. Ferromagnetic and paramagnetic particles are extracted from the slurry while the diamagnetic fraction passes through the magnetized volume. Later, the magnetic fraction is flushed from the matrix when the magnetic field is reduced to zero or the matrix is removed from the magnetized volume.

When metal ions are in solution, biomagnetic separation can be effected with HGMS through the pretreatment of the solution with microorganisms (Ref. 4). The metal may be taken up intracellularly or by metal deposition onto the surface of the microorganism. An elegant technique has also been developed that results in a high concentration of phosphate anions at the cell surface which reacts with metal ions present in solution to form a precipitate on the cell wall of the microorganism. The microorganisms, when coated with paramagnetic materials, behave like paramagnetic material in a magnetic field and are efficiently separated by HGMS. Calculations have shown that very low ultimate levels are possible for materials of interest to the nuclear industry. For example, for Am^{3+} the ultimate level is 2.43×10^{-9} ppm; for UO_2^{2+} the level is 5.38×10^{-9} ppm; and for PuO_2^{2+} the level is 4.37×10^{-9} ppm (Ref. 1). Further, a number of microorganisms can produce sulfide and give rise to sulfide precipitates and metal sulfide precipitates can be scavenged using HGMS. For example, the ultimate level to which Hg^{2+} metal ion concentrations can be reduced is 8.02×10^{-43} ppm. In experimental work on

industrial effluents from the Netherlands, the Hg concentration has been reduced from 2000 ppb to 2 ppb in a single stage (Ref. 1).

Figure C-2.1. Simplified High Gradient Magnetic Separation (HGMS) Diagram

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Since the matrix present inside the separation chamber consists of steel wool or other material that would physically limit the passage of large debris, it is essential that larger materials be removed from the waste stream upstream of the HGMS. HGMS is especially useful on particles less than 45 microns and as small as 0.1 microns. (Particles as large as 0.1 mm can also be handled with HGMS techniques.) The chemical environment of the solids impacts the separation only in so far as it influences the particle dispersion and the surface-charge density of the particles. For example, effective separations for soils require added surfactant. The best

separations occur with 0.2% $(\text{NaPO}_3)_6$ surfactant and adjustment of the slurry pH to 10 in the work performed at LANL on soils with actinide surrogates as the waste. Both the $(\text{NaPO}_3)_6$ surfactant and the pH adjustment behave as soil dispersing agents because they increase the surface-charge density of the clay particles.

Requirements for biomagnetic separation are dictated by the chemical environment and pH needs of the microorganisms (Refs. 1, 3, and 4).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

High gradient magnetic separation has been in use in the processing of ceramic clay on a commercial basis for many years. This process was developed for and in conjunction with the kaolin industry in the U.S. to improve kaolin clay through reduction of the iron concentration. Systems are being used for tramp iron removal and ore beneficiation, and have been tested for purification of waste water and stack gas from steel mills (Ref. 5). Systems using superconducting coils have been commercialized for the clay industry in the U.S., UK, and Czechoslovakia. The benefit of this "mature" technology in the ceramic industry is in the increase in "fired" brightness produced through a decrease in the iron concentration of the clay. Two clay feed systems have been considered: the axial feed system, in which the clay moves parallel to the axis of the solenoid, and the radial feed system, in which the clay is passed down a central tube that feeds the clay radially outwards through the matrix, where it is collected in an annular space in which it again flows axially out of the solenoid. The process is a cyclical one consisting of a feed part and a washing part.

A typical high gradient separator used in the kaolin industry consists of an iron bound solenoid, weighing about 200 tons. The magnetic field of 2 Tesla is produced in a cylindrical hole by copper coils weighing 60 tons, approximately 2 m in diameter, and 0.6 m long. Into this space are packed pads of ferromagnetic stainless-steel wool with voidage of 95%. The power consumption is 300 kW to 500 kW (Ref. 1).

Experimental work has shown that various metals can be taken up by microorganisms, either intracellularly or by metal deposition into the microorganism surface, and subsequently separated by the high gradient magnetic field process. Tests have been performed to remove paramagnetic uranyl ions, cobalt, and mercury ions to very low levels (concentrated by factors up to 10^7) (Ref. 6).

Eriez Magnetics successfully installed a superconducting magnet HGMS unit that went on line May 8, 1986 (Ref. 1). The system has the following characteristics:

Canister	213.36 cm diameter, 51 cm deep
Magnet size	391.16 cm ² , 210.82 cm deep
Magnet weight	227 tons
Ramp time	1 min, maximum
Helium usage	2 L per cycle at 1 min ramp time
Liquifier capacity	20 Lh ⁻¹ from gas at 300-4.2 K
Compressor power	47.8 kW (nominal)
Field strength	20,000 gauss

English Clays Lovering Pochin (ECLP) and Cryogenic Consultants Limited (CCL) have produced reciprocating cannister systems (RCS). These systems, also used in the purification of clays, allow the change out of the matrix chamber without turning off the magnet power (two separate cannisters are used: one is cleaned while the other separates material). This method results in significant savings in electrical power consumption.

The Nuclear Materials Division and the Mechanical and Electronic Engineering Division at Los Alamos National Laboratory are pursuing the use of HGMS for soil decontamination, tank waste remediation, and plutonium and uranium chemical processing (Ref. 7). These technologies may also be applicable in the MWTP as indicated above. For example, application of HGMS as a head-end unit operation in remediation may offer significant advantage to present chemical processing methods. HGMS can remove and concentrate most of the TRU and fission products before chemical processing begins. Hence, the chemical processing capacity downstream can be reduced, diminishing floor space required in the facility and reducing the volume of process chemicals used. Also, because a HGMS unit can be made transportable, the process is suitable for application at the site of the waste.

High gradient magnetic separation is being developed jointly by LANL and AWC/Lockheed under TTP #AL124102 - Magnetic Separation CRADA - for the Nevada Test Site ID. This technology can be applied to effect the selective extraction of actinide contaminants from soils, clays, and silts such as those found at NTS, Rocky Flats, and Fernald. Preliminary results show that over 90% of the plutonium can be extracted from certain recycle Pu residues using open gradient magnetic separation, and Pu simulants can be extracted from solids and slurries to ppm levels using high gradient magnetic separation. Several other TTPs have been submitted by LANL to develop high gradient magnetic separation technology for various applications; the current funding status of these TTPs is not known. These include the following:

- * TTP #AL1312P7 - Magnetic Separation for MWLID: Magnetic separation for metal and radionuclide removal from mixed waste landfill soils

- * TTP #AL1311Q2 - Magnetic Separation of UST Wastes
- * TTP #AL1312P0 - Magnetic Separation for USID: Magnetic separation for uranium removal from contaminated soil
- * TTP #AL1312P9 - Magnetic Separation for BWID: Magnetic separation for actinide removal from BW and contaminated soil
- * TTP #AL1312Q1 - Magnetic Separation for WeDID: Magnetic separation for weapon component waste disposal ID.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintenance requirements have yet to be determined.

3.3.3 Secondary Waste Streams

Because the process relies on physical properties rather than chemical properties, separations can be achieved while producing a minimum of secondary waste.

3.3.4 Separation Efficiency

Separation efficiency is dependent upon many factors including application, particle chemistry, particle size, physical bonding, etc. In some cases separation efficiency may be limited to less than < 25%, but in others factors exceeding 1,000 have been achieved. Section 3.3.1 gives some data for plutonium. The use of biomagnetic separation shows great promise for the separation of dissolved ions precipitated onto cellular walls of microorganisms made paramagnetic with separation factors of 1,000 in a single pass.

3.3.5 Safety and Health

Safety and health may be an issue with respect to increased concentrations of actinides and/or other contaminants.

3.3.6 Operational Complexity

The operational complexity of this technology is similar to other industrial systems commonly found in the chemical industry.

3.3.7 Glovebox Capability

An HGMS system can be made transportable and is amenable to operating as an entirely closed system.

3.3.8 Environmental Impact

Since an HGMS system can probably be operated as a closed system, its impact to the environment can be easily controlled and managed.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Estimated operating costs (\$US) of HGMS for clay processing for conventional and superconducting magnets as of 1988 are shown below (Ref. 1):

Operating Costs	Conventional Magnet	Superconducting Magnet
Deprec. per 10,000 h	20	43
Magnet power	15	3
Pumping & cleaning	10	10
Labor	18	18
Maintenance	11	11
Total (\$ h ⁻¹)	74	85
Relative cost per ton	1.52	0.88

3.5 TECHNOLOGY COMPARISON

This process allows weakly magnetic particles of colloidal size to be manipulated on a large scale at high processing rates. A comparison of biotechnologies including biomagnetics for use in waste treatment can be found in Ref. 8.

4.0 DEMONSTRATION REQUIREMENTS

Demonstration requirements are presently being defined by the Nuclear Materials Division and the Mechanical and Electronic Engineering Division at Los Alamos National Laboratory through a CRADA with AWC/Lockheed.

5.0 VENDOR LIST

The following is a list of vendors that sell commercial HGMS equipment:

Eriez Magnetics
P.O. Box 10608
Erie, PA 16514-0608
Phone: (814) 833-9881

Cryogenic Consultants, Inc.
1176-T N. Irving St.
Allentown, PA 18103
Phone: (215) 439-0419

Pacific Electric Motor Co.
1009 66th Ave.
Oakland, CA 94621-3535
Phone: (415) 569-7621

Cryomagnetics, Inc.
1006 Alvin Weinberg Dr.
Oak Ridge, TN 37830
Phone: (615) 482-9551

6.0 REFERENCES

1. Watson, J. H. P. "High Gradient Magnetic Separation." In *Solid-Liquid Separation*. L. Svarovsky, ed. Butterworth-Heinemann: Oxford, 1990.
2. Harding, K, and W. Baxter. "Application of High Gradient Magnetic Separation to Ferric Hydroxide Filtration." *IEEE Transactions on Magnetics* MAG-17, No. 6 (1981) 2795.
3. Bahaj, A. S., D. C. Ellwood, and J. H. P. Watson. "Extraction of Heavy Metals Using Microorganisms and High Gradient Magnetic Separation." *IEEE Transactions on Magnetics*, 27 No. 6 pt 2 (1991) 5371.
4. Bahaj, A. S., J. H. P. Watson, and D. C. Ellwood. "Determination of Magnetic Susceptibility of Loaded Microorganisms in Biomagnetic Separation." *IEEE Transactions on Magnetics*, 25 No. 5 (1989) 3809.
5. Drehmel, D., and C. Gooding. "High Gradient Magnetic Particulate Collection." Published in *American Institute of Chemical Engineers (AIChE) Symposium Series*. 74 No. 175 1978.
6. Watson, J. H. P., D. C. Ellwood, and A. S. Bahaj. "A Biomagnetic Separation Process for the Removal of Heavy Metal Ions from Solution." *Proceedings of the Low Temperature Engineering and Cryogenics Conference* (1990), Burton, M. J. ed. University of Southampton: Southampton, U.K. 1990.
7. Avens, L. R., U. F. Gallegos, and J. T. McFarlaw. "Magnetic Separation as a Plutonium Residue Enhancement Process." *Sixth Symposium on Separation Science and Technology for Energy Application Separation Science and Technology*. 25 (1990) 1967.
8. Ashley, N. and V. Roach, and J. W. Daniel. "Review of Biotechnology Applications to Nuclear Waste Treatment." *Journal of Chemical Technology and Biotechnology*. 49 No. 4 (1990) 381.

APPENDIX D FREEZE CRYSTALLIZATION

1.0 TECHNOLOGY DESIGNATION

Freeze crystallization is a process for separating pure solvents such as water from dissolved solids, undissolved solids, and organic contaminants. The process converts liquid solvents to pure crystalline solids and subsequently recovers them from the mother liquor. Purification factors, ranging from 100 to 1000 per freeze cycle, are routinely achieved. Freeze crystallization is being considered as an alternate technology since this one process may replace activated carbon adsorption, distillation, and numerous polishing steps such as reverse osmosis, ion chromatography, etc., in the baseline design.

2.0 NEED FOR THE TECHNOLOGY

This process would be used on the section 100 aqueous liquids treatment line to separate purified water from organics and dissolved or undissolved solids. Ninety-eight percent of the aqueous waste stream is recyclable within the plant, but the remainder must be discharged. One cycle of freeze crystallization should provide sufficient purification to permit internal recycling. The number of cycles required to permit discharge to the environment will depend upon the specific contaminants and their concentrations.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Freeze crystallization is a general separations process used to separate water from solutions (including hazardous waste) by cooling the solution until ice crystals begin to form. Crystals produced in this manner invariably have high purities. Once small, uniform crystals have been produced, they are separated from the remaining impurities and washed to remove surface impurities. The resulting brine is recycled to the crystallizer, so that as much solvent as desired can be recovered. The pure crystals are usually melted in a heat-pump cycle, which further improves the energy efficiency of the process. Salts that were dissolved in the water crystallize at saturation and are removed from the process as a sludge, thereby concentrating the hazardous components of the liquid waste into a smaller volume.

Fractionation processes may be used to separate the crystallized solids. With freezing, conditions can be varied to selectively crystallize specific solutes. When one or more of the solutes exceeds its solubility, additional crystal forms are produced, but they are formed

separately from each other and from the solvent crystals. Since in most waste applications the solvent is water (ice is always less dense than the solution and solutes usually more dense), it is easy to separate these crystals by gravity. Freeze crystallization processes are divided into two categories: indirect heat transfer and direct heat transfer.

3.1.1 Indirect Heat Transfer

Heat is transferred through a heat exchanger. Both scraped and nonscraped designs have been used in industry. Figure D-1 presents a process schematic diagram for the freeze crystallization process. Aqueous feed is introduced into the shell side of a tube and shell heat exchanger. A refrigerant gas such as ammonia is introduced into the tubes and both flow concurrently down the exchanger. This arrangement minimizes cold spots which might lead to ice blockage of the heat exchanger.

For this particular application the aqueous feed must have a minimal salt concentration that corresponds to an 8°F freezing point depression to control the ice crystal growth rate. If the initial aqueous feed is too dilute, ice crystals will tend to plug the crystallizer. If the salt concentration becomes too high, the resulting ice crystallization rate becomes too low and the ice crystals are too small and are difficult to separate from the mother liquor. Salt may be added initially to reach the appropriate minimal operational range.

After passing through the heat exchanger, the ice/salt slurry is pumped into a separation chamber where the ice is separated gravitationally from the concentrate and washed to remove the mother liquor.

After harvesting, the ice is melted and discharged as product. Typically purification factors of 1000 per cycle are achieved for both organic and inorganic contaminants. The salt water concentrate is recycled through the process until the freezing point reaches 20°F. Approximately 90% of the aqueous feed can be purified by this technique. The remaining concentrate must be thermally processed to recover the residual dissolved solids. The used refrigerant gas is recompressed and recycled also.

3.1.2 Direct Heat Transfer Process

In this process, aqueous feed and compressed refrigerant are mixed in the heat exchanger. Heat is transferred directly from the aqueous solvent to the refrigerant causing the refrigerant to boil to a gas forming a 10-15 weight percent ice-salt slurry in the crystallizer. This slurry is pumped to a settling chamber where salts and solids settle and are blown down to form a wet solid sludge. This sludge would be transferred to the wet solids line. The ice crystals float to

Figure D-1. Process Schematic for Freeze Crystallization

the top of the settling chamber and are pumped to a wash column. The ice rises within the wash column and is counterwashed with product melt liquid. This ice is skimmed from the column top and is melted to produce a purified aqueous stream.

Concentrated liquid from the bottom of the wash column is recycled to the crystallizer, where further crystallization takes place. The principal components of the process and the equipment variations that have been devised include:

3.1.3 Crystallizers

Crystallization can be induced by either of two methods: (1) by removing heat through a heat-transfer surface, or (2) by direct contact of a boiling refrigerant with the process fluid. The direct-contact refrigerant can be either the solvent (operating at its triple point) or a secondary refrigerant chosen for its operating properties.

3.1.4 Crystal Separators

Ice can be separated from the concentrate by filtration, by centrifugation, or by wash columns. Each of these separation devices must wash the ice to remove adhering concentrate. The wash column allows counter-current washing, and is therefore, more efficient than the other devices.

3.1.5 Crystal Melters

Any crystal that melts at a temperature below ambient can be used to condense the refrigerant and improve the energy efficiency of the process. These crystals can be melted either by direct contact with the condensing refrigerant or in a heat exchanger.

3.1.6 Refrigeration System

The purpose of the refrigeration system is to remove heat in the crystallizer and reject it to a convenient sink. The sink may be either melting crystals or cooling water. Conventional refrigeration equipment has been adapted for this purpose.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The freeze crystallization feed stream may contain hazardous chemicals, organics, or complex mixtures. No pretreatment is required other than filtering to remove solids. Organics separate into a second phase during the freeze concentration process and may be removed as such. The reject sludge will typically contain 40-50% water. This sludge mixture can be shipped to the wet solids line without further processing.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Freeze crystallization is a fairly new process developed during the 1950s when the first continuous equipment was developed. Several direct and indirect contact processes have been developed for the oil, chemical, and food industries, and for sea-water desalting. The technology is being commercialized for hazardous waste treatment by Freeze Technologies Corp. (Raleigh, NC) who is using a direct contact process, and HPD, Inc. (Naperville, IL) who is using an indirect process. All of the equipment necessary for a freeze crystallization plant is commercially available.

In 1992, HPD, Inc. installed a 24,000 gal./day indirect heat exchange plant for treating waste solutions from the paper and pulp industry in British Columbia. This plant was built without the benefit of extensive pilot plant testing and was subsequently abandoned because the compositional variability in the feed solution caused freezing point fluctuations beyond the design basis.

In the late 1960s, Envirovac (then a division of Colt Industries) built a 100,000 gal./day freeze crystallization plant for the Department of Interior for seawater desalination. This plant proved uneconomic for desalination.

A Direct Heat Exchange freeze crystallization pilot plant was built by FTC for the U.S. Department of the Interior, Office of Water Research and Technology, Department of Saline Research, at the Wrightsville Beach Test Facility, Wrightsville, NC from 1979 through 1981. This plant was designed to process 25,000 gal./day of sea water. It was operated from five to seven days per week for three years.

Although technically successful, this plant was abandoned in 1981, because reverse osmosis of seawater proved more economical than freeze crystallization. Reverse osmosis is very successful where the feedstream is a dilute salt solution without significant organic contamination, where significant concentration of the reject phase is not required, and where the reject salt stream can be easily returned to the environment.

Factors which favor freeze crystallization are concentrated complex solutions which must be dewatered, organics which may foul membranes, halides which may lead to unacceptable corrosion rates in thermal evaporators, and reject solids and solutions which require further processing.

Other corporations which have built freeze crystallization pilot plants include Carrier Corp., and Avco.

A large effort is currently underway to develop refrigerant gases that are more compatible with the environment. Freon gases are rapidly being phased out of industry. Some freon substitutes are already known and others are currently being researched. This affects primarily the direct heat transfer process since ammonia has already been demonstrated to be the refrigerant of choice for the indirect process.

3.3.2 Reliability and Maintenance Requirements

Equipment common to both the direct and indirect processes are:

- * Compressors for the refrigerant gas
- * Slurry pumps for the ice-salt slurry and to pump the blowdown solids from the separator to the wet solids line
- * Centrifugal pumps for aqueous solutions
- * Remotely operated valves.

This equipment is commercially available, mature, and reliable. Process reliability should benefit from the equipment reliability.

Equipment unique to the direct heat exchange process is a vacuum pump to initially remove nonrefrigerant gases from the crystallizer and to strip refrigerant from the melted ice.

Direct freeze crystallization can be integrated with other plant processes with exceptional flexibility since:

- * The process is dynamically stable because of the large holdup-to-throughput ratio.
- * The direct freeze process is not highly dependent on the feed composition or feed flow rate. The freeze plant maintains constant flows of either product (clean water) or concentrate, or both over short time intervals. This is done by automatically controlling product-concentrate split, by varying the amount of ice being produced, and by allowing the inventory of material within the process to change.
- * The freeze process can adapt quickly to the needs of other processes if the final disposal equipment has variable capacity based on waste characteristics or process variables. Variable flow of concentrate from the process has little effect on the operations of the freeze process, due to the comparatively large holdup in the system.
- * The freeze plant can be turned down to a fraction of its capacity quickly, and brought to full capacity on demand.

3.3.3 Secondary Waste Streams

Secondary waste streams are the organic, the wet solids, and the aqueous waste stream that is discharged. The organic and the wet solids waste stream can be directly transferred to

the 200 and 300 lines, respectively. The aqueous waste stream can be discharged once the environmental discharge limits are met.

3.3.4 Separation Efficiency

Each freeze crystallization cycle provides a decontamination factor that ranges from 100 to 1000. One cycle is all that is required for the internally recycled water. Water, which must be discharged to maintain a stable plant inventory, may require several freeze cycles.

3.3.5 Safety and Health

There are no safety or health issues related directly to freeze crystallization. The safety issues are generic to the nature of the mixed hazardous waste. Freeze crystallization equipment completely contains the wastes, and therefore, protects personnel from direct contact, from exposure to hazardous vapors, and from exposure to ionizing radiation. If criticality of fissionable materials within the wastes is a possibility, the pipes and tanks can be designed to be geometrically safe.

3.3.6 Operational Complexity

Freeze crystallization is a moderately complex unit operation. It is not as mechanically simple as ion exchange or reverse osmosis. It is, however, the only unit operation which can separate the water from all contaminants without the aid or assistance of other unit operations. Freeze crystallization is therefore the least complex system that can be devised for the aqueous waste line.

3.3.7 Glovebox Capability

Freeze crystallization can be designed into a glovebox; however, it may not be necessary since the steel walls of the pipes and tanks offer complete containment. A second barrier could be a cell in which the equipment is placed.

3.3.8 Environmental Impact

The only environmental impacts identified for freeze crystallization are the aqueous waste stream that must be discharged, the refrigerant gases that may escape, and the electrical power that is used. The aqueous wastes must be purified to meet environmental discharge limits. The refrigerant gases will be environmentally compatible, release of refrigerant gases will be minimized, and the electrical power used is less than the base case process. The environmental impact is therefore considered negligible.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

Despite the knowledge and experience of the commercial companies listed here, further development is desirable before a commercial plant is built. Development costs depend to some extent on whether a direct or indirect heat exchange process is chosen. Previous development proposals have been in the \$500,000 range. The capital cost for a freeze crystallization plant built of carbon steel operating at 10,000 Btu/h is \$3,000,000. These estimated costs include:

- * Process equipment
- * Installation materials and labor
- * Engineering design and installation
- * Indirect charges
- * Fees.

Costs not included in these estimates are royalties, site preparation, in-house engineering and management, and off-site incremental costs such as administration buildings, electrical distribution systems, etc.

The capital cost estimate for the base case aqueous line is \$7,429,000 and this is undoubtedly low by a factor of two, since the amount of polishing to meet environmental discharge regulations has not been adequately defined. Freeze crystallization will therefore yield a large capital cost saving.

Operating costs will vary from region to region depending upon labor rates, electrical power costs, scale of plant and throughput capacity, materials of construction, and design philosophy, etc. However, a range of \$2.00 per cubic meter for large systems to \$7.00 per cubic meter for small systems should cover the operating costs. Operating costs for this plant should run about \$3.00 per cubic meter. Operating cost estimates for the base case plant have not been published.

3.5 TECHNOLOGY COMPARISON

The process is economically and technically competitive on very contaminated streams. For example, wastes with heavy metals require concentrations of 1,000 to 10,000 mg/l to be economically recoverable with freezing.

Freeze crystallization has several advantages for remediation and waste recovery applications. First, it is a very efficient volume reduction process, producing a concentrate that has no additional chemicals added to it. When a large fraction of the solvent (usually water) is removed from a waste, the remaining impurities often begin to crystallize as well—they are

often sufficiently pure to have by-product value for resale. Other advantages include the following:

- * The process is energy efficient.
- * Water is converted to ice which is mechanically separated from the concentrate.
- * Pretreatment is usually not required. The process is not affected by saturated salts or organics which just form additional solid or liquid phases.
- * Phase equilibria can be altered chemically and physically with the process to promote selective precipitation.
- * All contaminants are reduced proportionally in the treated water; the melt contains from 0.01 to 0.1% of the concentration of contaminants in the feed.
- * Several commercial equipment options are available.

The main disadvantage of this process is its relatively high cost for treating streams with low concentrations of contaminants. The process is also relatively complex, requiring numerous pieces of equipment, compressors, heat exchangers, and pumps. Other disadvantages include the following:

- * Technology is new and pilot testing is usually required.
- * High capital costs.
- * Long-term O&M costs and reliability are unproven.
- * Few applications have been studied or tested.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data normally considered in the design of a freeze crystallization plant include:

- * pH
- * Specific gravity
- * Conductivity
- * Turbidity
- * Total solids
- * Total organic carbon
- * Aqueous feed rate
- * Inorganic chemical constituents
- * Organic chemical constituents.

Both FTC and HPD Corporations have extensive pilot plant data for freeze crystallization systems. Their information will be required for expedient plant design. Tests should be conducted over the feed composition range to verify the variables listed above.

4.2 TESTING REQUIREMENTS

One must conclude from this review that despite 30 years of industrial interest and some pilot plant development, the field of freeze crystallization is still an immature industry with very few industrial successes. The improvements listed in Sections 4.2.1 and 4.2.2 should be verified under pilot plant conditions before any more industrial plants are built.

4.2.1 Indirect Heat Transfer Process

Three areas need further research:

- * A wider range of freezing temperatures must be established to increase the operational stability of the system.
- * Better methods of moving the ice from the crystallizer to the separation chamber must be demonstrated. Current methods allow some line plugging to occur.
- * Better methods of separating the ice from the mother and wash liquors must be established.

4.2.2 Direct Heat Transfer Process

Three areas of improvement are also defined for the direct process:

- * Refrigerant gases other than halo or hydrohalocarbons must be developed. Environmental concerns are rapidly closing the available permitted uses of these refrigerants.
- * Better methods of moving the ice from the crystallizer to the separation chamber must be demonstrated. Current methods allow some line plugging.
- * Better methods of separating the ice from the mother and wash liquors must be established.

5.0 VENDOR LIST

Freeze Crystallization Technologies Acquisition Corporation
Raleigh, North Carolina
(919) 571-2936

HPD Corporation
Naperville Illinois
(708) 357-7330

Envirovac, Inc.
Rockford, Illinois
(815) 654-8300

6.0 REFERENCES

1. Barron, T.S. "Use of Freeze Crystallization Systems for Concentration of Liquid Hazardous Wastes." Hazardous Materials Management Conference and Exposition, Anaheim, California, 1986.
2. Heist, J.A. "Freeze Crystallization." *Chem. Eng.* 86:(10) McGraw-Hill: New York, March 7, 1979.
3. Heist, J.A. and T.S. Barron. "Freeze Separation Processes - Energy Efficiency by Flexibility." Fifth Industrial Energy Conservation Technology Conference and Exhibition, Houston, 1983, Texas Industrial Commission (Austin), 1983.
4. Klarman, A.F. and J.A. Heist. "Hazardous Waste Minimization by Reuse and Recycling at a Naval Aviation Depot." 24th Annual Aerospace/Airline Plating and Metal Finishing Forum and Exposition, SAE, Phoenix, Arizona, April 4-7, 1988.
5. Robinson, R.S. "Developmental Testing of a Secondary Refrigerant Freezing Desalination Pilot Plant at the Wrightsville Beach Test Facility." NTIS No. PB296-811, U.S.D.I. Office of Water Research and Technology, Washington, D.C., 1979.

APPENDIX E PHASE SEPARATORS

1.0 TECHNOLOGY DESIGNATION

Liquid/liquid phase separation technology will be described in this appendix.

2.0 NEED FOR THE TECHNOLOGY

Phase separation technology may be required in both the aqueous and liquid organic treatment lines.

This technology will be used in the aqueous treatment line to remove and concentrate immiscible organic liquids from water when the concentration of organics may be too high for membrane or media bed processes. Although the aqueous stream is defined as containing less than 1% organics, condensate from steam stripping operations, or concentrate from other operations designed to remove the organics from the aqueous waste stream, may be highly concentrated with organics. The organics will require further concentration before transferring them to the WDS System, or to the organic liquid treatment line.

Phase separation technology will be used in the organic liquid treatment line to further separate the organics from water, and concentrate the organic liquids prior to destruction in the WDS System.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION (REF. 1)

The separation of immiscible liquid phases is distinctive compared to other phase separations (gas/liquid, liquid/solid, gas/solid) in that the important density difference between the phases is usually very small, sometimes less than 0.1 g/cm^3 . Separation of phases with small density differences requires large equipment, application of large forces, or unique equipment geometries. The common separation mechanisms are gravity, centrifugal force, impaction and interception, and electromotive effects.

3.1.1 Gravity Separation

A wide variety of designs are used for gravity separation in immiscible-liquid separators: horizontal or vertical vessels, troughs (API separators), and vessels with various internal configurations or parallel plates. The vessels are often referred to as decanters and may operate in a batch or continuous operation.

The performance of gravity separators is dependent on two parts: (1) the movement of dispersed-phase drops to the interface and (2) the coalescing of the dispersed phase drops at the interface. Either part could be the controlling factor. The coalescence is dependent on the purity of the phases and the interfacial tension. There is no simple relation to predict the time required for coalescence; which may range from a fraction of a second to 2-3 minutes. The time gets shorter as the density difference between the phases increases, the continuous-phase viscosity decreases, the viscosity inside the drop decreases, and the interfacial tension increases.

The presence of a surface-active agent or fine dispersed solids can interfere with the coalescing process and result in a stable emulsion. Many liquid/liquid separators form a stable emulsion at the interface because of these agents and may require draw-off nozzles near the interface to prevent accumulation. This emulsion is like a foam, is typically stabilized by fine solids, and when drawn off may be de-emulsified by filtration, heating, or chemical addition.

Long horizontal vessels, as shown in Figure E-1, provide the most desirable geometry for vessels up to about 12 feet in diameter. In such horizontal decanters, the continuous phase flows perpendicular to the drops. This causes turbulence which interferes with the settling process. Batch operated gravity separators avoid the complications of turbulence in continuous separators.

Since all gravity settling depends on the distance a drop must travel to reach an interface, or the interface area available for coalescence, various designs having parallel plates are available. The parallel plates create individual flow channels producing many separators in parallel. The maximum distance a dispersed-phase drop must travel to reach an interface is the distance between plates (ranging from 0.75 in. to several inches), rather than several feet in a large open vessel. The parallel plates also address the problem of turbulence by decreasing the hydraulic diameter for flow, and therefore the Reynolds number, allowing laminar flow.

Most of the plates are placed on an angle to allow the light and heavy phases to disengage as they pass through the plate section. By the time the bulk flow reaches the disengagement volume at the plate exit, the dispersed phase has coalesced into large droplets that separate by gravity as they exit the plate surfaces.

3.1.2 Centrifugal Separators

Mechanical centrifuges are used commercially for immiscible-liquid separation. The most common liquid/liquid centrifuge is the disk type design similar to that shown in Figure F-5.5, Appendix F. The lower-density liquid phase moves to the top of the channel between disks and toward the center of the centrifuge. The higher-density liquid moves toward the outside of the bowl but also exits at the top through a separate channel. Some solids can be handled with

either periodic shutdown and cleaning, or an automatic solids ejection by either parting the bowl momentarily or opening nozzles to eject the solids.

Figure E-1. Simple Horizontal Vessel Decanter

Capacities of disk centrifuges range from 0.011 to 1.11 ft³/s. The specific gravity difference of the pure components should be at least 0.01 and the drop size of the dispersed phase should be at least 1 μ m. Experimental results report removal of water from aviation fuel down to 0-5 ppm on feed streams of 15% water in the dispersed phase at machine capacities of 200 gpm (Ref. 2).

3.1.3 Interception

Mixtures of immiscible liquids can be separated by an interception method analogous to mesh pads or fiber beds in gas/liquid systems. The mixture is passed through a dense bed of fibers or wire mesh and the dispersed drops contact with media surface. Most systems are designed with media materials that are preferentially wetted by the dispersed drops. The dispersed material is held by the media until enough material coalesces and large globules disengage from the media and separate by gravity. These devices are often referred to as coalescers.

Metal wires are generally wetted by aqueous phases, while organic polymeric materials are usually wetted by organic chemicals. Glass or treated glass fibers can be tailored for either aqueous or organic phase wetting. Particles down to 1-5 μ m have been removed successfully. Coalescers are good for clean liquid/liquid systems and are effective for removing all oil components except soluble oils. However, systems containing solids will rapidly plug the media unless prefiltration is used, and there is a potential for biological fouling (Ref. 3).

The performance of coalescers cannot be predicted theoretically and such systems require experimental work to determine sizing, using the same media, flow rate per unit area of media, and dispersion characteristics. Tests need to be run over sufficient time to ensure that the media is fully loaded with the dispersed phase and that steady-state operation has been obtained.

Another impactation technique is flotation. Gas bubbles are used to intercept dispersed liquid drops and float them out of the bulk phase. Flotation techniques and methods of generating bubbles are discussed in Appendix F-2. Separation efficiencies of greater than 90% are obtained with 50-250 ppm oil concentration feed (Ref. 1). This technique is effective for the removal of dispersed and emulsified oil with chemical addition; however, a chemical sludge is generated when coagulants are used (Ref. 3).

Ultrafiltration and microfiltration membranes are another variation of an impact or interception separation mechanism. Membrane technology is discussed in more detail in Appendix H. Ultrafiltration membranes have discrete pores about 0.001-0.02 μm in diameter that allow the continuous phase to pass, while trapping the larger individual drops that are usually greater than 0.1 μm . These devices are good for clarifying continuous phase, for example, removing dilute oil from water. However, the dispersed phase can only be concentrated, not truly separated, since a strong continuous-phase velocity is required across the surface of the membrane to resuspend trapped dispersed-phase material to prevent fouling and blinding of the pores. An example is feeding a 2-3% oil in water mixture with a clear water stream passing through the membrane containing about 0.0005% oil, and an exit bulk flow of about 20-30% oil (Ref. 1). The exit bulk flow could then be separated by more conventional settling devices.

Laboratory tests with membrane systems have demonstrated soluble oil removal. However, these systems require extensive pretreatment, have low flux rates, and are subject to membrane fouling and limited membrane life (Ref. 3).

3.1.4 Electroseparators

Electrical charging methods may be used to remove aqueous materials and solids from organic fluids as in crude oil desalting. Dispersed materials passed between electrodes are charged with either dipoles or net charges such that they are attracted either to each other or to an electrode surface where they coalesce with other dispersed-phase material. The coalesced materials are readily separated by gravity settling. Commercial equipment handling up to 7400 m^3/day of crude oil are in use (Ref. 2).

3.2 DEMONSTRATED PERFORMANCE

Phase separators have long been used as a unit operation in the manufacture of various products in the chemical-process industries. Their primary use has been in conjunction with liquid/liquid extraction with the subsequent separation of the solvent phase, or extract, from the raffinate, or residue. Other applications include separation techniques for oily wastewater.

3.2.1 Technology Status

Phase separation technology is well developed and commercially available. Various types of liquid/liquid separators are readily available for use to separate organic liquid/aqueous streams having various characteristics. However, tests will be required to determine the characteristics of the input stream so as to select the correct type of separator, and pilot plant tests will be required to determine design parameters and size the equipment.

3.2.2 Reliability and Maintenance Requirements

Phase separation technology is fairly simple and reliable requiring periodic maintenance for cleaning and repair. Liquid characteristics described previously, the type of separator, and materials of construction will determine maintenance frequency and cleaning requirements. Centrifuges will require the most maintenance because of the high-speed moving parts and high forces involved.

3.2.3 Secondary Waste Streams

In general there are no secondary waste streams. The waste streams consist of the heavy and light phases, each of which may require additional treatment. However, flotation methods may require the addition of chemical coagulants or flocculants that produce a chemical sludge.

3.2.4 Separation Efficiency

Separation efficiency depends on the waste stream characteristics and the technology used to perform the phase separation. Some examples of separation efficiency were presented in the discussions of the various separation methods.

3.2.5 Safety and Health

There are no safety and health issues with this technology.

3.2.6 Operational Complexity

Phase separation is a simple process with minimal complexity. Complexity will depend on the type of equipment required for the waste stream. The major control requirement is flow control to ensure required settling or coalescing time and to minimize turbulence.

3.2.7 Environmental Impact

Phase separation produces two waste streams, both of which may require further processing or disposal.

3.3 COST OF THE TECHNOLOGY OR EQUIPMENT

Capital costs are difficult to generalize owing to the wide range of feed properties, output specifications, and materials of construction. Table 1 is a relative positioning of the various separation techniques.

Operating costs of the various devices vary from essentially no cost for gravity chambers with weir outlet controls, to significant electrical and maintenance costs for high-speed centrifuges. Some periodic costs for clean-out of solids accumulations may be required with most of the devices.

Table 1. Relative Capital Costs of Liquid/Liquid Separators (Ref. 1)	
Low Capital	
	Decanter vessels
	Open-trough separators (API type)
	Plate separator devices
Moderate Capital	
	Coalescers
	Flotation systems
High Capital	
	Electro separators
	Membranes
	Centrifuges

3.4 TECHNOLOGY COMPARISON (REF. 1)

Systems with greater than 30% concentration of dispersed phase are difficult to handle in anything but large-volume gravity settlers. Coalescence will be a dominant factor due to the high frequency of dispersed-phase drop interaction. Coalescence will be greatly affected by the physical properties of the fluids, especially the interfacial tension. Fluid pairs with interfacial

tension greater than 10 dynes/cm should readily coalesce, while those < 1 dyne/cm will readily emulsify. Concentrations less than 30% disperse material can be handled by disk centrifuges. Below 15%, plate settlers can be used because settling, not coalescence, is likely to be the dominant mechanism. Below 5% concentration, all equipment is applicable and selection must be based on other criteria.

Dispersions with drop size less than 25 μm require techniques other than gravity settling such as fiber coalescers, flotation, or centrifugation to obtain good separation efficiency.

Emulsions are another category of dispersion with particles generally less than 1 μm and with low interfacial tension. Dense media coalescers and membranes are sometimes effective. Chemical or heat treatment may be needed to break the emulsions by changing the interfacial tension followed by conventional separation techniques. For water dispersed in an organic emulsion, the electroseparators may be applicable.

The required effluent quality is a major factor in determining the separator system configuration. Combinations of two or more separation devices or techniques may be needed. Gravity separators can perform a gross separation of drops down to 150 μm . Centrifuges, fiber bed coalescers, or membranes would be required for very high efficiencies for particles down to 1 μm . To clear a mixture of 30% dispersed-phase concentration to only a few ppm residual would require gravity settling followed by a polishing device.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Tests will be required to determine the characteristics of the input stream so as to select the correct type of separator, and pilot plant tests will be required to determine design parameters and size the equipment. In general, the performance of phase separators cannot be predicted in detail by theoretical means and such systems require experimental work to determine sizing using the same waste stream characteristics.

4.2 TESTING REQUIREMENTS

Tests will be required to determine the waste stream characteristics including dispersed phase concentration, droplet size, the physical/chemical characteristics of the phases, and solids content.

5.0 VENDOR LIST

Osmonics, Inc.
5951 Clearwater Dr.
Minnetonka, MN 55343
(800) 848-1750

Membrane Systems

Heil Process Equipment Corp.
34252 Mills Rd.
Avon, OH 44011
216-327-6051

Plate Separators

Permutit Co., Inc.
30-T Technology Dr.
Warren, NJ 07059
908-668-1700

Flotation Systems

Petrolite Corp.
16010-T Barker Point Lane
Houston, TX 77079
713-558-5200

Electrocoalescers

6.0 REFERENCES

1. Jacobs, L.J. and W.R. Penney. "Phase Segregation." in *Handbook of Separation Process Technology*, R.W. Rousseau, ed. John Wiley & Sons: New York, 1987.
2. Hooper, W.B. and L.J. Jacobs, Jr. "Decantation." in *Handbook of Separation Technologies for Chemical Engineers*. P.A. Schweitzer, ed. McGraw-Hill Book Co.: New York, 1988.
3. Corbitt, R.A. "Wastewater Disposal." in *Standard Handbook of Environmental Engineering*. R.A. Corbitt, ed. McGraw-Hill, Inc.: New York, 1990.

APPENDIX F MECHANICAL SOLID/LIQUID SEPARATION

The purpose of these technologies is to separate high concentrations of suspended solids from a liquid using gravitational, centrifugal, buoyancy, or filtration effects. Centrifuges and hydrocyclones use centrifugal forces to force heavier particles toward the circumference of a conical chamber where they fall out of suspension. Sedimentation uses gravity to allow heavier particles to settle out of a liquid suspension. Flotation techniques use buoyancy effects to float light particles to the top of a liquid.

Several soil decontamination processes in the Netherlands use gravity concentration and flotation for removal of fine particles and organics from extracting agents. Systems similar to this are in the pilot-stage in the United States. Pilot plant testing at Rocky Flats in the early 1970s showed that soils contaminated with 45, 284 and 7,515 pCi/g plutonium were reduced to 0.5, 12, and 86 pCi/g, respectively, using physical separation. The cleaned soil fraction ranged from 58% to 87% of the original volume. These technologies described in this appendix are as follows:

- F-1 Traditional Coagulation and Flocculation
- F-2 Flotation
- F-3 Foam Fractionation
- F-4 Sedimentation/Decantation
- F-5 Centrifugal Sedimentation
- F-6 Hydrocyclones
- F-7 Filtration

APPENDIX F-1 TRADITIONAL COAGULATION AND FLOCCULATION

1.0 TECHNOLOGY DESIGNATION

The purpose of coagulation and flocculation is to destabilize a colloidal solution and promote the growth of settleable solids. Coagulation refers to the reduction of the net electrical repulsive charges surrounding very small colloidal particles. Flocculation is a physical process where particles which have been treated with a coagulant are mechanically agitated to promote agglomeration.

2.0 NEED FOR THE TECHNOLOGY

The processing of aqueous liquids with suspended colloidal solids may require coagulation and flocculation to be considered as a separation technology. The primary use of coagulation/flocculation is in the Aqueous Treatment line as a primary treatment mechanism (block 150.2). Coagulation and flocculation are always followed by sedimentation and sometimes by a filtration step.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Colloidal dispersions in water consist of discrete particles held in suspension by their extremely small size (1-200 nm), state of hydration, and surface electrical charge. The purpose of coagulation and flocculation is to destabilize a colloidal solution and promote the growth of settleable solids. Coagulation refers to the reduction of the net electrical repulsive charges surrounding very small colloidal particles. Flocculation is a physical process where particles which have been treated with a coagulant are mechanically agitated to promote agglomeration. In this process, the first stage involves addition of a coagulant and/or coagulant aid during rapid mixing to ensure complete dispersion of the chemical. Next, flocculation (particle size growth) is promoted by mixing at lower velocities and for longer periods of time.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Stable colloidal solutions generally range up to a few percent solids. Very high solids content solutions should have the settleable solids removed in a primary clarifier before coagulation and flocculation. After final sedimentation, the solids content of the exiting stream is usually very low.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Coagulation and flocculation are commonly used water and wastewater treatment methods and are routinely used in plants treating millions of gallons per day. A variety of commercially available equipment is available. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected. While it is conceivable that a very special filtration application may be needed the screening of potential vendors cannot be made until more detail is known about the application.

No major technology development applications are known. However, most wastewater treatment operations employ coagulation or flocculation to some degree. New coagulants, polymers, and flocculation equipment are continually being evaluated.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintainability are a function of design but coagulation and flocculation are typically low-maintenance and highly reliable if correctly designed for the application. This is primarily due to the simple designs with few moving parts.

3.3.3 Secondary Waste Streams

The secondary waste streams from coagulation and flocculation systems are the settled solids. The addition of coagulants and polyelectrolytes may increase the overall volume of secondary wastes, but this additional volume is not prohibitive. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

This technology is highly efficient at removing most colloidal solids.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Depends on design but generally is not a complex system.

3.3.7 Glovebox Capability

These systems are generally used in large-scale wastewater treatment facilities and are not commonly used in small scale glovebox operations. However, if adequate hydraulic retention times and volumes are designed into the process, there is no technical reason why glovebox operations would be precluded.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Capital costs are generally low to medium, while operating costs are low.

3.5 TECHNOLOGY COMPARISON

Traditional filtration without coagulation or flocculation may be appropriate for small volume process streams where generation of secondary filter media is not a concern or where adequate retention times are impossible. However, for large volume streams, coagulation and flocculation followed by sedimentation is the preferred approach since the generation of secondary filter media is minimized.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of these systems requires information about the characteristics of the fluid being treated, the solids being removed, and the capacities required.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. Standard testing of these systems, referred to as "jar testing" is used to establish the dosage rates of coagulants and mixing speeds of flocculation tanks.

It is difficult, if not impossible, to simulate or predict the settling characteristics of a colloidal solution. The use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

Coagulation and flocculation are commonly used water and wastewater treatment methods and are routinely used in plants treating millions of gallons per day. A variety of commercially available equipment is available. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected. While it is conceivable that a very special filtration application may be needed the screening of potential vendors cannot be made until more detail is known about the application.

6.0 REFERENCES

None

APPENDIX F-2 FLOTATION

1.0 TECHNOLOGY DESIGNATION

Flotation is the removal of suspended solids and oil and grease from wastewaters and for the separation and clarification of sludges.

2.0 NEED FOR THE TECHNOLOGY

Flotation is the removal of suspended solids, and oil and grease from wastewaters and for the separation and clarification of sludges. Application in the MWTP is in the Aqueous Treatment Line, blocks 140.2 (organics feed), and 150.2 (primary treatment).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Flotation is a process by which solids are selectively floated to the surface of a slurry by means of attached gas bubbles. The injection of air into a liquid suspension can cause low-density solids and hydrocarbon solids and liquids to float to the surface for removal. Microbubbles formed by injection of air attach to particles, become trapped under larger particles, or become part of flocs. These particles with the attached air bubbles have a combined specific gravity less than that of water and float to the surface. The key to successful flotation is the selective adhesion of air bubbles to the material that is to be floated. The actual separation, after the material has been made lighter by air-bubble attachment, is usually by frothing.

The first step is the reduction of particle size to the point where flotation can occur. The second step is the addition of conditioning agents to assist the selective adhesion of the collection agent. Conditioning is necessary because of the dirty nature of most slurries, in which various materials can react with and adversely affect the action of the collection agent. This may simply involve a pH adjustment or addition of a detergent. After conditioning, a collection agent is added to cover the materials to be floated with a water repellant film which allows easy attachment of air bubbles. The collection agents may be selective so as not to coat the other materials in the slurry.

Once the particles have been treated so that the desired ones will adhere to air bubbles, a frothing agent is added and the slurry is aerated or otherwise agitated to produce the froth.

Various frothing agents are available, but a typical agent is soap. The froth is then removed from the top of the flotation cell by a mechanical scraper.

Another way to generate air bubbles is to pressurize the waste flow to 50-70 psi in the presence of sufficient air to approach saturation. When this pressurized air-liquid mixture is released to atmospheric pressure in the flotation unit, minute air bubbles are released from solution. The suspended solids or organic globules are floated to the surface by the air bubbles and are skimmed off. The principle components of a flotation system are a pressurizing pump, air-injection facilities, a retention tank, a back-pressure regulation device, and a skimming mechanism.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Flotation is the removal of suspended solids and oil and grease from wastewaters and for the separation and clarification of sludges. The stream characteristics depend on design and application, however the goal is to produce a wastewater solution which is clarified (i.e., free of suspended matter).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Flotation is not used as often as the more traditional solids removal techniques because performance is reduced by inconsistent feed streams. However, a large number of commercial vendors supply equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected.

This method is used extensively in the mining industry for concentration of minerals. Flotation and other physical separation techniques are used to recover copper, uranium, zirconium, and magnetite by the Palabora Mining Company in South Africa. The method has also been used for removal of radium mill tailings in Elliot Lake. During laboratory testing, flotation was found to reduce radium concentrations from 290 pCi/g to 57 pCi/g. It is also used to recover glass and plastics from municipal wastes.

For efficient operation, it is critical to match particle size distribution to bubble size and quantity. Methods for generating air bubbles typically include mechanical agitation, nucleation of gas from solution, or electrolysis of the aqueous phase. A microbubble generator, recently developed at Virginia Polytechnic Institute and State University, can provide 90 liters/minute of treated water and air, hydrogen peroxide or pure oxygen. This system can assist in flotation systems that concentrate primary and secondary sludges or for bioremediation.

3.3.2 Reliability and Maintenance Requirements

These requirements depend on the wastewater characteristics and the flotation system design.

3.3.3 Secondary Waste Streams

Secondary wastes include the chemicals added to induce flotation.

3.3.4 Separation Efficiency

Flotation can achieve very high separation rates if the materials are suited to such treatment.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Flotation can be a complex process depending on the pretreatment and chemicals required, the characteristics of the waste stream, and the nature of the material to be removed.

3.3.7 Glovebox Capability

Flotation is normally used in large-scale wastewater treatment and are not commonly used in small-scale glovebox operations. However, if the process conditions make it economically feasible, there is no technical limitation which would preclude glovebox operation since laboratory scale systems are available.

3.3.8 Environmental Impact

None are specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Capital costs are low to medium. Operating costs are generally low but can increase significantly as maintenance increases.

3.5 TECHNOLOGY COMPARISON

Flotation systems are very similar to sedimentation systems in concept. They are easy to design and operate and have few mechanical parts. The efficiency of the process depends on

the relative concentrations and densities of the contaminants in the waste stream. Flotation is employed when the organic content or the densities of suspended solids make it more appropriate than sedimentation.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of flotation systems requires information about the characteristics of the fluid, the solids being removed, and the capacities required. The primary variables are pressure, recycle ratio, feed solids concentration, and retention period.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible; however, laboratory tests are easily scalable. When not possible, maximum flexibility should be part of the overall design. Since it is difficult to simulate or predict the flotation characteristics of a specific process stream, the use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

Flotation is not used as often as the more traditional solids removal techniques because performance is reduced by inconsistent feed streams. However, a large number of commercial vendors supply equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected.

6.0 REFERENCES

Eckenfelder, W. Wesley, Jr. *Industrial Water Pollution Control*. 2nd ed., McGraw-Hill Book Company, 1989.

APPENDIX F-3 FOAM FRACTIONATION

1.0 TECHNOLOGY DESIGNATION

Foam fractionation is used to remove suspended solids and organics from aqueous solution. Foam fractionation is a variation of traditional flotation in which reagents are added to combine with dissolved species in solution, thereby allowing them to affix to air bubbles and become buoyant.

2.0 NEED FOR THE TECHNOLOGY

Application in the MWTP is in the Aqueous Treatment Line, blocks 140.2 (organics feed), and 150.2 (primary treatment).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

While flotation separates insoluble material, foam fractionation separates dissolved material. Surface inactive species can be removed from solution by adding an appropriate surface-active material to unite with the species so that it can be adsorbed at the bubble surface. This can occur through the formation of a chelate, electrostatic attraction, or some other mechanism. The surface-active material, or surfactant, acts as a mobile ion exchanger; a cationic surfactant can scavenge surface-inactive anions from solution, and a chelating surfactant can form a surface active complex with metallic ions.

In batch foam fractionation, foamate is continuously removed and the original solution is continuously depleted of the foaming agent. In continuous systems, feed solution is continuously added to the column while foamate and residue are withdrawn continuously. Foam separation, like other separation methods, can be conducted in a series of single stages or in one multistage countercurrent column. If the operation is to remove a surface-inactive material by complex formation with a suitable surfactant, the foamate (complex) may be broken by a chemical reaction to form an insoluble compound of the removed surface-inactive material, thus regenerating the surfactant. The insoluble compound is filtered from solution and the regenerated surfactant is recycled. It has been demonstrated that surfactant-Hg or -Cd complexes removed as foam can be broken down with H_2S or Na_2S and the HgS or CdS precipitated and filtered.

Foam fractionation techniques can be used to remove a large number of anions, cations and various organic and inorganic molecules from solution depending on the surfactant used. This technique has been used to separate Cr, Hg, Cd, Pb, chromate, cyanide, and many other species.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The stream characteristics depend on design and application, however the goal is to produce a wastewater solution which is clarified (i.e., free of suspended matter). Foam fractionation is similar to flotation except that reagents are added to improve the efficiency of the process. The output stream characteristics would necessarily differ depending on the chemical nature of the reagent.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

See corresponding section on Flotation, Appendix F-2. No significant differences exist.

3.3.2 Reliability and Maintenance Requirements

These requirements depend on the waste water characteristics, the system design, and the chemicals used to enhance flotation.

3.3.3 Secondary Waste Streams

The secondary waste streams consist primarily of the separated solids and unrecycled chemicals or surfactants. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

Separation efficiency depends upon the characteristic of the feed stream.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Depends on design but the technology is relatively simple.

3.3.7 Glovebox Capability

Foam fractionation is normally used in large-scale wastewater treatment and are not commonly used in small-scale glovebox operations. However, if the process conditions make it economically feasible, there is no technical limitation which would preclude glovebox operation.

3.3.8 Environmental Impact

None are specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Capital costs are low to medium. Operating costs are generally low but can increase significantly as maintenance increases.

3.5 TECHNOLOGY COMPARISON

See corresponding section on Flotation, Appendix F-2. No significant differences exist.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of foam fractionation systems requires information about the characteristics of the fluid, the solids being removed, and the capacities required. The primary variables are pressure, recycle ratio, feed solids concentration, and retention period.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design. Since it is difficult to simulate or predict the flotation characteristics of a specific process stream, the use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

See corresponding section on Flotation, Appendix F-2. No significant differences exist.

2 of 5

6.0 REFERENCES

Eckenfelder, W. Wesley, Jr. *Industrial Water Pollution Control*. 2nd ed., McGraw-Hill Book Company, 1989.

APPENDIX F-4 SEDIMENTATION/DECANTATION

1.0 TECHNOLOGY DESIGNATION

Sedimentation is the removal of solid particles from solution by gravity and generally refers to a large quiescent tank with sufficient hydraulic retention times to allow gravity settling of the majority of the particles suspended in solution.

2.0 NEED FOR THE TECHNOLOGY

Sedimentation commonly follows (and sometimes precedes) coagulation and flocculation of colloidal solutions. The use of sedimentation with or without coagulation and flocculation is in the Aqueous Treatment line as a primary treatment mechanism (block 150.2). Settling of solid particles from organic solutions in the Organic Treatment line is possible but slower settling characteristics in organics and smaller solution volumes restrict the practical use of sedimentation in this way.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Often the separation of the solid and liquid phases of a suspension is a two stage process. The first stage, known as thickening, involves the conversion of particles of the suspension into a thickened underflow with a clear overflow, often by the addition of a coagulant or flocculant. The second stage is usually an engineering operation to reduce the remaining water content of the thickened underflow by a suitable solid-liquid separation process.

Sedimentation processes are classified into four categories (Type I, Type II, zone, and compression) depending on the character of the particles. Type I refers to settling of discrete particles. Type II refers to hindered settling of flocculent materials. Zone settling is the mass sedimentation of flocculent particles in concentrations higher than Type II. Compression settling results when the solids concentration increases to the point where the particles are in physical contact with each other. The settling characteristics of a solution are determined by testing of actual process solutions. Sedimentation tanks are commonly referred to as clarifiers. Design criteria include overflow rate, depth, weir loadings, solids removal mechanism, and solids removal rates.

Two forms of sedimentation vessels are in common use. The clarifier is used for the clarification of a dilute suspension (usually less than 1% suspended solids content by volume) to obtain an overflow containing minimal suspended solids. The thickener is used to thicken a suspension of higher solids concentration to obtain an underflow with a high solids concentration while also producing a clarified overflow.

Particle size, particle density and fluid viscosity are obvious factors influencing the sedimentation process. Other factors influencing the separation process include particle shape and orientation, particle concentration, the distortion of a deformable particulate such as a floc, the interference of one particle with another (particularly when concentrations are high), the nearness of the wall of the container, container diameter relative to the height of the suspension, convection currents, etc. Materials with particle diameters of the order of a few microns settle too slowly for most practical operations. However, such particles can be agglomerated, or flocculated, into relatively large clumps called flocs, that settle out more rapidly.

Thickening devices usually consist of relatively shallow tanks from which the clear liquid is removed from the top and the thickened liquor from the bottom. The settling capacity of sedimentation units is directly proportional to the area of the vessel or tank and the settling rate of the solids in suspension. To obtain the largest possible throughput, the rate of sedimentation should be as high as possible. In most cases, this rate is increased by the addition of a coagulant or flocculant.

The tanks are circular with rotating arms to convey the settled solids to the point of discharge located at the bottom center of the tank. Thickener tanks are constructed of steel or concrete, with steel being the most economical in sizes of less than 25 m in diameter. Centrifugal slurry pumps, positive displacement diaphragm pumps, or progressive cavity pumps are used to withdraw the underflow through a tunnel system under the tank.

High capacity thickeners are available that provide high solids handling capacity in relatively small areas. However, the effectiveness of these systems depends on the selection of very effective flocculants and subsequent efficient mixing and dispersion of the flocculant solutions. These types of thickeners include the deep cone type, the Enviroclear thickener, the Eimco Hi-capacity thickener, and the lamella or inclined plate clarifier and thickener. The deep cone thickener design ranges from 3 to 4 m in diameter, 4.3 m deep and one is capable of handling 70 m³/hr of feed at 6% solids by weight to produce a final discharge ranging in moisture content from 25% to 35% by weight.

The only driving force for sedimentation is the difference in specific gravity between phases so that, although this process is highly efficient, it has a relatively low process capacity and may have limiting factors beyond the control of engineering design. On the other hand,

sedimentation systems are relatively cheap, are suited for batch or continuous operation, can be automated, and sedimentation is a well proven technique.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The input streams to sedimentation tanks consist of wastewaters with high suspended solids. They may also contain coagulants or settling aids added in pretreatment steps. The output stream is a clarified solution with low suspended solids.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Sedimentation systems are routinely used in water and wastewater treatment in plants treating millions of gallons per day. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. While it is conceivable that a very special application may be needed the screening of potential vendors cannot be made until more detail is known about the application.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintainability are a function of design but sedimentation systems are low-maintenance and highly reliable if correctly designed for the application.

3.3.3 Secondary Waste Streams

The secondary waste streams from sedimentation systems consist primarily of the settled solids. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

Sedimentation systems are very effective and have a long performance history.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Depends on design but are generally quite simple in design.

3.3.7 Glovebox Capability

These systems are generally used in large-scale wastewater treatment facilities and are not commonly used in small-scale glovebox operations. However, if adequate hydraulic retention times and process volumes are designed into the process, there is no technical reason why glovebox operation would be precluded.

3.3.8 Environmental Impact

None are specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Capital costs are low to medium, depending on the scale of operation. Operating costs are generally low.

3.5 TECHNOLOGY COMPARISON

Traditional filtration without coagulation or flocculation and sedimentation may be appropriate for small volume process streams where generation of secondary filter media is not a concern or where adequate retention times are impossible. However, for large volume streams, coagulation and flocculation followed by sedimentation is the preferred approach since the generation of secondary filter media is minimized.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of sedimentation systems requires information about the characteristics of the fluid being clarified, the solids being removed, and the capacities required.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design.

It is difficult, if not impossible, to simulate or predict the settling characteristics of a colloidal solution. The use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

Sedimentation systems are routinely used in water and wastewater treatment in plants treating millions of gallons per day. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. While it is conceivable that a very special application may be needed the screening of potential vendors cannot be made until more detail is known about the application. However, following are several vendors that supply this type of equipment:

Infilco Degremont, Inc.
Dorr-Oliver, Inc.
Walker Process Corp.
FMC Corp.
Oberlin Filter Co.
Chemical Waste Management

6.0 REFERENCES

Eckenfelder, W. Wesley, Jr. *Industrial Water Pollution Control*. 2nd ed., McGraw-Hill Book Company, 1989.

APPENDIX F-5 CENTRIFUGAL SEDIMENTATION

1.0 TECHNOLOGY DESIGNATION

The purpose of centrifugal sedimentation is to separate solids from a liquid stream or to dewater and/or thicken sludges and slurries. Solids are removed from the liquid stream flowing through a machine under the influence of a centrifugal field of 100-600 times the force of gravity. The fundamental difference between designs is the method of solids collection and discharge. The solids being removed can be granular, fibrous, flocculent, or gelatinous and differ in settling and compaction characteristics. Therefore, the type of centrifuge adopted is determined by the particular stream being treated.

2.0 NEED FOR THE TECHNOLOGY

Centrifuges are normally employed for dewatering and thickening sludges and slurries. Some designs are also used as filtration devices. As with other solid/liquid separation techniques, the potential applications in the MWTP are numerous. Specifically in the Aqueous Treatment line, solid/liquid separation is needed in blocks 155.2 (drum filter), 180 (solids dewatering) , and 150.1 (special operations). In the Organic line, solids removal is needed in blocks 250.1 (solids separation), 250.2 (filter), and 250.3 (filter).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Centrifugal sedimentation is based on density differences between solids and liquids (or between two liquid phases); the particles are subjected to centrifugal forces which make them move radially through the liquid either outwards or inwards, depending on whether they are heavier or lighter than the liquid. In commercial centrifuges the force of gravity is typically amplified by from 2 to 5 orders of magnitude. The term *ultracentrifuge* is commonly applied to any ultrahigh-force centrifuge. Ultracentrifuges are usually smaller in size due to the high centrifugal forces involved (over 300,000 g), and are usually used to separate small particles (less than 0.1 μm).

A sedimenting centrifuge consists of an imperforate bowl into which a suspension is fed and rotated at high speed. The liquid is removed through a skimming tube or over a weir while the solids either remain in the bowl or are intermittently or continuously discharged from the

bowl. Five types of industrial sedimenting centrifuges may be distinguished according to the design of the bowl and of the solids discharge mechanism.

The tubular centrifuge (Figure F-5.1) is a vertical tube with a large length-to-diameter ratio which rotates at high speed about its vertical axis. Liquid is introduced at the bottom and the flow is essentially axial. The liquid overflows over a weir at the top of the tube, and the solids are retained in the centrifuge. This is a batch operation in which the centrifuge must be stopped and cleaned (usually manually) when the solids content in the bowl reaches a certain level. Tubular centrifuges are usually used for liquid clarification with suspensions that contain less than 1% solids by volume.

The imperforate basket centrifuge (Figure F-5.2) is similar to the tubular centrifuge but with a much smaller length-to-diameter ratio causing a lower separation efficiency. This centrifuge is semi-continuous in operation and has intermittent discharge which may be automated. At the end of an operation cycle, usually triggered by a cake thickness detection device, the supernatant liquid that remains on top of the cake is skimmed off to produce a dryer cake on discharge. Solids are skimmed off with a ploughing knife and drop through the open bottom of the bowl. The solid content is usually low (3 - 5% by weight) to prevent frequent cleaning. Typical applications include dewatering of sludges and recovery of solids from waste streams. A triple bowl centrifuge has been used successfully to clean metal-working coolants.

The multi-chamber centrifuge (Figure F-5.3) uses a closed bowl that is sub-divided into several concentric vertical cylindrical compartments through which the suspension flows in series. The suspension passes through zones of progressively higher acceleration resulting in a classification effect, with the coarsest fraction being deposited in the innermost chamber, and the finest fraction in the outermost chamber. Another advantage is the machines large solids holding capacity. The efficiency of the multi-chamber centrifuge is high because of the long residence time of the suspension in the unit. This is a batch type system requiring manual discharge and cleaning thereby limiting this type of machine to suspensions containing less than 5% solids by volume. These centrifuges are mainly used for the clarification of beer, wine, fruit juice and varnish.

The scroll-type continuous conveyor discharge centrifuge (Figure F-5.4) operates and discharges continuously. This is a horizontal device with a conical bowl that contains a screw conveyor that rotates in the same direction as the bowl but at a slightly higher or lower speed. Centrifugal forces are lower than in other types of equipment. The slurry enters through an axial tube at the center of the rotor, passes through openings in the screw conveyor and is thrown to the rotor wall. Deposited solids are moved by the screw conveyor out of the liquid through an annular opening around the inlet tube. Liquid overflow exits the opposite end of the centrifuge.

93-0024-F-5.1

Figure F-5.1. Schematic Diagram of a Simple Tubular Centrifuge

(Reproduced with permission of Butterworth-Heinemann from Ref.1)

Figure F-5.2. Schematic Diagram of an Imperforate Basket Bow In Cross-Section

(Reproduced with permission of Butterworth-Heinemann from Ref. 1)

Figure F-5.3. Schematic Diagram of a Multi-Chamber Bowl in Cross-Section

(Reproduced with permission of Butterworth-Heinemann from Ref. 1)

Figure F-5.4. Schematic Diagram of a Scroll-Type Centrifuge Bowl in Cross-Section (Cono-Cylindrical Bowl)

(Reproduced with permission of Butterworth-Heinemann from Ref. 1)

When operated as a clarifier, this type of centrifuge recovers medium and coarse particles from feeds at high or low solids content from 2% to 50% by volume. This equipment has been used to recover crystals and polymers, and for the dewatering of municipal and industrial sludges and coarse solids.

The disc type centrifuge (Figure F-5.5) contains a stack of conical discs inside a cylindrical bowl. The liquid flows in thin layers between the discs, radially inwards, towards the outlet which is an annulus around the feed tube at the top center. Particles settle on the lower surface of the upper of the two discs that form each "disc channel". As the particles settle on the disc surface, they slide downward and outward toward the disc periphery and subsequently impinge on the wall of the bowl. The concept is to increase the settling capacity by using several layers in parallel, similar to the lamella systems used in gravity sedimentation. Disc centrifuges are operated up to 12,000 rpm, depending on bowl diameter, and can achieve flow rates up to $100 \text{ m}^3/\text{hr}$.

Figure F-5.5. Schematic Diagram of a Disc Centrifuge Bowl In Cross-Section

(Reproduced with permission of Butterworth-Heinemann from Ref. 1)

There are three types of disc centrifuges: the solids retaining type which is a batch type and requires manual cleaning, the nozzle type which allows continuous discharge of the slurry, and the solids retention type in which the solids are ejected intermittently. The underflow-to-throughput ratio for the nozzle type is normally between 5% and 50% depending on the number

and size of nozzles. Applications have been in the kaolin clay dewatering, tar dehydration, and clarification of wet process phosphoric acid. The solids ejecting type of disc centrifuge is used where there is a medium concentration of solids in the 2% to 6% range. Applications include clarification of juices and food extracts, and purification of fuels.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Like traditional sedimentation, the input streams consist of wastewaters with high suspended solids. They may also contain coagulants or settling aids added in pretreatment steps. The output stream is a clarified solution with very low suspended solids as a result of the high centrifugal forces.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Centrifugal sedimentation is not used as often as the more traditional filtration techniques because of higher maintenance and cost. However, a large number of commercial vendors supply equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. While it is conceivable that a very special application may be needed, the screening of potential vendors cannot be made until more detail is known about the application.

3.3.2 Reliability and Maintenance Requirements

Because of their high speed moving parts, centrifuges are higher maintenance items than traditional solid/liquid separation devices. Reliability can be a problem when used with inconsistent feed streams. All centrifuges must be maintained properly to ensure balance and adequate system operation. However, these devices are in wide use in industry and the maintenance needs are not prohibitive. Because of the high g-forces and rotational speeds, ultracentrifuges are generally small laboratory devices with high maintenance requirements. Ultracentrifuges are generally not suited for waste treatment systems.

3.3.3 Secondary Waste Streams

The secondary waste streams from centrifuges consist primarily of the removed solids and liquid overflow. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

Due to the extra energy added to the separation process, high efficiency separations can be achieved. However, this increased efficiency is offset by higher capital and maintenance costs.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Depends on design but can be quite a complex system.

3.3.7 Glovebox Capability

Centrifuges have been demonstrated in glovebox environments. Ease of operation and remote handling are primary concerns.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Capital costs are anticipated to be low to medium. Operating costs are generally low but can increase significantly as maintenance increases.

3.5 TECHNOLOGY COMPARISON

For harder to clarify solutions, centrifugal sedimentation is desirable to prevent long sedimentation times in sedimentation tanks. However, the mechanical nature of this process make it more expensive in equipment and maintenance costs.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of centrifugation systems requires information about the characteristics of the fluid being filtered, the solids being removed, and the capacities required.

4.2 TESTING REQUIREMENTS

Testing should be done in field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design.

Since it is difficult to simulate or predict the filtration characteristics of a specific process stream, the use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

Centrifugation is not used as often as the more traditional filtration techniques because of higher maintenance and cost. However, a large number of commercial vendors supply equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. While it is conceivable that a very special filtration application may be needed, the screening of potential vendors cannot be made until more detail is known about the application.

6.0 REFERENCES

Svarovsky, L. *Solid-Liquid Separation*. Butterworth-Heinemann: Oxford, 1990.

APPENDIX F-6 HYDROCYCLONES

1.0 TECHNOLOGY DESIGNATION

The hydrocyclone is a device that uses high centrifugal forces to separate solids from liquids.

2.0 NEED FOR THE TECHNOLOGY

Hydrocyclones are generally used for classification of soil particles in the 35 mesh to 1 μm range.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The hydrocyclone is a device that uses high centrifugal forces to separate solids from liquids. Usually the hydrocyclone consists of an upper cylindrical section fitted with a tangential feed connection and a lower conical section having a bottom concentric apex opening for solids discharge. The closed top of the cylindrical section has a downward protruding vortex finder pipe, ending below the tangential feed location, through which the liquid fraction discharges from the device (Figure F-6.1).

93-0024-F-6.1

Figure F-6.1. Schematic Diagram of a Typical Hydrocyclone

Pressurized slurry is introduced to the hydrocyclone tangentially through the feed connection which creates a downward spiraling action developing high centrifugal forces. As the

fluid moves downward, the solids in suspension are driven by the centrifugal force to the cyclone wall and progress toward the apex opening at the bottom of the conical section. At the apex, the solids, along with a small portion of liquid, continue on and leave the device by virtue of their inertia. As the apex is approached, the fluid phase reverses axial direction and spirals upward, exiting the hydrocyclone through the vortex finder pipe. Since those solids removed through the apex have been eliminated, the overflow fluid is substantially free of solids or, at a minimum, devoid of the larger or heavier solids fraction.

The advantages of the hydrocyclone are its intrinsic simplicity, low initial-capital cost, low-operating cost, and low-maintenance requirements.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Like centrifugal sedimentation, the input streams consist of wastewaters with high suspended solids. They may also contain coagulants or settling aids added in pretreatment steps. The output stream is a clarified solution with very low suspended solids as a result of the high centrifugal forces.

Cut sizes for most solids range from 2 to 250 μm , and flow rates for single hydrocyclone units range from 0.1 to 7200 m^3/hr .

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Mature

3.3.2 Reliability and Maintenance Requirements

Highly reliable with few maintenance requirements since hydrocyclones have no moving parts.

3.3.3 Secondary Waste Streams

The secondary waste streams from hydrocyclones consist of the removed wet solids and liquid overflow.

3.3.4 Separation Efficiency

The underflow solids concentrations that can be achieved with hydrocyclones rarely exceed 45% or 50% by volume, depending on the size of the unit, operating conditions, and the nature of the solids. Separation is based on the density difference between phases and particle size.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology.

3.3.6 Operational Complexity

Very simple.

3.3.7 Glovebox Capability

Hydrocyclones have been demonstrated in gloveboxes and are easy to operate remotely.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required other than testing for a specific application. Capital and operating costs are low.

3.5 TECHNOLOGY COMPARISON

Hydrocyclones can be used to clarify liquids, concentrate slurries, classify solids, wash solids, and separate immiscible liquids. They are simple and cheap to purchase, install, and operate, and they require little maintenance. However, once installed they are inflexible with low turn-down ratio due to the dependence of separation performance on flow rate, feed concentration, and particulate characteristics.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of hydrocyclones requires information about the characteristics of the fluid and solids being separated as well as the capacities required.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design.

Since it is difficult to simulate or predict the separation characteristics of a specific process stream, the use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

This is not a complex or new technology so many vendors listed in the Thomas Register will be able to supply this equipment.

6.0 REFERENCES

Svarovsky, L. *Solid-Liquid Separation*. Butterworth-Heinemann: Oxford, 1990.

APPENDIX F-7 FILTRATION

1.0 TECHNOLOGY DESIGNATION

Filtration is a unit operation designed to separate suspended particles from a fluid stream by passing the solution through a porous medium. As fluid is forced through the voids or pores of the medium, solid particles are retained on the medium's surface or in the pores, while the fluid, or filtrate, passes through.

2.0 NEED FOR THE TECHNOLOGY

Filtration processes will most likely be the most heavily used processing technology in the MWTP. Filters and filtration devices will be used throughout the Aqueous Treatment line and routinely in the Organic and Wet Solids treatment lines. Specifically in the Aqueous Treatment line, solid/liquid separation is needed in blocks 155.1 (grit removal), 155.2 (drum filter), 180 (solids dewatering), and 150.1 (special operations). In the Organic line, filtration is needed in blocks 250.1 (solids separation), 250.2 (filter), and 250.3 (filter). In the wet solids line, block 330 (grit screen) requires a separation technique. *It is important to remember that as the process flow diagrams become more detailed, the applications for filtration techniques will grow substantially.*

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Filtration is a method for separating solid particles from a fluid through the use of a porous media. The driving force is a pressure gradient caused by gravity, centrifugal force, vacuum, or pressure greater than atmospheric. There are two major types of filtration: cake filtration, and filter-medium (or depth) filtration.

In cake filtration, the solid particles are retained on the surface of a porous medium. The solids accumulate as a cake of increasing thickness. Eventually, the cake becomes the filter medium as the solids continue to build up on the cake. At the end of the filtration cycle the cake can be dewatered by mechanical compression or by air drying. The cake is then removed from the filter and the medium is washed and reused. Several technologies use the cake filtration process; these include rotary vacuum belt filters, rotary vacuum precoat filters, filter presses, and the belt filter press.

In depth filtration, the liquid containing typically less than 100 ppm of suspended solids is forced through a porous medium and the solid particles become entrapped within the pore

structure of the filter medium. The filter medium is usually granular-media filters, screen filters, or disposable cartridge filters. The filtration cycle is stopped when either the pressure drop or solids concentration in the effluent exceeds established limits. The filter medium must then be either replaced or cleaned.

To select filtration equipment, two important parameters must be considered: the method used to force the liquid through the medium, and the material that makes up the filter medium. In addition, filter aids may be used to prevent the penetration of fine particles into the pores of the filter plate when processing low-concentration suspensions. Filter aids build up a porous, permeable, rigid lattice structure that retains solid particles on the filter medium surface, while permitting liquid to pass through.

Filtration devices are manufactured in an abundance of different designs. The operating requirements depend on the design of the specific filtration device. While filtration devices can be designed for almost any application, the choice of method will depend on the characteristics of the fluid, particle size and size distribution, particle characteristics, temperature, etc.

For large scale filtration, the most common example is gravity granular-media filtration. This technique consists of filtration through beds of granular media and works best for removing colloidal material from aqueous solutions. A variety of designs for granular media systems are commercially available. Other frequently used designs are cake filtration units and vacuum assisted units.

For smaller throughput systems, there are a multitude of in-line cartridge systems available. These devices can be specified to operate in the normal range of flows and particle sizes of a waste stream. For reusable filters, these units should be designed for easy cleaning. For non-reusable designs, the filtration system should minimize the final volume of waste material (filter and filtered solids). If incineration of the solids is planned, then an ashless filter material, such as polypropylene, is highly desirable.

3.1.1 Cake

Cake filtration is the most common form of filtering employed in industry. With high solids concentration suspensions, even relatively small particles (compared to pore size) will not pass through the medium but will tend to remain on the filter surface. The most favorable filtration operation with cake formation is a process whereby no clogging of the filter medium occurs. Such a process is observed at sufficiently high concentrations of solid particles in suspension. This concentration may conditionally be assumed to be in excess of 1% by volume. To prevent pore clogging in the filter medium when handling relatively low solids concentrations (i.e., 0.1% to 1% by volume), general practice is to increase the solids concentration in thickeners before the suspension is fed to the filter.

The filtration cycle is initiated with a low but gradually increasing pressure gradient at an approximately constant flow rate. The process is then operated at a constant pressure gradient while experiencing a gradual decrease in process rate. On achieving a certain thickness, the cake is removed from the medium by various mechanical devices or by inverse filtrate flow (backflushing). After completion of cake formation, treatment of the cake depends on the specific filtration objectives. Depending on the disposal method and particulates, the cake may be discarded in a dry form or as a slurry.

Cakes are normally dewatered directly on the filter medium after filtration if no washing is required. Air is usually blown through the cake under pressure to remove excess water. Additional cake dewatering to concentrations below the residual moisture level can be achieved by blowing hot or dry air through the pores. Dewatering can also be performed under vacuum or by a centrifuge; however, some moisture may be left in the micropores and as adsorbed moisture. Virtually all retained moisture can be removed by thermally drying the cake.

3.1.2 Filter Media

A filter medium is, by nature, inhomogenous, with pores nonuniform in size, irregular in geometry and unevenly distributed over the surface. Pores with passages extending all the way through the filter medium are capable of capturing solid particles that are smaller than the narrowest cross-section of the passage. This is generally attributed to particle bridging or physical adsorption. For practical reasons filter medium openings should be larger than the average size of the particles to be filtered. The filter medium chosen should be capable of retaining solids by adsorption, and interparticle cohesive forces should be large enough to induce particle flocculation around the pore openings.

Solid particles undergoing separation from the suspension may be captured both on the surface of the filter medium and within the inner pore passages. This phenomena is typical in the separation of low-concentration suspensions, where the suspension consists of viscous liquids such as oils with fine particles dispersed throughout. The penetration of particles into the filter medium increases the flow resistance until eventually, filtration can no longer proceed at reasonable throughputs and the medium must be replaced. Filtration pore blocking occurs when suspensions have the following characteristics: relatively small particles, high viscosity, and low solids concentration.

3.1.3 Liquid Filtration Equipment

Proper selection must be based on detailed information of the slurry to be handled, cake properties, anticipated capacities, and process operating conditions. Continuous filters involve several operations which may include solids separation and cake formation, cake washing if

required, cake dewatering and drying, cake removal, and filter media washing. Either continuous or batch filters can be employed in cake filtration. In filter-medium filtration, however, where particulates are retained within the framework of the filter medium, only batch systems are applicable.

3.1.3.1 Deep Bed

Depth type filters have a broad pore-size distribution. During filtration, liquid flows preferentially through the larger pores so that depth type filters give greater flow rates. When a particle contained in a liquid is subjected to depth-type filtration, it may encounter a pore smaller than itself in the surface of the filter and will, therefore, be retained on the surface by sieve capture. However, because of the broad pore-size distribution, the particle may also encounter one of the larger pores and will penetrate into the depth of the filter before it is retained. Because a large amount of particulate matter can be retained in the inner surfaces of a depth-type filter before it clogs, these filters have a high particulate loading capability. This large dirt-holding capacity, coupled with their low cost means that depth-type filters provide a high degree of particulate removal at low cost. However, the broad pore size distribution means that particles may also penetrate completely through the filter so that they are not totally reliable for particle retention.

3.1.3.2 Centrifugal

Slurry is fed into a rotating basket or bowl having a slotted or perforated wall covered with a filtering medium such as canvas or metal-reinforced cloth. The angular acceleration produces a pressure that transports the liquor through the filter medium, leaving the solids deposited on the filter medium surface as a cake. When the feed stream is stopped and the cake spun for a short time, residual liquid retained by the solids drains off. This results in final solids that are considerably drier than those obtained from a filter press or vacuum filter.

Principal types of filtering centrifuges are suspended batch machines, automatic short-cycle batch machines, and continuous conveyor centrifuges. A widely used design combines the features of a centrifuge and a screen. Feed enters the unit at the top and is immediately brought up to speed and distributed outward to the screen surface by a set of vanes. The liquid is forced by the sudden centrifugal action through the screen openings into an effluent housing. As solids accumulate, they are gently moved down the screen by the slightly faster rotating helix. With the increase in screen diameter, higher centrifugal forces are encountered and solids are dispersed over a gradually increasing area, thus forming a thin, compact cake from which the remaining liquid is extracted. The relatively dry solids are blown out the bottom of the rotor by a set of vanes into a conical collection hopper.

3.1.3.3 Vacuum

Vacuum filters dominate cake filtration operations because they can be designed for continuous operation and because capital costs for a vacuum filter are normally considerably less than capital costs for a centrifuge. Vacuum filters are limited to a maximum pressure differential of 1 atm., and performance in handling high viscosity liquids is significantly inferior to the performance of a centrifuge or pressure filter. Vacuum filters are not normally considered for high temperature operations or volatile solvents because provisions for solvent containment are minimal and flashing of the solvent can overload the vacuum pumping system. The requirement for a closed system will normally preclude consideration of conventional vacuum filters for applications involving toxic materials.

3.1.3.4 Rotary Drum Filters

A countercurrent mode filter is one in which the filtrate flows parallel to and opposite to the direction of gravity. These filters are operated under either vacuum or pressure. The principal advantage of these filters is the continuity of their operation; however, total filtration cycles are limited to short time intervals. Therefore, it is necessary to maintain nearly constant slurry properties because changes can lead to wide variations in required times for the filter process. These filters are used for separating low concentration, stratified suspensions. They are less useful in handling suspensions containing particles with wide size ranges because fouling by small particles is a problem.

The conventional rotary drum vacuum filter provides high capacity in a single unit, can handle both dewatering and clarification operations, and in most applications will cost less than disk or horizontal filters of equal capacity. The multicompartment metal drum rotates partially submerged in the feed slurry (Figure F-7.1). A vacuum is maintained on the inside of the drum by pulling through the supporting axle. The surface of the drum is covered by the filter medium supported by a drainage grid. As the drum rotates, an automatic valve operates to provide vacuum for those sections passing through the slurry. The pressure differential across the filter medium causes the filtrate to flow through the medium, the drum's internal piping, and the automatic valve to the filtrate receiver. The solids are left on the surface of the filter medium, and the cake forms as the drum rotates through the slurry. Vacuum is maintained through dewatering and washing, if required, releasing at the point at which the cake is discharged.

- 1 = Hollow Drum
- 2 = Filtration Compartments
- 3 = Drive
- 4 = Hollow Trunion

- 5 = Automatic Valve
- 6 = Tank for Suspension
- 7 = Knife for Cake Scraping

Figure F-7.1. Rotary-Drum Vacuum Filter with External Filtration Surface

(From Cheremisinoff, N.P. and D.S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

Cake discharge is a major concern. There are at least five methods for discharging the cake (belt, scraper, precoat, roll, and string), and none are consistently satisfactory over a wide range of applications. When the rotary drum is used in applications involving toxic solvents, the filter is enclosed and the enclosure is maintained under vacuum. This procedure increases capital costs and limits access to the filter.

Drum filters with approximately 1600 ft² of surface area (roughly 14 ft in diameter and 36 ft long) have been built. Filtration rates, based on feed slurry throughput, are normally in the range 20 to 60 lb/hr ft² of filter area, depending on the characteristics of the slurry and the cake. The conventional rotary drum filter operates at low rotational speeds (typically 0.3 to 3 rpm), and energy requirements are not significant in evaluating the costs of installation and operation.

3.1.3.5 Cocurrent Filters

Cocurrent, or top feed filters, employ flat and cylindrical filter media in which the filtrate flow is parallel to and in the direction of gravity. Filter designs include sophisticated rotary

drum filters, continuous belt filters, Nutsch batch filters, and filter presses with horizontal chambers.

3.1.3.5.1 Internal Rotary Drum

In the internal rotary drum filter (Figure F-7.2), the filter medium is contained on the inner periphery of the drum. This design is suited for rapid settling slurries that do not require a high degree of washing. This filter is capable of handling heavy, quick-settling materials, and variations in feed consistency cause few or no difficulties.

Figure F-7.2. Section View of an Interior Medium Rotary-Drum Vacuum Filter

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

The feed slurry is discharged to the bottom of the inside of the drum and is maintained as a pool. As the drum revolves, the compartments of the drum successively pass through the slurry pool, where a vacuum is applied as each compartment becomes submerged. Slurry discharge is accomplished at the top center where vacuum is cut off and gravity (usually

assisted by blowback) allows the solids to drop off onto a trough. From there, a screw or belt conveyor removes the solids from the drum.

3.1.3.5.2 Nutsch Filters

A Nutsch (Figure F-7.3) is a tank equipped with a false perforated bottom that supports a filter medium. The lower chamber is designed for negative pressure and to hold the filtrate. Filtration is accomplished by dumping the slurry onto the filter medium and pulling a vacuum underneath the false bottom. The open Nutsch is used in small batch operations involving simple filtrations and nontoxic materials. The Nutsch is simple to fabricate and costs considerably less than competitive equipment.

Figure F-7.3. Nutsche Filter

(From Ryan, J.L. and D.L. Roper. Process Vacuum System Design and Operation, 1986. McGraw-Hill Book Co., New York, NY. Reproduced with permission of McGraw-Hill)

Operation of the standard Nutsch is very labor intensive. Discharging a dry product requires that the operator shovel the cake off the Nutsch, an operation that invariably damages the filter medium dictating use of a disposable medium. Capacity is limited to approximately 2000 gal. of slurry, with filter area seldom exceeding 50 ft². The principal disadvantage of the open Nutsch involves safety and health considerations—application is limited to nontoxic materials. However, a continuous filter is available that consists of a series of Nutsch filters on horizontal rotating trays.

3.1.3.5.3 Horizontal Rotary Filters

The horizontal rotary vacuum filter (Figure F-7.4) is adapted to filtering quick-draining crystalline solids. Its horizontal surface prevents solids from falling off or being washed off by wash water, and allows an unusually heavy layer of solids to be tolerated. The basic design consists of a circular horizontal table that rotates about a central axis. The table consists of several hollow, pie-shaped segments with perforated or woven metal tops. Each section is covered with filter media and is connected to a central valve mechanism that times the vacuum inside the hollow segment for removal of filtrate and wash liquid, and the dewatering of the cake during each revolution. Each segment receives a slurry in succession, wash liquid is sprayed onto each section, and the cake is dewatered by passing dry air through it. Finally, the cake is scooped off the surface by a discharge scroll.

Figure F-7.4. Cross-Section of a Rotary Horizontal Vacuum Filter Showing Filtrate Removal System, Filter Cloth, and Discharge Scroll

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

3.1.3.5.4 Belt Filters

Belt filters consist of a series of Nutsch filters moving along a closed path. Each unit is displaced along its path by driving and tensioning drums. Nutsch filters are equipped with supporting perforated partitions covered with the filtering cloth. The washed cake is removed by turning each unit over; sometimes cake removal is assisted with a shaker mechanism. Other belt filter designs consist of an endless supporting perforated rubber belt covered with the filter cloth. Advantages include their simplicity of design compared to filters with automatic valves, and the ability to provide countercurrent washing and removal of thin layers of cake (usually ranging from 1 to 25 mm). Their disadvantages include large area requirements, inefficient use of the total available filter area, and poor washing at the belt edges.

3.1.3.6 Cross-Mode Filters

Filters of this type have a vertical flat or cylindrical filtering partition, and the filtrate flows perpendicular to the direction of gravity. In the separation of heterogeneous suspensions, nonuniform cake formation along the height of the filter can occur because larger particles tend to settle out more rapidly. The cake may also creep down the filter partition due to gravity, particularly in the absence of a pressure gradient across the filter medium. However, the vertical partitioning makes these filters especially useful as thickeners, since it is convenient to remove cake by reverse filtrate flow.

3.1.3.6.1 Filter Presses

The common filter press is the plate-and-frame design (Figure F-7.5), consisting of a metal frame made up of two end supports rigidly held together by two horizontal steel bars. Varying numbers of flat plates covered with cloth filter media are positioned on these bars. The number of plates depends on the desired capacity and cake thickness. The plates are clamped together so that their frames are flush against each other forming a series of hollow chambers (Figure F-7.6). The plates and filter cloth have holes that register with connections on the frames, so that when the press is assembled these openings form a continuous channel over the length of the press and register with the slurry inlet connection on the fixed head. The channel opens only into the interior of the frames. At the bottom of the plates, holes connect the faces of the plates to filtrate outlet cocks. As the filterable slurry is pumped through the feed channel and into the frames, pressure builds up to force the filtrate through the filter cloth. The filtrate runs down the grooved face of the plates and passes out through the discharge cock. When the press is full, it is opened and dumped.

Figure F-7.5. Plate-and-Frame Filter Press Designed for Use with a Filter Aid for Removal of Metallic Hydroxides

(From Cheremisinoff, N.P. and D.S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

In terms of initial investment and floor area requirements, plate-and-frame filters are inexpensive compared to other filters. They can be operated at full capacity (all frames in use) or at reduced capacity by blanking off some of the frames by dummy plates. However, the combination of labor charges for removing the cake and downtime charges may constitute a high percentage of operating costs.

3.1.3.6.2 Leaf Filters

Leaf filters (Figure F-7.7) are similar to plate-and-frame filters in that cake is deposited on each side of the leaf, and the filtrate flows to the outlet in the channels provided by a coarse drainage screen in the leaf between the cakes. The leaves are immersed in the sludge when filtering and in wash liquid when washing. Therefore, the leaf assembly may be enclosed in a shell, as in pressure filtration, or immersed in sludge in an open tank, as in vacuum filtration.

Figure F-7.6. Sectional View of Filter Press

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

Figure F-7.7. Sectional View of a Filter Leaf Showing Construction and Approximate Location of Cake

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

In operating a pressure leaf filter, the sludge is fed under pressure from the bottom and equally distributed. The clear filtrate from each leaf is collected in a common manifold and carried away. The filter cakes build on each side of the leaf and filtration continues until the required cake thickness is achieved.

3.1.3.6.3 Disk Filters

Disk filters consist of a number of concentric disks mounted on a horizontal rotary shaft and operate on the same principle as rotary-drum vacuum filters (Figure F-7.8). The disks are formed by using V-shaped hollow sectors assembled radially around the shaft. Each sector is covered with filter cloth and has an outlet connected to a manifold extending along the length of the shaft and leading to an outlet port on the filter valve. The sectors rotate through the sludge in a tank, and as each sector enters the sludge, a vacuum is pulled inside the sector drawing in filtrate. As the disk rotates, the built up cake is removed with a doctor's knife and drops into a container.

- 1 = Section
- 2 = Filtering Disks
- 3 = Automatic Valve

- 4 = Manifold for Vacuum and Filtrate Discharge
- 5 = Piping for Compressed Air
- 6 = Doctor's Knives for Cake Removal

Figure F-7.8. Rotary-Disk Vacuum Filter

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

Compared to drum filters, the greatest advantage of the disk filter is that, for the same filtering area, it occupies considerably less floor space. However, because of vertical filtering surfaces, cake washing is not as efficient as with a drum filter. The disk is ideal when the cake is not washed and floor space is at a premium.

3.1.3.6.4 Cartridge

Cartridge filters are tubular cartridges normally operated as depth or surface type filters, depending on the filter media and filter design. Unfiltered liquid enters the inlet (bottom) port. It flows upward, around and through the filter medium, and filtered liquid discharges through the outlet (top port). Filtration normally takes place in the direction radially inward, through the outer face of the element into the hollow core. Filter cartridges may be stainless steel or fabric screen reinforced by a perforated stainless steel backing, paper, sintered metal, woven cloth, needle felts, activated carbon, or various membranes of pore size down to 0.2 μm . Factors to be considered in selecting filter media include solids content, type of contaminant, particle size and shape, amount of contaminant to be removed, viscosity, corrosiveness, abrasiveness, adhesive qualities, liquid temperature, and required flowrate.

Cartridge filtration is limited to liquid polishing or clarification, i.e., removing very small amounts of solids, in order to keep the frequency of cleaning and cartridge replacement down. Typically, suspensions of less than 0.01% volume concentration of solids are treated with cartridge filters.

Using quick-coupling connectors, the media can be removed from the housing, inspected, cleaned or replaced. Multiple filters are common consisting of two or more single filter units valved in parallel to common headers. These filters have the ability to sequentially backwash each unit in place while the others remain online providing continuous operation. These units can be fully automated to eliminate manual backwash with the control based on changes in differential pressure between the inlet and outlet headers.

3.1.3.7 Diaphragm Filters

Diaphragm filters are specially designed filter presses with the ability to reduce sludge dewatering costs by a squeezing cycle using a diaphragm (Figure F-7.9). Diaphragm filters combine an initial pumping followed by a squeezing cycle that can reduce the process cycle time by as much as 80%. During the filtration cycle, sludge is fed at approximately 100 psi into each chamber through an inlet pipe in the bottom of the filter plate. The number of chambers can range from a few dozen to more than 100. The sludge feed pump continues to feed sludge into the chamber until a predetermined filtering time has been achieved. Filtrate passes through cloth

on both sides of the chamber. Short filtration cycles produce cake thicknesses of 0.5 to 0.75 inches.

Figure F-7.9. Operating Cycles of a Diaphragm Press

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

Once the filtration cycle is complete, the sludge pump is stopped and a diaphragm in the chamber is expanded by water pressurized up to 213 psi. This compresses the sludge on both sides of the chamber into a thin, uniform cake with a solids content of more than 35%. On completion of the filtration and squeeze cycles, the chambers are automatically opened and the cakes are discharged, usually onto a belt conveyor. No precoating is required. Cake discharge from the filter press is fast. After a number of cycles (depending on the sludge type), the filter cloth will require cleaning. This can be accomplished manually or can be performed automatically at preset time intervals using a jet of 1000-psi wash water. Where even faster cake discharge is required or where sludge cakes are sticky, automatic cloth vibrators can be provided.

3.1.3.8 High-Pressure Filters

Thin-cake staged filters have been used effectively at high flowrates per unit area in Europe. Use of ultrathin cakes is a useful technique for increasing flowrates. Filtration surfaces are recessed plates equipped with rotating turbines that maintain permanent precoat-type thin cakes throughout the filter (Figure F-7.10). Cake thickness is prevented from growing beyond the

Figure F-7.10. Principal Components of a Staged, Thin-Cake Filter Thickener

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

in situ precoat formed during the first few minutes of the operation by blades on a rotating shaft passing through the axis of the filter. As liquid is removed, the thickening slurry moves from stage to stage. The unit acts as a filter-thickener, producing a continuous extrudate that may contain a higher solids content than is normally produced in conventional filters. The combination of high pressure (300 psi) and thin cakes produces high filtration rates.

3.1.3.9 Screw Presses

Dewatering is an important step in the filtration process and a necessary operation prior to drying to provide a higher percentage of solids feed. The material is conveyed by a screw inside a perforated cage (Figure F-7.11), and the available volume continuously diminishes. This can be done either by reducing the pitch of the screw in a cylindrical cage, or by reducing the diameter of the screw in a conical cage. Each successive stage presses the material harder; the high pressure forces the liquid out of the solids and through the perforated cage. Power requirements are high, and the screw press is only suitable for dewatering rough organic material, pastes, sludges, etc., because it does not include a filtration stage.

Screws are indicated by dotted lines

Figure F-7.11. Plan and Side Elevation Views of a Four-Stage Press

(From Cheremisinoff, N.P. and D.S. Azbel. Liquid Filtration. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

3.1.3.10 Strainer and Filter Bag Baskets

Strainer filter baskets and filter bag baskets are used as prefiltering devices to stop the larger contaminated particles and extend the life of the entire system. Strainer baskets have solid flat bottoms, and baskets for filter bags have perforated bottoms and accept standard size filter bags (Figure F-7.12).

Figure F-7.12. Details of Basket Seal

(From Cheremisinoff, N.P. and D.S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983. Reproduced with permission of Butterworth-Heinemann)

Dual-stage straining/filtering action is achieved by insertion of a second, inner basket supported on the top flange of the outer basket. Both baskets can be strainers (with or without wire mesh linings) or both can be baskets for filter bags. They may also be a combination: one a strainer basket, the other a filter bag basket. Dual-stage action increases strainer or filter life and reduces servicing needs.

Fabric bag filters are capable of providing removal ratings from 20 mesh to nominal 1 micron, for both Newtonian and viscous liquids. Wire mesh or fabric baskets can be cleaned and reused, or are disposable if they cannot be cleaned. A disadvantage of these units is that they require manual cleaning and servicing

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

All ranges of particle sizes are common for filtration depending on design and application. Filtration applications usually include clarification, separation for solids recovery, separation for both solids and liquid recovery, and separation to improve downstream plant operation.

Applications fall into two general categories:

- * Clarification in which suspended solid particles in concentrations typically less than 100 ppm are removed from an aqueous stream. This is usually accomplished by depth or cross-flow filtration to produce a clear aqueous effluent. The suspended solids may be concentrated to a slurry form for further dewatering.
- * Dewatering of slurries of typically 1 to 30% solids by weight. The aim is to concentrate the solids into a paste or solid form by cake filtration. The concentration of solids in suspension must be high enough to allow the formation of sufficiently thick cake for discharge as a solid mass before the rate of flow is significantly reduced.

Filtration will not:

- * Remove dissolved substances.
- * Separate chemical components in the same phase, except for membrane filters.
- * Filter sludges or tars that are highly viscous.

Process-oriented enhancements can be implemented to intensify particle separation. This involves pretreatment of the suspension with filter aids, flocculants, or electrolytes to produce a cake with minimal resistance. Prefiltration steps may also include thickening, coagulating, heating, conditioning, pH adjustment, or the production of an unstable floc.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Since filtration is such a widely used technology, there are hundreds of vendors which manufacture commercially-available equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially

available equipment are expected. While it is conceivable that a very special filtration application may be needed (such as a completely remote device in a highly corrosive and radioactive environment) the screening of potential vendors cannot be made until more detail is known about the application.

No major technology development applications are known. However, all operations that process liquid streams are continually evaluating filtration systems as part of normal operations.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintainability are a function of design, but filtration systems are typically low-maintenance and highly reliable if correctly designed for the application.

3.3.3 Secondary Waste Streams

The secondary waste streams from filtration systems consists primarily of the filtered solids. For non-reusable systems, a disposal method must also be found for the filter media. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

Filtration systems can be designed to almost any performance standard but will require knowledge of particle size, size distribution, and particle and fluid characteristics.

3.3.5 Health and Safety

There are no health and safety issues specific to this technology except where manual filter media replacement or cake removal is required.

3.3.6 Operational Complexity

Depends on design, but filters are generally not complex systems.

3.3.7 Glovebox Capability

Filtration systems are routinely used in glovebox environments. Ease of operation and remote handling are the primary design factors.

3.3.8 Environmental Impact

None are specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless a highly specific application is needed. Both capital and operating costs are considered.

3.5 TECHNOLOGY COMPARISON

Standard filtration may be compared with membrane separation and electrofiltration. This technology comparison will be determined at a later date.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of filtration systems requires information about the characteristics of the fluid being filtered, the solids being removed, and the capacities required.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design.

Since it is difficult to simulate or predict the filtration characteristics of a specific process stream, the use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

Since filtration is such a widely used technology, there are hundreds of vendors which manufacture commercially available equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. While it is conceivable that a very special filtration application may be needed (such as a completely remote device in a highly corrosive and radioactive environment) the screening of potential vendors cannot be made until more detail is known about the application.

6.0 REFERENCES

1. Svarovsky, L. *Solid-Liquid Separation*. Butterworth-Heinemann: Oxford, 1990.
2. Cheremisinoff, N. P. and D. S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983.
3. Ryan, J. L. and D. L. Roper. *Process Vacuum System Design and Operation*. McGraw-Hill Book Co.: New York, 1986.

APPENDIX G MEDIA BEDS

Media beds are generally beds of granular material through which a contaminated liquid is passed. The contaminant is removed from the liquid onto the bed material by adsorption or ion exchange. The technologies described in this appendix are as follows:

- G-1 Granulated Activated Carbon Adsorption
- G-2 Powered Activated Carbon Adsorption
- G-3 Alternative Rohm and Haas Process
- G-4 Activated Alumina Adsorption
- G-5 Ferrite Adsorption
- G-6 Silica Gel Adsorption
- G-7 Ion Exchange
- G-8 Chromatography
- G-9 Ion Specific Chromatography
- G-10 Bioadsorption

APPENDIX G-1 GRANULATED ACTIVATED CARBON

1.0 TECHNOLOGY DESIGNATION

The technology described in this section is known generally as media bed adsorption. This section describes the application of one specific adsorbent known as granulated activated carbon (GAC) (Ref. 1).

2.0 NEED FOR THE TECHNOLOGY

GAC beds are generally used for removal of small amounts of organic chemical contaminants from aqueous streams. Large amounts of organics can be removed from an aqueous stream with the use of various designs of separatory vessels for the separation of distinct liquid phases. The small organic fraction remaining can be removed with the use of technologies such as media bed adsorption using granular activated carbon, air or steam stripping, ozonolysis, UV destruction, supercritical water oxidation, membrane techniques such as reverse osmosis, as well as others. Per the CPTS F&OR document (Ref. 2), the activated carbon media bed (or beds) will comprise unit 190 of the CPTS, and shall be considered as the baseline technology against which the other technologies previously mentioned should be compared. As shown in the F&OR document, GAC beds (unit 190) will be used as polishing for the final removal of organics and limited inorganics from the aqueous treatment line (line 100), just upstream of unit 195, which is the inorganics polishing station (Ref. 2).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Granular Activated Carbon (GAC) adsorption is used to remove a wide variety of contaminants from a liquid or gaseous stream. It is most frequently used to remove organic compounds, although some inorganic species are efficiently adsorbed. The process may be non-specific and used as a broad-spectrum treatment operation, or the carbon may be specially prepared to remove a specific pollutant. GAC adsorption is based on the attraction of organic molecules in solution to the surface of the activated carbon. The adsorption process is dependent on the strength of the molecular attraction between the carbon and the organic contaminant, the type and characteristics of the carbon, and the pH and temperature of the solution. Nonpolar organic compounds of low water solubility are most easily adsorbed. A schematic diagram of a GAC air-cleaning system is shown in Figure G-1.1.

Figure G-1.1. Schematic of a GAC Air Cleaning System

Being efficient and relatively simple to operate, GAC adsorption is one of the most frequently used techniques for treating aqueous streams contaminated with organics. The carbon is placed in flow through column reactors that are operated until the effluent concentration reaches unacceptable levels. Since the adsorption process is reversible, the adsorbed contaminants can be removed after the adsorption capacity of the carbon has been exhausted thereby regenerating the bed for reuse. Thermal regeneration is usually employed to destroy or desorb the organic contaminants, depending on the nature of the contaminant and the regeneration temperature. Pretreatment is typically required for removal of oil, grease, and suspended solids (Ref. 1).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Carbon adsorption is a potential technology for removal of organic contaminants that are nonpolar, of low solubility, or of high molecular weight. Certain inorganic compounds will also adsorb to activated carbon, but the technology is not widely used for this application. This is because of problems in the regeneration process when high levels of adsorbed inorganics are present, and because processes that are more cost-effective are frequently available (Ref. 1).

Due to the nature of the carbon adsorption process, there is not a strictly quantifiable upper limit to the amount of organics in the feed stream. Larger amounts of organics in the feed will simply require earlier regeneration of the GAC or earlier replacement and disposal of the cartridges containing the granulated carbon. Input concentrations are typically in the 10 ppm range (Ref. 3).

On the output side, a similar situation exists in that if the GAC is capable of adsorbing more organic contaminant, it will do so with concentrations in the effluent in the low (~10) ppb range (Ref. 3).

Required pretreatment of the influent stream includes the removal of suspended solids to less than 50 mg/L and reduction in the concentration of oils and grease to less than 10 mg/L. Other pretreatments which extend GAC lifetime, but are not strictly required, include the removal of hardness and other inorganics as well as pH treatment (Ref. 1).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The use of GAC adsorption is a mature technology. It is not currently under development.

3.3.2 Reliability and Maintenance Requirements

This is a very reliable technology. The effectiveness of the GAC is determined by the continuous measurement of the concentration of organics in the effluent. As a result of this monitoring, operators know in real time when a problem exists.

There is no fixed or scheduled maintenance required. The GAC simply becomes unusable when the effluent shows a certain predetermined concentration of organics. At that point, the carbon is either sent for regeneration or the cartridges are replaced and the spent cartridge disposed.

3.3.3 Secondary Waste Streams

If a system does not require either pressurization or the treatment of large quantities (> 15 gal/min) of influent, then GAC filter cartridges can be used. In this case, the secondary waste stream will consist of a spent filter cartridge containing GAC and adsorbed organics (Ref. 4).

3.3.4 Separation Efficiency

Generally, aqueous streams with organic constituents in the 10 ppm range can be reduced to the 10 ppb range in one pass through a continuously operating system.

3.3.5 Safety and Health

Health and safety issues are not a source of controversy with the use of this technology. GAC is non-toxic, and when it is contaminated with organics, it still is relatively safe to handle due to the fact that the adsorption is only reversible at higher temperatures.

Operation of the GAC bed can easily be fully automated, however the effluent stream requires continuous monitoring for organic contamination. The chemical monitoring can also be automated, but requires periodic maintenance to ensure reliable results.

3.3.6 Operational Complexity

Although the basic operation of a GAC bed is quite simple, several operational difficulties are commonly encountered. Either bacterial growth or the accumulation of suspended solids can lead to an unacceptable pressure drop through the reactor. Backflushing can be used to solve this problem, however. Another operational problem occurs when a large molecular weight constituent of the feed stream (which is slow to adsorb onto the GAC) essentially 'masks' the GAC from other organic constituents which may exit the reactor without adsorbing. This may give the operator the incorrect notion that the GAC requires regeneration when in reality it may not. A knowledge of the feed stream composition helps in this situation.(Ref. 1)

3.3.7 Glovebox Capability

This technology is available to glovebox operations, comparable in complexity to ion exchange operations for which there is considerable experience within the DOE complex.

3.3.8 Environmental Impact

The use of this technology has very little negative environmental impact. When the GAC is regenerated (generally at temperatures exceeding 950 Degrees C), the furnace used will be fitted with both particulate and off-gas control (i.e., scrubbers). The disposal of the combustion particulates, GAC which has been fouled or reduced to an unusable particle size, and captured off gases is the only environmental effect resulting from the use of this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Disposable GAC cartridges can be used for the treatment of low-flow aqueous streams where pressurization is not required.

Disposable cartridges can be purchased from Tigg Corp. as follows: 5 gal/min - \$420 and 15 gal/min - \$635(1993 dollars) (Ref. 5).

The installed costs for an unknown application are shown in Reference 1 in 1983 dollars. For a 1 million gallon per day plant, total installed costs were approximately \$1 million. This includes site preparation, foundation, building, feed and backwash pumps, an air compressor, electrics, controls, and engineering, overhead and profit. The regeneration system costs were also reported. For a 10,000 lbs/day facility, total installed costs were reported as \$1.25 million,

with operating costs at \$500,000 per year. Again, these costs are in 1983 dollars. Also, the regeneration can be provided by vendors, thereby eliminating the capital costs of regeneration (Ref. 1).

3.5 TECHNOLOGY COMPARISON

The GAC bed adsorption of organics from an aqueous stream can be compared with powdered activated carbon, Amborsorb[®], air or steam stripping, ozonolysis, UV destruction, supercritical water oxidation, as well as others.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Test data requirements include a detailed knowledge of the chemical constituents of the feed stream, the amount and particle size of any entrained solids and perhaps details concerning any microbiological contamination. In addition, to assess the feasibility of adsorption for a particular application, it is generally necessary to perform an adsorption isotherm on the waste stream(s) of interest. This data will provide an estimate of the adsorption capacity. When combined with data on the contaminant concentration in the waste stream, effluent goal, waste flow rate, and desired carbon regeneration (or replacement) frequency, isotherm data can be used to estimate the size and cost of an adsorber (Ref. 1).

4.2 TESTING REQUIREMENTS

It is recommended that regeneration efficiency studies be completed to optimize regeneration conditions.

Actual column studies are recommended to assess optimum flow rates and adsorbent usage to maintain effluent quality to a set breakthrough concentration.

Bench-scale treatability studies should be performed once it is determined that carbon adsorption can produce an effluent of acceptable quality at a reasonable cost, on the basis of the equilibrium concentration and carbon-usage estimates obtained from the isotherm tests. It is imperative that bench-scale tests be designed to accurately represent the intended full-scale system (Ref. 1).

The most efficient approach to pilot-scale involves continuation of bench-scale and modeling activities until all design and operational variables have been optimized. It is highly recommended that pilot-scale studies be conducted as the next step, in order to verify that the design can be successfully scaled up and to fine tune the optimization of variables (Ref. 1).

5.0 VENDOR LIST

Hydro Group
Environmental Products Division
97 Chimney Rock Road
Bridgewater, NJ 08807

Phone (908) 563-1400
or (800) 524-2725

Envirex Ltd.
P.O. Box 1624
Waukesha, WI 53187

Phone (414) 547-0141
FAX (414) 547-4120

Calgon Carbon Corp.
P.O. Box 717
Pittsburgh, PA 15230

Phone (800) 422-7266

Envirotrol, Inc.
P.O. Box 61-T
Sewickley, PA 15143

Phone (412) 741-2030
FAX (412) 741-2670

Tigg Corp.
P.O. Box 11611
Pittsburgh, PA 15228

Phone (412) 563-4300

6.0 REFERENCES

1. Voice, Thomas C. "Activated Carbon Adsorption." in *Standard Handbook of Hazardous Waste Treatment and Disposal*, H.M. Freeman, ed., McGraw-Hill; New York, 1988, pp 6.1-6.21.
2. Thompson, T.K. "Functional and Operational Requirements for an Integrated Treatment Facility." Mixed Waste Treatment Project (Los Alamos National Laboratory), Subcontract 9-XY2-Y9590-1, Task 014, August 30, 1992.
3. Brochure ENV LTD 300 (11/92) of Envirex LTD, describing the GAC Fluid Bed Skid-Mounted Systems.
4. Phone conversation with Frank Lenzo of Hydro Group on 2/4/93.
5. Phone conversation with a Tigg Corp. sales engineer (David) on 2/4/93.

APPENDIX G-2 POWDERED ACTIVATED CARBON

1.0 TECHNOLOGY DESIGNATION

The technology described in this section is known generally as reactor adsorption. This section describes the application of one specific adsorbent known as powdered activated carbon (PAC) (Ref. 1).

2.0 NEED FOR THE TECHNOLOGY

PAC reactors are generally used for removal of small amounts of organic chemical contaminants from aqueous streams. Large amounts of organics can be removed from an aqueous stream with the use of various designs of separatory vessels for the separation of distinct liquid phases. The small organic fraction remaining can be removed with the use of technologies such as media bed adsorption using powdered or granular activated carbon, air or steam stripping, ozonolysis, UV destruction, supercritical water oxidation, membrane techniques such as reverse osmosis, as well as others. Per the CPTS F&OR document (Ref. 2), the activated carbon media bed (or beds) will compromise unit 190 of the CPTS, and shall be considered as the baseline technology against which the other technologies previously mentioned should be compared. As shown in the F&OR document, GAC beds (unit 190) will be used as polishing for the final removal of organics and limited inorganics from the aqueous treatment line (line 100), just upstream of unit 195, which is the inorganics polishing station (Ref. 2). PAC reactors are being considered as one alternative to GAC.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Powdered activated carbon is generally utilized in stirred reactors. The minus 200 mesh PAC (Ref. 3) is used as a dilute slurry in either of two reactor configurations. In the completely mixed batch (CMB) reactor, the water to be treated is stirred in a tank and the PAC is fed into the tank, where it adsorbs any organics present. The tank is then simply mixed, and additional PAC is added to the tank until the organics concentration drops to the desired level. At this point, then, the PAC must be removed by filtration or clarification before the water may be discharged. This process is labor intensive in that an operator must periodically test the water, although this also allows assurance that the effluent will meet the desired level of contamination prior to discharge.

In another reactor called the completely mixed flow reactor (a continuous process), the aqueous feed and PAC are both fed in predetermined quantities into a stirred vessel. The slurry produced is also discharged from the reactor at the same flow rate, and so the adsorption process must occur within the time window that both the water and the PAC are being well mixed within the reactor. Automation is possible with this continuous reactor. The problem here lies in the fact that a changing feed stream being treated with a fixed amount of PAC will have a varying concentration of contaminant in the effluent, unless an excess of PAC is continuously used.

The powdered activated carbon treatment (PACT) process incorporates biodegradation and physical adsorption to remove organic constituents from an aqueous stream. The reaction is carried out in an aeration basin. Powdered activated carbon added to the aeration basin adsorbs organics from the wastewater stream and acts as a substrate for microorganism growth. Non-biodegradable components remain adsorbed on the powdered activated carbon. A clarifier is used to separate treated water from spent powdered activated carbon and biomass. The powdered carbon is regulated until its adsorptive capacity is reached after which it is either regenerated or disposed (Ref. 1).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Due to the nature of the carbon adsorption process, there is not a strictly quantifiable upper limit to the amount of organics in the feed stream. Larger amounts of organics in the feed will simply require increased consumption of PAC. Input concentrations are typically in the 10 ppm range (Ref. 1).

On the output side, a target concentration of organics can be met with any of the processes described above.

Pretreatments are not required with PAC usage, although large amounts of oil or grease will cause increased and otherwise unnecessary PAC consumption.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The use of PAC adsorption is a mature technology. It is not currently under development.

3.3.2 Reliability and Maintenance Requirements

This is a very reliable technology. The effectiveness of the PAC is determined by the continuous measurement of the concentration of organics in either the reactor or the effluent. As

a result of this monitoring, operators know in real time when a problem exists.

There is no fixed or scheduled maintenance required. The PAC simply becomes unusable when the effluent shows a certain predetermined concentration of organics. At that point, the carbon is either sent for regeneration or is disposed.

3.3.3 Secondary Waste Streams

The secondary waste produced from the utilization of PAC is the PAC itself containing adsorbed organics. This waste stream can be eliminated if the PAC is regenerated.

3.3.4 Separation Efficiency

Generally, aqueous streams with organic constituents in the 10 ppm range can be reduced to the 10 ppb range.

3.3.5 Safety and Health

Health and safety issues are not a source of controversy with the use of this technology. PAC is non-toxic, and when it is contaminated with organics, it still is relatively safe to handle due to the fact that the adsorption is only reversible at higher temperatures. The use of PAC can create a dust hazard, however, and so the standard precautions must be taken in order to ensure safe utilization of the technology.

3.3.6 Operational Complexity

The use of PAC is quite simple, but in either batch or continuous modes, the operation must be performed under more or less continuous process monitoring (Ref. 1).

3.3.7 Glovebox Capability

This technology is amenable to glovebox operations, comparable in complexity to ion exchange operations for which there is considerable experience within the DOE complex.

3.3.8 Environmental Impact

The use of this technology has very little negative environmental impact. When the PAC is regenerated (generally at temperatures exceeding 950 Degrees C), the furnace used will be fitted with both particulate and off-gas control (ie: scrubbers). The disposal of the combustion particulates, PAC which has been fouled or reduced to an unusable particle size, and captured off gases is the major environmental effect resulting from the use of this technology. The potential for dust generation necessitates cautious handling of the unused PAC.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Costs associated with the use of this technology have not been determined at the time of this writing.

3.5 TECHNOLOGY COMPARISON

The PAC bed adsorption of organics from an aqueous stream can be compared with GAC beds, Ambersorb[®] beds, with air or steam stripping, ozonolysis, UV destruction, supercritical water oxidation, as well as others. The literature indicates that PAC is noticeably less efficient than GAC, which is less efficient than Ambersorb[®].

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Test data requirements include a detailed knowledge of the chemical constituents of the feed stream and the regulatory requirements for the aqueous effluent.

4.2 TESTING REQUIREMENTS

For batch operation, the information required for system optimization includes determination of the quantity of PAC required to meet the effluent target, reactor residence time, and effluent clarification requirements.

For a continuous operation, the flowrates of the feed stream and the PAC, reactor volume required to yield an acceptable residence time and again the clarification requirements must be determined.

5.0 VENDOR LIST

Calgon Carbon Corp.
P.O. Box 717
Pittsburgh, PA 15230

Phone (800) 422-7266

Tigg Corp.
P.O. Box 11611
Pittsburgh, PA 15228

Phone (412) 563-4300

6.0 REFERENCES

1. Voice, Thomas C. "Activated Carbon Adsorption." in *Standard Handbook of Hazardous Waste Treatment and Disposal*. H.M. Freeman ed., McGraw-Hill: New York, 1988, pp 6.1-6.21.

2. Thompson, T.K. "Functional and Operational Requirements for an Integrated Treatment Facility" Mixed Waste Treatment Project (Los Alamos National Laboratory), Subcontract 9-XY2-Y9590-1, Task 014, August 30, 1992.
3. Phone conversation with Frank Lenzo of Hydro Group on 2/4/93.

APPENDIX G-3 ALTERNATIVE ROHM AND HAAS PROCESS

1.0 TECHNOLOGY DESIGNATION

Alternative Rohm and Haas process uses Ambersorb® carbonaceous adsorbents, a proprietary material developed by Rohm and Haas, to remove volatile organic compounds (VOCs) from liquid and gas streams.

2.0 NEED FOR THE TECHNOLOGY

The technology is being considered as a final polishing step for removal of organic contaminants from aqueous and off-gas streams exiting the Chemical/Physical treatment section of the MWTP base-line process. Since input stream information and criteria for the product and by-product streams exiting this section of the flowsheet is not available at this time, further information cannot be provided regarding this process's performance. The applicability may change as this information becomes better known.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Ambersorb® carbonaceous adsorbents are a family of unique synthetic adsorbents useful for the removal of volatile organic compounds (VOCs) from liquid and gas streams. The Ambersorb® adsorbents are patented synthetic adsorbents. They are hard, black, spherical beads with exceptional physical integrity and variations in surface area, pore size distribution and surface properties.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

3.3 DEMONSTRATED PERFORMANCE (REFS. 1, 2)

The starting material for the Ambersorb® carbonaceous adsorbents is a highly sulfonated styrene/divinylbenzene macroreticular (highly macroporous) ion exchange resin with moderate surface area. This resin is pyrolyzed in a patented process. During pyrolysis, the macroreticular structure remains intact while there is a large increase in microporosity (pore diameter < 20 angstroms) and a slight increase in mesoporosity (20 to 500 angstroms) as measured by nitrogen porosimetry. Two other important consequences of pyrolysis are the ability to control the

surface properties (degree of hydrophobicity) and mechanical stability. Final surface areas range from 550 to 1100 m²/g.

Pressure drops (psi/ft bed depth) range from approximately 0.3 at 1 gpm/ft² to 20 at 100 gpm/ft².

The phenomenon of physical adsorption onto solids is due to electrostatic and covalent interactions between the adsorbate and the solid surface. These interactions include van der Waals, dipole-dipole and hydrogen bonding forces. Although it is difficult to accurately predict which species will be adsorbed well by a given adsorbent, a general guideline is that non-polar molecules or portions of molecules are attracted to hydrophobic surfaces, and polar materials are attracted to hydrophilic surfaces. The family of Ambersorb® adsorbents covers a wide range of surface polarities which offers the potential for effective adsorption of many types of organic compounds.

The Ambersorb® adsorbents are supplied as dry, black, spherical beads. For vapor phase treatment, they can be utilized directly. For aqueous applications, they must first be hydrated. Some hydrate immediately, while others may take several days.

For a liquid phase operation, Ambersorb® adsorbents can be used effectively in either a batch or column mode. For better performance efficiency, column operation is preferred. A typical system would involve three basic operations: service cycle, regeneration, and superloading.

In a fixed bed column operation, the adsorbent is packed in a vertical column. Prior to initial service, introduction of water in an upflow direction at a low flow rate (<0.25 gpm/ft²) is recommended to remove entrapped air from the column. For optimum performance, all suspended matter should be removed prior to introduction to the column.

The Ambersorb® adsorbents can be used in either a downflow or upflow service mode. The system configuration will be dependent on a number of variables including the effluent criteria, regeneration technique, and vessel design constraints. Typically, if extremely low leakage levels must be met (such as Maximum Contaminant Level drinking water standards), then countercurrent regeneration is recommended. Cocurrent operation is usually less difficult from an operational standpoint but will result in slightly higher leakage levels once the column is returned to service after regeneration.

Service flow rate will be dependent on a number of factors including influent concentrations, effluent targets, adsorptivity of compounds present, vessel efficiency, and so on. Adsorption flow rates can vary from 0.25 gpm/ft³ adsorbent up to 8 gpm/ft³. Column studies must be completed on prospective feed streams to optimize flow rate conditions. Typically, a flow rate of 3 to 4 gpm/ft³ adsorbent provides desired throughput while maintaining acceptable effluent water quality.

A minimum bed depth of one foot is generally recommended. If there is any possibility for buildup of particulate matter on the top of the bed, then the vessel should be designed to allow sufficient room for back-washing (up to 100% bed expansion). Suspended solids and particulate matter can cause pressure drop problems, channeling in the bed, and possibly foul the adsorbent. Prefiltration (deep bed filter, cartridge filter or other suitable filtration device) is recommended, especially if the column will be in a service cycle for an extended period of time.

Ambersorb® adsorbents readily expand upon backwashing at much lower linear velocities than for other adsorbents such as GAC. For this reason, backwashing during the service cycle is not recommended because of the possibility of disrupting the mass transfer zone which could significantly impair column performance.

Preliminary results indicate that Ambersorb® 563 adsorbent is considerably less corrosive to mild steel than GAC. General guidelines for use of competitive adsorbents such as GAC should be followed when utilizing the other Ambersorb® grades.

Operating capacity is a function of several variables. Static adsorption isotherm data can be used to approximate the weight or volume of an adsorbent required at a given contaminant concentration level. Flow rate constraints (gpm/ft³ adsorbent) can then be used to estimate how long the column can remain in service. Actual column studies are recommended, however, to assess optimum flow rates and adsorbent usage to maintain effluent quality to a set breakthrough concentration. An example result of column studies is shown in Figure G-3.1.

The capability to easily regenerate the adsorbent bed in situ is a key parameter in the process economics for an adsorbent system. The proper regenerant will depend on the solubility of each adsorbate as well as the ease of handling and disposal of the concentrated contaminant or spent regenerant stream. The Ambersorb® adsorbents can be easily regenerated with steam or other cost-effective regenerants such as methanol or acetone. Steam flow rates (measured as condensate) of 0.5 to 2.0 bed volumes per hour can be used. Up to 20 bed volumes of steam as condensate are required to consistently meet more stringent effluent criteria such as Maximum Contaminant Level (MCL) drinking water standards. This results in less than one bed volume of concentrated contaminant and approximately 19 bed volumes of saturated aqueous phase to be retained for reloading (Superloading). Typically 85 to 90% of the contaminants are removed from the adsorbent bed after the first five to ten bed volumes of steam are passed through the bed. The adsorbent bed will have to be cooled down for at least 2 hours after steam regeneration. It is recommended that treated water be introduced upflow at a low flow rate (0.25 gpm/ft²) to rehydrate the bed and remove air pockets taking care not to disturb the bed. If particulate matter buildup is a problem, a full backwash can be done at this point to remove suspended solids.

Recycle of unseparated organics from steam stripping can be accomplished by passing the solution through the column right before the next regeneration is performed (Superloading). The effluent quality during the Superloading step is reported to be only slightly above normal. The Superloaded adsorbent is then regenerated using standard procedures. A typical process is shown in Figure G-3.2.

Figure G-3.1. Example Bed Depth/Service Time Curve

Figure G-3.2. Ambersorb Process Schematic

In solvent regeneration, an appropriate solvent such as methanol or acetone is passed through the bed at a flow rate of 2 bed volumes per hour. Either upflow or downflow regeneration is acceptable. Typically about 3 or 4 bed volumes of regenerant can recover most of the material adsorbed. In many cases, much less regenerant can be used to achieve a complete regeneration depending on the regenerant and adsorbate. It is recommended that regeneration efficiency studies be completed to optimize regeneration conditions. Following regeneration, a rinse with water or steam is recommended to remove any residual regenerant prior to the next adsorption cycle.

These adsorbents have been extremely effective in the removal of chlorinated organics from contaminated water. They can also remediate streams containing aromatic compounds such as benzene, toluene, ethyl benzene, and xylene (BTEX). Ambersorb® adsorbents have five to ten times the capacity of granular activated carbon (GAC) when the contaminants are present at low concentrations (i.e., ppb to ppm levels), and can operate at higher flow rates than GAC while maintaining effluent water quality below drinking water standards. Furthermore, these Ambersorb® adsorbents can be regenerated in their own adsorber vessel using steam, and eliminating the liability and cost associated with offsite regeneration (Refs. 4 and 5).

In vapor phase applications, Ambersorb® adsorbents have been found to be more hydrophobic than GAC. Consequently, they are less prone to capacity loss when subjected to high relative humidity air streams. One application of Ambersorb® is in air filters where pollen, mist droplets, and dust down to a particle size of 0.005 mm are completely removed (Ref. 3).

3.3.1 Technology Status

Several field studies have been successfully completed on industrial waste streams and groundwater remediation (Ref. 4).

3.3.2 Reliability and Maintenance Requirements

This is a very reliable technology, comparable to GAC in reliability. The advantage over GAC is the ability to perform in situ regeneration, avoiding the necessity to remove the GAC for remote regeneration.

3.3.3 Secondary Waste Streams

Secondary wastes consist of steam condensate or solvents used for regeneration. The frequency of regeneration and Ambersorb® replacement is to be determined based on the waste stream contaminants and levels of contamination. Also, volume reduction levels (volume of

initial waste stream versus volume of regenerant) needs to be determined and will be a function of the waste stream contamination levels.

3.3.4 Separation Efficiency

Generally aqueous streams with organic constituents in the ppm range can be reduced to the ppb range in one pass through a continuously operating system.

3.3.5 Safety and Health

Health and safety issues are not a source of controversy with this technology. Ambersorb® is nontoxic, and when compared with organics, it still is relatively safe to handle due to the fact that adsorption is only reversible at higher temperatures. Operation of the Ambersorb® bed can easily be automated; however, the effluent requires continuous monitoring for organic contamination. The chemical monitoring can also be automated but requires periodic maintenance to ensure reliable results.

3.3.6 Operational Complexity

The basic operation is quite simple. Bacterial growth is not a problem as in GAC; however, particulates can lead to unacceptable pressure drops in the reactor (Ref. 2). Backflushing is an acceptable solution.

3.3.7 Glovebox Capability

Though there is no mention of use of this technology in glovebox operations it appears comparable in complexity to ion exchange operations for which there is considerable experience within the DOE complex.

3.3.8 Environmental Impact

The use of this technology should have very little environmental impact, significantly less than GAC since steam stripping (20 to 30 psi at 125° to 135°C) is used. The condensate by-product is collected for phase separation of the organics and the effluent recycled back through the Ambersorb®.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT:

Cost comparisons were provided by Rohm and Haas comparing Ambersorb® 563 with GAC (Ref. 1). Following is a brief summary:

	<u>Ambersorb® 563</u>	<u>GAC</u>
Installation Costs (\$K)	3,100	1,400
Annual Operating Costs (\$K)	880	2,400
NPV (20 yrs)	8,100	16,600
Cost/Acre Foot (\$)	109	220

Additional hypothetical cost comparisons were provided comparing Ambersorb® 563 with GAC on a well (Well #6387) at various flow rates at Rocky Flats Plant (Ref. 1):

	<u>Gallons Per Minute</u>		
<u>Ambersorb®</u>	<u>15</u>	<u>100</u>	<u>500</u>
# of Adsorbent	175	1,000	5,000
Installation Costs (\$K)	195	364	843
Annual Operating Costs (\$K)	0.84	0.76	142
Cost/Thousand Gallons (\$)	3.56	0.71	0.28
 <u>GAC</u>			
# of Adsorbent	650	6,000	20,000
Installation Costs (\$K)	105	273	538
Annual Operating Costs (\$K)	901	234	880
Cost/Thousand Gallons (\$)	3.89	1.29	0.81

3.5 TECHNOLOGY COMPARISON

The Ambersorb® bed adsorption of organics from an aqueous stream can be compared with GAC, air or steam stripping, ozonolysis, UV destruction, and supercritical water oxidation, as well as others.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

The Ambersorb® adsorbents can be used in either a downflow or upflow service mode. The system configuration will be dependent on a number of variables including the effluent criteria, regeneration technique, and vessel design constraints.

Service flow rate will be dependent on a number of factors including influent concentrations, effluent targets, adsorptivity of compounds present, vessel efficiency, and so on.

4.2 TESTING REQUIREMENTS

It is recommended that regeneration efficiency studies be completed to optimize regeneration conditions.

Actual column studies are recommended to assess optimum flow rates and adsorbent usage to maintain effluent quality to a set breakthrough concentration.

5.0 VENDOR LIST

Ambersorb® is a proprietary material developed by Rohm and Haas, Philadelphia, Pennsylvania. Contacts include:

Dr. William H. Brendley, Jr.
Director, Specialty Purifications
Rohm and Haas
Building 20, Suite 100
727 Norristown Road
Spring House, Pennsylvania 19477
(215) 641-7801
Fax: (215) 283-2875

Dr. Stephen G. Maroldo
Research Section Manager
Specialty Purifications Research
Research Laboratories
Spring House, Pennsylvania 19477
(215) 641-7318
Fax: (215) 283-2578

6.0 REFERENCES

1. Personal conversation with Dr. William H. Brendley, Jr. and Dr. Stephen G. Maroldo of Rohm and Haas on December 1, 1992.
2. "Ambersorb® Carbonaceous Adsorbents - Specialty Purifications." Rohm and Haas; Philadelphia, PA, October, 1990.
3. Correspondence with Dr. Michael A. Koals of Rohm and Haas on December 22, 1992.
4. Parker, G. R. and S. M. Bortko. "Groundwater Remediation Using Ambersorb® Adsorbents." presented at the Florida Environmental Chemistry Conference, October 30 through November 1, 1991.
5. Parker, G. R. "Comparison of Ambersorb® 563 Carbonaceous Adsorbent and Granular Activated Carbon for the Removal of TCE from Water at Short Empty Bed Contact Times." presented at the AIChE Annual Conference: Miami Beach, FL, November 4, 1992.

APPENDIX G-4 ACTIVATED ALUMINA ADSORPTION BED

1.0 TECHNOLOGY DESIGNATION

This appendix presents an evaluation of activated alumina adsorption technology relative to chemical/physical treatment required in a mixed waste treatment process.

2.0 NEED FOR THE TECHNOLOGY

The basic need for activated alumina adsorption in the mixed waste treatment process is in the separation of cations and anions from water. An activated alumina adsorption bed could be used after the Condensate Check Tank (Unit 190.3) in the aqueous treatment line as a polishing treatment unit prior to clean water distribution. Due to the high selectivity and pH dependence of this technology, its applicability would depend on the components present in the condensate and the levels of those components in relation to the NPDES permit.

Another potential need for activated alumina adsorption would be in the removal of water from the organic feed to the Concentrated Organics Burner (Unit 380) in the thermal treatment line. The level of water in the organics and the sensitivity of the burner to water in the feed would dictate the need for this technology.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION (Refs. 1, 2, 3, 4, 5, 9, 10)

Adsorption is a separation process based on the tendency of molecules from an ambient fluid phase of either a gas or liquid (adsorbate) to adhere to the surface of a microporous solid (adsorbent). Adsorption can be classified as either chemical or physical depending on the nature of the surface forces. Physical adsorption results from van der Waals interactions which are weak molecular interactions between the adsorbate and the adsorbent. Chemical adsorption involves stronger chemical bonds formed at the solid surface due to electron sharing or transfer between the adsorbate and the adsorbent. Adsorption is employed when high selectivity is needed because it is considered a more complex operation than other separation methods.

Activated alumina is a highly porous aluminous adsorbent made by the thermal processing of certain forms of hydrated alumina or aluminum hydroxide to remove the water of constitution. The resulting material has a relatively large surface area (50-400 m²/g) and a high affinity for water. Activated alumina is classified as a polar adsorbent because it adsorbs

water more strongly than organics. The most important industrial applications for activated aluminas are in drying processes to remove water from gases and organic liquids.

Activated alumina has also been used in water treatment to remove fluoride, arsenic, selenium, silica, and humic materials from drinking water. The adsorption of cations and anions is highly pH dependent with each adsorbate and relative to the zero point of charge (ZPC) of the activated alumina. pH higher than the ZPC favors the adsorption of cations while pH lower than the ZPC favors the adsorption of anions. Problems can occur due to competition from major background ions such as calcium, magnesium, or sodium which may need to be removed, and from silicate and phosphate ions. Activated alumina is not commonly used in wastewater treatment but has been proposed that it be considered where a high degree of selectivity is required or as a polishing treatment after a primary contaminant removal treatment.

Adsorption equipment is simple in design and normally consists of a single packed bed column. A standby column is also specified for use when the operating bed is being regenerated. A typical process flowsheet is shown in Figure G-4.1. A second bed can be added in series to improve product purity or in parallel to increase throughput. The service cycle for an activated alumina bed consists of conditioning the alumina with an acid (normally an HCl or H₂SO₄ solution), exhaustion of the bed, backwash of the bed with water, regeneration of the alumina with a caustic solution (normally a NaOH solution), and return to acid conditioning. Adjustment of the pH may be required prior to adsorption to improve removal efficiency.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Inputs to the adsorption bed could be aqueous streams containing specific inorganic or organic species that could be removed by activated alumina. Input stream requirements are discussed for specific species in Section 3.3.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

3.3.1.1 Fluoride Removal (Refs. 5, 9)

Removal of fluoride from drinking water using activated alumina has been practiced since the 1940s. Adsorption is employed rather than ion exchange because fluoride is one of the ions most preferred by alumina whereas with resins, fluoride is the least preferred. Activated alumina adsorption is the cheapest alternative compared to other accepted methods for fluoride removal such as reverse osmosis and electrodialysis. The mechanism for the

Figure G-4.1. Schematic of an Activated Alumina Adsorption Bed

adsorption is chemical in nature and is most effective at a pH of 5.5 to 6.0. Activated alumina systems are capable of reducing the fluoride level in effluents to 100-3000 µg/L.

3.3.1.2 Arsenic Removal (Refs. 5, 6, 9)

Activated alumina has been reported to be an effective and economical adsorbent for removing arsenic from water supplies. Anion exchange competes with activated alumina as an arsenic removal process. Activated alumina is preferred over ion exchange in waters with high total dissolved solids (TDS) levels (>500 mg/L) or sulfate levels (>25 mg/L) because the specificity of alumina adsorption reduces the affect of these variables. High chloride concentration does not reduce the adsorption capacity. Arsenic can occur in two forms, arsenate [As(V)] and arsenite [As(III)]. Arsenate removal by chemisorption is maximized at a pH of 5 while arsenite removal is less effectively removed at a pH of 8. Arsenite removal can be improved by oxidizing arsenite to arsenate prior to activated alumina adsorption. Activated alumina systems are capable of reducing the arsenic level in effluents to 10-60 µg/L.

3.3.1.3 Selenium Removal (Refs. 5, 9)

Selenium occurs in the selenite [Se(IV)] and selenate [Se(VI)] forms in water. Adsorption of selenium using activated alumina has been demonstrated as an effective process for selenite removal at a pH of 5 to 6. Removal of selenate at the same conditions is relatively poor. Ion exchange can also be used in selenium removal. The choice of ion exchange or activated alumina as a removal treatment depends on the oxidation state of selenium. Ion exchange is more appropriate for selenate removal even with high TDS and sulfate levels, while alumina is preferred for selenite removal. If both species are present, oxidation with chlorine followed by ion exchange is the preferred treatment. Activated alumina systems are capable of reducing the selenium level in effluents to 5-20 µg/L.

3.3.1.4 Dissolved Organic Carbon Removal (Refs. 5, 7, 8)

Activated alumina adsorption has been reported as a method for dissolved organic carbon (DOC) removal from natural aqueous systems. DOCs are large naturally occurring humic substances with molecular weights greater than 1000 and with humate and fulvate anions. Removal of these compounds is desired because they are trihalomethane (THM) precursors which are undesirable in water treatment processes. This application of activated alumina is still at the research level and more information is needed before it can be used for DOC removal in water treatment.

3.3.2 Reliability and Maintenance Requirements

Activated alumina has been used since the 1940s for fluoride removal and does not appear to present any unusual reliability or maintenance requirements. The specific requirements would depend on the contaminant being removed.

3.3.3 Secondary Waste Streams

The spent activated alumina is a secondary waste stream from this process along with the spent regenerant and backwash material.

3.3.4 Separation Efficiency

The separation efficiency would have to be determined based on the specific contaminant being removed.

3.3.5 Safety and Health

This process has been used for many years in water treatment. No unusual safety or health issues have been identified.

3.3.6 Operational Complexity

No complex operational situations would be expected from this process.

3.3.7 Glovebox Capability

To our knowledge, glove box capability has not been demonstrated.

3.3.8 Environmental Impact

Environmental impact has not been addressed.

3.4 COSTS OF TECHNOLOGY OR EQUIPMENT

The cost of an activated alumina system will be dependent on its performance requirements, including the processing rate of the unit, the contaminant which is targeted for removal, the contaminant level in the feed, and the desired level of contaminant in the effluent from the bed. The design of the equipment is that of a tank with support screens for the adsorption bed material and should be similar in cost to an ion exchange bed or carbon adsorption bed. This equipment could be supplied by many vendors.

3.5 TECHNOLOGY COMPARISON

Adsorption of metals and radionuclides is a standard technique for removal and concentration of these contaminants. The major disadvantage of adsorption processes is that they produce a concentrated liquid side stream resulting from regeneration. If not regenerated, the sorbent must be disposed as a solid waste.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Application of the activated alumina would have to be demonstrated using waste streams expected in the treatment plants to determine separation efficiency and other operational data.

4.2 TESTING REQUIREMENTS

Application of the activated alumina would have to be demonstrated using waste streams expected in the treatment plants.

5.0 VENDOR LIST

The vessel that would be used to contain the bed and the activated alumina should be commercially available from a number of manufacturers.

6.0 REFERENCES

1. *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th Edition, Vol. 1, John Wiley and Sons: New York, 1991.
2. Mantell, C.L., Adsorption. McGraw-Hill, New York, 1951.
3. Perry, R.H. and Green, D.W. (Editors). *Perry's Chemical Engineer's Handbook*, 6th Edition, McGraw-Hill, New York, 1984.
4. Rousseau, R.W. (Editor), *Handbook of Separation Process Technology*. John Wiley and Sons, New York, 1987.
5. Pontius, F.W. (Editor), *Water Quality and Treatment: A Handbook of Community Water Supplies*. 4th Edition, McGraw-Hill, New York, 1990.
6. Schlicher, R.J. and M.M. Ghosh. "Removal of Arsenic from Water by Physical-Chemical Processes." *AIChE Symposium Series - Separation of Heavy Metals and Other Trace Contaminants*. No. 243, Vol. 81, 1985.

7. Chen, A.S.C. and V.L. Snoeyink. "Activated Alumina Adsorption of Dissolved Organic Compounds Before and After Ozonation." *Environmental Science and Technology*. Vol. 21, No. 1, 1987, pp 83-90.
8. Davis, J.A. and R. Gloor. "Adsorption of Dissolved Organics in Lake Water by Aluminum Oxide: Effect of Molecular Weight." *Environmental Science and Technology*. Vol. 15, No. 10, 1981, pp 1223-1229.
9. Lankford, P.W., and W.W. Eckenfelder Jr. *Toxicity Reduction in Industrial Effluents*, Van Nostrand Reinhold. New York, 1990.
10. Patterson, J.W. *Industrial Wastewater Treatment Technology*. 2nd Edition, Butterworth-Heinemann, Boston, 1985.
11. Sircar, S. and A.L. Myers. "Liquid Adsorption Operations: Equilibrium, Kinetic, Column Dynamic, and Applications.", *Separation Science and Technology*. Vol. 21, Nos. 6 and 7, pp 535-562.

APPENDIX G-5 FERRITE ADSORPTION BED

1.0 TECHNOLOGY DESIGNATION

This appendix presents an evaluation of ferrite adsorption technology relative to chemical/physical treatment required in a mixed waste treatment process.

2.0 NEED FOR THE TECHNOLOGY

The basic need for ferrite adsorption in the mixed waste treatment process is in the separation of metals from water. Ferrite adsorption could be used for Primary Treatment (Unit 150.2) in the aqueous treatment line to remove dissolved metals prior to carbon bed adsorption. If a variety of metals are present, ferrite adsorption may be a better technology than precipitation due to its non-selective nature.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION (REFS. 1, 2, 3, 4, 5, 9)

Adsorption is a separation process based on the tendency of molecules from an ambient fluid phase of either a gas or liquid (adsorbate) to adhere to the surface of a microporous solid (adsorbent). Adsorption can be classified as either chemical or physical depending on the nature of the surface forces. Physical adsorption results from van der Waals interactions which are weak molecular interactions between the adsorbate and the adsorbent. Chemical adsorption involves stronger chemical bonds formed at the solid surface due to electron sharing or transfer between the adsorbate and the adsorbent.

Ferrites are a class of mixed valence iron oxide compounds having the crystal structure of spinel. They are commonly manufactured by adding ferrous ion to water followed by the addition of base and subsequent air oxidation. In the manufacturing process, it was discovered that heavy metal impurities present in solution were removed by ferrite when the metal ions replaced the iron atom in the spinel structure. This led to the development of techniques for separating metal from aqueous waste. With further investigation ferrite was found to have applications in the separation of particulate material and suspended solids, organic materials, and biological matter from wastewater. Ferrites have also been used to separate noxious gases from waste gas streams by acting as catalysts for the degradation of the noxious compounds and have been investigated in the removal of actinides from process waste. Because they are

not as selective as other adsorbents, they have found limited use outside the waste treatment field.

Two basic methods are used for separations with ferrite. In the *in situ* method (Figure G-5.1), ferrite is manufactured in the waste solution and the contaminating species is incorporated into the lattice of the ferrite crystal. The resulting mixture of ferrites are then magnetically separated from the treated water. The ferrites removed are not susceptible to leaching by alkaline, neutral, or even weakly acidic solutions. Most of the process steps can be performed in heated mix tanks. More complex process equipment may be selected to improve control or operating conditions.

The second method is the preformed ferrite process (Figure G-5.2). Ferrite is prepared separately and then placed in contact with the waste solution. Under alkaline conditions, the metal ions form insoluble hydroxide species. The hydroxide ions in the metal hydroxides are strongly adsorbed onto the surface of the ferrite particles thus also binding the metal to the surface. The ferrites with the adsorbed species can be magnetically separated. Most of steps in this process can also be performed in mix tanks.

Contaminants adsorbed onto the ferrite surface are generally not susceptible to leaching by water from natural sources so they can be sent directly to disposal. They can also be acid washed to remove the metals and the ferrite reused.

Research is presently being conducted on a third technique which uses sand coated with ferrihydrite. The coated sand when used in a granular filter provides for both metal removal due to adsorption on the ferrihydrite and solids removal due to the filtration in the bed. The bed is backwashed to remove particulates and regenerated with an acid solution to desorb the metal species. Equipment for the adsorption process would be similar to a commonly used sand filter. However, because the coated sand is not a commercial product, equipment would also be needed to coat the ferrihydrite on the sand. Even coating of ferrihydrite on the sand is important for successful removal and may require further development effort.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Inputs to a ferrite process in the chemical/physical treatment scheme could be aqueous streams containing metal ions. Specific metals that have been removed are listed in section 3.3.1.1. The output stream characteristics would depend on which separation method is used as described in section 3.1.

Figure G-5.1. In Situ Ferrite Method

(From Boyd, T.E., Cusick, M.J., Navratil, J.D., Ferrite Use in Separation Science and Technology, 207-232, in Recent Developments in Separation Sciences, Li, N.N., Navratil, J.D. eds., CRC Press: Boca Raton, Florida, 1986, with permission)

Figure G-5.2. Preformed Ferrite Method

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

3.3.1.1 Metals Removal (Refs. 5, 6, 7, 8)

Ferrites are effective and capable of removing a wide variety of metals. Dissolved metals that have been reportedly removed by ferrites include americium, arsenic, bismuth, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, plutonium, silver, tin, vanadium, and zinc. Titanium, silicon, and their dioxides have also been reportedly removed. Aqueous waste streams that have been successfully treated using ferrite adsorption include those from incinerator off-gas scrubbers, laboratories, radioactive sources, electroplating processes, fertilizer plants, dye manufacture plants, pickling liquor processes, and fly ash leachates.

One advantage of using ferrite comes from its non-selectivity. In precipitation processes the optimum precipitation conditions for different metals are not the same (ex. zinc and aluminum). With ferrites most metal ion impurities can be effectively removed in one step even if their initial concentration is relatively high.

An advantage of using ferrite involves highly oxidized species such as chromate and permanganate. In conventional precipitation processes one or several reduction treatment steps are required prior to hydroxide precipitation. In the ferrite process these species can be removed without pretreatment. The ferrite process is also not seriously affected by high salt concentration.

Maximum removals that have been observed for various dissolved metal species are shown in Table G-5.1.

3.3.1.2 Particulate Removal (Ref. 5)

Ferrites have been used to separate fine particulate material and suspended solids from aqueous solutions using the same methods employed for metal removal. The particulate material binds to the surface of the ferrite. The adsorption can be enhanced using a coagulating agent to improve efficiency. Ferrites offer an advantage in processing because they can be regenerated and reused. Particulates concentration has been reduced from several hundred ppm to approximately 10 ppm in several waste solutions.

Table G-5.1. Removals Observed for Various Dissolved Metal Species

(From Boyd, T.E., Cusick, M.J., Navratil, J.D., Ferrite Use in Separation Science and Technology, 207-232, in Recent Developments in Separation Sciences, Li, N.N., Navratil, J.D. eds., CRC Press: Boca Raton, Florida, 1986, with permission)

Maximum Removal Observed for Various Dissolved Metal Species (Ref. 5)		
<i>Element</i>	<i>Initial Concentration</i>	<i>Final Concentration</i>
	(ppm)	(ppm)
Cadmium	1,120	0.01
Chromium	6,590	0.112
Copper	9,500	<0.5
Iron	570	<0.05
Lead	6,800	<0.1
Manganese	285	<0.05
Mercury	1,000	<0.005
Nickel	20,300	<0.5
Plutonium	0.49	0.00007
Vanadium	46,000	<0.2
Zinc	2,400	0.015

3.3.1.3 Organics Removal (Refs. 5, 10)

Separation of a variety of organic materials from aqueous solutions has been reported. Phenol and aniline have been reduced in wastewater from dye manufacture from 0.012 ppm and 0.10 ppm, respectively, to <0.004 ppm and below the limits of detection. Organic content reduction as measured in BOD and COD has also been reported in food processing operations.

Organic removal of sparingly soluble organic chemicals has been examined using sodium dodecyl sulfate (SDS) coated ferrihydrite. The coating of ferrihydrite with an anion surfactant such as SDS produces an aggregate structure called a hemimicelle. The interior of a hemimicelle is similar to a micelle and is capable of incorporating hydrophobic organic compounds just as a micelle. The experiment demonstrated that the SDS-coated ferrihydrite was able to remove toluene, p-xylene, and trichloroethylene from solution. This application of ferrites is still at the research stage.

3.3.2 Reliability and Maintenance Requirements

Ferrites have been used commercially for metals removal, however, reliability and maintenance requirements were not available.

3.3.3 Secondary Waste Streams

The secondary waste stream generated would depend on the ferrite process used. In the *in situ* and preformed methods the secondary waste stream would be the ferrites produced. For the filter containing sand coated with ferrihydrite, the waste streams would be the spent filter material and the backwash material.

3.3.4 Separation Efficiency

The efficiency of separation depends on the metal ions being removed. Some reported metal removal efficiencies are shown in section 3.3.1.1.

3.3.5 Safety and Health

Ferrites have been used commercially for metals removal, however, information on safety and health issues was not available.

3.3.6 Operational Complexity

No complex operational situations would be expected from this process.

3.3.7 Glovebox Capability

To our knowledge, glovebox capability has not been demonstrated.

3.3.8 Environmental Impact

Environmental impact has not been addressed.

3.4 COSTS OF TECHNOLOGY OR EQUIPMENT

The cost of a ferrite system will be dependent on the ferrite method (*in situ*, preformed, or coated sand) and the performance requirements of the system such as the processing rate of the unit, the contaminants which are targeted for removal, the level of the contaminants in the feed, and the desired level of the contaminants in the effluent. If either the *in situ* or preformed methods are used, the equipment will primarily consist of stirred tanks and a magnetic separator. These items should be readily available. If the coated sand method is used the equipment design would be similar to a sand bed filter which is commonly used in wastewater

treatment and should also be readily available. One drawback of the ferrite coated sand system is that the coated sand is not a commercial product and may require including a sand preparation step.

3.5 TECHNOLOGY COMPARISON

Adsorption of metals and radionuclides is a standard technique for removal and concentration of these contaminants. The major disadvantage to adsorption processes is that they produce a concentrated liquid side stream resulting from regeneration. If not regenerated, the sorbent must be disposed as a solid waste.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Application of the ferrite processes for the metals in the waste streams expected for the treatment plant would have to be demonstrated. Additional development work would be required for the process using coated sand since it is still at the bench scale.

4.2 TESTING REQUIREMENTS

Use of the currently used ferrite processes would have to be demonstrated using the waste streams expected at the treatment plant. The ferrite process using ferrihydrite coated sand would have to be demonstrated at a larger scale.

5.0 VENDOR LIST

This process is not commercially available as a package from a vendor. The equipment would have to be purchased separately. The individual equipment should be commercially available from a number of manufacturers. The ferrihydrite coated sand is not a commercial product. If this process were used, the plant would also have to include equipment to make the filter material.

6.0 REFERENCES

1. *Kirk-Othmer Encyclopedia of Chemical Technology* 4th ed. Vol. 1, John Wiley and Sons: New York, 1991.
2. Mantell, C.L., *Adsorption*. McGraw-Hill: New York, 1951.
3. Perry, R.H. and D.W. Green, eds. *Perry's Chemical Engineer's Handbook*. 6th ed. McGraw-Hill: New York, 1984.

4. Rousseau, R.W. (ed.), *Handbook of Separation Process Technology*. John Wiley and Sons: New York, 1987.
5. Boyd, T.E., M.J. Cusick, and J.D. Navratil, "Ferrite Use in Separation Science and Technology." *Recent Developments in Separation Science*. Vol. VIII. CRC Press: Boca Raton, FL, 1986.
6. Benjamin, M.M., K.F. Hayes, and J.O. Leckie. "Removal of Toxic Metals from Power-Generation Waste Streams by Adsorption and Coprecipitation." *Journal WPCF* Vol. 54, No. 11, 1982, pp 1472-1481.
7. Schultz, M.F., M.M. Benjamin, and J.F. Ferguson. "Adsorption and Desorption of Metals on Ferrihydrite: Reversibility of the Reaction and Sorption Properties of the Regenerated Solid." *Environmental Science and Technology*. Vol. 21, No. 9, 1987, pp 863-869.
8. Edwards, M. and M.M. Benjamin. "Regeneration and Reuse of Iron Hydroxide Adsorbents in Treatment of Metal-Bearing Wastes." *Journal WPCF* Vol 61, No. 4, 1989, pp 481-490.
9. Edwards, M. and M.M Benjamin, "Adsorptive Filtration Using Coated Sand: A New Approach for Treatment of Metal-Bearing Wastes." *Journal WPCF*: Vol. 61, No. 9, 1989, pp 1523-1533.
10. Holsen, T.M., E.R. Taylor, Y-C Seo, and P.R. Anderson. "Removal of Sparingly Soluble Organic Chemicals from Aqueous Solutions with Surfactant-Coated Ferrihydrite." *Environmental Science and Technology*. Vol. 25, No. 9, 1991, pp 1585-1589.

APPENDIX G-6 SILICA GEL ADSORPTION BED

1.0 TECHNOLOGY DESIGNATION

This appendix presents an evaluation of silica gel adsorption technology relative to chemical/physical treatment required in a mixed waste treatment process.

2.0 NEED FOR THE TECHNOLOGY

Potential needs for silica gel adsorption in the mixed waste treatment process could be in the drying of off gas or the removal of water from the organic feed to the Concentrated Organics Burner (Unit 380) in the thermal treatment line. The level of water in these streams and the sensitivity of the units downstream would dictate the need for this technology.

Adsorption using surface modified silica gel might also be used in removal of metals after the Condensate Check Tank (Unit 190.3) in the aqueous treatment line or in the separation of specific organics in the organic treatment line. This type of adsorption has been used in laboratory separations but has not been developed for plant scale operations.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION (Refs. 1, 2, 3, 4, 5)

Adsorption is a separation process based on the tendency of molecules from an ambient fluid phase of either a gas or liquid (adsorbate) to adhere to the surface of a microporous solid (adsorbent). Adsorption can be classified as either chemical or physical depending on the nature of the surface forces. Physical adsorption results from van der Waals interactions which are weak molecular interactions between the adsorbate and the adsorbent. Chemical adsorption involves stronger chemical bonds formed at the solid surface due to electron sharing or transfer between the adsorbate and the adsorbent. Adsorption is employed when high selectivity is needed because it is considered a more complex operation than other separation methods.

Silica gel adsorbents are composed of a rigid three-dimensional network of spherical particles of amorphous colloidal silica (SiO_2). The silica gel surface has an affinity for both water and organics, although water is preferred. It is a widely used desiccant and its major uses have been in the dehydration of gases and liquids.

Silylated silica gel has been suggested as an adsorbent for removing contaminants from industrial wastewater. A silylated silica is a silica gel that has been modified by the reaction of

an organo-silicate compound with a silica substrate to form an immobilized organic complex. Functional groups with different affinities for waste such as metal chelators have been used to form the immobilized compounds. Other compounds with affinities to organic substances have also been immobilized on silica. If the contaminants can be chemically removed, the substrate can be recoated and used again. Applications of the silylated silica gels have been in chromatographic and other separations.

3.2 DEMONSTRATED PERFORMANCE (Refs. 5, 6)

Silica gels are widely used as a desiccant in the dehydration of gases and liquids and was used for many years to recover hydrocarbons from natural gas streams.

Modified silica gels have been used in analytical separation techniques to remove metals in solution. Immobilized diamine on silica gel in a column test was successful in removing copper from wastewater obtained from an electroplating facility. The column was most effective in removing copper and zinc and least effective in removing nickel and chromium. Levels of the metals met those required for discharge. Metal-organic compounds have been removed from natural waters in experiments conducted with long-chain (C₁₈) modified silica gels.

Development work is need to scale-up the analytical separations to a wastewater treatment application.

Silica gel has also been examined at the laboratory scale as an adsorbent for uranium (VI) and zirconium (IV) for acid solutions. This application is still at the research stage.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Inputs to the adsorption bed in the chemical/physical treatment scheme could be aqueous streams containing specific metals or organic streams containing specific organics that could be removed by a surface modified silica gel.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

To be determined.

3.3.2 Reliability and Maintenance Requirements

Use of silica gel for these applications has been in analytical separations. Reliability and maintenance requirements are not known.

3.3.3 Secondary Waste Streams

The spent silica gel would be a secondary waste stream from this process.

3.3.4 Separation Efficiency

This method is not used at a commercial scale for this type of separation. The separation efficiency is not known.

3.3.5 Safety and Health

This process has only been demonstrated at the analytical scale. Safety and health issues have not been fully addressed. However, since the process is conducted at ambient temperature and pressure, no unusual problems would be expected.

3.3.6 Operational Complexity

No complex operational situations would be expected from this process.

3.3.7 Glovebox Capability

To be determined.

3.3.8 Environmental Impact

This process has only been demonstrated at the analytical scale. Environmental impact has not been addressed.

3.4 COSTS OF TECHNOLOGY OR EQUIPMENT

Use of silica gel in mixed-waste treatment would be different from its current industrial uses and significant development would be required. The cost of a silica gel system would be dependent on the data obtained from the development effort and on the performance requirements for the system. The design of the equipment should be similar in design to an ion exchange bed or an activated carbon bed and would be available from many vendors.

3.5 TECHNOLOGY COMPARISON

Adsorption of metals and radionuclides is a standard techniques for removal and concentration of these contaminants. The major disadvantage to adsorption processes is that they produce a concentrated liquid side stream resulting from regeneration. If not regenerated, the sorbent must be disposed as a solid waste.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATE REQUIREMENTS

Application of the surface modified silica gels has been in chromatographic and other analytical separations. Additional development work on the process would be required to determine what type of surface modification would be required to perform the suggested separations and the efficiency of the separations.

4.2 TESTING REQUIREMENTS

Use of the surface modified silica gels would have to be demonstrated at a larger scale.

5.0 VENDOR LIST

This process has only been demonstrated as a analytical laboratory separation and is not available commercially from a vendor. The type of silica gel that would be applicable would have to be determined and may not be commercially available. The vessel that would be used to contain the bed should be commercially available from a number of manufacturers.

6.0 REFERENCES

1. *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th ed. Vol. 1, John Wiley and Sons: New York, 1991.
2. Mantell, C.L. Adsorption. McGraw-Hill: New York, 1951.
3. Perry, R.H. and D.W. Green, eds. *Perry's Chemical Engineer's Handbook*. 6th ed. McGraw-Hill: New York, 1984.
4. Rousseau, R.W. ed. *Handbook of Separation Process Technology*. John Wiley and Sons: New York, 1987.
5. Jones, L.W. and P.G. Malone. "Use of Surface-Modified Silica Gels in Wastewater Treatment." *Toxic and Hazardous Waste: Proceedings of the Fifteenth Mid-Atlantic Industrial Waste Conference*. Butterworth Publishers: Boston, 1983.
6. Milonjic, S.K., M. R. Boskovic, and T.S. Ceranic. "Adsorption of Uranium (VI) and Zirconium (IV) from Acid Solutions on Silica Gel." *Separation Science and Technology*. Vol. 27, No. 12, 1992, pp 1643-1653.

APPENDIX G-7 ION EXCHANGE

1.0 TECHNOLOGY DESIGNATION

Ion exchange can be used for the removal of undesirable anions and cations from a wastewater stream. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions or bicarbonate ions. Most ion-exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. Functional ionic groups are usually introduced by reacting the polymeric matrix with a chemical compound containing the desired group. Exchange capacity is determined then by the number of functional groups per unit mass of resin.

Ion exchange techniques typically are used to detoxify large flows of waste water containing relatively low levels of heavy-metals, salts and acids. These techniques are generally more efficient for such applications than many other processes. The purified water can be discharged to the environment, and the heavy metals recovered from the resin by chemical regeneration with acids or alkalis. The resulting waste stream must then be disposed of as a hazardous waste, or the heavy metals recovered for reuse.

2.0 NEED FOR THE TECHNOLOGY

Ion exchange is a simple and well understood technology that is used for the concentration and removal of materials from solutions. The technology has been used by the nuclear industry for many years.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Two ion exchange processes appear to be the most suitable ones for removal of plutonium and/or americium from scraps or wastes. Other ion exchange processes such as chloride anion exchange may have application to certain wastes. Plutonium nitrate anion exchange is based on the very selective absorption of plutonium (IV) from solution $>3M$ nitrate (typically $6-8 M$) by anion exchange resins as the $Pu(NO_3)_6^{2-}$ complex. Almost all other elements (except Np and Th) are not significantly absorbed and are easily removed with a nitrate solution wash. Elution is carried out by about 0.35 to $0.5 M$ HNO_3 where the $Pu(NO_3)_6^{2-}$ complex is not stable.

Cation exchange processes can very effectively remove plutonium and americium from relatively low ionic strength acid or salt solutions. Capacities depend on both the overall ionic strength and the charge of the other ions present. Plutonium and Americium are absorbed as the +3 ions and capacity and selectivity are best if the extraneous ions are of low charge and the total ionic strength is low. Selectivity and separation of Pu and Am from trivalent ions such as Fe, Al and Cr is low.

Other ion exchange processes such as chloride anion exchange for Pu may have applicability to the treatment of certain types of wastes such as chloride salts.

Ion exchange, as a process operation, is very simple. Although more complex equipment has been designed for specialized cases (high continuous throughput, unclarified feeds, etc.), most applications consist of a bed or column of particulate ion exchange resin or absorbent (spherical beads or granular material) through which the feed solution is flowed until some predetermined breakthrough of the component being absorbed occurs. Such simple column operation normally provides many theoretical stages of separation. The bed can then be washed with a solution chosen to remove weakly absorbed impurities. The bed or column is then eluted with a solution chosen for its ability to remove the absorbed component from the exchanger. Columns or beds are sometimes loaded and washed in series followed by removal and elution of only the first column of the series in order to maximize the exchanger capacity at low feed breakthrough.

Equipment for plutonium ion exchange is designed to be safe with regard to criticality at any conceivably possible plutonium concentrations that might be encountered. At high possible plutonium concentrations this restricts columns to not more than 5 to 6 inches diameter. Such equipment is normally built for the purpose from glass or stainless steel pipe instead of purchased.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

All ion exchange processes if operated in the typical column operation with multiple theoretical stages, requires feed clarification in order to prevent plugging of the resin beds by solids filtering out. Ion exchange has been operated in several cases with a few stages of stirred or agitated batches of exchanger and for some application this has been satisfactory but much higher separation factors can be obtained with column operation on clarified feed.

Plutonium nitrate anion exchange operates at high nitrate concentrations (~4 to ~9 M), and if HNO_3 is the chief source of nitrate, optimum absorption is at about 7 M HNO_3 . Only Pu in the tetravalent state is absorbed strongly which means that any Pu(VI) in the feed solution must be reduced (Pu(III) is easily oxidized by the nitrate solution). The best reductant for dilute Pu solutions is ferrous sulfamate, and at higher Pu concentrations, hydrogen peroxide is

useable. The output from Pu nitrate anion exchange is a dilute ($\sim 1 \text{ M}$) HNO_3 solution of Pu which is separated from other solution components and is markedly concentrated relative to feed input.

Cation exchange operates from a low ionic strength solution (preferably $< 1 \text{ M}$) where Pu(III), Pu(IV), and Am(III) are very strongly absorbed relative to monovalent and divalent ions. There is usually advantage to reducing Pu (IV) to Pu (III) to remove Pu (V) and (VI) and to minimize complexing of Pu (IV) by various anions as well as to increase ease of elution. The output is $\sim 5 \text{ M}$ HNO_3 containing much more concentrated Pu and Am than the feed with significant separation from monovalent and divalent cations and anions and minimal separation from trivalent cations.

Chloride anion exchange removes Pu (IV) and Pu (VI) from solution, the latter more efficiently so an oxidant such as sodium chlorite is advantageous. Chloride feed concentrations of $> 8 \text{ M}$ are needed for Pu (IV) and $> 6 \text{ M}$ for Pu (VI). The output is diluted ($< 1 \text{ M}$) HCl solution of Pu much concentrated from the feed. Separation of many common metal ions except iron and a few other transition metals is good.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Ion exchange is a mature technology and has been used extensively in the nuclear industry. Ion exchange materials are currently being developed that are more specific and useable over a wide range of conditions. Equipment will be dependent on needs and requirements and more than likely require a unique design for a given plant.

Most ion exchange equipment used in processing of radionuclides (other than possibly in nuclear reactor water treatment) is designed and built specifically for the proposed application. This equipment is of rather simple design often consisting simply of glass or stainless steel pipe with retaining screen in the bottom to hold the exchanger and connections for feed and effluent, venting, etc. A variety of cation/anion exchangers are available from vendors such as Dow, Rhom and Haas, Reilley Chemicals, Mobay Chemicals, etc. Certain of these resins have very significant advantages over others for some Pu ion exchange applications.

Recent advances in adsorbent resins show promise in the treatment of organic wastes. By controlling the pore size, porosity, surface area, and degree of hydrophilicity, it is possible to tailor adsorbents to a range of organic adsorption applications. Various ion exchange processes, particularly for the selective removal of certain fission products are in development stages. Even though selective ion exchangers are available for Cs removal from wastes, further

work is being carried out. Much of this is particularly aimed at absorption of Cs from very high pH solutions and to higher exchange capacities and includes work on selective organic exchangers at SRL and specially designed silico titanate exchangers at Sandia and PNL. The use of titanates to remove Pu and Sr from certain alkaline wastes is also being studied.

Titanate ion exchangers are being developed at Sandia National Laboratories under Technical Task Plan AL2312P4 for the Underground Storage Tank (UST) ID to remediate radioactive waste. The objective is to develop, engineer, and demonstrate the use of titanate ion exchange materials and ion exchange processes to support waste separation and treatment for the UST ID. Titanate ion exchange technology will be demonstrated for removal of radioactivity from supernate solutions, in-tank processing, fixation of strontium removed from sludge, and treatment processes to produce reduced-volume low-level waste forms. Use of inorganic vs. organic resin ion-exchange materials, such as the titanates, offers the advantage of stability in the presence of intense radiation.

The materials to be investigated include hydrous titanium oxide (HTO), and newly discovered alkoxide-derived crystalline titanate. When used as a conventional ion exchange column, titanate materials will produce effluent streams that can be treated as chemical, rather than radioactive or mixed waste. The titanates can also be incorporated into the matrix of organic anion exchange resins without affecting the anion exchange properties of the resin or the cation exchange properties of the titanate. This technology produces a single, engineered material capable of both cation and anion exchange for treatment of liquid wastes. When spent, the ion exchange material can be calcined to remove the organic portion, leaving a stable ceramic for interim storage. Based on previous studies at Sandia the HTO materials can be converted to stable, leach resistant ceramic form using processing technology developed in Australia. Because of their crystalline nature, the ceramic forms are expected to be stable over geologic time frames. Also, HTO materials can be incorporated into vitreous waste forms within the titanium limits specified for vitrified waste.

Ion exchange of sodium, in the sodium titanate, for other cations in aqueous solution can be empirically represented by:

The HTO materials can also function as anion exchangers in acidic solutions, allowing absorption of oxygenated anions, such as PO_4^{-3} , and metals that exist as aqueous oxygenated anions such as molybdates. However, low pH (<5) is required to take full advantage of this property.

This project includes:

- * Development of new crystalline titanates for efficient, selective absorption of Cs isotopes
- * Studies of TRU and Sr-90 partitioning with bulk or thin film amorphous hydrous titanium oxide ion exchange material.
- * Development of ion exchange processes to remove radioactivity (primarily Cs-137) from supernate solutions and salt cake.
- * Development of processes that can remove Sr-90 from sludge.
- * Development of enhanced titanate technology to treat LLW streams to produce a reduced volume LLW waste form.

One of the major applications of ion exchange is the removal of chrome from industrial plating streams. Other anions or cations from wastewater streams can be removed. Macroreticular resins are used for the removal of specific organic compounds such as chlorinated pesticides and aromatic hydrocarbons. This technology has been used successfully for the remediation of heavy metals and uranium from wastewater and groundwater at the Hanford and Savannah River sites.

Ion exchange is used extensively in the nuclear industry in common feedwater and condensate systems, transuranic extractions, boron recovery systems, spent-fuel pool cleanup, and radioactive waste processing. The condensates from evaporators used to concentrate hazardous and radioactive wastes are polished by ion exchangers to remove the last traces of radioactive material. The depleted resins are not normally regenerated but are disposed as LLW. Inorganic ion exchangers (e.g., zeolites or porous glass based ion exchangers) offer significant advantages in applications involving the separation of isotopes such as cesium and strontium. These isotopes can also be retained on zeolites or glass and encapsulated for long term storage.

3.3.2 Reliability and Maintainability Requirements

Past history indicates that because of the inherent simplicity of ion exchange systems they are very reliable if used as intended and correctly designed. A system uses a minimum of moving parts (pumps, valves etc.) and is easy to maintain if located in a glove box or hood. The system becomes more complicated if installed in a hot cell. The ion exchange resin needs to be replaced on a periodic basis as does some of the equipment. Ion exchange beds can be plugged by solids if present in the feed. For this reason ion exchange processing of streams containing solids needs to include feed clarification such as filtration or centrifugation so the maintenance of these steps is also required.

3.3.3 Secondary Waste Streams

Secondary waste streams produced will depend upon the waste streams being treated and what they are being treated for. The ion exchange resin will require replacement from time to time and the same is true for the equipment, but certainly on a less frequent basis. Acid waste streams could be recycled or evaporators could be used to recover solids. Plant requirements and needs will be the driving factor as to what waste streams will be produced.

3.3.4 Separation Efficiency

The ability of the equipment to efficiently separate stream components using ion exchange techniques has been shown to be possible on many waste streams within the DOE complex.

3.3.5 Safety and Health

Ion exchange processes do not normally involve gas release and the solid exchangers are generally of very low toxicity. Organic ion exchange resin like other organic materials can under certain conditions react exothermally with strong oxidants such as strong nitric acid and some radiolytically degraded exchangers may be more sensitive. For this reason, exchangers adequately stable to the expected solution compositions should be used. Pressure relief devices on columns can be used if deemed necessary.

3.3.6 Operational Complexity

Ion Exchange processes are generally simple with a minimum of moving parts and instrumentation required. Operation is usually simple and straight forward.

3.3.7 Glovebox Capability

Ion exchange systems have been very successfully used in gloveboxes by the nuclear industry for the past 40 years with very few problems.

3.3.8 Environmental Impact

Ion exchange processes are expected to have minimal environmental impacts. The amount of solid waste (spent resin) and equipment are normally rather small. Spent organic exchangers can be processed by incineration, other oxidation routes, or they can be grouted, etc.

Their chief hazard is probably residual radionuclides or metal ions remaining on them.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Ion Exchange technology has been used for over 40 years by the nuclear industry. The equipment requirements are known; however, each plant usually designs components to fit the needs of the plant. Off the shelf equipment used by other industries is not usually suitable due to the requirements of criticality, chemicals used, radiation damage to elastomers, etc.. The cost is usually minimal when compared to other systems such as solvent extraction that requires much more complex equipment.

3.5 TECHNOLOGY COMPARISON

One of the advantages of ion exchange is that the removed product from the wastewater stream can be recovered and reused or concentrated for more controlled disposal.

A disadvantage is the other ions within a waste stream can compete with the ion of interest in the exchange process thus reducing the capacity. For instance, iron in groundwater competes for the exchange of more hazardous ions like chromium or uranium.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Many ion exchange processes for Pu, Am and other metals recovery are well developed. These processes, such as plutonium anion exchange, have been used with a wide range of feeds and their use may require little or no data development. On the other hand, new processes and exchangers are being developed for which even feasibility remains to be proven.

4.2 TESTING REQUIREMENTS

Testing requirements for some well-developed ion exchange processes can be very minimal when applied to new streams, provided that the streams do not contain large amounts of interfering species such as fluoride. Even when these are present, testing can normally be performed on the laboratory scale since scale-up in ion exchange processes is straight forward. Any planned features of ion exchange column design, such as novel ways of adding and removing resins from columns, should be tested with non-radioactive materials.

5.0 VENDOR LIST

Ion exchange columns are usually fabricated from standard stainless steel (or glass or plastic) pipe, stainless steel screen, etc.. The rest of the equipment consists of standard

tankage, valves, pumps, etc. constructed from stainless steel. Organic ion exchangers are available from a variety of sources, some of which are listed below:

Dow Chemical Company
Rohm and Haas Company
Mobay Chemical Company
Reilly Industries

6.0 REFERENCES

1. Ryan, J. L., 1974, "Ion Exchange of the Transuranium Elements." in *Gmelin's Handbuch der Anorganischen Chemie*. Band 21, Transurane, Teil D2. G. Koch ed. Verlag Chemie, G.m.b.H.: Weinheim, Germany, 1974. pp 373-437.
2. Katz, J. J., G. T. Seaborg, and R. L. Morss, eds., *The Chemistry of the Actinide Elements*. 2nd edition. Chapman & Hall: New York, 1986, pp 550-564 and 894-897.
3. Schulz, W. W., *The Chemistry of Americium*. TID-26971. Energy Research and Development Administration: Oak Ridge, TN, 1976, pp 233-255.
4. Cleveland, J. M., *The Chemistry of Plutonium*. Gordon and Breach Science Publishers: New York, pp. 142-159.

APPENDIX G-8 CHROMATOGRAPHY

1.0 TECHNOLOGY DESIGNATION

Chromatography is a process by which a solute is immobilized on a stationary bed of adsorbent material.

2.0 NEED FOR THE TECHNOLOGY

As with other media bed technologies, chromatography may be used to remove specific contaminants from an aqueous waste stream. This technology has the potential of separating the adsorbed species through subsequent solvent extraction from the adsorbent.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION (Ref. 1)

If a solution is poured on top of a column of a suitable adsorbent, the solute will be immobilized into the stationary phase. By washing the adsorber bed with an appropriate solvent, the solute will be resolved into a series of concentrated bands each moving at different rates. Each component of the original mixture will be represented by a band into which that component is concentrated, and each component may be recovered in relatively pure form by dividing the column into segments and eluting the component from the adsorbent.

Only the solvent outside the particles of the bed is moving (external porosity). The stationary material is the fluid volume inside the particles (internal porosity) plus the solute held up on the solid. The solute may be held up on the surface of the solid by adsorption, or it may be dissolved in a thin layer of liquid coated on the solid. Also, since the pores are small and not uniform in size, large molecules may be excluded from some fraction of the internal void volume.

The solutes move at a rate equal to their solute velocities which is a function of the fraction of internal void volume that a species can penetrate, and the equilibrium between the amount of solute adsorbed and the solute concentration in the fluid. If the equilibria and rates of adsorption and desorption are sufficiently different for the different solutes, a slight separation is effected while traveling a short distance down the column. The separation is increased successively as the solution flows down the entire length of the column. However, due to mass transfer and diffusion effects the concentration bands are broadened and may overlap.

Alumina, silica gel, magnesia, powdered glass, charcoal, and other adsorbents are used, depending on the application. These solid beds may be used to provide mechanical strength while organics, such as organosilanes and ligands, are bonded to the surface to provide selectivity or improve the separation capability of the bed.

In operation, feed and recycle material are fed to the column as a pulse through an injector to produce plug flow. The solvent is fed continuously and is usually reused. A timer or detector is used for splitting the column outlet stream. Different product streams are sent to different separators, as shown in Figure G-8.1, where solvent is removed from the product. For liquid systems the separator may be a distillation column or evaporator. Since column separation is low for large systems, a mixed product fraction is collected and recycled to the column. The recovered solvent may require cleanup to remove traces of solute before it is returned to the column.

Figure G-8.1. General System for Large-Scale Chromatography

(Handbook of Separation Processes, R.W. Rousseau, ed., copyright © 1987 by John Wiley and Sons, Inc., Reprinted by permission of John Wiley and Sons, Inc.)

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Waste stream pretreatment requirements depend on the waste stream characteristics, species to be removed, and the adsorbent used.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The successful separation of the rare earth elements to a high degree of purity by fractional adsorption on organic resins is one application of chromatography. Large scale operations are used to separate sugars for enrichment of fructose and separating cane molasses. Size exclusion chromatography has been used to separate large molecules such as proteins from small molecules such as salts. Ion-exchange chromatography has been used to purify hydrometallurgical solutions and waste streams.

Moving-feed and simulated moving-bed systems are commercially available for liquid adsorption and ion-exchange systems. Several companies supply activated supports to which specific ligands can be attached.

3.3.2 Reliability and Maintenance Requirements

Chromatography does not appear to present any unusual reliability or maintenance requirements.

3.3.3 Secondary Waste Streams

Secondary waste streams may consist of unrecovered solvent and spent media.

3.3.4 Separation Efficiency

Separation efficiency depends on the species to be separated and the design of the chromatograph column.

3.3.5 Safety and Health

No unusual safety or health issues have been identified.

3.3.6 Operational Complexity

The operation is somewhat complex requiring media regeneration and an additional separation process to separate the solute from the solvent.

3.3.7 Glovebox Capability

Glovebox capability should be the same as for other media bed technologies.

3.3.8 Environmental Impact

Environmental impact has not been addressed.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

The cost of chromatography systems will depend on the required performance, processing rate, contaminants targeted for removal, contaminant level in the feed, and solvent usage.

3.5 TECHNOLOGY COMPARISON

Difficult to separate solutes can be efficiently separated into individual waste streams. High-performance liquid chromatography offers greater separating power for chemical mixtures of similar components than any other commonly used separation or purification process. There are several chromatographic techniques that can be used individually, but when coupled together can separate and purify chemical mixtures virtually unseperable by other methods.

Methods for many separations have not been standardized. Process is complex, requires bed regeneration, and requires final separation of the solute from the solvent.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data requirements have not been addressed.

4.2 TESTING REQUIREMENTS

Testing requirements have not been addressed.

5.0 VENDOR LIST

Vendors of this technology or equipment have not been identified at this time.

6.0 REFERENCES

1. P. C., Wankat, "Large-Scale Chromatography." in *Handbook of Separation Process Technology*. R. W. Rousseau, ed. John Wiley and Sons: New York, 1987.

APPENDIX G-9 ION SPECIFIC CHROMATOGRAPHY

1.0 TECHNOLOGY DESIGNATION

Ion Specific Chromatography is a process whereby ions may be selectively complexed and removed from a multitude of other ions.

2.0 NEED FOR THE TECHNOLOGY

Efficiently removing one or a few hazardous ions from head end processes may greatly ease the problems in processing the remaining wastes. Reducing actinide ion concentrations below 100 nanocuries per gram will relax the TRansUranic (TRU) waste classification. It also would remove criticality design constraints upon plant processes and equipment. Removing volatile elements such as mercury could also reduce off-gas constraints.

The technology requirements are:

- * The availability of ion specific ligands or the ability to synthesize them as required.
- * A chromatographic process line

The operational requirements are:

- * The process must be designed to treat a maximum aqueous feed stream of 129,936 gross kg/week. The feed stream will not normally exceed 10% dissolved solids by weight or 30% undissolved solids. No more than 1% organics are permitted in this stream.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

3.1.1 Bonding Theory

One of the fundamental rules of chemistry is that all atoms find stability by giving up energy. The electronic energy is minimized by filling each major energy shell. Those atoms which do not possess filled major energy shells, seek to give up or gain electrons through chemical bonding to move toward the filled shell position.

When atoms bind together, the atomic electronic orbitals overlap in space and are converted into molecular orbitals which usually have two centers of positive charge, however three or more are possible. Sigma molecular bonds result from frontal atomic orbital overlap, and because of superior overlap characteristics are usually stronger bonds than pi molecular

bonds resulting from the overlap of atomic orbitals whose major axes are essentially parallel. Permanent sigma and pi bonds typically form when unpaired electrons with opposite spin and similar binding energies are donated equally by the contributors.

Weaker coordinate bonds form from the overlap of filled p atomic orbitals from a donor atom with empty d or f atomic orbitals on a metal ion. The very weakness of this bond is used advantageously in separation sciences to manipulate the chemical environment of each metal ion by forming and releasing coordinate bonds with a donor substrate. By this means the metal ion can be bound to a solid substrate and released on command or can be solubilized from an aqueous to an organic phase and recovered again.

3.1.2 General Chromatography

Chromatographic processes depend upon the desired metal ions bonding coordinately to donor atoms (hereinafter called ligands). When one donor atom is involved, the term monodentate is applied meaning "one-toothed" because one coordinate bond is formed. When a given molecule possesses two donor atoms spaced geometrically so that both donor atoms can overlap orbitals with the metal ion, a ring is formed which incorporates the receptor ion. The stability of the complex is greatly improved by ring closure. These ligands are called bidentate or "two toothed" for obvious reasons. The term chelate (from the greek language meaning claw) is also used to designate a molecule which possesses two arms with a donor atom on the tip of each arm. The two arms close on the metal ion like a claw, therefore the name. The most stable chelate rings are composed of 5-8 members with 6 being most common. A smaller ring endures steric strain in obtaining ring closure, and a larger ring cannot maintain simultaneous complexation of both ligands as easily.

Each complex which forms is a unique chemical compound. Properties such as solubility, electro or nucleophilicity, ionic charge, etc. can be used to differentiate a particular complex from other ions or complexes in solution. The concentration of a given complex in solution depends upon:

- * The activities of the respective reactant atoms or ions
- * The solution temperature
- * The free energy for the complexation process

Homologous ions such as the alkali metal ions have similar outer shell electronic structures and tend to give similar coordinate binding energies. Separation of major classes of homologous ions (such as alkali metals, alkaline earth metals, 1st, 2nd, and 3rd transition series metals, lanthanides, and actinides) was one of the early triumphs of complexation chemistry. Some success was enjoyed in separating members within a homologous series by exploiting

different oxidation states, however separations between members of the same homologous series in the same oxidation state was considered difficult.

3.1.3 Ion Specific Chromatography

3.1.3.1 Crown Ethers (Poly-Oxo)

Separation of ions within a homologous series became easier when it was recognized that ligands may be synthesized which are sensitive to the ionic radius of a metal ion. An example of this class of ligands are the crown ethers. A primary crown ether is created by repeating O-CH₂-CH₂ segments sequentially in a chain structure which is allowed to cyclize into a ring. The monocyclic ring (commonly referred to as a coronand) can be of varying sizes depending upon the number of segments incorporated into the ring structure. The ring is named by stating the total number of atoms in the ring, the letter C for crown, and the number of ligands in the ring. An example of a common crown ether (the 18-C-6 ring) is given below.

Figure G-9.1 Crown 18-C-6 Monocyclic Ether

For simplicity's sake, the two hydrogens attached to each carbon have been omitted. It is seen that each ring forms a cavity and that metallic ions can be inserted into the cavity and will be complexed by unpaired electrons from each oxygen. Ionic specificity is determined by the following parameters:

- * The match between the ionic and ring radii.
- * The choice of ligands incorporated into the ring such as oxygen, nitrogen, sulfur, and phosphorus.

3 of 5

- * The displacement of solvo molecules.
- * The flexibility of the ring structure which may or may not allow the ring to conform to the ion surface.
- * The substituents attached to the ring.

Other ring structures have also been synthesized which contain features more complex than the repeating ether structure; however, most coronands which have been synthesized are of this type.

Studies (Ref. 1) have shown that the equilibrium complexation constant increases by one to two orders of magnitude when a straight chain homolog is cyclized into a ring structure.

Figures G-9.2 through G-9.5 are presented to reveal some of the factors which affect the complexation of metal ions by these crown ethers.

Figure G-9.2. Equilibria for 15C5 in Water

This figure shows that lithium is not significantly complexed with the coronand 15C5 in water, however the rest of the alkali metal ions are complexed to approximately the same degree. Due to the small ionic radius of lithium ion (0.76 Å), and the corresponding high positive electrostatic field near the surface, waters of solvation are tightly complexed and not easily exchanged. The low equilibrium constants and the lack of specificity within the remaining alkalis is an indication that the cavity within the coronand 15C5 is not large enough to properly incorporate such large cations. The alkaline earths have higher complexation constants than the alkali ions because of their higher charge, however they are still not differentiated significantly because none are sterically fitted to this small ring. The 3rd transition metal ions follow the alkaline earths closely since their charge and dimensions are very similar.

Figure G-9.3 is presented next for the coronand 18C6.

Figure G-9.3. Equilibria for Coronand 18C6 In Water

The coronand 18C6 provides much stronger complexing of the alkali metal ions and also demonstrates good selectivity. This selectivity is an indication that the ring size is a good match for the alkali ions. The best fit is apparently obtained for potassium at 1.38 angstroms. The better steric fit (of 18C6 compared to 15C5) is not limited to alkali ions but is also true for the alkaline earths. The alkaline earths have ionic radii in the same general range and because of their higher positive charge, have correspondingly higher complexation constants.

Two metals from the 3rd transition series, Mercury (+2) and Thallium (+1) are also plotted. The absolute value of the complexation constants show an increase as 18C6 is substituted for 15C5 however the percentage of increase is not as high as for the alkali and alkaline earth ions. This is an indication that the steric fit for these transition metals is not as good as for the alkali and alkaline earths.

The degree of complexation by solvo molecules plays an important role in the equilibria established by competing ligands. Solvents with weak complexing power such as methanol are not very competitive and as a consequence the equilibrium constants of more competitive ligands rise in such solvents. Figure G-9.4 gives a comparison of complexation of alkali ions by 18C6 in water and methanol.

Figure G-9.4. Equilibria for 18C6 in H₂O and MeOH

The equilibrium constants for 18C6 are increased by approximately 10,000 in methanol. This phenomena is generally true for all other metal ions and coronands, however the absolute values of the constants vary to some degree.

If two or more rings are connected by a bridge-head, such as nitrogen, a 3 dimensional cavity (called a cryptand) can be created.

Figure G-9.5 gives the structure for the cryptand 2.2.2.

Figure G-9.5. Structure of Cryptand 2.2.2

This structure is very similar to the coronand 18C6 however two bridgehead nitrogens have been substituted for oxygens at the equator and an eight membered chain containing two oxygens connects the bridgehead nitrogens. The 3 dimensional bonding increases the equilibrium complexation constants by factors ranging from 3 to 15 orders of magnitude. Once bonded most metal ions are held securely in place and are "buried in the crypt" hence the name.

For the alkali metals and alkaline earths, the increase in complexation constants for the cryptand over the coronand homolog is approximately 1000. Similar increases are seen for the lanthanides, and the 1st and 2nd transition series. The complexation constants for mercury and lead from the 3rd transition series are increased by 10 to 15 orders of magnitude. The factors causing such a tremendous increase are not well understood but this result appears very useful for removing these hazardous species from waste waters.

The ionic specificity is much higher in cryptands than in coronands because the correspondence between cavity size and complex stability is more pronounced. Figure G-9.6 illustrates the ionic selectivity which can be obtained between the alkalis in 95% MeOH.

Figure G-9.6. Cryptand 2.2.2 and Alkalis In 95% MeOH

This figure clearly shows the tremendous complexation of alkalis which can be achieved by the cryptand 2.2.2 in 95% MeOH. It also shows the distinct differences which can be achieved in the complexation constants of adjacent alkali metal ions.

Figure G-9.7. Equilibria for Cryptand 2.2.2 In Water

One sees from Figure G-9.7 that the complexation constants are very large for cryptands compared to coronands, and the constants are not as large in water as in methanol. The differentiation between adjacent members is also not as large.

Comparisons of $\log K$ for Mn^{+} -cryptand interaction in aqueous solution vs. the ionic radius of Mn^{+} show interesting effects. The monovalent alkali metal ions show the lowest complex stability with the cryptands, but exhibit a moderately strong stability dependence on cation size. Complexes formed by the alkaline earth cations are more stable. The bivalent transition- and post-transition-metal cations, which fall in a lower range of ion sizes than the alkaline earth metal ions, form complexes of highest stability and show the greatest dependence of $\log K$ on cation size. However, this trend is not sustained in the case of trivalent lanthanide cations which form complexes which are comparable in stability to those of the alkaline earth cations and whose stabilities show almost no dependence on the cation radii. $\log K$ values for the reaction of Eu^{2+} with 2.2.1 and 2.2.2 are larger than those for the corresponding reactions involving Sr^{2+} by 2.5 and 5 $\log K$ units, respectively, despite the fact that these cations have nearly identical ionic radii.

3.1.3.2 Crown Ethers (Polyamines)

Substitution of sp^3 nitrogen for ether oxygen in the coronand ring reduces the affinity of the ligand for the alkali and alkaline earth metal ions. A large number of monocyclic

polyamines having three to six functional groups in the ring have been synthesized. A majority of these have four functional groups more or less evenly distributed in a ring consisting of 12 to 16 atoms.

Most monocyclic polyamine macrocycles form metal complexes in which four almost equivalent nitrogen atoms are coordinated in a single plane about the metal ion and two other groups are bound in the axial sites above and below the plane. Relatively few log K values are available for metal ion binding to macrocycles of this type. Some log K values for saturated macrocyclic polyamine ligands with 5 to 6 nitrogen donor atoms and ring sizes of 15 to 18 members are available. These ligands are particularly effective for complexing bi-valent transition metal ions.

3.1.3.3 Crown Ethers (Polythio)

Coronands containing three, four, six, and eight sulfur atoms substituted for oxygen in the ring have been reported. The configuration of the metal ion-coronand complex is a function of the ring size and of the number of sulfur atoms in the ring. For example, a tridentate macrocycle gives a sandwich-type 2:1 (ligand:metal) complex with Ni^{2+} . Sexadentate ligands with 18-20 ring members have four of the sulfur atoms in a plane with the metal atom and two other sulfur atoms occupying positions above and below the plane. The nickel complex of an octadentate ligand contains two Ni^{2+} ions. Stoichiometry of 4:1 (ligand:metal) for two palladium and platinum complexes is reported indicating bridging by the sulfur donor atoms. Binding constants for the reaction of Cu^{2+} with a number of cyclic polythio ligands in 80% methanol have been determined.

3.1.3.4 Crown Ethers (Mixed Donors)

Many coronands have been synthesized with a mixture of oxygen, nitrogen, and sulfur donor atoms. Substitution of nitrogen for some of the oxygen atoms in coronands such as 18C6 and B218C6 results in macrocycles which have less affinity for potassium than did the parent macrocycle. Log K values in these cases decrease in the order of decreasing electronegativity of the substituted group, $\text{O} > \text{NR} > \text{NH}$. However replacing oxygen donor atoms by nitrogen results in increased K values for Ag^+ complexation. The different stability orders in the cases of K^+ and Ag^+ are likely a reflection of different types of bonding in the complexes of these cations; K^+ binding being primarily electrostatic whereas Ag^+ binding may involve both electrostatic and covalent contributions.

Substitution of sulfur for oxygen in several crown-3, crown-4, crown-5, crown-6, and crown-8 macrocycles produces dramatic effects on K values for metal ion-ligand interaction. In aqueous solution, little or no reaction occurs between the sulfur-containing macrocycles and

either alkali or alkaline earth metal ions. Compared to the oxygen-containing macrocycles, the stabilities of metal complexes with Ag^+ and Hg^{2+} are enhanced markedly and those with Tl^+ and Pb^{2+} are reduced by sulfur substitution. For many of the cyclic thioethers, Ag^+ and Hg^{2+} complexes have 1:2 (cation:ligand) stoichiometries. However, Tl^+ and Pb^{2+} give 1:1 complexes. If the donor sulfur atoms were to point into the ring cavity, the size of the cavity would be decreased considerably. However, X-ray studies indicate that even for crown-4, crown-5, and crown-6 rings, sulfur atoms are directed away from the cavity. Hence, binding of sulfur-containing crowns to Ag^+ and Hg^{2+} may not be of the inclusion type. Formation of 2:1 (metal:ligand) complexes in these systems points to the above possibility.

3.1.3.5 Crown Ethers Substitution on the Ring

Addition of benzene groups to 18C6 alters the cation selectivity of the ligand. The K value for the formation of the Ba^{2+} -18C6 complex in methanol solvent is larger than that for formation of the K^+ complex by a factor of 10. On the other hand, B218C6 (where B stands for the benzyl group) displays the opposite preference, binding K^+ better than Ba^{2+} in methanol by approximately the same amount. The change due to aromatic substituents may be attributed to some combination of ligand bulkiness leading to the isolation of the cation from the solvent, and the electron-withdrawing power of the benzo group(s) which weaken the electron-donor ability of the oxygen atoms resulting in a weaker metal-ligand interaction.

3.1.4 Actinide Extractants

Because of the danger of criticality reactions in chemical processing operations, and the special restrictions and expense involved with (TRU) waste, their extraction from the wastes will be discussed. Both group and ion specific separations are possible.

3.1.4.1 Un-ionized Oxygen Donor Extractants - Non-Phosphorous

Un-ionized extractants with the oxygen donor atom attached to one or two carbon atoms are historically important and are still occasionally used. Examples are:

- * Diethyl ether $(\text{C}_2\text{H}_5)_2\text{O}$
- * Methyl Isobutyl Ketone $\text{CH}_3\text{OCH}_2\text{CH}(\text{CH}_3)_2$

The ethers and ketones were used without diluents. Hexone in equilibrium with dilute aqueous nitrate systems was the most widely studied. With S representing the hexone molecule and the subscripts A and O representing equilibrated aqueous and organic phases, the stoichiometries of extraction for U(+6) and Pu(+6) are represented as:

These reactions are not used industrially today because of the flammability of the solvents and the amount of salting required to obtain good extraction coefficients.

3.1.4.2 Neutral Mono-Phosphorous Based Extractants

In most applications these extractants are used in a diluent, generally a saturated hydrocarbon. The organic solvent containing the extractant is equilibrated with an aqueous dilute nitric acid solution containing the actinides.

Examples of such extractants are:

- * Tributyl Phosphate ((C₄H₉O)₃PO) or TBP
- * Dibutyl Butyl Phosphonate ((C₄H₉O)₂(C₄H₉O)PO) or DBBP
- * Trioctyl Phosphine Oxide ((C₈H₁₇)₃PO or TOPO

Illustrative extraction stoichiometries for the various actinides may be represented as:

It is seen that in each case the actinide adds enough nitrate to form a neutral complex and then several TBP molecules to gain solubility in the organic phase. Other neutral phosphorous complexants follow the same pattern as TBP.

The strength of the coordination bond varies with each actinide, its oxidation state, and the particular ligand which forms the coordination bond, and since the actinide ion must compete with other metal ions including hydrogen ion, considerable selectivity may be exerted through the choice of these variables. As an example, the extraction of Pu(4) may be favored at the expense of Am(3) by choosing an extractant such as TBP which does not have high extraction coefficients, by adjusting the oxidation state of all Pu to +4 to maximize the Pu complexation strength, and adjusting the acidity to a value of 2 to 3 molar where the acid competes effectively with Am(+3) but not Pu(+4) for the TBP ligand.

TBP has been used very widely in the nuclear process industry because it is widely available, inexpensive, quite stable, and relatively non-flammable; its extraction coefficients are

moderate which makes it ideal for processing rich feeds, and the solubility of its complexes in the organic phase are quite high. Use of large concentrations of an extractant whose actinide complex has a low solubility in the organic phase can lead to a phenomena called third phase formation. Third phase formation is not desired because it can interfere with column operations and is somewhat similar to gunpowder in explosive strength.

Although these extractants have been widely used in the nuclear process industry for processing rich feeds, their utility is not as high for extracting actinides from wastes because their extraction coefficients are not high enough to insure complete separation of all actinide species from these wastes.

3.1.4.3 Amine Extractants

Extraction systems using primary, secondary, and tertiary amines and quaternary ammonium salts have been reported. In general, the aqueous phase contains excess mineral acid so the amine extractant is present in the organic phase as a substituted ammonium salt. The stoichiometry is complicated by the tendency of the amines and of their mineral acid salts to form polymeric aggregates.

In general it is assumed that the extracted metal is present in the organic phase as a negatively charged complex which is neutralized by the substituted ammonium ion. No bonding of the nitrogen atom of the amine to the extracted metal atom is assumed. For example, the extraction of UO_2^{+2} from an aqueous nitrate phase by a solution of trioctylammonium nitrate in o-xylene has been represented as:

where TOA represents trioctyl amine.

The extractability of Pu by amines from both nitrate and sulfate acid solutions varies with oxidation state in the order $\text{Pu}(4) > \text{Pu}(6) > \text{Pu}(3)$. Extraction from nitrate solutions was considerably higher with quaternary and tertiary than with secondary and primary amines. From sulfate solutions, it was highest with primary amines.

When no salt was present, $\text{Pu}(4)$ extraction coefficients vs nitric acid concentrations went through maxima, near 2 M HNO_3 with tertiary amines and near 8 M HNO_3 with the quaternary, secondary, and primary amines tested. Most, but not all, systems showed higher extraction coefficients when most of the nitric acid was replaced by nitrate salt. The measured dependences of extraction coefficients on amine concentration varied from first to about fourth power; it is doubted that these dependences correspond directly to the ligand numbers. $\text{Pu}(6)$

and Pu(3) extraction coefficients increased with increasing nitric acid concentration to at least 8-9 M HNO₃, but even these were much lower than the corresponding Pu(4) coefficients. In the presence of 2 M Al(NO₃)₃ (i.e., 6 N) and <0.5 M HNO₃, however, Pu extraction coefficients from Pu(3) solution were 10-100 with 0.12 M tertiary amine, suggesting oxidation to Pu(4) even in the presence of holding reductants.

From sulfate solutions, Pu(4) extraction coefficients are extremely high with 0.1 M primary amine. The coefficients varied with the third power of the amine concentration, and inversely with the first power of sulfuric acid concentration in unsalted solution. They were increased by replacing sulfuric acid with sulfate salt. Pu was also extracted from reduced sulfate solution, even in the presence of much ferrous ion. The extraction probably involves some oxidation.

Extracted Pu nitrate was stripped with "water" (very dilute nitric acid) only when tertiary amine concentration was low; stripping was more effective with a reductant or a complexer such as sulfate. Extracted Pu sulfate was stripped by displacement with nitrate.

3.1.4.4 Acidic Extractants with Oxygen Donors

Extractants of this type are generally assumed to extract through chelate formation. But in nearly all cases the chelation has been assumed but not proved. It is assumed that the anion of the extractant becomes attached to the metal atom being extracted through two oxygen atoms, thereby forming a ring of which the metal atom is one member. In a system using a monoprotic extractant HY which is monomeric, the extraction of M⁺P may be represented as:

Beta diketones- Acetyl acetone, CH₃C(O)CH₂C(O)CH₃ is historically important as an extractant. In most studies it has been used without a diluent. For many applications it has two disadvantages—its relatively high solubility in water and its relatively small tendency to ionize to the enol anion.

Thenoyltrifluoroacetone (HTTA) does not suffer from these disadvantages. This extractant is widely used by nuclear scientists in effecting separation and purification of actinides. HTTA and other B diketones coexist in keto and enol forms and as enol anions. The equilibrium may be represented, without regard to hydration and internal hydrogen bonding as:

That is,

These equilibria are not established rapidly, and the equilibrium constants depend upon the system employed.

The extraction of M^{+P} from an aqueous mineral acid phase into a benzene solution of HTTA has been represented for actinides as:

(X)(Y)PO(OH) Extractants - The two most widely studied examples of this type of extractant are dibutyl phosphoric acid, $(n\text{-C}_4\text{H}_9\text{O})_2\text{PO}(\text{OH})$ and di(2-ethylhexyl) phosphoric acid, $(2\text{-C}_2\text{H}_5\text{-C}_6\text{H}_{12}\text{O})_2\text{PO}(\text{OH})$. In each of these $\text{X}=\text{Y}$ and two C-O-P linkages are involved. But X may differ from Y, and either or both may be attached to the P atom through a C-P bond.

The $\text{PO}(\text{OH})$ group, present in each of these compounds, is formally analogous to the carboxylic group $\text{CO}(\text{OH})$. But it differs from the carboxylic group in two important respects:

- * it is far more acidic,
- * it participates in hydrogen bonding to a far greater degree.

Simple carboxylic acids in a suitable diluent form dimers through the joining together of the carboxylic groups to create an 8-member ring containing 2 carbon, 4 oxygen, and 2 hydrogen atoms. But the hydrogen bonding is relatively weak, and consequently the presence of a monomeric form of the acid may be demonstrated.

Dimerization of a compound containing the $\text{PO}(\text{OH})$ group may be explained similarly, the assumption being that two $\text{PO}(\text{OH})$ groups join together to form a similar 8-member ring, but the hydrogen bonding is so strong that the monomer is virtually nonexistent.

Extraction of +3 actinides by HDEHP is presented as:

where HY represents the monomeric form of HDEHP.

Similarly the extraction of U(+6) is presented as:

(X)PO(OH)₂ Extractants - Extraction with these complexants may be represented as follows:

For trivalent actinides Peppard (Ref. 2) reported:

3.1.5 Actinide Extractants for Waste

Almost all of the above extractants exhibit moderate distribution coefficients and are useful in processing rich feeds. Waste processing requires extractants which have much higher equilibrium complexing constants and higher distribution coefficients to efficiently remove small amounts of actinides from large waste feed streams.

3.1.5.1 Extractants for Acid Solutions

Carbamoyl Methylene Phosphinates

The following structure:

has proved fundamentally useful in actinide extractions from aqueous acid solutions. Both oxygens bond coordinately to the actinide ions forming a six-membered ring. This bidentate bonding gives very high complexation stability constants. Hydrogen ions do not compete nearly as effectively for the ligand since hydrogen can only bond monodentately because it possesses only one empty orbital.

Many R substituents have been tested but two seem to have come to the foreground. The first, Diethyldihexylcarbamoylmethylenephosphine oxide, (DHDECMP) has the following structure.

Early synthesis methods produced an impure product and as a result early tests were somewhat nonreproducible. Recently Occidental Petroleum has perfected a synthesis which produces this compound in extremely high yield.

A second compound octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) is shown below:

CMPO has been the extractant of choice for the proposed TRUEX process. Marsh (Ref. 3) compares these two extractants and gives Figures G-9.8 and G-9.9.

Figure G-9.8. Am Extraction with CMPO and DHDECMP

One sees from Figure G-9.8 that the extraction of Am(3) with CMPO does not vary significantly with acid molarity. This is a positive feature if one needs to extract Am from dilute acid; however, it is a negative feature if one needs to back extract the Am since a simple nitrate molarity adjustment does not suffice.

The extraction of Pu(4) and U(6) is shown in Figure G-9.9:

Figure G-9.9. Pu(4) and U(6) Extraction with 0.25 M CMPO and 0.75 M DHDECMP and 1M TBP

One sees from this figure that the extraction coefficients are again higher in CMPO than DHDECMP, however the invariance of extraction coefficients with acid molarity again means that CMPO will be difficult to strip with a simple nitrate molarity adjustment.

Factors which favor the use of DHDECMP are wastes which are already rich in nitrate, chlorides, and uranium as compared to Am or Pu. Factors which favor the use of CMPO are wastes which are lean in nitrates or chlorides and where Pu may be the principal actinide specie.

Addition of relatively large amounts of TBP is necessary to increase the solubility of CMPO and DHDECMP and to prevent 3rd phase formation.

3.1.5.2 Actinide Extraction from Neutral Solutions

Various measurements show that Pu exists primarily in the +5 oxidation state in neutral solutions. Extraction of this PuO_2^+ ion has proved very difficult from groundwater because of the formation of the very stable tris carbonato complex. A new class of organic extractants has recently been synthesized and is shown below:

Figure G-9.10. Structure of PuO_2 Complex

hydrogen bonding between the polar oxygen and the hydrogen which is attached to the nitrogen. This structure is very similar to that exhibited by the cryptands which were discussed earlier in the crown ether section. Ion specificity is gained by adjusting the length of the R segments to fit the PuO_2^+ or PuO_2^{++} ion exactly. The value of x in the carbon chain is 2 or 3.

It is quite possible that the ether oxygens are also coordinating to the metal atom forming a 6-membered ring. In any case the stability of this complex is very high and Pu(5) is readily extracted from the tris carbonato complex found in ground or seawater.

Various organic structures may be designed into the carbon chain to make the entire complex either aqueous or organic soluble. This provides flexibility in the chromatographic applications.

3.1.6 Attachments of Ligands to Substrates

3.1.6.1 Absorption Into Resin Beads

Macroreticular resins are resins which are synthesized in the presence of tiny droplets of a water insoluble alcohol. These water immiscible droplets are incorporated into the resin bead structure and are responsible, upon drying, for void spaces in the resin interior which gives the resin a high internal surface area and provides for very high internal diffusion coefficients. These same resins can either contain a functional group (causing them to function as ion exchange resins) or may not contain a functional group. In the latter configuration the resin is used as an organic absorbent. One use is to absorb water soluble organic substances of relatively low molecular weight from aqueous systems. Another use is to absorb and fix organic complexants for chromatographic applications. Amberlite XAD-4 resin is a commercial example of such a resin.

The highly aromatic, and consequently hydrophobic, structure of Amberlite XAD-4 imparts to it an affinity for the hydrophobic portion of organic molecules. The adsorption of these species onto the resin occurs, not through ion exchange, but through van der Waals' interactions, the binding ability of which is a function of the relative hydrophobicity of the solute, the solvent and the adsorbent. To better understand the phenomena through which the resin functions, consider the individual beads to be an agglomeration of a large number of very small micro-spheres, fused together into a spherical agglomerate.

The macroreticular structure results in a continuous solid phase as well as a continuous void, or pore, phase so that water, or other solvent, can very readily penetrate the pores. This type of structure results in a very high surface area in each bead. In adsorption, that portion of the organic molecule with less affinity for water (or other polar solvent), that is, the hydrophobic portion, is preferentially adsorbed onto the hydrophobic surface of the adsorbent,

the organic molecule with less affinity for water (or other polar solvent), that is, the hydrophobic portion, is preferentially adsorbed onto the hydrophobic surface of the adsorbent, while the hydrophilic portion of the molecule remains oriented in the aqueous, or solvent, phase which fills the pore volume of the bead.

The selectivity and extent of adsorption of the organic by the resin increases as the hydrophobicity of the solute increases. For this reason molecules such as DHDECMP, CMPO, or the crown ethers load very well on these resins and are not removed to any appreciable extent by aqueous loading or stripping operations.

Because of the high concentrations of extractant which can be achieved in these resins, very high adsorption coefficients for adsorbed ions have been found. Figure G-9.11 gives adsorption coefficients for actinides for a CMPO loaded resin.

Figure G-9.11. Adsorption of Actinides on CMPO Resin

The capacity of the resin is important as well as the equilibrium distribution coefficients. The capacity is a function of the loading of the organic complexant on the resin. Best results are obtained when the complexant is forced on the resin by a water-alcohol mixture during the loading step.

3.1.6.2 Silica-Gel Bound Ligands

The procedure for the attachment of crown ligands to silica gel is shown as follows:

By attaching the crowns to silica gel the expensive crowns are not leached and lost during the chromatographic process. This enables one to reuse the crowns through many, many column cycles. The key to making this a useful concept is to maximize the ligand density on the silica gel and therefore in a corollary sense the distribution coefficient of the gel for the adsorbed ion. To be useful industrially the adsorbent must meet or exceed the ratio defined as follows:

$$V_{\text{feed}}/V_{\text{column}} > 50 > K_d \cdot W_R$$

Where V_{feed} is the volume of feed which can be passed through the column before the final concentration equals the initial concentration.

V_{column} is the volume of adsorbent material

K_d is the distribution coefficient

W_R is the mass of one column volume of adsorbent

To maximize the ligand density and therefore the K_d value, one must use a silica gel with a high specific surface area.

The process described in Figure G-9.12 for attaching a crown ether to silica gel is a general syntheses procedure and can be used to attach any organic ligand to silica gel. Further research is necessary to demonstrate this for CMPO or DHDECMP.

Figure G-9.12. Attachment of Crown Ethers to Silica Gel

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Pretreatment requirements depend on the waste stream contaminants, the contaminants to be removed, and the ligands used in the chromatography column.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

3.3.1.1 Current Vendors

Commercial vendors are limited for these products since so many are just now being reported in the literature from bench scale tests.

The only commercial vendor for these products that we are aware of is EICrom Industries Inc. of Evanston Ill. EICrom is a small-business entity involved in the commercialization of unique, patented technology developed at Argonne National Laboratory.

3.3.1.2 Status of Separation Methods In Development

3.3.1.2.1 Crown Ethers

Literally hundreds of crown ethers have been synthesized and bench tested. None have been used industrially for large scale applications yet, however at least one has been offered by EICrome Inc. for radioactive strontium removal from wastes. This lack of industrial application stems from the fact that the technology is so new and because of the relatively high cost associated with synthesis of the crowns. By binding the crowns to silica gel and allowing this cost to be amortized over a longer operating lifetime, the cost factor may be reduced.

3.3.1.2.2 Actinide Extractants

Actinide extractants have been widely used for 40 or more years on an industrial scale. Only monodentate extractants have been used in the industrial liquid/liquid solvent extraction cycles for the actinides. The large scale extraction of actinides from wastes is a very new application. Bidentate extractions have been demonstrated on a bench scale but have not been applied industrially.

3.3.1.3 Availability of Equipment

3.3.1.3.1 Liquid/Liquid Solvent Extraction

Historically industrial solvent extraction began with batch contactors but quickly shifted to continuous column operations when they became available. One of the most popular has been the pulsed column. A new technology is emerging called centrifugal contactors. Centrifugal contactors perform the same overall function as columns but occupy much less

space and are very fast. Because of their mechanical and electrical complexity, it is by no means certain that their development is advanced enough to provide the reliability needed to replace column technology in the plants.

3.3.1.3.2 Liquid/Solid Solvent Extraction

Ion Exchange solvent extraction is considered a mature industry. More recent applications, such as the EIChrome type resins or the silica gel supported ligands, have been bench scale tested, appear very promising and are ready for large scale tests.

3.3.2 Reliability

Equipment and process reliability are expected to be excellent for these applications.

3.3.3 Secondary Waste Streams

Secondary waste streams are the solvents and liquid complexants for liquid/liquid extraction processes. Some of these are routinely lost to the aqueous acid waste stream due to limited solubility in the aqueous phase and due to inadequate phase separation. Radiolytic and/or chemical degradation products of the solvent and the complexant are found in the aqueous waste stream. Also, chemicals placed in the feed stream to maximize the complexation process, to assist the stripping cycle, or to clean the solvent are also found in the secondary wastes.

3.3.4 Separation Efficiency

Removing trace quantities of hazardous materials from large waste masses is a far greater challenge than the industrial processing of relatively rich feeds. Fortunately the new bi and multidentate extractants are designed to increase the efficiency and degree of the separation processes. Distribution coefficients ranging from 400 to 600,000 are readily available.

3.3.5 Safety and Health

No safety or health issues are prominent in the use of these technologies that are not germane to the hazardous nature of the feed materials.

3.3.6 Operational Complexity

These are simple unit operations which are founded on many years of industrial experience. They are not considered operationally complex.

3.3.7 Glovebox Compatibility

These types of operations have been operated in sealed cells or gloveboxes since the inception of the nuclear industry.

3.3.8 Environmental Impact

No environmental impacts have been identified.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

The plant equipment to implement these technologies is standard equipment. The only development costs would be associated with continued R&D to develop new and more efficient ion selective adsorbents. This R&D effort should be continuously funded for the next several years.

No Capital cost estimates have been developed for this application. An estimate will be forthcoming.

No operating and maintenance cost estimates are available at this time.

3.5 TECHNOLOGY COMPARISON

This technology is similar to supported liquid membranes described in Appendix H-5. Comparison with other separation technologies will be performed at a later date.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Distribution coefficients are required for separating the sought for ions from the waste matrix as a function of acidity, temperature, and reagent types and concentrations.

Stability of the extraction systems is required to measure their useful lifetimes.

Synthesis costs are required to accurately project the economics of some of these chromatographic processes.

Some data will be available from ElChrome Inc. However much of this data will have to be drawn from operating experience at the various DOE sites.

4.2 TESTING REQUIREMENTS

Complete pilot scale tests should be initiated on any of these advanced ion specific chromatographic processes to gain more industrial scale experience. These tests should begin as soon as possible.

5.0 VENDOR LIST

ElChrome Industries Inc.
Evanston Ill.

Ion Selective Consultants

Rohm and Haas
Philadelphia Pa.

Resins supplier

6.0 REFERENCES

1. Izatt, R.M., J.S. Bradshaw, S.A., Nielsen, et al. "Thermodynamic and Kinetic Data for Cation-Macrocyclic Interaction." *Chem Rev.* 1985, 85, pp 271-339.
2. Peppard, D.F. "Liquid-Liquid Extraction of the Actinides."
3. Marsh, F.S. and S.L. Yarbrough. "Comparative Evaluation of DHDECMP and CMPO as Extractants for Recovering Actinides from Nitric Acid Waste Streams." LA-11191. Los Alamos National Laboratory, February 1988.
4. Bradshaw, J.S., J.E. Krakowiak, et al., "Silica gel-bound Aza-Crowns for the selective removal and concentration of metal ions." *Pure & Appl. Chem.* Vol 61, No 9, 1989, p 1619.
5. Raymond, K.N. and T.S. Franczyk. "Specific Complexation of Metal Oxo Cations." U.S. Patent A7628256.
6. Horner, D.E. and C.F. Coleman, "Plutonium Extraction from Nitrate and Sulfate Solutions by Amines and Organo-phosphorous Compounds." ORNL-3051. Oak Ridge National Laboratory: Oak Ridge, TN.

APPENDIX G-10 BIOADSORPTION

1.0 TECHNOLOGY DESIGNATION

Biosorption refers to the use of biologically-based materials (biosorbents) for the selective adsorption or absorption of specific contaminants from wastewater or contaminated groundwater. Biosorbents are usually made up of non-living biological material (biomass), in the form of whole cells or pieces of cellular material (typically cell walls), which have been trapped or immobilized within a polymer matrix in the shape of a bead, or which have been immobilized on a membrane. Bacteria, algae, fungi, and plants can all serve as sources of biomass from which biosorbent materials can be made.

2.0 NEED FOR THE TECHNOLOGY

The cleanup process necessarily generates large volumes of waste water that may be combined with corrosive solutions and washdown liquids from a variety of sources. Any of these liquids could contain arsenic, cadmium, chromium, lead, mercury, and an unknown number of other hazardous or radioactive elements that eventually must be removed. However, many of these elements have the potential to interfere with subsequent remediation processes due to their toxicity and reactivity. In addition, the radioactive elements may compound the cleanup effort by binding to, and thereby contaminating, otherwise innocuous components of the remediation process. This could actually result in a net increase in the volume of waste, rather than a decrease. The success of the waste treatment may thus be predicated on the removal of these metals from aqueous liquids early in the process, before other chemical or biological techniques are employed.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The bioadsorption process involves the use of biomass from fungi, algae, and bacteria to remove, concentrate, and recover a variety of metals, including uranium. This technology is based on the observation that metals reversibly bind to polysaccharides and other cellular components of bacteria, algae, and fungi. Since this binding does not usually depend upon biological activity, it is often sufficient to use "biomass," a collection of cells and cell wall polymers, which is not necessarily alive, to adsorb and concentrate the metals. Adsorption occurs directly from free solution, and is generally most efficient in solutions that are slightly

acidic. Metals may be removed by washing the biomass with a dilute base, such as sodium bicarbonate. This regenerates the adsorbent, which can be reused many times.

Biosorption technology itself is a specialized type of ion exchange chromatography in which the biological material forms the basis for the resin used in the ion exchange column. The presence of various charged chemical groups on the cells or cell pieces from which the biosorbent material is made makes it possible for the biomass to bind ions. Because the cell walls of different organisms and different species or strains of the same organism are made up of different components, biosorbent materials from different sources are able to bind different target ions, often with high affinity and high specificity.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Algae and fungi can adsorb metals over a very wide concentration range. Bacteria are not as well characterized, but at least two strains of photosynthetic bacteria and one strain that metabolizes ammonia have shown comparable adsorption behaviors. Since the binding is characteristic of the particular biopolymers expressed by the organism, it differs among species and among strains within a species. Thus, the choice of a biomass consortium may be driven by a need to optimize the adsorption of specific metals. Alternately, a collection could be used to provide broad capability.

In most cases, the input stream should not have to be diluted, and the presence of organic solvents will not influence binding. However, since the charge relationship between the metal and biopolymer is important, the pH may have to be adjusted. Uranium, for example, binds best at pH 4.5. The lower concentration limit of binding for most metals has not been well characterized, but adsorption is known to exceed 95% in the microgram per milliliter concentration region.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Biosorption is useful for the removal of heavy metals from contaminated wastewater and groundwater. Biosorbent resins have been developed which can bind uranium, mercury, chromium, copper, zinc, lead, and other heavy metals to varying degrees. It should be noted, however, that many of these biosorbents have not yet been perfected and are not yet ready to be commercialized.

Most biomass is easily grown or collected. The materials can be prepared on site or may be shipped dry over long distances. Unfortunately, vendors of biomass adsorption products have not been identified at this time. That is not to say that they do not exist, since patents

have been granted on processes to remove metals from mine wastes, and to recover uranium from fuel processing operations. There are no unusual requirements for the equipment required to contain the adsorbent, either during use or during regeneration.

Research is proceeding to identify organisms for use in the recovery of many metals, including uranium, manganese, silver, copper, mercury, gold, and thorium. Promising candidates have been found in the genera *Rhizopus*, *Scytalidium*, *Rhodobacter*, and *Rhodospirillum*, among others.

3.3.2 Reliability and Maintenance Requirements

Biomass media, especially when immobilized on a matrix that preserves good flow characteristics and protects the cells from degradation, can be recycled. Once they are saturated, the media can be regenerated by removing metals and metallic oxoanions using either acids or bases. They require the same maintenance as conventional ion exchange systems.

3.3.3 Secondary Waste Streams

Metals are recovered at high concentration in dilute base. In time the binding ability of the biomass will become exhausted, requiring that it be dried and incinerated, or disposed of in some other manner. There may be an appreciable residue of bound metals at that time, the nature of which will depend, of course, upon the nature of the solutions it has encountered.

3.3.4 Separation Efficiency

As a rule of thumb, most biomass will bind between 10 and 20 percent metal, when calculated as a percent of dry mass. This binding may be affected by the presence of other elements, especially metals such as aluminum which lowers the total adsorption of other species. Organisms, however, differ in the extent to which they are sensitive to such competition, and the temperature ranges over which binding is effective. There may also be differences in the extent to which high concentrations of sodium or potassium interfere with the adsorption process.

3.3.5 Safety and Health

The system lends itself to automation. Unless the media need to be replaced, which can be done after regeneration, the operators are not exposed to hazardous materials.

3.3.6 Operational Complexity

Typical installations are frame-mounted, with five or six large cannisters to hold the separation media. Input and output streams are contained within tubing. Operation is not complicated.

3.3.7 Glovebox Capability

There is no inherent reason why the system could not be operated in a glove box.

3.3.8 Environmental Impact

Since this technology concentrates waste, its impact is primarily related to its ability to reduce the volume of hazardous material, and to make eventual storage and containment safer.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Cost estimates have been requested.

3.5 TECHNOLOGY COMPARISON

As a remediation technology, biosorption offers a promising alternative to, and could be more effective than, other technologies such as reverse osmosis and precipitation. Reverse osmosis requires the use of multiple pass units, removes ions other than the target ion(s), and is expensive (especially when the initial metal ion concentrations are low). Precipitation has disadvantages not found with biosorption, such as the production of large volumes of sludge effluents containing high concentrations of salts.

An advantage of biosorbents is that they can be significantly less expensive to manufacture or synthesize than commercially available highly selective ion exchange materials. Biological material such as algae and bacteria are very easy to grow in large quantities.

The binding specificity of biosorbents is a real advantage over other ion exchange media. Biosorbents have been designed which are insensitive to dissolved solids in waste water and are not inhibited by the presence of other ions such as the components of hard water, Ca^{+2} and Mg^{+2} , or monovalent cations, such as Na^{+} or K^{+} . These ions are frequently present in high concentrations in groundwater and are known to inhibit conventional ion exchange resins from binding heavy metals. Biosorbents can also be much more stable and resilient than other ion exchange material with a high resistance to fouling by organic molecules.

Biosorption represents a potential new addition to the field of remediation, although it still requires more R&D and more testing and evaluation to perfect and expand its uses to more contaminants.

4.0 DEMONSTRATION REQUIREMENTS

Requirements for demonstration involve a waste stream containing less than 1% organic content, from which solids have been removed by settling and/or filtration. Adjustments in pH may have to be made to optimize the binding of contaminating metals.

4.1 DATA REQUIREMENTS

In determining whether a particular biosorbent is practical for decontamination of a particular water stream, it must be shown that the biosorbent will bind the contaminant with high affinity and specificity. The biosorbent should only bind the metal of interest, and should do so with a high enough affinity that the effluent coming out of the column meets clean up standards.

Another criterion for a good biosorbent is that the binding be reversible. After the biosorbent has been loaded with metal, it must be able to withstand being stripped of the metal, regenerated, and reused for further decontamination. The more times a biosorbent can be recycled, the less expensive it is to operate since the overall cost of a water purification system is often dominated by the cost of the biosorbent material. Moreover, the best biosorbents are those that can be stripped with the lowest possible volume of stripping solution; the less used the more concentrated is the contaminant metal and the better the overall volume reduction of the contaminant.

4.2 TESTING REQUIREMENTS

This technology has been tested on aluminum, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, uranium, vanadium, and zinc. Tests involving one particular vendor have been performed on uranium and mercury-containing groundwater from Oak Ridge, Savanna River, and Hanford. Units capable of processing in excess of 100 gallons per minute of industrial point source waste have been tested.

5.0 VENDOR LIST

Upon completion of successful preliminary arrangements, units for testing and demonstration can be made available by Bio-Recovery Systems, manufacturers of biological sorption equipment for groundwater and industrial wastes. Their address is: 2001 Copper Avenue, Las Cruces, NM 88005. Contact Tom Powers, (503) 523-0405.

6.0 REFERENCES

None

APPENDIX H MEMBRANES

A wide variety of separations may be achieved using membranes. A membrane is a thin film interposed between two fluid phases, the selective permeation through which is governed by particle or molecular size, chemical or physical affinity to the membrane material, and/or the mobility of the permeating species within the membrane. To achieve separation, work must be done on the system—either chemically, electrically, or mechanically. The purpose of energy input is to provide a driving force for mass transfer. The nature of the driving force is a useful means of classifying the membrane processes described in this appendix as follows:

- * Pressure driven by a pressure gradient - Reverse Osmosis, Ultrafiltration, and Microfiltration
- * Electrically driven by a potential (voltage) gradient - Electrodialysis
- * Chemically driven by a concentration gradient - Supported Liquid Membranes and Pervaporation.

These technologies are described in this appendix are as follows:

- H-1 Reverse Osmosis
- H-2 Ultrafiltration
- H-3 Microfiltration
- H-4 Electrodialysis
- H-5 Supported Liquid Membranes
- H-6 Pervaporation

APPENDIX H-1 REVERSE OSMOSIS

1.0 TECHNOLOGY DESIGNATION

Reverse Osmosis (RO) is primarily used as a method to remove salts from a feed stream containing inorganic ions to produce high purity water and as an economical roughing demineralizer to pretreat feed streams prior to ion exchange.

2.0 NEED FOR THE TECHNOLOGY

Reverse osmosis is a potential secondary treatment technology for removal of dissolved organics, colloids, and dissolved solids. This separation technology is fairly nonselective and may be preceded by solvent extraction or liquid membrane extraction for the selective recovery of actinides or other metals.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

During reverse osmosis, high pressure is applied to the feed stream as it passes over a semipermeable membrane. Provided that the applied pressure is greater than the osmotic pressure of the feed solution, pure water will flow through the membrane leaving behind dissolved salts, organics, colloids, or microorganisms. Typical operating pressures are 200 to 1100 psi. The process produces a concentrated waste stream of reduced volume that requires further treatment or disposal.

Generally speaking, the pores in the skin of an RO membrane intended for removal of salt are larger (e.g., 10-40Å) than the hydrated ions (e.g., Na^+ , Cl^- , Ca^{2+} , SO_4^{2-}) they are intended to repulse. However, these pores are filled with water that is strongly influenced by the polymeric walls of the pores. Such water becomes "ordered" which, because of its ordering, has too low a dielectric constant to dissolve salt ions, in contrast to bulk water. Thus, salt rejection in a useful membrane is based on the lack of solubility of the hydrated ions in the ordered water within the pores, not on the size of the pores. In practice, both water and salts cross the membrane, but at different rates.

Reverse osmosis membranes are manufactured in the form of hollow fibers or flat sheets. DuPont is the principal manufacturer of hollow-fiber modules. This configuration permits very high specific membrane areas to be achieved at relatively low cost. However, hollow-fiber

modules are more susceptible to fouling by suspended matter. Spiral-wound modules are more commonly used in industry because of their better resistance to fouling.

The more common membrane formulations include cellulose acetate or aromatic polyamides. The cellulose acetate membranes tend to be more rugged, less expensive, and more resistant to moderate concentrations of chlorine. They are susceptible to biological attack and to hydrolysis in highly basic solutions.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Feedwater to the RO system must be pretreated to remove particulate and colloidal matter that cause membrane fouling. Typical pretreatment processes include media filtration (e.g. sand) and cartridge filtration at a particle size of 5-10 μm . If the feed is highly turbid, the filtration stage needs to be preceded by coagulation and sedimentation. Chemical pretreatment of the feedwater may also be required for pH control and inhibition of membrane fouling.

Reverse osmosis is best suited for feed streams containing from 3,000 to 10,000 ppm dissolved salt. With proper design, product water with less than 500 ppm total dissolved solids can be achieved in a single stage. Water recovery rates, defined as the ratio of the product flow rate to the feed flow rate, of 30% can typically be achieved in a single stage unit. With multistage arrays, as shown in Figure H-1.1, water recovery rates of 75-88% are possible.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The RO process has been developed and extensively applied for desalination of brackish waters and in treating metal wastes from plating baths. In addition to these more common applications for inorganics and metals, the technology has been applied for treating waste streams of organics and radionuclides.

Removal of organic contaminants from dilute waste streams were reported by the EPA, and pilot-scale testing of an RO unit demonstrated 90-98% removal from the permeate for 1,2-dichloroethane, chloroform, diethyl ether, and tetrahydrofuran. Trichloroethane, benzene, bromoform, hexane, 1,1,1-trichloroethane, and 1,1-dichloroethane showed 99% or greater removal from permeate. PCBs and pesticides were also successfully removed from groundwater in test applications of a mobile RO unit at waste sites in Canada.

RO was also used to treat groundwater containing a mixture of radioactive materials—including uranium and technetium—and nitrate. All contaminants in the effluent stream were reduced to concentrations below MCLs.

Figure H-1.1. Two Possible Multi-Stage Module Arrays for Reverse Osmosis. The top array represents a 75% water recovery system, while the bottom array represents 87.5%.

There are a number of U.S. manufacturers of RO membranes. The major companies are listed in Section 5.0. Membrane manufacturers typically supply small pilot-scale units for testing. Approximately 75% of the membranes sold are of spiral-wound configuration. Other module designs available include tubular, hollow fiber, and plate-and-frame modules.

Most membrane elements are standardized with regard to size and flowrates and therefore are interchangeable. Compared to electrodialysis and distillation, reverse osmosis has the lower energy usage. For treatment of complex feed streams, membrane fouling is likely to be a severe problem requiring chemical pretreatment of the feed in the form of pH adjustment and the addition of antiscalants. Once fouled, membrane cleaning is not always successful and requires a trial and error approach.

3.3.2 Reliability and Maintenance Requirements

RO membrane performance is a function of two major factors: the membrane material and the configuration of the membrane module. Several module designs are available, including tubular, spiral wound, hollow fiber, and plate and frame. Hollow-fiber elements are particularly prone to fouling and, once fouled, are hard to clean. Thus, application of these fibers require a great deal of pretreatment to remove all suspended and colloidal material from the feed stream. Spiral-wound modules, due to their relative resistance to fouling have a broader range of applications. A major advantage of the hollow-fiber modules, however, is the fact that they can pack 5000 ft² of surface area in a 1-ft³ volume, while a spiral-wound module can only contain 300 ft²/ft³.

3.3.3 Secondary Waste Streams

Secondary waste streams would be comprised of membrane wash solutions. With proper feed pretreatment, membrane washing may only be required on rare occasions.

3.3.4 Separation Efficiency

Feedwater to the RO system is pumped first through a micrometer filter, which is usually a replaceable cartridge-element filter, to remove turbidity and particulate matter. A RO system can remove 95% or more of the dissolved solids in raw water, together with suspended matter. The exact percent of product purity, product recovery, and reject water depends on the amount of dissolved solids in the feedwater, the temperature at which the system operates, and the system design including the number of RO stages.

Membranes in RO units are typically impermeable to fine particles and many dissolved species. In general, good removal can be expected for high molecular weight organics and charged anions and cations. Multivalent ions are treated more effectively than univalent ions.

3.3.5 Safety and Health

RO membranes are operated at fairly high pressures. Safety systems would have to be in place in case of a leak in the pressurized system. For example, the high pressure pumps should be located inside a glovebox or shielded cell. The process does not require direct operator involvement but the process does concentrate the radionuclides present in the feed stream. There is the possibility that a non-TRU feed could be concentrated sufficiently to become a TRU stream.

3.3.6 Operational Complexity

As with other membrane processes, there are no moving parts except for the pumps used to feed the liquid solutions across the membrane surface. A number of membrane modules can be stacked in a cascade arrangement to increase water recovery rates.

3.3.7 Glovebox Capability

There should not be any particular difficulty in operating an RO process in a glovebox. Changing membranes and modules should not be difficult to accomplish in a glovebox.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

The cost of electricity for operating the pumps is probably the single highest operating cost for RO. Some of this energy can be recovered with a turbine. The size of a mixed waste plant may not be large enough to justify the capital costs involved in providing for energy recovery.

3.5 TECHNOLOGY COMPARISON

Advantages include low operating costs and low energy consumption because (1) an energy intensive phase change is not required; (2) capital costs are low; and (3) operators only require a low degree of skill. The primary advantage of RO is that this process can be used to successfully treat different types and combinations of contaminants in water to relatively low concentration levels.

Disadvantages are that contaminants are not destroyed by this process but are concentrated to a smaller liquid volume that still requires treatment or disposal. Pretreatment of the influent stream to prevent fouling, plugging, and chemical attack on the membrane is required. This process also requires the use of cleaning solutions that will require treatment or disposal.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Feed stream composition, flow rates, and product specifications must be known at the early stages of flowsheet design.

4.2 TESTING REQUIREMENTS

Testing requirements are to be determined.

5.0 VENDOR LIST

The principal suppliers of Reverse Osmosis membrane manufacturers are listed below:

DuPont
Separation Systems-Permasep
Glasgow Site,
Newark, DE 19714
(302) 999-6781

Desalination Systems, Inc.
1238 Simpson Ave
Escondido, CA 92029
(619) 746-8141

FilmTec Corp.
7200 Ohms Lane
Minneapolis, MN 55435
(612) 835-5475

Fluid Systems
10054-T Old Grove Rd
San Diego, CA 92131
(619) 695-3840

Aqua Man, Inc.
2568 Turquoise Cir.
Newbury Park, CA 91359
(805) 498-5707

Desalination Systems, Inc.
1238A Simpson Way
Escondido, CA 92029
(619) 746-4995

Flowmatic Systems, Inc.
617 D Lakeview Rd.
Clearwater, FL 34616
(813) 461-3077

Fluid Systems Corp.
10054 Old Grove Rd.
San Diego, CA 92131
(800) 525-4369

HPD, Inc.
HPD Place, Box 3032
Naperville, IL 60566
(708) 357-7330

Lifestream Intl. Water Systems
Box 92408
Long Beach, CA 90807
(800) 468-5426

Medro Systems, Inc.
416 E. Industrial
Mckinney, TX 75069
(214) 542-8200

Hydranautics
11111-T
Flintkote Ave
San Diego, CA 92121
(619) 536-2500

Millipore
80 Ashby Rd
Bedford, MA
(800) 225-1380

Mobile Water Technology
2070 Airways Box 14867
Memphis, TN 38114
(800) 238-3028

Osmonics, Inc.
5951 Clearwater Dr.
Minnetonka, MN 55343
(800) 848-1750

Permutit Co.
30 Technology Dr. Cn. 4920
Warrens, NJ 07059
(908) 668-1700

Pollution Measurement Corp.
1013 Lyman Ave.
Oak Park, IL 60304
(708) 383-7794

Polymetrics, Inc.
101 Nicholson Lane
San Jose, CA 95134
(800) 822-7659

Western Filter Co.
Box 16323
Denver, CO 80216
(303) 288-2617

6.0 REFERENCES

1. Stitt, E. H. "Membrane Separation." In *Solid-Liquid Separation*. L. Svarovsky, ed. Butterworth-Heinemann: Oxford, 1990.
2. Cheremisinoff, N. P. and D. S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983.
3. Rautenbach, R. and R. Albrecht. *Membrane Processes*. John Wiley & Sons: New York, 1989.

APPENDIX H-2 ULTRAFILTRATION

1.0 TECHNOLOGY DESIGNATION

Ultrafiltration membranes (UF) have a permeate cutoff that lies between RO and microfiltration (MF). UF methods use pressure to separate the nonionic materials from a solvent, and is particularly effective for the removal of suspended solids, oil and grease, large organic molecules, and complexed heavy metals from wastewaters.

2.0 NEED FOR THE TECHNOLOGY

This technology is a candidate for primary treatment in the main treatment line and can be used for treatment of secondary waste streams. More sophisticated forms of ultrafiltration such as micellar-enhanced UF are candidates for the removal of dissolved organics and metal ions.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

This process uses special membrane material in equipment very similar to that used for reverse osmosis. As with RO, several types of membrane configurations are available that differ in cost, membrane area/volume ratio, and resistance to fouling.

The most common type of UF membranes used in industrial applications is the thin-skinned membrane which allows enhanced flowrates (low friction factors) at given pressure differentials. Lower pressures than those used in RO (generally less than 100 psi) are sufficient to promote permeation, and molecules that differ by a factor of ten in their molecular weights can usually be separated. However, it is the size of the molecule, not its molecular weight, that is the most important factor in determining the separation capabilities of a UF process.

Most UF processes are operated in the cross flow mode. In this process, the influent (or feed stream) is separated into two effluent streams: the "permeate" or clean stream, and the "concentrate" which retains all of the suspended solids rejected by the membrane. Only the permeate actually passes through the membrane. The feed and concentrate streams flow parallel to the membrane surface, resulting in the term "crossflow." In this type of element, the solids are swept away with the concentrate, eliminating or greatly reducing the potential for the element to plug. The membranes are typically polymers although a few membranes prepared from ceramic materials can be found. Concentration polarization, plugging, and fouling are

factors that degrade membrane performance. To reduce concentration polarization, the membrane modules are operated under turbulent flow, at high Reynolds numbers. Membrane fouling refers to the degradation of membrane performance due to adsorption of material onto the membrane surface. Fouled membranes require chemical cleaning to restore their flux. This leads to secondary waste streams to be either treated further or disposed of as is.

UF filters have screen or sieve-type retention properties that provide for absolute removal of particles of a specific size. In this case, the particle is simply too big to pass through the pore, so it becomes trapped on the top surface of the membrane acting as a sieve or screen. To achieve the desired absoluteness of removal from sieve retention, the largest pores of the filter selected must be smaller than the smallest size particle of the particle size distribution. In practice, this is not always possible to do with assurance because the particle size distribution is usually not known. Membrane filters are selected because they have a narrower pore-size distribution than other types of filters, and they are selected based on their pore size relative to whatever is known about the particle size.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

UF is applicable to wastewaters that contain contaminants in particulate form. For example, plutonium is often present as particulates, and ionic contaminants may also be removed if they are first complexed to high molecular weight compounds. Dissolved metals and radionuclides can also be removed by this process if they are first precipitated in a pretreatment process step.

If oil-in-water emulsions cannot be separated by water-wetted MF filters, then UF becomes appropriate and the pore size is selected to reject the dimensions of the emulsified oil droplets. UF is also used to remove particles and high-molecular-weight species from water prior to hollow-fiber RO desalination.

The contaminants to be removed using UF methods are larger in size and may first be chelated to a high molecular weight compound to allow them to be removed by filtration. The membrane material used has a much larger pore size than reverse osmosis membranes. Operating pressures are much lower, typically 50 to 100 psi versus 200 psi and above for reverse osmosis.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Ultrafiltration is used for the removal of suspended solids and emulsified oil from waste waters, and can be combined with chemical treatment for the removal of dissolved radioactive

elements. In this capacity, ultrafiltration processes are proving to be very effective for the treatment of alpha-bearing wastes (Ref. 3). The addition of inorganic absorbers (such as hydrous titanium oxide and polyantimonic acid) to aqueous streams containing Pu and Am, followed by ultrafiltration, was able to produce permeates with activities as low as 5×10^{-5} Bq/mL (Ref. 3).

Micellar-enhanced ultrafiltration has also been investigated as a means of removing dissolved organics and metal ions from aqueous streams (Ref. 1, 2). The separation approach involves the addition of a surfactant to the waste stream at a concentration high enough to produce micelles. Partitioning of the target pollutant compounds or metal ions to the micelles results in their removal when the solution is passed through an ultrafilter having a pore size smaller than the micelle diameter. Obviously, solutes having high partition coefficients for the surfactant micelles are more effectively removed than more soluble solutes having low micelle partition coefficients. A schematic of the micellar-enhanced ultrafiltration process is shown in Figure H-2.1.

Figure H-2.1. Schematic of Micelle-Enhanced Ultrafiltration (from Ref. 1)

(Reprinted from Ref. 1, pg. 32, by courtesy of Marcel Dekker, Inc.)

British Nuclear Fuels (BNF) is designing a new effluent treatment plant for its fuel reprocessing facility. In the process, sodium hydroxide is added to the iron-bearing acidic effluent to increase its pH to 9.5 creating a ferric hydroxide floc. Most of the actinides coprecipitate with the floc and the solids are separated from the liquid using a graphite/zirconium-oxide membrane. The solids will be encapsulated and the liquid can be discharged.

BNF has also developed a remotely maintainable ultrafilter for the filtration of low activity effluents. A single module capacity is approximately 70 m³/day and techniques have been developed for in-service cleaning and out-of-service chemical cleaning.

3.3.2 Reliability and Maintenance Requirements

Ultrafiltration is used on a large-scale basis in several industries. The process has proven to be quite reliable. About the only need for maintenance is the periodic washing necessary to minimize fouling or scaling of the membrane surface.

3.3.3 Secondary Waste Streams

The major secondary waste streams generated by this technology would be aqueous wash solutions used to rinse the membrane surfaces. These solutions would contain small amounts of radionuclides.

3.3.4 Separation Efficiency

The separation characteristics of a membrane separation unit will depend on (1) the selectivity of the membrane, (2) the fluid dynamics in the module, (3) the driving force, and (4) the flow pattern in the module (ie., co-current or counter-current flow).

When used for oil/water separations, ultrafiltration processes can produce a final concentrate containing about 40% oil. Water recovery of 95% or better can be expected. If incineration of the oil product is to be considered, the oil stream must be concentrated further by evaporation.

3.3.5 Safety and Health

Ultrafiltration systems are completely enclosed and, therefore, should reduce worker exposure and minimize the risk of spills. However, these membrane systems are operated under slight pressure. A leak in a transfer line or the membrane housing would lead to spills contaminating the area around the leak.

3.3.6 Operational Complexity

For simple, single-pass flow, the membrane unit requires little space and support equipment. To attain higher recovery levels, it may be necessary to use several stages. These stages can be arranged in a number of different cascade patterns either with or without reflux.

3.3.7 Glovebox Capability

There should be no problem with operating an ultrafiltration unit in a glovebox. The only moving parts are located in the liquid pumps.

3.3.8 Environmental Impact

The ultrafiltration process is a completely enclosed system. The only effluents from the process are liquid streams.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Costs will be developed.

3.5 TECHNOLOGY COMPARISON

This process offers the advantage of improved removal efficiencies over conventional filtration. The process is easily automated, and pre-engineered package systems are readily available. The primary disadvantage is relatively higher costs over conventional filtration.

4.0 DEMONSTRATION REQUIREMENTS

Pilot-scale units can be purchased from manufacturers. Pilot-scale testing is recommended with actual waste feeds before settling on a flowsheet design and purchasing full-scale equipment.

4.1 DATA REQUIREMENTS

Feed stream characteristics must be known before a pilot-scale design can be started. The feed flowrates and the product specifications must also be known. Since the membrane materials are organic, estimates of the radiation field that the membrane will be exposed to should be available. The required particle size cutoff of the membrane must be determined.

4.2 TESTING REQUIREMENTS

Testing requirements are to be determined.

5.0 VENDOR LIST

The principal suppliers of Ultrafiltration equipment are listed below:

Amicon
72 Cherry Hill Dr.
Beverly, MA 01915
(800) 426-4266

Osmonics, Inc.
5951 Clearwater Dr.
Minnetonka, MN 55343
(800) 848-1750

Alcoa Separations Technology, Inc.
Box 560
Rockford, IL 61105
(815) 877-3041

HPD, Inc.
HPD Place, Box 3032
Naperville, IL 60566
(708) 357-7330

Fast Systems, Inc.
3240 N. Broadway
St. Louis, MO 63147
(314) 621-2536

Koch Membrane Systems
Wilmington, MA

New Logic International, Inc.
1155 Park Ave
Emeryville, CA 94608
(415) 655-7307

Allied Signal
San Diego, CA

A G Technology Corp.
34 Wexford St
Needham, MA 02194
(617) 449-5774

Romicon
Woburn, MA

Western Filter Co.
Box 16323
Denver, CO 80216
(303) 288-2617

DSI
Escondido, CA

6.0 REFERENCES

1. Christian, S. D. and J. F. Scamehorn. "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics from Aqueous Streams." In *Surfactant-Based Separation Processes*. J. F. Scamehorn and J. H. Harwell, eds. Marcel Dekker: New York, 1989, pp. 3-28.
2. Scamehorn, J. F., S. D. Christian, and R. T. Ellington. "Use of Micellar-Enhanced Ultrafiltration to Remove Multivalent Metal Ions from Aqueous Streams." In *Surfactant-Based Separation Processes*. J. F. Scamehorn and J. H. Harwell, eds. Marcel Dekker: New York, 1989, pp. 29-51.
3. Cross, J. E., G. J. Holwell, and E. W. Hooper. "Summary of Experimental Work During 1886/87 on Actinide Decontamination to Low-Levels." Report AERE R 12856. Harwell Laboratory: 1987.
4. Stitt, E. H. "Membrane Separation." In *Solid-Liquid Separation*. L. Svarovsky, ed. Butterworth-Heinemann: Oxford, 1990.
5. Cheremisinoff, N. P. and D. S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983.

APPENDIX H-3 MICROFILTRATION

1.0 TECHNOLOGY DESIGNATION

Microfiltration (MF) is particularly effective for the removal of suspended solids having particle diameters between approximately 0.1-10.0 μm . Design considerations include choice of operation mode and module design.

2.0 NEED FOR THE TECHNOLOGY

Microfiltration will be needed as a pretreatment step ahead of any reverse osmosis treatment system. Additionally, microfiltration will be required as a pretreatment stage before any solvent extraction or supported liquid membrane unit operation.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

MF methods use pressure to separate the nonionic materials from a solvent, and are particularly effective for the removal of suspended solids, oil and grease, large organic molecules, and complexed heavy metals from wastewaters. This process uses special membrane material in equipment very similar to that used for reverse osmosis. As with RO, several types of membrane configurations are available that differ in cost, membrane area/volume ratio, and resistance to fouling.

MF membranes are operated in one of two ways: (1) as a straight-through filter, commonly referred to as dead-end filtration, and (2) in a cross-flow configuration. In dead-end filtration, essentially all of the liquid feed appears in the permeate. Plugging and fouling is a serious problem and only those feed streams containing less than 0.5% suspended solids are candidates for dead-end filtration. Feeds containing less than 0.1% solids are almost always filtered in dead-end configuration.

In cross-flow filtration, the feed is continuously swept over the membrane surface, producing a clarified product stream and a retentate containing most of the solids. In this filtration mode, typically less than 20% of the feed liquid is transported across the membrane per stage. Higher recoveries require recycle and/or multiple stages. Several different module designs are available. Dead-end filter housings include disk filters, pleated cartridges, dead-end spiral, and air-pulsed capillary. Cross-flow filters are available as flat-sheets in plate-and-

frame modules and as spirals and hollow fibers. Reverse flow, air-purging, and chemical treatment are methods used to restore membrane flux after partial blockage from fouling.

The membrane materials are typically polymeric and include nylon, polypropylene, polysulfone, polyvinylidene fluoride, polyvinyl chloride, and cellulose nitrate/cellulose acetate. Newer microfiltration membranes include ceramics based on alumina (Alcoa); aluminum oxide (Anotec); carbon membranes (GFT); glass; and sintered metal membranes. In addition, dynamically formed membranes are also used in microfiltration. The most common dynamic membranes employ a bed of zirconium oxide deposited on a porous support. The membrane is formed by passing a suspension of ZrO_2 across the porous support and laying down a semipermanent layer. The ZrO_2 coating can be removed when desired. Rhone-Poulenc is the primary supplier of this membrane type.

MF filters have screen or sieve-type retention properties that provide for absolute removal of particles of a specific size. In this case, the particle is simply too big to pass through the pore, so it becomes trapped on the top surface of the membrane acting as a sieve or screen. To achieve the desired absoluteness of removal from sieve retention, the largest pores of the filter selected must be smaller than the smallest size particle of the particle size distribution. In practice, this is not always possible to do with assurance because the particle size distribution is usually not known. Membrane filters are selected because they have a narrower pore-size distribution than other types of filters, and they are selected based on their pore size relative to whatever is known about the particle size.

When correctly sized for an application, membrane filters are absolute in the retention of all particles present in the liquid. However, depending on the nature of the particles, large loadings may block the filter's surface interfering with further filtration. This is the weak point of MF; the filter may accommodate only a small surface loading of particulates before its useful life is compromised. Therefore, MF filters are not used by themselves where large particle concentrations are involved. Instead, they are usually used in combination with prefilters, usually deep-bed filters, to reduce the particulate concentration to prevent premature blocking of the MF membrane. However, a new automated, flat-plate MF system has been developed and tested that automatically dumps the filter cake and replaces the filter medium on a semi-continuous basis (Ref. 4).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

This process is applicable to wastewaters that contain contaminants in particulate form. For example, plutonium is often present as particulates, and ionic contaminants may also be removed if they are first complexed to high molecular weight compounds. Dissolved metals and radionuclides can also be removed by this process if they are first precipitated in a

pretreatment process step. Oil and water mixtures can be successfully separated by MF membranes as long as the mixture is not an emulsion

The contaminants to be removed using MF methods are larger in size and may first be chelated to a high molecular weight compound to allow them to be removed by filtration. The membrane material used has a much larger pore size than reverse osmosis membranes. Operating pressures are much lower, typically 50 to 100 psi versus 200 psi and above for reverse osmosis.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 TECHNOLOGY STATUS

There are a number of commercial suppliers of membranes and filtration equipment. Current process applications of microfiltration include pharmaceutical/biological, beer sterilization, wine clarification, fluid purification(food producers).

3.3.2 Reliability and Maintenance Requirements

As with all membrane separation processes, the membranes must be cleaned if fouling or scaling is a potential problem. The ceramic and carbon/ ZrO_x based membranes would be more resistant to radiation damage. The ZrO_x membranes of Rhone-Poulenc are being used for nuclear applications in Europe (Ref. 3). Ceramic-based membranes can be cleaned by backflushing, reducing secondary waste volumes.

3.3.3 Secondary Waste Streams

The only secondary waste streams would be aqueous cleaning solutions used to remove adsorbed material from the membrane surfaces. With tubular membranes, reversing the flow across the membrane is often sufficient to clean the membrane. In this case there would not be any secondary wastes produced.

3.3.4 Separation Efficiency

For separating particulates, the separation is absolute. Particles larger than the membrane pore size are retained in the concentrate stream. Pore diameter is typically between 0.1 and 3 microns for PTFE (Gore) and PE (Celgard) membranes.

3.3.5 Safety and Health

No specific safety and health issues peculiar to this technology.

3.3.6 Operational Complexity

Process control consists of regulating feed pressure and flow rates. More complex flowsheets would consist of several separation stages arranged in a cascade.

3.3.7 Glovebox Capability

The units could be installed in a glovebox. Changing the membranes, if ever necessary, could be a problem. To reduce worker exposure and simplify the task of membrane replacement, it may be more effective to simply replace the entire membrane module.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Costs are highly dependent on the feed stream composition, flowrates, and the size of separation being performed.

3.5 TECHNOLOGY COMPARISON

This process offers the advantage of improved removal efficiencies over conventional filtration. The process is easily automated, and pre-engineered package systems are readily available. The primary disadvantage is relatively higher costs over conventional filtration.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Feed stream characteristics must be known before pilot-scale design can be started. The feed flowrates and the product specifications must also be known. Since the membrane materials are organic, estimates of the radiation field that the membrane will be exposed to should be available. The required particle size cutoff of the membrane must be determined.

4.2 TESTING REQUIREMENTS

Information regarding the feed composition, flow rates, particle size, and product composition is required to design a membrane separation system. The expected radiation fields will dictate whether or not organic-based membranes could be considered. It is highly recommended that a pilot-scale test be carried out before installing a full-scale treatment circuit.

5.0 VENDOR LIST

The principal suppliers of Microfiltration membranes and equipment are as follows:

Millipore
80 Ashby Rd.
Bedford, MA
(800) 225-1380

Pall Process Filtration Co.
2200 Northern Blvd.
East Hills, NY 11548
(800) 645-6532

Amicon
72 Cherry Hill Dr.
Beverly, MA 01915
(800) 426-4266

Anotec Separations
226 E. 54th St. Ste. 501
New York, NY 10022
(212) 751-3770

Alcoa Separations Technology, Inc.
Box 560
Rockford, IL 61105
(815) 877-3041

Asahi Glass America, Inc.
1185 Ave. of the Americas
New York, NY 10036

Gelman Sciences
600 S. Wagner Rd.
Ann Arbor, MI 48106
(313) 665-0651

Hoechst-Celanese
5200-77 Center Dr.
Charlotte, NC 28217
(704) 559-6030

Osmonics, Inc.
5951 Clearwater Dr.
Minnetonka, MN 55343
(800) 848-1750

Rhone-Poulenc
P.O.B. CN 7500
Cranbury, NJ 08512-7500
(609) 860-3567

W. L. Gore
P.O.B. 1010
Airport Rd.
Elkton, MD 21921
(410) 392-3200

6.0 REFERENCES

1. Stitt, E. H. "Membrane Separation." In *Solid-Liquid Separation*. L. Svarovsky, ed. Butterworth-Heinemann: Oxford, 1990.
2. Cheremisinoff, N. P. and D. S. Azbel. *Liquid Filtration*. Ann Arbor Science: Woburn, MA, 1983.
3. Kientz, G. Private communication. Rhone-Poulenc, Cranbury, NJ 08512-7500.
4. Martin, J. F. et al. "Demonstration of Microfiltration Technology," *J. Air Waste Management Assoc.*, Vol 41, No. 12, pp 1653-1657, December 1991.

APPENDIX H-4 ELECTRODIALYSIS

1.0 TECHNOLOGY DESIGNATION

Electrodialysis is used to remove ionic components from water producing moderate purity water. This technique relies on ion-exchange membranes in a direct-current electrical field to separate ionic species from solution.

2.0 NEED FOR THE TECHNOLOGY

This is a candidate technology for the primary treatment of aqueous waste feeds for the removal of ions. Specialized forms of electrodialysis such as electrodialytically regenerated ion exchangers are capable of reducing metal concentrations to ultra-low levels.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Electrodialysis is a membrane separation process that can be used to separate and remove ionic species from an aqueous stream. A typical electrodialysis cell consists of an anode and a cathode separated by a series of anion- and cation-exchange membranes arranged in an alternating pattern as shown in Figure H-4.1. Each pair of ion exchange membranes forms an individual cell. As an electrical current is applied across the cell, the ions are drawn through the semipermeable membranes to the appropriate electrode. An electrodialysis system generally consists of many thin cells stacked in parallel. The efficiency of the separation process is mainly determined by the ion-exchange membranes used in the system. The energy required to remove ionic species depends on the feed concentration and the current utilization. The maximum current that can pass through a membrane is limited by the ion concentration on the diluate side of the membrane. If the limiting current density is exceeded, the applied electrical power is converted to waste heat and the excess current results in the splitting of water into H^+ and OH^- .

Electrodialysis can be applied as a treatment method for the removal of metal ions and other ionic species from water. Electrodialysis has been used extensively on a commercial scale for desalination of water. It is effective at concentrating reverse osmosis brines. Because of the high osmotic pressures, concentration of brines by reverse osmosis cannot exceed certain values. Treatment of metal-bearing hazardous waste streams, such as plating wastes, is another typical application for electrodialysis.

Figure H-4.1. Schematic of Electrodialytic Regeneration of Mixed Bed Ion Exchange Resins

Recently, electrodialysis, in combination with the use of ion exchange, has been used for the production of ultrapure water. In this approach, ion exchange beads are placed between the electrodes of an electrodialysis stack. The application of an electric current results in the continual sweeping of adsorbed ions from the ion exchange media. The feed water is almost completely deionized without the chemical regeneration of the ion exchanger. This process has been commercialized by millipore.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Input stream requirements and output stream characteristics are to be determined.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

This is a well-established technology of which there are a number of manufacturers of membranes and complete dialysis units. Over 2000 plants have been established worldwide for desalting brackish water. The process operates at atmospheric pressure and does not require the addition of any chemical reagents, except for cleaning the membranes. Typically, a direct current of 30 amperes is sufficient to transfer about 1 gram-equivalent per hour. Current is limited to about 100 amperes per square meter of membrane area. A full-scale stack can transfer about 1000 gram-equivalents per hour (Ref. 1).

3.3.2 Reliability and Maintenance Requirements

The only maintenance requirement would be the periodic cleaning of the membranes. The cleaning schedule would depend on the concentrations of foulants present in the feed stream.

3.3.3 Secondary Waste Streams

The only secondary waste streams would be cleaning solutions used to remove deposits from the membrane surfaces. The presence of nonionic organics in the feed stream can lead to membrane fouling. This can become excessive, in which case another primary concentration step, such as freeze fractionation, must be employed. Electrodialysis can then be used as a polishing step.

3.3.4 Separation Efficiency

Electrodialysis is primarily used to treat dilute electrolyte streams. It can typically remove 90-95% of the dissolved solids in the feed stream and concentrate these solids to the 5-10% range. In a typical process, about 90% of the feed is recovered as the dilute stream and 10% recovered in the concentrate stream.

3.3.5 Safety and Health

No safety and health issues peculiar to this technology.

3.3.6 Operational Complexity

Electrodialysis is a simple unit operation. There are no moving parts except for the pumps used to move the liquid streams through the dialysis unit. A DC current is the driving force for the separation.

3.3.7 Glovebox Capability

The membrane unit could, in principle, be placed in a glovebox. The membrane size, however, will be the determining factor as to whether this is possible or not.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

Costs will be determined.

3.5 TECHNOLOGY COMPARISON

Electrodialysis is an effective method for concentrating some charged species from a waste stream into a reduced volume of wastewater. Compared to reverse osmosis, the membranes used in electrodialysis are more tolerant of the chemical environments of waste streams and are easier to clean.

Contaminants are not destroyed by electrodialysis, but are concentrated into a lower volume waste stream that requires treatment and disposal. Pretreatment of some influent streams may be required to prevent membrane fouling.

4.0 DEMONSTRATION REQUIREMENTS

Pilot-scale units can be purchased from manufacturers. Pilot-scale testing is recommended with actual waste feeds before settling on a flowsheet design and purchasing full-scale equipment.

4.1 DATA REQUIREMENTS

To determine the required membrane area, small-scale pilot tests must be performed. The treatment capacity per unit of membrane area will vary with the salt concentration, the temperature, and the salt recovery ratio. The presence of solids in the feed may require pretreatment if the solids are prone to precipitate. The pH of the feed solution must also be known. Ideally, the feed should be a neutral solution.

5.0 VENDOR LIST

The commercial suppliers of electrodialysis equipment and membranes are shown below:

Asahi Glass America, Inc.
1185 Ave. of the Americas
30th Floor, New York, NY
(212) 764-3155

Ionics, Inc.
65 Grove St.
Watertown, MA 02172
(617) 926-2500

Millipore Corp.
80-T Ashby Rd.
Bedford, MA 01730
(617) 275-9200

Pall Corp.
2200 N. Blvd.
East Hills, NY 11548
(516) 484-5400

6.0 REFERENCES

1. Reed, P. B. "Recent Advances in Separation and Purification Equipment." Paper No. 52b, presented at the 1984 AIChE Meeting, 21 August, Philadelphia, PA.

APPENDIX H-5 SUPPORTED LIQUID MEMBRANES

1.0 TECHNOLOGY DESIGNATION

In supported liquid membrane extraction, the organic solvent is immobilized within a microporous membrane support. The support is usually a hydrophobic polymer such as microporous polypropylene. The organic solvent is held within the membrane pores by capillary forces, and thus allows the membrane to be placed between an aqueous feed stream and aqueous strip solution. This geometry permits extraction and stripping to take place simultaneously. Compared with conventional solvent extraction, a much smaller solvent inventory is required for this membrane process and there is the added advantage of low solvent losses due to entrainment together with the elimination of the need for liquid/liquid phase separation.

2.0 NEED FOR THE TECHNOLOGY

This technology is a candidate for the primary treatment of aqueous waste streams. It would be used for the selective extraction and recovery of specific metal ions such as the actinides or RCRA metals.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

In supported liquid membrane extraction, the organic solvent is immobilized within a microporous membrane support. The support is usually a hydrophobic polymer such as microporous polypropylene. The organic solvent is held within the membrane pores by capillary forces, and thus allows the membrane to be placed between an aqueous feed stream and aqueous strip solution. This geometry permits extraction and stripping to take place simultaneously (see Figure H-5.1). Compared with conventional solvent extraction, a much smaller solvent inventory is required for this membrane process and there is the added advantage of low solvent losses due to entrainment together with the elimination of the need for liquid-liquid phase separation.

The general mechanism for solute extraction is through facilitated transport. A membrane carrier is used as a shuttle, carrying the solute across the membrane phase. With coupled transport, a solute can be extracted from the feed solution and concentrated on the strip solution. Coupled transport involves the simultaneous diffusion of two different solutes which

undergo reversible complexation with a mobile carrier. The downhill transport of one solute supplies the energy to pump the other solute up its concentration gradient.

Figure H-5.1. Schematic diagram of metal transport across a Supported Liquid Membrane. The Cotransport of H^+ can be used to pump metal ions up their concentration gradient

Membranes used in microfiltration and ultrafiltration make good supports for liquid membrane extractors. Hollow-fiber modules can be used to achieve high specific surface areas, and hence, high extraction rates.

The major problem facing liquid membrane extraction systems is instability of the membrane phase. Membrane instability can manifest itself in several different ways. Each of these represents catastrophic failure. Solvent loss from the membrane phase due to dissolution into the aqueous feed and strip solutions is one form of failure. Although organic diluents and metal extractants typically have a very low solubility in aqueous electrolyte solutions, the volume ratio of aqueous feed to organic solvent can be significantly greater than 10^6 . Additionally, osmotic pressure gradients across the liquid membrane can easily be 40 atm or greater. Pressure gradients of this magnitude can easily force the organic phase out of the pores of the membrane support. This is the chief cause of membrane failure. To counteract this effect, supports with very small pores that generate a large capillary force are used.

An alternative approach, which combines aspects of conventional solvent extraction with membrane extraction is the membrane contactor (Refs. 1 and 2). In this configuration, a microporous membrane is used to separate the bulk aqueous and organic phases and thus

prevents the dispersion of the liquid phases. In a hollow-fiber module, the feed would flow through the lumens of the fibers, and the organic phase would flow counter-currently on the shell side. The interface of the immiscible liquids is immobilized at the pore mouths of the microporous membrane. The use of composite hydrophilic-hydrophobic membranes eliminates the need to maintain one of the phases at a slight excess pressure in order to keep the interface immobilized at the membrane surface. A second module can be used to strip the loaded organic phase. Alternatively, one can use two sets of hollow fibers in a single module where one carries the aqueous feed and the other carries the aqueous strip solution. The organic solvent is located on the shell side of the module.

The advantages of this technique are as follows: (1) a very high specific area is easily achieved with the use of hollow-fiber modules, (2) there is no need to have a difference in phase densities, (3) there is a very wide range of liquid phase flow rates possible, (4) there is no flooding, and (5) scale-up to larger systems is simplified.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The range of solutes that can be extracted are identical to those treatable by conventional solvent extraction. The solvent system must be custom-designed for a particular feed composition.

Extraction systems are always designed with the recycle of the organic solvent in mind. The solvent can be recycled by first stripping the loaded metals and then adjusting the pH if necessary.

The aqueous product stream would be concentrated in the desired metal species. The concentration factor can be as high as 100-fold or more. Because of the membrane barrier at the liquid/liquid interface, there is very low other-phase carryover. This means that the aqueous product stream would contain at least 10-100 times less organic entrainment than what would be expected for conventional solvent extraction.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

As with conventional solvent extraction, the solvent system is tailored specifically to the feed composition and usually is effective only for certain components in the feed. The development of an extraction system and flowsheets for specific applications requires development studies to be carried out at the pilot scale before a technology can be transferred to the plant scale. The development and introduction of new extractant systems requires extensive research efforts followed by pilot-scale studies. The benefits of a well-designed

solvent extraction system are high selectivity for targeted species and extremely high decontamination factors.

3.3.2 Reliability and Maintenance Requirements

In general, the membrane extraction units are very stable and can be expected to operate for very long periods of time with little or no maintenance. The only moving parts are ancillary equipment such as pumps or pressure valves.

3.3.3 Secondary Waste Streams

The secondary waste streams would include any special aqueous scrub solutions that might be required to regenerate the organic solvent before recycling it back to the extraction module and any scrub solutions that might be needed to rejuvenate the membrane supports. These streams would become slightly contaminated with radionuclides.

3.3.4 Separation Efficiency

The separation efficiency of a membrane extraction unit can be orders of magnitude higher than conventional solvent extraction systems because of the dispersion-free mode of operation. In conventional solvent extraction, the effective partition coefficients of extracting species are often limited by the amount of other-phase carryover. This factor is eliminated in membrane extractors because the other-phase carryover is virtually zero.

3.3.5 Safety and Health

As with any solvent extraction operation, the process will concentrate the extractable radionuclides from at least 10-fold to several orders of magnitude. This could, for example, generate a TRU stream from a non-TRU feed stream. The increased activity due to the extraction and concentration of any gamma/beta emitters must be dealt with accordingly.

3.3.6 Operational Complexity

Supported membrane extraction systems are mechanically very simple. There are no moving parts except for the external pumps used to move the liquids through the membrane module.

3.3.7 Glovebox Capability

The membrane units tend to be more compact than other types of solvent extraction equipment and, consequently, there should be no problem with operating a supported liquid membrane unit or a membrane extractor within a glovebox.

3.3.8 Environmental Impact

The extraction system is operated as a completely enclosed system. The membrane modules are manufactured completely from plastic materials and could be disposed of by incineration.

3.4 COST OF THE TECHNOLOGY OF EQUIPMENT

The cost of installing a membrane extractor should be significantly less than any other solvent extraction system. Cellgard hollow fiber membrane modules can be purchased for as little as \$350-\$450. A 15-20 cm long unit has a flow capacity in the liter per min range but can be operated at flow rates as low as 50-100 mL/min.

3.5 TECHNOLOGY COMPARISON

The advantages of using supported liquid membrane extractors versus conventional solvent extraction are (1) the ability to handle solids in the aqueous feed stream, (2) the large and well-defined interfacial area obtained with the membrane support, (3) the ability to independently vary the flow rates of the two liquid streams over very wide ranges, (4) no need to have any density difference between the organic and aqueous phases, and (5) the ability to handle liquid/liquid systems with very low interfacial tension.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

To properly design and size an extraction system, information regarding the feed composition, the product stream specifications, and the flowrates is essential. Batch extraction data for all of the feed components would be required to optimize the initial pilot-scale design.

4.2 TESTING REQUIREMENTS

The commercially supplied membrane extractor units use a polypropylene membrane. Since this is an organic material, sufficient pilot plant testing would be required to ensure that the membrane could withstand the expected radiation exposures. These tests should be carried out using actual waste feeds.

5.0 VENDOR LIST

The major supplier of membrane extractor units is

Hoechst-Celanese
5200-77 Center Dr.
Charlotte, NC 28217
(704) 559-6063

Various membrane materials can be used for liquid membrane supports and can be obtained through suppliers of microfiltration membranes.

6.0 REFERENCES

1. Prasad, R. and K. K. Sirkar. "Solvent Extraction with Microporous Hydrophilic and Composite Membranes." *AIChE J.* 33, 1057-1066, 1987.
2. Kathios, D. and B. Smith. Private communication. Los Alamos National Laboratory, 1993.

APPENDIX H-6 PERVAPORATION

1.0 TECHNOLOGY DESIGNATION

This appendix presents an evaluation of pervaporation technology relative to chemical/physical treatment required in a mixed waste treatment process.

2.0 NEED FOR THE TECHNOLOGY

The basic need for pervaporation in the mixed waste treatment process is in the necessary separation of organics (which ultimately are oxidized and released to the atmosphere) from water, which is the single usable product from the process. Pervaporation could potentially be used in the aqueous liquids treatment line or the organic liquids treatment line of the mixed waste treatment process. Pervaporation would most logically be used as a secondary treatment step (Unit 190) in the aqueous liquids treatment line, removing residual, dissolved organics from water. The primary treatment step (Unit 150.2) may not remove organics to the purity requirements for the "clean water" product, and if so, pervaporation may be used in conjunction with or in partial replacement of this treatment to perform this required separation.

In the organic liquids treatment line, pervaporation could be used to remove dissolved water from any of the streams feeding the Concentrated Organics Tankage (Unit 240) or the Sludge/Slurry Preparation (Unit 265). The tolerance of the Concentrated Organics Burner (Unit 380) and the Heavy Organics Combustor (Unit 213) for water will determine the need for pervaporation upstream of these units. Another potential use of pervaporation in the organics treatment line would be upstream of the Organics Oxidation step (Unit 270). The efficiency of Liquid Separation (Unit 250.4) and the economics of partial bypass of the Organics Oxidation (Unit 270) will determine the need for pervaporation in this service.

An additional potential need for pervaporation in the mixed waste treatment process would be to recover for reuse any solvents used in special treatment steps.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Pervaporation is a membrane technology for separation of liquids. The separation is brought about because of the differences in permeation of the components in the mixture through the membrane. In contrast to other membrane separation processes, pervaporation is a multiphase process, in which the liquid feed is in direct contact with the membrane, and the

permeate is withdrawn as a vapor at the back side of the membrane. The driving force of the pervaporation process is the difference in chemical potential of the permeating component between the feed side and the permeate side.

The transport mechanism of pervaporation involves the sorption of one or more components of a liquid mixture into the membrane on the feed side, diffusion of these components (the permeate) through the membrane, and desorption of the permeate into the vapor phase at the back side of the membrane.

A typical flowsheet is shown in Figure H-6.1. The pervaporation process consists of heated feed being fed to a series of membrane modules in a vacuum vessel, with interstage heaters between modules and a condenser on the permeate stream. Pervaporation modules are commonly of a plate-and-frame design and constructed of stainless steel. Other configurations consist of hollow-fiber and spiral-wound modules. A vacuum pump is used to maintain a moderate vacuum in the vessel. The condenser temperature and vacuum level are dependent on the desired product concentration, and the feed-side operating pressure is set to avoid boiling the feed mixture. Typical system operating pressures are in the 30-60 psi range, and typical operating temperatures are ambient to 200°F.

Figure H-6.1. Typical Pervaporation Process Flow Diagram

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The feed stream to a pervaporation unit needs to be an organic or aqueous/organic liquid with negligible solids. Dissolved salts or impurities may interfere with the process. The products of the process are most typically two liquids, an organic which is typically suitable for reuse and an aqueous waste or product.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

As of the beginning of 1992, more than 50 pervaporation systems had been installed worldwide to recover solvents, separate mixtures of hydrocarbons, remove organics from waste streams, dehydrate ethanol and isopropanol, and dealcoholize wines and liquors (Refs. 1 and 2). The majority of industrial-scale units are being used to dewater organic solvents or alcohol fuels (Refs. 2, 3, 4, 5, 6, 7 and 8). Reference 3 lists 83 organic chemicals which can be dehydrated by pervaporation, and—in addition to many alcohols, ketones, ethers, esters, and amines—includes aniline, benzene and jet fuel. It should be noted that most of the industrial applications of pervaporation have been performed on solutions of few components, and most commonly on binary or ternary azeotropic systems. Also, many of the industrial applications use pervaporation in combination with another technology to achieve the required separation.

Recent developments in pervaporation have included treatment of hazardous waste streams, focused primarily on the removal of chlorinated hydrocarbons from aqueous waste streams (Refs. 9, 10, 11, 12, 13, 14 and 15). Separation factors of up to 10,000 have been achieved in the removal of dichloromethane, trichloroethylene, and carbon tetrachloride from water (Refs. 9, 10, and 11). To date, while testing of pervaporation has been performed on some hazardous waste, no testing has been reported on radioactive or mixed waste.

3.3.2 Reliability and Maintenance Requirements

To be determined.

3.3.3 Secondary Waste Streams

The waste streams are dependent on the feed composition and separation objectives. Removal of organics from aqueous waste will result in a highly concentrated organic stream, which can be destroyed thermally or possibly reused. Removal of water from an organic liquid mixed waste will result in a low-level aqueous waste plus a concentrated organic stream.

3.3.4 Separation Efficiency

To be determined.

3.3.5 Safety and Health

No safety and health issues peculiar to this technology.

3.3.6 Operational Complexity

Pervaporation units are generally small, simple, easy to operate, and have low maintenance.

3.3.7 Glovebox Capability

Pervaporation has no experience in glovebox configurations.

3.3.8 Environmental Impact

Negligible environmental impact expected.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

The cost of a pervaporation system will be highly dependent on its performance requirements, including feed rate and composition and required effluent concentration. For use on mixed waste streams, development will be required and will significantly add to the costs.

The capital cost of a pervaporation unit treating 100 m³/day of waste water with up to 1000 ppm 1,1,2-trichloroethane to a level of 5 ppm was estimated at \$125,000, and included the pervaporation unit, condenser, phase separator, and vacuum pump (Ref. 16). Total operating cost, which includes depreciation, labor, module replacement and energy, was estimated at \$1.96/m³ of feed (Ref. 16). This unit, in terms of feed rate, is approximately four times the capacity of the aqueous liquids treatment line and 200 times the capacity of the organic liquids treatment line in the mixed waste treatment process.

In a supplier's proposal dated May 1992, a pervaporation unit to recover 99% isopropanol from a 74% isopropanol/26% water feed at the feedrate of 77 kg/hr was priced at \$157,000 (Ref. 17). This unit includes six pervaporation modules, a vacuum vessel, interstage heaters, a permeate condenser, a feed/product heat exchanger, a feed pump, a product pump, a vacuum pump, and associated piping and instrumentation. This unit, in terms of capacity, is approximately four times that of the organic liquids treatment line in the mixed waste treatment process.

Based on the above two reference points, a "ballpark estimate" for the capital cost of a pervaporation unit in the mixed waste treatment process would be \$100,000-\$200,000.

Development costs to demonstrate performance on simulated and/or actual mixed waste may range from 1-5 times this amount.

3.5 COMPARISON OF PERVAPORATION WITH COMPETITIVE TECHNOLOGIES

3.5.1 Comparison with Single-Phase Membrane and Adsorbent Bed Processes

Vapor permeation, gas-phase membrane separation, and reverse osmosis are other membrane processes having some overlap with pervaporation in application. Molecular sieves and carbon-bed adsorption also overlap with pervaporation in applications. Vapor permeation is a modification of pervaporation in which the feed is vaporized prior to membrane exposure. Because of the need to vaporize the entire feed, vapor permeation, gas-phase membrane separation, and molecular sieves usually have higher operating and capital costs compared to pervaporation. For dewatering applications, pervaporation can process feed of a much higher water content than molecular sieves. Another advantage of pervaporation over molecular sieves and carbon-bed adsorption is that regeneration is not required.

Pervaporation is a less developed technology than all of the above with the exception of vapor permeation. Compared to reverse osmosis, the current applications for pervaporation are more limited. Pervaporation has been used in combination with reverse osmosis or adsorption processes to take advantage of the unique advantages of each process.

3.5.2 Comparison with Distillation

For recovery of organic solvents from aqueous mixtures, and particularly for azeotropic mixtures, pervaporation is an alternative to the more conventional technology of distillation. Pervaporation offers advantages over distillation in that no chemical entrainers are required to break azeotropes, energy demands are greatly reduced, capital costs are typically less, pervaporation systems are easier to start up and operate, pervaporation systems are more flexible in terms of feed composition, and process conditions are typically more mild (Refs. 1, 2, 6, 18 and 19).

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Included in 4.2

4.2 TESTING REQUIREMENTS

Prior to procurement of a pervaporation system for the mixed waste treatment process, testing will be required to:

1. Select the most appropriate membrane for the specific separations required
2. Demonstrate stability of the membrane toward minor and trace components expected in the waste streams
3. Demonstrate stability of the membrane within the expected range of radiation exposure
4. Determine separation efficiency, flux rates, and other process performance data.

Facilities and pervaporation equipment are available (listed in Section 5.1) to support demonstration testing using simulated waste with no modification required to the equipment. For demonstration of pervaporation of actual mixed waste, equipment would need to be procured. Commercially available pervaporation test units may be of full-scale for the specific service to which it would be applied in the mixed waste treatment process, or may be easily modified to meet capacity requirements.

5.0 VENDOR LIST

5.1 PERVAPORATION SYSTEM TESTING

1. Peterson, Eric S., Chemical and Materials Research and Engineering Group, EG&G Idaho, 1955 Fremont St., P. O. Box 1625, Idaho Falls, ID 83415 - 2208, (208) 526-1521 FAX (208) 526-8514
2. Lechleider, R., Carbone of America Corporation, 14 Eastmans Road, Parsippany, NJ 07054, (201) 503-0777 FAX (201) 503-0225 (testing performed at Separations Technology Laboratory, 540 Branch Drive, Salem, Virginia 24153 (703) 389-7535)

5.2 PERVAPORATION SYSTEM EQUIPMENT

1. Lechleider, R., Carbone of America Corporation, 14 Eastmans Road, Parsippany, NJ 07054, (201) 503-0777 FAX (201) 503-0225
2. Bakish, R., Bakish Materials Corporation, 171 Sherwood Place, P. O. Box 190, Englewood, N. J. 07631, (201) 567-5873 FAX (201) 567-6684

6.0 REFERENCES

1. "Pervaporation Offers Advantages in Solvent Recovery." *Chemical Processing*. January, 1992: pp. 33-36.
2. Fleming, H. L. "Consider Membrane Pervaporation." *Chemical Engineering Progress*. July 1992: pp. 46-52.
3. Tusel, G. F. and H. E. A. Brüscke. "Use of Pervaporation Systems in the Chemical Industry." *Desalination*. 53, 1985: pp. 327-338
4. Fleming, H. L. "Membrane Pervaporation: Separation of Organic/Aqueous Mixtures." *Separation Science and Technology*. 25, 1990: pp. 1239-1255.
5. Brüscke, H. E. A. "State of Art of Pervaporation." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 2-11.
6. Asada, T. "Dehydration of Organic Solvents. Some Actual Results of Pervaporation Plants in Japan." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 379-386.
7. Kraetz, L. "Dehydration of Alcohol Fuels by Pervaporation." *Desalination*. 70, 1988: pp. 481-485.
8. Sander, U. and P. Soukup. "Design and Operation of a Pervaporation Plant for Ethanol Dehydration. " *J. of Membrane Science*. 36, 1988: pp. 463-76.
9. Peterson, E. S., M. L. Stone, W. F. Bauer, and A. K. Gianotto. "The Removal of Organics From Waste Streams Using Polyphosphazine Membranes." *Proceedings of Euromembrane-92*. Paris, France, October 5-8, 1992: pp. 381-387.
10. Côté, P. and C. Lipski. "Mass Transfer Limitations in Pervaporation For Water and Wastewater Treatment." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 449-462.
11. McCaffrey, R. R. and D. G. Cummings. U. S. Patent 5,022,996, 1991.
12. Dotremont, C., S. Goethaert, and C. Vandecasteele. "The Removal of Chlorinated Hydrocarbons by Means of Pervaporation." *Proceedings of Euromembrane-92*. Paris, France, October 5-8, 1992: pp. 269-274.
13. Meckl, K., R. N. Lichtenthaler. "Removal of Organic Compounds From Aqueous Solutions by Pervaporation," *Proceedings of Euromembrane-92*. Paris, France, October 5-8, 1992: pp. 195-198.

14. Abouchar, R. and H. Bruschke. "Extraction of Organics From Industrial Waste Water by Pervaporation." *Proceedings of Euromembrane-92*. Paris, France, October 5-8, 1992: pp. 175-181.
15. Aptel, P., E. Julien, N. Ganne, R. Psaume, Y. Auelle, and M. Roustan. "Pervaporation Situation Among Other Competitive Techniques in Halogenated Solvents Removal From Drinking Water." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 463-475.
16. Kaschemekal, J., J. G. Wijmans, R. W. Baker, and I. Blume. "Separation of Organics From Water Using Pervaporation." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 405-412.
17. Carbone of America Proposal to EG&G, Idaho. "Membrane Pervaporation For Dehydration Of Isopropanol." May 1992, (attached to EG&G Engineering Design File NPR-MHTGR-0510, "Status of Target Demonstration Line Isopropanol Recovery Design Support," R. O. Whipple, September 21, 1992.)
18. Pearce, G. K., "BP's New Pervaporation Technology." *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*. Nancy, France, September 19-22, 1988: pp. 493-500.
19. Bruschke, H. E. A. and G. F. Tusel. "Economics of Industrial Pervaporation Processes." *Proceedings European and Japanese Membrane Processes*, 1984: pp. 581-586.

APPENDIX I NITRATE DESTRUCTION/SEPARATION

It is expected that most of the nitrate-containing mixed wastes will ultimately be solidified for final disposal, although the final methods and criteria for solidification and disposal are still being developed. The nitrates in the waste will generally increase the volume and/or reduce the integrity of all of the waste forms that have been proposed for ultimate disposal, so nitrate destruction prior to solidification will normally be beneficial, although the cost-benefit relationship for nitrate destruction is not yet certain. Nitrates are also a concern as a source of groundwater contamination, since they will leach out of most solid waste forms.

In addition to meeting final waste form requirements, destruction or removal of nitrates may be required for other reasons such as: to meet environmental discharge limits for aqueous waste water, to reduce nitrogen dioxide gas emissions from the incinerator, or to reduce the hazard of vigorous exothermic reactions.

In the baseline process nitrates are removed from the aqueous waste stream in the tertiary polishing step, after all other contaminants and problem species are removed. However, if significant quantities of nitrates are removed in these previous removal/separation processes and subsequently end up in the dry solids sent to waste destruction or final forms processing, then a selective nitrate removal/destruction process may be required early in the treatment process prior to tertiary polishing.

The compounds of Nitrogen are many and display a wealth of chemical reactions. Beginning with elemental nitrogen (N_2), one can oxidize to the nitrate anion (NO_3^-) or reduce to ammonium cation (NH_4^+). Many chemical species fall in between these two extremes, and the chemical conversion between species can be accomplished by oxidation/reduction methods involving either chemicals in solution or with the use of an electrochemical cell through various pathways.

Technologies based on these and other processes are described in this appendix. The following technologies are destruction technologies except for salt splitting, which is a separation technology described in Appendix I-8.

- I-1 Nitrate to Ammonia and Ceramic (NAC) Process
- I-2 Electrochemical Ion Exchange
- I-3 Biodenitrification
- I-4 Chemical Reduction
- I-5 Hydrothermal Process
- I-6 Calcination
- I-7 High Temperature Processes
- I-8 Salt Splitting

APPENDIX I-1 NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

1.0 TECHNOLOGY DESIGNATION

This appendix presents an evaluation of the NAC process which involves the destruction of nitrate and/or nitrite salts in aqueous mixed waste solutions.

2.0 NEED FOR THE TECHNOLOGY

The need for the NAC process in the mixed waste treatment process is in the treatment of aqueous wastes containing nitrates. See the introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Sodium nitrate-based wastes are common to many Department of Energy facilities. The nitrate anion is very mobile and difficult to immobilize, especially in the relatively porous, cement-based grout that is currently used. The NAC process is an innovative, low temperature process that uses aluminum metal reduction to convert alkaline, nitrate-based aqueous waste to ammonia and an aluminum oxide-sodium aluminate-based solid.

The NAC process involves the chemical reduction of nitrate ions to ammonia by powdered aluminum. The aluminum is converted to aluminum hydroxide and sodium aluminate, as shown in the following stoichiometric reaction.

The solid aluminum hydroxide irreversibly dehydrates to Gibbsite:

The proposed flowsheet for the process is shown in Figure I-1.1. Aluminum, which may include DOE-contaminated scrap, is shredded and fed to the reactor along with the nitrate-based aqueous waste. Reactor pH is controlled at 11-12.5 by the addition of sodium hydroxide. The reaction is highly exothermic but can be controlled to maintain a temperature of 50°C to 60°C by adjusting aluminum feed and reactor coolant feed rates.

Figure I-1.1. General Flow Sheet for the Nitrate to Ammonia and Ceramic (NAC) Process

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. The primary solid product of the reaction is Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) with a small percentage (3-4%) of sodium aluminate. This product is crystalline, white in color, hard (2.5-3.5 Mohs) and dense (2.42 g/cc) and upon aging is quite insoluble in nearly all acids and only sparingly soluble in hot caustic. Silica is added to the product from the reactor and the material is then calcined, pressed, and sintered to form a ceramic. After pressing and sintering, Gibbsite may be an acceptable high level waste form.

The process has an added bonus in that it also precipitates most cations, metallic and non-metallic, from solution as highly insoluble aluminum spinels. Strontium should form an insoluble spinel similar to the calcium spinel. Bench tests have been performed to measure the distribution of Co-60, Sr-85, Cs-137, Ce-144, and Tc-99 between the insoluble Gibbsite phase and the aqueous phase. Sr-85 and Ce-144 (a stand-in for Pu) were fixed in the solid phase. Co-60 distributed between both the solid and liquid phases. This fortuitous property of aluminum means that most metal and nonmetal cations will enter the dense, solid ceramic matrix as a very insoluble mineral.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Inputs to the process are high nitrate concentration aqueous mixed waste and aluminum. Bench scale batch tests using simulated ORNL Melton Valley Storage Tank (MVST) supernate waste (270 g/l) and Hanford High Level Waste (3 to 6 M NO_3^- , 183 g/l) and using aluminum powder or shot, have shown that approximately twice the theoretical amount of aluminum is required to reduce essentially all of the nitrate to ammonia. Typically 1.6 kg of aluminum was required to treat 1 kg of NaNO_3 (1.9X stoichiometric), with most of the excess aluminum required to react with the last 10% of the nitrate (Ref. 1). As the nitrate concentration decreases, more aluminum reacts with water to form hydrogen gas. Lab-scale tests have demonstrated that a smaller excess of aluminum (1.1X stoichiometric) is required to destroy essentially all of the nitrate using a continuous-flow reactor (Ref. 2). Sensitivity of the process to the aqueous nitrate feed composition has not been investigated. Radioactively contaminated aluminum scrap from DOE facilities could be beneficially used in the process.

This process occurs in alkaline solutions ($\text{pH} > 11.5$) at slightly elevated temperatures ($> 50^\circ\text{C}$) and atmospheric pressure. Thus, the alkaline waste solutions that are stored at Hanford, Oak Ridge, and Savannah River will not require any pretreatment prior to nitrate destruction, although acidic waste solutions, will need to be pretreated to raise the pH to 11.5. The reaction is highly exothermic (-381 kcal/mole of NaNO_3), so the solution will need to be cooled after the reaction is initiated. For high nitrate concentration waste solutions, water

would need to be added to keep the slurry diluted enough to mix. The reaction products form a granular, sand-like material that can be dried, pressed, and sintered to form an insoluble alumina-silica ceramic as the final waste form. Silica is added to the reactor to immobilize the sodium in the ceramic waste form. The volume of the final solid waste form from a continuous flow process will be about 70% less than the starting solution for a 4 M NaNO_3 solution. 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 insoluble final waste form.

If oxygen is present, the off-gas will be flammable because of the ammonia and the small amount of hydrogen produced, so an inert gas blanket will be required for the reactor. The off-gas will need to be treated to remove ammonia, probably by catalytic oxidation to convert the ammonia to nitrogen gas and water.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Bench top feasibility studies have been completed on the denitration of a supernate surrogate representing solution from Hanford single-shell tank waste. Between 85 to 99% of the nitrate was converted to ammonia. The batch type NAC process achieved a volume reduction of 50 to 55% compared to expected volume increases of 35 to 50% for supernate that was grouted. Indications are that greater volume reductions are achievable with continuous flow processes. Engineering data from bench top studies indicate the process will be economical to operate.

Additional work on the process is continuing in FY93 focusing on greater volume reduction and the addition of silica to the reactor to form silica-alumina-based ceramics for final forms testing. Some issues that need to be addressed before a pilot- or full-size system can be built include optimization of the aluminum feed requirement, determination of the design and operational parameters for a future plant, determination of the maximum acceptable amount of nitrate in the waste form, determination of the characteristics and acceptability of the ceramic waste form, determination of the fate of the total sodium present, determination of the operability of the reaction system, and characteristics of the solids produced using an actual "hot" supernate.

3.3.2 Reliability and Maintenance Requirements

This process has only been demonstrated at the bench scale. Reliability and maintenance requirements are not known.

3.3.3 Secondary Waste Streams

The products from the process are ammonia gas and a ceramic solid. Treatment of off-gas from the waste form preparation steps will be required. No other waste streams are generated.

3.3.4 Separation Efficiency

Between 85 to 99% of the nitrate is converted to ammonia in the process, and volume reduction from batch processing is from 50 to 55% after reaction, drying, and uniaxially pressing at 5,000 psi (Ref. 1). The ammonia off-gas from the reactor can be passed over a heated, catalytic bed and converted to nitrogen and water prior to discharge to the atmosphere.

3.3.5 Safety and Health

This process has only been demonstrated at the bench scale so safety and health issues have not been fully addressed. However, the process converts nitrate to ammonia rather than nitrogen gas, so further off-gas treatment will be required. The ammonia and hydrogen gas produced by the reaction are potentially explosive, so an inert gas must be maintained in the system. Finally, the process is highly exothermic, so safety controls will be required to prevent a run-away reaction.

3.3.6 Operational Complexity

This process has only been demonstrated at the bench scale. The proposed flowsheet does not indicate any complex operational situations.

3.3.7 Environmental Impact

The NAC process produces an ammonia off-gas which can be converted to nitrogen and water which will not be of environmental concern. The ceramic waste form produced by the process is expected to be acceptable for final disposal but has not yet been qualified.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

The cost of a system using the NAC process will be highly dependent on the performance requirements and optimization of the bench-scale process. Development work in this area is continuing.

Preliminary costs associated with construction and operation of the NAC process plant based on the proposed flowsheet have been estimated in 1992 by D. E. Brashears of Martin Marietta Energy Systems Central Engineering. For a batch plant to process 1200 kg NO_3^- /hr of Hanford SST waste over 20 years, the estimated capital cost was \$20M with an operating cost

of \$2.01 to \$2.66/kg NO_3^- -destroyed (Ref. 1). This compares to published literature costs for an electrolytic process and a thermal process of \$5.13/kg of nitrate in 1957. If the ceramic product is acceptable as a final waste form, it will offer additional cost savings by eliminating final form processing steps.

3.5 TECHNOLOGY COMPARISON

The NAC process will convert essentially all of the nitrate or nitrite in the waste to ammonia, while producing an insoluble alumina-silica ceramic waste form that is significantly smaller in volume than the starting waste solution. The waste form will trap many of the radionuclides and heavy metals that are originally present in the waste. Most other nitrate destruction processes convert sodium nitrate solutions to sodium hydroxide solutions. Leaving the waste solution in a liquid form would be an advantage if further processing or recovery operations were planned, but solidification would be required before final disposal. Grouting the liquid waste would result in a volume increase of about 40%, compared to a decrease of 70% for the NAC process. The NAC process will only work in alkaline solution ($\text{pH} > 11.5$), so any acidic wastes would require pH adjustment.

Advantages of this process are:

- * It is a simple chemical process which uses inexpensive reagents.
- * It fixes most of the metal and nonmetal cations in an insoluble matrix which may function well as a high level waste form after pressing and sintering.
- * Approximately 50% volume reduction in solids is achieved in batch processes, and 70% volume reduction in continuous processes.

Disadvantages are:

- * The waste form must be qualified by extensive leach and stability tests.
- * Hydrogen gas is generated in large quantities and the entire reaction must be run under an inert atmosphere to reduce the explosion hazard.
- * Ammonia rather than nitrogen is the principal gaseous reduction product. This must be scrubbed from the off-gas stream producing a waste that approximates the bulk of the original nitrate waste volume, or the ammonia must be passed over a heated, catalytic bed where it can be converted to nitrogen and water prior to discharge to the atmosphere.

3.5.1 Comparison with Cement-Based Grout

Immobilization of nitrate waste in a cement-based grout results in volume increases of between 35 to 50% depending upon the formulation used compared with volume reductions of 50 to 55% with the NAC process. Because the NAC process product (Gibbsite) has small,

dense particles, the solid produced from it will have smaller pores than cement-based material, and less water from the outside will be able to penetrate thus reducing diffusion into the environment.

3.5.2 Comparison with Thermal Conversion to NO_x

Decomposition of nitrate starts at about 588°C and is 70% complete at about 940°C. All the water must be evaporated before the conversion to NO_x can occur making this a very energy intensive process. At the high temperatures needed for decomposition, volatilization of the radioelements can also occur. Both NO_x and radioelements can be difficult to scrub out of the off-gas. In addition, organics present in the nitrate-based waste may initiate an explosion depending upon concentration and other catalyzing metals or species which may be present in the waste.

3.5.3 Comparison with Electroreduction

Nitrates can be converted to N₂ and NH₃ using electrolytic cells. Such cells are subject to a number of problems including the production of sodium hydroxide from sodium nitrate rather than products such as aluminum oxide and sodium aluminate from the NAC process which present fewer problems for final disposal; the crystallization of salts within the cells which foul the electrodes and lower current efficiency; the plating of metals and some radioelements onto the electrode surfaces which lowers cell efficiency; and the reduction in cell efficiency that can occur due to the presence of trace amounts of chromium due to the cyclic oxidation and reduction of chromium in such cells.

4.0 DEMONSTRATION REQUIREMENTS

Development work should include pilot-scale tests to further define the operating limits, through-puts, required process/safety controls and economics of the processes, and small-scale tests on actual waste solutions to identify any potential problems caused by minor waste constituents.

4.1 DATA REQUIREMENTS

Additional work on the process is continuing in FY93 and is addressing optimization of the aluminum feed requirements, determination of the design and operational parameters for a future plant, determination of the maximum acceptable amount of nitrate in the waste form, determination of the characteristics and acceptability of the ceramic waste form, determination of the fate of the total sodium present, and determination of the operability of the reaction system and characteristics of the solids produced using an actual "hot" supernate.

4.2 TESTING REQUIREMENTS

The process must be demonstrated at a larger scale before a full-size system can be constructed. Further bench-scale testing is underway to further define data and testing requirements for the planned pilot-scale system.

5.0 VENDOR LIST

This technology is being developed at Oak Ridge National Laboratory, so there are no commercial suppliers at present. The equipment needed for the process is standard industrial equipment that is readily available.

6.0 REFERENCES

1. Mattus, A.J., D.D. Lee, T.A. Dillow, L.L. Farr, S.L. Loghry, W.W. Pitt, and M.R. Gibson. *A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process (Draft)*, Oak Ridge National Laboratory, Oak Ridge, TN, ORNL/TM-12245, October 1992.
2. Mattus, A.J. and D.D. Lee. "The Nitrate to Ammonia and Ceramic (NAC) Process - A Newly Developed, Low Temperature Technology." To be presented at the Second International Mixed Waste Symposium, Baltimore, MD, August 1993.
3. Taylor, P.A., D.E. Kurath, and R. Guenther. *Evaluation of Nitrate Destruction Methods (Draft)*, DOE/MWIP-10, Oak Ridge National Laboratory, Oak Ridge, TN, March 1993.

APPENDIX I-2 ELECTROCHEMICAL ION EXCHANGE

1.0 TECHNOLOGY DESIGNATION

The process involves the destruction of nitrate salts from mixed wastes by first isolating the nitrate anion using an ion exchange resin, migrating them to the anode of an electrolytic cell, and then reducing them to nitrogen gas at a cathode.

2.0 NEED FOR THE TECHNOLOGY

The need for the electrochemical ion exchange process in the mixed waste treatment process is in the treatment of aqueous wastes containing nitrates. See the introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Electrochemical destruction of nitrate and nitrite containing mixed wastes shows promise in reducing the volume of residual wastes in effluent waste streams as well as being competitive with other wet processing approaches on at least the basis of power consumption. This method of destroying nitrates is under development by Bradtec, Inc. (Bristol, United Kingdom), AEA Industrial Technology (Oxfordshire, United Kingdom) and by researchers at the Savannah River Plant (SRP). It has been tested on simulants for radioactive waste streams expected at the Rocky Flats Plant (RFP) (Ref. 1) and SRP (Refs. 2 and 3). In both cases, the process involves first a separation process followed by a destruction process.

The approach being investigated for the RFP involves a process that is being demonstrated for a variety of applications (Refs. 1 and 4). Bradtec's electrochemical ion exchange (EDX) process consists of separation of the nitrate from the waste stream by an anion exchange resin followed by migration of the nitrate anions to an anode as shown in Figure I-2.1. The resin is contained between two anion selective membranes "A," on one side of which is the cathode compartment and on the other the anode compartment. The resin is continuously regenerated by a hydroxide flux that regenerates the anion sites and displaces the nitrate ions which then migrate to the anode compartment. Hydroxide ions are continuously generated by the cell at the cathode allowing for continuous cell operation. 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.

Figure I-2.1. Principle of Nitrate Electrochemical Ion Exchange

By making the nitrate/anolyte mixture follow a circuitous route through a series of bipolar electrodes in the destruction cell as shown in Figure I-2.2, the nitrate is electrochemically reduced to nitrogen at the cathodes and the anolyte returned to the anode compartment for reuse. Monopolar electrochemical destruction has been considered by several investigators, but the bipolar cell design has been found to be more effective (Ref. 2). The cells also have the potential of oxidizing organics in the waste at the anode.

Concentration of nitrates from dilute aqueous streams, such as ground water, has been investigated by incorporating electrochemical ion exchange process along with the destruction cell (Refs. 1 and 4). For aqueous wastes with dilute concentrations of nitrates, destruction can be facilitated by concentration of the nitrates (Ref. 1). However, separation and subsequent concentration of nitrate in the anolyte is not expected to be necessary for efficient destruction for nitrate/nitrite rich feed streams.

The conversion of nitrate to nitrogen, the preferred product, or ammonia is achieved through a series of sequential reduction steps. Because some of the intermediate species are unstable and short lived, only the important reactions in the destruction process are given below.

Measurable quantities of NH_4^+ , N_2O , H_2 , and O_2 can be expected as additional products in destroying nitrates and nitrites (Refs. 1 and 3).

Figure I-2.2. Schematic of Nitrate Destruction Process

Figure I-2.1 shows hydroxide as the regenerating ion; however, the catholyte chemistry controls the species of regenerating ion. Two anions that have been tested are hydroxide and bicarbonate. In the first case, sodium hydroxide is the catholyte that is maintained by the dissociation of water, which produces hydroxide ions for migration while generating hydrogen gas at the cathode. In the case of sodium bicarbonate catholyte, the bicarbonate ion migrates to the resin to replace nitrate ions, and the catholyte is maintained by the dissociation of water and the addition of carbon dioxide gas, thus producing hydrogen and regenerating sodium bicarbonate.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Electrochemical methods of reducing the amount of nitrate and nitrite in mixed waste at SRP have been investigated for several years using single and multiple cell electrolysis compartments. Investigations on SRP wastes indicate that electrolysis is a viable means of destroying nitrates and nitrites. However, the presence of chromium in the waste solution can reduce the electrical

efficiency of the process due to cyclic oxidation and reduction. The electrical efficiency can be reduced from >90% to <40% by 16 mg/L chromium (Ref. 2).

The electromigration of nitrate to the anode compartment is accompanied by the migration of other anions (Cl^- , SO_4^{2-} , HCO_3^-), which reduces the process efficiency. Once in the anolyte, these ionic species build up in concentration until a sufficient chemical concentration gradient exists to induce the back diffusion of the ions through the membrane. When this equilibrium is reached, the effect is that these anions pass through the EIX cell and appear in the effluent in the same concentration as in the feed. This process will occur with any anion, including nitrate, unless that ion is removed from the anolyte. Therefore, the selective removal of any species promotes forward migration and selective separation (Ref. 4).

Use of the hydroxide ion as a regenerant will produce regions of high alkalinity in the resin. Thus, the feed solution must be devoid of cations susceptible to alkaline precipitation, such as calcium. However, tests by Bradtec have shown that bicarbonate ion is an acceptable regenerant in the case where calcium is present in the feed (Ref. 1).

3.3 DEMONSTRATED PERFORMANCE

Destruction of nitrates by electrolysis has been investigated for a number of years for its applicability to radioactive mixed wastes (Refs. 1 to 4). The EIX process has been examined specifically for wastes from RFP and a pilot-scale plant has been proposed (Ref. 1). Research on SRP wastes has determined that the efficiency of the reduction of nitrates and nitrites depends on the current density, presence of chromate ion, temperature, and electrode spacing (Ref. 2).

There are a number of advantages in using the electrochemical process to destroy nitrates. Of significant importance is that there are no secondary wastes formed with the simple use of a destruction cell as the process does not require addition of significant quantities of other chemicals. The process could be used on acidic or alkaline waste streams without pretreatment. For acidic solutions, the waste will be neutralized while the nitrate is being destroyed. There is the potential for simultaneously destroying organics at the destruct cell anode. For dilute nitrate wastes, where an ion exchange resin might be used in the EIX process, the resin is used continuously and requires no additional regeneration.

Electrolysis affects ions other than just the nitrates that are intended to be destroyed. In some cases the products plate out on electrodes, although this problem can be solved partially by proper electrode selection, reversing electrode currents where possible, or removing problem ions prior to destruction (Refs. 2 and 3). Use of porous membranes has also resulted in some problems with fouling (Ref. 2). Chromium concentrations above 1 mg/L significantly reduce the electrical efficiency of the process.

Release of the off-gases will require further evaluation. The NH_3 and N_2O may have to be treated depending on the amounts produced and on local and national environmental regulations. The possible formation of NO_2 as a result of NO (g) combining with O_2 (g) in separation of nitrates from dilute nitric acid may warrant evaluation (Ref. 4). Hydrogen generation at the cathode presents a safety concern in that there is a potential for the formation of an explosive mixture of gases.

The electromigration of ions in aqueous solutions is accompanied by electroosmosis in which water diffuses through the membrane. This can, if not controlled, lead to volume imbalances over long treatment periods. In addition, the electrolysis process consumes water and will require significant quantities of makeup water. The treated solutions may require solidification for final disposal, which will increase the volume by about 40%.

3.3.1 Technology Status

All of the equipment for the recommended processes is commercially available. The electroreduction process assisted by anion exchange (The Bradtech process) is currently commercially available from the Bradtech Corp. and has been tested at Rocky Flats Plant.

3.3.2 Reliability and Maintenance Requirements

This process and equipment are in general considered very reliable except for the fact that the membranes employed are subject to fouling.

3.3.3 Secondary Waste Streams

This process converts sodium nitrate and sodium nitrite to nitrogen and oxygen gases and sodium hydroxide. The residual aqueous phase which contains the dissolved solids can be dehydrated and placed in grout or glass as a final waste form.

3.3.4 Separation Efficiency

These processes can reduce the nitrates/nitrites to an insignificant level. Decontamination factors (ratio of influent concentration to effluent concentration) of over 100 have been demonstrated in some cases (Ref. 1).

3.3.5 Safety and Health

The safety and health issues are only unique because of the nature of the mixed wastes which are being processed. Complete containment of these wastes must be assured at all times. Criticality concerns are met by the standard equipment and procedures in use in the nuclear industry.

3.3.6 Operational Complexity

The operational complexity of these processes is not great. Simplicity was strongly considered in the acceptance criteria.

3.3.7 Environmental Impact

No environmental impact is expected from any of these processes since no secondary waste streams will be injected into the environment which do not meet the EPA discharge limits. However, release of the off-gases, such as NH_3 and N_2O , will require further evaluation.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

To treat 0.1 gpm of a high nitrate concentration feed (1 M nitrate) would require 20 ion exchange cells at a cost of approximately \$100,000. The addition of a nitrate destruction cell would be an additional \$50,000 (Ref. 1).

The costs for this technology have not been estimated for treating DOE mixed wastes. Bradtec estimates that power requirements are about 0.96 kWh/g mole of NO_3^- destroyed or a total of 1.6 kWh/g mole for both separation by EIX and destruction (Ref. 3). Such power consumption at \$0.03/kWh would result in power costs of \$0.46/kg NO_3^- to destroy nitrates.

3.5 TECHNOLOGY COMPARISON

This is commercially known as the Bradtech process. It has been commercially implemented, however, it will continue to benefit from the further development of anode materials for the cell. It is more complex than the simple ER cell, but achieves the same degree of waste reduction and produces the same off-gas stream. The process economics are relatively good but not quite as high as the simple ER cell.

The electrochemical destruction process will work in acidic or alkaline solutions. The process of nitrate destruction produces hydroxide, so acidic waste solutions will be neutralized during nitrate treatment, but concentrated alkaline wastes will contain very high levels of sodium hydroxide. The process can potentially destroy all of the nitrate in the waste, and does not produce any secondary solid wastes.

4.0 DEMONSTRATION REQUIREMENTS

Development work should include pilot-scale tests to further define the operating limits, through-puts, plugging/fouling control, required process/safety controls and economics of the process, and small-scale tests on actual waste solutions to identify any potential problems caused by minor waste constituents.

Tests on an RFP feed stream indicated that americium-241 was retained in the resin compartment and that plutonium-238 in the feed was not detected in any of the effluent samples analyzed. It was assumed that under the conditions of the test the plutonium had precipitated as a highly insoluble polymer or hydroxide (Ref. 1). Thus, tests are required to determine the behaviour of radionuclides in the waste under operating conditions.

4.1 DATA REQUIREMENTS

Data required in any demonstration will include:

- * Degree of nitrate/nitrite reduction
- * Off-gas composition
- * Process economics
- * Secondary waste stream compositions
- * Behavior of other species during operation.

4.2 TESTING REQUIREMENTS

Test requirements will include:

- * Process data development
- * Process safety issues
- * Equipment reliability
- * Process stability and flexibility

5.0 VENDOR LIST

Electrochemical destruction of nitrates is under development by Bradtec, Inc. (Bristol, United Kingdom), AEA Industrial Technology (Oxfordshire, United Kingdom), and by researchers at the Savannah River Plant (SRP). Commercial units are available for treating low concentration ground water, and lab-scale units have been tested on simulants for DOE mixed waste solutions.

6.0 REFERENCES

1. Atkins, K.J., D. Bradbury, G.R. Edler, and S.M. Scrivens. *Electrochemical Ion Exchange Treatment of Plutonium-Bearing Nitrate Waste*. BRADTEC Ltd., Bristol Polytechnic, Coldharbour Lane, Bristol BS16 1QY, United Kingdom, November 1992.
2. Hobbs, D. T., and M. A. Ebra. "Electrochemical Processing of Alkaline Nitrate and Nitrite Solutions." In *AIChE Symposium Series - Electrochemical Engineering Applications*, No. 254, Vol. 83, pp. 149-155, 1987.

3. **Electrosynthesis Company, Inc., *Electrochemical Processing of Nitrate Waste Solutions*. WSRC-TR-90-491, Westinghouse Savannah River Company, Aiken, South Carolina, May 31, 1992.**
4. **Bradbury, D., G. R. Elder, and G. L. Kalinauskas. *Removal and Destruction of Nitrates from Wastewater and Groundwater*. Bradtech-US, Inc., Atlanta, Georgia, and Bradtech Ltd., Bristol, United Kingdom, 1992.**

APPENDIX I-3 BIODENITRIFICATION

1.0 TECHNOLOGY DESIGNATION

The purpose of biodenitrification is to convert nitrite and nitrate ions in waste solutions to nitrogen gas, thereby reducing the toxicity of process effluents to biota.

2.0 NEED FOR THE TECHNOLOGY

The use of nitric acid as a process chemical is routine in actinide processing and the MWTP may be required to treat these solutions. Other nitrate sources may include spent nitrate salts and dilute nitric acid solutions from decontamination of process equipment. While biodenitrification is not specifically included in the MWTP design, it may be necessary to meet permit restriction on nitrates in process effluents.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 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, is needed to act as a hydrogen donor and to supply carbon for biological synthesis. The products of biodenitrification are nitrogen gas, carbon dioxide, water, and small quantities of biomass.

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. The nitrate is converted to nitrogen gas, carbon dioxide and water. A readily biodegradable organic carbon source is supplied to the bacteria, and moderate temperatures (15 to 50°C) and pH (7.5 to 8.5) must be maintained in the bioreactor for optimal denitrification rates. The feed stream to the Y-12 bioreactors contains about 5 M total nitrate (mostly aluminum nitrate) and about 1.5 M nitric acid. Calcium acetate is supplied as the organic carbon source. The bioreactors can treat about 2 g NO_3^-/L of reactor volume/day. The denitrification reaction produces enough alkalinity to neutralize the feed and maintain a pH of about 7.5 in the bioreactor as long as the feed solution contains less than 1.5 M free nitric acid. The bioreactor produces a sludge that contains calcium carbonate, aluminum hydroxide and biomass (Refs. 1 and 2).

Feeding highly concentrated nitrate wastes to a bioreactor is only feasible if the cations in the waste will precipitate in the bioreactor. For soluble cations, such as sodium, the

concentration of the waste stream fed to the bioreactor is limited by the tolerance of the bacteria for the cation. In the case of sodium, high denitrification rates have been observed at sodium concentrations up to 1.2 M. It may be possible to isolate or develop bacterial strains that could tolerate even higher sodium concentrations. Acute radiation experiments have demonstrated that 0.3 rad/s should not adversely affect the denitrification bacteria (Ref. 3).

Equipment for biodenitrification systems generally consists of process tanks, mixing equipment, and a sludge removal mechanism. All engineered biological treatment systems require rigid control of process variables such as temperature, feed-to-microorganism ratio, retention times, choice of organism, influent and effluent nitrate concentrations, etc.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Stream characteristics depend on design and application. Normally biodenitrification is used after the majority of the metals have been precipitated out of solution, and it is usually followed by carbon columns to adsorb any unreacted organic species.

However, this technology is used at the Y-12 Plant to treat bulk aqueous wastes containing all types of metal and organic contaminants. A wide variety of contaminants are fed to this system with no attempt at segregation. The large processing volume tends to dilute the effect of specific contaminants. However, contaminants harmful to people are also detrimental to the bacteria (e.g., Ni, Cr, Pb, and As), but the bacteria can be acclimated to most species. Sudden changes in the process chemistry will shock the bacteria and be more detrimental than specific contaminants.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Biodenitrification systems are currently available through commercial industry. Biological denitrification has been used for over 15 years to treat high nitrate concentration mixed wastes at the Oak Ridge Y-12 Plant. The Y-12 Plant currently operates a 500,000 gallon batch system to treat process wastes. These wastes contain low concentrations of uranium, but do not contain fission products like most of the currently stored mixed wastes. The process has not been tested on the high sodium nitrate concentration mixed wastes that are stored at DOE facilities.

Biodenitrification systems are often used in wastewater treatment plants treating millions of gallons per day. All necessary equipment for these processes is currently available through commercial industry. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintainability are high for this technology. However, adequate feed characterization is required to ensure proper pH, and an organic to microorganism ratio.

3.3.3 Secondary Waste Streams

The secondary waste streams from biodenitrification systems consist primarily of the biomass that is settled from solution. No toxic materials of incomplete destruction have been detected in the Y-12 Plant biodenitrification effluent; however, whether or not these materials are produced depends on the MWIP feed stream. As with all process equipment, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

These systems are very effective and have a long performance history.

3.3.5 Safety and Health

No health and safety issues specific to this technology exist.

3.3.6 Operational Complexity

This technology is generally quite simple in design.

3.3.7 Glovebox Capability

These systems are generally used in large-scale wastewater treatment facilities and are not commonly used in small-scale glovebox operations. However, if adequate hydraulic retention times and process volumes are designed into the process, there is no technical reason why glovebox operation would be precluded.

3.3.8 Environmental Impact

None specific to this technology.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

No significant development effort is required unless the waste stream contains a co-contaminant that is toxic to the denitrification organism. Capital costs are low to medium, depending on the scale of operation. The cost for operating the Y-12 Plant bioreactors is about \$4/kg NO_3^- . Costs for a remote-handled facility would be much higher, but have not been quantified.

3.5 TECHNOLOGY COMPARISON

Most nitrate removal technologies operate by collecting the nitrate ion on an ion exchange resin or through electrochemical destruction. Biological processes are generally more efficient and result in less secondary waste streams. The main advantages of biological denitrification is that essentially all of the nitrate in the waste is converted to relatively innocuous end products (carbon dioxide, nitrogen and biomass) at ambient temperature and pressure, its ability to process large batches, and the maturity of the technology. The required equipment is also simple, readily available, and easy to operate.

The disadvantage is the same for all biological processes in that they must be carefully controlled to maintain a healthy biological culture. The pH and salt concentration ranges that the bacteria can tolerate are narrow, and the denitrification rate is slow, which dictates large bioreactors. Wastes that contain high sodium concentrations, which includes most of the stored wastes, will require dilution prior to treatment. The sludge produced during the process would require further treatment to stabilize or destroy the biomass in order to prevent off-gassing during storage.

Unless an order-of-magnitude improvement is found in sodium tolerance for denitrification bacteria, the high-pH mixed wastes stored at Hanford, Oak Ridge, and Savannah River would need to be diluted significantly before biodenitrification could be used to destroy the nitrates. Also, the waste would have to be neutralized, which would require large amounts of acid, and might solubilize additional radionuclides and heavy metals. Significant effort has been expended in the past to reduce the volume of these stored wastes as much as possible, so diluting the wastes for nitrate treatment would be very undesirable. The treated waste would require further treatment, such as biomass destruction and grouting prior to final disposal to solidify the waste and prevent off-gassing during storage.

Acidic waste streams, such as those at Rocky Flats and Idaho National Engineering Laboratory, appear to be better candidates for this technology, although these streams are currently being solidified. Any dilute mixed waste streams that may be produced in the future would be good candidates for biodenitrification.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Design of biological systems requires information about the characteristics of the fluid being treated. All engineered biological treatment systems require information on temperature requirements, feed-to-microorganism ratio, retention times, choice of organism, influent and effluent nitrate concentrations, etc.

4.2 TESTING REQUIREMENTS

Design of biological systems must be performed through bench and pilot testing with actual waste streams. Denitrification rates would need to be measured for specific waste streams in order to size a bioreactor for treating the waste. Required dilution ratios and neutralization requirements would need to be determined for high sodium concentration waste solutions.

5.0 VENDOR LIST

The equipment needed for denitrification (stirred bioreactors or columns, pumps, controllers, etc.) is readily available from many industrial equipment suppliers. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. As mentioned previously, only minor modifications of commercially available equipment are expected. Some companies that specialize in applications of biological processes include:

- * BioGenesis, Inc.
- * Bio-Rem, Inc.
- * BioTrol, Inc.
- * ECOVA Corporation
- * International Technology Corporation
- * Remediation Technologies, Inc.

6.0 REFERENCES

1. Clark, F. E., C. W. Francis, and J. W. Strohecker. *Denitrification of Acid Wastes From Uranium Purification Processes*. Y-1990, Union Carbide-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, TN, November 1975.
2. Clark, F. E., J. M. Napier, and R. B. Bustamante. "Biological Treatment of Concentrated Nitrate Wastes." *1977 National Conference on Treatment of Industrial Wastewaters and Residues*, Houston, TX, 1977.
3. Francis, C. W. and C. W. Hancher. "Biological Denitrification of High-Nitrate Wastes Generated in the Nuclear Industry." In *Biological Fluidised Bed Treatment of Water and Wastewater*. P. F. Cooper and B. Atkinson, eds. Ellis Horwood Limited: Chichester, England, 1981.
4. Benefield, L.D., et al. *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall, Inc., 1984.

5. **U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. "The Superfund Innovative Technology Evaluation Program: Technology Profiles Fifth Edition." EPA/540/R-92/077, 1992.**

APPENDIX I-4 CHEMICAL REDUCTION

1.0 TECHNOLOGY DESIGNATION

The technology described involves the destruction of nitrate and/or nitrite salts in aqueous mixed waste by chemical reduction.

2.0 NEED FOR THE TECHNOLOGY

The need for chemical reduction in the mixed waste treatment process is in the treatment of aqueous wastes containing nitrates. See the introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION

3.1 DESCRIPTION

A wide range of reducing agents, such as formic acid, formaldehyde, sugar and ammonia, can be used to convert nitrate to a mixture of nitrogen gas and NO_x's. Examples of the reactions that can occur with formic acid are shown below (Ref. 1).

The denitration of high level waste (HLW) using formaldehyde has been performed for many years at the Marcoule and La Hague plants in France and at the Tokai-Mura plant in Japan. Formaldehyde is metered into a boiling solution of HLW at a controlled rate. The process is mainly used to adjust the acidity and nitrate concentration of the HLW prior to extraction processes, so destroying all of the nitrate is not a goal of these facilities. There is normally an induction period after the formaldehyde is added to the HLW before the reaction initiates. If excessive amounts of formaldehyde build up in the solution before the reaction starts, rapid reaction rates could produce high pressures in the reaction vessel. Several incidents of this type have occurred in the full-scale facilities with minor consequences (Ref. 2). There is also the

possibility of an unstable oscillatory reaction, caused by periodic build-up of reactants followed by very rapid reaction occurring if noble metals, such as palladium, are present in the waste solution (Ref. 3).

The off-gas will contain high concentrations of NO_x , so treatment will normally be required. The gas could be scrubbed, but this will produce large volumes of radioactively contaminated nitric acid or nitrate salts that will require further treatment for disposal. The preferred treatment for the off-gas would be catalytic reduction with ammonia, which will produce nitrogen gas (Ref. 4).

3.2 DEMONSTRATED PERFORMANCE

Nitrate reduction with formaldehyde has been used for many years to reduce the acidity of HLW at full-scale facilities in France and Japan. The process is potentially unstable, but has been successfully used for many years with only minor incidents.

The nitrate is converted to nitrogen oxides rather than nitrogen gas, so further off-gas treatment would be required. The alkaline wastes stored at Hanford, Oak Ridge and Savannah River would need to be acidified prior to treatment, which would require huge amounts of acid and would solubilize heavy metals, transuranics and other radionuclides. The process is potentially unstable, so safety controls will be required to prevent a runaway reaction. The process is not normally capable of destroying all of the nitrate, so substantial concentrations of nitrate would still be present in the waste after treatment. The treated waste would need to be solidified before final disposal, which would increase the volume.

3.3 COST OF TECHNOLOGY

The cost of this process for treating DOE wastes has not been estimated, but should be similar to the NAC process.

3.4 TECHNOLOGY COMPARISON

The chemical reduction process has been used for many years in France and Japan without serious incident, in spite of the potential for unstable or runaway reactions. The treated solution would require solidification prior to final disposal. As presently developed the process is limited to acidic solutions, so the alkaline wastes stored at most DOE facilities would need to be acidified prior to nitrate treatment. The process is not normally capable of destroying all of the nitrate, so substantial concentrations of nitrate would still be present in the waste after treatment.

4.0 DEMONSTRATION REQUIREMENTS

The process has not been tested on the alkaline mixed wastes stored at DOE facilities. Unless methods are developed to use the process under alkaline conditions, large amounts of acid would be required for pH adjustment prior to treatment. Extensive development work would be required before a facility could be designed and built to process DOE wastes.

5.0 VENDOR LIST

The process has been commercialized in Japan and Europe, but has not been used in the United States.

6.0 REFERENCES

1. Cecille, L. and M. Kelm. "Chemical Reactions Involved in the Denitration Process With HCOOH and HCHO." In *Denitration of Radioactive Liquid Waste*. L. Cecille and S. Halaszovich, eds. Graham and Trotman: Norwell, MA, 1986.
2. Breschet, C., D. Pageron, F. Drain, and V. Decobert. "Industrial Application of Denitration of HLW By Means of HCHO." In *Denitration of Radioactive Liquid Waste*. L. Cecille and S. Halaszovich, eds. Graham and Trotman: Norwell, MA, 1986.
3. Schulenberg, T. "Safety Aspects About Denitration." In *Denitration of Radioactive Liquid Waste*. L. Cecille and S. Halaszovich, eds. Graham and Trotman: Norwell, MA, 1986.
4. Donato, A. "Abatement of the NO_x Evolved During Denitration of Reprocessing Concentrate." In *Denitration of Radioactive Liquid Waste*. L. Cecille and S. Halaszovich, eds. Graham and Trotman: Norwell, MA, 1986.

APPENDIX I-5 HYDROTHERMAL PROCESS

1.0 TECHNOLOGY DESIGNATION

The technology described involves the destruction of nitrate and/or nitrite salts in aqueous mixed waste by hydrothermal processes.

2.0 NEED FOR THE TECHNOLOGY

The need for hydrothermal processes in the mixed waste treatment process is in the treatment of aqueous wastes containing nitrates. These processes may also destroy certain organic species depending on operating conditions. See the introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION

3.1 DESCRIPTION

The hydrothermal process is a variation of the chemical reduction process, with the chemical reduction occurring at higher temperatures and pressures. The same range of reducing agents could be used, but other more refractory compounds, such as ferrocyanides, that may already be present in the waste will also react with the nitrate under these conditions.

Lab-scale tests have shown that formic acid can be used to destroy essentially all of the nitrate in a 3 wt% NO_3^- solution within 2 hours under acidic ($\text{pH}=4$) or basic ($\text{pH}=13$) conditions in a pressurized vessel ($T=350^\circ\text{C}$ and $P=19$ MPa). In the acidic solution essentially all of the nitrate was converted to nitrogen gas, but in the basic solution only about 50% was converted to nitrogen gas and the remainder was unaccounted for (Ref. 1). Other reductants, such as ammonia, urea, methane and hydrogen, were tested under similar conditions, but were found to be less effective, particularly at high pH.

Lab-scale tests have demonstrated that various organics and ammonia will react with nitrate under supercritical or near supercritical conditions (450 to 525°C and 30 MPa). A mixture of nitrogen gas and nitrous oxide is produced from the nitrate. Potassium ferrocyanide, which is present in the Hanford waste, will react with nitrate at 500°C and 30 MPa. Most salts are only slightly soluble in supercritical water; for example, sodium nitrate has a solubility of 293 ppm at 525°C and 24.8 MPa. Low solubility may make it difficult to get high sodium nitrate concentration solutions into the reactor, but also opens the possibility for removing the reaction products (i.e., sodium hydroxide) and other radionuclides and heavy metals as a solid waste (Ref. 2).

3.2 DEMONSTRATED PERFORMANCE

This technology has been tested in lab-scale experiments using a surrogate for the Hanford tank waste and other more dilute nitrate solutions. This technology is similar to the chemical reduction process. The main advantages are that organics present in the waste could be used to destroy nitrate, converting the organics to carbon dioxide and minerals. Also, both acidic and alkaline solutions could be treated using this process. Under some conditions almost all of the nitrate can be converted to nitrogen gas. It may be possible to separate most of the salts, and some radionuclides and heavy metals as a solid waste. If the majority of the salts are removed, the dilute water solution left could be greatly reduced in volume by evaporation prior to solidification for final disposal.

Nitrates and other salts have limited solubility in supercritical water, so plugging of the lines to and from the reactor is a concern. The high temperatures and pressures used in the process will increase corrosion rates, so exotic materials will probably be required for the reactor increasing system cost. Further processing, such as grouting, will be required to solidify the waste prior to final disposal. Off-gas treatment may be required for NO_x 's.

3.3 COST OF TECHNOLOGY

The cost of this technology has not been estimated, but will probably be higher than the NAC and Chemical Reduction processes because of the higher pressures and exotic materials requirements.

3.4 TECHNOLOGY COMPARISON

This process has the potential for destroying nitrates in both acidic and alkaline wastes without any required pre-treatment. Under some conditions the nitrate is converted almost completely to nitrogen gas. Organics that are present in the waste will be destroyed at the same time as the nitrate, which is the major advantage of this process. The treated solution will require solidification prior to final disposal, although the volume of solid waste may be greatly reduced if the salts are separated from the supercritical water in the reactor. Extensive development work would be required before a facility could be designed and built.

4.0 DEMONSTRATION REQUIREMENTS

The development work should include pilot-scale tests to further define the operating limits, throughputs, required process/safety controls, plugging control and economics of the processes, and small-scale tests on actual waste solutions to identify any potential problems caused by minor waste constituents.

5.0 VENDOR LIST

Supercritical water oxidation units are commercially available for treating dilute wastewaters, but would likely require significant modification before DOE mixed wastes could be treated.

6.0 REFERENCES

1. Cox, J. L., M. A. Lilga and R. T. Hallen. *Thermochemical Nitrate Reduction*. PNL-8226, Pacific Northwest Laboratory, Richland, WA, September 1992.
2. Robinson, J. M., et al. *Destruction of Nitrates, Organics, and Ferrocyanides by Hydrothermal Processing*. LA-UR-93-456, Los Alamos National Laboratory, Los Alamos, NM, 1993.

APPENDIX I-6 CALCINATION

1.0 TECHNOLOGY DESIGNATION

The technology described involves the destruction of nitrate and/or nitrite salts in aqueous mixed waste by the calcination process.

2.0 NEED FOR THE TECHNOLOGY

The need for the calcination process in the mixed waste treatment plant is in the treatment of aqueous wastes containing nitrates. This processes may also destroy certain organic species depending on operating conditions. See the Introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION

3.1 DESCRIPTION

Aqueous radioactive wastes at INEL are stabilized and solidified in a fluidized-bed calcining facility called the New Waste Calcining Facility (NWCF). The 1.5-meter diameter calciner, which is heated to 500°C by in-bed combustion, will process about 200 gal/hr of waste, producing a dry granular solid for storage. The NWCF treats a variety of wastewaters, including wastes high in aluminum, zirconium, fluoride and ammonia, as well as nitrate. The concentration of sodium nitrate in the feed is strictly controlled to prevent caking of the calcine. Sodium nitrate melts at 308°C, and mixtures of sodium nitrate with potassium, calcium or magnesium nitrate melt at even lower temperatures. Sodium nitrate decomposes to produce Na_2O and NO_2 in the range of 600 to 900°C, which is above the temperature limit for the NWCF (Ref. 1). Small amounts of sodium bearing wastes are calcined by mixing them with other waste solutions, but inventories of sodium wastes are accumulating because of the limited amount of sodium allowed in the NWCF.

Pilot-scale tests have demonstrated that the ratio of sodium wastes entering the NWCF can be increased by adding sucrose to the waste solution. The sucrose reacts with the nitrate to produce NO_x , as described in Appendix I-4. Potential problems identified in the pilot-scale tests include possible plugging of off-gas filters by unburned sucrose, increasing the amount of fines produced and increased caking of the solids during storage. Further development tests were recommended (Ref. 2).

3.2 DEMONSTRATED PERFORMANCE

Calcination has been used at INEL for almost 30 years to solidify low sodium wastes. Wastes with moderate concentrations of sodium can be processed by appropriate blending with other waste streams. Pilot-scale tests have demonstrated that adding sugar to the waste solution can increase the allowable concentration of sodium nitrate by chemically reducing the nitrate during calcining.

The calcination process used at INEL will not work for the alkaline wastes stored at Hanford, Oak Ridge and Savannah River, which are primarily sodium nitrate. The sodium nitrate melts, but does not decompose, at the calciner's operating temperature of 500°C. The off-gas from the calciner must be treated to remove NO_x , which is the primary decomposition product of metal nitrates at 500°C.

3.3 COST OF TECHNOLOGY

The cost for calcining waste in the NWCF is about \$37/L (\$130/kg NO_3^-) (Ref. 3). This is the only technology that is currently being used on highly radioactive mixed waste at a DOE facility. The cost is much higher than the estimates for several of the other nitrate destruction technologies, even though the process is not more complicated, which casts doubt on the other cost estimates.

3.4 TECHNOLOGY COMPARISON

Calcination is a well-established process for solidifying low sodium concentration wastes. However, using the technology to treat the high sodium nitrate concentration wastes stored at most DOE facilities is not feasible at the present. The process converts nitrate to NO_x gas, so off-gas treatment would be required.

4.0 DEMONSTRATION REQUIREMENTS

The process is well established for low sodium concentration wastes. Further development work may establish treatment methodologies for higher sodium wastes.

5.0 VENDOR LIST

The calcination process was developed at Idaho National Engineering Laboratory.

6.0 REFERENCES

1. Berreth, J. R. *Potential Calcining Stoichiometries and Their Effects On Waste Volumes*. WINCO-1070, Idaho National Engineering Laboratory, Idaho Falls, ID, December 1989.

4 of 5

2. Newby, B. J., T. D. Thomson and B. H. O'Brien. *Calcination of Fluorinel-Sodium Waste Blends Using Sugar As a Feed Additive*. WINCO-11879, Idaho National Engineering Laboratory, Idaho Falls, ID, June 1992.
3. B. H. O'Brien, Idaho National Engineering Laboratory (INEL), personal communication.

APPENDIX I-7 HIGH TEMPERATURE PROCESSES

1.0 TECHNOLOGY DESIGNATION

The process described involves the destruction of nitrates and/or nitrites from aqueous mixed wastes using high temperature processes including thermal and plasma incineration.

2.0 NEED FOR THE TECHNOLOGY

The need for high temperature processes in the mixed waste treatment plant is in the simultaneous destruction of nitrates and organic species. See the introduction to Appendix I for a discussion on the need for nitrate destruction technology. Although thermal destruction is part of the WDS System, it is discussed here in the context of nitrate destruction to identify the pros and cons of sending nitrate salts directly to thermal destruct.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Sodium nitrate melts at 307°C, and begins decomposition at 588°C which is about 70% complete at 940°C. Typical decomposition reactions are:

These are disproportionate redox reactions wherein the formal oxidation number of nitrogen is reduced and the number for oxygen is increased. High reaction rates are obtained because of the high temperatures. Thermal destruction can be a very efficient method for destroying nitrates; however, two problems are noted:

- * Release of NO_x gases to the environment is strictly controlled by the Environmental Protection Agency (EPA) because of the potential for creating acid rain. Trapping these acid gases in a caustic trap is counter productive since this recreates the nitrate-nitrite compounds that were originally destroyed.
- * The relatively high vapor pressure of sodium nitrate will cause some of the nitrates to distill. These nitrates can condense in the off-gas system and can create a fire or explosion hazard. It is important that sufficient retention time is achieved within the combustion zone to ensure the thermal degradation of nitrate vapors, as well as solids and liquids.

Despite the above problems, destruction of nitrates by incineration is routinely performed for feedstreams which have a small nitrate concentration and a high organic concentration. Under these conditions the carbon, carbon monoxide, and hydrogen released by the organics successfully removes oxygen from the NO_x gases. Nitrate rich streams can also be incinerated if the NO_x gases are further reacted in an afterburner zone with a fuel rich gas such as propane. For these reasons front-end removal of nitrates may not be required if mixed wastes are to be incinerated and if an appropriate afterburner is designed into the off-gas system.

At higher temperatures ($>2000^\circ\text{C}$) nitrates can be converted directly to nitrogen gas. One of the most promising thermal treatment systems for nitrates is plasma incineration. Plasma processing breaks all of the chemical bonds at these higher temperatures, and upon rapid quenching, nitrogen and oxygen gas are the primary products. Pilot-scale tests using a plasma torch have demonstrated that a mixture of sodium and potassium nitrate can be converted to solid carbonates and nitrogen gas. The equipment consisted of a plasma torch, which generates extremely high temperatures by passing nitrogen or argon gas through a magnetically rotated electric arc producing an incandescent stream of ionized gas, and a graphite-lined, coke-filled furnace that served as a reaction chamber (Ref. 1). The coke reacted with the sodium and potassium oxides produced by the torch to yield carbonates.

An aqueous waste, consisting of magnesium, aluminum and calcium nitrates and nitric acid, which simulated a raffinate waste produced at the Feed Materials Production Center at Fernald, Ohio, was also calcined using a Westinghouse Marc 3 plasma torch. The torch was operated at a power level of 98 to 173 kW with air as the carrier gas, which yielded a reactor temperature of about 1200°C . The raffinate simulant was fed to the torch at a flowrate of 0.25 L/min. The reaction product was primarily metal oxides containing $<1\%$ nitrates. With air as the carrier gas, the torch generated about 1800 ppm NO in the off-gas prior to feed addition, that increased to about 2100 ppm NO after feed addition. Most of the nitrates in the feed were converted to nitrogen gas (Ref. 2).

3.2 DEMONSTRATED PERFORMANCE

High temperature processing, such as with a plasma torch, can decompose nitrates to nitrogen gas and NO_x and would destroy any organics in the waste. Pilot-scale tests using waste surrogates have demonstrated that a plasma torch can convert a solution of metal nitrates to solid metal oxides and can decompose a solid mixture of sodium and potassium nitrate. The nitrates are primarily converted to nitrogen gas.

A plasma torch system for destroying nitrates in mixed waste would require extensive development work before a full-scale facility could be designed and built. Sodium nitrate would be converted to sodium oxide, which is very reactive and hygroscopic. Using a coke-filled

furnace would convert the oxides to carbonates, which are stable, but would make the solids difficult to recover. The amount of radionuclides that would be volatilized during the process has not been determined.

3.3 COST OF TECHNOLOGY

Costs for building and operating a high temperature nitrate destruction system have not been estimated.

3.4 TECHNOLOGY COMPARISONS

Incineration is considered a safe and mature technology. The prospect of an explosion is always a possibility; however, with reasonable care and supervision, explosives have been excluded from the feed streams. Incinerators are not considered mechanically complex, they have good process economics, and they achieve good waste volume reduction. Although incinerators have an off-gas problem to deal with, treating or scrubbing incinerator off-gases is a well-developed art, and the residual incinerator ash can be immobilized as glass or grout.

Since an incinerator is already required to destroy hazardous organics and to stabilize the inorganic residues, it should be considered for use in treating waste streams with low levels of nitrate contamination. Thermal incineration of low nitrate concentrations requires no additional development activity. Thermal incineration of high nitrate concentrations is not recommended unless the following conditions are met:

- * A temperature not in excess of 950°C to ensure that NaOH and not Na₂O is the reaction product because of ash handling problems.
- * Removal of all reducing compounds to lessen the hazard of explosions.
- * A fuel rich afterburner to react the NO_x gases in the off-gas stream.

High temperature processes, such as a plasma torch, can convert sodium nitrate to nitrogen gas and sodium oxide, which is very reactive and would require stabilization. Enough energy would need to be supplied to evaporate all of the water from the waste solutions. The fate of the radionuclides in the waste has not been determined. Unlike lower temperature calcination, most of the nitrate would be converted to nitrogen gas rather than NO_x's.

Plasma incineration is not a mature technology. It is a moderately complex process because of the electronic equipment required to sustain the plasma and because of the high temperatures achieved in the plasma zone. The off-gas composition is very favorable since nitrates convert to nitrogen and oxygen gases. Waste volume reduction is achieved because some of the products are gases and can be released to the environment. The rest are recovered as metal oxide residues. The process economics are not yet thoroughly understood because of the immaturity of the process.

4.0 DEMONSTRATION REQUIREMENTS

Extensive development work would be required before a full-scale treatment system could be designed and built. Methods for remotely recovering the ash from the torch or incinerator and stabilizing the reactive solids must be developed.

5.0 VENDOR LIST

All of the equipment for the recommended processes is commercially available except for the plasma torches that are being developed. Suppliers of thermal incinerators for combusting hazardous wastes include Combustion Engineering in Windsor CT. Only Westinghouse at Pittsburgh, PA has reached true commercial vending status with a plasma incinerator. Other plasma torches are under development by Retech at Ukiah, CA and by UCLA in Los Angeles, CA.

6.0 REFERENCES

1. Johnson, A. J., and P. M. Arnold. "Waste Generation Reduction - Nitrates, Comprehensive Report of Denitrification Technologies." RFP-3899, Rockwell International, Golden, CO, March 1986.
2. Falk, D. E., E. J. Lahoda and J. L. Mitchell. "Nitrate Destruction By a Plasma Torch." FMPC/SUB-020, Westinghouse Materials Company of Ohio, Cincinnati, OH, September 1988.
3. Falk, D.E., E.J. Lahoda, and J.L. Mitchell. "Nitrate Destruction by a Plasma Torch." Feed Materials Production Center, Cincinnati, Ohio, FMPC/SUB-0210, September 1988.
4. Newby, B.J., T.J. Nichols, and A.P. Hoskins. "Calcination of WM-183 Waste." Exxon Nuclear Idaho Co., ENICO-1128, June 1983.
5. Armstrong, K.M. and L.M. Klinger. "Nitrate Waste Processing by Means of the Joule-Heated Glass Furnace." Monsanto Research Corp., Miamisburg, Ohio, MLM-3304, October 18, 1985.
6. Cowan, R.G., R.J. Cash, T.J. Owen, and G.E. Shook. "Nitrate Destruction in an Elutriated Fluid-Bed Calciner." Westinghouse Hanford Co., Richland Washington, WHC-EP-0062, September 1987.

APPENDIX I-8 SALT SPLITTING

1.0 TECHNOLOGY DESIGNATION

This process described involves the separation of nitrate salts from mixed wastes by first splitting the salts into their respective anions and cations, followed by conversion into acids and bases using an electrodialysis method.

2.0 NEED FOR THE TECHNOLOGY

Salt splitting separates the salts into their respective acids and bases that may either be recycled and reused within the DOE system, or further processed to destroy the HNO_3 and dispose of the NaOH . See the introduction to Appendix I for a discussion on the need for nitrate destruction technology.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

This electrodialysis method is characterized by its ability to split salts into their respective acids and bases, the ability to produce concentrated streams from dilute streams, and low energy consumption. The principle of operation is simple: ions in an electric field will migrate toward the electrode of opposite charge until they encounter an ion barrier. By proper selection and placement of ion selective barriers (membranes), salts can be concentrated. By inclusion of a bipolar membrane that splits water into H^+ and OH^- , the salts can be converted back into the acids and bases from which they were originally made.

Using electrodialysis, a center compartment of an electrodialysis cell is separated from a cathode compartment by a permeable cation exchange resin membrane, and from an anode compartment by a permeable anion exchange resin membrane. If a solution of sodium nitrate is placed in the center compartment and the anode and cathode are connected to a direct current source, the sodium ions will exchange on the cation resin displacing hydrogen (H^+) ions. Under the induced current, the Na^+ will be transported to the cathode and concentrated along with an equivalent amount of hydroxide ions (OH^-) which are generated at the cathode from the electrolysis of water. Similarly, the nitrate ion (NO_3^-) will exchange on the anion resin in the center mixed-bed compartment and will migrate with the induced current to the anode compartment. Hydrogen ions generated at the anode will combine with the nitrate ion to form HNO_3 . The ion exchange resins are constantly regenerated by the OH^- and H^+ formed by electrolysis.

This technology is not new, but must be matched with DOE streams to be treated. Commercial applications of this technology exist; however, the commercial applications do not contend with intensely radioactive solutions and such complex organic and inorganic mixtures as may be encountered in DOE wastes.

Salt splitting is economically and politically feasible in the commercial world where a ready market exists for all of the acids and bases which can be produced. Because of the vast amounts of nitrate/nitrite salts in DOE wastes, the limited need within DOE for acids and bases, and the political barriers to transferring any previously contaminated chemicals to the commercial markets, salt splitting should only be considered to satisfy the limited DOE market for acids and bases. Salt splitting is considered a safe process. It compares in safety to the electrolytic reduction (ER) process; however, process economics will not be as good for this technology as for ER since this process uses membranes that can fail or foul.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Because most metal hydroxides are not soluble in basic solutions, except for those in Group I of the periodic table, all heavy metal ions must be removed by preprocessing. Within a cell stack, cations permeate through one of the membranes into a basic solution. The heavy metal ions that permeate into this solution will precipitate onto the exit face of the membrane, thus fouling the membrane and rendering the entire cell stack inoperable (Ref. 1).

It is desirable to remove as much of the radionuclides as possible before the salt solution is introduced to the stack. Membrane materials that show a high degree of resistance to degradation by oxidizing acids, are quickly degraded by moderate doses of ionizing radiation. On the other hand, commercial membranes that exhibit good radiation resistance have poorer chemical resistance (Ref. 1).

The output consists of an acid and a base stream, both of which may be contaminated.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The development work principally needed for salt splitting is the development of robust membranes. This robustness must be maintained even when exposed to strong oxidizing acids, and ionizing radiation. Commercial membranes are highly selective for ions of a particular charge, and typically last for about one year. Membranes should be developed which compare favorably for the DOE wastes.

3.3.2 Reliability and Maintenance Requirements

This process and the general equipment necessary to run it are considered to be reliable; however, the membrane material is subject to fouling, and chemical or radiolytic degradation, and is therefore a source of difficulties.

3.3.3 Secondary Waste Streams

This process converts salts into the respective acids and bases from which the salts were originally produced. Waste volume reduction is not realized until the acids and bases find a beneficial use. Since the supply of salts vastly exceeds the demand for acids and bases, this process does not significantly reduce the waste inventory. There is no significant off-gas from this process; therefore it must rate highly on this factor. The residual aqueous phase that contains the dissolved solids can be dehydrated and placed in grout or glass as a final waste form.

3.3.4 Separation Efficiency

These processes can reduce the nitrates/nitrites to an insignificant level.

3.3.5 Safety and Health

The safety and health issues are only unique because of the nature of the mixed wastes which are being processed. Complete containment of these wastes must be assured at all times. Criticality concerns are met by the standard equipment and procedures in use in the nuclear industry.

3.3.6 Operational Complexity

The operational complexity of these processes is not great. Simplicity was strongly considered in the acceptance criteria.

3.3.7 Environmental Impact

No environmental impact is expected from any of these processes since no secondary waste streams will be injected into the environment that do not meet EPA discharge limits.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

The costs associated with this technology have not been determined at the time of this writing.

3.5 TECHNOLOGY COMPARISON

Salt splitting technology has several issues regarding membrane degradation and fouling that must be resolved before it can be considered for use in a mixed waste treatment system. However, other membrane based technologies may have the same problems that will require further development. The main disadvantage with salt splitting is that the process has the potential of generating two contaminated waste streams unless preprocessing removes radionuclides from the feed stream. However, unless there is significant need for the resulting acid and base, additional processing for disposal and/or destruction will be required. Therefore, nitrate destruction processes should be used in the first place rather than salt splitting.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Membrane life must be determined at operating conditions that will include exposure to a mixed acid product and possibly to ionizing radiation.

Data required in any demonstration will include:

- * Degree of nitrate/nitrite reduction.
- * Off-gas composition.
- * Process economics.
- * Secondary waste stream compositions.

4.2 TESTING REQUIREMENTS

Test requirements will include:

- * Process data development.
- * Process safety issues.
- * Equipment reliability.
- * Process stability and flexibility.

5.0 VENDOR LIST

Commercial applications of this technology exist; however, the commercial applications do not contend with intensely radioactive solutions and such complex organic and inorganic mixtures as may be encountered in DOE wastes. Wastren, Inc. of Golden, CO is developing an electrodialysis technology in collaboration with EG&G Rocky Flats, Inc.

6.0 REFERENCES

1. Hickman, R.G. "Waste Salt Recovery, Recycle, and Destruction." *Proceedings of the Information Exchange Meeting on Waste Retrieval, Treatment and Processing*. Houston, TX, March 15-17, 1993.

APPENDIX J PRECIPITATION

Precipitation technologies described in this appendix are as follows:

- J-1 Standard Precipitation Methods
- J-2 TRU/CLEAR®
- J-3 Sequestering Agents

APPENDIX J-1 STANDARD PRECIPITATION METHODS

1.0 TECHNOLOGY DESIGNATION

In wastewater treatment, precipitation is a physicochemical process, whereby some or all of a substance in solution is transformed into a solid phase and is subsequently removed from the solution.

2.0 NEED FOR THE TECHNOLOGY

Precipitation of dissolved chemical species may be needed in the MWTP in the Aqueous Treatment Line blocks 150.2 (primary treatment), 190 (secondary treatment), or 192 (tertiary treatment).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Precipitation is the process of making dissolved chemical constituents insoluble so that they can be separated from the liquid. This is usually accomplished by chemical reaction by adding a chemical that forms an insoluble compound with the target contaminant, or by changes in the composition of the solvent to decrease the solubility of the substance in it.

The precipitant used will depend on the composition of the waste stream including the metals to be removed, as well as other materials that may inhibit precipitation. Typical precipitating agents include sodium hydroxide, lime, ferric hydroxide, and sodium sulfide. Hydroxide and sulfide precipitation are commonly used for removing heavy metals. Sodium borohydride is a reducing agent that can be used to precipitate metals from solution as the insoluble elemental metal. Displacement is a process in which a metal is displaced and precipitated from solution by a metal higher in the electromotive series. The precipitates are often flocculated into larger particles (flocs) with the help of coagulants prior to solids removal. The precipitated solids can then be removed by settling and/or filtration.

3.2 INPUT AND OUTPUT STREAM CHARACTERIZATION

Pretreatment may be required to remove complexing agents that inhibit or prevent the use of conventional precipitation methods. Common complexing agents in waste streams include ammonia, cyanide, and ethylenediaminetetraacetic acid (EDTA).

Contaminants which would hinder a precipitation process may also require removal. Such contaminants are those which would form a soluble species with the ion or compound which you desire to precipitate. An example of this is the presence of the carbonate ion when attempting to precipitate uranium at high pH. The formation of insoluble uranium species is hindered because the uranyl carbonate complex is highly soluble at high pH. Another example of a contaminant interfering with a precipitation is the presence of iron when attempting to precipitate uranium with hydrogen peroxide at low pH. The iron reacts with the hydrogen peroxide preferentially, thus preventing the uranium-hydrogen peroxide reaction to take place.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

A large number of commercial vendors supply precipitation equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected. Ongoing development activities conducted by many organizations include investigating precipitation methods for selective precipitation of contaminants.

The K-1232 Liquid Chemical Treatment Facility at Oak Ridge uses chemical precipitation for removal of heavy metals from plating operations aqueous wastes. The treated wastewaters are released under the National Pollution Discharge Elimination System (NPDES) standards.

An iron coprecipitation process has been used at Oak Ridge for removing uranium from nitrate containing wastes, and in the Uranium Mill Tailing Remedial Action (UMTRA) program for removing uranium, radium, and other contaminants from surface runoff wastes generated during remedial action. During pilot-scale testing of this process at Hanford, reduction of uranium in groundwater from 3,460 ppb to 1 to 7 ppb was demonstrated.

3.3.2 Reliability and Maintenance Requirements

Reliability and maintenance requirements are to be determined at a later date.

3.3.3 Secondary Waste Streams

The secondary waste streams from precipitation processes consist primarily of precipitated solids. The addition of precipitation chemicals may also sufficiently alter the chemical characteristics of the feed stream to warrant secondary treatment. As with all process operations, periodic replacement of hardware as a function of normal operations will be necessary and will need disposal.

3.3.4 Separation Efficiency

Separation efficiency depends upon the characteristic of the feed stream and the design of the process.

3.3.5 Safety and Health

Health and safety issues specific to this technology will depend on the selection of process chemicals and their reaction characteristics.

3.3.6 Operational Complexity

Depends on design but may range from simple to quite complex.

3.3.7 Glovebox Capability

The technology is amenable to glovebox operations.

3.3.8 Environmental Impact

Environmental impact depends on the application.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Costs associated with the technology or equipment depends on the application and will be determined at a later date.

3.5 TECHNOLOGY COMPARISON

Chemical precipitation systems are relatively simple to operate and equipment and chemicals are readily available. However, the method generates a sludge that requires further treatment or disposal. If present, organometallic complexes may inhibit precipitation of the metals. There is no upper concentration limit for treatment but the lower concentrations are limited by equilibrium solubilities of the individual precipitates. The removal efficiencies are determined by the solubility products of the salts formed. However, some contaminants may be coprecipitated with the sludge that is formed, and may be removed to concentrations below their solubility limits. Treatability testing is generally required.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data requirements depend upon the application and will be determined at a later date. It is impossible to specify the quantity of waste stream information to design a chemical process without knowledge of the specific chemical process involved. In general, the more robust the precipitation process, the less information is needed. For processes which are highly sensitive to contaminants, a more detailed waste stream characterization is needed.

4.2 TESTING REQUIREMENTS

Testing should be done in the field with actual process streams where possible. When not possible, maximum flexibility should be part of the overall design. The use of surrogates in place of actual process streams should only be used where no other option is available.

5.0 VENDOR LIST

A large number of commercial vendors supply precipitation equipment. As detailed performance specifications become available for each application, the competitive bid process will be used to screen potential vendors. Only minor modifications of commercially available equipment are expected.

6.0 REFERENCES

1. Chung, N. K. "Chemical Precipitation" in *Standard Handbook of Hazardous Waste Treatment and Disposal*. H. M. Freeman, ed. McGraw-Hill Book Co.: New York, 1989.
2. EG&G Rocky Flats. "Final Site Wide Treatability Studies Plan." U.S. DOE, Rocky Flats Plant: Golden, CO, June 3, 1991.

APPENDIX J-2 TRU/CLEAR®

1.0 TECHNOLOGY DESIGNATION

Flocculation/precipitation is one of the treatment technologies used for the removal of transuranic waste from the aqueous liquid waste stream. This technology removes contaminants that are water soluble including alpha emitting radioisotopes, heavy metals, and organics. The technology described in this section is not a process, but rather a chemical substitute within the flocculation and chemical precipitation processing steps.

2.0 NEED FOR TECHNOLOGY

For aqueous wastes not suitable for processing in the primary treatment unit (Unit 150.2) such as dissolved impurities which may foul the activated carbon beds, special neutralization and chemical precipitation is needed to act as a prefilter to protect the primary treatment line operations. This feed is pumped to the flocculation and precipitation system. The flocculation/precipitation system is designed to remove suspended solids, heavy metals, and alpha emitting radioactive elements from a waste stream. Analytical Development Corporation (ADC) has developed a wastewater treatment chemical, TRU/CLEAR®, that utilizes potassium ferrate (K_2FeO_4) as a replacement for conventional precipitation agents, such as lime, ferrous/ferric sulfate, or ferric chloride.

The TRU/CLEAR® treatment product would be used in the flocculation/ precipitation treatment step (process #150.1) of the aqueous liquid waste stream after the liquid/solid separation step (process #150). The TRU/CLEAR® or ferrate(VI) technology can be used in most existing wastewater treatment plants incorporating a rapid mixer, flocculation unit, and clarifier. The purpose of potassium ferrate technology is the significant reduction in waste for disposal. Additionally, potassium ferrate may be used in pretreatment technologies or polishing as post treatment for air stripping.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

To remove high concentrations of suspended, and/or dissolved solids in the aqueous liquids stream, the stream is fed through the "prefiltering stages" (flocculation/ precipitation

system mentioned above). These stages consist of a pH adjustment, an agitator, and a settling tank for separation of the flocculants.

The chemistry of the process involves reduction of Fe(VI) to a final product of Fe(III) and each intermediate redox state attaches to a colloid of insoluble contaminant causing it to flocculate. Potassium ferrate (iron VI) differs from other inorganic coagulants such as alum or iron salts. Unlike these inorganic coagulants, which almost instantly form large flocs indicating the rapid precipitation of the Fe(III) hydroxide ($\text{Fe}(\text{OH})_3$) or the aluminum hydroxide ($\text{Al}(\text{OH})_3$), the ferrate ion (FeO_4^{2-}) is highly soluble in alkaline solutions (approximately 50 g/L). For the ferric or alum ion to be an effective coagulant, it must collide with the negatively charged colloids in order to destabilize the colloidal particles and start the floc formation process. It is often necessary to add large quantities of ferric or aluminum salts to form sweeping floc and ensure that flocculation is effective in removing small quantities of contaminants. Ferrate(VI), however, destabilizes colloids by the formation of multicharged cation iron species when Fe(VI) is reduced to Fe(III). Ferrate(VI) will reduce to ferric(III) and result in the formation of ferric hydroxide precipitates which agglomerates the colloid particles into larger, settleable solids. When Fe(VI) in an aqueous system reduces to Fe(III), it is then possible for many multicharged cation iron species [Fe(V), Fe(IV), Fe(III)] to form and adsorb onto the surface of the negatively-charged colloids and destabilize the colloids through charge neutralization.

3.2 INPUT AND OUTPUT STREAMS CHARACTERISTICS

For implementation of ferrate technology into the Mixed Waste Aqueous Wastewater Treatment, process adjustments must be made. Treatability studies typically are required to determine the required residence times and potassium ferrate dosage. The engineering technology issues have not been addressed that are required to build a treatment system, or the minor modifications which may be required for a chemical replacement in the existing schematic, and the solid waste handling after decontamination with ferrate wastes. However, current technology should be applicable to ferrate waste. Bench scale testing will have to be performed to define optimal operating parameters. However, typical operating parameters are summarized in table J-2.1.

The output streams have an alkaline pH of 11. The effluent from the floc may be filtered further to remove colloidal particles. Given specifications of the waste stream including flowrates, system modifications to existing equipment for MWTP application may be identified. With vendor assistance, the proper ferrate formulation may be selected. After selecting the proper formulation, bench scale testing for formula optimization need to be performed on the specific aqueous waste stream, with samples drawn and analyzed by an independent vendor.

TABLE J-2.1. TYPICAL OPERATING PARAMETERS

(Courtesy of Analytical Development Corp., TRU/CLEAR® Wastewater Treatment Technology)

PARAMETER	OPTIMUM CONDITIONS
Flow rates	10 to 2000 gpm
Potassium ferrate dosage (as Fe+6)	1 to 5 mg/l
Influent pH	8 to 12
Temperature	64 to 95°F
Residence times	15 min to <1 hr as needed

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The flocculation and precipitation system is well developed and functional. The chemical substitute potassium ferrate(VI) technology was first commercially applied for treatment of wastewater at West Valley Nuclear Services in 1990. ADC has demonstrated bench tests for removal and reduction of transuranic and solid waste for disposal at many DOE facilities.

The reaction mechanisms discovered to date during investigation of ferrate chemistry and application indicate a possible violation of equilibrium solubility behavior as it is understood today. The experimental results indicated that, by using this chemistry, transuranic metal elements can be removed to lower concentrations in solution than can be predicted by empirically measured equilibrium solubility constants. It is believed that several mechanisms are operating simultaneously in the system which contribute to the overall removal characteristics of the technology, including localized kinetically controlled reactions. These mechanisms are being investigated in conjunction with the engineering development of the technology. The total engineering effect of these mechanisms and properties is precipitative removal of transuranic elements from wastewater to unprecedented low concentrations, not predictable by standard analysis.

3.3.2 Reliability and Maintenance Requirements

It should be noted that nitrates in the system will accelerate degradation of ferrate causing larger flocs to form and ultimate paralysis of the ferrate technology claims. If this happens, the system must include a recycling loop for two or more passes; without recycling the efficiency decreases, and the amount of disposable waste increases. It is paramount to define the waste stream, and possibly pretreat the waste stream converting the nitrates before the destabilization stage.

3.3.3 Secondary Waste Streams

The flocculation and precipitation system has two streams that exit the system; solid and liquid. The flocculant that drops out of the settling tank (or solid), and the aqueous waste water stream (liquid). As with the use of any coagulant, sludge is generated by the flocculation and precipitation system. Settled sludge is dewatered by rotary kiln and disposed. The liquid stream is then sent to the primary treatment unit (Unit #150.2).

3.3.4 Separation Efficiency

It has been estimated that the volume of settleable solids generated is five to ten times lower using ferrate(VI) technology instead of ferric sulfate and lime. In general, for MWTP purposes, flocculation/precipitation removes, via oxidation, foulants, dissolved solids and transuranics. The flocculation and precipitation system with potassium ferrate minimizes radionuclide discharge (meeting and exceeding radionuclide limits set in DOE Order 5400.5) and efficiently removes priority pollutant metals from waste streams with a removal efficiency of 99%. (Note: After defining the application this percentage may vary depending on number of treatment steps.)

3.3.5 Safety and Health

TRU/CLEAR® is a strong oxidizer (potassium ferrate) and should be handled with the same care and procedures as other oxidizers. OSHA regulations require the storage of oxidizers away from flammables and explosives. The chemical should be used only in the solid powder form. While handling TRU/CLEAR® materials, appropriate protection should be worn (gloves, eyewear, lab coat, and mask). Fine particles are easily airborne during loading. In general, the safety and health plan for the facility should include the operation of these units, as well as the chemicals being used.

3.3.6 Operational Complexity

For pilot plant use, the TRU/CLEAR[®] processing units are mobile and contained in trailers. The operation is relatively simple to use, requiring three technicians (one per 8-hour shift) and a daily supervisor, preferably a Health Physicist. The system is automated with the exception of adding the potassium ferrate into the rapid (vortex) mixer. The mixer may be automated by adding a solid flow feed mixer. It includes an accumulation tank with an 8-hour holding capacity. Once a technician conducts sampling and analysis, the wastewater effluent may be discharged into a permitted water treatment unit.

3.3.7 Glovebox Capability

A pilot plant unit, rated at a capacity of 115 gal/min, is contained in two tractor trailers. There is no need for a glovebox. The levels, during tests at Fernald, OH, for example, were not high enough to use a glovebox; however, they were at levels that require protective clothing.

3.3.8 Environmental Impact

No significant impacts are anticipated to occur during routine installation and operation. This is based on assessment of effects on the environment in three areas: 1) construction; 2) waste generation; and 3) permitted discharge of effluent off-site. Workers may incur nominal exposure to the hazardous substances associated with plumbing and welding activities during installation. Otherwise, construction is not an issue, since the units are self-contained in trailers. Use of TRU/CLEAR[®] technology is not believed to impact environmental air quality, because this is a non-volatile, aqueous line and the cyclones are enclosed. Before actual use, all required environmental permits should be in effect (i.e., National Pollution Discharge Elimination System (NPDES) permit). An emergency response plan must be in place in the event of an accidental release.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

See Table J-2.2 below.

3.5 TECHNOLOGY COMPARISON

This technology may offer the ability to remove radionuclides to lower levels than achievable with conventional precipitation processes. It is also reported to produce much less sludge than conventional processes. The primary disadvantage is that the process is based on a proprietary chemical, which would have to be purchased from a single supplier.

A treatment study performed in December 1990 at Los Alamos National Laboratories using TRU/CLEAR® technology found that 165,000 gallons of wastewater treated using current ferric sulfate/lime treatment generated ten-55 gallon drums of sludge compared to the proposed TRU/CLEAR® treatment which generated one-55 gallon drum of sludge. This is an extreme example, generally the waste reduction ratio may range from 1 to 5 and 1 to 10 TRU/CLEAR® treatment versus the current ferric sulfate/lime treatment. To further illustrate this point, Table J-2.2 below shows how the total management of this waste could yield approximately \$200,000 in savings per million gallons of aqueous wastewater treated using the ferrate(VI) technology instead of ferric sulfate and lime.

TABLE J-2.2. FERNALD ENVIRONMENTAL MANAGEMENT PROJECT ANNUAL TOTAL WASTE MANAGEMENT COST COMPARISON (REF. 2)

	TRU/CLEAR® \$35/lb.	TRU/CLEAR® \$18/lb.	LIME \$0.05/lb.
Chemical Costs:			
TRU/Clear®	\$217,000	\$111,600	\$0
Sodium Hydroxide	\$8,010	\$8,010	\$0
Lime	\$0	\$0	\$5,170
Drums of Sludge	434	434	775
Monitoring Costs (\$5/drum)	\$2,170	\$2,170	\$3,880
Kiln Operating Costs (\$50/drum)	\$21,700	\$21,700	\$38,750
Drums of Dry Sludge	304	304	543
Disposal Costs (\$145/cu.ft.)	\$321,780	\$321,780	\$574,770
Total Waste Management Costs	\$570,660	\$465,260	\$622,570
Treatment Costs	\$0.09/gal	\$0.08/gal	\$0.10/gal

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Typical data requirements consists of waste stream flowrates, influent pH, temperature, and residence times.

4.2 TESTING REQUIREMENTS

In order to successfully demonstrate the efficiency of TRU/CLEAR® or potassium ferrate technology, several steps need to be taken:

- * Determine flow rate to properly size unit processes
- * Characterize waste to properly select coagulation feed chemicals and to predict treatment effectiveness
- * Determine total suspended solids to predict solid generation rates and properly size sedimentation process
- * Determine total dissolved solids to predict solid generation rates and determine what other constituents will precipitate in addition to transuranics
- * Determine alkalinity to predict chemical requirements for pH adjustment
- * Specify effluent requirements (based on regulatory drivers) to predict technology effectiveness, and evaluate need for additional treatment downstream

5.0 VENDOR

Analytical Development Corp.
 4405 North Chestnut St.
 Colorado Springs, CO 80907
 Michael E. Potts
 Applications Chemist
 (719) 260-1711

6.0 REFERENCES

1. ADC Potassium Ferrate Wastewater Treatment Technology Brochure, January 20, 1992
2. Personal communications with Michael E. Potts, Analytical Development Corp., 1993.

APPENDIX J-3 SEQUESTERING AGENTS

1.0 TECHNOLOGY DESIGNATION

Sequestering agents are chelating or macrocyclic chemical reagents that form highly stable and soluble complexes with metal cations, often with great selectivity. They are used to concentrate or extract various cations, especially heavy metals and radionuclides, in analytical applications and waste treatment processes. Sequestering agents that complex with inorganic anions also exist but are not as well developed.

2.0 NEED FOR THE TECHNOLOGY

Sequestering agents could be used in the MW process to remove hazardous metals within the Aqueous Liquids Treatment Line. Specifically, all the actinides and other radionuclides may be removed by sequestering agents in Process Number 150.1 (Special Treatment). Sequestering agents may also find applications in the Secondary Treatment Unit (190) where ion-specific technology is necessary for the removal of any remaining inorganic cations from the clean water stream.

All the actinides and various other radionuclides (e.g., Sr^{90} , Tc^{99} , and Cs^{137}) can be concentrated and removed in Special Treatment using sequestering agents. Elimination of the actinides and minimization of radioactivity before Primary Treatment may obviate the need of glovebox operations for the remainder of the process, simplifying downstream processing requirements. Other hazardous (RCRA) metal ions (e.g., Cd, Hg, and Pb) can also be extracted through the use of sequestering agents.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Because of favorable thermodynamics and spatial relationships, highly stable complexes are formed between sequestering agents and selected cations. Formation of complexes is often highly selective. Sequestering agents can be made miscible with organic solvents such that liquid/liquid extraction can be performed on aqueous samples. This is, however, sometimes costly. It is preferable to have sequestering agents sorbed onto an inert stationary support (e.g., resin with small particle size) such that cations may be extracted by passing the aqueous liquid through a packed column of the support (*extraction chromatography*).

No special equipment is required so long as the sequestering agents are allowed to mix intimately with the waste stream and can be physically separated from it afterward. Very efficient separations can be obtained as separation factors may reach 10^5 or even higher. However, effective extraction very often can only be achieved under rather restricted conditions; for example, the distribution coefficients are highly pH-dependent and a narrow pH range is normally required. Most sequestering agents can be regenerated and recycled for further use.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The waste streams to be treated with sequestering agents are aqueous liquids. Pretreatment is sometimes necessary, depending on the cations and sequestering agents being considered, to modify the chemical characteristics of the waste streams for the separation to be effective. Adjustment of pH and removal of interfering anions are the most common pretreatment procedure. When waste streams with very high concentrations of cations are being treated, it is also necessary to ensure that capacities of the sequestering agents are not exceeded. Many sequestering agents are generally quite resistant to oxidation and high temperatures: solutions containing high concentrations of nitric acid and peroxide can be used up to the boiling point of the solvent involved. Targeted ions can be removed down to non-detectable levels in the product streams with no additions to the stream being treated.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The development of commercially available sequestering agents is relatively new. Consequently, only a limited number of vendors exists. However, sequestering agents are routinely used for analytical applications (e.g., extraction of actinides), and in a few cases they have been used on an industrial scale to extract specific elements (e.g., recovery of noble metal ions from mine waste waters). Systems are available on a commercial basis that have wide ranging separation capabilities across the periodic table (e.g., SuperLig[®] based products, IBC Advanced Technologies, Inc.). Automation has been demonstrated on these systems as fixed bed systems and system components can be obtained which are designed for radiation environments. Initial tests have shown that performances of these systems are not severely degraded by high-intensity gamma radiation.

Improved products designed for special applications (e.g., extraction of Sr by Sr•Spec and U by U/TEVA•Spec, ElChroM Industries, Inc.) that provide better separation and higher selectivity, have also appeared and will become more widely available.

A variety of programs are in place to develop new sequestering agents and extraction chromatography materials. Some of these programs are proprietary in nature. A Technical Task Plan exists among the Office of Technology Development, national laboratories, industry, and universities to identify, develop, and test solid-based sequestering agents to remove Cs, Sr, and transuranics from basic and acidified High Level Wastes. Improved products for Cs and Sr separations should be available within one year.

3.3.2 Reliability and Maintenance Requirements

Frequent replacement of sequestering agents or column materials (i.e., sequestering agents and solid support) is expected even with regeneration of these materials since they only have a limited useful lifetime. Their availability in sufficient quantity and on a continuous basis depends on the separations involved and the existing capacities for their syntheses.

3.3.3 Secondary Waste Streams

Unlike ion exchangers, sequestering agents extract the ions of interest with no chemical additions to the stream being processed. However, minor loss of sequestering agents and organic solvents, whether in liquid/liquid extraction or column chromatography, does occur and contaminate the aqueous waste stream. The level of this contamination varies and depends on the specific system; in some cases this contamination is eliminated by chemically attaching (covalent bonding) the sequestering agents onto the substrate.

Sequestering agents used to extract radionuclides become mixed wastes but can be disposed of relatively conveniently with the proper design (e.g., use of silica gel as support material which can be vitrified). If the sequestering agents are to be regenerated, the systems typically are eluted with common acids or salts (e.g., HCl, NaCl, and EDTA) and the eluent may become mixed waste.

3.3.4 Separation Efficiency

Sequestering agents offer extremely high separation efficiency because of the very large complex-formation constants (up to 10^{60}). Commercial systems currently in operation can separate metals in high purity from each other and from large excesses (>1000 fold) of other metals in highly acidic matrices. Separation of various trace contaminants (at or below ppm levels) from very concentrated base metal and/or electroplating streams is also performed on a commercial basis. Decontamination factors of 10^5 and higher have been achieved using a variety of sequestering agents on simulated nuclear waste streams.

3.3.5 Safety and Health

The majority of sequestering agents are organic macrocycles or metal chelators while most support materials are chemically inert resin, synthetic polymer, or silica gel. The chemical toxicity of these materials varies and they should be handled with appropriate cautions to avoid ingestion. In practice, however, they are well contained in columns and other containers and do not generally come into contact with the operators. This is especially true since most systems can be automated.

3.3.6 Operational Complexity

The use of sequestering agents in extraction chromatography is relatively simple; their operation is based on well-known engineering specifications common to fixed-bed systems and they can be easily automated. Due to their highly selective and efficient uptake of targeted ions, systems involving sequestering agents are many times smaller than ion exchange, solvent extraction, or precipitation systems.

3.3.7 Glovebox Capability

Although sequestering agents are routinely used in gloveboxes for analytical applications, no large-scale demonstration of their use in gloveboxes is known. Industrial-scale applications of liquid/liquid extraction and extraction chromatography involve large equipment; their demonstration will require a specially designed glovebox.

A large number of sequestering agents, however, have been subjected to intense gamma radiation and found not to degrade excessively.

3.3.8 Environmental Impact

The use of sequestering agents, especially in extraction chromatography, has been described as environmentally friendly since they can be recycled with eluents that are often environmentally benign. Little or no organic solvent is necessary in extraction chromatography while most sequestering agents can be broken down chemically. A number of different support materials are available such that careful designs may minimize undesirable environmental impact.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Many systems have already been developed and implemented for a wide range of ions, across the periodic table. There is, however, significant developmental work to be done for other ions, as well as appropriately engineered systems for Mixed Wastes. The effort and cost

required for those development and testing programs can be defined only when a specified project is identified.

Installation and start-up of an extraction chromatography system are fairly routine and normally consists of a fixed bed system hook-up; only a few system parameters need to be controlled (e.g., flow rate, pH). Consequently, while sequestering agents are relatively quite expensive, there is very little associated capital costs. The exact costs vary widely and depend on the specific applications.

The operating costs of an extraction chromatography system are:

- * Energy cost: low since the system is a simple fixed-bed
- * Maintenance cost: low since the associated mechanical system is relatively simple
- * Replacement cost: replacement of column materials will be required frequently even if they are regenerated since they can only be recycled a limited number of times. Cost varies depending on applications, but column materials are generally expensive.
- * Secondary materials: they are not required unless the sequestering agents are to be regenerated by elution. If elution is required, the eluent normally consists of common mineral acids or salts.
- * Disposal cost: low since there is no special disposal requirement and most sequestering agents can be broken down chemically.

The operating costs of a solvent extraction system, on the other hand, are generally higher because a more complex mechanical system and large amount of organic solvents are required.

3.5 TECHNOLOGY COMPARISON

The primary advantages of sequestering agents over other separation techniques are selectivity, high separation factors, and rapid kinetics.

Other advantages may include:

- * Effective extraction even in the presence of large excesses of acids and salts
- * Eluents for regeneration are common acids or salts
- * A variety of support formats is possible.

Specific advantages (of extraction chromatography) over ion exchange include:

- * High selectivity. As only targeted ions will bind, concentration of impurities in the sample has little effect on extraction.
- * Rapid kinetics. Flow rates up to 50 times greater than ion exchange are possible without an adverse effect on extraction capacity.
- * Recovery of ions of low concentration. Since an ion exchange mechanism is not involved and the binding constants are high, sequestering agents can be used to extract ions of very low concentration.

Specific advantages (of extraction chromatography) over solvent extraction include:

- * **Rapid kinetics.** A complete phase separation is not required which may take a long time.
- * **Reduced capital investment.** There are fewer engineering and space requirements; remote control and automation are more easily engineered.
- * **Reduced secondary wastes.** No organic solvent needs to be used and the input stream is not changed.
- * **Organic solvents.** Only a small amount of organic solvent used is used in attaching the sequestering agents onto the support and, in a few cases, no organic solvent is necessary as sequestering agents can be made to chemical bond directly to the support material.

The major disadvantage, compared to ion exchange, is the higher cost. Sequestering agents are typically much more expensive than ion exchangers and can only be recycled a limited number of times. However, the cost of certain critical separations using sequestering agents may actually be lower because of its high selectivity.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

In order to properly employ sequestering agents in the extraction of hazardous and mixed wastes, the following data must be available:

- * **Waste Stream Characterization.** The physical characteristics and chemical composition of the waste stream (e.g., pH, nature of cations and anions present) must be known to determine the applicability of sequestering agents and to provide the optimal extraction condition.
- * **Distribution coefficients, separation factors, and capacity of the sequestering agents.**
- * **Proper extracting conditions:** pH, temperature, and flow rate.
- * **The resistance of the column materials to chemical attack and extractant loss induced by acid wash/aqueous stream.**
- * **Interactions between sequestering agents and possible interfering ions in the waste stream.**

A variety of vendor data are available—the quantity and type of data depend on the separation involved and the amount of experience the vendors have with that separation. Partition coefficients, separation factors, capacities, pH and temperature ranges, and recommended flow rates are well-known for fully developed systems. Other data available

may include: physical constants of support material, resistance toward chemical attack, and thermodynamic and kinetic parameters for sequestering agent-ion interactions.

4.2 TESTING REQUIREMENTS

There are relatively few requirements for lab-scale and pilot-scale tests: simulated wastes (nonradioactive or radioactive), the sequestering agents (prepacked columns are commercially available for extraction chromatography), and a chemical analytical capability. Tests can therefore be planned and initiated easily; a number of tests are actually underway or have been completed for various programs (e.g., Pacific Northwest Laboratory and IBC Advanced Technologies have investigated the usefulness of some SuperLig® materials for their usefulness in treating nuclear wastes).

While tests involving nonradioactive simulated wastes can be performed by both federal and private (vendor) laboratories, very few private laboratories are equipped and permitted to handle mixed wastes. Consequently, tests that use radioactive mixed wastes very likely need to be performed at federal laboratories, perhaps with some participation from the vendor if new sequestering agents are involved. Because of the limited testing requirements, relatively little time and funding are necessary to carry out these tests. However, a large number of tests may be required, depending on the kinds of application and the number of sequestering agents to be demonstrated.

5.0 VENDOR LIST

The suppliers of Sequestering Agents are shown below:

EiChroM Industries, Inc.
8205 S. Cass Ave., Suite 107
Darien, IL 60561
(800) 422-6693
(708) 963-0381 (FAX)

IBC Advanced Technologies
P. O. Box 656
Provo, UT 84603
(801) 375-1600
(801) 375-3200

In addition, the following people are engaged in research on sequestering agents:

Prof. Abraham Clearfield
Department of Chemistry
Texas A & M University
College Station, TX 77843

Prof. Reed Izatt
Department of Chemistry
Brigham Young University
Provo, UT 84602
(801) 378-5474 (FAX)

6.0 REFERENCES

1. Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*. Cambridge University Press: Cambridge, 1989.
2. Meade, T. J. and D. H. Busch. *Prog. Inorg. Chem.* 1985, 33, 59-126.
3. Izatt, R. M., J. S. Bradshaw, S. A. Nielson, J. D. Lamb, and J. J. Christensen. "Thermodynamic and Kinetic Data for Cation-Macrocyclic Interaction." *Chem. Rev.* 1985, 85, 271-339.
4. Izatt, R. M., K. Pawlak, J. S. Bradshaw, and R. L. Bruening. "Thermodynamic and Kinetic Data for Macrocyclic Interaction with Cations and Anions." *Chem. Rev.* 1991, 91, 1721-2085.
5. Horwitz, E. P., M. L. Dietz, and D. E. Fisher. "Separation and Preconcentration of Strontium from Biological, Environmental, and Nuclear Waste Samples by Extraction Chromatography Using a Crown Ether." *Anal. Chem.* 1991, 63, 522-525.
6. Horwitz, E. P. "New Chromatographic Materials for Determinations of Actinides, Strontium, and Technetium in Environmental, Bioassay, and Nuclear Waste Samples." Chemistry Division, Argonne National Laboratory, May 1992, (preliminary report).
7. Camaioni, D. M., N. G. Colton, and R. L. Bruening. "Investigation of the Potential of Silica-Bonded Macrocyclic Ligands for Separation of Metal Ions from Nuclear Waste." PNL-7894, Pacific Northwest Laboratories, January 1992.

APPENDIX K PYROCHEMICAL PROCESSING

1.0 TECHNOLOGY DESIGNATION

Pyrochemical processing is a thermal process for transformation of solid and liquid carbonaceous materials into gaseous components, and a solid residue containing fixed carbon and ash.

2.0 NEED FOR THE TECHNOLOGY

The technology is being considered as a final step for inerting reactive species found in salts exiting the chemical/physical treatment section of the MWTP base-line process. Molten pyrochemical waste salts containing reactive species can be sparged with oxygen or chlorine to produce an inert salt. The sparging processes are referred to simply as the Oxygen Sparging (OS) process and the Chlorine Sparging (CS) process.

The pyrochemical processes at the Rocky Flats Plant (RFP) produced waste salts that contain reactive species such as calcium and magnesium. The presence of such species has two serious effects on the handling, storage, and transportation of those salts. First, the presence of the reactive species in a pyrochemical waste salt places that salt under the purview of the Resource and Recovery Act (RCRA) as a mixed waste. Second, the Department of Transportation (DOT) regulations prohibit the transportation of pyrophoric materials and the DOT definition of pyrophoric includes water-reactive species. Thus, the RFP pyrochemical waste salts must be treated to eliminate the reactive species to remove those salts from RCRA regulation and prior to any shipment of the salts. This process is applicable to on-site treatment of pyrophoric material or to the MWTP, if pyrophoric material is produced as a by-product of mixed waste processing and treatment.

Since input stream information and criteria for the product and by-product streams exiting this section of the flowsheet are not available at this time, further information cannot be provided regarding this process's performance. The applicability may change as this information becomes better known.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

A variety of chemical treatments can be used to oxidize the reactive species in the pyrochemical waste salts. Such treatments include the complete dissolution of the salt in water

and the sparging of an oxidizing gas into the molten waste salt. The following discussion focuses on the sparging treatment. Sparging the molten pyrochemical waste salt with sufficient oxygen or chlorine will result in the complete conversion of the reactive species to inert species.

The sparging processes (OS or CS) require standard pyrochemical stationary furnaces. The furnace heads must be adapted to accommodate a sparging tube and an exit gas tube. The gloveboxes must have the appropriate fixtures to allow a flow of air, oxygen, or chlorine into the furnace along with a flow of argon. The exit gas tube must be connected to a scrubber system to allow any chlorine gas to be processed.

For the CS process, an on-demand chlorine gas generating system needs to be used. Such a system eliminates the hazards associated with the storage of bulk quantities of chlorine. In a catastrophic accident, the only amount of chlorine released would be the amount in the tubing between the generating system and the furnace.

In the production-scale pyrochemical stationary furnaces at RFP, about 1 to 1.5 kilograms of salt could be processed per sparging run. An important concern about the sparging processes is that currently ceramic crucibles are used to contain the molten salt. Those crucibles can only be used one time. However, work on reusable crucibles is proceeding. In addition, stainless steel crucibles are being considered for the pyrochemical waste salts in the sparging process. Stainless steel normally cannot be used for containment of actinides as stainless steel alloys with the actinides. However, as the actinide content of the pyrochemical waste salts is minimal, such alloying would probably be insignificant and no breach of containment would occur. Testing of the stainless steel crucibles is required. An oxidized tantalum crucible backup would be recommended.

The sparging processes can treat the entire array of pyrochemical waste salts to eliminate the reactive species. In the CS process the chloride species are soluble in the salt matrix and no segregation is expected. However, in the OS process, the actinide oxides and oxychlorides will segregate away from the salt phase if sufficient oxygen is sparged into the molten salt to oxidize all of the actinides.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

To be determined.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

The Los Alamos National Laboratory (LANL) has developed the OS process as an actinide separation process for the recovery of plutonium from LANL electrorefining residue

salts. The LANL work has shown that the plutonium can be concentrated in a dense phase with the americium remaining in the salt matrix if oxygen is sparged into the molten salt for a short time. Development work on an OS process for the plutonium recovery from LANL molten salt extraction residue salts is proceeding. No work has been done with the objective to oxidize all of the reactive species without regard to actinide separation.

A chlorine on-demand generator has been identified by EG&G Rocky Flats (RF) personnel for use in the CS process. A purchase requisition has been approved by RF for the Colorado School of Mines (CSM) to install and test that chlorine generator. The contract is under negotiation between RF and CSM.

Currently, Residue Treatment Technology personnel at RFP are proposing that the pyrochemical laboratories in Building 779 at RFP be used for the OS and CS processing of pyrochemical waste salts. If approval is received for this proposal, the work could begin once the appropriate modifications to the furnace heads are made and a scrubber system is installed. About two years would be needed for development work on RFP pyrochemical waste salts.

3.3.2 Reliability and Maintenance Requirements

To be determined.

3.3.3 Secondary Waste Streams

The main secondary waste from the sparging processes is the crucible waste. However, if stainless steel containment vessels can be used for the pyrochemical waste salts, then the secondary waste stream is reduced primarily to the scrubber wastes.

3.3.4 Separation Efficiency

To be determined.

3.3.5 Safety and Health

To be determined.

3.3.6 Operational Complexity

To be determined.

3.3.7 Glovebox Capability

To be determined.

3.3.8 Environmental Impact

To be determined.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Much of the equipment already exists at RFP in Buildings 779 and 776. Modifications to the furnace heads and installation of the sparging system and installation of a scrubber system would be required. Cost estimates of required modifications have not been completed at this time.

3.5 TECHNOLOGY COMPARISON

To be determined.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

See Section 4.2 below.

4.2 TESTING REQUIREMENTS

Testing of the stainless steel crucibles is required. An oxidized tantalum crucible backup would be recommended.

No work has been done with the objective to oxidize all of the reactive species without regard to actinide separation. About two years would be needed for development work on RFP pyrochemical waste salts.

5.0 VENDOR LIST

Contacts include:
Alice Murray
EG&G Rocky Flats
Building T779A
P.O. Box 464
Golden, CO 80402-0464
Phone: (303) 966-7798
Fax: (303) 966-8027

6.0 REFERENCES

None.

APPENDIX L SOLVENT EXTRACTION

Solvent extraction is a physical separation process used to transfer constituents from one liquid solution or solid matrix to another liquid solution. The separation efficiency depends on the relative solubilities of the constituent to be separated, the solvent, and the feed. Supercritical fluids are a special type of solvent in which a liquid or gas is brought to the supercritical state by applying high pressure and temperature. The processes described in this appendix are as follows:

- L-1 Conventional Solvent Extraction**
- L-2 Supercritical Fluid Extraction**
- L-3 TRUEX Actinide Segregation**
- L-4 Cloud Point Extraction**

APPENDIX L-1 CONVENTIONAL SOLVENT EXTRACTION

1.0 TECHNOLOGY DESIGNATION

The term solvent extraction is used to refer to two different types of processes. One, known as liquid/liquid extraction, is the selective partitioning of solutes between two immiscible phases. When used for the separation of metal ions, an aqueous feed containing a mixture of metal ions is contacted with an immiscible solvent that is comprised of an organic diluent and a metal extractant. The other process, known as leaching, is the separation of constituents from solids by contact with a liquid in which the constituents dissolve (Ref. 1).

2.0 NEED FOR THE TECHNOLOGY

Like ion exchange or liquid membrane extraction, this technology is a candidate for the primary treatment of aqueous waste streams. It could be used for the selective extraction and recovery of specific metal ions such as Cs and Sr, the actinides or RCRA metals. The removal of high energy beta/gamma emitters at the front end would eliminate the need for extensive shielding around processing equipment during downstream processing.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Solvent extraction is applicable, in principle, to the physical separation of organic constituents and some heavy metals from aqueous or organic solutions (liquid/liquid extraction) or from sludge or solid mixtures (leaching). The chosen solvent and the matrix to be treated are mutually insoluble. This method is used to transfer constituents from one liquid solution (or solid matrix) to another. In practice, an appropriate solvent must be found that has a high selectivity and saturation solubility for the desired constituent, and a low solubility in the feed material or waste stream.

A solvent extraction process involves a multiple number of stages in which extraction, scrubbing, and stripping are carried out. During extraction, metal ions are selectively transferred to the organic solvent through a reversible reaction with an organic metal extractant. After extraction the loaded solvent may be scrubbed with a suitable aqueous phase to remove small amounts of impurities that have been co-extracted during the extraction stage. After the scrubbing stage, the metal ions are stripped from the solvent by an aqueous solution which reverses the metal/extractant complexation reaction. Usually, the metal ions are recovered in a

strip solution that is fairly concentrated and is only a fraction of the initial feed volume. Once the solvent is stripped, it is recycled back to the extraction stage.

Each section of a flowsheet (e.g., extraction, scrubbing, and stripping) may actually involve the use of a number of contactors. The contactors are designed to maximize the amount of dispersion and mixing between the two immiscible liquid phases. Solvent extraction processes are typically carried out under continuous, counter-current operation at ambient temperature and pressure.

The selectivity of the separation achieved by solvent extraction is determined by the physico-chemical properties of the metal complexes formed in the aqueous and organic phases. Thus, significant research has gone into the development of extractants that are capable of selectively complexing only certain metal ions present in complex mixtures. The reversibility between extraction and stripping is often achieved by a change in pH.

Because of the large variety of extractants and the complexity of solvent extraction systems, it is not practical to present a detailed discussion of the factors that must be considered in choosing a solvent for a given extraction. Suffice it to say that this choice requires a detailed knowledge of the feed composition and the processing goals.

A wide variety of contactor devices have been used in solvent extraction. The major classes of contactors include: (1) mixer-settlers, (2) centrifugal contactors, (3) unagitated columns, and (4) agitated columns. Mixer-settlers and centrifugal contactors operate as discrete stages in which the immiscible phases are mixed and separated before proceeding to the next contactor unit. The approach to equilibrium is often better than 95-98% in a centrifugal contactor but may be only 50-60% in a mixer-settler. In systems with poor chemical kinetics, large mixer-settler units with high residence times are required to achieve stage efficiencies greater than 90%.

In column extractors, mass transfer takes place along the full length of the device and the phases are separated only at the end of the unit. Contactor geometry is an important consideration in choosing a unit for use with feeds containing flammable materials. The device must maintain a noncritical geometry at all times.

Mixer-settlers require a relatively large floor space to achieve high flowrates because of the area of the settler. Because of the inefficiency of the unit, more stages may be required to perform a separation process with slow extraction/stripping kinetics.

Column extractors have a much smaller footprint than mixer-settlers but can require specially built high-bay areas due to their height. Increased mass transfer efficiency is obtained by incorporating porous packing within the column to act as an aid in droplet formation and to reduce axial mixing. The feed streams entering a packed column are often pulsed in an effort to enhance mass transfer by increasing dispersion of the dispersed phase as it passes through the

packing material. Pulsed columns have been used quite extensively for nuclear applications because of the simplicity of the design, which provides for the elimination of seals that may eventually leak.

Centrifugal contactors have been used in the nuclear industry for a number of decades and have undergone significant design improvements in the past 10-15 years. The advantages of this device include: (1) higher throughput, (2) higher mass transfer rates, (3) small compact size, (4) rapid rate of approach to steady-state, and (5) critically safe geometry. In addition, the Argonne-designed contactor, shown in Figure L-1.1, has all inter-stage lines placed on the exterior of the unit thus permitting changes in flowsheet design to be accommodated easily by re-plumbing the units.

Figure L-1.1. Schematic of Argonne Centrifugal Contactor (from Ref. 3)

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

As a general rule solvent extraction systems do not react well to the presence of suspended solids in the feed solution. Fine particles in the feed can lead to emulsification, interfacial crud formation (which impedes mass transfer), and blocked passages in the contactor equipment.

Solvent extraction is applicable to a wide variety of constituents. However, most solvents will be effective for particular types of constituents and will not be effective for other types. In addition, it is possible that some constituents may not be amenable to solvent extraction. Each system must be tested to select appropriate solvents.

Solvents containing extracted constituents should be regenerated, if possible, to allow economical treatment. This process does not destroy the extracted constituents. Further treatment of extracted constituents may be required prior to ultimate disposal.

The process is not applicable to constituents that may not be removed from the solvent during regeneration. Matrix conditions, such as pH, or the presence of surfactants or emulsifiers, may alter the effectiveness of the process.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Solvent extraction processes such as the PUREX process have been used in the processing of nuclear materials for the past 40 years. Considerable experience with mixer-settlers, pulsed columns, and centrifugal contactors has been accumulated during this time. Equipment design has evolved to accommodate remote use in gloveboxes or shielded cells. A recent publication describes the advances in centrifugal contactor design for implementing the TRUEX process (Ref. 3). Centrifugal contactors manufactured from polyvinylidene fluoride (Kynar) have been used at Los Alamos for processing chloride waste streams (Ref. 4). Those units were purchased commercially from Robatel, which is a French company with offices located in Pittsfield, MA. Pulsed columns are available commercially. For example, Eries, a subsidiary company of Robatel, offers pulsed columns for use in the nuclear industry. However, the various column components are available from individual vendors and often times the columns are custom assembled by the user.

For installation in new facilities, centrifugal contactors probably have the overall advantage over other types of contactors because of their small size and high throughput. They have been designed for remote operation and have a critically safe geometry.

Bradtec has developed and tested a dilute, aqueous-based, chemical extraction process for the treatment of soils and other materials contaminated with radionuclides. This process (ACT*DE*CON process) combines dissolution with dilute selective solvents, contaminant recovery, and solvent regeneration to remove strontium, cesium, technetium, radium, actinides (uranium and transuranics), barium, mercury, and lead. Other contaminants may be treatable, but testing has not been performed to verify performance.

The solvent chemistry combines established carbonate recovery chemistry with a chelant (EDTA) and oxidant (hydrogen peroxide). The oxidant is required to raise the oxidation state of the contaminant to allow formation of carbonate complexes.

The treatment process uses countercurrent solvent extraction to dissolve and recover the contaminants. Several extractor stages are used. The number and residence time in each extractor is determined by both the contamination level and the level of decontamination required. Decontamination factors of 10 to 20 are typically achievable with two extractors. The treated material that exits the final extractor is filtered to recover the treated solids. The solvent (with contaminants) is treated by either selective ion exchange or evaporation. Use of ion exchange recovery requires the waste stream be free of organic contamination, or pretreatment performed to remove the organics.

3.3.2 Reliability and Maintenance Requirements

Once the chemistry of a solvent extraction process is established, the processes are generally very reliable. Sudden changes in feed composition, however, can cause serious problems. The most effective solvent extraction processes are fairly feed-specific. Wide changes in pH or metal concentrations can cause problems.

The contactor equipment used in solvent extraction processes is generally very reliable. Equipment designs have been continually improved over the past 40-50 years.

3.3.3 Secondary Waste Streams

The major secondary waste stream from solvent extraction processes are the spent solvents and any aqueous streams that are used to scrub or regenerate the organic solvent so that it can be recycled. These waste streams are likely to contain radioactive contaminants and may be a mixed waste if RCRA metals are present.

3.3.4 Separation Efficiency

The separation efficiency depends on the relative solubilities of the constituent to be separated, the solvent, and the feed.

3.3.5 Safety and Health

Solvent extraction processes can be operated remotely in shielded facilities or in gloveboxes. There has been a trend in recent years to replace toxic diluents with more benign chemicals. However, the less toxic diluents, such as aliphatic hydrocarbons, are very flammable. Fire hazard is a significant safety issue with almost all solvent extraction processes.

3.3.6 Operational Complexity

Complexity depends on the waste stream characteristics, the material to be extracted, and the solvents used.

3.3.7 Glovebox Capability

Solvent extraction processes can be operated in glovebox facilities. This mode of operation, however, eliminates certain kinds of contactor equipment. For example, pulsed columns would be too tall to fit in a glovebox and typically require a high bay area with at least a 15-20 ft ceiling height. Mixer-settlers and centrifugal contactors would easily fit into a glovebox. Centrifugal contactors require the smallest amount of space but are the most expensive type of contactor available.

3.3.8 Environmental Impact

Solvent extraction processes can be operated as totally enclosed systems. When the solvent and the waste are contacted, the contaminants of concern transfer from the waste matrix to the solvent. The waste and solvent may then be separated. At this point, the waste matrix may be disposed of or treated further, as appropriate. The solvent may be regenerated for use. In open systems, the extract (solvent and organic waste) may be burned as fuel or incinerated, and the raffinate, which may be an aqueous solution retaining radioisotopes, can be captured for treatment or disposal.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

The most significant items, in terms of cost, are the solvents and the contactor equipment. The cost of newly developed extractants for nuclear waste processing can be very high. For example, the current cost of CMPO is in excess of \$200/lb. Of course, with increased demand the unit costs of the more specialized extractants like CMPO will drop dramatically. The costs of centrifugal contactors can be quite high. Since these are custom-made units that can be manufactured from corrosion-resistant materials, costs of about \$100K per stage would not be unusual. This high cost is somewhat offset by the smaller footprint of these units. Mixer

settlers are significantly cheaper but require more stages to reach the same level of efficiency as that of a centrifugal contactor.

3.5 TECHNOLOGY COMPARISON

The primary advantages of solvent extraction are its applicability to a wide range of contaminants and the widespread use of solvent extraction in industrial applications. Solvent extraction may be readily bench-tested.

Costs of solvent extraction are higher than for absorption or stripping methods. In most cases, solvent extraction will be effective for a limited number of the constituents in the waste matrix, necessitating further treatment of the waste. Recovered contaminants will require treatment prior to disposal.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

The data necessary to design a solvent extraction flowsheet include the identification of all species present in the feed stream. The extraction and stripping partition coefficients for these species must be measured using the proposed solvent system. The decontamination factors required must be known so that the required number of extraction stages can be determined. Any expected variation in the feed stream composition must also be known so that appropriate steps can be taken to minimize their influence on process performance.

4.2 TESTING REQUIREMENTS

The use of pilot plant testing of solvent extraction processes should be considered a prerequisite to full-scale plant testing. These pilot facilities should be kept functional in the event that major changes in feed composition may necessitate a change in solvent composition. The advances in thermodynamic modeling capabilities that have taken place in recent years can help to reduce the extent and costs of flowsheet testing.

5.0 VENDOR LIST

There are a large number of vendors that sell contactor equipment for solvent extraction applications. One vendor for each type of contactor is listed below.

Robatel Inc.
29 Wendell Ave
Pittsfield, Ma 01201
(413) 499-4818
(centrifugal contactor)

Artisan Industries Inc.
73 Pond St.
Waltham, MA 02254
(617) 893-6800
(pulsed columns)

MEAB Metallextraktion AB
PO Box 83
S-42121 Vastra Frolunda
Sweden
46 (0)31 681988
(mixer settlers)

6.0 REFERENCES

1. Berkowitz, Joan B. "Solvent Extraction." In *Standard Handbook of Hazardous Waste Treatment and Disposal*. H. M. Freeman, ed. McGraw-Hill Book Co.: New York, 1989.
2. Chemical Waste Management, Inc. and BradTec. ACT*DE*CON Technical Note.
3. Leonard, R. A. "Recent Advances in Centrifugal Contractor Design." *Sep. Sci. Technology*. 23, 1473, 1988.
4. Palmer, M. Personal communication. Los Alamos National Laboratory, Los Alamos, NM.

APPENDIX L-2 SUPERCRITICAL FLUID EXTRACTION

1.0 TECHNOLOGY DESIGNATION

Supercritical fluid extraction is a form of solvent extraction that may be used in a closed system to remove organics from a waste stream or from solids. Carbon dioxide is commonly used as the fluid for this process.

2.0 NEED FOR THE TECHNOLOGY

The technology is being considered as an alternative step for extraction or removal of hazardous organic species from waste streams entering the Chemical/Physical treatment section of the MWTP process.

Supercritical fluid extraction is a process that employs a flowing, noncombustible, nontoxic, environmentally safe supercritical fluid as a solvent. Supercritical carbon dioxide (SCO₂) is that phase of CO₂ which has been heated and compressed above 31°C and 1078 psi and behaves primarily as a liquid with solvating properties. This type of process has been used to decaffeinate coffee and tea on an industrial level and has been shown capable of removing several different types of hazardous organic contaminants from a limited number of materials and waste water. In waste cleanup applications, SCO₂ is used to dissolve the hazardous components and extract them from the substrate material. After a rarefaction step, these contaminants precipitate out of solution, allowing the CO₂ to be recycled. Residual waste would then be treated simply as radioactive rather than mixed. A typical SCO₂ system is shown in Figure L-2.1.

Since input stream information and criteria for the product and by-product streams exiting this section of the flowsheet are not available at this time, further information cannot be provided regarding this process's performance. The applicability may change as this information becomes better known.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Pure carbon dioxide, when subjected to pressures above 1078 psi (P_c) and temperatures greater than 31°C (T_c), is said to be in a supercritical state. Since this supercritical phase exists above the critical temperature (T_c), it is not a liquid although it exhibits liquid-like densities and displays both good solubilizing properties and favorable mass transport characteristics. These

attributes make SCO_2 an effective solvent for nonpolar organic compounds. Since CO_2 itself is relatively inexpensive, nontoxic and nonflammable, it becomes an ideal solvent for use in the extraction of hazardous organic compounds from a variety of substrates because it does not produce a hazardous secondary waste stream.

Figure L-2.1. Supercritical Carbon Dioxide Extractor

Solubilities of organic compounds in SCO_2 are related to the density of the SCO_2 which, in turn is a strong function of pressure, especially near the critical point. Up to several orders of magnitude change in solubility can be achieved by moderate changes in pressure near the critical point. In the range $P_C < P < 2P_C$, solubility is also strongly affected by temperature and may increase or decrease with increasing temperature. Temperature dependence is significantly reduced at pressures $> 2P_C$ and for this reason, most extraction studies are conducted at temperatures above T_C and pressures greater than $2P_C$.

It is believed that mutual solubility can be predicted for solvent/solute pairs with similar (Hildebrand) solubility parameters. Since this solubility parameter is related to the density of the supercritical fluid medium, then SCO_2 can be made an effective solvent for a variety of solutes by changing its pressure and hence its density to match that of the solute of interest. This pressure/density relationship is therefore an important control parameter in the SCO_2 process in that it affects the "dissolving power" for specific organic solvents and oils. Use of the Hildebrand solubility parameter for polar solvents is widely discouraged. However, tests are being performed at Sandia to evaluate the effects of co-solvents, such as water, on the solubility of polar compounds in SCO_2 (Ref. 1).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Input requirements would vary with the metal of interest, but are not expected to be demanding. The output would consist of the decontaminated solid metal, organic waste, and recyclable CO_2 gas.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Work is being done at SNL, EG&G Rocky Flats, EG&G Mound, and LANL as part of a DOE effort to understand and implement SCO_2 cleaning where feasible (Ref. 1). EG&G Mound has obtained encouraging results for removing machine oil from stainless steel (Ref. 1). Work at EG&G Rocky Flats is directed toward using SCO_2 to remove oil contaminants from plutonium. At SNL, they are studying the solubility of contaminants in SCO_2 , and the behavior of water as a nontoxic, nonflammable cosolvent in SCO_2 , including potential corrosive effects, if any (Ref. 1). SCO_2 is likely to be very useful in separating hazardous organic wastes from TRU wastes, thereby permitting the separation of mixed wastes into radioactive and hazardous waste components.

SCO_2 cleaning has been demonstrated at Rocky Flats Plant on a laboratory scale for removing light oils and solvents from steel and uranium substrates. It has been used for both very low residue cleaning of metal substrates and for removing bulk quantities of oil from steel fines. Rocky Flats has also conducted experiments which indicate that ultrasonically induced cavitation in SCO_2 may improve the organic extraction in complex geometries. Results can be found in numerous internal RFP technical reports (Ref. 2).

An SCO_2 test system has been manufactured for EG&G Rocky Flats by Fluitron Inc., of Ivyland, PA, to investigate removal of organic contaminants from RFP waste. This system has been installed at the University of Colorado where testing will be conducted on various

candidate waste forms, including, but not limited to, combustibles, glass, metals, and leaded materials. Initial solvents to be examined include TCE, TCA, carbon tetrachloride, and methylene chloride. The system is a microprocessor-controlled, closed-loop system equipped with a 4-liter extraction vessel. The system has the capability to achieve a maximum CO₂ pressure in the extraction vessel of 5000 psi and a maximum operating temperature of 100°C. Pressure is provided by a single-stage, triple-diaphragm compressor. The system is operated by means of an Allen-Bradley SLC 500 programmable logic controller (PLC). Carbon dioxide from a liquified bulk supply is piped to a storage vessel in the Fluitron unit. From there, the CO₂ is recompressed by the single-stage, diaphragm compressor to the desired operating pressure (typically >1078 psi.) Pressurized CO₂ then passes through a heat exchanger where it is further heated to the desired operating temperature and piped to the extraction vessel containing the solvent-contaminated waste. In the extraction vessel, solvents and oils are dissolved in the SCO₂. Solvent-contaminated CO₂ is then piped to the separation vessel where the pressure is rapidly reduced, causing SCO₂ to undergo phase transformation to gaseous CO₂. The dissolved organic contaminants separate and condense in the bottom of the separation vessel. Uncontaminated, gaseous CO₂ is then piped to the storage vessel for recirculation while the extracted solvents and oils are removed for disposal (Ref. 2).

Krupp Research in West Germany has developed a recycling process for waste oil based on supercritical ethane extraction. Feeds are waste oils contaminated with dissolved metals, water, and PCBs. The oil is extracted into the ethane, and the heavier components leave as column bottoms. In addition, the food processing industry uses scaled-up commercial equipment (Ref. 3).

3.3.2 Reliability and Maintenance Requirements

Since the system has no complex or high technology components, reliability and maintainability should not be a major issue.

3.3.3 Secondary Waste Streams

The technology addresses the solvent extraction of undesirable organics or organometallic compounds from solids or liquids without production of a solvent-contaminated waste stream.

3.3.4 Separation Efficiency

System has same degree of separation capability as conventional solvent extraction.

3.3.5 Safety and Health

High pressure system required. Temperatures are only modestly elevated. The technology is capable of being automated.

3.3.6 Operational Complexity

The process is not considered to be complex and size will depend upon scaling.

3.3.7 Glovebox Capability

Gloveboxes are possible for small scale systems.

3.3.8 Environmental Impact

Environmental impact is considered insignificant. The system would have one concentrated solid waste output and pure solvent (i.e., CO₂) which is recycled. During any leak, the depressurization of the solvent precipitates contaminants and only pure CO₂ is released.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Development costs would be based on the effort to synthesize new metal-specific ligands which can then be dissolved in SCO₂. A crude estimate may be one manyear of research per ligand. The 4-liter test system described in Section 3.3.1 costs \$175,000. A 20-gallon system, capable of a 30-minute turnaround, would cost approximately \$750,000. These costs are approximations, and, of course, could vary significantly depending on design requirements and other unknown factors (Ref. 1).

3.5 TECHNOLOGY COMPARISON

SCO₂ is nontoxic, nonflammable, inexpensive, recyclable and has properties that make it attractive as a non-hazardous solvent such as its gas-like transport properties (i.e., diffusivity and viscosity), liquid-like density, and negligible surface tension. These properties and the solubility of materials in SCO₂ are very pressure-temperature dependent. Consequently, the dissolving power can be very fine-tuned to the contaminant to be removed. Although polar organic molecules are not very soluble in SCO₂, their solubility can be increased by adding to SCO₂ polar cosolvents or modifiers such as water, isopropanol, or methanol.

One of the positive aspects of SCO₂ is that it is recyclable. The material to be treated is placed in a high pressure extractor and the SCO₂ circulates through the extractor and dissolves the contaminant (Figure L-2.1). The CO₂ then passes through a pressure reducer and separator,

and is recycled back to the extractor. Because the dissolving power of CO₂ generally decreases as the pressure is decreased (at constant temperature), the contaminant is collected in a low pressure separator. Due to the complexity and cost of high pressure equipment, the use of SCO₂ may not be economical compared to other traditional solvents. However, if other solvents require special handling and disposal, then SCO₂ may become attractive.

There are other efforts involving supercritical hydrocarbon extractants, but working with SCO₂ is much more convenient. It is easier to troubleshoot since it can be seen if there is a leak. Also, the contaminants are contained in the carbon dioxide, and it is easier to recycle. There are no issues regarding venting of CO₂ to the atmosphere as there are with hydrocarbons.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data to be obtained in the experimental equipment at the University of Colorado include extraction efficiency for the solvents of interest on the respective substrates as a function of time and the cost effectiveness of this approach. Examination of various solvent concentrations on complex substrates, with or without the use of modifiers, will also be examined. The use of ultrasonics will also be evaluated for its role for potential improvement in extraction efficiency.

4.2 TESTING REQUIREMENTS

See Section 4.1 above.

5.0 VENDOR LIST

Celeste Marsh
EG&G Rocky Flats
Building T779A
P.O. Box 464
Golden, Colorado 80402-0464
Phone: (303) 966-7618
Fax: (303) 966-7925

Val Krukonis
Phasex Corporation
Lawrence, MA

Doug Ruch
Fluitron, Inc.
Ivyland, PA

Bill McGovern
CF Systems, Inc.
Woburn, MA

W. Alan Propp
Idaho National Engineering Laboratory

Robert Sievers, John Brock
CIRES
University of Colorado

6.0 REFERENCES

1. BCM Newsletter, April 1992, Sandia National Laboratory, Albuquerque, NM.
2. Marsh, C. M. Personal conversation. 4 December 1992.
3. Berkowitz, J. B. "Solvent Extraction." In *Standard Handbook of Hazardous Waste Treatment and Disposal*. H. M. Freeman, ed. McGraw-Hill Book Co.: New York, 1989.

APPENDIX L-3 TRUEX ACTINIDE SEGREGATION

1.0 TECHNOLOGY DESIGNATION

TRUEX (transuranic extraction) is a conventional aqueous/organic solvent extraction system.

2.0 NEED FOR THE TECHNOLOGY

TRUEX (transuranic extraction) is a conventional aqueous/organic solvent extraction system capable of decontaminating waste streams to below the transuranic limit of 10 nCi/g.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

TRUEX is a conventional aqueous/organic solvent extraction scheme. It may be employed using pulse columns or centrifugal contactors and is conceptually analogous to the PUREX system which has been used in the nuclear industry to recover uranium from spent fuel. TRUEX will recover all the actinide elements resulting in a non-TRU effluent.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

TRUEX requires an acidic input to be effective. Maximum extraction efficiency is achieved with molar acid concentrations. The output will consist of the TRU-free effluent (this will still be contaminated with non-TRU radioactivity) and the stripping solutions containing complexed TRU. The organic can be recycled many times, although a scrub stage may be required to remove radiolysis products of the extractant.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

TRUEX is established technology. Although research is complete, a pilot plant operation may be required depending upon the specific application. This process requires building and operation of a plant on a par with a fuel reprocessing plant, depending upon the desired scale.

The extractant is supplied by M&T Chemicals (Rahway, NJ). The patent holder on the process is E.P. Horwitz at ANL.

3.3.2 Reliability and Maintenance Requirements

Similar to any large-scale chemical process.

3.3.3 Secondary Waste Streams

The process produces a non-TRU radioactive acidic aqueous effluent; aqueous TRU strips; a mildly radioactive, non-TRU aqueous scrub; and a recyclable organic stream.

3.3.4 Separation Efficiency

TRUEX has been demonstrated to have an excellent ability to reduce TRU content of spent fuel solutions to non-TRU.

3.3.5 Safety and Health

The safety and health aspects of operating a TRUEX plant are the same as operating a PUREX plant, except that they are highly dependent upon the waste stream being purified. The system would handle radioactive materials, acids, and organic solutions. The technology can be largely automated.

3.3.6 Operational Complexity

This system is a large, complex process system. TRUEX is a plant-scale operation. There are no competing technologies for TRU extraction.

3.3.7 Glovebox Capability

TRUEX has been operated on a small scale in gloveboxes. These operations are usually laboratory research work but may be satisfactory for decontamination of small volumes of material.

3.3.8 Environmental Impact

Possible impacts are due to leaks or irresponsible operation.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Building a full-scale TRUEX plant is a major commitment of resources, probably running into the hundreds of millions of dollars, depending on size.

3.5 TECHNOLOGY COMPARISON

To be determined.

4.0 DEMONSTRATION REQUIREMENTS

TRUEX is essentially proven technology. Some tests may be done for unusual feed streams or pilot plant work. This commitment need not be large.

4.1 DATA REQUIREMENTS

To be determined.

4.2 TESTING REQUIREMENTS

To be determined.

5.0 VENDOR LIST

To be determined.

6.0 REFERENCES

To be determined.

APPENDIX L-4 CLOUD POINT EXTRACTION

1.0 TECHNOLOGY DESIGNATION

Cloud Point Extraction is an aqueous process that uses detergents or emulsifiers to extract organic waste or possibly heavy metal waste from soils or sludges.

2.0 NEED FOR THE TECHNOLOGY

This technology would be used in the wet solids part of the mixed waste process between the special feed tank and the main feed tank in one of three situations: (1) the solids are wet with some organic liquid; (2) the solids contain an organic solid that can be washed out with a suitable cleaning agent; or (3) there is an aqueous solution containing a metal that must be removed prior to drying.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The process is an aqueous process that uses detergents to separate unwanted organic or inorganic compounds from sludge. The unique attribute of this process is that the detergents are recovered and recycled. Equipment used are tanks, stirrers, heaters, and phase separators. Process capabilities and limitations are not yet known.

The proposed cleanup strategy involves the following processes:

- (1) A "washing" step, in which the sample is agitated in a micellar detergent solution, solubilizing the lipophilic components--this will be carried out at room temperature.
- (2) Heating of the suspension until clouding and phase separation occur--depending on the detergent used, this happens in the range of 25-80°C. For economic (fuel) considerations, it will be preferable to choose a detergent with a low cloud point.
- (3) Separating the detergent phase, containing the organic pollutants, from the aqueous bulk--this is essentially similar to solvent extraction in that the contaminants are now concentrated in a small volume that can be physically separated. The advantage of the proposed method is that the detergent phase has low toxicity, low volatility, and potentially low cost.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The process may be sensitive to pH and is sensitive to temperature. No pretreatment requirements are known, but that does not mean that none would be discovered for a particular feed. Input and output ranges for all the possible sludge feeds have not yet been defined. Different feeds will probably respond better to different detergents.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

This technology is best described as being in the research stage. Two months ago it was on the list of funded activities by OTD for the MWIP. The technology is not available now and the availability date depends on actions taken by DOE HQ and available funding.

3.3.2 Reliability and Maintenance Requirements

The technology is very simple and expected to be very reliable.

3.3.3 Secondary Waste Streams

The secondary waste stream is a nonhazardous detergent.

3.3.4 Separation Efficiency

The separation is expected to be limited by fluid removal from the solids, and that is about 90% per stage. With better fluid removal, 95+% separation per stage can be anticipated.

3.3.5 Safety and Health

There are no safety or health issues that have been identified. On the contrary, the detergents are used at ambient conditions prior to cloud point separation. They are nonvolatile and nontoxic. The only hazard comes from whatever specie(s) are removed by the detergent.

3.3.6 Operational Complexity

Operational complexity is minimal. Size will be determined by batch size of sludge treated rather than by the process hardware.

3.3.7 Environmental Impact

There is no known adverse environmental impact known for the technology or equipment.

3.4 COST OF TECHNOLOGY OR EQUIPMENT

The cost to complete the development is not known because the technology is in the early stage of research. However, it would be possible to determine if the technology should be moved to the development stage for less than half a million dollars. Capital costs for recyclable detergent and hardware will be small compared to the cost of the glovebox if one is needed. Operating costs should be low. Chemical makeup is minimal and the process can be automated to cut labor costs. Equipment is easy to maintain and the chemical environment is noncorrosive. Energy costs will be small (mixing and filtering).

3.5 TECHNOLOGY COMPARISON

The competing technologies for sludge washing are generally in the area of liquid/liquid extraction, and the liquids are usually more expensive, more toxic, more flammable, or more difficult to separate and recycle. Today, a quantitative comparison cannot be made.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Data are needed to establish the sludges that can be washed, how much liquid phase can be removed after the contacting, how much of the contaminant is removed by the detergent phase, how complete the separation is between the liquid phases, the time required to accomplish these steps, and costs of equipment and chemicals.

4.2 TESTING REQUIREMENTS

Testing is required to obtain data described in Section 4.1. Tests will be done in university and federal laboratories, at least until it is assured that the technology is economically viable. Surrogate materials probably are not needed unless the organic being removed is highly toxic. With adequate funding, testing will be completed two years after it starts. It will cost less than half a million to decide if the technology should be moved into development. A pilot-scale facility seems in order at this point in time and could be built and tested for about a million dollars.

5.0 VENDOR LIST

There are no vendors.

6.0 REFERENCES

1. Thornton, J. *Science and Practice of Liquid-Liquid Extraction*. Vols. 1 and 2. Clarendon Press: Oxford, 1992.
2. Cecille, L., et al., eds. *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*. Elsevier Applied Science: New York, 1991.
3. Myers, D. *Surfactant Science and Technology*. VCH Publishers: New York, 1988.
4. Loran, C. and R. Von Wandruszka. *Anal. Chim. Acta*. 285, 335, 1992.

APPENDIX M THERMAL TECHNIQUES

Thermal processes described in this appendix are as follows:

M-1	Conventional Evaporators
M-2	Thin Film Evaporators
M-3	Drying
M-4	Distillation
M-5	Air Stripping
M-6	Stream Stripping

APPENDIX M-1 CONVENTIONAL EVAPORATORS

1.0 TECHNOLOGY DESIGNATION

This technology involves the application of heat to evaporate a volatile solvent, thereby decreasing the waste stream volume and leaving a concentrated solution or sludge. The technology described in this section is conventional evaporation.

2.0 NEED FOR THE TECHNOLOGY

Evaporation technology has been proposed in the aqueous stream baseline process to concentrate and/or dewater solids (process #180), and for secondary polishing (process #190.1) (Ref. 1). Evaporation can be applied to a wide variety of liquid wastes to concentrate relatively nonvolatile contaminants from solutions with high solids content. It is widely used in nuclear fuel-cycle facilities, and is most suitable for processing liquid waste that has a high total dissolved solids (TDS) concentration and requires a high degree of separation of the contaminant from the liquid. However, for large volumes of liquids (over 3800 m³/yr), economic considerations may favor other methods because of the high energy costs of evaporation. In addition, if the electrical conductivity is less than 100 μ mho/cm at 25°C, liquid waste has generally been processed by filtration and ion exchange, but if the conductivity is higher, evaporation has been used (Ref. 2).

The purpose of evaporation is to remove the solvent as a vapor from a solution or slurry to produce a concentrated solution, thick liquor, or slurry. In practice, evaporation will be used to concentrate the aqueous waste stream into a sludge to be sent to the wet solids line, and to produce clean condensate for clean water discharge.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Evaporation is a process whereby nonvolatile components in a solution or slurry are concentrated by vaporizing the solvent, normally water, thereby decreasing the volume of the waste to be treated and/or disposed. Evaporation is applicable to volatile liquids containing (relatively) nonvolatile solutes, where the solvent and solute are stable at the evaporation temperature. Organics, inorganics, metals, and radionuclides may be separated by this process, but evaporation does not treat the hazardous constituents. The residue is usually a sludge with

a high solids content that is handled as the mixed waste concentrate, and in most cases will require further treatment.

Evaporation involves the addition of heat and/or application of a vacuum to remove a volatile liquid from a nonvolatile liquid or dissolved solid. The evaporated liquid is condensed (usually the heat of condensation is recovered to preheat incoming liquid) and recovered for reuse or disposal. The nonvolatile constituents become concentrated in the residual liquid. In some applications, the waste may be evaporated to the extent that some solids precipitate out of solution.

Evaporators are applied in nuclear plants to concentrate aqueous wastes and to obtain relatively pure water for recycle or for acceptable discharge to the environs. Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs) frequently use evaporators to process miscellaneous radioactive and chemical wastes from equipment and floor drains, backwash and/or blowdown solutions, regenerant solutions, decontamination solutions, and miscellaneous aqueous wastes. Among the important elements of evaporator design are heat transfer, separation of evolved vapor from residual liquid, volume reduction, prevention of fouling of the heated surface, and conservation of energy.

An evaporator consists basically of a device to transfer heat to the solution and a device to separate the vapor and liquid phases. Evaporators coupled to efficient deentrainment devices provide capability for a high degree of separation for most dissolved materials. However, the inherently high operating cost of evaporation limits its applicability to those liquids that have a high concentration of dissolved solids and require high decontamination factors. Common problems in mixed waste evaporators are foaming, severe scaling, and corrosion. To resist corrosion, evaporators are usually constructed of stainless steel and operated at as low a temperature as is practical. Scale has to be removed periodically, either mechanically or chemically. Foaming can be avoided by foam-breaking devices inside the evaporator or by antifoam agents (Ref. 3).

3.1.1 Methods of Operation

Evaporators may be operated batchwise or continuously. Batch operation generally requires more energy than continuous operation. Batch evaporators are operated such that filling, evaporating, and emptying are consecutive steps so that the body must be large enough to hold the entire charge of the feed and the heating element must be placed low enough not to be uncovered when the volume is reduced to that of the product. Batch operations may be used for small systems, for products that require large residence times, or for products that are hard to handle.

A more frequent method of operation is semibatch in which feed is continuously added to maintain a constant liquid level until the entire charge reaches the final concentration. Continuous-batch evaporators usually have continuous feed, and over at least part of the cycle, a continuous discharge. One method of operation is to circulate from a storage tank to the evaporator and back until the entire tank is at a specified concentration and then finish the evaporation in batches. Continuous evaporators have continuous feed and discharge such that concentration of both feed and discharge remain constant during operation.

Evaporators may be operated as once-through units or the liquid may be recirculated through the heating elements. In once-through operation all the evaporation is accomplished in a single pass so the ratio of evaporation to feed is limited. Thin film evaporators are frequently operated once through (see Appendix M-2). Once-through evaporators are also frequently required when handling heat-sensitive materials.

Recirculated systems require that a pool of liquid be held within the equipment. Feed mixes with the pooled liquid and the mixture circulates across the heating element. Only part of the liquid is vaporized in each pass across the heating elements; unevaporated liquid is returned to the pool. All the liquor in the pool is therefore at maximum concentration. Recirculated evaporators, however, can operate on a wide range of concentrations.

3.1.2 Types of Evaporators

Jacketed Vessels

When liquids are to be evaporated on a small scale, the operation is often accomplished in some type of jacketed vessel or kettle with the heating medium in the annular space between the tank and the jacket. This may be batch or continuous but the rate of heat transfer is generally lower than for other types of evaporators due to limited heat transfer surface area. Jacketed evaporators are used when the product is very viscous, the batches are small, good mixing is required, or ease of cleaning is important (Ref. 4).

Coils

The most common type of coil evaporator is coils inside a tank with the evaporation process outside the coils and an appropriate heating medium inside the coils as shown in Figure M-1.1. Evaporation can also occur inside the coils, with downflow or upflow of the process, and with the heating medium outside the coils. Coils are used for the following reasons: small capacity, difficult to handle product, high operating pressures, or use of spiral flow will increase heat transfer or reduce fouling (Ref. 4).

A - Product
B - Vapors
C - Concentrate

D - Heating Steam
E - Condensate

Figure M-1.1. Stirrer Evaporator with Propeller-Type Stirrer and Built-In Heating Coil (for products with favorable behavior and average viscosity)

(©Noyes Publications with permission from Reference 4.)

Horizontal Tube Evaporators

This type, shown in Figure M-1.2, is seldom used except for a few special applications. The simplest design is a shell and horizontal tube arrangement with the heating medium in the submerged tubes and evaporation on the shell side. Modifications include the use of U-tubes to facilitate removal of the tube bundle for cleaning.

Initial investment is low and this type of evaporator is well adapted for nonscaling, low viscosity fluids. Heat transfer rates may be low, the unit may be susceptible to vapor binding, and foaming liquids cannot usually be treated. Advantages include relatively low cost for small capacity applications, low headroom requirements, large vapor-liquid disengaging area, relatively good heat transfer with proper design and extended surfaces, and the potential for easy semiautomatic descaling (Ref. 4).

A - Steam Inlet	E - Liquor Outlet
B - Vent for Noncondensed Gases	F - Sight Glasses
C - Condensate Outlets	G - Vapor Outlet
D - Liquor Inlet	

Figure M-1.2. Horizontal-Tube Evaporator

(©Noyes Publications with permission from Reference 4.)

A modification of the horizontal tube evaporator is the horizontal spray-film evaporator shown in Figure M-1.3. This is essentially a horizontal, falling-film evaporator in which the liquid is distributed by recirculating through a spray system. Advantages include: noncondensables are more easily vented, distribution is easily accomplished, precise leveling is not required, vapor separation is easily accomplished, operation is reliable under scaling conditions, and the evaporator is easily cleaned chemically. Disadvantages include: viscosity range is limited, crystals may adhere to the tubes, more floor space is required, and there is limited application for once-through evaporation (Ref. 4).

Figure M-1.3. Horizontal Spray-Film Evaporator

(©Noyes Publications with permission from Reference 4.)

Short Tube Vertical Evaporators

Figure M-1.4 illustrates the standard short tube vertical evaporator, or calandria, with natural circulation. Tubes from 4 to 10 feet long are located vertically inside a steam chest enclosed in a vertical shell. Circulation through the tubes is induced by natural circulation. Modifications to the standard calandria include the basket type evaporator in which the downcomer is annular between the steam chest wall and the shell making evaporator removal for cleaning and repair easier; inclined tube evaporators, shown in Figure M-1.5, perform well with foaming products due to the sharp change in flow direction of the vapor head; and propeller calandrias, shown in Figure M-1.6, provide a higher heat transfer rate.

The short tube evaporator offers several advantages: low headroom, high heat transfer rates at high temperature differences, ease of cleaning, and low initial investment. Disadvantages include: high floor space and weight, relatively high liquid holdup, and poor heat transfer at low temperature differences or high viscosity. Applications include evaporation of clear liquids, mild scaling liquids requiring mechanical cleaning, crystalline product when propellers are used, and for some foaming product when inclined (Ref. 4).

Figure M-1.4. Cross-Sectional Diagram of Standard Vertical-Tube Evaporator with Natural Circulation

(©Noyes Publications with permission from Reference 4.)

Figure M-1.5. Natural-Circulation Inclined-Tube Vaporator with Downcomer Integral with Steam Chest

(©Noyes Publications with permission from Reference 4.)

Figure M-1.6. Propeller Calandria Evaporators

(©Noyes Publications with permission from Reference 4.)

Long Tube Vertical Evaporators

These types of evaporators use tubes from 12 to 30 feet long and are generally the cheapest per unit capacity. A typical unit is illustrated in Figure M-1.7, and a typical batch type unit is illustrated in Figure M-1.8 for solutions having a high evaporation-to-feed ratio and where frequent cleaning of the heat exchanger is required (Ref. 5). Long tube units may be operated as once-through or recirculating systems. In rising film evaporators the vapor travels faster than the liquid in the core of the tube causing the liquid to rise up the tube in a film on the tube surface. The liquid film is highly turbulent causing high heat transfer rates, and residence time is low permitting application to heat-sensitive materials.

Figure M-1.7. Long-Tube Vertical Evaporator

(©Noyes Publications with permission from Reference 4.)

Figure M-1.8. Batch-Type LTV Evaporator

(From Sweitzer, P.A., ed. Handbook of Separation Techniques for Chemical Engineers 2E (1988). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

Falling film evaporators. Illustrated in Figure M-1.9, eliminated problems associated with hydrostatic head in rising film units. Liquid is fed at the top of long tubes and allowed to fall down the walls as a film. Evaporation occurs at the surface of the highly turbulent film and not at the tube surface so that temperature differences must be relatively low. Vapor and liquid are separated at the bottom of the tubes so that the liquid must be evenly distributed to all tubes and a significant amount of liquid must be circulated to the tubes. Disengagement of the vapor from the liquid is facilitated by the sharp change in direction required for the vapor to escape the unit. The falling film evaporator is widely used for concentrating heat-sensitive materials because the residence time is low. These units are also used in fouling service because boiling occurs on the surface of the film and any salt resulting from vaporization is swept away and not deposited on the tube surface. They are also suited for handling viscous fluids (Ref. 4).

Figure M-1.9. Falling-Film Evaporator

(From Sweitzer, P.A., ed. Handbook of Separation Techniques for Chemical Engineers 2E (1988). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

The advantages of the long tube evaporator include: low cost, large units, low holdup, small floor area, and good heat transfer over a wide range of applications. Disadvantages include: high headroom is needed, recirculation is frequently required, and the long tube evaporator is generally unsuited for salting or severely scaling fluids. The long tube evaporators

are best applied when handling clear fluids, foaming liquids, corrosive fluids, or large evaporation loads (Ref. 4).

Forced Circulation Evaporators

These evaporators maintain circulation, regardless of evaporation rate or heat duty, by pumping the liquid through the heating elements with relatively low evaporation per pass. Typical units are shown in Figures M-1.10 and Figure M-1.11. These systems are generally more expensive than natural circulation systems, but may have higher heat transfer rates and lower maintenance costs. The majority of applications are designed to prevent boiling in the tubes thereby decreasing the tendency for salting or scaling. Instead, the process fluid is recirculated by pumping, heated under pressure to prevent boiling, and subsequently flashed to vaporize the liquid. In other designs, the heated liquid enters the fluid body below the surface and boiling occurs after the heated liquid mixes with the cooler body liquid and vapor is evolved from the liquid surface. When forced circulation is combined with a conical bottom, the undissolved solids in the evaporator can be kept in suspension by the high circulation rate. During concentrate pumpout, the reboiler pump is kept in operation resulting in a reduction in the buildup of radioactive solids in the evaporator vessel bottom.

Figure M-1.10. Forced-Circulation Evaporator - Submerged-Tube Type

(From Sweitzer, P.A., ed. Handbook of Separation Techniques for Chemical Engineers 2E (1988). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

Figure M-1.11. Forced-Circulation Evaporator with an External, Vertical Single-Pass Heater and Restriction Device to Prevent Boiling in Tubes (Ref. 7)

Forced circulation evaporators have proven to be the most suitable for radioactive waste and nuclear process related applications (Ref. 6). The use of a pump makes possible separation of the heat-transfer, vapor-liquid separation, and crystallization functions. Because the circulation rate is independent of the evaporation rate, this type of evaporator is well suited to crystallization operations where solids must be maintained in suspension at all times. In radioactive waste applications, evaporators are designed to process a wide variety of feed streams, with solids concentrations typically ranging from less than 100 ppm to 2 wt%. The bottoms discharge concentration can vary from 4 to 50 wt% solids. Natural circulation units were unable to achieve design throughput rates and experienced operating difficulties due to tube fouling, plugging, and control problems.

Advantages of forced circulation evaporators include: high rate of heat transfer; positive circulation; relative freedom from salting, scaling, and fouling; ease of cleaning, and a wide range of applications. Disadvantages include: high cost, relatively high residence time, and maintenance and operating costs associated with pumps. These systems are best applied when treating crystalline products, corrosive products, or viscous fluids, and in uses requiring a high degree of concentration and close control of concentration. Among the difficulties reported to be frequently encountered with forced-circulation evaporators are: (a) plugging of tube inlets by salt deposits detached from the walls of equipment; (b) poor circulation caused by higher than

expected heat losses; (c) salting due to boiling in the tubes; and (d) corrosion/erosion. These problems can be minimized or eliminated by appropriate design and operation (Ref. 6).

Evaporators/Crystallizers

Crystallization is the controlled precipitation of solids from a saturated solution containing water and dissolved solids. The evaporative-crystallization process first generates a super-saturated solution by evaporating the water from the solution. The process then controls the combined effects of nucleation rate, growth rate, heat balance, and material balance to provide the desired crystals and concentrated liquor (Ref. 7). Forced-circulation evaporators are well suited to concentrating salting liquors and therefore function well as evaporator/crystallizers. A typical evaporator/crystallizer is shown in Figure M-1.12.

Figure M-1.12. Evaporator/Crystallizer (Ref. 7)

The forced circulation crystallizer has become the primary tool for production of dry, or nearly dry, waste salts with zero liquid discharge (Ref. 8). The crystallizer can process waste streams with widely varying composition leaving a circulating crystal slurry of up to 25 wt% suspended solids. Because the crystallizer circulates a slurry, some method of dewatering is required. In order of solids dewatering effectiveness, and cost, the following options are available (Ref. 8):

- Centrifuge—highest cost, 10-20% retained liquid
- Belt filter—automatic operation, 40-50% retained liquid
- Filter press—manual/semi-automatic, 40-60% retained liquid
- Hydrocyclone—least cost, no moving parts, 50-70% retained liquid.

The entrained liquid may be as high as 50% dissolved solids, so in many cases the hot crystals can absorb all the residual water into water of hydration, leaving dry solid at room temperature (Ref. 8).

Plate Evaporators

Plate evaporators are constructed of flat plates that are usually corrugated to provide turbulent flow between the plates as shown in Figure M-1.13. Flat plate, or plate-and-frame, evaporators are constructed by mounting a number of embossed plates with corner openings between a top carrying bar and a bottom guide bar. The plates are gasketed and arranged to form narrow flow passages when a series of plates is clamped together in the frame. Fluids are directed through the adjacent layers between the plates, either in series or parallel, depending on the gasketing arrangement. These type of evaporators are well adapted to evaporating heat-sensitive, viscous, and foaming materials. They afford fast startup and shutdown, are compact with low headroom, and are easily cleaned and modified. The high turbulence in the channels prevents scaling (Ref. 9).

Figure M-1.13. Corrugated Plates Can Be Assembled as Shown or Rearranged to Optimize Heat Transfer

(Reprinted by special permission from *Chemical Engineering* (Feb. 23, 1970)
Copyright © (1979), by McGraw-Hill, Inc., New York, NY 10020.)

These evaporators can be designed to operate as rising or falling film evaporators, thin film evaporators, or crystallizers (Ref. 10). A major disadvantage is the large gasketed area limiting the operating pressure to approximately 300 psi. However, because all fluids are gasketed independently to the atmosphere, intermingling of fluid cannot occur and leakage can be avoided by proper selection of gasketing material and assembly.

Submerged Combustion Evaporators

Submerged combustion is the process of burning a fuel in a specially designed burner under the surface of a liquid. The hot combustion gases exit the burner directly into the surrounding liquid and heat is transferred directly from the gas to the liquid as illustrated in Figure M-1.14. There are many different types of submerged combustion evaporators, many of which use an external combustor. However, these evaporators tend to be less efficient than those burning the fuel beneath the surface of the liquid due to heat loss between the burner and the evaporator.

Figure M-1.14. Evaporator Vessels for Submerged Combustion Evaporator

(©Noyes Publications with permission from Reference 4.)

Submerged combustion evaporators are frequently smaller than other types, and can be economically constructed from corrosion resistant materials. Thermal efficiencies are high—ranging from 90 to 99% of the net heat output. Since the vapor is mixed with large quantities of noncondensable gases, it is difficult to reuse this heat in the vapor; however, the heat may be used to preheat the incoming feed stream. Direct contact heat transfer overcomes the built-in thermal losses associated with the separation of fluid streams by an intervening solid wall in

conventional evaporators, and eliminates the deterioration of heat transfer effectiveness with time due to fouling of heat transfer surfaces (Ref. 11).

Water vapor is formed during combustion. To prevent its condensation into the liquid, the gas and liquid must exceed 140°F. Above this temperature the water derived from combustion is not sufficient to saturate the dry combustion gases, and water will be evaporated from the liquor to achieve saturation.

Bubbling combustion gases through the liquid results in a significant boiling point reduction. When burning natural gas with 8% excess air, the boiling point of water has been found to be approximately 192°F. Similar boiling point depression has been found with aqueous salt and acid solutions. As the amount of excess air increases, the boiling point decreases accordingly (Ref. 4).

The problems resulting from submerged combustion evaporation have been related to entrainment and stack emissions. Uniformity of gas phase dispersion is important because thermal effectiveness decreases rapidly with nonuniformity of dispersal. Another disadvantage is that design methods for determining required dimensions of equipment are not well established. These type of evaporators are best suited for corrosive, scaling, salting, and highly viscous liquids which are not heat-sensitive and where water carbonation can be tolerated. Other advantages include low equipment cost and low pressure drop for gas flow (Ref. 11). They can also be used as crystallizing evaporators and are widely used to concentrate waste streams (Ref. 4).

Mechanical Vapor Compression Evaporators

With mechanical vapor compression, water vapor boiled off in the evaporator is passed to an electrically powered compressor and is compressed to 1-3 psi. This raises the pressure and saturation temperature of the vapor which is then used as the heating medium in the evaporator. The heat present in the vapor is used to evaporate more water instead of being rejected in a condenser. Due to inefficiencies in the compression cycle, excess vapor is often produced which can be used to compensate for vent and radiation losses and, in some cases, assist in preheating the feed (Ref. 10). Mechanical vapor compression is a proven means to significantly reduce energy required for evaporation (Ref. 4).

Mechanical vapor compression achieves the highest possible energy savings, but at the expense of higher capital investment and increased electrical power consumption. High boiling point rises makes vapor compression less economical because of the high compression ratio required and the attendant high energy use and increased capital cost. Vapor compression evaporation finds wide application when temperature differences across the evaporator are low (10°C to 15°C), boiling point rise is low (< 6°C), vapors are not extremely corrosive, fouling is not excessive, and the cost of electricity is low (Ref. 4).

3.1.3 Vapor - Liquid Separation

Losses or carryover into the vapor stream result from droplets in the vapor that cannot separate because of the vapor velocity. The extent of entrainment is a function of the size distribution of the droplets and the vapor velocity. Entrainment may be generated from the atomization at a liquid surface by a high gas velocity, from a spray contacting operation, or from the disengagement of gas and liquid in a contacting process. This latter mechanism is the most common (Ref. 4). Bubbles breaking the surface cause drops of different sizes to be propelled upward. The smaller ones are caught in the upward flowing gas and carried overhead as entrainment, while the larger ones return to the surface.

Entrainment can be separated from a gas stream with a variety of mechanisms, including gravity, inertial impact, interception, centrifugal force, and Brownian motion. Separators in common use and classified according to construction are as follows: flash tanks, vane impingement separators, wire mesh separators, Karbate strut separators, centrifugal separators, cyclones, and special types. Except for flash tanks and some special separators, the efficiency of all these separators tends to increase with increasing velocity up to a maximum allowable limit. In this region the efficiency seems to depend primarily on gas velocity and particle size, and to be somewhat insensitive to gas and liquid physical properties.

Various entrainment separators are compared in Table M-1.1 (Ref. 4).

Flash Tanks

In flash tanks the velocity is reduced to a value that permits the droplets to settle out rather than being carried by the vapor. Flash tanks are generally used when the liquid entrainment exceeds 20 wt% of the gas flow. Proper sizing of the tank should result in a residual entrainment under 3 wt% of the gas flow rate. However, it is often not practical to provide a vapor body large enough to accomplish the desired disentrainment.

Wire Mesh Separators

Knitted wire mesh, either metal or plastic, is often used inside vapor heads for entrainment separation. Knitted mesh can be used effectively where it will not be fouled or plugged by solids in the liquid, although wire mesh may sometimes be washed to remove solids. Any significant corrosion will cause rapid disintegration of the mesh. The performance of the mesh depends on wire surface area and free volume. Vapor flows easily through the mesh while droplets of liquid impinge on the wire surfaces, coalesce, flow back, and drop away from the demister pad. Knitted mesh has very good separation characteristics when the gas density is low and poor characteristics when it is high. Separation efficiency (percent of inlet entrainment removed) can be expected to increase from 80% at 2 ft/sec to 95% at 3 ft/sec to 99+% at 5 ft/sec (Ref. 4).

TABLE M-1.1. COMPARISON OF SEPARATORS

SEPARATOR TYPE	ADVANTAGES	DISADVANTAGES
Vane (Line Separator)	<ol style="list-style-type: none"> 1. High efficiency 2. Good turndown characteristics 3. Relatively inexpensive 4. Low pressure drop - typically less than 0.5 psi 	<ol style="list-style-type: none"> 1. Liquid loading is limited to roughly 5 - 10% of gas mass flow rate 2. Pockets can plug with solids 3. Difficult to clean unless vanes are removable
Vane (Vertical Gas Separator)	<ol style="list-style-type: none"> 1. Better efficiency than line separator 2. Good turndown characteristics 3. Will separate liquid slugs 4. Will operate efficiently with high liquid loading 	<ol style="list-style-type: none"> 1. Pockets and drain piping can plug with solids 2. Difficult to clean unless vanes are removable 3. Relatively inexpensive
Mesh Separator	<ol style="list-style-type: none"> 1. Generally good efficiency at low pressure 2. Inexpensive if installed in existing vessel 3. Available in a variety of materials 4. Very low pressure drop - less than one inch water 	<ol style="list-style-type: none"> 1. Very susceptible to plugging 2. Expensive if new tank is needed to house mesh pad 3. Highly susceptible to corrosion
Karbate Separator	<ol style="list-style-type: none"> 1. High efficiency 2. Good turndown characteristics 3. Very low pressure drop - less than one inch water 	<ol style="list-style-type: none"> 1. Only available in Karbate 2. Liquid loading limit 3. Somewhat difficult to clean 4. A trap device is needed for liquid collection
Centrifugal (Line)	<ol style="list-style-type: none"> 1. Inexpensive 	<ol style="list-style-type: none"> 1. Lower efficiency than vane line separators 2. A trap device is needed for liquid collection 3. Limited liquid handling capacity
Cyclone	<ol style="list-style-type: none"> 1. Can be designed in-house 2. Less susceptible to plugging than other types 3. Can be operated at high inlet velocity (with high pressure drop) 	<ol style="list-style-type: none"> 1. Lower efficiency than vane line separators 2. A trap device is usually needed for liquid collection
Fiber Mat (Brink)	<ol style="list-style-type: none"> 1. Very high efficiency 2. Relatively low pressure drop (approximately 6-8 inches water) 	<ol style="list-style-type: none"> 1. Relatively expensive 2. Highly susceptible to plugging

(©Noyes Publications with permission from Reference 4.)

Brink mist eliminators are filtering separators consisting of a bed of fine glass or synthetic fibers sandwiched between two screen supports. High-velocity (H-V) and high-efficiency (H-E) models are available. The H-V models can separate droplets more efficiently than the

conventional mesh because the fibers are much smaller in diameter, but the liquid handling capacity is less. The H-V separator uses inertial impact while the H-E unit is based on capture by Brownian motion and is used for droplets in the submicron range. Because velocities are quite low (often 0.5 ft/sec), large capacity requires large surface area.

Vane Impingement Separators

Vane impingement separator elements consist of parallel zig-zag plates or vanes with collection pockets, similar to those shown in Figure M-1.15. As entrainment-laden gas flows through the separator, the liquid droplets are forced by inertia onto the vane surfaces. The resultant liquid film flows to the collection pockets where it drains away by gravity. Each change of direction is a stage of separation, and by employing several such flow reversals, manufacturers are able to achieve very good separation efficiencies.

Figure M-1.15. Vane Impingement Separator Elements

(©Noyes Publications with permission from Reference 4.)

Vane impingement separators are built in a variety of configurations for various locations in an evaporator system as shown in Figure M-1.16. It is often more economical to provide a line separator with required piping rather than provide an internal separator. Vertical gas separators are used when very high separation efficiencies are required or when the liquid entrainment to the separator is in the range of from 5 to 20 wt% of the gas flow. Vertical collection surfaces stay cleaner longer than horizontal surfaces because of better liquid drainage. Vane separators are usually purchased from the vendor on a performance basis. Pockets can plug with solids and are difficult to clean unless the vanes are removable.

Figure M-1.16. Types of Vane Impingement Separators

(©Noyes Publications with permission from Reference 4.)

Centrifugal Separators

Centrifugal separators impart a spin or rotation to the liquid-laden gas. Blades or a special passage are used to impart the rotation and the resultant centrifugal force. Entrained liquid collects on the wall and flows through a drain connection. Centrifugal separators are usually line-type separators and are purchased from the manufacturer on a performance basis. These type of separators have lower separation efficiency than vane separators and have a limited liquid handling capacity.

Cyclones

Cyclone separators admit entrainment-laden gas through a tangential inlet. The gas then spirals around the central tube, called a vortex finder, and finally exits through it. Cyclone efficiency is not as good as other separators. Good separation usually results from high velocities (up to 300 ft/sec) with resultant high pressure drops.

Other Separators

Other separator types include: streamline struts, banks of tubes, zig-zag baffles with no liquid collection pockets, packed beds, and fibrous filters.

3.1.4 Input and Output Stream Characteristics

Evaporation is not suitable for application to cases in which the solvent and solute(s) have similar volatilities. The waste stream must be completely characterized and relatively homogeneous in nature (Ref. 12). However, there does not appear to be a limit on the input liquid characteristics, including solids content, while the typical solids content of the output stream is 4-50 wt%. In general, conventional evaporators are limited to liquid viscosities below approximately 1000 centipoise (Ref. 4). Practical application of evaporation technology is significantly affected by the properties and characteristics of the solution to be concentrated. The presence of resin beads or resin fines in the feed may create serious fouling and corrosion problems (Ref. 6). The resin decomposes in the evaporator heating tubes, releasing chlorides, sulfates, amines, and other organic compounds. Some of the more important properties of evaporating liquids are discussed below.

Concentration

As the liquor is concentrated the solution properties may drastically change. The density and viscosity may increase with solid content until the heat transfer performance is reduced or the solution becomes saturated. Continued evaporation of a saturated solution may cause crystals to form which often must be removed to prevent plugging or fouling of the heat transfer surfaces. The boiling point of the solution also rises considerably as the solids concentration increases.

Foaming

Foam often results from the presence of colloids, surface tension depressants, or finely divided solids. These often concentrate at the liquid surface and can sometimes be removed by a surface blowdown or use of antifoam agents. Other causes of foaming are air leakage below the liquid surface or the presence of dissolved gases in the liquid. Stable foams cause excessive entrainment. When foam begins to build in an evaporator, the foam layer can often continue to grow until it fills the evaporator and is carried out the top. Foam cannot be broken by conventional entrainment separators unless the foam is highly unstable. Foams may be suppressed by operating at low liquid levels, by mechanical or hydraulic means.

Salting

Salting refers to the growth on evaporator surfaces of a material having a solubility that increases with an increase in temperature.

Scaling

Scaling is the growth or deposition on heating surfaces of a material which is either insoluble or has a solubility that decreases with an increase in temperature. It may also result from a chemical reaction in the evaporator. Both scaling and salting liquids are best handled in an evaporator that does not rely on boiling for operation.

Fouling

Fouling is the formation of deposits other than scale or salt. They may be due to corrosion, solid matter entering with the feed, or deposits formed on the heating medium side.

Corrosion

Corrosive properties of the liquid influence the material of construction or evaporator type. Corrosion and erosion are often severe in evaporators due to the high vapor and liquid velocities, the presence of suspended solids, and the concentrations required.

Other Fluid Properties

Other fluid properties may influence the type of evaporator or mode of operation including toxicity, explosive hazards, temperature sensitivity, radioactivity, and ease of cleaning. Salting, scaling and fouling result in steady decrease of heat transfer rates, until the evaporator must be shut down and cleaned. Temperature-sensitive materials require control of the time/temperature relationship, and low-holdup-time requirements may dictate the use of certain evaporator types.

3.2 DEMONSTRATED PERFORMANCE

Evaporation has long been used as a unit operation in the manufacture of various products in the chemical-process industries. In addition, it is currently being used for the treatment of hazardous wastes such as radioactive liquids and sludges, metal-plating wastes,

and other organic and inorganic wastes. In industries that generate large volumes of aqueous waste with dilute hazardous constituents, evaporation is used to concentrate the waste for additional treatment or disposal. If an aqueous hazardous waste contains moderately volatile organic constituents, treatment after evaporation may be required to separate these organics from the water phase (Ref. 12).

3.2.1 Technology Status

Evaporator technology is well developed and commercially available. Various types of evaporators are readily available for use to concentrate mixed aqueous waste streams. However, tests will be required to determine the characteristics of the input stream so as to select the correct type of evaporator, and pilot plant tests will be required to determine design parameters and size the equipment.

In addition, experiments are needed to determine the reasons for decontamination factors (DFs) lower than theoretical and to find ways to increase them. Engineering correlations are needed to describe mist formation versus physical properties and operating conditions. With a knowledge of how mists are formed, designs could be chosen to minimize mist formation. Experimental studies are needed to determine the factors limiting demister performance. If the phenomena that limit demister performance are understood, improved designs can be found. More studies are needed on multiple-effect evaporators (i.e., several evaporators (or effects) connected so that the vapor from one effect serves as the heating medium for the next) to determine whether they can give improved (higher) DFs and better energy utilization. Evaluation of the factors that influence availability and reliability of evaporators and crystallizers (e.g., corrosion, maintenance, controls, etc.) is needed (Ref. 13).

Rod Williamson, Vice President of Sales for LICON Inc, an evaporator manufacturer, believes research should be focused on systems engineering to refine and integrate existing technologies for treating mixed wastes (Ref. 14). Other areas that are believed to require further development include:

- Addressing of carryover problems. Current DFs for nonvolatile constituents are 10^5 to 10^7 .
- Removal of volatile organics prior to evaporation of the bulk aqueous streams. This may include flashing off the volatiles under deep vacuum.
- Automation with possible use of robotics.
- Determination of the best type of evaporator to use and the supporting equipment to use with it (i.e., ultrafiltration, reverse osmosis, carbon beds, ion exchange polishing, etc.).
- Develop better pre- and post-chemical treatment for scale prevention.

3.2.2 Reliability and Maintenance Requirements

Evaporation technology is fairly simple and reliable requiring periodic maintenance for cleaning and repair. Liquid characteristics described previously, the type of evaporator, and materials of construction will determine maintenance frequency and cleaning requirements. Corrosive service requires units that are easy to repair, or have removable tube bundles. Removal of various scale and deposits by chemical cleaning is a common cleaning practice. However, chemical cleaning is not always effective and some types of fouling can be removed only by physical or mechanical means such as hydroblasting, scraping, wire brushing, drilling, cutting, or sandblasting. For batch operations, scheduled maintenance should not have a major impact on operations. However, unscheduled maintenance will interrupt waste processing. In addition, problems may arise when manually cleaning or repairing evaporator components due to the potential hazardous and radioactive nature of the deposits remaining in the evaporator. Thus, evaporator types that can be modified for automated cleaning and/or component replacement should be considered.

The evaporator should be designed so that chemicals for cleaning can be easily added, and so that easy and quick maintenance can be accomplished to minimize exposure of personnel to radiation. Generally, this means that evaporator components should be separated to the maximum extent possible, be placed in separate cubicles, or be separated by shielding walls.

Evaporation systems with moving parts, such as pumps for forced circulation systems or compressors for mechanical vapor compression, may have higher maintenance requirements and be less reliable than other types of evaporators.

3.2.3 Secondary Waste Streams

Secondary waste streams consist of the concentrated product and entrained liquid in the evaporated vapor stream. Noncondensable gases from the condenser may also form a secondary waste stream. Offgas from submerged combustion, or other direct contact evaporators, will also form a secondary waste stream consisting of hot air or combustion products.

3.2.4 Separation Efficiency

The separation factor (SF) is defined as the bottoms-to-distillate concentration ratio. Evaporators are designed to produce a specific SF at the maximum bottoms concentration. Separation factors in the range of 10^5 - 10^6 for nonvolatiles can be obtained for a simple evaporator with a cyclone separator. The addition of a reflux column to the evaporator plus an

entrainment separator can add several orders of magnitude to the SF. However, reductions in the SF (and DF) may result from foaming, splashing, entrainment, or volatilization of solute (Ref. 6).

The volume-reduction (VR) factor is defined as the ratio of feed volume to bottoms volume. Evaporator/crystallizers have been proposed for the treatment of low level waste (LLW) as partial volume reduction systems; the VR factor is expected to range between 2 and 5 (Ref. 7), and up to about 50 wt% solids may be concentrated in the bottoms (Ref. 6).

The decontamination factor (DF) for radioactive waste evaporators is normally expressed as the ratio of the contaminant concentration in the feed to the contaminant concentration in the condensate. The most significant influences on the attainable DFs are: (a) the evaporator type and design, (b) the design and performance of associated liquid droplet deentrainment devices, and (c) volatilities of feed-solution contaminants. Evaporative decontamination is not recommended for radioactive iodine, ruthenium, technetium, and tritium because of the volatility of these elements (Ref. 2).

Provision of effective entrainment separation is the most important operating factor. It is also important to maintain operating conditions such as reflux, pH, and temperature so that they suppress volatilization. A system DF of 10^6 is theoretically predicted for a single-effect evaporator used to separate water from a nonvolatile solute. However, average system DFs of 10^4 can be expected for nonvolatile fission and corrosion products in natural and forced-circulation evaporators, but an average system DF of approximately 10^3 can be expected for iodine. Spray film and submerged U-tube evaporators produce DFs that are 5-10 times lower (Ref. 7).

3.2.5 Safety and Health

Safety and health issues may arise from the following: spills or leaks of flammable or hazardous fluids or gases, uncontrolled reactions, process upsets, operating errors, mechanical equipment failure, improper equipment venting or pressure relief, and poor housekeeping. The ASME code requires all equipment to be protected by pressure relief devices to prevent the pressure from rising above the maximum allowable working pressure. However, venting must be into an enclosure to prevent exposure of personnel to potentially hazardous vapors or gases.

The equipment may require cleaning, which may involve manual operations in a hazardous environment, depending on the nature of the equipment and liquid and solid constituents.

3.2.6 Operational Complexity

Evaporation technology can range from simple to complex depending on the type of equipment selected and the controls required. The equipment is large and requires ancillary equipment in the form of condensers, pumps, and valves and actuators.

3.2.7 Environmental Impact

Evaporation produces a condensate, bottoms stream, and potentially a noncondensable offgas, all or one of which may require further processing or disposal.

3.3 COST OF THE TECHNOLOGY OR EQUIPMENT

Evaporation is an expensive technology, both in terms of capital cost and operating costs. Capital costs depend on the type of evaporator selected, its size, the materials of construction for the tubes and body, and the auxiliary equipment required for proper operation. Capital and operating costs for a forced circulation evaporator/crystallizer using steam heating and mechanical vapor recompression (MVR) are shown in Table M-1.2 (Ref. 8). Cost are based on a single unit system at 100% of design capacity.

TABLE M-1.2. FORCED CIRCULATION EVAPORATOR/CRYSTALLIZER COSTS

Flow (gpm)	Steam Heated		MVR	
	Capital Cost	Operating Cost	Capital Cost	Operating Cost
10	0.9	75.5	1.25	48
20	1.35	69.5	1.8	39
30	1.7	67	2.3	35

Source (Ref. 8)
Capital Cost in \$ Millions
Operating Costs in \$/1000 gallons

Assumptions:
Power = \$0.045/kwh
Operating Labor = \$20.00/hr
Steam Use = 1160 Btu/lb
Steam Cost = \$5.00/mmBtu
MVR Compressor = 150 kwh/1000 gal feed
Capital Recovery = 10%/yr

Operating labor costs generally are attributed to one person who can easily control an evaporator system if an adequate number of control instruments are used. Occasional maintenance labor is required for the repacking of pumps and valves and the repair of piping. The main maintenance requirement may be for mechanical cleaning and tube replacement. Total maintenance cost, including retubing cost, is about 1% of installed equipment cost per year for

evaporators in noncorrosive service. Where corrosion is moderately severe, maintenance costs are on the order of 3% per year (Ref. 15).

3.4 TECHNOLOGY COMPARISON

The advantages and disadvantages of natural circulation, forced circulation, and submerged U-tube evaporators, described in Section 3.1.2, are compared in Table M-1.3. Evaporators of these types are expected to yield concentrates containing 40 to 50 wt% solids. The solids content of the concentrates can be increased significantly by using a wiped-film evaporator or an evaporator/crystallizer (Ref. 2).

TABLE M-1.3. ADVANTAGES AND DISADVANTAGES OF EVAPORATOR TYPES

Evaporator Type	Advantages	Disadvantages	Best Applications	Frequent Difficulties
Natural Circulation	Low cost, large heating surface, in one body, low holdup, small floor space, good heat transfer coefficients at reasonable temperature differences (rising film), and good heat transfer coefficients at all temperature differences (falling film)	High headroom, generally unsuitable for salting and severely scaling liquids, poor heat transfer coefficients for rising-film version at low temperature differences, and recirculation usually required for falling-film version	Clear liquids, foaming liquids, corrosive solutions, large evaporation loads, high temperature differences for rising film, low temperature differences for falling film, and low-temperature operation for falling film	Sensitivity of rising film units to changes in operating conditions and poor feed distribution to falling film units
Forced Circulation	High heat transfer coefficients, positive circulation, and relative freedom from salting, scaling, and fouling	High cost, power required for circulating pump, and relatively high holdup or residence time	Crystalline product, corrosive solutions, and viscous solutions	Plugging of tube inlets by salt deposits detached from walls of equipment, poor circulation because of higher than expected head losses, salting because of boiling in tubes and corrosion/erosion
Submerged U-tube	Very low headroom, large vapor-liquid disengaging area, good heat-transfer coefficients, and easy semi-automatic descaling	Unsuitable for salting liquids, high cost, and relatively high holdup or residence time	Limited headroom, small capacity, and severely scaling liquids	Slow response to changes in control settings and poor level control in vacuum units

The primary advantage of evaporation is that it reduces the volume of waste requiring treatment, thus lowering treatment costs. Evaporation is a well-known, mature technology, available from a large number of vendors and applicable to a variety of conditions.

The main disadvantage of evaporation is that it has relatively high operating costs. The equipment may require cleaning, which may involve manual operations in a hazardous

environment, depending on the nature of the equipment and liquid and solid constituents. Evaporation concentrates hazardous constituents in a residual liquid requiring further treatment.

Other technologies that can concentrate an aqueous waste stream include membrane technology (reverse osmosis and electrodialysis).

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Properties of the liquid to be evaporated are critical in the final selection of an appropriate evaporation system. These properties include heat capacity, heat of vaporization, density, thermal conductivity, boiling-point rise, and heat-transfer coefficient.

Other considerations are the potential for corrosion, foaming, entraining, salting, and scaling. Some of these concerns can be largely eliminated by use of proper construction material and/or proper design choice. The appropriate design is specific to the liquid to be treated and must be determined through the use of pilot units.

4.2 TESTING REQUIREMENTS

Tests are conducted to determine capacity, heat transfer rates, steam economy, product losses, and cleaning cycles. Performance tests may also be required to establish that a new evaporator system has met performance guaranteed by the supplier. Tests may also be required to determine evaporator capacity under different operating conditions.

Evaporator testing can be costly, especially if the data obtained are not sufficient to meet the test objectives. Adequate personnel must be available to gather all necessary data over a relatively short period.

Parameters that cannot always be precisely determined make it nearly impossible to define all the problems during the design stage. These parameters include: composition changes, fouling, validity of heat transfer data, and changes in utilities. It may be necessary to evaluate the performance of an evaporator at other than design operating conditions.

5.0 VENDOR LIST

LICON, Inc.
Pensacola, FL
Bill Pergande, President
Rod Williamson, VP of Sales
904-434-5088

Vacuum, vapor compression,
and multi-stage flash evaporators

APV Crepaco, Inc.
Tonawanda, NY
716-692-3000

Plate, rising/falling film tubular,
and MVR evaporators

Ambient Technologies, Inc.
North Miami Beach, FL
305-937-0610

Vacuum evaporators

T-Thermal
Conshohocken, PA
215-828-5400

Submerged combustion

HPD Inc.
Naperville, IL
708-357-7330

Submerged combustion, vacuum,
crystallizers, freeze crystallization,
electrodialysis, and reverse osmosis.

6.0 REFERENCES

1. Bechtel, Inc. *Mixed Waste Treatment Project Process Systems and Facilities, Design Study and Cost Estimates*, September 1992.
2. EG&G Idaho, Inc. *Low-Level Radioactive Waste Treatment Technology*, Report DOE/LLW 13Tc, Idaho Falls, ID: National LLRW Management Program, 1984.
3. Benedict, M., T. Pigford, and H. Levi. *Nuclear Chemical Engineering*, McGraw-Hill Book Co.: New York, 1981.
4. Minton, P.E. *Handbook of Evaporation Technology*, Park Ridge, NJ.: Noyes Publications, 1986.
5. Schweitzer, P.A., ed. *Handbook of Separation Techniques for Chemical Engineers*, McGraw-Hill Book Co.: New York, 1988.
6. Coplan, B.V. and P.J. Mayo. "Liquid Waste Management." *Radioactive Waste Technology*, A.A. Moghissi et al., eds., ASME: New York, 1986.
7. Jolley, R.L., et al. *Low-Level Radioactive Waste From Commercial Nuclear Reactors, Volume 2, Treatment, Storage, Disposal and Transportation Technologies and Constraints*. ORNL/TM-9846/V2. Oak Ridge National Laboratory: Oak Ridge, TN, 1986.
8. Wolfe, T.D. *Evaporation and Crystallization of Brines for Zero Discharge*. Unpublished report, HPD Corporation, Naperville, IL, 1993.

9. Usher, J.D. "Evaluating Plate Heat-Exchangers" in *Process Heat Exchange*, V. Cavaseno, ed. (chemical engineering). McGraw-Hill Publishing Co.: New York, 1979.
10. APV Crepaco, Inc. *APV Evaporator Handbook*. 3rd ed. EHB-1189. Tonawanda, NY: APV Crepaco.
11. Kreith, F. and R.F. Boehm. *Direct-Contact Heat Transfer*. Hemisphere Publishing Corp.: New York, 1988.
12. Freeman, H.M., ed. *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill Book Co.: New York, 1989.
13. Kibbey, A.A. and H.W. Godbee. *A State-of-the-Art Report on LLW Treatment*. ORNL/TM-7427. Oak Ridge National Laboratory: Oak Ridge, TN, 1980.
14. Letter from R.C. Williamson, Vice President Sales, LICON Inc., February 11, 1993.
15. Perry, R.H. and D. Green, eds. *Perry's Chemical Engineers' Handbook*. 6th ed. McGraw-Hill Book Co.: New York, 1984.

APPENDIX M-2 THIN-FILM EVAPORATORS

1.0 TECHNOLOGY DESIGNATION

The technology described in this section is thin-film evaporation. This technology involves the application of heat and mechanical agitation to spread a thin film over the heat transfer surface to evaporate a volatile solvent thereby decreasing the waste stream volume and leaving a concentrated solution or sludge.

2.0 NEED FOR THE TECHNOLOGY

Thin-film evaporation technology will be used in the aqueous stream baseline process to concentrate and/or dewater solids from the backwash and/or blowdown streams from other plant processes (process #180). The purpose of thin-film evaporation is to increase the solids content of the waste stream beyond the capabilities of conventional evaporators prior to transferring the waste to the wet solids line.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The thin-film evaporator is also called an agitated-, scraped-, wiped-, or turbulent-film evaporator. Thin-film evaporators are mechanically aided, turbulent film devices. The heating surface is a single large-diameter cylindrical or tapered tube, and the liquid being concentrated is spread out onto a thin, highly turbulent film by the blades of the rotor. These evaporators are designed to spread and continuously agitate and renew a thin layer of liquid on one side of a metal surface, with heat supplied to the other side. A thin-film evaporator has three major components: a vapor body, a rotor, and a drive system (Ref. 1) as illustrated in Figure M-2.1.

Product enters the feed nozzle above the heated zone and is transported by gravity and mechanically by the rotor in a helical path down the inner heat transfer surface. The liquid forms a highly turbulent thin film from the feed nozzle to the product outlet nozzle. Only a small quantity of process fluid is contained in the evaporator at any instant. Residence times are low and gases or vapors are easily disengaged. The blades may also act as foam breakers. Typically about one-half pound of material per square foot of heat transfer surface is contained in the evaporator.

A variety of basic designs are available commercially. They are either vertical or horizontal, and can have cylindrical or tapered thermal bodies and rotors as illustrated in

Figure M-2.2. The rotor may be one of several "zero-clearance" designs, a rigid "fixed-clearance" type or, in the case of tapered rotors, an adjustable clearance type. One vertical design includes an optional residence-time control ring to manipulate the film thickness to some extent. The majority of thin-film evaporators are the vertical design with a cylindrical fixed-clearance rotor shown in Figure M-2.1 (Ref. 2).

Figure M-2.1. Flow Path for Thin-Film Evaporator

(From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

A - Vertical Cylindrical Thermal Zone
B - Vertical Tapered Thermal Zone

C - Horizontal Cylindrical Thermal Zone
D - Horizontal Tapered Thermal Zone

Figure M-2.2. Horizontal and Vertical Thin-Film Evaporation

(From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Agitated thin-film evaporation has a potential for removing volatile organics from those waste streams that would foul or plug conventional evaporators, or which require low operating pressures during evaporation. Certain slurries, sludges, or viscous wastes that cannot be handled by conventional equipment can be successfully processed in agitated thin-film evaporators. Mechanical agitation of the heat transfer surface allows processing of high-viscosity liquids, in some cases up to 100,000 cP (Ref. 3), and liquids with suspended solids. Agitation promotes heat transfer and keeps solids in suspension, thereby preventing or minimizing fouling of the surface. The solids content of the concentrates from a thin-film

evaporator can at least be doubled (40-50 wt%) over that from a conventional evaporator (Ref. 4). Some types of this equipment have been developed that are capable of discharging dried solids (Ref. 3).

Thin-film evaporators can be used to remove or recover organic components from waste streams. The bottoms of the evaporator will have smaller amounts of volatiles than the feed, either because of the reduction in concentration or the reduction in volume (or both). For mixed (water and organics) waste streams, a thin-film evaporator can selectively remove the water (the organics are high-boiling) to improve the Btu value of the bottoms, or selectively remove the organics (the organics are low-boiling) so that the the organics can be burned. These units can also be used to separate volatile compounds from the solids in sludges.

Hazardous wastes that can be treated in a thin-film evaporator include waste solvents, and halogenated and nonhalogenated organics can be recovered together with alcohols, ketones, esters, glycols, ethers, aromatic hydrocarbons, petroleum naphthas, freons, and specialty solvents. Still bottoms, spent lubricating oil, coating residues, obsolete paints, and inks can be treated in a thin-film evaporator (Ref. 2).

Chemical processing applications for thin-film evaporators may be classified into four broad categories (Ref. 1):

1. Heat-sensitive products. Under high vacuum and moderate temperatures, the mean residence times of a vertical thin-film evaporator can be between 2 and 100 seconds with a very narrow time distribution.
2. Materials that tend to foul. Because of high turbulence imparted by the rotor and excellent localized mixing, fouling of the thermal surface is not generally a problem.
3. Viscous liquids. Fluid with viscosities up to 50,000 cP can be processed in a standard thin-film evaporator. Zero-clearance rotors do not exhibit the range of viscosity application that fixed-clearance rotors exhibit. Some firms manufacture thin-film evaporators and vertical extruders for the 50,000-2,000,000 cP range where fluids cease to flow under the influence of gravity alone.
4. Miscellaneous applications. Various special application problems have been solved by thin-film evaporators: evaporation with chemical reaction; two-phase flow (immiscible fluids, slurries, suspensions); and others.

As with conventional evaporators, practical application of evaporation technology is significantly affected by the properties and characteristics of the solution to be concentrated. Thin-film evaporators do not work well for wastes which react immediately when heated. Filtering is required if the solids in the waste are comparable in size to the clearance of the rotors (Ref. 2).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Thin-film evaporator technology is well developed and commercially available. Various types of evaporators are readily available for use to concentrate liquid waste streams. However, tests will be required to determine the characteristics of the input stream so as to select the correct type of evaporator, and pilot plant tests will be required to determine design parameters and size the equipment.

3.3.2 Reliability and Maintenance Requirements

Because thin-film evaporators are rotating machinery, they are precision machines and preventive and corrective maintenance are important considerations. Bearings and mechanical seals must be properly applied and maintained.

At the drive end of the rotor, a double mechanical seal is most often supplied. A coaxial design like the Crane 151 seal, which is more durable and accommodates more vibration, has a typical life expectancy of about four years. Because of torque and some axial loading by the multiple belt drive, a self-aligning roller bearing is recommended; it also has a life of about four years. The bearing and seal can be inspected and serviced without removing the top cover of the rotor (Ref. 2).

Reasons for premature failure include failure of the double mechanical seal and the self-aligning roller bearing. The double mechanical seal can fail as a result of the loss of cooling fluid, the presence of solids or abrasives in the seal coolant, chemical attack on elastomeric O-rings, or abnormal vibration. The self-aligning roller bearing can fail as a result of inadequate lubrication or mixing of lubricant types; sporadic lubrication, which can permit water or other fluids into the bearing; or abnormal vibration (Ref. 2).

The internal bearing most commonly used at the discharge end of vertical machines is a non-load bearing design. The full weight of the rotor is supported at the top, and the function of the lower bearing is to center the rotor in a carbon cup bushing. Typical life of the bushing is two years. Premature bearing failure may be caused by loss of lubricant, poor lubricating properties of the lubricant, or process upsets with liquid backing up into the rotor area.

Original equipment rotors typically last from 10 to 30 years with little or no maintenance (Ref. 2).

3.3.3 Secondary Waste Streams

A thin-film evaporator has three streams which exit the system—the distillate which was evaporated and then condensed back to the liquid phase, the concentrates stream which was not evaporated, and the noncondensable gases that are vented from the condenser.

In the case of volatile organics removal from hazardous waste, the distillate will contain the organics that have been removed from the waste. Depending on water content and miscibility, it may be possible to separate the organics and water by decanting. In some cases, it may be desirable to pass the distillate through activated carbon to remove the organics by adsorption.

The exhaust vent of the condenser contains noncondensable gases (primarily air) and, potentially, a small amount of organic vapors. This exhaust can be further processed by passing it through activated carbon to remove the organics by adsorption.

3.3.4 Separation Efficiency

Combinations of evaporator and entrainment separators provide a separation efficiency between 80% and 99+% depending on equipment used and vapor velocity.

3.3.5 Safety and Health

Safety and health issues may arise from the following: spills or leaks of flammable or hazardous fluids or gases, uncontrolled reactions, process upsets, operating errors, mechanical equipment failure, improper equipment venting or pressure relief, and poor housekeeping. The ASME code requires all equipment to be protected by pressure relief devices to prevent the pressure from rising above the maximum allowable working pressure. However, venting must be into an enclosure to prevent exposure of personnel to potentially hazardous vapors or gases.

The equipment may require cleaning, which may involve manual operations in a hazardous environment, depending on the nature of the equipment and liquid and solid constituents.

3.3.6 Operational Complexity

Thin-film evaporation technology can range from simple to complex depending on the type of equipment selected and the controls required. The equipment is large and requires ancillary equipment in the form of condensers, pumps, valves and actuators, and cooling water for the condenser and seals.

3.3.7 Environmental Impact

Thin-film evaporation produces a condensate, bottoms stream, and potentially a noncondensable offgas, all or one of which may require further processing or disposal.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Evaporation is an expensive technology, both in terms of capital cost and operating costs. Thin-film evaporators are from 20 to 30 times more expensive than conventional evaporators (Ref. 1).

1984 budget prices for four standard thin-film evaporators with 316L stainless-steel wetted parts are listed in Table M-2.1.

TABLE M-2.1. BUDGET PRICES: THIN-FILM EVAPORATORS

Heating Surface Area m ² (ft ²)	Budget Price (1984)
0.1 (1)	\$16,000
1.0 (11)	45,000
5.0 (54)	120,000
15.0 (160)	210,000

From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

Table M-2.2 compares the cost of the evaporator alone to the installed-system cost for two cases. In the case designated *simple*, the heating medium is assumed to be steam, and the system is controlled manually. In the case designated *sophisticated*, the heating medium is a recirculating thermal fluid and the system is completely automated. The cost of the heat generator (steam boiler) is not included.

Operating and maintenance costs (1984 prices) are provided in terms of unit costs in Reference 2 as \$0.0075/liter of waste treated, or \$0.37/liter of volatile organic compounds (VOCs) removed.

3.5 TECHNOLOGY COMPARISON

A major advantage is that volatile organic compounds can be removed from viscous liquids, and viscous liquids can be reduced in volume. A concentrate can be produced with much higher solids content than conventional evaporators with minimal fouling, if any. As with conventional evaporation, an advantage is reduction in volume of waste requiring treatment,

5 of 5

thus lowering treatment costs. Also, thin-film evaporation is a well-known, mature technology, available from a large number of vendors and applicable to a variety of conditions (Ref. 1).

TABLE M-2.2. COST DISTRIBUTION OF THIN-FILM EVAPORATOR SYSTEMS

	Simple	Sophisticated
Evaporator	100	100
Components as % of evaporator		
Main auxiliaries (condenser, pumps, vacuum system, controls)	30	150
Piping, fittings (materials only)	10	20
Structural frame	5	5
Installation (foundation, erection, piping, wiring, insulation)	100	100
Total installed cost	245	375
Evaporator as % of installed cost	41	27

Source: Ref. 2
Cost in \$ thousands

(From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Co., New York, NY. Reproduced with permission from McGraw-Hill)

Disadvantages include the need to leave a fraction of the organics in some sludges to maintain fluidity. The cost of thin-film evaporators is significantly higher than conventional evaporators. As with conventional evaporators, evaporation concentrates hazardous constituents in a residual liquid requiring further treatment (Ref. 1).

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

As with conventional evaporators, properties of the liquid to be evaporated are critical in the final selection of an appropriate evaporation system. These properties include heat capacity, heat of vaporization, density, thermal conductivity, boiling-point rise, viscosity, and heat-transfer coefficient. Other considerations are the potential for corrosion, foaming, entraining, salting, and scaling. Some of these concerns can be largely eliminated by use of proper construction material and/or proper design choice. The appropriate design is specific to the liquid to be treated and must be determined through the use of pilot units.

4.2 TESTING REQUIREMENTS

Tests are conducted to determine capacity, heat transfer rates, steam economy, product losses, and cleaning cycles. Performance tests may also be required to establish that a new evaporator system has met performance guaranteed by the supplier. Tests may also be required to determine evaporator capacity under different operating conditions.

Evaporator testing can be costly, especially if the data obtained are not sufficient to meet the test objectives. Adequate personnel must be available to gather all necessary data over a relatively short period.

Parameters that cannot always be precisely determined make it nearly impossible to define all the problems during the design stage. These parameters include: composition changes, fouling, validity of heat transfer data, and changes in utilities. It may be necessary to evaluate the performance of an evaporator at other than design operating conditions.

5.0 VENDOR LIST

Blaw-Knox Company (Buflovak Division) Buffalo, NY	716-895-2100 Dryers & Evaporators
Cherry Burrell (Chemetron Division) Louisville, KY	502-491-4310
Luwa Corporation Charlotte, NC	704-394-8341
Kontro Company, Inc. Orange, MA	508-544-2536
Pfautler Company, Inc. Rochester, NY	716-235-1000
Artisan Industries, Inc. Waltham, MA	617-893-6800

6.0 REFERENCES

1. Minton, P.E. *Handbook of Evaporation Technology*. Noyes Publications: Park Ridge, NJ: 1986.

2. Freeman, H.M., ed. *Standard Handbook of Hazardous Waste Treatment and Disposal*. McGraw Hill Book Co.: New York, 1989.
3. Schweitzer, P.A., ed. *Handbook of Separation Techniques for Chemical Engineers*. McGraw Hill Book Co.: New York, 1988.
4. Tang, Y.S. and J.H. Saling. *Radioactive Waste Management*. Hemisphere Publishing Corp.: New York, 1990.

APPENDIX M-3 DRYERS

1.0 DESIGNATION OF THE TECHNOLOGY

This appendix will discuss dryer technology including direct, indirect, and microwave dryers.

2.0 NEED FOR THE TECHNOLOGY

Dryers are used to dry wet solids and sludges from internal and external sources. A low-temperature vacuum dryer (process #355) will be required for drying heat-sensitive materials such as nitrates which are subsequently sent to final forms processing. A standard dryer (process #350) will be used to dry and pulverize most of the wet solids which are then sent to homogeneous dry solids processing.

Pumpable solids may be dewatered first by filtration, filter pressing, or centrifugation. The resulting wet solids will then be dried.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Dryers can be classified as indirect and direct. Indirect dryers use a hot surface to heat the solids by conduction or radiation using little or no hot gas, such as air, to drive the drying process. The basic operation is to conduct heat into the particles by the hot metal walls of the containing vessel and agitator. The particles that are heated in turn heat others. The primary driving force is a temperature difference and, since little or no gas is present, the solid and its liquid are heated above the liquid's boiling point. Evaporation causes some degree of expanding, contracting, and cracking of the solids, in addition to the expansion of liquid to vapor. The high temperatures required also cause thermal expansion of the dryer structure so that indirect dryers are usually massive steel structures. To avoid heat damage to the solid, and to sweep moisture out of the dryer, some air or vacuum operation may be necessary thereby increasing the complexity of the system. Drying costs are generally higher due to higher heating costs caused by restrictions on temperature, and higher labor and maintenance costs. When either moisture recovery or maximum cleanliness is required, then indirect drying should be used (Ref. 1).

Direct dryers heat the solids by contacting them directly with a hot gas (usually air). When a gas is present, the solid and its entrained liquid are heated to a temperature below the

liquid's boiling point. The high vapor pressure of the liquid drives vapor into the dry gas which has a lower vapor pressure. Thus, liquid evaporates at a low pressure and temperature, even if the air is quite hot. This keeps the solids relatively cool as long as they retain some moisture. The need for large amounts of air flow requires more complex systems and a means for collecting fines from the exhaust air.

The method of heating determines how the drying solids will be agitated, transported, and collected. The split between heating methods is not sharp, however, because most indirect dryers use hot air to sweep out the vapor, and some direct dryers also use indirect heating. Another important distinction is the feed material's physical state. Liquids vary from thin solutions to thixotropic pastes, and solids vary from nearly dry granules to sticky sludges. Spray and drum dryers can be fed only liquids. All other common dryers accept wet solids, although certain liquids can be pumped into some of them, usually through a spray nozzle.

Drying is usually preceded by pretreatment operations to reduce the moisture content of the input stream, thereby decreasing the cost of drying, or to modify the consistency of the input stream for improved drying. Some liquids (usually solutions) can be concentrated by evaporation with the wet sludge in the bottom of the evaporator sent to a dryer. Insolubles can be converted to wet solids by decanting, filtering and dewatering, or centrifuging.

Determining which type of dryer, if any, is most suitable for a specific material requires testing. Without tests there is no way to determine with confidence whether or not even closely related feeds will dry in the same manner and at the same conditions. Test results are useful only for a specific application and as a guide for other tests. Tests are run to determine the optimum conditions including heating temperatures, exposure time, the flow rate of solids, and their concentration in the feed. To obtain the desired result, the dryer may have to be altered (different plows or mixing devices), the feed altered, or an altogether different dryer tested.

Ordinarily dryers cannot accept feeds unless they flow freely. A wet solid needs the consistency, dryness, and particle size and shape to allow it to flow properly; otherwise it must be mixed with enough dry material to allow proper flow. Other factors that affect drying include: (1) stickiness of the material to itself and to dryer surfaces as it enters the dryer, (2) some materials pass through the sticky or plastic phase as they dry, (3) particle size, (4) the case hardening of some materials, which seal in the moisture and fuse particles into a block, and (5) impurities, even in trace amounts, which can affect the dryer's performance (Ref. 1).

3.1.1 Indirect Dryers

Indirect dryers have a relatively simple flow pattern with the feed usually into one end of a drum, and the dry material exiting the other end. The dryer is usually sloped to aid transport of the solids, and heat is provided to the jacket and agitator by steam or heat transfer oil. The

jacket may be zoned for different temperatures, including cooling in the last zone if necessary. If a vacuum (or air sweep) is required, the air and vapor exhausting from the dryer must pass through a collector to remove fines from the air stream and to protect the vacuum pump. The limited amount of air and vapor are then passed through a condenser and then to thermal treatment to destroy vaporized organics that may be present.

Indirect dryers use little or no air, and they heat the solids through a metal wall rather than by direct contact with hot air. Compared to direct dryers, they have lower maximum drying temperatures and lower maximum throughput; they also agitate the solids mechanically and have a heavier construction. There is often an upper limit to the temperature set by the rigid construction. Thus, temperatures above those reached by steam heating are generally not practical. The most common indirect dryers have either horizontal housings that are rotating cylinders or stationary housings with one or more rotating agitators.

Most products benefit from intensive mixing and mechanical agitation which continuously expose cooler particles to the heating surface. As a secondary function, proper selection of agitator design can provide blending of the mass. Thus, most of the common types of indirect dryers heat and agitate a bed of material inside the heated housing. A major difference between many drum dryers is the configuration of the agitators and plows used to mix the drying solids. Two major exceptions are the drum dryer in which a layer of liquid feed is laid on the outside of a heated cylinder, and the high-speed paddle dryer which throws a layer of feed particles on the inside of a heated cylinder. The variety of agitation components for horizontal equipment is broad, as shown in Table M-3.1.

TABLE M-3.1. AGITATORS USED WITH HORIZONTAL-SHELL DRYER CONFIGURATIONS (REF. 2)

Type Agitator	Fig. No.	Extended Heat Transfer Surface	Ratio of Heat-Transfer Surface to Process Volume	Heat Transfer Rates	Folding Action of Agitator
Hollow interrupted flight	M-3.1	Yes	Good	Excellent	Excellent
Hollow, disk	M-3.2	Yes	Excellent	Good	Good
Hollow, screw	M-3.3	Yes	Excellent	Good	Good
High-speed paddle	M-3.4	No*	Poor	Good	Poor
Ribbon	M-3.5	No*	Poor	Poor	Poor

*Shaft may be hollow and used for heat transfer

93-0024-TR-Q-13

The main problem for dryers comes when feeding sticky or very wet solids. When these materials first contact the heating surface, they may stick or cause other problems. They may be preconditioned by backmixing with dry product in a mixer outside the dryer or inside the dryer, depending on the agitator design and the nature of the feed. A wet feed requires a high evaporation rate so that it is best dried at a high heat transfer rate with relatively short exposure time. Conversely, if bound moisture is to be removed, a long exposure time is needed. To remove large amounts of both free and bound moisture, two drying stages are often the best solution (Ref. 1).

3.1.1.1 Disc Dryers

These dryers have hollow, full-circle discs, closely spaced on one or more shafts as shown in Figure M-3.1 and M-3.2. This arrangement provides both agitation and a high heat transfer surface area per unit volume. Feed flows either parallel to one or more shafts, or perpendicular to several shafts. The housing is also heated and may be zoned for improved temperature control. Feeds should be free flowing; if they stick to hot surfaces they must be backmixed with dry product. Most applications need a relatively long exposure time, from 10 minutes to 1 hour, but exposure time can be varied up to several hours for diffusion-dominated drying. The heating surface per unit volume is high, as are the heat transfer rates, but the overall heat transfer rate is about half that of a high-speed paddle dryer (Ref. 1).

3.1.1.2 Screw Conveyor Dryers

This dryer has helical, hollow screws and a jacketed trough, both of which can be heated (Figure M-3.3). The material is pushed along gently with little intermixing—close to ideal plug flow. Heat transfer rates are low for plug flow operation.

3.1.1.3 Paddle Dryers - High Speed

The high-speed paddle dryer is best suited to applications dominated by heat transfer rather than diffusion. It functions as either an indirect or a direct dryer, and usually as a combination of both. The jacketed shell is heated and can be zoned. The unheated agitator paddles (Figure M-3.4) throw a thin layer of particles around the inner surface of the shell giving a high heat transfer rate. The action of the paddles breaks up many materials, which improves drying but adds fines to the product and air stream. A high heat transfer rate makes the unit suitable for a range of feed consistencies including wet and sticky pastes, and some slurries, which need a flow of air to carry off the vapor. A wide range of feed consistencies can be handled with proper adjustments to the agitator's clearance, angle settings, and speed. Exposure times typically range from a few seconds to less than 20 minutes. For low final

Figure M-3.1. Hollow Interrupted-Flight Agitator

(Reprinted by special permission from Chemical Engineering (March 19, 1973),
Copyright© (1979), by McGraw-Hill, Inc., New York, NY 10020.)

Figure M-3.2. Hollow Disk Agitator Gives Good Heat Transfer

(Reprinted by special permission from Chemical Engineering (March 19, 1973),
Copyright© (1979), by McGraw-Hill, Inc., New York, NY 10020.)

Figure M-3.3. Hollow Screw Design of Agitator

(Reprinted by special permission from Chemical Engineering (March 19, 1973),
Copyright© (1979), by McGraw-Hill, Inc., New York, NY 10020.)

Figure M-3.4. High-Speed Paddle Dryer

(From Cook, E.M. and H.D. DuMont. Process Drying Practices (1991).
McGraw-Hill Book Company, New York, NY. Reproduced with permission of McGraw-Hill.)

moisture content, a secondary dryer with a long exposure time suitable for diffusion drying may be required (Ref. 1).

3.1.1.4 Paddle Dryers - Low Speed

The low-speed paddle dryer is intended for materials needing long exposure time (from 30 to 90 minutes) with drying dominated by diffusion. It typically functions as a secondary dryer. T-bar shaped, unheated agitators are mounted on a central shaft and rotate slowly with the horizontal bar of the "T" close to the jacketed shell to remove stuck solids.

3.1.1.5 Disc Dryer with Segmented Discs

These dryers, also called paddle dryers, use wedge-shaped, hollow segmented discs that are curved around a center shaft as shown in Figure M-3.6. One design uses from two to four shafts rotating oppositely. The discs are intermeshed to aid in mixing and self cleaning. The hollow shaft and the dryer jacket are heated. The wedge shape and intermeshing action scrape hard against the particles which helps to keep the discs clean, increases heat transfer rate, and promotes local mixing. Some very wet and sticky feeds can be handled because of the agitator action, but difficult feeds require backmixing before drying. Average exposure is 10 minutes to 2 hours (Ref. 1).

3.1.1.6 Rotary Dryers

Although the cost is relatively high, the different designs of this type of dryer have important niches—in handling material with little dust loss, for operating as a closed system, and for operating under vacuum. The dryer consists of a cylindrical shell and from one to four rows of tubes, concentric about the shell centerline, that rotate as a unit. Generally steam is used to heat the tubes inside the shell. This type of dryer generally uses no air, or just an air sweep, and handles materials that require both heat transfer and diffusion dominated drying. The feed must be free-flowing to avoid fouling of the tubes which cut through the material to provide some cascading, mixing, and breaking of lumps. Sometimes external, hinged knockers are used that fall against the shell as it rotates to jar loose solids stuck inside. Typical exposure times are 20 minutes to 2 hours (Ref. 1).

3.1.1.7 Drum Dryers

Drum dryers may have single or double drums. Feeds must be sufficiently liquid to coat the rotating drum from a trough, or to be applied to its surface by rollers. Product is scraped off by a blade and vapors are exhausted by a fan through a hood. Temperature and exposure time

Figure M-3.5. Ribbon Agitator Gives Excellent Folding Action

(Reprinted by special permission from Chemical Engineering (March 19, 1973), Copyright© (1979), by McGraw-Hill, Inc., New York, NY 10020.)

Figure M-3.6. Segmented Disc Paddle Dryer Shafts

(From Cook, E.M. and H.D. DuMont. Process Drying Practices (1991). McGraw-Hill Book Company, New York, NY. Reproduced with permission of McGraw-Hill.)

(normally no more than 20 seconds) are regulated independently. Film thickness and solids content can also be controlled. Practical temperatures are relatively low, and massive, rigid construction is required to maintain proper alignment and reduce cost of maintenance (Ref. 1).

The double drum dryer, shown in Figure M-3.7, is very versatile and can be used to dry materials of widely varying densities and viscosities including dilute solutions, heavy liquids, or pasty materials (Refs. 3 and 4). This type of dryer, with a top feed, is also effective for fairly heavy sludges, although splash-fed twin drum drying (Figure M-3.8) may be better for some applications. Drum dryers can be enclosed in a vacuum chamber or placed under a hood to collect vapor. They may use a pendulum or perforated tube for top feed, or dip pan, spray, or splash for bottom feed (Ref. 4).

3.1.2 Vacuum Drying

The thermal sensitivity of the material fixes the maximum allowable temperature which varies inversely with the time of retention. Thus, whenever the time for drying is long, operation under vacuum is needed to bring the evaporation temperature down to safe levels. Vacuum drying is also used to reduce dusting and to improve drying rates when the material must be dried to extremely low moisture content. Vacuum dryers are usually of the double-cone or rotary type (Ref. 5).

3.1.2.1 Double-Cone Dryers

The double-cone rotary dryer shown in Figure M-3.9 is used extensively for batch operations. It is a double cone within a double cone (double-walled construction is standard). The heat transfer medium is introduced between the walls, and the vacuum connection is through a rotary mechanical seal (or packing gland) mounted in the trunnion on one side of the dryer. Smooth interior surfaces promote complete discharge of the solids from the bottom and facilitate cleaning. Mixing of the solids is achieved by rotating the cones, producing a gentle rolling action. The principal disadvantage of the double-cone design involves materials that tend to stick to the dryer walls, thereby fouling the walls and decreasing the heat transfer rate. Another problem arises when certain materials form lumps, which tend to grow larger and thus will hinder heat transfer and drying (Ref. 5).

3.1.2.2 Rotary Dryer

The rotary dryer is used to handle paste and slurries that tend to stick to dryer walls. The dryer consists of a stationary cylindrical shell, agitator blades mounted on a central shaft, and associated agitator drives. The rotary direct dryers described in Section 3.1.1 can be designed for vacuum operation usually down to 29 inches Hg. The dryer is charged through a

Figure M-3.7. Double Drum Atmospheric

(Courtesy of Buflovak Div., Blaw Knox Food and Chemical Equipment Company.)

Figure M-3.8. Twin Drum Atmospheric

(Courtesy of Buflovak Div., Blaw Knox Food and Chemical Equipment Company.)

Figure M-3.9. Double-Cone Vacuum Dryer

(From Ryan, J.L. and D.L. Roper. *Process Vacuum System Design and Operation* (1986). McGraw-Hill Book Company, New York, NY. Reproduced with permission from McGraw-Hill.)

port at the top and emptied through one or more discharge ports at the bottom. The agitator is usually a single or double continuous spiral (Fig. M-3.5). Product buildup is eliminated by using spring-loaded scrapers, mounted in the agitator blades, to scrape the dryer walls. The heating medium is circulated through the jacket surrounding the shell, and in larger units, through the hollow central shaft. The rotary dryer is often a better choice, based on economics, than the double-cone dryer for applications involving free-flowing powders (scraper blades not required). The working volume of the rotary dryer is generally 50% of the total volume and may be as high as 85%. The entire operation from feed to discharge can be automated. Dust filters on top of the dryer are standard, and a condenser is installed downstream to protect the vacuum pumping system. The rotary dryer is difficult to seal and air leakage around the agitator shaft seal and air locks can shut the system down.

3.1.3 Direct Dryers

For most direct dryers, heated air flow is in the once-through, or open, mode. This air is heated and forced through the vessel. The dried product is separated from it in one or more collectors and the air and vapor are discharged to a condenser and then to thermal treatment to incinerate any noncondensable organics. The need for this excess amount of air to be handled by the thermal treatment system may cause design problems with this system and overload the offgas system.

Considering only the drying operation, direct heating, if possible, is generally preferred for several reasons. The material is heated primarily by convection from the surrounding air, the temperature of which can be closely controlled so the material is never warmed above a specified temperature. In general, direct dryers are cheaper than those indirectly heated due to the absence of jackets or tubes to hold the heating media. Except for rotary dryers, the chamber construction can be out of sheet metal which is lower in cost and permits more trouble-free thermal expansion.

Direct drying also has disadvantages. The exhaust air is still warm and the overall thermal efficiency is low; however, this can be alleviated by recirculating a fraction of the humid outlet air or recovering some of the heat content by the incoming air. Recovery of the moisture and fine particulates in the vented gases, and treating the vented gases in the offgas system is difficult and costly. However, particulate loading can be decreased by lowering the air velocity, or collecting particles in a cyclone or bag filter. Moisture can be recovered in a condenser, and noncondensable organics recovered by adsorption. These ancillary components may also be required with indirect dryers, but would be larger and more costly for direct dryers due to the larger volumes of air and higher particulate loading.

Direct dryers all have one common feature: air supplies the heat and carries off the evaporated moisture. But they differ greatly in how the solids move. The particles may be at rest on tray dryers, ride on conveyor dryers, stirred and tumbled in rotaries, fluidized in beds, thrown up in flash dryers, or atomized into a mist in spray dryers. The action of the air varies from gentle motion over a static bed to making violent contact with every particle.

For a given dryer and airflow, evaporation rate and air temperature difference are the major influences on the production rate. The best drying efficiency comes at the highest air temperature at the inlet and the lowest air temperature at the outlet. The maximum at the inlet is limited by the strength-temperature properties of the metals and the heat sensitivity of the solids. Also, if a high-temperature operation is to be free of fires and scorching, product buildup must be avoided. At the low-temperature end the minimum is set by the moisture specification for the solids and the potential for moisture condensation on cool surfaces (Ref. 1).

3.1.3.1 Conveyor Dryers

Well-suited for drying materials of mostly large sizes, but when designed properly a conveyor dryer can also handle particulates. For these it uses a continuous metal screen or belt on which the materials ride and which is usually perforated so heated air can pass through the bed of particulates. Fine particles require a nonperforated belt and air impinges on or flows across the material. The enclosure is a rectangular, insulated housing. Feeds are usually granular. Heavy pastes can be extruded onto the belt but must be dry enough to avoid reagglomeration

into a mass. Feed must cover perforated belts evenly to avoid air bypass around the edges and nonuniform drying.

3.1.3.2 Flash Dryers

Flash drying vessels are vertical ducts in which wet particles are entrained in hot air flowing upward as shown in Figure M-3.10. Solids loading is limited by the need to convey wet feed, and air velocity must be kept above a minimum. This limits exposure time to a few seconds so only unbound moisture can be removed. In most cases the feed must be granular. To assure uniform drying, feed must be deagglomerated or milled before or after entering the drying duct. A classifier may be installed to remove the fines (which dry faster) and to recycle the heavier particles that move more slowly up the duct. For special applications some flash dryers are designed to give longer exposure time with expanded sections of the duct or spiral paths for the particles (Ref. 1).

Figure M-3.10. Direct Drying System with Backmixing, Milling, Classifying, Product Recycle, and Heat Recovery

(From Cook, E.M. and H.D. DuMont. Process Drying Practices (1991). McGraw-Hill Book Company, New York, NY. Reproduced with permission of McGraw-Hill.)

3.1.3.3 Fluid-Bed Dryers

Fluid beds have a turbulent mixing action and a wide range of designs, temperatures, and residence times. Figure M-3.11 shows a typical configuration. In operation, air enters a plenum below a screen that is perforated to retain solids and yet allows air to pass through it. A pressure drop through the screen distributes hot air evenly to the bed to heat the particles. To

reduce the air velocity over the fluidized bed, the upper portion of the chamber may be enlarged so that only fines are entrained in the exhaust. The bed area and depth give the necessary residence time as determined by testing. Some sticky feeds can be handled because the active bed is a true backmixer; however, deeper beds and longer residence times are required. Not all materials can be fluidized. Particles should be in the range of 100 microns to 10 mm, must not be excessively sticky, and must resist lumping and abrasion. The material must not be too dense or cause uneven air distribution (Ref. 1).

Figure M-3.11. Fluid-Bed Drying Chambers

(From Cook, E.M. and H.D. DuMont. *Process Drying Practices* (1991). McGraw-Hill Book Company, New York, NY. Reproduced with permission of McGraw-Hill.)

Another type of fluidizing dryer is the swirl fluidizer designed to dry filter cakes, pastes, or thick viscous liquids (Ref. 6). The dryer consists of a cylindrical drying chamber with an air disperser, a rotating disintegrator, and a drying section. The hot air enters the air disperser tangentially and is directed into the drying section as an intense, controlled swirling air flow. The rotating disintegrator is mounted at the base of the drying section. The feed is introduced into the dryer by a screw feeder or pump. Under the action of the swirling air and disintegrator, the feed is broken up into small particles which are dried and pass out of the dryer with the

exhaust air for collection in a filter. For this type of dryer to be applicable, the feed must break up into a fluidizable powder (Ref. 3).

3.1.3.4 Rotary Dryers

Direct rotary dryers, like indirect rotaries, have a sloped, rotating cylinder as shown in Figure M-3.12. They have the lowest operating cost for many materials, particularly those dried in bulk and at high temperature. Wide particle size distributions can be handled if the fines are dried quickly and airborne out of the dryer while heavier particles stay in the dryer longer. Drying takes place as the solids cascade off lifting flights on the side of the rotating drum and hot air passes through the particles. Even some liquids and sludges can be sprayed into a bed of dry material and dried successfully with the right dryer and feeder design. External knockers or internal chains are needed to unstick some materials from the shell, but the noise makes them unacceptable in some locations.

Figure M-3.12. A Through-Circulated Rotary Dryer

3.1.3.5 Spray Dryers

Spray drying is limited to liquid feed so that energy and airflow requirements are high to accommodate the high evaporation load. However, some spray dryers can handle material with up to 80% solids content (Ref. 3). Any liquids that can be pumped and sprayed into fine drops may be considered for spray drying as long as they are not too viscous. Feeds are atomized by

using nozzles or spinning discs called atomizer wheels. Average droplet size in typical drying chambers range from 10 to 150 microns (Ref. 1). Chambers come in various sizes and designs with cocurrent and countercurrent air/droplet flow depending on the required residence time and particle size. Typical spray drying configurations are shown in Figure M-3.13.

Figure M-3.13. Flow Arrangements in Spray-Drying

The Leafflash spray dryer is a French technology for rapid drying of wet radioactive waste such as spent ion exchange resins (beads or powder), sludges, and evaporator concentrates (Ref. 7). It is based on the "Leafflash" process developed by Rhone-Poulenc Research to

dry certain chemical and food products and is licensed to Technicatome. The process uses hot gas injected at a high speed at the edge of a "well vortex" created by a diaphragm burner/injector. The waste to be dried is sucked into the partial vacuum in the center of the vortex and sprayed into the hot gas by simple entrainment, resulting in instantaneous drying.

In the Leafflash process, hot gas is produced in a cold wall, hot gas generator, which also uses the leafflash principle of very low thermal inertia. The gas is injected into the upper part of the dryer, where it crosses the well vortex at high speed, carrying along with it the waste products that are being dropped by gravity through the top of the dryer into the vortex. The gas is air-cooled at the outlet of the dryer, and conveys the dry product to a cyclone where the dry product is removed by the grate at the bottom of the cyclone. The gas exiting the top of the cyclone passes through a venturi scrubber and a re-heater before final filtration and release to the atmosphere. Advantages to this spray drying process include the following: no failure-prone mechanical systems are used except for the feed systems and dry product removal; very low thermal inertia allows discontinuous operations to be conducted; and temperatures can be controlled to prevent damage to heat-sensitive products (low heat) or to calcine others (high heat).

3.1.3.6 Tray Dryers

Traditional tray dryers operate in a batch mode and, depending on size and design, are referred to as tray, truck, or tunnel dryers. The equipment cost is the lowest of all the dryers, but with manual loading and unloading the operating cost is the highest. The continuous rotating tray dryer, shown in Figure M-3.14, overcomes the static tray dryers most serious disadvantages—high labor and space needs, uneven heating, and long exposure times. The trays are circular, and the top tray receives the material from a conventional feeder. After one revolution the material is wiped off and drops to the next lower tray. This process continues, and on each tray the material is leveled and raked by stationary arms so the particles are dried more uniformly. Hot air from centrally mounted blowers heats the top of the material and the trays. The resulting dried product is not always particulates, but may be small lumps or cakes that must be ground and screened.

3.1.4 Microwave Drying

Microwaves generate heat by molecular-dipole oscillations. At microwave frequencies (3–300,000 MHz), the amount of heating done decreases exponentially with depth from the surface, and the depth of penetration is inversely proportional to the frequency (Ref. 8). The advantages of microwave heating (also termed dielectric heating) stem from the fact that the heat is generated directly within the work material allowing for precise control of the amount of

heat and where it is generated. Because of the inherently shorter thermal time constants involved, it tends to be much faster than processes that require transfer from a heated medium outside the material to be dried.

Figure M-3.14. Turbo-tray Dryer

Microwave, or dielectric, heating has selective applications in drying sheet materials or thin layers of particulates. For effective drying of sludges, a thin layer would be laid down on a flat conveyor belt and transported through the electrode region of the radio frequency (RF) generator. A low velocity air stream would be required to exhaust the vapor from the drying chamber. Factors that affect dielectric heating include material properties such as the dissipation factor and dielectric constant; characteristics of the RF generator including voltage, frequency, power, and time of application; and heat loss from the material being heated (Ref. 9).

Probably the most important factor in dielectric heating is the dissipation factor which is high in materials with polar molecules and quite low in materials with nonpolar molecules. Generally, dielectrics that lend themselves to dielectric heating have a dissipation factor of 0.01 or greater. The dissipation factor varies with frequency, temperature, humidity, and in some cases applied voltage. These variations can be explained by the transition time of the dipole moment of the molecule. When the period of the excitation voltage equals the transition time of the molecules, the dissipation factor is at its maximum. Also, the transition time is related to the viscosity of the material which is proportional to its temperature.

The dielectric constant also varies with frequency, temperature, humidity, and applied voltage. Although not as important as the dissipation factor in determining the heatability of a

material, it becomes very important when heating dielectrics composed of several different types of materials. Although increased voltage will increase the power loss and therefore the heat generated within a dielectric, a practical limit is reached when the dielectric undergoes voltage breakdown. The frequency used is determined by the application, and although any frequency could be used for dielectric heating, specific frequency bands established by the Federal Communications Commission are usually used. Finally, because heat is generated within the dielectric, heat flows from the material so that with thin materials there may be sufficient heat loss to prevent achievement of the required temperature increase. This may require insulating the material to be heated, or heating the surrounding ambient by conventional means (Ref. 9).

3.1.5 Ancillary Equipment

Systems must be tailored to suit the requirements for preparing the feed, conditioning the product, and treating the exhaust or extracting heat from it. Equipment generally required to complete a drying system includes the following: feeders, heaters, and product collectors.

3.1.5.1 Feeders

Leakage of air into an indirect dryer is minimized by the use of choke-type feed and discharge screw conveyors. These units run full and block off entry of air.

Spray and drum dryers accept only liquids, but viscosities can vary over a wide range. Most other dryers need somewhat granular feeds, although some pastes or slurries (when backmixed with enough dry product) can be brought to the right consistency. Most wet feeds must be kept from dropping directly onto a hot surface.

For wet solids several feeders are available with variable drives for control. A mixer-type feeder serves as both feeder and external backmixer. The agitation in some dryers gives a degree of backmixing without adding dry powder. Other types of feeders used for wet solids include screw conveyors, rotating tables, vibratory trays, and rotary air locks. Slurries that settle quickly may require special agitation before and during feeding (Ref. 1).

3.1.5.2 Heaters

Direct heaters heat air by mixing it with combustion gases, while indirect heaters heat the air through the walls of a heat exchanger. The cost of direct-fired heating is less, and direct-fired heating helps preserve those products that require a low oxygen content in the drying air. Indirect heaters have low thermal efficiencies which can be improved by heat recovery from exhaust gases.

Most indirect dryers are heated with steam or thermal fluids which are, in turn, indirectly heated by gas or oil burners, or heated by direct contact with electrical heating elements. Thus, an external heating system with associated equipment will be required for indirect dryers.

3.1.5.3 Product Collectors

There are four basic types of product collectors used to separate powder from the air stream—the drying vessel itself, cyclones, bag filters, and wet scrubbers. The product is normally discharged directly from the drying vessel by gravity. However, fines are entrained in the air stream in direct dryers, and in the sweep air in indirect dryers. The amount entrained in indirect dryer air depends on the particle size and air velocity which is typically very low.

Specialized collectors may be required for direct dryers to remove large quantities of fines from the air/vapor stream to minimize particulate loading on the thermal treatment system. If a scrubber is used the wet fines—in the form of a sludge—must be dried again.

3.1.6 Drying Sludges and Slimes

Major problems that such materials cause are fouling of the dryer heat transfer surfaces, preventing or restricting the escape of vapor from the particles due to the formation of agglomerates or case hardening, and formation of a plastic stage during which the material turns with the agitator without moving forward (Ref. 1).

Plate and frame filter presses, belt filter presses, rotary vacuum filters, and centrifuges are used to dewater sludges produced from wastewater processing. However, they cannot remove enough water and the sludge may still retain 70% to 90% liquid. Many sludges are tacky or sticky. This stickiness is often limited to a specific moisture range which may occur briefly during the drying process. Dry product can be backmixed into the feed if consistency is a severe problem thereby raising the solids content and bypassing the problem.

Conventional disc dryers are difficult to operate continuously because their surfaces foul and the solids do not transfer properly in the dryer. On the other hand, dual shaft units with segmented discs that scrub, rather than smear, the solids against the surfaces keep them relatively clean. The intermeshing of the discs and counter-rotation of discs on companion shafts produces a kneading action that, together with drying, breaks up lumps.

Slime, such as that produced at copper anodes, also goes through a sticky phase that continues well into the drying cycle. Slime also has a tendency to ball up and for the balls to case harden. To help overcome both problems a pug mill can be installed for backmixing, kneading the dry powder into the slime and cutting and dicing the resulting mass. Use of segmented disc paddle dryers also reduces the sticking effect (Ref. 1).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

Input streams may vary from flowing liquid to thixotropic or highly viscous fluid to wet or nearly dry solid particles. Stream characteristics depend on preprocessing and the characteristics and contents of the input waste stream.

3.3 DEMONSTRATED PERFORMANCE:

Drying has long been used as a unit operation in the manufacture of various products in the chemical process industries. In addition, it is currently being used in the treatment of hazardous wastes such as radioactive liquids and sludges, metal-plating wastes, and other organic and inorganic wastes. In industries that generate large volumes of aqueous waste with dilute hazardous constituents, drying is used to drive off the volatile component to reduce the volume and concentrate the waste into a dry solid for additional treatment or disposal.

3.3.1 Technology Status

Drying technology is well developed and commercially available. Various types of dryers are readily available for use to dry concentrated, mixed aqueous and organic liquid waste streams. However, tests will be required to determine the characteristics of the input stream so as to select the correct type of dryer, and pilot plant tests will be required to determine design parameters and size the equipment.

3.3.2 Reliability and Maintenance Requirements

Drying technology is fairly simple and reliable requiring periodic maintenance for cleaning and repair. Liquid characteristics described previously, the type of dryer, and materials of construction will determine maintenance frequency and cleaning requirements. Corrosive service requires units that are easy to repair or clean. Removal of fouling and deposits by physical or mechanical means (such as hydroblasting, scraping, wire brushing, or sandblasting) may be necessary. For batch operations, scheduled maintenance should not have a major impact on operations. However, unscheduled maintenance will interrupt waste processing. In addition, problems may arise when manually cleaning or repairing dryer components due to the potential hazardous and radioactive nature of the deposits remaining in the dryer.

Because many dryers are rotating machinery or use rotating equipment such as air blowers or pumps, preventive and corrective maintenance are important considerations. Bearings and mechanical seals must be properly applied and maintained.

Reasons for premature failure include failure of the mechanical seal in rotating shaft dryers as a result of wear or powder entering the seal, or the loss of seal coolant if coolant is

used; the presence of solids or abrasives in the seal coolant; or abnormal vibration. The bearings can fail as a result of inadequate lubrication or mixing of lubricant types; sporadic lubrication, which can permit water or other fluids into the bearing; or abnormal vibration.

3.3.3 Secondary Waste Streams

Secondary waste streams consist of entrained particles and volatile organics in the dryer vapor stream. Particles are usually captured by a filter between the dryer and condenser; however, soluble organics may be retained in the condensate. Noncondensable gases from the condenser may also form a secondary waste stream. The major secondary waste stream is the dried solids product that is sent to thermal treatment or final forms.

3.3.4 Separation Efficiency

Drying efficiencies over 99% may be achievable depending on the nature of the solid particles, and the time—temperature relationship in the dryer.

3.3.5 Safety and Health

Safety and health issues may arise from the following: spills or leaks of flammable or hazardous fluids or gases, uncontrolled reactions, process upsets, operating errors, mechanical equipment failure, improper equipment venting or pressure relief, and poor housekeeping.

Most dryers, if not specially built to be airtight, leak to some extent, even when new. In addition, parts will wear, and become corroded or out of shape over time. These issues must be factored into the operational and safety procedures and maintenance schedule. The equipment may also require cleaning, which may involve manual operations in a hazardous environment, depending on the nature of the equipment and liquid and solid constituents.

3.3.6 Operational Complexity

Dryer technology can range from simple to complex depending on the type of equipment selected and the controls required. The equipment is large and requires ancillary equipment in the form of feeders, condensers, pumps, and valves and actuators.

3.3.7 Environmental Impact

Drying produces a condensate, dry solids, and potentially a noncondensable offgas, any of which may require further processing or disposal.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Drying costs are generally higher for indirect dryers due to limits on temperature restricting capacity, and higher heating costs. Labor expenses for operating are about the same, but are more per unit of output for indirect dryers. Maintenance costs are also higher due to the mechanical drives and rotating seals to be maintained and there is the need to keep close tolerances between parts. However, major costs associated with direct drying that offset its benefits include air handling and product collecting equipment and the additional offgas treatment equipment.

In general, there are advantages to first mechanically dewatering evaporator bottoms, sludges, and other wet solids thus reducing plant installation and operating costs of the final drying stage. Any water that can be removed mechanically means that less energy will be required in the drying stage. However, economic tradeoffs should be made between concentrating dissolved solids or suspended fines through mechanical means (i.e., filter presses, centrifuges, etc.), and the use of evaporators, or spray dryers for liquid waste. Evaporation generally requires less energy than spray drying, but for small waste streams, the capital cost per pound evaporated is higher than for spray drying (Ref. 3).

Although development costs are not required, there will be costs incurred for testing to determine the optimum type and size of dryer. Approximate costs of various types of dryers are provided in Table M-3.1 based on cost curves in Reference 10.

TABLE M-3.1. APPROXIMATE CAPITAL COSTS OF VARIOUS DRYERS (REF. 10)

<u>Dryer Type</u>	<u>Cost Per Unit Area (Volume)</u>
Spray dryer	\$800/ft ² cross-sectional area
Rotary dryer	\$50/ft ³ shell volume
Conveyor dryer	\$360/ft ² conveyor area
Fluidized bed	\$1500/ft ² bed cross-section
Flash dryer	\$14,000/ft ² column cross-section
Double-cone dryer	\$1250/ft ² cross-section
Drum dryer	\$220/ft ² drum surface area
Tray dryer	\$20/ft ² tray area

3.6 TECHNOLOGY COMPARISON

The primary advantage of drying is that it reduces the volume of waste requiring treatment to dry solids, thus lowering treatment costs. Drying is a well-known, mature

technology, available from a large number of vendors and applicable to a variety of conditions. Most vendors can provide complete systems including feeders, condensers, and dust collecting equipment.

The main disadvantage of drying is that it has relatively high operating costs. The equipment may require cleaning, which may involve manual operations in a hazardous environment, depending on the nature of the equipment and liquid and solid constituents. Drying concentrates hazardous constituents in residual solids requiring further treatment.

Drying is the only technology that can produce a dry solid from either an aqueous or nonaqueous waste stream. The technology comparison that needs to be made is between direct and indirect dryers, and between the dryer types within each group.

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Most process equipment can be designed based on calculations using general, empirical equations relating the design to material flow rates and properties. The lack of such relations for dryers means that virtually every application requires testing to answer these questions:

1. Is drying feasible?
2. Does the dried product have the desired properties?
3. Does the drying system run without buildup or other equipment problems?
4. What are the best operating conditions?

In practice, all dryers must be designed by making test runs of the material in question on a small-scale model of the type of dryer under consideration. However, heat transfer rates in small dryers run about 40%–60% of those in larger equipment; thus careful analysis of test data is required (Ref. 1). When a piece of test equipment is used to determine the heat transfer coefficient (U), certain conditions are fixed such as the amount of heat to be transferred, the heat transfer area of the unit, the agitator configuration, and often its speed. Experience indicates that in most instances the calculated U is erroneous and equipment improperly selected because of this (Ref. 2). Thus, the results of pilot test must be carefully evaluated.

Typical data needed from pilot test runs include the following (Ref. 2):

1. Change of condition, heat transfer rate, and composition data against time
 - Change in temperature of heat-transfer medium versus time
 - Change of temperature of process mass versus time
 - Change of composition of process mass versus time
 - Inlet and outlet operating pressures of heat-transfer medium and process mass versus time

- Input rates of heat-transfer medium and process mass
- Output rates of process mass
- 2. Properties of process mass
 - Particle size
 - Bulk density
 - Specific heat, heat of fusion, heat of vaporization
 - Vapor pressure
- 3. Heat-transfer area
- 4. Speed and power consumption
- 5. Visual observations
 - Stickiness
 - Mixing characteristics
 - Scaling (and other pertinent observations)

4.2 TESTING REQUIREMENTS

Testing requirements include use of surrogate material in the vendor's facility to determine equipment type, size, and method of agitation. Vendors typically will have dryers and other equipment available for testing for a nominal fee. However, no dryer manufacturer has the ideal—full range of direct and indirect dryers—so the best procedure is to investigate and run tests at several laboratories regardless of the cost and time impacts. The Mixed Waste Treatment Plant (MWTP) may have special needs such as separate facilities for greater safety or cleanliness; large test dryers to assure more accurate scaleup; test units set up where the feed originates for better security or control of toxicity. But the main goal of testing is to determine dryer suitability and to generate design data for scaleup to an operating system.

Pilot scale testing should initially be performed on surrogate material, but eventually actual material must be used to verify the selection of dryer type and to determine the final dryer design and scaleup factors. Monitoring will be required to determine offgas treatment and particle collection requirements.

5.0 VENDOR LIST

Many dryer manufacturers are listed in the Thomas Register, and most manufacture a limited variety of dryers, or only one type of dryer. Following are several selected manufacturers (selection is not based on experience or knowledge of the manufacturers capabilities) and the types of dryers manufactured.

Manufacturer**Product**

Krauss Maffei
Process Technology Division
7095 Industrial Road
Florence, KY 41042-6270
(606) 283-0200

Direct, indirect, continuous, and
batch type dryers or drying systems
including vacuum dryers.

Heyl & Patterson
Renneburg Division
P.O. Box 36
Pittsburgh, PA 15230
(412) 788-6900

Flash dryers, fluidized bed dryers,
rotary sludge dryer-extruder

Niro Atomizer
9165 Rumsey Rd.
Columbia, MD 21045
301-997-8700

Spray, fluidized bed, flash

ABB/ASEA Brown Boveri, Inc.
Stamford, CT
800-626-4999

Sludge dryers

Buflovak (a Division of
Blaw-Know Corporation)
Box 1041
Buffalo, NY 14240
716-895-2100

Drum dryers

United McGill Corp.
Columbus, OH
614-443-0192

Vacuum dryers

APV Crepaco Inc.
9525 West Bryn Mawr Ave.
Rosemont, IL 60018
708-678-4300

Spray, flash, conveyor, tray,
vacuum, and drum dryers

6.0 REFERENCES

1. Cook, E.M. and H.D. DuMont. *Process Drying Practices*, McGraw-Hill, Inc: New York, 1991.
2. Root, W.L. and R.A. Nichols. "Heat Transfer in Mechanically Agitated Units." In Process Heat Exchange, V. Cavaseno, ed., (Chemical Engineering). McGraw-Hill Publishing Co: New York, 1979.
3. Personal communication, Glen Selch, Selch Process Systems, 1993.
4. Buflovak Dryers, *Bulletin D0891*.

5. Ryans, J.L. and D.L. Roper. *Process Vacuum System Design and Operation*, McGraw-Hill Book Co: New York, 1986.
6. Niro Atomizer Sales Literature, B-Na-551/US.
7. Numatek, Inc. "Product Summary, Rapid Drying of Wet Radioactive Waste." In *French Decontamination and Decommissioning Capabilities*, NUMATEC, Inc: Bethesda, MD, 1991.
8. Keey, R.B. *Drying Principles and Practices*, Pergamon Press: New York, 1972.
9. Moffit, P. "Dielectric and Microwave Heating" in *Handbook of Applied Thermal Design*, E.C. Guyer, ed., McGraw-Hill Book Co: New York, 1989.
10. APV Crepaco Inc. *Dryer Handbook*, DRH-889. Tonawanda, NY: APV Crepaco.

APPENDIX M-4 DISTILLATION

1.0 TECHNOLOGY DESIGNATION

Distillation is a chemical separations process which uses vaporization and condensation to separate components within a liquid or gas stream based upon their differences in volatilities.

2.0 NEED FOR THE TECHNOLOGY

In the mixed waste (MW) process, it is envisioned that distillation could be used for liquid separation and product recovery/recycle in aqueous, organic, and other liquid waste streams. For aqueous waste streams, distillation could be used to separate aqueous waste from dilute organics and for high efficiency treatment of the remaining aqueous streams. For organic waste streams, distillation could be used to separate dilute organics from concentrated organics. In addition, the process could be used to recover mercury in liquid waste streams during the mercury control portion of the MW process.

Currently, distillation has been selected as one of the technologies to be examined in process #250.4 for separating organic liquid waste streams. The other technologies include automatic decantation and automatic separation based on route switching as a function of liquid density. Distillation is also being considered in process #595 for recovering the mercury product stream for reuse.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

The basic distillation process consists of applying heat to a liquid mixture, causing subsequent vaporization of part of the mixture, and then removing heat from the vaporized portion. The resulting condensed vapor is richer in the more volatile components and the residual unvaporized bottoms are richer in the less volatile components (Ref. 1). A distillation system's column design can either be single-staged, also referred to as "flash" distillation, or be multi-staged for increasing the processes' separation efficiency. The two general types of distillation system designs are batch and continuous.

Batch distillation equipment (Ref. 1) basically consists of a heated vessel, or "still," a rectifying column, a condenser to condense the overhead vapor, a splitter for returning a portion of the distillate as reflux, and several receiving vessels for collecting the overhead and bottoms (Figure M-4.1). This distillation process operates by introducing a batch of feed into the

heated still. As feed is heated, the more volatile components will begin to separate from the less volatile components and are collected in the condenser. This overhead product is then condensed and some of it may be returned to the top of the column as a reflux. Multiple staging in the column design is used to increase separation efficiency and is achieved by bringing the reflux liquid into intimate contact with the rising vapors.

Figure M-4.1. Batch Distillation. Still with Fractionating Column.

(From Freeman, H., Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Company. New York, NY. Reproduced with permission of McGraw-Hill.)

Continuous distillation (Refs. 1 and 2) is the most common form of distillation used by the chemical, petroleum, and petrochemical industries and involves the constant introduction of feed stream(s) into a distillation column. The column in which the feed stream is introduced contains plates or packing designed to provide intimate contact between vapor and liquid. The column consists of two sections: the rectifying or enriching section and the stripping section depending upon whether each section is above or below the feed introduction point (Figure M-4.2). The vapor rising through the rectifying section of the column is washed with liquid to remove the less volatile components, while the liquid in the stripping section of the column is stripped of the more volatile components by the rising vapor in that section. A condenser is used to condense the overhead vapor that exits the rectifying section of the column. A portion of this condensate is continuously withdrawn as the overhead product, while the remainder of the condensate is returned to the column through the reflux pump. In the reboiler, liquid that exits the stripping section is collected and a portion of that liquid is heated to produce a vapor

stream that is returned to the column. The unvaporized portion of the liquid is continuously withdrawn as the bottoms product.

Figure M-4.2. Continuous Distillation. Continuous Fractionating Column with Rectifying and Stripping Sections.

(From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Company. New York, NY. Reproduced with permission of McGraw-Hill.)

Distillation is capable of high efficiency separation and product recovery for a variety of liquid waste streams. However, the efficiency of this process is limited by capital and operating costs which can be relatively high depending upon the characteristics of waste streams processed and desired product purity. These costs may be offset by recovering some of the product for recycle or resale or to make this process more economically feasible. Also, this process is generally not economical for liquid waste streams with less than 7% organic content, with relative volatilities between 0.9 and 1.1, or a high solids content. Distillation systems typically require energy between 250 to 1200 Btu per pound of feed (Ref. 1) and the maximum operating temperature of the process in between 350° to 500 °F (Ref. 1).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

The most suitable waste streams for treatment by distillation are liquid organics, including organic solvents and halogenated organics. Generally, the waste stream should be a free-flowing fluid and produce negligible plugging or fouling effects of the column's internals. However, there are some free-flowing fluids such as organic peroxides, pyrophoric organics, and most inorganic wastes that cannot be treated by distillation (Ref. 1). In continuous distillation, the waste stream must also have a negligible solids content. For batch distillation, the unit may have a high solids content, or contain tars or resins since such materials will usually settle out in the pot and are removed at the termination of the process, thus not contaminating the column internals. Also, batch distillation is usually preferred when the composition of the feed varies significantly because the single system is flexible in terms of changing reflux ratios, boil-up rates, and number of components separated in the same column (Ref. 2). As discussed in Section 3.1, this process is generally not economical for liquid waste streams with less than 7% organic content, with relative volatilities between 0.9 and 1.1, or a high solids content. Pre-treatment would generally be needed for any waste stream containing solids, highly viscous liquids, or polymeric materials; otherwise, special equipment or maintenance procedures may be required at an added cost.

For waste streams containing azeotropes (i.e., liquid mixtures that maintain a constant boiling point and produce vapor of the same composition as the mixture when boiled) and other feed solutions that are difficult to separate, a third component is usually added to the mixture. For example, this additive could be used to form a new boiling point with one of the original constituents of an azeotrope or to alter the relative volatility of the original constituents (Ref. 2).

Since distillation will only serve to separate and reclaim volatiles in a more concentrated form, the output stream characteristics will be similar to the input waste stream characteristics.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Distillation is considered a mature technology and has been used widely by industry for purification in chemical manufacturing and in processes involving internal solvent recycling for many years. Bench-scale to full-scale distillation equipment is readily available through various commercial sources. Because of the large number of variable process factors that must be considered, most distillation systems are custom-designed. However, for common distillation

functions such as solvent-recovery or stream-purification, complete package systems can be provided in preassembled modular or skid-mounted units.

Distillation has been used to separate organic compounds from radioactive aqueous solutions such as regenerative solutions, decontamination solutions, biological wastes, and scintillation liquids (Ref. 3). However, this process has not been widely used in the radwaste treatment industry.

3.3.2 Reliability and Maintenance Requirements

Since this technology is mature, issues associated with equipment reliability should not be a significant factor. Maintenance procedures should be well defined and repair parts should be readily available. Associated shutdowns would probably be based upon the characteristics of the waste streams and the type of distillation unit. As mentioned in Section 3.2, certain types of wastes will more likely cause fouling. These waste types should be avoided to minimize these shutdowns due to fouling. Equipment availability would be different for batch and continuous distillation systems. Batch systems, because of their cyclic nature, would have frequent start-ups and shutdowns. Thus, any scheduled and unscheduled shutdowns would not tend to cause the same operational problems as a continuous unit would.

3.3.3 Secondary Waste Streams

Distillation serves to reclaim volatiles in a more concentrated form. These volatiles would still have to be disposed of using appropriate waste disposal techniques. Any materials recovered for recycle or resale may require declassification as a hazardous waste. In addition, the column packing material may become a secondary waste.

3.3.4 Separation Efficiency

Separation efficiency appears to be obtainable at any degree up to 100% (Refs. 1 and 2) provided that there are no limitations in cost. The degree of component separation for a given system configuration is dependent upon the operating conditions, the number of stages, and the amount of reflux.

3.3.5 Safety and Health

Safety and health issues associated with distillation are determined to be insignificant. Various vendors have indicated that this process can or has been automated, thus minimizing operator exposure.

3.3.6 Operational Complexity

Because of the inherent thermodynamic constraints, distillation tends to be a rather large and complex operation in comparison with competing technologies. First, the equipment and auxiliaries are usually comparatively large (heights exceeding 200 ft) and cover large areas. In addition, distillation equipment is often complex and must be operated by highly skilled personnel.

3.3.7 Glovebox Capability

Since this technology has been used to separate organic compounds from radioactive aqueous solutions, it is assumed that this technology has been demonstrated in a glovebox. However, since these systems are considered to be large and complex, operation of a full-scale system in a glovebox may be considered to be impractical.

3.3.8 Environmental Impact

As far as environmental impact issues, distillation is considered to create no air or liquid effluent problems that cannot be easily averted. Nonetheless, the potential exists for the emission of volatile organics into the air. Sources of these emissions include the condenser vents, accumulator tank vents, and storage tank vents (Ref. 1). Even though emissions from the condenser vent should be primarily noncondensable gases, volatile organic compound (VOC) air emissions could become significant if the condenser should become overloaded for any reason. To minimize the amount of volatiles emitted, a vent condenser is typically used after the main condenser (Ref. 1).

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Since this technology is considered to be mature, development or testing costs are anticipated to be minimal. Depending upon the waste streams treated, the process equipment could be purchased off-the-shelf with no additional development or testing.

Because distillation systems are normally large, capital costs of implementation are considered to be high for a distillation system. Equipment costs are dependent upon such design variables as size and type of reboiler, column height, column diameter, column internals, degree of automation, and materials of construction which are determined by the feed stream to be processed and the component separation required. For example, equipment costs would be in the order of \$350K to process a 190° proof ethyl alcohol from a 50 gal/min stream containing 3% alcohol (Ref. 2). Equipment installation costs will vary based upon the type and size of

equipment, the geographical location, and site characteristics. Sources (Refs. 1 and 2) indicate that installation costs may vary from 0.25 to 2 times equipment costs.

Operating costs are generally high because the process is considered both labor and energy intensive. As discussed previously, nominal energy requirements are about 250 to 1200 Btu/lb of feed. Separation difficulty is a major driver in operating costs which will depend on variables such as feed concentration, degree of separation required, relative volatility of feed components and presence of contaminants. For example, the annual operating cost of a 70 gal/min distillation system which recovers ethanol from an aqueous waste stream containing about 3% ethanol in addition to suspended sludge and yeast solids is about \$165K (Ref. 1).

3.5 TECHNOLOGY COMPARISON

Distillation has the advantage of being a mature technology and is capable of separating liquids at relatively high efficiencies. However, its processing costs can be relatively high, making other technologies more cost-competitive. If the products can be recycled or sold, distillation would be able to compete with more economical liquid separation technologies. In general, distillation is considered the preferred method of recovery where salable products are involved (Ref. 1).

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

Since this technology is mature, distillation systems can be custom-designed for processing for a particular type of waste stream with minimal demonstration. To design a system, data are needed on the waste's physical characteristics and chemical composition, desired product purity, and production rate. Data on the waste's physical characteristics would be used to determine the feasibility of the process and to design the distillation unit. Waste chemical composition data are needed to determine several design parameters including relative volatilities, auto-ignition temperatures, decomposition temperatures of components and azeotrope presence. Product purity data would be used for system design and establishing operating parameters. Production rate data would be used to size the system.

There are extensive data from a variety of vendors on the types of waste streams for which they have designed distillation systems. The specific waste streams and waste processing requirements would have to be more clearly defined so that available vendor data can be reviewed to identify areas requiring further testing.

4.2 TESTING REQUIREMENTS

At the present time, there are no ongoing tests within DOE EM-50 being performed on this technology. Future tests may be scheduled once additional data gaps are identified. Testing would be needed to optimize a system design and operating conditions for new waste streams. In addition, these tests would be conducted to develop pre-treatment methods for difficult-to-separate waste streams such as azeotropes.

5.0 VENDOR LIST

AQUA-CHEM, Inc. Water Technologies Div P.O. Box 421 Milwaukee, WI 53201	414-359-0600
APV Crepaco, Inc. 395 Fillmore Avenue Tonawanda, NY 14150	716-692-3000
Glitch Package Plants 1055-T Parsippany Blvd. Suite 503 Parsippany, NJ	201-299-9350
VARA International 1201 19th Place Vero Beach, FL 32960	407-567-1320

6.0 REFERENCES

1. Freeman, H.M., ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*. McGraw Hill Book Co.: New York, 1989.
2. APV Crepaco, Inc. *Distillation Handbook*. 3d ed. DH-187. Tonawanda, New York.
3. R. L. Jolley, et al. *Low-Level Radioactive Waste from Commercial Nuclear Reactors*. ORNL/TM--9846-Vol.2. Oak Ridge National Laboratory: Oak Ridge, TN, May 1986.

APPENDIX M-5 AIR STRIPPING

1.0 TECHNOLOGY DESIGNATION

The technology described in this section is known as air stripping. Air stripping is a hazardous waste treatment process for the removal of volatile organic compounds (VOCs) from either water or aqueous waste streams.

2.0 NEED FOR THE TECHNOLOGY

It is proposed that the air stripping station be contained in the aqueous treatment line (Code 100) (Ref. 1) downstream of the organics feed tank (Code 140.2) but prior to the organics oxidation unit (Code 270). Depending on the composition of the feed stream, the relative position of the organics feed tank may have to be moved as compared to where it is shown in Reference 1 because of the necessity that particulates and dissolved iron salts be removed upstream of the air stripper.

One might ask why the air stripper is needed in the aqueous treatment line in view of the fact that any liquid organics have been physically separated and sent to the organic treatment line (code 200). The answer lies in the fact that a crude physical separation cannot be 100% effective in separating liquid phases. At best, the organic phase could be removed with little or no aqueous contamination; however, the aqueous phase will always be contaminated with small amounts of the organic phase. The reverse situation holds true in that the aqueous phase could be removed free of organics, but the organic phase would be contaminated with small amounts of the aqueous phase. The air stripping technology is proposed to be applied at this point in the aqueous treatment line, therefore, to easily remove the small amount of the organic phase left behind after liquid phase separation. Of course, the situation may exist in which there is not enough free organic phase in the aqueous stream for a bulk separation to be possible. In this case, air stripping could be used to remove the volatile organic contaminants.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Air stripping is a continuous process for the removal of volatile substances from water or aqueous streams by use of countercurrent flows of the aqueous stream and air. In the most common applications of air stripping, a tower is packed with randomly distributed media of various designs. The aqueous stream is pumped to the top of the tower and flows downward

under the influence of gravity over the packing creating a very large wetted surface area. Air is supplied via a blower to the tower from below the lowest level of packing and flows upward, removing volatile substances from the aqueous stream as it travels upward within the packed column (Figure M-5.1).

Figure M-5.1. Packed-Tower Air Stripper (Ref.2)

(From Freeman, H., Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Company. New York, NY. Reproduced with permission of McGraw-Hill.)

The principle of operation exploits Henry's Law which states that the partial pressure of a volatile substance above a dilute solution of that substance is directly proportional to its concentration (this can also be expressed as mole fraction) in the solution. This is of course an equilibrium condition. In air stripping, the non-equilibrium condition is encountered and in fact provides the driving force behind the volatilization of the VOCs. As the contaminated aqueous stream travels downward through the column, it encounters ever fresher air while at the same time the concentration of the contaminant in the aqueous stream becomes less and less. Eventually, almost all of the volatile contaminants will be stripped from the aqueous stream if the stripper is designed and operated properly for that specific waste stream. Reductions up to 99.999% of VOCs input into the air stripper are feasible. Stripper design and operating parameters are shown in Table M-5.1.

TABLE M-5.1. AIR STRIPPER DESIGN AND OPERATING PARAMETERS

PARAMETER	VALUE
Single Tower Water Flow Rate	10 to 500 gpm*
Contaminant Range	Dependant upon composition of aqueous stream, however generally applicable to contaminants less than 100 mg/L
Water Inlet Temperature	50 to 75 Degrees F
Packing Depth Within Tower	10 to 40 ft
Nominal Packing Size	0.5 to 3.0 in diameter (various designs available)
Range of Hydraulic Loading Rates	10 to 30 gpm/ft ² (must prevent tower flooding)
Air Flow Rate/Blower Motor	4000 cfm with 10 HP
Stripping Efficiency	Dependent upon composition of waste stream, stripping conditions and column design. Can be as high as 99.999%.
Construction Materials	PVC, fiber-reinforced plastic or aluminum

* **Note:** Volumetric air/water ratios can vary from as low as 10:1 to as high 300:1, depending upon feed stream requirements (Ref.2)

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

For the air stripping technology to be effective, particulates and dissolved iron must be removed from the feed stream upstream of the stripper. The technology will be effective only on dissolved (or suspended) volatile species that have Henry's Law constants above 10 atm, with the upper limit of concentrations roughly 100 mg/L (Ref. 2). The reduction in the concentration of the VOCs can be as high as 99.999% and the composition of the vapors produced depend upon the composition of the feed stream, with the vapors containing almost no water.

In all cases, the VOCs must have Henry's Law constants above 10 atm (if solution concentration is expressed as mole fraction) (Ref. 2) or above 0.003 atm-m³/mole (if solution concentration is expressed in chemical units) (Ref. 3). Table M-5.2a shows some representative VOCs and their Henry's Law constants. Table M-5.2b shows some general classes of VOCs which can be air-stripped.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 TECHNOLOGY STATUS

Vendors that are capable of supplying complete operational systems for sale or rent include Hoffman Process, Hydro Group, Delta Cooling Towers, and Environmental Restoration

Systems. The vendors listed above require information on feed stream composition and quantity and also effluent requirements. With this information, a custom-designed air stripper system can be designed and costed.

TABLE M-5.2a. HENRY'S LAW CONSTANTS (H) FOR SOME REPRESENTATIVE VOCs

COMPOUND	H*.ATM
Vinyl Chloride	3.55×10^5
Carbon tetrachloride	1.29×10^3
Tetrachloroethylene	1.1×10^3
1,1,1-Trichloroethane	5.5×10^2
Toluene	4.0×10^2 (25°C)
Benzene	3.4×10^2
Chloroform	1.7×10^2
1,2-Dichloroethane	61
Bromoform	35
Methylethylketone**	5.0 (24°C)
Acetone**	2.0 (25°C)
Pentachlorophenol**	0.12

* 20°C

** Note: Not easily air stripped

(From Freeman, H. Standard Handbook of Hazardous Waste Treatment and Disposal (1989). McGraw-Hill Book Company. New York, NY. Reproduced with permission of McGraw-Hill.)

TABLE M-5.2b. AIR STRIPPABLE CLASSES OF VOCs (Ref.3)

COMPOUND CLASS	REPRESENTATIVE VOC
Halogenated Non-polar Aromatics	Pentachlorobenzene
PCBs, Halogenated Dioxins, Furans	Hexachloro-dibenzofurans
Other Halogenated Polar Aromatics	Benzyl chloride
Halogenated Aliphatics	TCE, PCE, Hexachloro-cyclopentadien
Other Halogenated Compounds	Toxaphene
Heterocyclics, Non-halogenated Aromatics	Xylene
Other Polar Non-halogenated VOCs	Dibutyl nitrosamine
Other Non-polar VOCs	Octane, Tributyl Phosphate

Depending on customer requirements, the vendors can supply designs only, equipment only, or complete systems including operations personnel. In general, the design of an air stripper system does not actually involve design, but rather the specification of parameters such

as tower diameter and height, packing depth and configuration, air flow rate, and the type of offgas treatment (if required for a specific application). Vendors such as Hydro Group routinely size air stripper systems at no cost to the customer, making their money later when a system is purchased through them.

Recent development work on air stripping includes both improved packing designs and high-temperature air stripping. The newer packing designs have many open structures which increase the available surface area for stripping while not increasing the pressure drop through the tower. The increased performance of the towers allows cost savings to be realized in that either throughput can be increased or stripper size decreased. Work on high-temperature air stripping has increased the applicability of air stripping to compounds not strippable at room temperature or below. Both the volatility and the Henry's Law constant of organic compounds increase with temperature. In addition, the viscosity of water decreases with increasing temperature, so that mass transfer is increased with decreased liquid-phase resistance, thereby allowing increased volatility of the organic contaminants.

3.3.2 Reliability and Maintenance Requirements

Air stripping towers have no moving parts. Ancillary equipment such as pumps, blowers, and blower motors have no special or involved maintenance requirements. Should the tower packing become fouled, the tower would require disassembly (generally this would not involve heavy equipment since most towers are fabricated from materials such as PVC) and replacement of the packing material.

3.3.3 Secondary Waste Streams

In general, the water effluent from an air stripping operation can be disposed of with no further treatment. However, this is highly dependent upon the upstream feed treatments employed as well as the composition of the feed stream entering the air stripper.

Offgases separated by the air stripper in general create an air pollution problem. Many offgas treatment technologies exist, however, and include condensation, adsorption onto activated carbon, and fume incineration as well as others. In addition, the tower packing material may become a secondary waste.

3.3.4 Separation Efficiency

For feed stream contaminant species having Henry's Law constants greater than $0.003 \text{ atm}\cdot\text{m}^3/\text{mole}$ (and this includes volatile radionuclides such as Radon-222), separation efficiency can be very nearly 100%. For other species which can be air-stripped by using higher temperatures, for instance, again the separation efficiency can approach 90+%, but the

technology cannot be as effective with these less volatile or diffusible species. In this case, a more energy-intensive technology such as steam stripping would probably be more appropriate.

3.3.5 Safety and Health

It is relatively simple to set up an air stripping system for completely unattended operation. Water and air flow rates are controllable by conventional equipment, as are other operational parameters such as sump level and column temperature. In view of this information, the health risks to operators are minimal.

Operational safety is generally not a problem in consideration of the fact that remote operation is possible. Also, the following information shows that operations personnel can work safely in the vicinity of the stripper; however, organic vapor respirators will be required if no vapor trapping is employed. The only moving parts involved are the feed pump and the forced (or induced) draft blower. Also, most operations are conducted at ambient temperatures. High pressures are not encountered, as the pressure provided by the forced draft blower is only that required to lift air to the top of the tower. The tower itself will be held firmly in place by guy wires.

3.3.6 Operational Complexity

The operation of air stripper system can be fully automated, with remote control of operations from a central location possible.

3.3.7 Environmental Impact

The environmental impact of air stripping is basically a trade-off of creating an air pollution problem while at the same time solving a water pollution problem. The aqueous effluent will in most cases be clean enough to discharge to the environment. In the case of VOCs remaining after air stripping, a polishing step such as activated carbon adsorption may be required. The organic vapors produced may not be a problem, depending upon the regulations imposed at the specific site where the air stripper is to be located. If the organic vapor discharge is a problem, then several treatment technologies exist to remedy the problem. Examples of the technologies include activated carbon adsorption, condensation and fume incineration.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

The costs associated with air stripping have not been determined at the time of this writing. Complete information on the feed stream including chemical composition and the

quantity to be processed must be known in order to size a system. The size of the system is what ultimately drives the cost of the technology.

3.5 TECHNOLOGY COMPARISON

Air stripping can be compared to wet air organics oxidation (the baseline technology), steam stripping, activated carbon adsorption, supercritical water oxidation, ozonolysis, ultraviolet organics destruction, and various membrane techniques including membrane-assisted solvent extraction (MASX/MADS).

4.0 DEMONSTRATION REQUIREMENTS

4.1 DATA REQUIREMENTS

The data requirements for air stripping include information on the feed stream characterization as well as on the requirements for the effluent (or secondary) streams and are shown in Table M-5.3. In order to properly size/design an efficient air stripping system, these data must be available (Ref.3).

TABLE M-5.3. DATA REQUIREMENTS FOR AIR STRIPPING

DATA REQUIREMENT	PURPOSE
Waste Stream Characterization	Required for determining the applicability of air stripping, for designing the stripping unit, and to measure the effectiveness of the technology
Required Removal Efficiency	Required for determining stripper size and operating parameters. Requirements are determined by the least volatile component
Henry's Law Coefficient	Required to determine mass transfer rates which affect stripper size and operating parameters
Gas Phase Diffusion Coefficient*	Required to determine mass transfer rates which affect stripper size and operating parameters
Feed Stream Flow Rate	Required for proper sizing of the unit
Feed Stream Temperature	Required for determining operating temperature of the tower
Ambient Air Temperature	Required for determining operating temperature of the tower
Feed Stream Inorganics Content	These compounds can affect stripper efficiency, especially dissolved iron and carbonate which can foul packing
Feed Stream pH	Extreme pH (pH<3 or pH>8) can cause corrosion and may decrease stripper efficiency

* Required for each volatile component

Data or specifications on specific equipment are available from a number of sources. An example of commercially available data is shown in a handbook produced by Delta Cooling Towers, Inc. In addition, many vendors have presented papers of general concern describing the technologies that they market. An example is Reference 4.

4.2 TESTING REQUIREMENTS

The required test data include the chemical characterization of both the aqueous and vapor effluent streams. All materials entering the air stripper must be accounted for in a material balance. From the chemical characterizations of the feed and effluent streams, the process efficiency can be determined.

5.0 VENDOR LIST

Hoffman Process, Inc. P.O. Box 345 Sewickley, PA 15143	412-741-6001
--	--------------

Hydro Group, Inc. Environmental Products Division 97 Chimney Rock Road Bridgewater, NJ 08807	800-524-2725
---	--------------

Delta Cooling Towers, Inc. P.O. Box 952 Fairfield, NJ 07004-2970	800-289-3358
--	--------------

Met-Pro Corp. Duall Division 1550 Industrial Drive Owosso, MI 48867	517-725-8184
--	--------------

Viron International 505 Hintz Road, Dept. 10 Owosso, MI 48867	517-725-8255 ext. 224
---	--------------------------

Advanced Industrial Technology Corp. Box 555-T Lodi, NJ 07644	201-265-1414
--	--------------

R.E. Wright Associates, Inc.	717-944-5501
------------------------------	--------------

Branch Environmental Attn: Bill Gilbert	908-526-1114
--	--------------

Glitsch, Inc. Attn: Bill Zellers P.O. Box 660053 Dallas, TX 75266	214-631-3841
--	--------------

Ensons Engineering
Services, Inc.
Attn: Ram Nagrani
9508 Ironmaster Drive
Burke, VA 22015

703-644-6694
(Fax) 703-644-9798

AWD Technologies
Rockville, MD

301-948-0040

6.0 REFERENCES

1. Thompson, T.K. *Functional and Operational Requirements for an Integrated Treatment Facility*. Mixed Waste Treatment Project, Subcontract 9-XY2-Y9590-1, Task 014. Los Alamos Laboratory, Los Alamos, NM: August 30, 1992.
2. Boegel, J.V. *Air Stripping and Steam Stripping*. In *Standard Handbook of Hazardous Waste Treatment and Disposal*. Freeman, H.M. ed. McGraw-Hill: New York, 1988.
3. Battelle Northwest Laboratories. *Air Stripping*. In *ReOpt-An Electronic Encyclopedia of Environmental Remedial Action Options*. Richland, WA.
4. Michal, J. "Air Stripping of Organic Compounds-An Overview." Presented at the Arizona Water and Pollution Control Association Annual Conference, Lake Havasu City, Arizona, 1988 (reprinted from *Pollution Equipment News*.)

APPENDIX M-6 STEAM STRIPPING

1.0 TECHNOLOGY DESIGNATION

The technology described in this section is known as steam stripping. Steam stripping is a hazardous waste treatment process for the removal of volatile organic compounds (VOCs) from either water or aqueous waste streams.

2.0 NEED FOR THE TECHNOLOGY

It is proposed that the steam stripping station be contained in the aqueous treatment line (Code 100) (Ref. 1) downstream of the organics feed tank (Code 140.2) but prior to the organics oxidation unit (Code 270). Depending on the composition of the feed stream, the relative position of the organics feed tank may have to be moved as compared to where it is shown in Reference 1 because of the necessity that particulates be removed upstream of the steam stripper.

One might ask why the steam stripper is needed in the aqueous treatment line in view of the fact that any liquid organics have been physically separated and sent to the organic treatment line (Code 200). The answer lies in the fact that a crude physical separation cannot be 100% effective in separating liquid phases. At best, the organic phase could be removed with little or no aqueous contamination; however, the aqueous phase will always be contaminated with small amounts of the organic phase. The reverse situation holds true in that the aqueous phase could be removed free of organics, but the organic phase would be contaminated with small amounts of the aqueous phase. The steam stripping technology is proposed to be applied at this point in the aqueous treatment line, therefore, to easily remove the small amount of the organic phase left behind after liquid phase separation.

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

Steam stripping is a continuously operating fractional distillation process without the rectification feature of the standard fractional distillation process. The feed stream enters a tower from the top and travels downward under the influence of gravity (Figure M-6.1). A countercurrent flow of steam enters the column from below and volatilizes or strips the more volatile components (in this case the hazardous contaminants) from the feed stream. The volatilized contaminant and steam emerge from the top of the column where they are first

condensed and then separated in an accumulator. The water and organic phases separate, the condensed organic phase is removed, and the water phase is recycled into the feed stream (Ref. 2).

Figure M-6.1. Steam Stripper

(From Freeman, H. *Standard Handbook of Hazardous Waste Treatment and Disposal* (1989). McGraw-Hill Book Company. New York, NY. Reproduced with permission of McGraw-Hill.)

In terms of equipment requirements, the difference between steam stripping and steam distillation is seen in the lack of a rectification section in the steam stripping tower. In steam distillation, the feed stream enters the column near the middle. Below the feed point, rising vapors strip the feed stream of its more volatile components (this is referred to as the stripping section). As the vapors rise into the rectification section of the column, returned condensate (that is, reflux) washes the rising vapors of its less volatile components, thereby allowing for a fine separation of the volatile components of the feed stream. In a remedial stripping process, the separation of organics from themselves is not of paramount importance.

The equipment necessary for steam stripping consists of a tower (of either packed or tray design, although packed steam stripper towers are generally reserved for smaller strippers), a boiler or some other source of steam, a water-cooled condenser, an accumulator which is the

vessel in which the separation of the condensed phase occurs, various pumps, piping, and possibly a heat exchanger or vacuum pump. A heat exchanger can greatly increase the efficiency of the system by using heat from the bottoms to preheat the feed stream. Also, the entire operation can be performed under vacuum, depending on the volatility of the organic contaminants to be removed from the aqueous feed (Ref. 2).

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

For the steam stripping technology to be effective, particulates must be removed from the feed stream upstream of the stripper as mentioned above. In addition, steam stripping should not be used on feed streams which contain noncondensable components such as vinyl chloride without taking precautions to prevent the loss of said components in the offgas. High concentrations of dissolved inorganics can interfere with efficient separation; therefore dissolved inorganics should be treated upstream of the steam stripper.

The technology will be effective in removing dissolved volatile organic species that are not strippable by air only because of their high concentration, low volatility (low Henry's Law constant), or low diffusivity in either water or air. The upper concentration range of volatile organics removable by steam stripping is determined by many factors, but with a properly sized tower, upwards of 5% organics can be removed. The aqueous effluent of the stripper can be as high as 100% free of volatile organics and the composition of the vapors produced depend upon the composition of the feed stream. The above performance levels can be achieved only with a properly designed and operated system. Steam strippers are not necessarily generic, and must be designed with a particular range of specific contaminants in mind (Ref. 2).

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

Steam stripping is a mature technology which has been used in the environmental remediation industry for over a decade. As such, the technology can be utilized almost immediately, with rental of the equipment available from a number of vendors. See Section 5.0 for a list of potential vendors for steam stripping equipment and services.

AWD Technologies has recently patented a steam stripping system combined with a vapor extraction system which removes non-condensable components and captures them on granular activated carbon (Ref. 3). The system is called AQUADETOX/VES and was demonstrated at Bldg. 175 at Lockheed Aeronautical Systems Company in Burbank, CA in September 1990. The system reduced TCE and PCE levels to less than the 5 µg/L regulatory requirement for these compounds (Ref. 3).

3.3.2 Reliability and Maintenance Requirements

In the two-year operation of the AQUADETOX/VES system at Bldg. 175 (Lockheed, Burbank), the system was operable 97% of the time. The 7% downtime listed in Reference 3 was comprised of both scheduled and nonscheduled downtime with no further breakdown, so unscheduled repairs cannot be fully quantified. The alkalinity of the water being treated did cause some scaling problems, resulting in downtime to descale and also necessitated pH control to be added to the feed stream (Ref. 3).

Maintenance of steam strippers in general will require treatment of the boiler water on a daily basis. Dissolved solids, pH, phosphate, and tannin levels must be controlled in order to keep the boiler operating properly, and this is complicated by the fact that the steam is condensed and recycled through the boiler. Since the tower has no moving parts, routine maintenance primarily consists of inspecting for fouling or scaling of the plates and walls of the tower. Ancillary equipment such as pumps, drives, the condenser, and accumulator vessels also require regularly scheduled inspections (generally once per month for continuously operated systems).

3.3.3 Secondary Waste Streams

In general, the water effluent from a steam stripping operation can be disposed of with no further treatment. However, this is highly dependent upon the upstream feed treatments employed as well as the composition of the feed stream entering the air stripper. In most cases the stripper column will not contain packing as is used in air strippers (trays are used instead). For smaller systems, however, column packing will be used and in this case the packing itself will become a secondary waste stream.

Offgases which have been separated by the steam stripper are not a problem, since the vapors are collected and the organics sent to the organic treatment line. Noncondensable organics can be trapped with granular activated carbon (GAC) beds as shown by the effectiveness of the AWD AQUADETOX/VES system (Ref. 3).

3.3.4 Separation Efficiency

AWD testing of their AQUADETOX/VES system was sponsored by EPA under the SITE Program in September 1990. The tests were conducted at Bldg. 175, Lockheed, Burbank. The results of the tests reduced 400-600 $\mu\text{g/L}$ TCE and 2000-2500 $\mu\text{g/L}$ PCE in the groundwater to less than the 5 $\mu\text{g/L}$ regulatory requirement for each contaminant, although TCE was reduced to a lesser extent than the PCE. Soil gases were reduced by 98.0-99.9 % in the cases where the GAC beds were regenerated often enough. When the GAC beds were

overdriven, contaminant removal efficiency dropped to as low as 93.4% (Ref. 3). These efficiencies can be expressed as volume reductions which in each case is greater than 99.9999%.

3.3.5 Safety and Health

It is relatively simple to set up a steam stripping system for completely unattended operation. Water and steam flow rates are controllable by conventional equipment, as are other operational parameters such as sump level and steam temperature. In view of this information, the health risks to operators are minimal.

Operational safety is generally not a problem in consideration of the fact that remote operation is possible; however, there are always safety concerns when steam is used in a process. Operators trained in boiler operations must be utilized in order to ensure safe operation of this equipment.

3.3.6 Operational Complexity

The operation of a steam stripper can be fully automated with the use of appropriate control equipment; however, trained and experienced operators must be used for the operation due to safety concerns as outlined above.

3.3.7 Environmental Impact

The environmental impact of operating a steam stripping system is generally not a problem if the unit is set up and operated properly. Offgases may contain noncondensable organics; however, systems such as AWD's AQUADETOX/VES trap offgases. In this case contaminated GAC is a secondary waste stream produced from the operation of the steam stripper. GAC is regenerable, however (Ref. 3). In addition, chemicals for boiler water treatment must be used. These include potassium hydroxide, potassium hexametaphosphate and a solids controlling product called tannin.

3.4 COST OF THE TECHNOLOGY OR EQUIPMENT

Bill Gilbert of Branch Environmental says that a small pilot-scale steam stripper can be set up for approximately \$50K.(Ref. 4) Frank Lenzo of Hydro Group says that a complete, full-scale steam stripper system can cost up to \$1M, and that without specific information on feed stream composition and quantity, a more accurate estimate of the capital costs cannot be made (Ref. 5).

3.5 TECHNOLOGY COMPARISON

Steam stripping can be compared to other technologies such as air stripping, distillation, and granular-activated carbon adsorption, as well as several membrane techniques such as membrane-assisted solvent extraction or membrane-assisted distillation stripping (Ref. 6).

4.0 DEMONSTRATION REQUIREMENTS

See Reference 3 for a description of the AWD AQUADETOX/VES demonstration as evaluated for EPA's Site Program.

4.1 DATA REQUIREMENTS

Data requirements for steam stripping include detailed feed stream characterization data, as well as a knowledge of permissible concentrations of contaminants allowable in the effluent. The above information combined with a knowledge of the amount of water to be treated allows the design of an efficient steam stripping system.

4.2 TESTING REQUIREMENTS

Typically in order to optimize a steam stripping operation, tests must be run to vary the parameters of: (1) groundwater feed rate, (2) steam flow rate, (3) steam temperature, and (4) steam pressure. If offgas treatment is required, then the important operating parameters for that technology must be included. In the case of the AQUADETOX/VES process, GAC bed regeneration frequency must be determined (Ref. 3).

5.0 VENDOR LIST

Hoffman Process, Inc. P.O. Box 345 Sewickley, PA 15143	412-741-6001
--	--------------

Hydro Group, Inc. Environmental Products Division 97 Chimney Rock Road Bridgewater, NJ 08807	800-524-2725
---	--------------

Met-Pro Corp. Duall Division 1550 Industrial Drive Owosso, MI 48867	517-725-8184
--	--------------

Viron International 505 Hintz Road, Dept. 10 Owosso, MI 48867	517-725-8255 ext. #224
---	---------------------------

Advanced Industrial
Technology Corp.
Box 555-1
Lodi, NJ 07644

201-265-1414

Environmental Restoration
Systems, Inc.

800-944-5515

Branch Environmental
Attn: Bill Gilbert
P.O. Box 5265
Somerville, NJ 08876

908-526-1114
(Fax) 908-526-2881

6.0 REFERENCES

1. Thompson, T.K. *Functional and Operational Requirements for an Integrated Treatment Facility Mixed Waste Treatment Project*. Subcontract 9-XY2-Y9590-1, Task 014. Los Alamos National Laboratory, Los Alamos, NM: August 30, 1992.
2. Boegel, J.V. "Air Stripping and Steam Stripping." In *Standard Handbook of Hazardous Waste Treatment and Disposal*, Feeman, H.M. ed. McGraw-Hill: New York, NY.
3. AWD Technologies. *Integrated AQUADETOX/VES System Evaluated by EPA's SITE Program*. White Paper: Rockville, MD.
4. Phone conversation with Bill Gilbert of Branch Environmental.
5. Phone conversation with Frank Lenzo of Hydro Systems.
6. Hutter, J.C. and G. F. Vandegrift. *Decontamination of Groundwater Using Membrane-Assisted Solvent Extraction*. Separation Science and Technology Division. Argonne, IL: Argonne National Laboratory.
7. 1992 Thomas Register.

APPENDIX N MERCURY SEPARATION PROCESSES

1.0 TECHNOLOGY DESIGNATION

This appendix presents evaluations of 19 technologies for separation of mercury from solid, liquid, and gas streams.

2.0 NEED FOR THE TECHNOLOGIES

Mercury-containing mixed wastes can occur in a number of physical forms such as aqueous and organic liquids, and combustible and noncombustible solids. Wastes composed primarily of organic material would go to the "waste destruction and stabilization" operation, and the subsequent gas cleanup operation would produce condenser/scrubber liquid and gas streams requiring mercury separation. Inorganic solids might be leached to transfer the mercury to a liquid phase, with subsequent removal of mercury from the liquid. More detailed flowsheets are presented in a Bechtel design study (Ref. 1).

3.0 DESCRIPTION AND EVALUATION OF THE TECHNOLOGY

3.1 DESCRIPTION

3.1.1 Solid-Phase Processes

For solids, the treatment technologies were designed to separate the mercury from the solids into liquid or gas phases where it can be concentrated into a small volume by the technologies listed under "aqueous liquids" and "gases." The mercury must be separated from radionuclides at some point. This might be done when the mercury is separated from the solid phase or when the mercury is subsequently removed from the liquid or gas phase. The only technology found for combustible solids was incineration. Noncombustible solids might be acid-leached or thermally treated at temperatures up to 600°C, depending on the composition of the solids and mercury speciation.

The EPA established roasting and retorting as the Best Demonstrated Available Technology (BDAT) for D009 high-mercury nonwastewaters (Ref. 2). Thermal treatment appears likely to be a strong candidate for many mixed wastes because many physical forms can be handled in the same process equipment. Acid leaching of the solids to dissolve mercury species may be a useful technology provided the nonradioactive constituents and the nonchemically hazardous constituents are not also dissolved. Acid leaching is the BDAT for

K071 nonwastewaters. A commercial process for K106 nonwastewaters using a sulfuric acid/sodium hypochlorite leach is the Innochem process.

The use of solutions containing "active" chlorine or "elemental" chlorine to produce soluble mercury chloride anionic complexes is established in two patents (Ref. 3,4). A patent application has been filed by General Electric for a process using a KI/I₂ solution to oxidize and form soluble mercury iodide complexes (Ref. 5). Tests on a synthetic soil matrix dosed with metallic mercury and several mercury compounds including oxides, chlorides, sulfide, phosphate, nitrate, and methyl mercury chloride gave excellent separation.

3.1.2 Liquid-Phase Processes

Organic liquids would be incinerated, followed by mercury removal from the combustion gases. The EPA has promulgated BDATs for only two mixed wastes, one of which is a hydraulic oil contaminated with mercury and tritium (Ref. 2).

For aqueous liquids, several sorbents and ion exchange technologies can be considered. Commercially available sorbent technologies are the activated carbon pellets impregnated with sulfur (Mersorb) and ion exchange resins containing thiol groups such as Ionac SR-4. If commercial suppliers of chelating resins are available, this technology would be available in the short term. Mersorb can be used over a fairly broad pH range, down to pHs of 3 to 4. It will absorb other metals which are disposed to form sulfides. If nontoxic metals are present in the liquid waste in high concentrations, the use of Mersorb may be expensive. The isothiuronium resin degrades at alkaline pHs but can be used at acidic pHs down to 1. The thiol resin can be used for alkaline solutions provided the mercury is in cationic form.

Mercury can be removed from aqueous liquids by borohydride reduction to the metallic form. This technology has a history of practice for gold and silver recovery. A commercial reagent is available. Borohydride reduction was developed by Merck & Company to remove mercury from an organomercury-containing liquid waste (Ref. 6). The method is not specific for mercury, and group VIII metals including ruthenium and above would also be removed, which includes rhodium, palladium, osmium, iridium, and platinum (Ref. 7). If ruthenium were present in the liquid to be treated, borohydride reduction would not be suitable. An effort is underway by the Chlorine Institute to make borohydride reduction the BDAT for mercury cell wastewaters.

A technology with unique potential advantages for treatment of aqueous liquid streams is the 3M membrane combined with IBC sequestering agents. This technology is currently under investigation through Battelle PNL for cesium and strontium removal. IBC has developed a system of making highly selective, non-ion exchange, organic ligands chemically bonded to solid supports such as silica particles. 3M has developed methods for incorporating these particles

into matrices resulting in teflon membranes that are highly porous to afford very high flow rates. For applications where highly selective removal of mercury may be required from an aqueous stream, this technology is promising (Ref. 8).

3.1.3 Gas-Phase Processes

Only three technologies were found for mercury separation from gases. These do not include condensing/scrubbing, which would be used to cool gases from incineration or thermal treatment and absorb soluble species. The condensate/scrubbing solutions would be treated for mercury removal by the methods listed under "aqueous liquids." Gases leaving a condenser or scrubber at temperatures below 100°C would carry extremely small amounts of mercury species other than metallic mercury. For example, an Antoine extrapolation of available vapor pressure data for mercuric chloride (corrosive sublimate) to 100°C gives a value around 10^{-5} mm Hg. This converts to about 0.1 ppm for one of the most volatile of the mercury salts.

The Mersorb technology listed for treatment of aqueous liquids is also used for gases. To prevent oxidation of the sulfur in the pellets, temperatures are limited to 100°C in oxygen-containing gases. The gas humidity in the pellet beds must be maintained below 90 percent to prevent condensation of water in the pellet voids. Vendors' literature gives a rule-of-thumb minimum contact time of 10 seconds (Ref. 9).

Two other technologies listed for gases are a patented polysulfide resin (Ref. 10) and the Boliden/Norzinc process. The resin was patented in 1986 and no information was found indicating whether the technology was commercialized. The commercial availability of this resin and its performance relative to Mersorb are not known. The Boliden/Norzinc process is the base-line process for the Mixed Waste Treatment Project.

3.2 INPUT AND OUTPUT STREAM CHARACTERISTICS

3.2.1 Solid-Phase Processes

Combustible solids would be treated by incineration. Most of the mercury would be volatilized and would be separated from the combustion gases by the off-gas treatment system. The incinerator nonwastewater residues that contain concentrations of mercury equal to or greater than 260 mg/kg (High Mercury Subcategory) must be retorted/roasted prior to disposal. Nonwastewater residues from retorting/roasting operations are not prohibited from land disposal provided they meet the TCLP standard of 0.2 mg/l. For D009 low-mercury nonwastewaters, EPA has promulgated a treatment standard of 0.2 mg/l.

Noncombustible solids might be retorted/roasted, volatilizing the mercury into an off-gas treatment system. Alternatively, acid leach processes would produce aqueous solutions of

soluble mercuric salts. The solids could be treated with chlorine-containing solutions to produce soluble mercury chloride complexes, or with KI/I₂ solution to produce soluble HgI₄⁻² solutions. The solids might also be contacted with aqueous alkaline sulfide solution to form soluble mercury polysulfide. The mercury would be recovered from these solutions by technologies discussed under ("Aqueous Liquids").

3.2.2 Liquid-Phase Processes

Mercury might be removed from aqueous streams by contact with activated carbon pellets impregnated with sulfur (Mersorb Process). These pellets would not be regenerated and would be an output stream. The aqueous stream could be treated with an alkaline solution of sodium borohydride to reduce the mercury (and other group VIII metal including ruthenium and above) to the metallic state, for removal by cementation, filtration, or carbon adsorption. The output stream would be a metal (probably iron) coated with mercury, mercury perhaps mixed with filter media, or carbon containing mercury. Dissolved mercury salts could be reacted with sulfide compounds in neutral or acidic solution to precipitate mercuric sulfide, which could be removed by filtration. The output stream would be mercuric sulfide. Dissolved mercury salts could be removed with various ion exchange resins, some of which could be regenerated to produce output streams of highly concentrated dissolved salts. Otherwise, the output stream from ion exchange would be the loaded resins. Dissolved mercury salts could be removed by extraction with liquid organic amines, in which case the output stream would be a regenerant nitric acid solution. Output streams for the 3M membrane process are not yet known. Output stream from biomedial adsorption would be the loaded biomedial.

3.2.3 Gas-Phase Processes

The condensate/scrubber waters would be treated by the processes discussed under "Liquid Processes," and the output stream characteristics would be as discussed there. Gas streams containing mercury could be cleaned by passing through a bed of Mersorb pellets or polysulfide resin pellets, and the output would be the loaded pellets. If the gas was cleaned by the Boliden/Norzinc process, the mercury would exit the process as a mercurous chloride sludge.

3.3 DEMONSTRATED PERFORMANCE

3.3.1 Technology Status

3.3.1.1 Solid-Phase Processes

Combustion is commercially available. A recent journal publication listed 44 full-scale thermal treatment remediation projects completed or in progress by 17 contractors (Ref. 7).

Acid leaching is commercially available. This is the BDAT for K071 nonwastewaters.

Thermal treatment is commercially available. This is the BDAT for high mercury nonwastewaters.

Chlorination requires development. This technology is the subject of two patents, but it is not known whether full-scale processes were developed. One patent was developed for application to brine filter sludge in chloralkali plants (K071 waste). The other patent was developed for "electrolytic cell caustic filter solids," which may also be K071 waste.

Soluble mercury polysulfide complexes require development. This technology is the subject of one patent. No documentation was found, which indicates scale-up to commercial operation. It was developed for application to electrolytic cell solids, comprising magnesium hydroxide, ferric hydroxide, and calcium carbonate.

Iodation requires development. A patent has been filed by General Electric describing this separation method followed by an electrolytic membrane process for iodine recovery and recycle.

3.3.1.2 Liquid-Phase Processes

Organic liquid combustion is commercially available. EPA promulgated incineration as the BDAT for hydraulic oil contaminated with mercury and tritium.

Sorption on activated carbon/sulfur pellets is commercially available. The material is available as "Mersorb," from Nucon International, Inc. A few bench-scale tests were reported in the ORNL Chemistry Division Annual Report (ORNL-6152) of 1985. Distribution coefficients of 10^5 to 10^6 liters/kg were measured. Vendors' literature gives a rule-of-thumb design throughput of 1 gpm/cuft of sorbent.

Borohydride reduction is commercially available. This process is currently used commercially to recover silver from spent photographic film and gold from jewelry scrap. Morton International sells a sodium borohydride solution under the VenMet trademark and is working with the Chlorine Institute to develop a process for mercury recovery from K106

wastewaters. The intent is to replace the current BDAT with borohydride reduction. The chlorine/caustic soda industry is the second largest user (after batteries) of mercury.

Precipitation of mercuric sulfide is commercially available. This is the BDAT for K071 wastewaters.

Ion exchange is commercially available. A vast variety of ion exchange separations are carried out commercially. Resin containing the iminodiacetic acid group will pick up cationic mercury selectively from calcium and magnesium, but copper and cobalt are also picked up. Mercury in the form of anionic complexes, e.g., HgCl_3^- or HgCl_4^- , can be picked up by anion exchange resins but not selectively. Savannah River Plant has used a thiol resin (Duolite GT-73) which is very selective for mercury in the cationic form. The resin was effective in both dilute waste streams and those containing concentrated salt. Regeneration was not recommended. Another thiol resin commercially available is Ionac SR-4.

Extraction with liquid organic amines requires development. This technology is the subject of one patent. No documentation was found indicating scale-up for process operations. The patent does not indicate the area of potential application.

3M membrane technology requires development. Development is at the bench-scale level for mercury separation applications. Battelle PNL and IBC Advanced Technologies, Inc. are working with 3M to develop an Empore membrane for strontium and cesium removal. The EPA has allowed five test methods involving Empore extraction disks with seven more pending (all for organic compounds).

Chelating resins requires development. The isothiuronium resin may have been used commercially for gold and platinum recovery, but it is no longer available from the original manufacturer (Ionac Chemical Company). No documentation was found indicating scale-up of the Japanese process. Processes using these resins would be similar to conventional ion exchange operations, except chelating resins cannot be regenerated or are regenerated with some difficulty. A resin containing an isothiuronium group was studied in 1971 for removal of both Hg^{2+} and CH_3Hg^- . The selectivity in the presence of dissolved iron, nickel, copper, and zinc at concentrations up to 10 g/l was complete. A second account of a chelate resin application was found in a U.S. patent assigned to a Japanese company.

Adsorption on biomedica requires development. Material is available from Biorecovery Systems, Inc. Uptake tests were done on Y-12 groundwaters, giving a relatively low equilibrium loading of 0.0001 mol/kg of sorbent.

Cementation (Amalgamation) is commercially available. This technology has been used in the mining industry for many years. More active metals (e.g., aluminum, copper, iron, and zinc) will reduce mercury to metallic form as they are dissolved. In the Innochem process, ground steel scrap is used in a rotary contactor.

3.3.1.3 Gas-Phase Processes

Sorption on activated carbon/sulfur is commercially available. The sorbent is commercially available as "Mersorb," from Nucon International, Inc. Vendors' literature gives recommended minimum contact time of 10 seconds. Contacting is done typically by passing gases through columns packed with the beads. Temperature is limited to 100°C in an oxygen-containing environment. Relative humidity must be below 90 percent to prevent condensation in pores.

Polysulfide resin requires development. No documentation has been found indicating scale-up to commercial operation. This is the subject of a U.S. patent. The resin is produced by contacting sodium polysulfide with a strongly basic anion exchange resin, resulting in a sorbent having about 8-10 percent sulfur content. The patent claims the sorbent is useful in removing mercury from gases at low concentration levels typified by natural gas.

Boliden/Norzinc process is commercially available. This process was selected by Bechtel for the Mixed Waste Treatment Project. Mercury-containing gases are scrubbed with a solution of mercuric chloride, which reacts to form mercurous chloride (which has a very low solubility). Some mercurous chloride is purged from the system, equivalent to the mercury scrubbed from the gases. The remainder is reacted with chlorine gas to produce mercuric chloride solution.

3.3.2 Reliability and Maintenance Requirements

To be determined.

3.3.3 Secondary Waste Streams

To be determined.

3.3.4 Separation Efficiency

To be determined.

3.3.5 Safety and Health

To be determined.

3.3.6 Operational Complexity

To be determined.

3.3.7 Glovebox Capability

To be determined.

3.3.8 Environmental Impact

To be determined.

3.4 COSTS OF TECHNOLOGY OR EQUIPMENT

Costs will depend strongly on scale of operation. Complete characterization of candidate waste streams is required before alternate flowsheets can be prepared and evaluated.

3.5 TECHNOLOGY COMPARISON

3.5.1 Solid-Phase Processes

Of the six processes found, three were rated as commercially available while the other three were judged to need development work. Combustion is the only feasible technology for solid wastes made up primarily of organic solids, and this technology is commercially available. Comparison of the various technologies for application to the many kinds of inorganic solid wastes will require development of flowsheets to identify the disposition of all components and to provide a basis for cost estimates. This work must await complete characterization of candidate wastes.

3.5.2 Liquid-Phase Processes

Ten processes were found, six of which were rated as commercially available. For organic liquids such as hydraulic oils, incineration is the BDAT. Comparison of the various technologies for application to the many kinds of aqueous wastes will require development of flowsheets to identify the disposition of all components and to provide a basis for cost estimates. This work must await complete characterization of candidate wastes.

3.5.3 Gas-Phase Processes

Three processes were found, two of which were rated as commercially available. Comparison of these technologies for application to the gases to be treated will require development of flowsheets to identify the disposition of all components in the entering gases and to provide a basis for cost estimates. This work must await complete characterization of candidate wastes.

4.0 DEMONSTRATION REQUIREMENTS

Development of flowsheets and economic feasibility studies will lead to the selection of technologies which require demonstration.

5.0 REFERENCES

1. *Mixed Waste Treatment Project Process Systems and Facilities: Design Study and Cost Estimates*, Bechtel Corporation, September 1992.
2. Rosengrant, L. and J. Labiosa. *Final BDAT Background Document for Mercury-Containing Wastes*, EPA/530-SW-90-059Q (May 1990) PB90-234170.
3. Wygasch, E. and G. Weiss. U.S. Patent 3,755,110; August 28, 1973; assigned to Badische Anilin- & Soda-Fabrik AG, Germany.
4. Carlson, G.A. U.S. Patent 3,785,942; January 15, 1974; assigned to PPG Industries, Inc.
5. Foust, D.F. *Extraction of Mercury and Mercury Compounds from Contaminated Material and Solutions*, U.S. Patent Application 07/963,225; October 15, 1992; assigned to General Electric Company.
6. Magliette, R.J. et al. "An At-Source Treatment for Organomercury-Containing Hazardous Liquid Waste," *Environmental Progress* 10 (August 1991): 1992..
7. Stennick, Robert S. et al. *Proceedings of the 1991 Ind. Waste Conf.* (46th) pp. 325-327.
8. Goken, G. Vendor's literature. 3M: St. Paul, MN.
9. Graves, K. Vendor's literature. NUCON International, Inc.: Columbus, OH.
10. Horton, R.L. U.S. Patent 4,591,490; May 27, 1986; assigned to Phillips Petroleum Company.

APPENDIX O DECONTAMINATION

1.0 INTRODUCTION

A variety of decontamination processes may be required in the Mixed Waste Treatment Plant (MWTP) to decontaminate containers, equipment, and debris. Containers are sent to the decontamination station from all the waste treatment lines, and equipment items and debris are sent to decontamination from the heterogeneous solids line. Reusable containers and recyclable clean equipment items are subsequently packaged and transported offsite (Ref. 1).

Decontamination technologies known to be in use, under development, or proposed were identified and evaluated for the Oak Ridge K-25 Site (Ref. 2). These technologies were grouped according to a generic decontamination method as shown in Table O-1. Surface decontamination will be the primary method used to decontaminate containers and equipment. These techniques take off the surface layer of the substrate (usually metal) and any fixed or loose contamination on the surface. Bulk decontamination and metal refining techniques remove contamination that is distributed throughout the substrate. Bulk decontamination techniques, such as solvent extraction or chemical leaching, may be used to decontaminate debris or in upstream processes to remove specific species from wet or dry solids. Metal refining technologies, if used to remove volume or surface contamination from metal debris, are the province of the Waste Destruction and Stabilization System TSG and will not be discussed in detail in this appendix.

Decontamination technology development and implementation needs were also developed in Reference 2, and the technologies were evaluated and ranked with respect to the K-25 Site requirements. The following technology summaries and evaluation results are based on the information in Reference 2. Reference 3 contains additional details regarding these decontamination technologies including technology status and deployment costs.

2.0 TECHNOLOGY SUMMARIES

2.1 MECHANICAL SURFACE REMOVAL METHODS

Most of the technologies in this generic group involve impacting or blasting a surface with a high-velocity stream of fluid or solid particles as indicated in Table O-1. Supercritical CO₂ blasting is under development by industry (Ref. 2). The centrifugal CO₂ blasting technology is being developed using the DOE Fusion Energy Program's centrifuge pellet acceleration method.

TABLE O-1. DECONTAMINATION TECHNOLOGIES (REF. 2)

Mechanical Surface Removal Methods	11. Solvent washing to remove radiological contamination 12. Solvent washing to remove organics 13. Strippable coatings 14. Vacuum (low pressure) 15. Ultrasonic cleaning
1. Ultra high-pressure water 2. Shot blasting 3. Scrabblers/scarifiers 4. Grit blasting 5. Centrifugal cryogenic CO ₂ blasting 6. Ice blasting 7. Supercritical CO ₂ blasting 8. Plastic pellet blasting 9. Hand grinding, honing, scraping 10. Automatic grinding 11. Metal milling 12. Concrete milling 13. Explosive	Chemical Surface Cleaning Methods
Thermal Surface Removal Methods	1. Chemical foams 2. Chemical gels 3. Organic acid treatment 4. Fluoroboric acid treatment 5. Inorganic acid treatment 6. Caustic treatment 7. REDOX treatment 8. Electropolishing 9. Gas phase 10. Biological 11. Laser-activated chemistry 12. UV/ozone (UV light activation) 13. Electromigration
1. Microwave scrubbing 2. Plasma torch 3. Laser heating 4. Laser etching and ablating 5. Plasma surface cleaning 6. Plasma etching/fluorination 7. Flashlamp cleaning	Bulk Decontamination Methods
Surface Cleaning Methods	1. Solvent extraction 2. Incineration 3. Biological 4. Dry heat 5. Chemical leaching 6. Catalytic extraction process 7. Vacuum (low pressure)
1. Compressed air cryogenic CO ₂ blasting 2. High-pressure water 3. Superheated water 4. Hot water 5. Steam 6. Hand brushing 7. Automated brushing 8. Sponge blasting 9. Hot air 10. Dry heat (roasting)	Metal Refining Methods
	1. Smelt purification 2. Electrorefining 3. Mond (nickel carbonyl) process 4. Leach/electro-winning

The others are accepted and used by industry for decontamination work. The grit and shot blasting technologies will remove the surface layer of most substrates. The other blasting methods will remove concrete surface layers.

For purposes of cost reduction and waste minimization, separation of the removed contamination and recycle of the working fluid or solid particles is desired. For technologies using CO₂, separation is facilitated as the solid or supercritical CO₂ converts to the gaseous phase during impact with the surface being decontaminated. But, containment and collection of the contaminated dust could be a problem depending on the configuration of the surface being blasted. For ultra high-pressure water (UHPW), effective methods for water recycling are needed. For shot and grit blasters, increased recycling of materials depends on the development of more durable and easily cleaned shot and grit.

Manual methods such as scraping tend to be labor-intensive and slow, and may result in excessive worker exposure to radiation or contamination. Grinding, honing and milling machines are commercially available for decontaminating surfaces; however, these machines are most suitable for regular surfaces.

Other mechanical methods are usually applied to decontamination of large concrete surfaces and are not expected to be needed in the MWTP. These include mechanical scarifiers and scrubbers, and selective detonation of explosive charges to shatter the surface of concrete. These methods can generate airborne contaminants, and scarifiers and scrubbers are slow.

Since the technologies in this generic group remove the surface layer of the substrate, essentially 100% decontamination should result (if the depth of penetration of the decontamination is less than the depth of surface removal, and if back-contamination can be prevented). For blasting technologies, the waste generated will consist of the particular blasting medium and the contaminated layer of substrate that is removed. If the blasting medium can be separated, the waste generated by the technologies in this group will consist primarily of the detached substrate layer. These techniques will also produce a small volume of contaminated filters. Recycle systems for UHPW will increase the aqueous waste stream and produce additional contaminated filters and media beds, filter cake and sludges.

2.2 THERMAL SURFACE REMOVAL METHODS

For surface removal of concrete, the microwave scrubbing, plasma torch, and flashlamp methods flash the water of hydration in the concrete to steam. The resulting volume expansion fractures the concrete surface and the removal of debris captures most of the contamination. Decontamination of concrete debris may be required in the MWTP.

The plasma torch, flashlamp, and laser methods remove the surface layer of other substrates by supplying enough heat to the surface to cause vaporization. The vaporized

materials and contaminants may then be captured by vacuum removal with a cover gas stream and a downstream filter system. The plasma torch method will produce a significantly higher gas-flow rate than the laser method. Because of the unidirectional nature of these technologies, application to complex geometries may be difficult. Burn-through could also occur when treating large surfaces such as glovebox walls.

In plasma cleaning, glow discharges may be used either to clean the inside surfaces of vessels or, in reactive plasma cleaning, to produce chemically reactive species that clean contaminated surfaces by the processes of chemisorption, reaction, and desorption or gasification. For example, with an oxygen plasma, oxygen atoms, ozone, and UV photons convert hydrocarbons to CO₂ and water vapor, and a fluorine plasma may provide for separation and recovery of uranium by converting it to UF₆. Because of the relatively low melting point of metal fluorides, "burn-through" with fluorine "hard" plasmas would have to be prevented if the item being decontaminated is to be reused. This could be done by monitoring the production of offgases and by controlling the plasma discharge parameters. Plasma cleaning is routinely used to clean the inside of fusion devices before the main plasma is initiated. A pollution control method for the effluent gas from the plasma treatment step will be needed.

For the technologies in this generic group that remove the surface layer of the substrate, essentially 100% decontamination should result if a sufficient depth of surface is removed. Thus, control of the depth of surface removal is a critical factor. The waste generated will consist primarily of the detached substrate layer.

These technologies produce smoke that has smaller particle sizes than the dusts resulting from mechanical surface removal. The smoke will be harder to remove by filtration and may require other offgas technologies, such as wet scrubbing, thereby producing a larger secondary aqueous waste stream.

2.3 SURFACE CLEANING METHODS

Surface cleaning methods remove the fixed and/or loose contamination without disturbing the surface of the substrate. They should be particularly effective for loose contamination. Several technologies that are described in the mechanical surface removal methods group may also be listed in this group in their less aggressive modes. These include scraping, UHPW, shot blasting, grit blasting, centrifugal cryogenic CO₂ blasting, ice blasting, supercritical CO₂ blasting, and plastic pellet blasting. Depending on the operating conditions or the particular substrate being treated, these technologies can achieve decontamination without affecting the substrate surface.

Other blasting technologies in this generic technology group are compressed air cryogenic CO₂ blasting, sponge blasting, high-pressure water, superheated water, hot water, and steam. In

this CO₂ blasting method, the cryogenic pellets are accelerated by compressed air rather than by centrifugal force. The sponge blasting technology decontaminates by blasting surfaces with various grades of patented, water-based urethane foam particles using 110 psig air as the propellant. The foam is absorptive and can be used either dry or wet to treat a variety of surface contaminants such as oils, greases, lead compounds, chemicals, and radionuclides. A nonaggressive grade of foam is used for surface cleaning of sensitive or otherwise critical surfaces. Aggressive grades, which are impregnated with abrasives, are capable of removing tightly adhered materials such as paints, protective coatings, and rust, and can roughen concrete and metal surfaces if desired. High-pressure (500 - 1000 psi) water sprays are used extensively in the nuclear industry for smearable contamination. Decontamination Factors (DFs) of 1.5 to 10 are typically obtained, depending on the amount of fixed contamination. Superheated water (300 - 400 °F and several hundred psi) machines are commercially available. Their use is usually limited to floors. Commercial equipment using steam and hot water jets for decontamination is also available. For technologies using water, effective methods are needed for treating the contaminated wastewater and recycling water to the blasting machine.

Manual decontamination methods of brushing and scrubbing will remove loose contamination but usually will be ineffective for fixed contamination. Also, they have the same undesirable features discussed for the mechanical surface cleaning group of technologies.

Solvent washing is typically used for organic contamination such as oils and PCBs. Loose or smearable contamination may also be removed. To minimize waste, solvent recovery is needed. All low-boiling organic solvents are RCRA hazardous and will increase the cost of operation.

The strippable coating technology involves painting a surface with, for example, a water-based organic polymer. When dry, the coating can be removed, along with the contaminants captured by the coating mechanically, chemically, or in the case of auto-release coatings, by vacuuming. DFs are reported to range from 3 or 5 up to several hundred, depending on how tightly the contaminants are bound to the surface.

The technology of dry heat (e.g., roasting) would be used to remove volatiles such as mercury, oils and PCBs.

The use of vacuum cleaners and their filters is accepted and widely used for removing and collecting loose contamination. It is often used to clean up during and after grinding, honing, scraping, and other surface removal methods. Vacuuming might be effective for removing loose contamination that has settled on girders, cell housings, other nonvertical surfaces, cracks, etc., within the decontamination area of the MWTP.

Ultrasonic cleaning has been used for many years for removing surface contamination from relatively small metal parts. Use of this technology on a large scale would likely require separation of the contaminants from the cleaning fluid so that the fluid could be recycled.

2.4 CHEMICAL SURFACE CLEANING METHODS

Technologies comprising chemical foams, chemical gels, acid treatments, caustic treatments, and redox treatments involve reaction with the contaminant to form species that can be dissolved in the cleaning solution and thereby removed from the substrate. Depending on the strength of the chemical solution, physical degradation of the surface can also occur. Foams and gels are used to enhance the performance of the chemicals and to reduce subsequent waste volumes by better holding the decontamination chemical in contact with the contaminated surface. These methods of application can be used for in situ decontamination of exterior surfaces. The other solutions may be applied in dipping baths, loop systems, or by spraying. Recovery would be a problem in the use of the spraying technique on exterior surfaces unless decontamination is done in a spray booth with suitable critically-safe drains. Spray booths similar to car washes are used at gaseous diffusion plants to decontaminate the interior and exterior of disassembled equipment. For waste volume reduction, regeneration and recycle of the chemical is necessary. Depending on the strength or reactivity of the chemical, DFs range from 5 or 10 to several hundred. British Nuclear Fuels, Ltd., uses several different chemical technologies to decontaminate equipment from the Capenhurst Diffusion Plant to below British below-regulatory-concern (BRC) limits. An issue to be considered is that once the chemicals are exhausted, they may be RCRA hazardous and require special treatment in the aqueous waste line.

Electropolishing selectively removes contaminant metal ions from a metal surface. This method, using an electrolyte and electricity, has usually been applied on small areas. For waste volume reduction, separation of the contaminant from the electrolyte and recycling of the electrolyte would be needed.

Gas phase decontamination uses a strong fluorinating gas to convert uranium fluoride and oxyfluoride deposits in the inside of gas-tight equipment to uranium hexafluoride gas, which could then be recovered with chemical or cold traps. (The fluorides of nickel and other materials used to construct the gaseous diffusion cascades are not volatile.) The excess fluorinating gas could be reused. Laboratory studies have shown that over 99.9% uranium removal can be obtained by reaction at room temperature. However, thorium and protactinium fluorides and most of the fluorides of elements formed in the decay chains of U-235 and U-238 are not volatile. In most cases, the levels of these contaminants are expected to be low enough that surface release criteria can be met. Further studies are needed to determine ultimate DFs.

Treatment of the offgas will generate wastes from liquid scrubbers and dry chemical traps when using current technology. Technetium may also be removed by this method.

Plasma etching and fluorination technologies may be used to enhance performance of gas phase decontamination. The plasmas of fluorinating gas can be created to promote room temperature chemical reactions of converting uranium fluoride and oxyfluoride deposits into uranium hexafluoride gas. A research project would be needed to perform a feasibility test to confirm the viability of this process.

The biological, laser-activated chemistry, and UV/ozone technologies are in the evolving technology stage. Research projects would be needed to investigate the feasibility of using these technologies for surface decontamination. UV/ozone cleaning technology is currently used in the semiconductor industry to clean organic material from surfaces.

Biological treatment is envisioned as applying a layer of microbes to a surface, supplying needed nutrients, and eventually removing the microbe layer from the decontaminated surface. Laser-activated chemistry is a proven technique for accelerating chemical reaction rates at surfaces and for selecting reaction paths and chemical stoichiometries.

In the use of UV/ozone to remove oils, greases, and solvents, UV light produces ozone from oxygen and also excites and/or dissociates contaminant molecules. These reactive species then produce CO₂ and water vapor (and HCl in the case of chlorinated solvents).

Electromigration uses an electric potential to cause migration of metal ions from a surface into an electrolyte. The technology may be applied in a localized area or in a batch fashion to contaminated areas or equipment. For waste volume reduction, separation of the contaminant from the electrolyte and recycling of the electrolyte would be needed.

2.5 BULK DECONTAMINATION METHODS

Bulk decontamination methods will generally be used in the wet and dry solids lines to remove selective contaminants from solids as part of the pretreatment process, or in the decontamination of debris. Several of these techniques, such as incineration and the catalytic extraction process which uses a furnace to produce a molten metal bath, are considered part of the WDS System and will not be discussed here.

Solvent extraction is discussed in Appendix L. This method removes organics and other species from bulk materials by dissolution. The technology could be applied as a bulk or continuous process. For waste volume reduction, separation of the contaminants from the solvent and recycling of the solvent would be needed. Also, the solvent would require removal from the decontaminated material by heating or vacuum. Chemical leaching is similar to solvent extraction. Chemical leaching and biological technologies are described under chemical surface

cleaning and biological technologies are described in Appendix A. Solvent extraction and chemical leaching are well-established technologies in current use.

Dry heat, as in the surface cleaning method, would be used to remove volatiles such as mercury, oils, and PCBs. Treatment of offgases to remove the volatilized contaminants would be necessary, and bench-scale studies would be needed to determine the applicability of the technology.

Very limited use of vacuum has been made for bulk decontamination. A proprietary vacuum-based process exists for removing water soluble Cr^{+6} from transite sheeting surfaces. Vacuum can also be used to remove contamination from porous materials by boiling solvents out of the material if the solvent foams out and can be collected. Because of their low-vapor pressures, the technique would probably be ineffective for most oils and PCBs.

2.6 METAL REFINING METHODS

Smelt purification is a technology that would be used in the WDS System as part of the metal melter technology being investigated for destroying organic contaminants and removing impurities from scrap metal.

Electrorefining is a well-established, commercial technology but is much less established for decontaminating radioactively contaminated metal. Electrorefining uses an electrolysis cell that contains an anode made from contaminated metal and deposits a cathode of pure metal. A voltage applied between the cathode and anode causes metal to ionize from the anode and to plate out on the cathode. Lab-scale tests with electrorefining of contaminated nickel resulted in plate-out of technetium with the nickel on the cathode. The electrolytic waste solutions from this process will be characterized as mixed wastes. Decontamination and recycle of the electrolytic solutions will be needed. Studies to determine the electropotentials, current densities, and concentrations to use might make this method successful. At the thermodynamic limit, this process can separate all elements adequately.

In the leach/electro-winning process, impure metal is dissolved, the solution is passed through a purification step, and purified metal is then plated out on a cathode in an electrolytic cell. This process is a well-established, commercial method for producing nickel from ore but is not used commercially to refine contaminated nickel metal. As in the case of electrorefining, decontamination and recycling of the electrolytic solutions will be needed. Technetium can be removed by ion exchange with the impure metal solution.

The Mond process involves reaction of CO at a high temperature and pressure with nickel to form nickel carbonyl. Under the proper condition, only the nickel reacts to form a carbonyl. The nickel carbonyl separates from the contaminants and is removed in the gas phase. Subsequent decomposition of the nickel carbonyl at a high temperature and at a reduced

pressure produces purified nickel. The International Nickel Company has used the Mond process for decades to refine nickel.

3.0 TECHNOLOGY NEEDS

The following discussion of technology needs is based on the discussion in Reference 2.

3.1 MECHANICAL SURFACE REMOVAL METHODS

For waste minimization, a water treatment and recycle system needs to be developed for the UHPW and ice blasting technologies. Also, improved vacuum systems are needed to recover the water to prevent the spread of contamination when cleaning equipment with complex geometries. For the abrasive blasting technologies—shot, grit, and plastic pellet—more durable materials that resist deformation and abrasion and can be recycled through the process more times are needed for waste minimization. Higher velocity and harder cryogenic CO₂ pellets are needed to increase the aggressiveness of this technology and extend its usefulness to more difficult decontamination applications. Better containment methods are again needed to limit the spread of contamination.

The supercritical CO₂ technology, which appears promising, requires development work to establish its acceptance. Better containment methods for the dust generated by grinding and milling technologies are needed. Development of remote operation capabilities are needed for the mechanical surface removal technologies for equipment contaminated with high levels of radiation or hazardous materials.

3.2 THERMAL SURFACE REMOVAL METHODS

The plasma torch heating technology requires laboratory-scale testing on various substrates with different contaminants to determine efficiencies and problem areas. The laser heating technology also needs similar evaluation. Plasma discharge cleaning could be an effective technique for decontaminating the inside of equipment. However, there is significant uncertainty regarding the effectiveness of plasma discharge and plasma etching/fluorination technologies, and extensive development and demonstration programs will be required to prove their effectiveness.

The needs of the plasma discharge cleaning technology include the following: (1) demonstration that the glow discharge plasmas can be ignited in vessels and equipment with complex shapes and that the plasma will reach into all of the crevices and corners within these vessels; (2) demonstration of the gasification of uranium and other deposits of interest using fluorine discharges; (3) construction and operation of prototypical equipment for generating reactive plasmas to remove hydrocarbon contaminants, to decompose PCBs, and to gasify

uranium and other radioisotopes; and (4) determination of the applicability of plasma cleaning to equipment internals with large surface areas.

3.3 SURFACE CLEANING METHODS

Commercial cryogenic CO₂ pellet blasting is commercially available. However, evaluation of this technology on a number of typically contaminated items would clarify how broadly applicable this technology could be. Brushing and vacuuming are accepted technologies. Vacuuming would benefit from the development of cleanable, reusable prefilters and high-efficiency recyclable particulate filters to minimize waste generation. The same is true of other decontamination technologies that require vacuum collection systems. The surface cleaning technologies that use either liquid, water or steam have the same needs for development of water recycle systems and improved vacuum systems as identified for UHPW and ice blasting under mechanical surface removal technologies.

In the removal of oils and PCBs, the hot air stripping and dry heat technologies will generate offgases. Specific needs will depend on the effluent treatment requirements.

The solvent washing and ultrasonic cleaning technologies need solvents that are more environmentally acceptable to be identified and demonstrated. Water is the standard for these technologies.

3.4 CHEMICAL SURFACE CLEANING METHODS

The fluoroboric acid technology generates a metal waste as a result of surface removal. The optimum material for solidification of this waste needs to be determined.

To advance the gas phase technology, laboratory studies need to be continued to determine the feasibility of the process. For MWTP application, this process needs to be expanded to allow decontamination of a range of radionuclide contaminants from internal surfaces. If recovery of an unreacted chemical agent is to be a part of the process, research will be needed to determine the best recovery method, and this method will require demonstration. Separation of reaction by-products could be a problem.

Several aspects of electromigration require fundamental evaluation. Selection of the best characteristics for an electrolyte to cause migration of all contaminants to the surface is needed. Concrete imbibing studies are needed to evaluate the flow or migration methods, and parametric studies are needed to optimize operating conditions, if concrete debris is to be decontaminated within the MWTP. Electrolyte gels need development for nonhorizontal surfaces. Systems that will recycle electrolytes must be designed and demonstrated.

Development of HNO₃/HF cleaning with or without ultrasonic agitation should be considered. For the organic acid technology, pilot plant studies of waste treatment (ion

exchange) are needed to meet regulatory requirements. Research and development of alkaline dissolution of surface oxide films is needed for the caustic treatment technology. Determination of the usefulness of the REDOX technologies for decontamination would require extensive R&D.

The biological, laser activated chemistry, and UV/ozone technologies are also in the evolving technology stage, and R&D projects would be needed to determine the feasibility of surface decontamination by these treatments.

3.5 BULK DECONTAMINATION METHODS

The needs of solvent extraction, biological, dry heat, chemical leaching, and vacuum technologies are the same as those described above for analogous technologies.

3.6 METAL REFINING METHODS

For the Mond (nickel carbonyl) process, bench-scale tests are needed to verify that nickel is separated from technetium and other radionuclides if specific decontamination of nickel is required in the MWTP. For the electrowinning technology, a method of removing various radionuclides is needed, and a recycle system for the electrolyte solution needs to be developed.

4.0 TECHNOLOGY EVALUATION

The application of a particular decontamination technology will depend on the assessment of several factors including the following (Ref. 2):

- * The contaminants present and their physical and chemical states
- * The surface and substrate material upon which the contamination is present
- * The size, configuration, and relationship to other surfaces of the contaminated surface
- * Accessibility of the contaminated area
- * Desired degree of decontamination to be achieved
- * Expected efficacy of the candidate technology
- * Equipment and materials available for use in decontamination
- * Worker safety and radiation dose minimization
- * Environmental regulations
- * Security and criticality requirements
- * Development, capital and operating costs
- * Quantity and nature of the secondary waste that will be generated.

Because of the varieties of substrates (type and configuration) and the contaminants, it may be impossible to choose a single decontamination technology as preferred for all problems. The Oak Ridge K-25 Site has ranked these technologies for their particular set of problems

(Ref. 2). It will be incumbent upon the Mixed Waste Treatment Program to identify the expected types of containers, equipment and debris to be decontaminated, the types of contaminants to be removed, the purpose of the decontamination effort and the level of decontamination required. Once these, and the above factors have been defined, specific technologies can be selected for further evaluation and development for the MWTP specific needs.

5.0 REFERENCES

1. Thompson, T.K. *"Mixed Waste Treatment Project: Functional and Operational Requirements for an Integrated Facility."* Prepared for Los Alamos National Laboratory under subcontract 9-XY2-Y9590-1, August 30, 1992.
2. Oak Ridge K-25 Site. *"Oak Ridge K-25 Site Technology Logic Diagram, Vol. 1, Technology Evaluation."* K-2073, Prepared for DOE Office of Technology Development, February 26, 1993.
3. Oak Ridge K-25 Site. *"Oak Ridge K-25 Site Technology Logic Diagram, Vol. 3A, Technology Evaluation Data Sheets."* K-2073, Prepared for DOE Office of Technology Development, February 26, 1993.

INTERNAL DISTRIBUTION

1. T. Abraham	16. G. Kamp
2. P. Backus	17. T. Malinauskas
3. M. Baker	18. L. Mezga
4-8. J. Berry	19. J. Perona
9. G. Bloom	20. M. Savage
10. C. Brown	21. P. Taylor
11. A. Croff	22. Central Research Library
12. T. Conley	23. Document Reference Center
13. R. Genung	24. ORNL Patent Section
14. B. Hightower	25-26. ORNL Laboratory Records
15. D. Hutchins	27. ORNL Laboratory Records, RC

EXTERNAL DISTRIBUTION

28. N. Askew, Westinghouse Savannah River Co., P.O. Box 616, Aiken, SC 29802
29. C. Baldwin, EG&G Rocky Flats, P.O. Box 464, Highway 93 & Cactus, Bldg. 881, Golden, CO 80402-0464
30. M. Ballestri, BDM Federal, 20251 Century Blvd., 4th Floor, Germantown, MD 20874
31. J. Bassi, EM-351, U.S. Department of Energy, 12850 Middlebrook Road, Germantown, MD 20874
32. J. Batdorf, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
33. S. Bates, EG&G Idaho, Inc., P.O. Box 1625, MS-3930, Idaho Falls, ID 83415-3930
34. T. Bergsman, Battelle Pacific Northwest Laboratory, Battelle Boulevard, MS P7-41, Richland, WA 99352
35. L. Borduin, Los Alamos National Laboratory, One Bikini Road, MS K557, Los Alamos, NM 87545
36. M. Brooks, Waste Policy Institute, 555 Quince Orchard Blvd., Suite 600, Gaithersburg, MD 20879
37. H. Burns, Westinghouse Savannah River Co., P.O. Box 616, Bldg. 704-61s, Aiken, SC 29808
38. G. Bryan, Pacific Northwest Lab, Battelle, Blvd., Richland, VA 99352
39. P. Castel, U.S. DOE/HQ, WINCO, 20201 Century Blvd., Rm. 408, Germantown, MD 20874
40. D. Chaiko, Argonne National Lab, CMT/Bldg. 205, 9700 S. Cass Ave., Argonne, IL 60439
41. C. Collier, BDM Federal, 20251 Century Blvd., 4th Floor, Germantown, MD 20874
42. C. Cooley, U.S. Department of Energy, EM-50, Trevion II, Washington, D.C. 20585-0002
43. T. Cooper, Westinghouse Hanford Corp., 2355 Stevens Dr., MS N3-12, Richland, WA 99352

44. A. Corstillo, FERMCO, 25 Merchant St., 3rd Floor Technology, Springdale, OH 45246
45. S. Couture, Lawrence Livermore National Lab, P.O. Box 808, L-591, Livermore, CA 94551
46. G. Coyle, EM-541, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874-1290
47. P. Coyle, EM-55, U.S. Department of Energy, 19901 Germantown Road, Germantown, MD 20874
48. J. Cunnane, Argonne National Lab, 9700 South Cass Ave., Bldg. 205, Argonne, IL 60439
49. J. Dalton, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
50. J. Dancz, SAIC, Quince Diamond Executive Center, 555 Quince Orchard Rd., Suite 500, Gaithersburg, MD 20878-4137
51. R. Darnell, EG&G Idaho, Inc., P.O. Box 1625, MS-3950, Idaho Falls, ID 83415-3950
52. L. Dewitt, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
53. S. Domotor, U.S. DOE, EM-351, Trevion II, Washington, D.C. 20585
54. P. Erickson, EPA-RREL, 5995 Center Hill Ave., Cincinnati, OH 45224
55. J. Fannon, U.S. DOE, HQ/EM-50, 20201 Century Blvd., Bellmeade Bldg. II, Rm. 402, Germantown, MD 20874
56. G. Fitzgibbon, WHC, P.O. Box 1970, MS H6-07, Richland, WA 99352
57. C. Frank, EM-50, U.S. Department of Energy, Forrestal Office Building, Washington, DC 20585
58. E. Franz, Brookhaven National Lab, Environmental & Waste Technology Center, North Railroad St., Bldg. 830, Upton, NY 11973
59. N. French, Sandia National Laboratory-Livermore, 7011 East Avenue, Livermore, CA 94550
60. M. Fuhrmann, Brookhaven National Laboratory, Building 703, Upton, NY 11973
61. A. Gatuchette, US EPA, Risk Reduction Engineering Lab, 26 W. Martin Luther King Blvd., Cincinnati, OH 45268
62. R. Gehrke, EG&G Idaho, Inc., 2151 N Blvd., MS-7111, P.O. Box 1625, Idaho Falls, ID 83415
63. R. Geimer, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
64. R. Gillins, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
65. K. Hain, EM-55, U.S. Department of Energy, 1000 Independence Ave., SW, Washington, DC 20585
66. T. Harris, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
67. P. Hart, U.S. Department of Energy, EM-542, Trevion II, 19901 Germantown Rd., Germantown, MD 20874-0002
68. J. Helt, Argonne National Laboratory, 9700 S. Cass Avenue, Bldg. 205, Argonne, IL 60439
69. D. Helton, Westinghouse Savannah River Co., P.O. Box 616, Bldg. 773-41 A., Rm. 228, Aiken, SC 29802
70. B. Hickman, Lawrence Livermore National Lab, 7000 E. Ave., Livermore, CA 94550
71. D. Hjeresen, AET, MS-P641, Bikini Road, Los Alamos, NM 87545
72. J. Hunter, Westinghouse Hanford Co., P.O. Box 1970, MS L531, Bldg. 3766, Rm. 14, Richland, WA 99352
73. D. Isbell, EM-40, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874

74. P. Jones, BDM Federal, 20251 Century Blvd., 4th Floor, Germantown, MD 20874
75. P. Kalb, Brookhaven National Lab, Environmental & Waste Technology Center, North Railroad Street, Bldg. 830, Upton, NY 11973
76. T. Kan, Lawrence Livermore National Lab., P.O. Box 808, L-467, Livermore, CA 94550
77. B. Kitchen, Savannah River Laboratory, Westinghouse Savannah River Co., P.O. Box 616, Aiken, SC 29802
78. K. Kostelnik, EG&G Idaho, Inc., P.O. Box 1625, MS-3930, Idaho Falls, ID 83415-3930
79. D. Kried, Battelle Pacific NW Lab, Battelle Blvd., Richland, WA 99352
80. O. Kruger, Westinghouse Hanford Company, 2355 Stevens Dr., Richland, WA 99352
81. M. Lankford, EM-552, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874
82. M. Larsen, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
83. G. Leatherman, SAIC, Quince Diamond Executive Center, 555 Quince Orchard Rd., Suite 500, Gaithersburg, MD 20878-0697
84. S. Lein, EM-54, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874-1290
85. J. Lippold, BDM Federal, 20251 Century Blvd., 4th Floor, Germantown, MD 20874
86. P. Lurk, EM-552, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874
87. J. Mayberry, SAIC, P.O. Box 50697, Idaho Falls, ID 83405-0697
88. W. McCulla, Los Alamos National Laboratory, SM 30 Warehouse, Bikini Road, MS J-563, Los Alamos, NM 87545
89. J. McFee, IT Corporation, 5301 Central Ave., NE, Albuquerque, NM 87108
90. K. Merrill, EG&G Idaho, Inc., 2151 N Blvd., MS-3930, P.O. Box 1625, Idaho Falls, ID 83415
91. R. Moats, BDM International, 12850 Middlebrook Road, Suite 300, Germantown, MD 20874
92. J. Moore, U.S. Department of Energy, P.O. Box 2001, Oak Ridge, TN 37830-8620
93. D. Musgrave, Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-440, Livermore, CA 94550
94. T. Myrick, SAIC, P.O. Box 2501, Oak Ridge, TN 37831
95. R. Nakaoka, Los Alamos National Laboratory, P.O. Box 1663, MS-6517, Los Alamos, NM 87545
96. M. Nawar, Office of Radiation Programs, Environmental Protection Agency, 401 M St. SW, ANR-461, Washington, DC 20460
97. G. Ordaz, EM-541, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874
98. C. Owens, EG&G Idaho, P.O. Box 1625, Idaho Falls, ID 83415-3960
99. R. Peters, Battelle-Pacific Northwest Lab, P.O. Box 999, MS P7-41, Richland, WA 99352
100. W. Phillips, Roy F. Weston Office of Technology Services, 12850 Middlebrook Road, Germantown, MD 20874
101. W. Pitt, Texas A&M University, Department of Nuclear Engineering, College Station, TX 77843
102. B. Place, Westinghouse Hanford Co., Solids & Liquids Waste Remediation, P.O. Box 1970, MS H5-33, Richland, WA 99352

103. W. Ross, Battelle-Pacific Northwest Lab, P.O. Box 999, MS P7-41, Richland, WA 99352
104. R. Schumacker, Westinghouse Savannah River Co., SRTC, P.O. Box 616, Bldg. 773-42A, Aiken, SC 29808
105. B. Schutte, EM-54, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874-1290
106. B. Schwinkendorf, BDM Federal, 1801 Randolph Rd., SE, Argonne, IL 60439
107. G. Seigny, Battelle-Pacific Northwest Lab, P.O. Box 999, MSIN P7-42A, Aiken, SC 29808
108. M. Shupe, EM-541, U.S. Department of Energy, Trevion II, Room 440, 19901 Germantown Road, Germantown, MD 20874-1290
109. D. Singh, Argonne National Lab, 9700 South Cass Ave., Bldg. 212, Rm. G-233, Argonne, IL 60439
110. D. Skrinicosky, Strategic Technology International, 20 Avon Meadow Ln., Suite 220, Avon, CT 06001
111. S. Slate, Battelle Pacific Northwest Laboratory, 902 Battelle Blvd., P.O. Box 999, KI-25, Richland, WA 99352
112. S. Stein, Battelle, Seattle Research Center, 4000 NE 41st, Seattle, WA 98105-5428
113. E. Steverson, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
114. P. Sydenticker, BDM Federal, 20251 Century Blvd., 4th Floor, Germantown, MD 20874
115. H. Turner, ARCO, 2300 W. Plano Parkway, Plano TX, 75075-8499
116. T. Timmerman, Mason & Hanger, Bldg. 11-2, P.O. Box 50697, Idaho Falls, ID 83405-0697
117. T. Uhlmeier, MD-Ferguson Co., 7295 Highway 94 South, St Charles, MO 63304
118. J. Vavruska, Equinox, Ltd., 872 Don Cubero Ave., Santa Fe, NM 87501
119. C. Ward, Westinghouse Savannah River, Building 773-A, D-1134, Aiken, SC 29808
120. S. Warren, EM-442, U.S. Department of Energy, 12800 Middlebrook Road, Trevion II, Germantown, MD 20874-1290
121. J. Witzeman, P.O. Box 398704, 7400 Willie Road, Fernald, OH 45030
122. S. Wolf, U.S. Department of Energy, Trevion II, 19901 Germantown Road, Germantown, MD 20874
123. W. Wolfe, SAIC, 545 Shoup Ave., P.O. Box 50697, Idaho Falls, ID 83405-0697
- 124-125. A. Wollerman, Trevion I, 12850 Middlebrook Road, Suite 400, Room 721, Germantown, MD 20874
126. M. Zenkovich, EM-323, U.S. Department of Energy, 12800 Middlebrook Road, Germantown, MD 20874
127. Office of Assistant Manager, Energy Research and Development, DOE-OR, P.O. Box 2001, Oak Ridge, TN, 37831
- 128-129. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831

**DATE
FILMED**

10/27/93

END