Evaluation of Pretreatment Processes for Supercritical Water Oxidation

C. M. Barnes

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**Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415**

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Prepared by

C. M. Barnes

C. M. Barnes, Senior Engineering Specialist
Chemical and Process Engineering

1-27-94

Date

Reviewed by

C. Mohr

C. M. Mohr, Senior Engineering Specialist
Chemical and Process Engineering

1/27/94

Date

Approved by

J. M. Beller

J. M. Beller, SCWO Program Manager
Waste Technology Development

2/4/94

Date

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ABSTRACT

This report evaluates processes to chemically treat U.S. Department of Energy wastes to remove organic halogens, phosphorus, and sulfur. Chemical equilibrium calculations, process simulations, and responses from developers and licensors form the basis for comparisons. Gas-phase catalytic hydrogenation processes, strong base and base catalyzed processes, high pressure hydrolysis, and other emerging or commercial dehalogenation processes (both liquid and mixed phase) were considered. Cost estimates for full-scale processes and demonstration testing are given. Based on the evaluation, testing of a hydrogenation process and a strong base process are recommended.

SUMMARY

U.S. Department of Energy (DOE) mixed wastes that are candidates for supercritical water oxidation (SCWO) are known to contain significant quantities of compounds that upon oxidation will result in mineral acids. These mineral acid precursors include halogenated hydrocarbons, sulfonated hydrocarbons, and tributyl phosphate. Modar, one of the developers of SCWO, expects corrosion problems if chlorine (Cl) in the SCWO system exceeds 100 ppm. Systematic studies to determine the maximum acceptable levels of the various corrosive species in SCWO systems have not been performed.

One process option to avoid the corrosive conditions in a SCWO process that would result from oxidation of these compounds is to react or remove the mineral acid precursors in a pretreatment process prior to SCWO. Processes with potential to adequately dehalogenate wastes include catalytic hydrogenation processes, catalytic hydrolysis processes, and base-catalyzed or strong base processes.

Equilibrium calculations showed that over a wide range of conditions, virtually complete conversion of chlorinated hydrocarbons via reaction to hydrogen chloride (HCl) or chloride salts via hydrolysis, hydrogenation, or reaction with a base was favorable. However, within conditions giving complete conversion, there was a smaller range that avoided the formation of graphitic carbon. Carbon formation could lead to catalyst deactivation or deposition problems. For some feeds, conditions could not be found in which significant amounts of carbon were not part of the equilibrium products. Temperatures of 250°C or above were generally needed to avoid carbon formation. In general, it was found that equilibrium yields were much more sensitive to the amount of hydrogenation agent or base than to the feed temperature. It was also found that thermal decomposition alone, at a temperature of 300°C, cannot be used to dechlorinate wastes because of low conversions for some common chlorinated compounds. Dechlorination with hydrogen was found to have some equilibrium advantages over dechlorination with steam.

In an evaluation that included performance, economic, and experience criteria, catalytic, gas-phase dehalogenation with hydrogen was found to have slight advantages over dehalogenation with steam, methanol, or natural gas. Although hydrogen is more expensive than the other sources of hydrogen, it has the advantage of better yields and more developed technology. Gas-phase dehalogenation with calcium hydroxide was found to have a slight advantage over using calcium oxide or sodium hydroxide.

Six commercial or emerging processes that could potentially dehalogenate nonvolatile compounds were evaluated. High pressure processes are expected to have corrosion problems similar to those seen in SCWO, low conversions or, if catalytic, potential deactivation. Processes using elemental sodium are well established for dechlorinating PCB-contaminated oils, but would have very limited application to DOE waste types. Alkaline polyethylene glycol (APEG) processes are capable of dehalogenating a broader variety of wastes, but the cost of the polyethylene glycol (PEG) reagent results in very high operating costs, especially for treating common chlorinated solvents such as carbon tetrachloride or dichloroethylene. Drying of the waste prior to treatment is needed for APEG processes, increasing capital and energy costs.

The potassium derivative of 2-methoxyethanol (KGME) process is similar chemically, but less well developed to the APEG process. Likewise, solvated electron processes are relatively new, and applicability to the broad range of DOE wastes is very uncertain.

The two most promising means of chemically pretreating DOE liquid wastes are via catalytic hydrogenation and use of a strong base. These two processes are recommended for testing with surrogate DOE wastes. Testing of either of these processes can be done either at the Idaho National Engineering Laboratory (INEL) or by a commercial company. A meeting with UOP is recommended to discuss testing its HyChlor™ process. Demonstration by UOP appears attractive because of its existing pilot plant facilities, expertise in catalyst development, and experience with the HyChlor process.

A proposal was received from ETG Environmental and Wright State University to test surrogate DOE wastes using a base catalyzed decomposition (BCD) process. Testing would be performed at the university, which has been involved in the development of the BCD process and recently performed a treatability study using this process on an INEL hazardous waste. Alternatively, testing of a strong base process could be performed at the INEL. Further discussions are recommended to determine the best testing arrangements. The strong base process, while it may be unable to dechlorinate PCBs or other aromatic hydrocarbons in DOE waste, could complement the hydrogenation process or be applicable to a broader range of waste types than hydrogenation.

Chemical treatment of DOE wastes is feasible for removal of halogens and sulfur, thus converting the waste into a feed that will be acceptable for SCWO. However, the cost of chemical treatment is likely to be of the same order of magnitude than the cost of SCWO. Also, the wide range of compositions may likely necessitate two or more different pretreatment systems, adding cost. While considerable development has made certain dechlorination systems ready or nearly ready for full-scale application, none can adequately treat certain types of DOE waste, such as solid combustible waste or tributyl phosphate. Additional development will be needed if these waste are to be processed by a SCWO system. Testing will also be needed to determine the capability of dechlorination processes to other halogens and forms of sulfur expected to be present in DOE wastes.

Information was also received for the Synthetica Technologies Detoxifier process, which dehalogenates wastes in a moving bed evaporator and then completes the destruction of organics by steam reforming. This treatment system appears to offer advantages over a pretreatment/SCWO system, and a more detailed comparison of the two technologies is recommended.

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ACRONYMS

ACFM	actual cubic feet per minute
APEG	alkaline polyethylene glycol
BCD	base catalyzed destruction
BHP	brake horsepower
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
gpd	gallon per day
gpy	gallon per year
INEL	Idaho National Engineering Laboratory
KGME	potassium derivative of 2-methoxyethanol
LDR	land disposal restriction
MBE	moving bed evaporator
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
PCP	pentachlorophenol
PEG	polyethylene glycol
PNL	Pacific National Laboratory
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
SCF	standard cubic feet
SCFY	standard cubic feet per year
SCWO	supercritical water oxidation

TBP	tributyl phosphate
TCE	trichloroethylene
TEG	tetraethylene glycol

Evaluation of Pretreatment Processes for Supercritical Water Oxidation

1. INTRODUCTION

U.S. Department of Energy (DOE) mixed wastes that are candidates for supercritical water oxidation (SCWO) are known to contain significant quantities of compounds that upon oxidation will result in mineral acids. These mineral acid precursors include chlorinated hydrocarbons, fluorinated hydrocarbons, sulfonated hydrocarbons, sulfur-containing solvents such as carbon disulfide, and tributyl phosphate. One process option to avoid the corrosive conditions that would result from oxidation of these compounds is to react or remove the mineral acid precursors in a pretreatment process prior to SCWO. This report evaluates pretreatment processes by comparing the thermodynamics, state of development, feedstock flexibility, and economics of these processes. Recommendations are also made of testing to demonstrate the process on simulated DOE wastes.

1.1 Equilibrium Analysis

Chemical thermodynamics can be used to determine the equilibrium composition of products of any reaction mixture. The SOLGASMIX-PV computer code was used to perform equilibrium calculations for a number of waste components at several temperatures. Effects of the amount of water, hydrogen, and type and amount of base on equilibrium compositions were determined for a variety of compounds and mixtures. A report summarizing the results of this equilibrium analysis is given in Appendix A.

It was found that over a wide range of conditions, complete conversion of chlorinated hydrocarbons to hydrogen chloride (HCl) or chloride salts was thermodynamically favorable. However, within these conditions there was a smaller range that avoided the formation of graphitic carbon. Carbon formation could lead to catalyst deactivation or deposition problems. For some feeds, conditions could not be found in which significant amounts of carbon were not part of the equilibrium products.

In general it was found that equilibrium yields were much more sensitive to the amount of water, hydrogen, or base than to the reaction temperature. Temperatures of 250°C or above were generally needed to avoid carbon formation. It was also found that thermal decomposition alone, at a temperature of 300°C, cannot be used to dechlorinate wastes because of low conversions for some common chlorinated compounds. Dechlorination with hydrogen was found to have some equilibrium advantages over dechlorination with steam.

1.2 Evaluation Method

The goal of this evaluation is to determine what testing needs to be performed to demonstrate a pretreatment process to remove mineral acid precursors from SCWO feeds. Initially, chemical equilibrium calculations were performed for a variety of organic liquids that are present in DOE wastes. These calculations resulted in conditions for hydrolysis, hydrogenation, and strong base reactions that would result in complete reaction of the halogenated or sulfur feed compound.

A wide range of organic liquid, sludge, and solid wastes are potential candidates for SCWO and may need pretreatment. However, in order to compare dehalogenation processes, a single "average waste" was defined as follows:

	Mole (%)	Weight (%)
Light hydrocarbons	40	29
TRIM®SOL	20	64
Water	40	7

The light hydrocarbons consisted of 15 mol% each of methanol, acetone, ethylene glycol, benzene, carbon tetrachloride, and dichloroethane, and 10 mol% monoethanolamine. TRIM®SOL is a petroleum-based commercial cutting fluid with both chlorinated and sulfonated long-chain hydrocarbons. The above "average waste" contains a total of about 19 wt% chlorine and 0.7 wt% sulfur.

Monoethanolamine is included in the waste because it is a constituent of DOE wastes, and may have an effect on dehalogenation processes. Amines have been shown to be acceptable in SCWO processes, forming N_2 rather than NO_x .

Heat and material balances were calculated for various processes. For dechlorination reactions, equilibrium was assumed. The heat and material balance provided a basis for operating costs and also for rough-sizing equipment, which in turn provided a basis for equipment cost estimates. The capacity used for the pretreatment process was assumed to be 500 gpd of organic liquids, based on a 5,000 gpd, 10% waste SCWO unit.^a

The evaluation consists of a series of comparisons. First, four processes of gas-phase dechlorination/desulfurization were compared. Based on material and energy balances for these four processes, differences in operating and capital costs were estimated. These processes apply only to the light hydrocarbons and water portion of the waste. The evaluation used weighting factors to combine measurable and intangible criteria into a total score for each process.

Another comparison was made of gas-phase reactions with three solid bases. Although these processes have been primarily developed to treat PCB-contaminated soil, the chemistry of dechlorination reaction is similar regardless of the state of the feed.

A third comparison was made of processes that could be used for dehalogenation of nonvolatile chlorinated waste. Six processes were selected for this evaluation. Conceivably, any hydrogenation or strong-base process, treating vapor could be combined with any liquid phase process to form a complete system for treating liquid waste.

a. EG&G Idaho Interoffice Correspondence, C. M. Barnes to T. R. Charlton, "Estimate of Capacity of SCWO Unit to Treat DOE Wastes," August 3, 1993.

A final comparison was then made of commercially available processes. This comparison included UOP's Hychlor™ process, ETG Environmental's base catalyzed process, SDTX Corporations' alkaline polyethylene glycol (APEG) process, and Synthetica Technologies' Detoxifier. HyChlor is a hydrogenation process, while the other three use strong bases. Process information received from the licensors/developers of these processes was used in their evaluation, including processing experience, estimated capital and utility costs, feedstock flexibility, waste stream quality, and safety and maintenance considerations.

2. COMPARISON OF HYDROGENATION PROCESSES

Hydrogenation of chlorinated hydrocarbons can be accomplished thermodynamically using a variety of sources of hydrogen. Processes that use hydrogen from four sources—hydrogen, natural gas, methanol, and water—were compared. The process using hydrogen is the best demonstrated of the four. Natural gas was included as a case using a hydrogen source much less expensive than hydrogen. For simplicity, natural gas was assumed to be 100% methane; the usual minor components in natural gas, ethane, propane, butanes, CO₂, and nitrogen are not expected to have any detrimental effect on the process.

Methanol was included because of successful demonstration dechlorination tests at the Idaho National Engineering Laboratory (INEL). Complete dechlorination was seen in tests using *p*-dichlorobenzene, orthochlorophenol, 2-chloro-1,1'-biphenyl, and 1,1-dichloroethane at temperatures from 180–350°C, and using an alumina-supported platinum catalyst.

Hydrogenation using steam has not been widely tested, but, if chemically successful, would offer another low cost process that would be very compatible with a SCWO process.

Differences were seen for these processes in the feedstock cost, the reactor size/cost, required utilities, and the equilibrium products. The stage of development of each of these processes was factored into the evaluation as well.

2.1 Yields

Two major differences are seen in the equilibrium yields from these four processes. Equilibrium yields for reaction mixtures on an equivalent hydrogen basis, in the amount of 2 moles H₂ per mole of hydrocarbon, show that carbon is produced in all cases. However, increasing the ratio of hydrogen to feed eliminates carbon formation for hydrogen and water, but not for methane and methanol.

Process simulations to obtain heat and material balances were run based on 4 moles hydrogen or water per mole of hydrocarbon, and 1 mole of methane or methanol per mole of hydrocarbon. At these conditions, for a 500 gpd hydrogenation facility, the carbon that would be produced at equilibrium would be:

Feed	Carbon (lb/hr)
Hydrogen	None
Water	2
Methane	13
Methanol	15

Slight changes in conditions would eliminate carbon in the case of water, but not for methane or methanol. Carbon formed in the reactor would likely reduce the activity of the catalyst, require equipment to physically or chemically regenerate the catalyst and which would result in secondary waste streams, and could potentially cause plugging or flow problems.

The second difference in yields is in the relative amounts of methane and CO₂ in the equilibrium products:

Feed	Molar ratio of methane to carbon dioxide in products
Hydrogen	130
Methane	52
Methanol	6.6
Water	1.6

High ratios of methane to CO₂ result in a fuel gas from which energy can be recovered. Other components of the equilibrium products are nearly equivalent for the different feed cases.

2.2 Feed and Utility Costs

The feed costs for the four cases are shown below:

Feed	Feed rate	Unit cost	Feed cost (yr)
Hydrogen	4.5 M SCFY	\$1.35/100 SCF	\$61,000
Water	26,000 gpy	\$25/month	\$300
Methane	1,030 M Btu/yr	\$2.50/M Btu	\$2,600
Methanol	15,000 gpy	\$98.50/54-gal drum	\$27,000

The unit cost for hydrogen was obtained from Air Products in Salt Lake and is the cost of delivered liquid hydrogen to the INEL. The cost does not include rental for a tank or installation fee of the tank. Liquid hydrogen is available at pressures up to about 120 psia. If high pressure hydrogen is required, the cost be considerably higher, estimated by Air Products to be greater by a factor of six. The unit cost of methane was taken from the *Oil and Gas Journal*. The unit price for methanol was obtained from a local supplier.

Utilities were estimated assuming all heat would be supplied by electricity at 5¢/kW and all cooling done by cooling water. The cost of cooling water was calculated from the power requirement of air cooler fans and the air coolers recooling hot cooling water.

The total utilities costs are:

Feed	Annual utilities (cost)
Hydrogen	\$2,200
Water	\$5,800
Methane	\$1,500
Methanol	\$2,400

The higher utility cost for the water case is due to the steam generator duty. The lower cost for methane reflects lower duties, both heating and cooling. A major difference in the processes, the required reactor duty, is masked by the low cooling water cost. Each reaction is exothermic; however, the reaction of methanol is nearly adiabatic (600 Btu/hr), while that of hydrogen is greater by two orders of magnitude (73,000 Btu/hr).

2.3 Capital Cost Differences

Rigorous cost estimates of equipment were not made because of the small size of the equipment. For example, the condenser area for the process using methane was 1.2 ft²; for methanol or hydrogen, 1.4 ft²; and for water, 2.2 ft². Capital costs differences at these exchanger areas are expected to be negligible. The calculated size of the accumulator drum for the three cases of hydrogen, methane, and methanol was identical at 1.5 ft diameter by 3.5 ft, while the accumulator for the water case was sized at 2 ft diameter by 4 ft.

Table 1 shows a list of equipment that is unique to a particular feed case. This list would suggest that the methanol case would have the lowest capital cost, while either water, due to the steam generation equipment, or hydrogen, due to the cryogenic tank, would have the highest.

Table 1. Equipment unique to each hydrogenation case.

Case	Equipment	Size
Water	Water tank	3 ft diameter by 6.5 ft
	Steam drum	1.5 ft diameter by 2.5 ft
	Steam generator	16 kW electric heater
	Feed water pump	1/4 hp
	Water pump	1/4 hp
	Demineralizer	1 gpm
Hydrogen	Liquid H ₂ tank	4 ft diameter by 11 ft
	Vaporizer	3 kW electric heater
Methane	Hold up tank	3 ft diameter by 7 ft
	Compressor	4 ACFM, CR=4.1, 1 BHP rotary or reciprocating
Methanol	Methanol tank	5 ft diameter by 10 ft
	Methanol pump	1/4 hp

Perhaps the major difference in capital cost would be due to the reactor. Assuming a residence time of 10 minutes for water and 1 minute for the other cases, the reactor would be 5 ft in diameter by 15 ft in length for the methane and methanol cases, 6.5 ft by 20 ft for hydrogen, and 14 ft in diameter by 42 ft in length for water. There is considerable uncertainty in these estimates of required residence time because of the lack of published data.

2.4 Overall Comparison

To combine both measurable differences with the more uncertain costs, the four options were ranked in seven areas with scores of 0 to 10. The ranking scores were multiplied by weighting factors to obtain total scores for each process. The rankings and scores are given in Table 2.

The above evaluation gives the edge to hydrogen, in spite of its higher feed cost. The major uncertainty regarding the hydrogen process is the pressure that will be required. If high pressure hydrogen is required, hydrogen has less advantage because of greater costs. The other three feed cases are very close in their total scores. Both methane and water have very low feed costs but, in the case of methane, no testing has been reported. Use of water is commercial for CS_2 , but very little testing has been performed using chlorinated hydrocarbon wastes. An uncertainty for all cases, but particularly for steam, is the required residence time; demonstration of a residence time on the order of a few seconds for any one of the cases could swing the economics to favor that case. Methanol offers advantages of the simplest handling of the feed and the least expensive equipment. Dechlorination of using methanol has been demonstrated at lab-scale. The greatest uncertainty with methanol is whether coking will cause catalyst deactivation and operational problems. In laboratory-scale testing at the INEL, no coking was observed.

Various catalysts have been tested or proposed for dechlorination reactions. Appendix B contains a brief evaluation of catalysts.

Table 2. Hydrogenation process comparison.

	Weighting factor	Rank:Score			
		Water	Hydrogen	Methane	Methanol
Feed cost	5	10:50	0:0	8:40	5:25
Reactor cost	4	0:0	8:32	10:40	10:40
Utilities cost	1	0:0	5:5	10:10	5:5
Other equipment	1	0:0	0:0	8:8	10:10
Carbon yield	3	9:27	10:30	0:0	0:0
CH_4/CO_2 yield	1	0:0	10:10	7:7	4:4
Demonstrated	5	5:25	10:50	0:0	5:25
Total score		102	127	105	109

3. COMPARISON OF STRONG BASE PROCESSES

Chemical thermodynamics are favorable for the reaction of bases such as metal oxides, hydroxides, or carbonates, with chlorinated hydrocarbons. Table 3 shows the Gibbs free energy change at 600 K for the reaction of metal oxides and hydroxides with carbon tetrachloride to produce the corresponding chloride salt plus carbon dioxide.

Material and energy balances were made for three bases—NaOH, $\text{Ca}(\text{OH})_2$, and CaO. Thermodynamic calculations showed that for CaO, steam was required to avoid carbon formation, while no steam was required for the other two bases. Thus, of the three cases CaO will have the highest capital cost because of the steam generation equipment and larger equipment required to handle the steam volume. Apart from the difference in the process due to steam, the processes are very similar in equipment, and equipment upstream of the reactor preheater is identical.

The dechlorination reaction using any of the three bases is exothermic, necessitating reactor cooling. Although this reactor cooling duty is nearly twice as large for the calcium oxide case as for either of the hydroxide cases, the incremental operation cost is only about \$300/yr. The major operating cost difference will be for the base, and is estimated to be \$1,000/yr for CaO, \$10,000/yr for $\text{Ca}(\text{OH})_2$, and \$60,000/yr for NaOH.

Table 3. Free energy change for reaction of metal hydroxides and oxides with CCl_4 .

Metal oxide/hydroxide	ΔG (kJ per mole of CCl_4)
Al_2O_3	-136.1
TiO_2	-239.8
Fe_2O_3	-249.6
MoO_2	-390.7
MgO	-398.0
CaO	-642.0
Na_2CO_3	-672.2
Li_2O	-775.8
NaOH	-903.8
KOH	-996.6
$\text{Ca}(\text{OH})_2$	-1104.2
Na_2O	-1132.6
K_2O	-1343.8
Cs_2O	-1695.0

Another difference between the three processes is the stability of the base. Sodium hydroxide has a melting point of 318°C, close to the expected operating reactor temperature of 300°C. Considering the highly exothermic reaction and the possibility that some organic compounds may require higher reactor temperatures, melting of the base could be a major operational problem. Melting would not be a problem for either calcium hydroxide or oxide. Calcium hydroxide decomposes to CaO at 580°C, and CaO melts at 2,580°C.

The base catalyzed decomposition (BCD) process using sodium bicarbonate has been developed jointly by the U.S. Environmental Protection Agency (EPA) Risk Reduction Engineering Laboratory, the Naval Civil Engineering Laboratory, and the Pacific Northwest Laboratory.¹⁻³ A flow diagram for soil treatment is shown in Figure 1. The development of this process has focused on PCB-contaminated soil. A destruction efficiency of 99.9999% was demonstrated in a 10 ton/hr unit treating PCB-contaminated sediments at Waukegan Harbor, Waukegan, Illinois, in 1992. The process was used to treat 40,000 yd³ of PCB-contaminated soil at a Superfund site in Brant, New York, in 1991-1992. Two liquid treatment systems were planned to be started in Australia in 1992.

Laboratory testing using different bases has been performed recently at Mississippi State University.⁴ Ca(OH)₂ was found to dechlorinate 4-chlorobiphenyl at temperatures of 250-400°C, while no reaction was observed for CaO.⁴

In a different type of process that uses sodium hydroxide to dechlorinate wastes prior to thermal reforming, 100% CCl₄ was successfully dechlorinated.⁵

An overall evaluation of the three bases is shown below:

	Weighting factor	Rank:Score		
		NaOH	CaO	Ca(OH) ₂
Operating cost	5	0:0	10:50	5:25
Capital cost	5	10:50	0:0	10:50
Base stability	5	0:0	10:50	8:40
Demonstrated	5	10:50	0:0	10:50
Total score		100	100	165

4. COMPARISON OF LIQUID PHASE PROCESSES

Many of the halogenated compounds expected in DOE waste are solvents of relatively low molecular weight and high volatility. However, heavier compounds of low volatility such as the chlorinated alkane polymer in TRIM®SOL, tributylphosphate, or sodium dioctyl sulfonate of the scintillation fluid Atomlite will require a liquid or mixed phase treatment process. Several liquid phase processes have been developed to remove PCBs from transformer oils. Other processes have been developed for application to PCB-contaminated soils, but can be adapted for liquid phase operation.

Six processes that could be used for pretreatment are discussed below and then compared. Information was obtained both from published literature and in response to inquiries to the developer or licensor of the process. Some of the processes are applicable to both volatile and nonvolatile wastes.

4.1 High Pressure Catalytic Process

A high pressure pretreatment process would have the advantage of being easily integrated into the SCWO process. A process has been developed at the Pacific Northwest Laboratory (PNL) to destroy hazardous organic compounds and chlorinated organic compound in aqueous solutions.⁶ The optimal operating conditions for the reactor were found to be 350–400°C, 2,000–4,000 psig, and 30–60 minute residence times. This range of conditions covers liquid, vapor, and supercritical regions. The reactor uses a catalyst. A flow diagram is shown in Figure 2.

Figure 2. Pacific Northwest Laboratory high pressure aqueous treatment process.

Fourteen commercially available catalysts were tested using 10% hexone in water at 400°C. Three reduced nickel catalysts gave conversions of greater than 99% while the other catalysts showed conversions of less than 24%. Carbon was formed on the catalyst at 350°C, but not at temperatures of 400°C or greater. Conversions greater than 99% were achieved for other compounds as well, including p-cresol, naphthalene, hexane, benzene, chlorobenzenes, and trichloroethylene (TCE). For TCE, 30% of the carbon present in the feed was deposited as carbon on the catalyst, and corrosion and pitting was seen in the reactor, which was constructed of Inconel 600.

It was concluded that additional studies were needed to apply this process to chlorinated hydrocarbons. The detrimental effect of HCl on catalyst activity and corrosion were of concern.

Based on the results of these tests and PNL, a high pressure catalytic process would not meet requirements for the SCWO pretreatment system. The PNL results show that the process has the same major problem as SCWO and corrosion, and in addition both HCl and carbon deposition could result in catalyst deactivation. Deactivation would lead to either inadequate conversion or the high expense of frequent catalyst replacement. In addition, the process destroys nonhalogenated compounds as well as halogenated compounds. Thus, if the level of destruction is sufficiently high, it is not a pretreatment process, but a treatment process that would eliminate the need for SCWO.

4.2 Sodium Processes

Several processes using sodium have been developed and used to remove PCBs from transformer oil. Sodium is dissolved in an aromatic such as biphenyl or naphthalene; often a second solvent such as tetrahydrofuran is also used. PCB-containing oils need to be either dry or dewatered prior to treatment. The process also limits the level of PCB in the waste from 1,000 to 10,700 ppm, depending on the particular commercial process.⁶ A secondary waste of polyphenyl polymer, sodium salts, and entrapped oil is produced, as well as an offgas containing nitrogen, hydrogen, water vapor, and hydrocarbons.

The major advantage of the process is that it is well demonstrated, having been used to treat more than 14 million gallons of transformer oil as of 1989.⁷ Both ENSR Operations and PPM, Inc., use variations of this process to treat wastes. Processing cost for the PPM process is \$1.75–2.00 per gal.

The major disadvantage of the process relative to treatment of DOE wastes is that it has been used only for PCB removal from transformer and similar oils. Testing of other types of organic liquids present in DOE wastes and other types of halogenated, sulfonated, and phosphorus components would be needed. These other wastes, as well as the high chlorine content of some DOE wastes, may make the sodium process more costly than other alternatives. The chlorine content of some DOE wastes (e.g., TRIM®SOL) is an order of magnitude higher than the present limit of the process. Additional disadvantages are the safety concerns handling metallic sodium and flammable solvents.

A process inquiry was sent to ENSR Operations regarding sodium treatment of DOE mixed waste. When evaluated by its technical personnel, it was concluded that the waste contained too many compounds that would interfere with the destruction of chlorinated compounds. Because an

elaborate separation system would be required, the high operating cost due to high reagent usage, and the complex compositions of the waste, ENSR declined to formally respond to the inquiry.

4.3 Alkaline Polyethylene Glycol (APEG) Processes

Because of the disadvantages of the sodium process for PCB decontamination of transformer oil, several companies have been involved in development and demonstration of an alternate process that uses an alkaline metal hydroxide and polyethylene glycol rather than the sodium/solvent reagent. Initial development was performed by the Franklin Research Center, and further development, demonstrations, and commercialization were performed by the EPA's Risk Reduction Laboratory, General Electric Corporate Research and Development Center, International Technology, and Galson Remediation Corporation. SDTX Technologies presently holds the rights to the Franklin Research Center's patents.

The process typically uses KOH in polyethylene glycol (PEG), and is most often referred to as the KPEG process. The reaction is carried out at mild conditions, typically 100–250°C, is complete in 10–120 minutes, and is not sensitive to the presence of water. A sketch of the General Electric process is shown in Figure 3.

Figure 3. General Electric APEG process.

A much broader spectrum of wastes has been processed with this treatment than the sodium process. A mobile system containing a 2,700-gal reactor was used to treat 9,000 gal of petroleum oil that had been collected from ground water at a wood-preserving site near Butte, Montana.⁸ The oil contained 3.5% pentachlorophenol plus parts-per-million levels of chlorinated dioxins and furans. Test data showed destruction of dioxins and furans to less than 1 ppb. Toxicity tests performed on the reaction wastes showed that they were not harmful to mammals or fish. The same unit was then used to treat 8,000 gal of a more heterogeneous waste at the Western Processing site in Kent, Washington.⁸ The waste contained oils, solids, water, and pesticides, and destroyed tetrachlordibenzodioxin to less than 0.3 ppb.

The process has been used to decontaminate soil at several sites, including processing over 30,000 tons of soil at the Wide Beach, New York, Superfund site. The capital cost of a 50 yd³/d system used to treat soil in Guam in 1989 was \$229,000, and operating costs as follows:⁸

	<u>\$/ton</u>
Chemicals	535
Utilities	34
Personnel clothing	35
Labor	676
Total	<u>1,280</u>

More recently, costs of a 250 ton/d unit have been estimated as follows:⁹

	<u>\$/ton</u>
Chemicals	86
Utilities	25
Labor	12
Mobilization/demobilization	7
Fixed costs, including royalty and return	103
Total	<u>233</u>

Appendix C contains the response of SDTX Technologies to the process inquiry for treated of simulated DOE wastes. Estimated costs for a 500 gpd unit are as follows:

Capital cost, without royalty	\$500,000
Operating costs (based on 200 d/yr)	
KPEG and NaOH	\$1,300,000
Utilities and other consumables	\$70,000
Labor	\$300,000
Total	\$1,880,000

Thus the total cost of a 500 gpd KPEG unit over a 5-year treatment schedule would be in the order of \$9 million.

The process proposed for DOE waste consists of a drying step using azeotropic distillation followed by dechlorination of the organics and SCWO of the aqueous stream. The treatment unit would yield a dechlorinated organics stream plus a NaCl solids/KPEG reaction products waste. The process could treat liquid wastes, organic sludges, spent carbon, and possibly tributyl phosphate (TBP). There is presently no basis to determine whether the process would dechlorinate solid combustible wastes containing polyvinyl chloride (PVC).

4.4 KGME Process

The KGME process is similar to the KPEG process except that it uses a proprietary reagent, prepared from KOH plus 2-methoxyethanol. A sketch of the process is shown in Figure 4. The process was designed to dehalogenate liquid wastes containing PCBs, dioxins, furans, and other halogenated aromatic and aliphatic compounds. It is a batch process, with the wastes and reagents added to a hot-oil jacketed reactor, that is held at reaction temperature for 3-9 hours. Water is used to quench the reaction, and then the contents are transferred to a decantation tank where organic and aqueous phases separate and are pumped to tanks prior to disposal. Vapors from the reactor pass through a refrigerated condenser and a series of carbon canisters prior to discharge to the atmosphere.

Figure 4. KGME process.

Advantages claimed for the process, which was offered by Chemical Waste Management, include using only one-fourth as much reagent required for the KPEG process, less waste produced than KPEG, and no polymeric residue. Testing has been performed mostly on PCB-contaminated oils; the first-pilot scale test was performed in 1992. Moisture in the feed is limited to 5%. In a recent reorganization of Chemical Waste Management, the KGME technology was transferred to Rust Remedial Services.

The KGME process is less developed than APEG processes, and the chemistry is similar. A drying step would be required for most wastes. In laboratory tests¹⁰ the molar ratio of reagent to waste (trichlorobenzene) was between 1.5:1 and 3:1, indicating a sizable expense for the alkoxide reagent. Based on these factors, the process is considered less suitable than other dehalogenation alternatives.

4.5 Solvated Electron Process

The solvated electron process uses a reagent of sodium or calcium dissolved in liquid ammonia. The reaction is low temperature, moderately high pressure, and liquid phase, and has a residence times typically of milliseconds. Ammonia can be recovered and recycled through vaporization, condensation, and recompression. The process is reported to be tolerant of moisture in the waste. Most testing to date has been performed on PCB-contaminated transformer fluid and soil. A process inquiry was sent to A. L. Sandpiper Corporation, which is developing the process, but no response was received.

4.6 Base Catalyzed Decomposition Process

The base catalyzed decomposition (BCD) process, discussed earlier as a possible candidate for gas phase dehalogenation reactions, could conceivably be used for nonvolatile compounds as well. The BCD process was developed and patented by the EPA's Risk Reduction Engineering Laboratory. The process is effectively a catalytic transfer hydrogenation process in which chlorine atoms present on chlorinated molecules are replaced by hydrogen atoms.

Several variations exist of the strong base or base catalyzed decomposition processes. Much development has focused on decontaminating soils using sodium bicarbonate. Other research has used a variety of other bases such as CaO, CaOH, MgO, and NaOH on a variety of types of waste containing chlorinated hydrocarbons. The solvated electron, APEG, and KGME processes can be considered variations of base dechlorination processes.

A treatability study using the base catalyzed decomposition process along with tetraethylene glycol was performed by Wright State University on an INEL hazardous waste.^b The waste consisted of laboratory debris such as pipets, gloves, vials, broken beakers, bottles with aqueous liquids, and Dowicide pellets. After removing the liquids and Dowicide pellets, the waste was subjected to multiple extractions until the concentration of known contaminants—pentachlorophenol (PCP), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)—was less than

b. Unpublished report by T. O. Tiernan, *Final Report on Hazardous Waste Treatability Study*, February 26, 1993.

the Resource Conservation and Recovery Act (RCRA) land disposal restriction (LDR) limits. The chlorinated wastes in aqueous, solid, and organic extractant forms were then treated in bench-scale and pilot-scale tests. Reaction temperature for all tests was in the range of 180–230°C. The duration of tests was from 4 to 12 hours, although some tests were continuations of previous ones. Destruction efficiencies for most PCDDs and PCDFs were greater than 99.99%. A final PCP concentration of 6 ppb was achieved, equivalent to a 99.99999% destruction efficiency.

Some brief preliminary tests of the BCD process have been performed on carbon tetrachloride and dichloroethane, using KOH and tetraethylene glycol (TEG) at temperatures from 21 to 50°C. Based on these tests, ETG Environmental and Wright State University propose similar treatability tests on the chlorinated components of simulated DOE wastes. The proposed tests would use KOH in twice the stoichiometric quantity of chlorinated hydrocarbon, TEG in a volume ratio of 1:8 TEG:chlorinated hydrocarbon, and an EPA proprietary catalyst in a quantity of 1 g per 100 ml of chlorinated hydrocarbon. Rough estimates by ETG of costs for a 500 gpd unit dechlorinating DOE wastes are:

Capital	\$1.0–1.5 million
Operating (including manpower and reagents)	\$2,000–3,000/day

4.7 Liquid-Phase Process Comparison

The following is a general comparison of three of the six potential processes for dechlorination of nonvolatile compounds. The high pressure catalytic process was eliminated from consideration because of the likelihood of high corrosion rates and catalyst deactivation. The KGME process was eliminated because of inadequate information, and could later be reconsidered as a variation of the KPEG process. ENSR Operations declined to propose a sodium-based treatment system for simulated DOE wastes. Rankings are relative because of the minimal data for some of the processes.

	Weighting factor	Strong base or BCD	Solvated electron	APEG
Capital cost	5	10	5	9
Operating cost	5	10	5	0
Destruction efficiency	5	8	10	9
Secondary wastes	5	10	8	5
Waste flexibility				
Aqueous liquids	2	10	5	2
Organic liquids	2	10	10	10
Sludges	2	7	5	10
Spent carbon	2	8	10	8
Solid combustible	2	7	10	10
Demonstrated	10	5	2	10
Total score		324	240	295

5. COMMERCIAL PROCESS EVALUATION

The engineering evaluations have shown that for volatile compounds, hydrogenation with hydrogen shows greater promise than using water, methanol, or natural gas and reaction with calcium hydroxide shows advantage over CaO or NaOH. For dehalogenation of nonvolatile wastes, reaction with a strong base shows the greatest promise, followed by APEG processes. Based on these evaluations, a hydrogenation and a strong base process are recommended for testing. Several processes that have had considerable development or are commercial fit into these recommended types. UOP offers the Hychlor process, which uses hydrogen to dechlorinate wastes. ETG Environmental holds a license from the EPA for the BCD process, and SDTX Technologies holds the patents on the KPEG process. Synthetica Technologies offers a treatment process that includes dechlorination with sodium hydroxide as a first step, followed by catalytic reforming to complete destruction of organics.

An inquiry was sent to the various vendors/developers of the above processes. Costs estimates and other data were requested for a 500 gpd plant treating the "average waste" as defined in Section 1.2. Information regarding the capability of the process to treat six other waste streams was also requested.

5.1 UOP Hychlor Process

UOP's response to a process inquiry is given in Appendix D. The Hychlor process uses two catalytic hydrogenation steps—one to remove sulfur and nitrogen and the other to remove chlorine. A continuous process would use two reactors; alternatively, a single reactor could be operated in a semi-batch mode to treat the waste first for sulfur and nitrogen and in a second step for halogens. Hydrogen is recovered and recycled. Each reactor effluent is scrubbed with caustic to neutralize and remove acid gases. The Hychlor process thus uses hydrogen and caustic to convert and remove mineral acid precursors, and results in two effluents—a waste brine and treated organics. Based on 100 lb of the feed composition given in Section 1.2 (64 wt% TRIM®SOL, 7 wt% water, 29 wt% mixed solvents and light organics), UOP estimates the organic effluent will consist of 8.6 lb of propane and lighter and 56.7 lb of butane and heavier organics.

The capital estimate for the UOP process is \$2.5 million, excluding licensing fee. A licensing fee minimum of \$750,000 is stated, although the fee varies with capacity and is likely negotiable. It estimates an operating cost of \$0.80 per gal for utilities and consumables. Hydrogen and caustic account for the major part of this cost, 41% and 35% respectively. With labor, the estimated operating cost would be \$380,000 per year. Of the seven waste compositions given in the process inquiry, UOP states that the Hychlor process could treat three of the organic liquids and the organic sludge, but not the tributyl phosphate waste, the spent carbon waste, or the solid combustible waste.

UOP states that the surrogate DOE waste is not significantly different from other hazardous wastes that it has successfully treated. However, it recommends a 3–5 week pilot plant verification of the process at their Research Center in Des Plaines, Illinois, using a sample of the surrogate waste. This pilot plant testing would be a cost-share arrangement, with DOE's cost approximately \$75,000 to \$80,000.

5.2 SDTX KPEG Process

The response of SDTX Technologies is given in Appendix C. The proposed process consists of azeotropic distillation to remove water followed by reaction in a plug flow reactor using NaPEGSM. NaPEG would be made onsite by the batch reaction of NaOH and PEG. Waste streams include water from the drying step, which would be sent to the SCWO unit, an organic-free water effluent from NaPEG production and released to the atmosphere, an NaCl effluent wet with organics, and the dechlorinated organics product. Apparently, no offgas is produced.

SDTX estimates a capital cost of \$500,000 for a 500 gpd unit. This cost excludes any royalty. SDTX holds the major patents in alkaline glycolate technology, and works with various remediation contractors and equipment suppliers on remediation projects. They estimate a operating cost of \$1.80/lb of liquid (or \$13/gal) for PEG and NaOH, and \$0.05–0.10/lb of liquid additional for utilities. With labor, total operating cost is estimated to be \$1,370,000 per year.

SDTX states that the process could likely treat five of the seven wastes. The two excluded are the TBP waste and combustible solids, although a currently planned research program may lead to capability for TBP. An alternative process configuration would be required for the spent carbon and organic sludge wastes. SDTX states that there is no KPEG unit now operating on organic liquids.

5.3 ETG Base Catalyzed Decomposition Process

The ETG response to the process inquiry is given in Appendix E. ETG prepared its response in consultation with Dr. T. O. Tiernan of Wright State University and Charles Rogers, the inventor of the EPA BCD process. Wright State University is one of the developers of the BCD process, and Tiernan recently performed a BCD process treatability study on a chlorinated insecticide waste from the INEL.

ETG made rough cost estimates of \$1–1.5 million capital and \$2,000–3,000/day operating for a 500 gpd unit. Five-year treatment costs would be \$3–4.5 million. No breakdown of costs or details of the full-scale process were given.

ETG proposes treatability tests to better determine the fundamental parameters for treatment of the DOE simulated wastes, and provide a better basis for cost estimates for a full-scale system. The treatability tests would be performed at Wright State University, and would include tests of carbon tetrachloride, dichloroethane, and possibly TRIM[®]SOL, and then the waste mixture. The test reactor proposed for the tests can operate at temperatures from ambient to 538°C, at pressures from atmospheric to 6,000 psi, and is constructed of Hastelloy. The reactor has valved sampling ports to permit removal of both liquid and gaseous samples at any time interval during the course of the test.

The ETG proposal states that if the treatability tests prove successful, then four of the six alternative wastes given in the inquiry are potentially treatable. These four include 100% TRIM[®]SOL, the CCl₄/TCE/Freon waste, the INEL organic sludge, and the spent activated carbon wastes. The other two—the TBP waste and the combustible solids waste—apparently are not compatible with the BCD process.

5.4 Synthetica Detoxifier

A process inquiry was sent to Synthetica Technologies because of its moving bed evaporator (MBE) that dechlorinates waste feed prior to high temperature catalytic steam reforming. The process has been tested on a variety of wastes including 100% CCl₄, Hanford tank waste surrogates, spent activated carbon, and combustible solid waste similar to DOE combustible waste. Rather than decouple its process to solely perform dehalogenation, Synthetica chose to respond to inquiry with information on its process to completely destroy organic waste. A sketch of the process is shown in Figure 5. The complete response is given in Appendix F.

For organic liquids, the process consists of evaporation of the organic material by exposure to steam at 300–550°C. Heavier organic liquids or sludges can be fed directly to the next stage of the process, the MBE. A shredder is used for some solid wastes. In the MBE, neutralization of acid gases takes place and dry salt falls into the bottom hopper. The dehalogenated organic material and steam enter the reformer, which decomposes the organics to hydrogen, CO, and CO₂. Following cooling, the effluent passes through absorber beds to remove trace organics and halogens. Part of the effluent is then recycled to vaporize additional waste, while the remainder is fed to a reactor that converts CO and hydrogen to CO₂ and water. This oxidized offgas is released to the atmosphere.

The estimated capital cost for a Detoxifier unit that processes about 1 ton/d (about 240 gpd) is \$900,000. Operating cost was estimated at \$600 per day, or based on 200 days per year, \$120,000 per year. Labor costs are lower than other options because the control unit is robust enough to allow the unit to run unattended.

Testing has been done on all the waste forms given in the process inquiry, including organic liquids, TBP, spent carbon, and solid combustibles. Plans are under way to test actual mixed waste with a Detoxifier unit that will be installed at Sandia National Laboratories. Another unit is scheduled to be delivered to ATG in Richland, Washington, for treatment of low level waste. Permits from EPA and Washington state have been obtained to construct this unit.

5.5 Comparison

A comparison of the commercial processes is given below:

	UOP Hychlor	ETG BCD	SDTX KPEG	Synthetica Detoxifier
Capital cost (\$M)	2.5	1–1.5	0.5	1.8
Annual operating cost (\$K)	(380)	400–600	(1670)	(360)
Consumables and utilities	80		1370	210
Labor	300		300	150
Total 5-yr life cost (\$M)	4.4	3–4.5	8.8	3.6
Flexibility				
Halogenated solvents	Yes	Yes	Yes	Yes
TRIM®SOL	Yes	Yes	Yes	Yes
TBP	No	No	?	Yes
Organic sludge	Yes	Yes	Yes	Yes
Spent carbon	No	Yes	Yes	Yes
Combustible solids	No	No	No	Yes

Drum Feed Evaporator

Organic Vaporization
 CCl_4 / TCE Desorbition
GAC Reactivation

Moving Bed Evaporator

Organic Decomposition
 CCl_4 / TCE Decomposition
HCl Neutralization
Nitrate Decomposition

High-Temperature Steam Reforming Reactor

Organic Destruction

Figure 5. Synthetica Detoxifier process.

The above cost estimates are for a 500 gpd organics unit, and based on estimates from the respective companies. For the Synthetica Detoxifier, the capital cost estimate is based on two 1-ton/d units, while the operating costs are calculated from three times the cost estimates given in the proposal, which are based on 1,200 lb/d. This comparison shows that while the SDTX has the lowest capital cost, its high operating cost make this technology prohibitive. Given the level of accuracy of the estimates, the total five-year life cost for the UOP Hychlor process, ETG BCD process, and Synthetica Detoxifier is essentially equivalent. However, the Hychlor and BCD processes would pretreat waste to be then fed to a SCWO unit, while the Detoxifier is a complete treatment process. The Synthetica Detoxifier process is also capable of processing a broader range of wastes than the other options.

6. TESTING ALTERNATIVES AND RECOMMENDATIONS

Testing of both a hydrogenation process and a base process is recommended. Testing of the hydrogenation process could be performed at the INEL or at UOP's Research Center. Testing at UOP has the advantages of using an existing pilot plant and a catalyst that has been demonstrated in previous testing of a variety of wastes. Likewise, testing of a base process could be performed at either the INEL or Wright State University.

UOP proposed a treatability study of a 20-L sample of the baseline waste for a 3-5 day test to verify product yields and product qualities. ETG proposed testing of four 200-mL samples, including CCl_4 , DCA, the chlorinated compound of TRIM®SOL, and then the waste mixture of TRIM®SOL, chlorinated solvents, and nonchlorinated compounds. Meetings with both UOP and ETG/Wright State University are recommended to obtain additional information regarding testing options, facilities, and costs.

If the INEL were to perform testing of both process, four series of tests are envisioned. In the first series, three catalysts would be tested with the baseline waste composition without TRIM®SOL and using hydrogen. Process condition would be sought within the temperature range of 200-350°C, pressure range of 50-2,000 psia, and H_2 to feed ratio of 0.5 to 4.0 to dechlorinate the feed to 1,000 ppm Cl, or 99.7% destruction efficiency. (The 1,000 ppm Cl limit is based on an acceptable level of 100 ppm Cl for SCWO, and a water to waste dilution of 10:1.) If initial tests with hydrogen show that high pressure is required, tests would be continued with methanol, water, or methane.

In the second series the same feed would be used with a solid base rather than a catalyst. Tests would be performed to determine acceptable temperatures and possibly also steam ratio. The third series would test the full waste stream with whichever system, hydrogenation or base, proved superior in the first two series. The final series would depend on the results of series 3, and be either the alternative system with the full waste, or the strong base system with TRIM®SOL only. An estimated 50-60 separate runs would be made.

A sketch of the testing apparatus is given in Figure 6. An equipment list with rough cost estimates is given below:

Reactor System #1	
Stirred reactor with heater	\$10,000-15,000
2 high pressure pumps	6,000
PC (286)	2,000
Data acquisition boards	1,000
Data acquisition software	1,000
Gas regulators	400
Thermocouples	150
Pressure transducer	1,000
Metering valve	200
Auto sampling valve	1,000
Gas chromatograph upgrade	5,000
Gas mass flow controller	1,500
Gas flow meter	1,000
Stainless steel tubing	200
Fittings and valves	900
Facility upgrade (minor)	5,000

Figure 6. Proposed INEL test scheme.

Reactor System #2

Stirred reactor with heater	\$10,000-15,000
2 high pressure pumps	6,000
Data acquisition boards	1,000
Gas regulators	400
Thermocouples	150
Pressure transducer	1,000
Metering valve	200
Auto sampling valve	1,000
Gas mass flow controller	1,500
Gas flow meter	1,000
Stainless steel tubing	200
Fittings and valves	900
Facility upgrade	<u>5,000</u>
Total	\$58,200-68,200

The above estimate assumes the use of an existing gas chromatograph. Some of the above equipment may be available from INEL Research Center surplus and would reduce total cost.

An overall cost estimate is as follows:

Labor

Test plan, equipment procurement, safety review, test procedure	440 hr	\$38.7K
Four series of experiments and analytical support	1,400 hr	\$104.7K
		<u>\$10.6K</u>
Data analysis and test report	120 hr	\$154.0K
Equipment, chemicals and lab supplies		<u>\$73.0K</u>
Total project (does not include study)	1,830 hr	\$227.0K

Total cost for INEL testing of just one of the two processes is estimated to be \$100,000 to \$120,000.

Because of the advantages of the Synthetica Detoxifier process, it is also recommended that development of this technology be followed closely in order to make updated comparisons with SCWO, and, if needed, testing be done of the Detoxifier process with the simulated DOE wastes defined for SCWO pilot plant tests.

7. REFERENCES

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Appendix A

Chemical Equilibrium Analysis of Pretreatment Processes

Appendix A

Chemical Equilibrium Analysis of Pretreatment Processes

A-1. INTRODUCTION

DOE mixed wastes that are candidates for supercritical water oxidation (SCWO) are expected to contain significant quantities of compounds that upon oxidation will result in mineral acids. These mineral acid precursors include chlorinated hydrocarbons, fluorinated hydrocarbons, sulfonated hydrocarbons, carbon disulfide, and tributyl phosphate. One process option to avoid the corrosive conditions that would result from oxidation of these compounds is to react or remove the mineral acid precursors prior to SCWO.

Engineering Design File (EDF) ID121217/1005 proposed a baseline process as well as alternative schemes for removal of mineral acid precursors. The recommendations of this EDF were based on published research and development information, which for many processes was limited. To more adequately evaluate possible pretreatment processes, in order to select processes for demonstration testing, additional analysis is needed. The first step is that of determining chemical equilibrium limitations. Equilibrium analysis will confirm that the requirements placed on the chemical reactors of the pretreatment process are thermodynamically possible, and will also guide the selection of reaction conditions and catalysts.

Equilibrium compositions were determined using the SOLGASMIX-PV computer code, a PC version that was developed at and received from Oak Ridge National Laboratory. SOLGASMIX-PV has a very complete databank for inorganic compounds and C_1 - C_3 hydrocarbons; for the C-H-O-Cl system, the databank includes 76 chemical species. To supplement this databank with compounds of specific interest to the study, thermodynamic data was added for chloroform, tetrachloroethylene, hexachloroethane, dichloroethylene, trichloroethylene, dichloroethane, trichloroethane, tetrachloroethane, ethylene glycol, acetic acid, acetone, methanamine, ethanamine, and 1,1,1,2-tetrachloro-2,2-difluoroethane.

A-2. GAS-PHASE HYDROLYSIS REACTOR

The proposed baseline pretreatment process in EDF ID121217/1005 partially vaporizes the liquid waste, and the vapor is fed to a gas-phase hydrolysis reactor. To analyze the chemistry that would occur in this reactor, 12 representative compounds were selected, and equilibrium compositions were first determined for each of these compounds at a variety of conditions of temperature, steam ratio, and type and amount of base. Following this analysis, equilibrium compositions were determined for a variety of mixtures aimed at being representative of organic liquid wastes.

A temperature of 300°C was used for most equilibrium calculations for the 12 single compounds. For a few of the compounds, the effect of temperature on equilibrium was also determined, but it was expected that reaction rate considerations rather than equilibrium would be the dominant factor in determining reaction temperature.

A-2.1 Pyrolysis and Hydrolysis of Chlorinated Light Hydrocarbons

In the absence of both water and any base to neutralize reaction products, HCl, CCl_4 , graphitic carbon, and methane are the predominate equilibrium products, as shown in Table 1. If the reactant contains no hydrogen, such as carbon tetrachloride, chlorine gas will be the predominant equilibrium form of Cl.

The significance of these results is that they show that thermal decomposition (pyrolysis) alone (at 300°C) cannot be used to dechlorinate common solvents because of low conversions for fully chlorinated compounds as carbon tetrachloride and C_2Cl_6 , and because of carbon formation in all cases. Formation of carbon could result in deposition, plugging, or catalyst deactivation.

Addition of steam, base, or a source of hydrogen is necessary to eliminate carbon from equilibrium reaction products. If no base is added, the minimum steam ratio required to eliminate carbon from the equilibrium products is 2 moles of steam per mole of hydrocarbon for C_1 chlorinated hydrocarbons and about 5.5 moles of steam per mole of hydrocarbon for C_2 chlorinated hydrocarbons. Table 2 shows the change in equilibrium composition as the steam ratio is changed for methyl chloride.

The addition of a base to the reaction results in formation of the a chloride salt rather than HCl, the formation of a carbonate salt rather than CO_2 , and the formation of a hydroxide salt rather than steam. Theoretically, by careful selection of the amount of steam and base, a gaseous effluent of only methane and hydrogen could be obtained, assuming equilibrium is reached in the reaction. For example, the only gaseous equilibrium products for the reaction of 1 mole of DCE with 6 moles of NaOH are 0.01 moles methane and 3.96 moles hydrogen, or for the reaction of 1 mole of C_2Cl_6 with 2 moles of water and 7 moles of CaO, 0.23 moles of methane and 0.06 moles of hydrogen.

Table 3 shows the effect of the amount of base, CaO or NaOH, on the conversion of chlorinated hydrocarbons.

Less steam is needed to avoid carbon formation when a base is present than when no base is present. For CaO, the minimum steam ratio is approximately 1 mole steam per mole of carbon, while for NaOH, no steam is required.

Table 1. Equilibrium composition for thermal decomposition of chlorinated hydrocarbons.

Reactant (1 mole)	Equilibrium composition at 300°C (moles)					
	CCl_4	HCl	Carbon	Methane	Cl_2	H_2
CCl_4	0.90	—	0.10	—	0.20	—
CH_3Cl	—	1.0	0.53	0.47	—	0.06
Cl_2CCH_2	—	2.0	2.00	—	—	—
$\text{Cl}_3\text{CCH}_2\text{Cl}$	0.40	2.0	1.60	—	0.20	—
Cl_3CCCl_3	1.35	—	0.65	—	0.30	—

Table 2. Effect of steam ratio on equilibrium composition for methyl chloride.

Moles steam per mole methyl chloride	Equilibrium composition at 300°C (moles)					
	CH ₄	CO ₂	Carbon	HCl	H ₂ O	H ₂
0.0	0.47	—	0.53	1.00	—	0.06
0.5	0.50	0.04	0.45	1.00	0.42	0.07
1.0	0.58	0.12	0.30	1.00	0.76	0.08
1.5	0.67	0.21	0.12	1.00	1.07	0.10
2.0	0.69	0.24	—	1.00	1.50	0.12
2.5	0.71	0.28	—	1.00	1.93	0.14

Table 3. Effect of amount of base on equilibrium composition of CCl₄ and CH₃Cl.

Equilibrium composition at 300°C (moles)									
1. 0.9 CCl ₄ + 0.1 C ₂ Cl ₄ + x CaO + 3 H ₂ O =									
x	CH ₄	CO ₂	H ₂	H ₂ O	CaCl ₂	CaCO ₃	Ca(OH) ₂	CaO	Carbon
2	0.04	1.06	0.06	2.87	2.00	—	—	—	—
3	0.03	0.07	0.09	2.85	2.00	1.00	—	—	—
4	—	—	0.20	1.90	2.00	1.10	0.90	—	—
6	0.05	—	0.01	—	2.00	1.05	2.89	0.05	—
2. CH ₃ Cl + x CaO + 1.5 H ₂ O =									
1	0.50	—	1.00	1.00	0.50	0.50	—	—	—
2	0.62	—	0.52	0.12	0.50	0.38	1.12	—	—
3	0.71	—	0.17	0.002	0.50	0.29	1.41	0.79	—
3. C ₂ H ₂ Cl ₂ + x CaO + H ₂ O =									
1	0.39	0.42	0.06	1.16	1.00	—	—	—	1.19
2	0.97	—	0.07	—	1.00	1.00	—	—	0.03
4	0.97	—	0.07	0.002	1.00	1.00	—	2.00	0.03
4. 0.9 CCl ₄ + 0.1 C ₂ Cl ₄ + x NaOH + 2 H ₂ O =									
x	CH ₄	CO ₂	H ₂	H ₂ O	NaCl	Na ₂ CO ₃	NaOH		
4	0.03	1.07	0.07	3.86	4.00	—	—		
6	0.02	0.08	0.13	4.83	4.00	1.00	—		
8	—	—	0.20	4.90	4.00	1.10	1.80		
5. CH ₃ Cl + x NaOH + 1.5 H ₂ O =									
1	0.72	0.28	0.12	1.94	1.00	—	—		
2	0.50	—	0.50	2.00	1.00	0.50	—		
3	—	—	3.00	1.50	1.00	1.00	—		

Table 4 shows the effect of temperature on the equilibrium composition of the hydrolysis of C_2Cl_6 , based on 2 moles of steam and 4 moles of CaO per mole of C_2Cl_6 .

Temperature has very little effect on concentrations of most equilibrium species. Below 250°C, graphitic carbon is formed.

A-2.2 Pyrolysis and Hydrolysis of Freon

The major equilibrium products of the pyrolysis of $C_2F_2Cl_4$ at 300°C are graphitic carbon, CCl_4 , CF_4 , Cl_2 , CCl_3F , and CCl_2F_2 . As steam is added to this mixture, HCl and CO_2 are formed from CCl_4 plus steam, and small amounts of $COCIF$, COF_2 and $COCl_2$ at the expense of the chlorofluoromethanes. As the amount of steam is increased to 3 moles of steam per mole of $C_2F_2Cl_4$ or greater, the equilibrium form of all Cl is HCl and of F is HF. Most carbon will be in the form of CO_2 , but a steam ratio greater than 5 is needed to eliminate graphite from the equilibrium products.

Sodium hydroxide is capable thermodynamically of dehalogenating Freon. Steam is not required. Less than stoichiometric NaOH, relative to the number of halogen atoms of the Freon, results in HF plus NaCl in the equilibrium products, while stoichiometric NaOH yields NaF. Excess sodium hydroxide results in formation of sodium carbonate as well as sodium fluoride and sodium chloride. Equilibrium yields at various temperatures for 1,1,1,2-tetrachloro-2,2-difluoroethane are given in Table 5, for a reaction mixture of 1 mole of freon and 7 moles of NaOH.

As in the case of C_2Cl_6 , temperature has very little effect on equilibrium conversion.

A-2.3 Pyrolysis and Hydrolysis of Carbon Disulfide

The equilibrium products for pyrolysis of carbon disulfide at 300°C are graphitic carbon and liquid elemental sulfur.

The equilibrium products for the hydrolysis of 1 mole of CS_2 with 1 mole of water at 300°C are:

	<u>Moles</u>
Graphite	0.43
CO_2	0.43
COS	0.13
CS_2	0.01
H_2S	1.00
$S_{8(g)}$	0.054
$S_{(l)}$	0.42

Increasing the amount of steam will shift the sulfur-containing products to H_2S and away from elemental sulfur, and shift the carbon species to CO_2 and methane and away from graphite.

As CaO is added to the reaction mixture, in increasing amounts, first the CaO will consume carbon to form calcium carbonate, then convert H_2S to calcium sulfide, and then consume water to form calcium hydroxide. Traces of calcium sulfate will also be formed. This trend is opposite of that

Table 4. Effect of temperature on equilibrium composition for C_2Cl_6 .

Temperature (C)	CH ₄	CO ₂	H ₂	H ₂ O	CaCl ₂	CaCO ₃	Carbon	CO (ppm)
150	0.18	0.68	0.002	1.63	3.00	1.00	0.14	0.5
200	0.23	0.73	0.01	1.54	3.00	1.00	0.05	7
250	0.24	0.76	0.02	1.49	3.00	1.00	—	53
300	0.24	0.76	0.06	1.47	3.00	1.00	—	286

Table 5. Effect of temperature on equilibrium composition for $C_2Cl_4F_2$.

Temperature (C)	CH ₄	CO ₂	H ₂	H ₂ O	NaCl	NaF	Na ₂ CO ₃
200	0.25	1.25	0.01	2.99	4.00	2.00	0.50
250	0.24	1.26	0.04	2.98	4.00	2.00	0.50
300	0.23	1.27	0.09	2.95	4.00	2.00	0.50
350	0.20	1.29	0.19	2.90	4.00	2.00	0.50

of the addition of CaO to chlorinated hydrocarbons, in which chloride salt is formed preferentially to carbonate.

A-2.4 Hydrolysis of Nonchlorinated Hydrocarbons

In contrast to the results found for chlorinated light hydrocarbons, both steam and base are needed to avoid carbon in the equilibrium products from benzene. The equilibrium products for the decomposition of benzene at 300°C are 76 mole% carbon and 24 mole% methane, *whether or not NaOH is added*. With excess base, a minimum of 6 moles of water per mole of benzene is required to avoid carbon formation for CaO, and a minimum of 4 moles of water per mole of benzene is required for NaOH. Graphitic carbon may also be formed at high steam ratios if inadequate base is present to convert all carbon to carbonate. Table 6 shows equilibrium compositions for benzene at a variety of conditions.

For acetone with CaO, methane and hydrogen are the predominant equilibrium products, and their yields somewhat insensitive to ratios of water or base in the feed. Increases in water or base to the feed results in increases in calcium hydroxide and unreacted CaO in the products. Even with excess CaO, nearly two-thirds of the total carbon is in the form of methane at equilibrium. In contrast, for acetone with NaOH, yields of hydrogen and methane were highly sensitive to feed water and base ratios, and all carbon is converted to carbonate to the limit of the sodium present in the reaction mixture.

Methanol, ethylene glycol, and monoethanolamine (MEA) follow the same pattern as acetone. The equilibrium form of nitrogen from MEA is diatomic nitrogen gas. Levels of NO_x are 10⁻²⁶ moles/

Table 6. Equilibrium yields for benzene.

Feed (moles per mole C ₆ H ₆)		Equilibrium composition at 300°C (moles)							
		CH ₄	CO ₂	H ₂	H ₂ O	Carbon	CaCO ₃	Ca(OH) ₂	CaO
Steam	CaO								
6	0	2.29	0.93	0.28	4.1	2.78	—	—	—
6	1	2.79	0.43	0.29	3.1	1.77	1.00	—	—
6	2	3.89	—	0.30	0.94	0.09	2.00	—	—
6	3	3.25	—	1.99	0.25	—	2.75	0.25	—
6	6	3.54	—	0.83	0.01	—	2.46	1.07	2.47
3	6	2.90	—	0.20	—	1.60	1.50	—	1.50

Feed (moles per mole C ₆ H ₆)		CH ₄	CO ₂	H ₂	H ₂ O	Carbon	Na ₂ CO ₃	NaOH
Steam	NaOH							
6	3	3.30	—	0.34	3.55	0.72	1.50	—
6	4	3.66	—	0.36	3.32	—	2.00	—
6	6	3.00	—	3.00	3.00	—	3.00	—
6	8	2.00	—	7.00	—	—	4.00	—
4	4	3.46	0.11	2.97	1.77	0.42	2.00	—
4	6	3.00	—	3.00	—	—	3.00	—
2	6	3.38	—	2.34	—	0.62	2.00	2.00
0	6	1.45	—	0.10	—	4.55	—	6.00

mole MEA at 300°C and increase to only 10^{-10} moles/mole MEA at 900°C. The more oxygen in the organic molecule, the less water is needed to avoid carbon formation. Yields for ethylene glycol and CaO are shown in Table 7.

Equilibrium conversion for ethylene glycol is very insensitive to temperature, as shown in Table 8. Yields of CO are very low from ethylene glycol, 0.03 ppm at 300°C, 1 mole steam per mole ethylene glycol, and 3 moles of CaO per mole ethylene glycol.

A-3. HYDROGENATION

Figure 1 shows the equilibrium yields of graphitic carbon, methane and hydrogen for varying amounts of hydrogen in the hydrogenation of C₂Cl₆. At ratios of 3 moles of hydrogen per mole

Table 7. Equilibrium conversion of ethylene glycol.

Moles per mole EG		Equilibrium composition at 300°C (moles)							
		CH ₄	CO ₂	H ₂	H ₂ O	CaCO ₃	Ca(OH) ₂	CaO	Carbon
1	0	0.95	0.51	0.12	1.98	—	—	—	0.54
1	1	1.00	—	1.00	1.00	1.00	—	—	—
1	2	1.08	—	0.66	0.08	0.92	1.08	—	—
1	4	1.18	—	0.28	—	0.82	1.36	1.82	—
2	3	0.87	—	1.51	0.87	1.13	0.87	—	—
2	4	1.18	—	0.28	—	0.82	2.36	0.82	—
2	6	1.18	—	0.28	—	0.82	2.36	2.82	—

Table 8. Effect of temperature on equilibrium conversion of ethylene glycol (1 mole steam and 3 moles CaO per mole ethylene glycol).

Temperature (C)	Equilibrium composition (moles)				
	CH ₄	H ₂	Ca(OH) ₂	CaCO ₃	CaO
150	1.25	0.001	1.50	0.75	0.75
200	1.24	0.02	1.49	0.76	0.76
250	1.23	0.09	1.45	0.77	0.77
300	1.18	0.28	1.36	0.82	0.82

A-10

Figure 1. Hydrogenation of C²Cl⁶.

C_2Cl_6 or higher, all chlorine is in the form of HCl. The figure shows that the minimum amount of hydrogen needed to avoid carbon formation is slightly greater than the stoichiometric amount needed to form HCl and methane. Results for other chlorinated and fluorinated hydrocarbons are similar.

In order to compare hydrolysis and hydrogenation, equilibrium compositions were determined for chlorinated hydrocarbons with three sources of hydrogen—hydrogen gas, methane, and methanol. Table 9 presents a comparison equilibrium compositions for hydrogenation and hydrolysis for DCE, Table 10 for methyl chloride, and Table 11 for chloroform. For all hydrogen sources, including water, the total hydrogen in the reaction mixture was equivalent.

All sources of hydrogen dechlorinate the reactant chlorine compound. Equilibrium concentrations of the fuel gases hydrogen and methane are notably less for water than the other three reactants. Methane is unique among the four hydrogen sources in that carbon is among the equilibrium products for each of the three chlorinated hydrocarbons, and for DCE, water was the only reactant that did not give any carbon in the equilibrium products. In each feed case, methane used the least CaO, while water consumed the most.

The same trends are seen with hydrogenation of CS_2 . Hydrogen gas, methane, methanol, and water are all able to completely convert carbon disulfide to hydrogen sulfide, assuming equilibrium is reached. Carbon shows up in the equilibrium products when methane is used. Water results in the least amount of fuel gases and requires the most base.

A-4. EQUILIBRIUM COMPOSITION OF MIXTURES

Equilibrium calculations were performed for the mixture of 20 moles TRIM®SOL, 6 moles methanol, 6 moles acetone, 6 moles ethylene glycol, 6 moles dichloroethane, 6 moles carbon tetrachloride, 6 moles benzene, and 4 moles monoethanolamine. The amount of water, hydrogen, and base was varied from run to run.

A-4.1 Dechlorination by Hydrogenation

It was found that a ratio of greater than 11 moles of hydrogen to one mole of hydrocarbon was needed to avoid carbon formation. Over the range of hydrogen to feed ratios of 2 to 11 and a temperature of 300°C, the equilibrium form of chlorine was HCl; of sulfur, H_2S ; of oxygen, steam; and of carbon, graphite and methane. Yields are shown in Table 12.

Table 9. Equilibrium composition of 1 mole DCE plus 6 moles CaO plus 2 moles of H_2 .

H_2 source	Equilibrium composition at 300°C (moles)						
	CH_4	H_2	Carbon	$CaCl_2$	$Ca(OH)_2$	$CaCO_3$	CaO
H_2	1.45	1.00	0.05	1.00	—	0.50	4.50
CH_4	1.45	1.00	1.05	1.00	—	0.50	4.50
CH_3OH	1.45	1.00	0.55	1.00	—	1.00	4.00
H_2O	0.94	0.22	—	1.00	0.89	1.06	3.06

Table 10. Equilibrium composition of 1 mole CH_3Cl plus 6 moles CaO plus 2 moles of H_2 .

H_2 source	Equilibrium composition at 300°C (moles)						
	CH_4	H_2	Carbon	CaCl_2	Ca(OH)_2	CaCO_3	CaO
H_2	1.00	1.00	—	0.50	0.50	—	5.00
CH_4	1.69	0.12	0.06	0.50	—	0.25	5.25
CH_3OH	1.42	0.33	—	0.50	0.33	0.58	4.59
H_2O	0.71	0.17	—	0.50	1.71	0.29	3.30

Table 11. Equilibrium composition of 1 mole CHCl_3 plus 6 moles CaO plus 2 moles of H_2 .

H_2 source	Equilibrium composition at 300°C (moles)						
	CH_4	H_2	Carbon	CaCl_2	Ca(OH)_2	CaCO_3	CaO
H_2	0.71	0.17	—	1.50	0.91	0.29	3.29
CH_4	1.21	0.08	0.04	1.50	—	0.75	3.75
CH_3OH	0.94	0.22	—	1.50	0.39	1.05	3.06
H_2O	0.23	0.06	—	1.50	1.97	0.76	1.76

Table 12. Equilibrium composition of waste mixture dechlorinated with hydrogen.

Moles H_2 to moles hydrocarbon	Equilibrium composition at 300°C (moles per mole HC feed)						
	CH_4	Carbon	CO_2	H_2	H_2O	HCl	H_2S
2:1	3.93	4.34	0.03	0.34	0.96	1.17	0.04
4:1	4.89	3.38	0.03	0.41	0.97	1.17	0.04
6:1	5.86	2.42	0.02	0.47	0.98	1.17	0.04
10:1	7.79	0.50	0.02	0.61	0.99	1.17	0.04
11:1	8.27	0.01	0.02	0.65	0.99	1.17	0.04

A-4.2 Dechlorination by Hydrolysis and Strong Base

With no base, a ratio of 12 moles of steam per mole of hydrocarbon is required to avoid carbon formation. However, addition of a base reduced the steam requirement drastically, and if a sufficient amount of base is added, no steam is required. Table 13 shows equilibrium yields for cases of steam and calcium hydroxide. Some yields are not shown in Table 13. Organic nitrogen in the feed will yield diatomic nitrogen with traces of ammonia. Sulfur will form H_2S in the absence of a base, of the sulfide salt if a base is present, with traces of H_2S . All chlorine in the feed will form HCl in the absence of a base, or the chloride salt if base is present.

A-5. CHEMICAL INTERACTIONS WITH ALUMINA

Alumina is a widely used catalyst support or cocatalyst for hydrogenation and dechlorination reactions. Based on SOLGASMIX-PV equilibrium calculations of reactions with no base present, no decomposition of Al_2O_3 will occur in the hydrogenation of CCl_4 at temperatures from 200–400°C. The same is true of the hydrolysis of DCE at 350°C, hydrogenation of DCE at 350°C, and the hydrogenation of dichlorobenzene at 350°C. With a feed of CS_2 , parts-per-billion levels of aluminum sulfide appear in the equilibrium products.

When calcium oxide is present in the reaction mixture along with alumina, the equilibrium form of Al is a combination of calcium aluminates, $CaAlO_4$ and $Ca_3Al_2O_6$.

Table 13. Equilibrium composition of waste mixture dechlorinated with steam and/or base.

Reactants (per mole HC)		Equilibrium composition at 300°C (moles per mole HC feed)							
H_2O	$Ca(OH)_2$	CH_4	CO_2	H_2	H_2O	Carbon	$Ca(OH)_2$	$CaCO_3$	yCaO
8	0	4.09	1.27	0.50	6.48	2.95	—	—	—
2	0	3.16	0.25	0.33	2.52	4.89	—	—	—
2	1.7	4.18	0.21	0.38	2.68	2.82	—	1.08	—
2	5.0	4.76	—	3.69	0.72	—	0.85	3.53	—
2	8.3	4.76	—	3.69	0.72	—	4.18	3.53	—
1	5.0	5.16	—	2.12	0.11	—	1.24	3.14	—
0	5.0	5.37	—	1.26	0.02	—	0.76	2.93	0.69

Appendix B

Dechlorination Catalyst Recommendation

INTEROFFICE CORRESPONDENCE

Date: December 13, 1993
To: Charles Barnes, MS 3625
From: Daniel Ginosar, MS 3625 *Daniel Ginosar*
Subject: SCWO PRETREATMENT VAPOR PHASE CATALYST SELECTION - DMG-02-93

A preliminary selection of catalysts for vapor phase reaction testing is complete. A final selection will be made following input from catalyst vendors and EG&G Idaho, Inc. personnel with catalysis expertise.

The following types of catalyst are proposed for testing:

NiMo/ γ Al₂O₃ - sulfided
PtPd/ γ Al₂O₃
CaCO₃ - potassium permanganate, copper chloride
Metal Alloy Oxide

The NiMo/ γ Al₂O₃ - sulfided catalyst has been studied^{1,2} for the vapor phase dechlorination of chlorobenzene and dichlorobenzene. Sulfiding the catalyst was necessary to obtain the catalytic activity¹. The NiMo/ γ Al₂O₃ catalyst was used at temperatures from 200 to 350°C, pressures of 100 atm and a hydrogen to organic ratio of 2.6. CoMo/ γ Al₂O₃ catalyst should in general have similar activity to the Ni based catalyst; however, the Co based catalyst ~~are~~ *is* currently 50% higher in price³. Both catalysts may be very active at pressures as low as 20 atm, and both are resistant to sulfur deactivation, used commonly to hydrogenate sulfur streams at 1500 ppm levels³. These catalysts are used for desulfurization and denitrogenation as well as dehaolgenation reactions.

Precious metal catalysts such as Pt and Pd can have higher activity; however, they are susceptible to deactivation by sulfur and are significantly higher in cost than NiMo catalyst. Pd/ α Al₂O₃ catalysts have been shown to catalyze the hydrodechlorination of Polychlorinated Biphenyls (PCB) at a temperature of 220°C, and 2.3 atm hydrogen pressure⁴. Additionally, a Pt based catalyst has been tested at EG&G Idaho for the hydrodechlorination of PCBs where either methanol or hexane was used as the source of hydrogen⁵. PtPd/ γ Al₂O₃ catalyst are being manufactured with higher sulfur resistance and are being used in 300 ppm sulfur streams³.

Base catalysts have the advantage of adsorbing the acid gasses produced during reaction, thereby eliminating continued gas phase chlorination reactions. A CaCO_3 - potassium permanganate, copper chloride catalyst was shown to be effective in the oxidation of trichloroethylene⁶ and might be applied to a hydrogenation reaction. The CaCO_3 portion of the catalyst is consumed in the reaction.

Metal alloy oxide catalysts are being developed at EG&G to replace Pt group based catalyst. These catalysts are similar to Pt group based catalysts in function, are lower in cost, higher in availability and are more resistant to deactivation by sulfur⁷. A metal alloy oxide catalyst could provide the high activity of the Pt or Pd based catalyst, have the ability to utilize methanol or hexane as a source of hydrogen, have the sulfur resistance of the NiMo based catalyst and have costs typical of NiMo based catalysts.

For each type of reaction, a source of hydrogen is required. This source may be either hydrogen gas, methane gas, methanol, water or hydrocarbons in the process waste. The process waste may not be a suitable choice due to the variation in feed composition expected.

In addition to in-house catalyst testing, the UOP Inc. Hychlor process should be considered. The UOP process utilizes a pre-treatment separation step to remove catalyst poisons, a catalytic hydrogenation reactor, and a post-treatment step to meet effluent specifications. The reactor uses hydrogen as a feed, and operates in a 15-69 atm pressure range with temperatures between 66 and 370°C. The process effluent are hydrogen gas for recycle to the reactor, an aqueous fraction containing salts and the decontaminated organic product⁸.

Based on the above, it is recommended that the four types of catalyst listed above be tested in-house for the vapor phase reactor. NiMo/ $\gamma\text{Al}_2\text{O}_3$ and PtPd/ $\gamma\text{Al}_2\text{O}_3$ catalyst samples may be obtained for testing from standard catalyst manufactures, such as Criterion Catalyst Co. or United Catalysts while the CaCO_3 - potassium permanganate, copper chloride and the metal alloy oxide catalyst samples may need to be produced in-house.

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blm

cc: J. J. McCarthy, MS 3625
Project File
Central Files, MS 1651
D. M. Ginosar Letter File

Appendix C

Response of SDTX Technologies to Process Inquiry

SDTX TECHNOLOGIES, INC.

706 Sayre Drive • Princeton, NJ 08540 • Tel: 609-452-0955 • FAX: 609-452-7670

82
December 14, 1993

VIA FACSIMILE

Mr. Charles Barnes
EG & G, Idaho
P.O.Box 1625
Idaho Falls, ID 83415 - 3625

Dear Mr. Barnes:

This letter responds to yours of November 8 as amplified by our telephone conversation of November 17.

EG&G wishes to consider KPEGsm dechlorination as a pretreatment to reduce the corrosivity of chlorinated wastes in supercritical water oxidation (SCWO). We both understand that once they have been completely dechlorinated, the wastes may not need as exotic a treatment as SCWO. I trust that you further understand from our conversations and the article I sent you that KPEGsm is a proprietary chemistry, not limited to a specific process implementation.

SDTX, however, has a particular competency in conceptualizing processes based on first principles and developing these processes based on appropriate experimental (Treatability) data. Although there is no data on KPEGsm dechlorination of your baseline feed and no KPEGsm unit now operating on liquids, we can provide a conceptual design and economics to support your present evaluation.

The paragraphs below follow the outline in your letter:

Process Description

We visualize a skid-mounted continuous mini-plant comprising the steps of first drying the feedstock by azeotropic distillation using the methanol and acetone in the feed then reacting the dry liquid with NaPEGsm in a cooled continuous plug flow reactor. NaPEGsm would be made, batchwise, on site from the reaction of NaOH and PEG. A block diagram is attached.

Capital Cost Estimate

At the 500 GPD level, such a unit would cost in the area of \$ 500,000, including engineering. This figure is provided to allow you to handle capital cost in a consistent manner.

Obviously, there are many options for how this project is handled. Depending, for example,

New York
8105 81st Street
Middle Village, NY 11379
Tel: 718-429-1620
FAX: 718-672-8744

Texas
1010 Lamar, Suite 450
Houston, Texas 77002
713-759-9070
FAX: 713-759-9590

Colorado
1700 Lincoln, Suite 5000
Denver, Colorado 80203
Tel: 303-832-3131
FAX: 303-894-9088

Mr. Charles Barnes page two

on whether SDTX sells or leases you a unit, or provides a service or merely a design, will govern the size and structure of our royalty. In any case, royalty should affect the choice between treatment options.

Operating Cost Estimate

My calculation from the data in your letter is that the contaminated liquid stream is about 15% chlorine by weight. Based on this, PEG consumption would be about 1.8 lbs/lb of total liquid and NaOH consumption would be about 1.35 lbs/lb. You can get up-to-date costs for these from Chemical Marketing Reporter, but I use \$1/lb of PEG for the combination; its been historically close. Other consumables and utilities would add about \$.05-.10/lb additional. The unit needs to be manned three shifts by two men per shift at your labor rate.

Testing, demonstration etc. of the process

$$\begin{aligned} 1.8/16 &= .1125 \\ .05 - .10/16 &= .003125 \end{aligned}$$

The chemistry of KPEGsm has a long history in liquids. In fact, much of the PCB contaminated transformer fluid in America has been treated with this chemistry.

Limitations of process for alternative feeds

The KPEGsm chemistry will dechlorinate alternative feeds 1,2,4 and 5. Different equipment configurations than that envisioned herein will, however, be required for the solid phase material of alternate feeds 4 and 5. There may be some reaction with stream 3; we expect to be doing a research program shortly which will throw some light on this. No basis to even guess at alternative stream 6.

Secondary wastes generated

The streams exiting the process are shown in the block diagram. The NaCl stream may be recovered as shown, or may be passed to the SCWO unit. In the former case, the SCWO sees no halogen, but a solids wetted with KPEGsm reaction products is generated. This would need to be considered from an overall system perspective.

Safety, reliability, etc.

There should be no problem in configuring a safe reliable and easy to operate unit.

Based on our experience, it is not clear that KPEGsm is the right dehalogenation option for your baseline feed. Given your timing constraints, however, we have responded with

Mr. Charles Barnes page three

economics. Once you have completed your December 10 evaluation, however, it may be worthwhile to return to this point. SDTX has other chemistries that may be more relevant.

SDTX does believe that KPEGsm is particularly suited to the 31000 m³ of solid waste mentioned in your letter. We understand that the present inquiry is not directed to this material; please, however, keep us in mind for this.

Should you need to reach me, please feel free to do so at my home office:

RR 1 Box 422
Hensonville, NY 12439
Phone: 518-734-4483
Fax: 518-734-5802

Yours very truly,

A handwritten signature in cursive script, appearing to read "Robert Hoch".

Robert Hoch
RH/is

BLOCK DIAGRAM
of
CONCEPTUAL
DECHLORINATION
for
JNER

ITEM NO.:

DATE:

SUBJECT:

MEMO OF CONVERSATION

Person Called Robert Hoch Date December 14, 1993
Representing SDTX Technologies Time 3:30 PM
Person Calling Charles Barnes Phone 518-734-4483
Representing INEL

Subject: Dehalogenation Processes

Conversation: I called Mr. Hoch because of his comment on p. 2 that said that it was not clear that KPEG[™] is the right process for our needs, and asked him to elaborate. He recognized that because of the expense of the KPEG[™] reagent, it would probably not be economic compared to alternative processes. When I asked him for his opinion of alternatives, he mentioned three. Using a strong base (without PEG) would be effective for dechlorinating aliphatics but not aromatics such as PCB. With aromatics, a base will replace one chlorine atom with a hydroxyl group, but then is resistant to further dechlorination.

The other two options he mentioned were catalytic hydrogenation and superoxidation. For the former, he said it would take some development finding the right catalyst and conditions, while the other would likely take considerable development.

Appendix D

Response of UOP to Process Inquiry

UOP
25 East Algonquin Road
Des Plaines, Illinois 60017-5017
Telephone: 708-391-2000
FAX: 708-391-2253
Telex: 211-442

November 30, 1993

Mr. Charles Barnes, Sr.
Engineering Specialist
Chemical and Process Engineering
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415

Dear Mr. Barnes:

Thank you for your letter of November 4, 1993 requesting additional information on UOP's technologies as they might pertain to the treatment of mixed hazardous and radioactive wastes. Undercover is a technical proposal specifically addressing the technical and economic questions you raised relative to the baseline case in your letter. In short, we believe our HyChlor Process, modified as described in the proposal, will achieve the performance goal you indicated: a maximum of 100 wt-ppm heteroatom contamination in the organic phase.

In addition to the baseline case, you inquired as to the viability of treating some alternative cases. Attached to this letter as Table 1 is a short summary of our assessment employing UOP's technology in the cases you raised.

If the technology and the approach recommended in the proposal look attractive to you, both technically and economically, I propose that we discuss convening a meeting at your offices in the near future to pursue any questions you may have and to talk about how to proceed to the next step. Mixed waste is a unique treatment problem and we would like the opportunity of working with you to solve it. Best regards.

Sincerely,

D. R. Hedden
Manager, Marketing & Sales
Environmental Control &
Management Systems

Enclosures

Table 1
Alternate Case Treatment Summary

<u>Alt. Case</u>	<u>Case Description</u>	<u>Technology Option</u>
1.	100% TRIM@SOL	Same as baseline case
2.	50% carbon tetrachloride, 48% tetrachloroethylene, 2% Freon 113	Second stage of baseline case
3.	45% Tributyl phosphate, 5% dibutyl phosphate, 50% c10-c14 n-paraffins	High temperature decomposition, no UOP technology option at this time
4.	Organic sludge containing 33 wt-% calcium silicate, 13 wt-% carbon tetrachloride, 7 wt-% 1,1,1 trichloroethane, 28 wt-% ethylene glycol, 19 wt-% Texaco Regal oil	Proprietary UOP Hydrogen Flash separation followed by second stage of baseline case
5.	Spent activated carbon containing 20 wt-% carbon tetrachloride	High temperature decomposition, no UOP technology option at this time
6.	Shredded and ground combustible waste containing 5 wt-% polyvinyl chloride, 35 wt-% polyethylene, and paper, cloth and wood	High temperature decomposition, no UOP technology option at this time

UOP HyChlor™ PROCESS

for the

**Conversion of Mixed Hazardous and Radioactive
Liquid Waste Solvents**

**EG&G-Idaho, Inc.
Idaho National Engineering Laboratory
Idaho Falls, Idaho**

Non-Proprietary Technical Proposal

November 30, 1993

**EG&G-Idaho, Inc.
Idaho Falls, Idaho**

UOP HyChlor™ Process

Executive Summary

Based on the information in connection with mixed hazardous and radioactive wastes contained in the letter from Mr. Charles Barnes Sr, dated November 4, 1993, UOP proposes that EG&G-Idaho, Inc. consider using UOP's fully demonstrated, proprietary HyChlor Process to convert the hazardous organic portions of the baseline waste characterized in the letter to materials containing less than 100 wt-ppm of halogens plus sulfur plus nitrogen.

The estimate of the erected capital investment for a Process unit with a capacity of 500 gallons per day is \$2.5 million. The utilities and consumables requirements are approximately \$0.80 per gallon of waste treated.

If the HyChlor approach meets the technical and economic requirements for the mixed waste treatment project, a treatability verification study on non-radioactive material could be performed in a 3-5 week period at a cost to EG&G-Idaho in the range of \$75,000-\$80,000.

**EG&G-Idaho, Inc.
Idaho Falls, Idaho.**

UOP HyChlor™ Process

Section I

Technology Background and Experience

A. Technology Basis

The increasing concern being shown worldwide for environmental protection and the associated increase in ever more restrictive legislation, most particularly hazardous waste incinerators, presents users and manufacturers of chlorine-based petrochemicals with unique challenges to the disposal, or possible reuse, of the hazardous chlorinated organic by-products and residues. For example, the by-product streams generated in the production of epichlorohydrin or propylene oxide represent complex mixtures of chlorinated hydrocarbons and oxygenates, some of which are highly toxic and thermally unstable. Incineration has been the traditional route selected for the disposal of these chlorinated materials requiring high operating temperatures ($>1,200^{\circ}\text{C}$) and generating large volumes of gaseous and liquid effluents. In addition, both the capital cost and permitting requirements associated with new hazardous waste incineration capacity provide an incentive for chemical users and producers to invest in recycling versus destructive technology.

UOP developed the HyChlor Process in an effort to advance recycling technology through the use of catalytic hydrodehalogenation. In contrast to thermal treatment processes, the HyChlor Process operates at relatively mild conditions ($100\text{-}300^{\circ}\text{C}$) and generates hydrogen chloride and hydrocarbon products that are suitable for recycle and reuse. The Process is environmentally friendly since it does not produce any greenhouse gases or products of incomplete combustion, such as dioxins or phosgene. In addition, the Process is a totally enclosed system such that if any unconverted materials were generated during an operational upset they can be captured for re-processing rather than being released to the environment. Most important, the Process's economics are competitive when compared at the same performance level as incineration; plus, the value of the recovered products and the lower maintenance requirements provide a more attractive operating cost.

B. HyChlor Process Experience

UOP has been developing and commercializing new technology since 1914 and has at the present time over 8,000 licensable patent rights.

The HyChlor Process was developed and patented in 1987 and since that time has been in operation on a wide variety of feed stocks in two continuous pilot plants located at UOP's Des Plaines, Illinois Research Center. In 1992 a fully integrated demonstration unit was successfully operated in Western Europe and a second demonstration unit is currently in operation with a target completion date of December, 1993. A few examples of the hazardous waste feed stocks that have been treated by the Process include:

- Still bottoms from the production of epichlorohydrin
- Heavy tar from the production of ethylene dichloride and vinyl chloride monomer
- Light ends from the production of ethylene dichloride
- Still bottoms from the production of propylene oxide (chlorine route)

The Process is based around fixed bed catalytic hydrogenation similar to that which has been practiced since the late 1940s in crude oil refineries to remove sulfur, nitrogen and similar contaminants from petroleum fractions. However, in the HyChlor Process the object is to recover the inorganic acid and hydrocarbon products for their inherent market value. All of the Process unit operations and equipment materials of construction have been rigorously, and successfully, demonstrated.

C. HyChlor Process Advantages

UOP's objective in developing HyChlor was to produce a treatment technology that (i) was flexible enough to treat a wide variety of organic liquid residues; (ii) would eliminate the production of toxic materials such as dioxins and furans; and, (iii) was economically competitive with hazardous waste incineration alternatives. The result is a new advanced technology that, when processing pumpable highly chlorinated liquid hazardous wastes, will:

- Meet or exceed U.S. destruction and removal efficiencies for the hazardous waste's principle organic hazardous constituents;
- Prevent discharges from both normal and abnormal operations that could be harmful to human health and the environment; and,
- Cost no more than current hazardous waste incineration options.

**EG&G-Idaho, Inc.
Idaho Falls, Idaho.**

UOP HyChlor™ Process

Section II

Process Description

A. Overview

The HyChlor Process has been developed to be flexible with respect to the material to be processed and simple with respect to its day to day operation. The individual unit operations comprising the Process are:

- Conversion Reactors
- Acid Gases Absorption and/or Neutralization
- Reaction Products Recovery System

The Process objective traditionally is to dechlorinate a raw highly chlorinated feed stock (i) without fouling the Process catalyst system or equipment; and, (ii) without corroding the Process equipment. Chlorinated organics tend to be very thermally unstable such that when heated they decompose forming polymers and in some instances coke. To eliminate this concern, the Process uses heated hydrogen to avoid directly heating the feed stocks by reboiling or heat exchange thus limiting the conditions for the materials to decompose and generate coke. As a basic Process philosophy, the feed stock never sees high temperature unless large amounts of hydrogen are present.

Given the mix of sulfur and nitrogen as well as halogenates in the EG&G-Idaho mixed hazardous and radioactive waste feedstock, the implementation of the Process will be modified. Following is a brief description of the Process scheme to treat the mixed wastes. A flow diagram of the proposed scheme is included at the end of this Section.

B. Process Description

The Process objective will be to convert the mixed waste feedstock in two stages. The first stage will use catalytic hydrogenation to remove the sulfur and nitrogen contamination from the feedstock followed by neutralization and recovery of the resultant inorganic reaction products. The second stage will also use catalytic hydrogenation to dehalogenate the organic portion of the first stage

waste again followed by neutralization and recover of the inorganic reaction products. Based on cost, treatment requirements and similar project issues, the two step Process can be considered as either a continuous sequential operation or a batch operation where the first and second stages are carried out using the same equipment.

1. First Stage Operation

The raw feed stock would be mixed with heated recycle hydrogen and charged to the first stage hydrogenation reactor. The reactor's feed temperature would be adjusted to achieve the desired levels of desulfurization and denitrification. The hydrogenation reactor uses a commercially available UOP catalyst and produces a reaction effluent which consists of hydrogen sulfide, hydrogen halides, ammonia, hydrogen, hydrocarbon, and the unconverted organohalides. The reactor's conditions are chosen to maintain a temperature above the dew point of the acid gases produced.

The reaction effluent would be scrubbed with caustic to remove the inorganic acid gases. The neutralized material would then go to the Product Separator where the hydrogen-rich gas phase, the aqueous brine phase and the organic product phase would be separated. The hydrogen gas would be heated and returned to the hydrogenation reactor along with fresh makeup hydrogen to replace the hydrogen that has been consumed in the first stage. The caustic neutralization solution would be continuously circulated and from this stream a small amount of brine would be removed and a corresponding amount of fresh makeup caustic added. The brine would be free of organohalides.

The destination of the organic product phase containing the unconverted organohalides depends on the continuous versus batch operation question mentioned above. If continuous, the hydrocarbon product would pass directly to the second stage. If a batch operation, the hydrocarbon product would have its light gases removed prior to the material going to storage.

2. Second Stage Operation

The first stage organic phase, either from the first stage Product Separator or from storage, would again be mixed with heated recycle hydrogen and charged to the second stage hydrogenation conversion reactor. The reactor's feed temperature would be adjusted to achieve the desired conversion of organohalides. The second stage reactor also employs a commercially available UOP catalyst. The reaction effluent in this case consists of halide

acid gases, hydrogen, hydrocarbon, plus any unconverted organohalides based on the selected conversion efficiency.

The reaction effluent would be continuously scrubbed with caustic to neutralize the hydrogen halides. As in the first stage, the neutralized material would go to a Product Separator where the hydrogen-rich gas phase, the aqueous brine and fully treated organic product would be separated. The hydrogen gas would be heated and returned to the second stage reactor with fresh makeup hydrogen added to replace the hydrogen that has been consumed. Again, as in the first stage, a caustic neutralization solution would be continuously circulated and from this stream a small amount of brine would be constantly removed and a corresponding amount of makeup caustic added. This brine would also be free of organohalides.

As with the continuous versus batch operation question, further recovery operations for the clean organic phase would be set by economic, not technical, boundaries. If there is interest, it would be possible using a product fractionator, to recover a butane and heavier liquid stream, a propane product and an ethane and lighter stream.

UOP HyChlor Process Unit

Mixed Hazardous and Radioactive Wastes

Schematic Flow Diagram (Batch Operation)

EG&G-Idaho, Inc.
Idaho Falls, Idaho.

UOP HyChlor™ Process

Section III

Preliminary Basis of Design

A. Feed Stock Description

Following is a description of the mixed hazardous and radioactive waste feed stock used as the basis for the Process yields and pro-forma economics contained in this proposal. The basis for the compositional data that follows is information furnished by Mr. Charles Barnes, Sr. in his letter to Mr. D. R. Hedden dated November 4, 1993, attached in Appendix I.

1. Composition

	<u>wt-%</u>
water	6.60
benzene	4.31
methanol	1.77
acetone	3.20
ethylene glycol	3.43
carbon tetrachloride	8.48
dichloroethane	5.46
monoethanolamine	2.25
Trim®Sol	64.50
Total	100.00

2. Physical and Chemical Characteristics, wt-ppm

heptane insolubles	500
evaporative residue	200

B. Preliminary Treatment Objectives

1. Processing Capacity	175 lbs/hr
2. Products	100 wt-ppm total halides plus sulfur and nitrogen in hydrocarbon product

C. Estimated Process Yields

Based on the preliminary treatment objectives, the estimated combined hydrogenation reactor yields from processing the mixed waste feed stock described above are as follows:

<u>In</u>	<u>wt-%</u>
mixed waste feed	100.00
Hydrogen	3.50
Total	103.50
<u>Out</u>	
ammonia	1.31
hydrogen sulfide	0.69
hydrogen halide	19.46
water	16.71
propane & lighter	8.62
butane & heavier	56.71
Total	103.50

D. Estimated Product Qualities

As indicated in the Process Description, there would be basically an aqueous brine effluent and an organic product resulting from the catalytic hydrogenation of the mixed wastes. The aqueous brine would contain the sulfur, nitrogen and halides now in benign inorganic forms suitable for discharge to a POTW. The hydrocarbon product(s) would have less than 100 wt-ppm of total halides, sulfur and nitrogen.

EG&G-Idaho, Inc.
Idaho Falls, Idaho

UOP HyChlor™ Process

Section IV

Pro-forma Economics

A. Pro-Forma Economics Basis

In addition to the environmental benefits of destroying highly chlorinated residues in a fully-enclosed unit, HyChlor's economics compare favorably with those of hazardous waste incineration alternatives. Detailed cost analyses have confirmed that HyChlor's economics are very competitive, both capital investment and operating costs, when hazwaste incineration alternatives are designed and operated to either the destruction and removal efficiencies (DREs) set by the United States or the hazardous waste incineration Directive being set by the European Community (EC). The key for such a comparison is ensuring the incinerative and hydrogenation approaches are on an equal basis, i.e., equivalent destruction and removal efficiencies and air/water emission standards.

B. Estimated Capital Investment

On a U.S. Gulf Coast, open shop basis, the estimated capital investment for the HyChlor Process unit assuming a batch operation with the capacity to treat 500 gallons per day of mixed waste would be:

Materials and Labor	US\$1.5mm
Design Engineering/Construction Expenses	US\$1.0mm
Estimated Capital Investment	US\$2.5mm

For the purposes of this estimate, the basic engineering design and the detailed engineering design of the unit are assumed to be in accordance with UOP standards and specifications and U.S. federal, state and local codes. No adjustments have been made for utilization of the licensee's design standards.

C. Estimated Operating Costs

The following operating cost estimate accounts for the utility and consumables required to operate the two stages of the Process unit.

Estimated Operating Costs
(\$ per gal feedstock)

	<u>Rate</u>	<u>Cost</u>	<u>\$/gal feed</u>
<u>Consumables</u>			
Hydrogen	3.50 wt% Feed	\$6/1000 SCF H ₂	\$0.33
Catalyst	one year life (both stages)		\$0.015
NaOH	22.2 wt% Feed	\$0.15/lb NaOH	\$0.28
<u>Utilities</u>			
Power	50 kwh	\$0.045/kwh	\$0.11
Fuel	0.25 mmBtu/hr	\$5.00/mmBtu	\$0.06
Total			\$0.795

Estimates of the maintenance and labor costs associated with the operation depend to a great extent on the existing infrastructure at the site. However, there are no unusual daily or annual maintenance requirements and therefore, as a reference, the annual maintenance would be in the range of 3-4% of the unit's capital investment estimate. Direct labor to operate the unit would equate to roughly 2 persons per shift.

**EG&G-Idaho, Inc.
Idaho Falls, Idaho**

UOP HyChlor™ Process

Section V

Commercial Basis

A. License Agreement

UOP furnishes the rights to use its Process technology under the terms of a unit License Agreement. The agreement allows the licensee to utilize UOP's patents and technical information to operate the Process. In return for the rights to use the Process, the licensee is asked to make a one time payment to UOP based on the Unit's design processing capacity. The bases for the royalty rate include the complexity of treatment, the quantity of material to be treated, and the available commercial and developmental alternatives for treatment. At the current time depending on the application of the technology, the royalty rates vary in the range \$100 - \$2,000 per metric ton (\$0.005 - \$0.11 per gallon) of unit design capacity with a minimum license fee of \$750,000 for a commercial unit.

B. Technology Transfer

UOP would undertake the engineering, fabrication and assembly of the Process unit on modules and deliver the unit's modules and equipment, f.o.b. point of manufacture, on a firm fixed price basis. We believe this to be the most cost effective and time efficient way for our customers to place the Process technology in service. With UOP's fixed price offer, 75-80% of the required capital investment for the Process unit can be fixed at the outset of the project.

When EG&G-Idaho is ready to commence a project to install a Process unit, UOP would prepare the engineering design for the unit developed from a design basis mutually agreed upon by EG&G-Idaho and UOP. Completion by EG&G-Idaho of a UOP "Basis of Engineering Design Questionnaire" would be required in order to furnish UOP with the battery limit requirements for the Process unit along with the utility systems and general site details needed for the design, engineering and construction of the unit. Once the Questionnaire is compiled, UOP and EG&G-Idaho would meet for a Design Basis meeting to review the Process unit's design basis and address any questions.

Preparation of UOP's firm fixed price offer would begin once the basic engineering design was completed and it was reviewed by EG&G-Idaho. The offer would be released to EG&G-Idaho approximately 6-8 weeks after EG&G-

Idaho advised their satisfaction with the unit's basic engineering design. Preparation of the basic engineering design would require 18 - 26 weeks depending on the Process unit's complexity. EG&G-Idaho would be expected to pay UOP for preparation of both the basic engineering design information and the firm fixed price offer. The cost for this work falls within the accuracy of the capital investment estimate presented in the previous section of this proposal.

C. UOP Process Performance Guarantees

In support of the Process performance expectations, UOP will provide warranties based on mutually agreed feed stock definition; treatment requirements; and, product qualities. Typically, UOP will warrant the following aspects of a Process unit's performance:

A.	Throughput	Minimum daily processing rate
B.	Hydrogen Consumption	Maximum quantity of hydrogen consumed per unit of Feed Stock processed
C.	Liquid Hydrocarbon Product Quality	Maximum total chloride content in the propane produced
D.	Catalyst Life	Minimum number of days the catalyst will perform at the Process guarantee levels

It has been UOP's practice throughout its 75+ year history to furnish our customers with the strongest assurances possible that UOP technology will perform as represented.

D Preliminary Process Performance Evaluation

Our initial conclusion from a review of the feed stock information is that it is not significantly different from other hazardous wastes that UOP technology has successfully converted albeit that experience has been with non-radioactive materials. We propose at this stage that both parties continue discussions with the objective of further defining the level of detail EG&G-Idaho requires to fully assess the Process technology and to determine the most effective way to integrate a Process unit into the proposed treatment facility.

Given our review of the analytical characterization of the feed stock furnished by EG&G-Idaho before proceeding with any engineering work, we would want to undertake at our Research Center in Des Plaines, Illinois a 3-5 week pilot plant verification of the Process product yields and product qualities

employing a sample of the feed stock material. In this type of confirmatory activity, the Process products would be analyzed in detail by UOP and sufficient pilot plant performance data would be collected to assure closed material balances. A sample of the final treated organic liquid product would be available for analysis by EG&G-Idaho upon request.

To perform the work, EG&G-Idaho would be asked under the terms of a treatability study agreement to arrange for shipment to UOP of a twenty (20) liter sample of the non-radioactive material. UOP would furnish EG&G-Idaho with the appropriate information to ensure compliance with U.S. and Illinois hazardous waste shipping requirements. During the pilot plant activities, UOP would periodically communicate results and progress to EG&G-Idaho and upon completion of the work, a Technical Report would be issued summarizing the pilot plant results. These results would be used as needed in the production of the aforesaid engineering design information. In addition to furnishing the feed stock sample, EG&G-Idaho would be asked to financially support a portion of the costs, nominally \$75,000 - \$80,000, to perform the pilot plant verification work and the requisite feed stock and product analytical characterizations.

APPENDIX 1

November 4, 1993

Mr. D. R. Hedden
UOP
25 East Algonquin Road
Des Plaines, Illinois 60017-5017

WASTE DEHALOGENATION PROCESS INQUIRY - CMB-11-93

Dear Mr. Hedden:

Thank you for the information you recently sent Mr. Dan Ginosar on UOP's hazardous waste and waste oil technologies.

The Department of Energy (DOE) possesses large quantities of mixed hazardous and radioactive wastes at various sites across the country, including the Idaho National Engineering Laboratory. One technology that is being developed to treat a portion of these wastes is supercritical water oxidation. Tests to date of supercritical water oxidation of DOE wastes have shown high levels of corrosion in the reactor and associated equipment due to mineral acids produced from halogen-containing wastes.

The largest portion of mineral acid precursors in DOE wastes are in the form of chlorinated hydrocarbons, both solvents such as carbon tetrachloride and dichlorethylene, and cutting oils such as TRIM•SOL which contains chlorinated alkane polymers. Lesser amounts of DOE waste contains fluorinated hydrocarbons, sulfonated hydrocarbons, carbon disulfide, and tributyl phosphate. One option being evaluated to avoid the corrosive conditions that would result from oxidation of these compounds is to react or remove the mineral acid precursors in a pretreatment process prior to supercritical water oxidation.

We would like the following information on UOP's dechlorination process in order to include it in our evaluation:

1. Process description
2. ROM capital cost estimate for the baseline feed case, including any engineering and licensing fees
3. Operating cost estimates for the baseline feed case
4. Summary of testing, demonstration and operation experience of the process

Mr. D. R. Hedden
November 8, 1993
CMB-11-93
Page 2

5. Description of capabilities or limitations of process for alternative feed cases
6. Quantities and compositions of secondary wastes generated by the process
7. Description of safety, reliability, and ease of operation and maintenance features.

We would also like to know your capability to perform treatability studies, including an estimated cost and schedule for a treatability study on the baseline feed.

The baseline feed is described in Table 1. Alternative feedstocks are given in Table 2. The baseline capacity of the facility is 500 GPD of organic liquid. Considerable uncertainty exists in the estimate of the amount of DOE waste that would need dehalogenation. The 500 GPD capacity is based on 5 treatment facilities at different sites. The final organic effluent is required to have a maximum of 100 ppm of halogens plus sulfur plus phosphorus, all in organic form. There is no incentive to recover any hydrocarbon component.

Although the actual DOE waste contains low levels of radioactivity, assume no radioactivity is present in the waste.

We would appreciate receiving the information by December 10 in order to meet the schedule of our evaluation. Please contact me at (208) 526-0864 in you have any questions.

Sincerely yours,

Charles Barnes, Sr. Engineering Specialist
Chemical and Process Engineering

blm

TABLE 1 - BASELINE WASTE COMPOSITION

AVERAGE WASTE:

	<u>Mole %</u>	<u>MW</u>	<u>Weight %</u>
Solvents & Light Hydrocarbons	40	78.4	28.9
Methanol	(6)	32	
Acetone	(6)	58	
Benzene	(6)	78	
Ethylene Glycol	(6)	62	
Carbon Tetrachloride	(6)	153.8	
Dechloroethane	(6)	98.9	
Monoethanolamine	(4)	60	
Cutting Oil (TRIM•SOL)*	20	350	64.5
Water	40	18	6.6
Total	100		100

TRIM•SOL:

*Estimated TRIM•SOL composition: $C_{20}H_{37.5}O_{1.65}Cl_{1.1}S_{0.11}N_{0.22}$

<u>Constituents:</u>	<u>CAS#</u>	<u>Range, %</u>
Petroleum oil	8002-05-9	30-40
Petroleum sulfonate	61789-85-3	20-30
Chlorinated alkane	68410-99-1	20-30
Nonionic surfactant	68991-48-0	1-10
Aromatic alcohol	68803-15-6	1-10
Glycols	68803-15-6	1-10
Substituted indole	63232-48-1	<1
Blue-green dye	68476-44-8	<1
Antifoam	9003-01-4	<1

TABLE 2 - ALTERNATIVE WASTES

1. 100% TRIM•SOL
2. 50% Carbon Tetrachloride, 48% Tetrachloroethylene, 2% Freon 113
3. 45% Tributyl phosphate, 5% Dibutyl phosphate, 50 % $C_{10}-C_{14}$ n-paraffins
4. An organic sludge consisting of 33 wt% calcium silicate, 13 wt% carbon tetrachloride, 7 wt% 1,1,1-trichloroethane, 28% wt% ethylene glycol, 19 wt% Texaco Regal Oil
5. Spent activated carbon containing 20 wt% carbon tetrachloride
6. A shredded and ground combustible waste containing 5 wt% polyvinyl chloride, 35 wt% polyethylene, and the remainder paper, cloth and wood

Appendix E

Response of ETG Environmental, Inc., to Process Inquiry

Environmental, Inc.

Providing creative environmental solutions

December 21, 1993

Mr. Charles Barnes
Sr. Engineering Specialist
Chemical and Process Engineering
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Post Office Box 1625
Idaho Falls, ID 83415

Dear Mr. Barnes:

ETG Environmental, Inc. has reviewed the waste characteristics of wastes at DOE facilities with Professor Thomas Tiernan of Wright State University (WSU) and Charles Rogers, the inventor of the EPA BCD technology.

The information on the chemistry and process of the BCD technology is described in the attached preliminary feasibility report. Since the fundamental parameters for optimum treatment of the chlorocarbons contained in the baseline waste have not been established in previous tests, ETG and WSU propose that treatability tests be conducted with each of the individual chlorocarbons contained in the baseline waste prior to treatability tests on the actual baseline waste mixture. The proposed treatability studies will be conducted in WSU Laboratories assuming no radioactivity is present.

The estimated costs for the treatability tests outlined in the preliminary feasibility report are as follows:

1. Treatability Test on Carbon Tetrachloride

a.	Reactor set-up and test run	\$ 9,000
b.	Analyses of liquid residue and gaseous products from 4 sample aliquots	<u>9,000</u>
c.	Total Test 1	\$ 18,000

2. Treatability Test on Dichlorethane

a.	Reactor set-up and test run	\$ 9,000
b.	Analyses of liquid residue and gaseous products from 4 sample aliquots	<u>9,000</u>
c.	Total Test 2	\$ 18,000

3. Treatability Test on Baseline Waste

a.	Reactor set-up and test run	\$ 9,000
b.	Analyses of liquid residue and gaseous products from 4 sample aliquots	<u>9,000</u>
c.	Total Test 3	\$ 18,000

4. Grand Total For Tests 1, 2, and 3 **\$ 54,000**

The indicated costs are only approximate. Actual costs will depend upon the outcome of the initial tests and the extent to which additional investigations of the reaction parameters (reaction time, temperature and proportions of reagents) prove to be required. These studies would best be conducted as an R&D investigation with sufficient flexibility to explore promising results and variable parameters in detail. A more definitive proposal and cost estimate can be provided once the scope of the project and the mechanism of funding are known.

ETG has constructed a 75 gallon pilot scale liquid reactor as part of the Therm-O-Detox[™] system used in a demonstration at the Koppers Superfund site in Morrisville, NC under EPA SITE Program. A program fact sheet for this site demonstration to treat soil contaminated with pentachlorophenol (PCP), dioxins and furans is enclosed for your information.

The capital and operating costs for the base line feed case will depend on the optimization parameters provided by the proposed treatability studies. Based on ETG's experience, the estimated capital cost for a reactor system with 500 GPD processing capacity will be in the range of \$1MM to \$1.5MM. The estimated operating costs including reagents and manpower will be in the \$2,000 - \$3,000/day range.

If you need any additional information, please contact me.

Sincerely,

Yei-Shong Shieh
Sr. Vice President
Technology & Business Development

ETG
Environmental, Inc.

**Preliminary Feasibility Report
For The Treatment Of The Halogenated
Hydrocarbons At Various DOE Facilities
Using Base Catalyzed Decomposition (BCD) Process**

Submitted To:

**Charles Barnes
Chemical and Processing Engineer
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, ID 83415**

Submitted By:

**ETG Environmental, Inc.
Attn: Dr. Yei-Shong Shieh
Sr. Vice President
Technology & Business Development
660 Sentry Parkway
Blue Bell, Pennsylvania 19422**

**Wright State University
Attn: Dr. Thomas O. Tiernan,
Professor of Chemistry
Toxic Contaminant
Research Program
Dept. of Chemistry, 175 Brehm Laboratory
3640 Colonel Glenn Highway
Dayton, Ohio 45435**

I. INTRODUCTION

Base-Catalyzed Decomposition (BCD) is a process for dehalogenating halogenated organic chemical compounds which was developed and patented by the U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory (EPA/RREL) in Cincinnati, Ohio. This process has been extensively tested and refined at the bench scale in collaborative studies conducted by Professor Thomas O. Tiernan's Laboratory at Wright State University, and in collaborative field demonstrations conducted by ETC Environmental, Inc.

The BCD process is effectively a catalytic transfer hydrogenation process, in which chlorine atoms present on chlorinated molecules are removed and replaced by hydrogen atoms. The overall process is typically represented by the chemical reaction,

The catalysts used in these reactions are proprietary to the U.S. EPA and are relatively inexpensive, readily available materials, in contrast to the costly noble-metal catalysts which have traditionally been used for such reactions. The "Acceptor-Cl" reagents here are, of course, the chlorinated organic molecules which are to be dechlorinated. The chlorinated organic compounds which are prominent hazardous waste constituents and which have

been investigated most extensively in studies of these reactions are aromatic compounds such as the chlorophenols (tri-, tetra-, and penta-), polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), and chlorophenoxy and other chlorinated herbicides (2,4,5-T; 2,4-D; Silvex; Lindane). Laboratory tests have demonstrated that these chemicals can be completely dechlorinated using the BCD process in relatively short reaction times. These tests involved the chemicals in neat form, as well as in complex waste mixtures containing oils and other components, in contaminated soil and sediments, and on solid sorbents such as spent activated carbon. Field demonstrations of the BCD process have shown that the process at full-scale is effective in treating PCB-contaminated soils, and liquid wastes and contaminated soils originating from wood-preserving sites, which contain chlorophenols, PCDD and PCDF. Laboratory tests have also demonstrated that a variety of chloroalkanes and chloroalkenes, including carbon tetrachloride, dichloroethane, methylene chloride and chloroform, can be dechlorinated using one version of the BCD process.

There are several versions of the BCD process which use somewhat different combinations of reagents and which differ in their effectiveness for particular wastes. Laboratory tests of the process have shown that the combination of reagents indicated in reaction (1) above is particularly effective and appropriate for liquid chemicals and waste formulations containing PCB, PCDD, PCDF, chlorophenols, and chlorinated pesticides. However, contaminated

soils and sediments containing these chemicals are more effectively treated by the two-step BCD process. In the initial step, a solid BCD reagent is mixed with the contaminated soil or sediment and the mixture is then heated in a thermal reactor with continuous stirring, while purging the soil with a continuous flow of nitrogen. In this step, the soil or sediment is purged, leaving a "clean" residual solid material and substantial decomposition/dechlorination of the degraded chemical also occurs. Any desorbed chemicals which are not fully dechlorinated are condensed and collected. This condensate is then treated in a liquid BCD reactor, using the reagents shown in Reaction (1) above. Still another combination of reagents, namely tetraethylene glycol and potassium hydroxide, (KTEG), and a catalyst, appears to be effective for treating chloroalkanes and chloroalkenes. In some instances, the latter process results in dehydrohalogenation (HCl loss) rather than chlorine atom replacement by hydrogen which, as already noted, occurs with the other BCD processes. Thus, the KTEG version of this process converts chloroalkanes initially to chloroalkenes, and with further reaction, to acetylenes.

II. BENCH-SCALE TREATABILITY TESTS ON BASELINE WASTE

The information provided by EG&G Idaho, Inc. regarding the Baseline Waste indicated that the objective of an initial treatment, possibly using a process such as Base-Catalysed Decomposition (BCD) process, is to dehalogenate the chlorinated

hydrocarbons which are potential precursors of hydrochloric acid, so that subsequent treatment to destroy the other organics in the waste using supercritical water oxidation (or other processes) is not subjected to highly corrosive conditions. As already noted, the BCD process is well-suited to this purpose, and one version of the process has previously been shown, in rather brief preliminary tests, to be effective for dechlorinating both carbon tetrachloride and dichloroethane which are present in the Baseline Waste. The only other chlorinated compound in this waste is indicated by EG&G Idaho to be a "chlorinated alkane", which was not specifically identified, but is likely also amenable to dechlorination by the BCD process.

It should be mentioned, however, that the BCD process was developed and has been utilized to date (with the exception of a few laboratory tests) only in open reactors which were fitted with condensers to trap volatile constituents which escaped the reactor vessel during heating. In the case of laboratory tests, the condensed organic components were recycled back into the reactor after removal of water from the condensate, if any was present. A schematic of the bench-scale reactor used for such tests is shown in Figure 1. This type of reactor was previously used by Wright State University to treat a sodium pentachlorophenate waste material in tests conducted for EG&G Idaho, Inc. for which Ms. Penny Pink was the technical monitor. The Baseline Waste to be treated in the present case contains significant quantities of rather volatile hydrocarbon solvents, including acetone and

benzene, as well as the chlorinated materials themselves (carbon tetrachloride and dichloroethane) which are also quite volatile at the temperatures which are anticipated to be used in the BCD process. The boiling point of these light hydrocarbons and chlorocarbons are in the range from about 56 to 84°C. The KTEG version of the BCD process was briefly tested earlier on carbon tetrachloride and dichloroethane at reaction temperatures from 21 to 50°C and the reaction rate, as expected, was shown to be temperature dependent.

Another important consideration with respect to the application of the KTEG version of the BCD process to dichloroethane is that on the basis of earlier studies, this dehydrohalogenation reaction apparently yields ethylene and acetylene as products, both of which are, of course, gases at atmospheric pressure and ambient temperature, and are highly flammable and potentially explosive. Consequently, these gases would have to be trapped as they evolved or alternatively, kept in the reactor by using a closed or sealed reactor. The previous studies of treatment of carbon tetrachloride with the KTEG version of the BCD process established that this compound is dechlorinated, but the reaction products were not specifically determined. It appeared that methylene chloride may have been initially formed.

The considerations discussed above suggest that it would be preferable to conduct laboratory treatability tests on the Baseline Waste using a closed reactor. Such a reactor is available at Wright State University and is illustrated schematically in Figure

2. This batch reactor is constructed of corrosion resistant Hastelloy and the contents of the reactor can be continuously stirred. This reactor can be heated to achieve and maintain reaction temperatures ranging from ambient to 1000°F (538°C). Temperature in the reactor interior is monitored by a thermocouple and the heater is regulated by a highly accurate proportional controller. The reactor can operate in the pressure range from atmospheric to 6000 psi and is fitted with a pressure gauge. Both reactor temperature and pressure are continuously monitored and displayed on a strip chart recorder. The reactor is also fitted with valved sampling ports to permit removal of both liquid and gaseous samples at any desired time interval during the course of the reaction. Since the fundamental parameters for optimum treatment of the chlorocarbons contained in the Baseline Waste have not really been established in previous tests, it is proposed that treatability tests be conducted with each of the individual chlorocarbons contained in the Baseline Waste in pure form, prior to treatability tests on the actual Baseline Waste mixture. The treatability tests described in the following are proposed for this study, all tests to be conducted using the closed reactor system shown in figure 2.

1. Treatability Test on Carbon Tetrachloride (CCl₄)

Carbon tetrachloride (CCl₄, 200 mL) will be combined with a twice-stoichiometric quantity of potassium hydroxide (KOH, = 224 g), 25 mL of tetraethylene glycol (TEG), and 2 grams of a proprietary catalyst in the reactor shown schematically in

Figure 2. The reactor will be sealed and heated to a temperature of 50°C, while stirring the mixture continuously for a total period of four (4) hours. Samples of both the residual liquid and the gaseous products will be withdrawn at one-hour intervals during this period and analyzed for CCl_4 and for lower chlorinated compounds, methylene chloride (CH_2Cl_2), and chloroform (CHCl_3), as well as for CO_2 and potential inorganic products such as sodium carbonate (Na_2CO_3) and sodium chloride (NaCl). Analysis of organics will be accomplished using GC-MS. Depending upon the results of this test, additional tests may be desirable at lower temperatures, and/or at different reaction times.

2. Treatability Test on Dichloroethane

A mixture of 100 mL each of 1,1-Dichloroethane and 1,2-Dichloroethane will be combined with the twice-stoichiometric quantity of KOH, 25 mL of TEG and 2 g. of the proprietary catalyst in the reactor shown in Figure 2. The mixture will be heated, with continuous stirring, to a temperature of 50°C for a total period of four (4) hours. Samples of both the residual liquid and the gaseous products will be removed for analyses at one-hour intervals during this period and analyzed for dichloroethane, ethylene, acetylene and vinyl chloride, using GC-MS. Again, depending upon the results of this test, additional tests at different temperatures and/or at different reaction times may be indicated. If the "chloroalkane"

specified to be present in the Trim-Sol cutting oil can be specifically identified, treatability tests on this compound would also be conducted.

3. Treatability Test on Baseline Waste

Assuming the BCD process can be optimized for the individual chlorinated components of the Baseline Waste in the tests described above, a final treatability test would be conducted on the Baseline Waste itself, again using the reactor shown in Figure 2. Quantities of reagents utilized and reaction time and temperature would be selected on the basis of the results of tests 1 and 2 above. Samples of the residual liquid and gaseous products would again be withdrawn at approximate intervals and analyzed for the chlorocarbons in the waste and for the expected chemical products using GC-MS.

III. ALTERNATIVE WASTES

If the treatability tests on the Baseline Waste prove to be successful, then some of the Alternative Wastes identified by EG&G Idaho should also be amenable to BCD treatment. Specifically, the wastes listed as Nos. 1,2,4, and 5 are potentially treatable by procedures similar to those described above, and treatability tests on these wastes could be accomplished if desired.

WRIGHT STATE UNIVERSITY LABORATORY SCALE REACTOR FOR BCD TREATMENT STUDIES

FIGURE

FIGURE 2

Appendix F

Response of Synthetica Technologies to Process Inquiry

SYNTHETICA

SYNTHETICA TECHNOLOGIES, INC.

November 18, 1993

Charles Barnes, Sr., Eng. Specialist
Chemical & Process Engineering
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-3625

FAX (208) 526-5142

SUBJECT: WASTE DEHALOGENATION PROCESS INQUIRY CMB-14-93

Dear Charles:

As we have discussed in our telephone conversation a few days ago and in my telephone conversation with your Program Manager, John Beller yesterday, we have agreed that we really should respond to the whole waste destruction task. This does seem clear since our simply dehalogenating the feed for the supercritical water downstream process, makes for a very expensive interface and problematic interface. As we agreed with our technology we can dehalogenate and destroy the wastes types provided in your list very easily by steam-reforming since it is a low pressure process and can handle all heteroatoms in your waste stream.

CAPABILITY FOR PROCESSING MIXED WASTE: As we discussed on the telephone, we have the capability for processing mixed radioactive and RCRA hazardous waste streams with our Synthetica detoxifier system consisting of the standard steam-reforming unit together with both a Drum Feed Evaporator and a Heated Shredder-Screw Feeder.

We have a system going to Sandia National Laboratory in Albuquerque, NM to be located in Area 5 that will be handling mixed waste types, nearly identical to those that you list. We also are scheduled to send a system to a private waste processing company, ATC, in Richland, Washington for handling LLW, and this operation already has an permit from the State & EPA for authority to construct. To date the Synthetica Building is constructed for a capacity for three units. Underway, are activities which will expand this capability to mixed waste. We are also one of the three technologies sponsored by DOE for the destruction of high level nitrate waste from Hanford.

ACTIVITIES WITH LAWRENCE LIVERMORE NAT'L LAB.: The activities here involve similar mixed waste, where we are considering putting one of our systems in Building 251 Hot Cells. This program has high level support from DOE Headquarters in Washington and Livermore.

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CHEMICAL WEAPONS DESTRUCTION: As we discussed we were invited by the National Academy of Engineering in Washington, DC to give testimony to their Congressional Blue Ribbon Committee on our approach to destroying chemical weapons on-site, as a viable and inexpensive alternative to incineration, such as at Johnson Island Atoll. Chemical weapons involve a large variety of heteroatoms (i.e. S, P, N, F, Br, Cl, etc.), and with our steam-reforming chemistry we convert these into non-toxic forms for easy disposal.

OTHER ACTIVITIES WITH SYNTHETICA TESTING: There are many other activities underway involving contracts with Sandia for looking at processing classified waste forms, propellants, energetics, etc. We have two contracts for Savannah River and Hanford activated carbon reprocessing, where the GAC contains almost entirely chlorinated solvent waste (i.e. TCE, PCE, CCl₄, and Chloroform) from groundwater contamination. We have a program for the destruction of stockpile Thorium nitrate waste with DOD, as well as a unique role for the destruction of napalm bombs at Camp Pendleton in southern California.

PROPOSAL: We have prepared the following brief scope of proposal to cover each of the points you have raised:

1. **Process Description:** The proposed system would involve our standard Synthetica Detoxifier consisting of our standard steam-reforming converter together with our Moving Bed Evaporator, vent condenser & CO converter. The collection of attached mechanical elevations & papers present the process details and discussion.
2. **Capital Cost Estimate:** We have provided for the baseline feed case a very rough capital cost estimate of \$900,000 for the above system, without any radiation shielding. The shielding issue will need to be covered with you in the future if it is needed. Since this is our standard system, our engineering fees are already included in the price. If shielding is needed, there will be engineering fees and maybe even testing at Sandia's Area-5.
3. **Operating Cost Estimate:** The operating costs are typically about \$150/day for electricity (480v, 3 Ø, 60 KW max), \$250/day for labor, \$50/day for consumables, \$100/day for our Support & Service Program & \$50/day miscellaneous. This totals \$600/day operating cost. We anticipate feed capacities for the MBE of at least 3 drums/day, or 1200 lbs/day; thus, operating costs around \$0.50/lb seem reasonable.
4. **Operating Experience:** A brief outline of our operating experience has been given above and some of the details are given in the attached papers.
5. **Capabilities & Limitations:** The MBE system can handle halogenated species at levels even up to 100%. This was demonstrated with 100% feed of CCl₄.
6. **Secondary Wastes:** The operation of the MBE on halogenated organics produces a dry salt material suitable for grout or vitrification (i.e. the French Glass Melter to produce glass logs). There are no other significant secondary waste forms.

1 Ton/D
Capacity

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7. Safety, Reliability, Ease of Operation, & Maintenance: We have some very forward looking safety controls (i.e. quadraply redundant controls: process computer with process model and digital feed-forward control, microprocessors on each of the minimum cutsets of the fault-tree, hard-wired-programmable array logic modules that do analog controls, and mechanical fail-safes on valves). The system is robust enough for us to allow the unit to run unattended. Because it is entirely computer controlled, it can be operated remotely by your staff &/or our Support & Service Center. We routinely start-up our units on Sunday afternoon remotely with nobody in our testbay and start testing on Monday morning. Our total hours of operation are around 60,000 hours, complete with maintenance cycles, etc. The operation is very simple, through a touch panel, very much like the automated bank tellers. We can bring in people off of the stree and with no instructions, they can run the unit. Remember, it is designed for use in hospitals and small industry by their unsophisticated staff.

CONCLUSIONS: I hope the above discussion explains why we feel that this approach is better for your waste stream and why it is entirely compatible with all of the other work underway at this time with DOE and DOD. We have attached literature that will help support what we are saying. We look forward in hearing from you soon as to what next step you want us to take.

Sincerely yours,

Dr. Terry R. Galloway, V.P.

INEL1

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F-5

SYNTHETICA® DETOXIFIER

ON-SITE DETOXIFICATION

- **Detoxifies gases, liquids and solids** – up to 5 drums of organic waste per day.
- **On-site installation** – integrates with on-going plant operations.
- **Accepts drums or continuous feeds** – adapts to in-line process or solvent recovery.
- **Reduces disposal costs and liability** – minimizes manifesting and costly off-site transportation, terminates liability.
- **Establishes predictable future costs** – eliminates dependence on off-site disposers.
- **Achieves on-site source reduction** – inert residue disposed of safely and easily.
- **Safe, simple operation, all automatic** – continuously monitors essential functions, minimum operator interaction, failsafe design.
- **Compact and efficient** – 8' by 12' floor space; simple installation, weighs only 3800 lbs.; only 50KW power.

- **Mobile waste detoxification service** – unit fits in truck van for on-site service.
- **Complete detoxification** – destruction levels of 99.99% or greater.
- **Favorably viewed by Regulatory Agencies and Environmentalists** – selected by the California DHS to demonstrate alternative technology. Supports source reduction and minimization programs.
- **Patents issued in U.S. and foreign countries**

Typical industrial applications for the Synthetica Detoxifier:

Waste Solvents	Mixed Organics
Aqueous Wastes	PCB Contaminated
Paint Sludges	Pharmaceutical Wastes
Laboratory Wastes	Biomedical Wastes
Degreasing Sludges	Low-Level Radioactives
Off-Spec Organics	Carbon Reactivation

MOVING BED EVAPORATOR

F-11

F-12

Detoxifier Process for LLW Waste

F-14