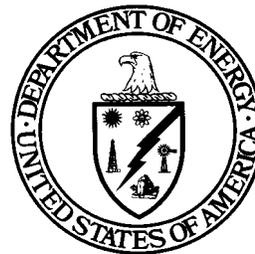


Direct Chemical Oxidation

Mixed Waste Focus Area



Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology

December 1998

Direct Chemical Oxidation

OST Reference #109

Mixed Waste Focus Area



Demonstrated at
Lawrence Livermore National Laboratory
Livermore, California

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://OST.em.doe.gov> under "Publications."

TABLE OF CONTENTS

1	SUMMARY	page 1
2	TECHNOLOGY DESCRIPTION	page 5
3	PERFORMANCE	page 9
4	TECHNOLOGY APPLICABILITY AND ALTERNATIVES	page 12
5	COST	page 15
6	REGULATORY AND POLICY ISSUES	page 17
7	LESSONS LEARNED	page 20

APPENDICES

A	References
B	TMS Data Elements
C	Acronyms

SECTION 1

SUMMARY

Technology Summary

The Best Demonstrated Available Technology (BDAT) for the destruction of organically contaminated mixed waste [generated from both past Department of Energy (DOE) nuclear operations and current cleanup activities] is incineration. However, there is interest in treatment alternatives to excess air, open flame combustion. This interest derives from public concern for potential stack emissions and the fact that large volumes of gaseous effluents conceivably could result in significant releases of environmentally harmful contaminants. End users in the DOE complex and stakeholders do not believe that adequate attention has been directed toward development of alternative oxidation techniques involving nonthermal, nonflame processes. Both in response to these concerns and pending Environmental Protection Agency (EPA) regulation changes that will impose additional emission limits and monitoring requirements, the DOE's Mixed Waste Focus Area (MWFA), an EM-50 program, sponsored the development of several technologies that are alternatives to incineration. These alternative processes are referred to as Alternative Oxidation Technologies (AOTs).

Direct Chemical Oxidation (DCO) is a nonthermal, near ambient (atmospheric) pressure, aqueous-based AOT that was developed to destroy the organic contaminants in hazardous or mixed wastes. DCO uses solutions of the peroxydisulfate ion, the strongest known chemical oxidant other than fluorine-based chemicals, to convert organic solids and liquids to benign carbon dioxide, water, and constituent minerals. Peroxydisulfate has also been used alone or with an Ag (II) catalyst in decontamination and etching solutions for removing PuO₂ (as dissolved plutonyl ion) from nuclear equipment. The expended oxidant may be electrolytically regenerated to minimize secondary wastes. Offgas volumes are minimal, allowing retention of volatile or radioactive components in the process fluid. For nearly all organic liquids, the rate of destruction at 90–100°C is roughly 200 kg (as carbon) per cubic meter of reaction vessel per day.

Among the benefits and limitations of the DCO technology are the following:

- DCO can treat a wide variety of organic wastes (liquids and solids; water-soluble or not) and waste matrices (soils, sands, clays; ceramic substrates; steel machinery, etc.) contaminated with organic constituents.
- Process operation and control is simple; scale-up or scale-down is straightforward; and common materials of construction are used (such as polymer- or glass-lined steel, earthenware, or stainless steel). No unusual or expensive containment materials are required; oxidation is best pursued in ceramic, polymer or glass-lined vessels, in earthenware, or in stainless steel.
- The rate of the oxidation reaction can be selected (through concentrations and temperature) to provide either complete destruction of organic substrates, or merely decontamination and etching of metal, ceramic or plastic debris.
- Peroxydisulfate oxidation generates no toxic byproducts, and the oxidation product (sulfate) can be recycled--thereby reducing oxidant costs and minimizing secondary wastes.
- Oxidants used in the process are readily available and transportable, and no unusual materials are required for process containment or oxidant storage.
- The nonthermal process operates below 100°C, thus minimizing the offgas volume, and precluding the potential for formation of dioxins and furans in the offgas and reducing the offgas treatment requirements and costs.
- Solid and liquid products of the oxidation reactions are of minimal volume; process outputs are compatible with conventional chemical separation techniques or are readily stabilized for burial.



The process is probably most attractive when a small amount of organic must be removed from a large amount of an inert solid matrix, such as sludge, soil, sand or filter material. Decontamination is similarly well-suited, using peroxydisulfate alone or with a mediated chemical oxidant couple such as Ag (I)/Ag (II), Ce (III)/Ce (IV), or Co (II)/Co (III). Prehydrolysis to promote better mixing between the organic phase and the aqueous oxidant is not chemically necessary, but is favored where it allows very volatile solvents to be oxidized without the complications of high-pressure containment of evolved gases. Processing of bulk organic materials is also simple, but the cost of oxidant recycle mitigates in favor of incineration whenever the latter is possible.

Demonstration Summary

Beginning in 1992, the DCO process was developed for applications in mixed waste treatment, chemical demilitarization and decontamination, and environmental remediation by engineers and scientists at the Lawrence Livermore National Laboratory (LLNL). The integrated DCO process (including hydrolysis) was demonstrated on the pilot-plant scale (15 kg/day, as carbon) using LLNL waste streams or surrogates containing chlorinated solvents. A broad spectrum of materials has been successfully oxidized using peroxydisulfate, including: acetic acid, formamide, ethylene glycol, tributyl phosphate, trialkyl amines, kerosene, methyl chloroform, trinitrotoluene (TNT) and other explosives, surrogates of biological or chemical warfare agents, paper and cotton, PCBs, pentachlorophenol, ion exchange resins (DOWEX), and carbon residuals found in simulated sludge. Further research is not deemed necessary before scale-up for implementation, but treatability studies should be undertaken on each candidate waste stream to ensure processability.

General conclusions based on DCO demonstration testing to date are:

- Chlorinated materials are readily destroyed by peroxydisulfate. Prehydrolysis is not necessary for oxidation, but enhances contaminant solubility, avoids the requirements for pressurizing the oxidation step (with CO₂ evolution), and avoids entrainment of the volatile solvents in the CO₂ offgas.
- Dilute pentachlorophenol and PCBs are also fully oxidized in the basic DCO media. Work is in progress to determine rates of destruction of high concentrations of PCBs (2% in oils).
- Testing in larger equipment with trichloroethane supports the premise that the process can be readily scaled up to desired production throughput.
- Though complete oxidation of non-cellulostic debris is possible, it is probably too slow and requires too much oxidant to support a practical throughput, so decontamination of these materials by surface oxidation is a more practical goal.
- The composition of the offgas stream will depend on the particular waste being processed, but will typically include carbon dioxide from the oxidation of organic matter, and some oxygen produced by a minor competing side reaction (oxidation of water). In acid solutions, some chlorine will be present in the offgas resulting from oxidation of chlorine-containing wastes, but use of DCO in alkaline solutions avoids the formation and release of chlorine from organic molecules, or the free inorganic chloride remains as the chloride ion in solution.
- In cases where the oxidant is recycled by electrolysis, then oxygen, ozone, and possibly chlorine (if chloride is present) will be added to the anode offgas. In industrial electrolysis cells, hydrogen gas is concurrently produced at the cathode; this gas may be oxidized to water (in a catalyzed bed) and the water internally recycled. Commercial catalysts are available for this purpose.
- At the process operating conditions, formation of dioxins and furans in the offgas is not believed possible, and analyses to check for these materials have been negative.
- Wastes containing finely divided aluminum or iron powders can be oxidized so rapidly that unsafe conditions can occur, however, this is common to most aqueous oxidants.



- Though peroxydisulfate readily destroys dilute organic contamination in aqueous solutions, the water present also dilutes the oxidant, making recycle impractical. This is also common to other AOT concepts, but the DCO process is still applicable to these waste streams.

LLNL is seeking to enter into coordinated demonstrations involving the use of one or more of its five pilot-scale reaction vessels. Ideally, LLNL equipment will be operated in field treatability studies, while identical equipment is retained and operated at LLNL on surrogates to provide technical and scientific support as needed.

Contacts

The following individuals can provide additional information in regards to the Direct Chemical Oxidation technology:

Technical

Principal Investigator

Dr. John F. Cooper
Chemistry and Materials Science Directorate, L-352
Lawrence Livermore National Laboratory
PO Box 808 Livermore, CA 94550
(925) 423-6649; fax 422-0049
E-mail: cooper3@llnl.gov

LLNL Management

Dr. Martyn Adamson
Program Leader--Waste Processing Development
Environmental and Earth Sciences Program
Lawrence Livermore National Laboratory
PO Box 808 Livermore CA 94550
(925) 423-2024

Management

DOE-ID Program Director

William Owca
Mixed Waste Focus Area
U.S. Department of Energy
Idaho Operations Office
785 DOE Place
Idaho Falls, ID 83401-1563
(208)-526-1983
FAX: (208)-526-5964
E-MAIL: owcawa@inel.gov

DOE-Oakland Operations Office

Sam Brinker, Project Manager
Oakland Operations Office
(925) 422-0710

MWFA Product Line Manager

Vince Maio, Advisory Engineer
Mixed Waste Focus Area
Lockheed Martin Idaho Technologies Company/LMITCO
Idaho National Engineering and Environmental Laboratory/INEEL
P.O. Box 1625
Idaho Falls, ID 83415-3875
(208)-526-3696
FAX: (208)-526-1061
E-mail: vmaio@inel.gov



Other

All published Innovative Technology Summary Reports are available on the OST Web site at <http://em-50.em.doe.gov> under "Publications." The Technology Management System, also available through the OST Web site, provides information about OST programs, technologies, and problems. The OST Reference Number for Direct Chemical Oxidation is 109.



SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

The DCO process, developed at the LLNL with internal R&D and EM50/MWFA support, is a nonthermal, low temperature, ambient pressure, aqueous based technology for the oxidative destruction of the organic components of hazardous or mixed waste streams. Program publications are given in the following references: (Adamson et al. 1995a) (Adamson et al. 1995b) (Adamson et al. 1995c) (Adamson et al. 1996) (Cooper et al. 1995) (Cooper et al. 1996) (Cooper, Krueger, and Farmer 1995) and (Cooper et al. 1997). The process uses solutions of sodium or ammonium peroxydisulfate to mineralize organic material to carbon dioxide and water. The expended oxidant (sodium or ammonium hydrogen sulfate) may be regenerated by electrolysis to minimize secondary waste or oxidant cost. The net waste treatment reaction is:



The peroxydisulfate process is an application of a well-established industrial technology. Acidified ammonium peroxydisulfate is one of the strongest oxidants known. It is comparable to ozone and exceeded in oxidative power only by fluorine and oxyfluorides. The process is primarily being developed for the treatment of organic liquids and solids contaminated with organic liquids. It will oxidize the organic fraction of sludge if the matrix is finely divided and slurried with the working solution. Destruction of some organic solids, such as paper, cloth, and styrene resins, is possible, and other plastics and inorganic debris will be partially oxidized and decontaminated. The oxidation potential of peroxydisulfate is high enough to oxidize nearly all organics; thus the process is virtually "omnivorous." However, perfluorinated polymers (e.g., Teflon) are inert, and reactions with polyethylene and PVC are slow, so surface oxidation to decontaminate rather than destroy the matrix is a more practical goal.

Many organics are oxidized by the process at ambient pressure and temperatures in the 80 to 100°C range. More recalcitrant materials, e.g., PVC polymers, benefit from higher temperatures (140–180°C, 24 h) to partially pyrolyze the material before oxidation by peroxydisulfate.

At room temperature, solid peroxydisulfate salts and moderately concentrated solutions are stable. The ion is thermally activated at moderate temperatures (>80°C) to produce the sulfate radical anion (SRA), which is a strong charge transfer agent:



This free radical initiates a cascade of oxidation reactions in the organic wastes producing intermediate organic molecular fragments, organic and hydroxyl free radicals, inorganic ions in high oxidation states [e.g., Ag (II) and Co (III) if these elements are present], and secondary oxidants such as peroxymonosulfate, hydrogen peroxide, ozone, and nascent oxygen. Equation [2] can also be catalyzed by ultraviolet (UV) radiation, transition metal ions, radiolysis, and noble metals. The chemistry has been reviewed by (House 1961), (Minisci 1983), and (Peyton 1993). In general, oxidation by peroxydisulfate in mild acid or base is first order in $[\text{S}_2\text{O}_8^{2-}]$ and follows the rate equation:

$$d[\text{R}]/dt = -k_a [\text{S}_2\text{O}_8^{2-}]. \quad [3]$$

with $k_a = 0.01\text{-}0.02 \text{ min}^{-1}$ when both $[\text{R}]$, the waste organic, and $[\text{S}_2\text{O}_8^{2-}]$ are expressed in units of normality (equivalents per liter). Table 1 shows the rates of destruction of a variety of organic chemicals with diverse functional groups, for initially low concentrations (<50 ppm, as carbon). Figure 1 shows the temperature dependence of the oxidation rate for dilute and concentrated organics, which extrapolates well to existing data on the rate of formation of the SRA at low temperatures. This indicates that the rate of destruction of the organic waste material at the higher temperature is highly dependent on the rate of SRA formation. The domain of operation of Direct Chemical Oxidation (DCO) at $T = 90\text{-}100^\circ\text{C}$ falls on the extrapolated rate of formation of the sulfate radical anion. More concentrated organics are destroyed at higher rates than dilute organics (concentrations <50 ppm), because of the accelerating effect of



intermediate free radicals on peroxydisulfate activation. The formation of organic free radicals can accelerate the formation of the SRA, leading to a doubling or tripling in the rate of organic destruction in initially concentrated solutions.

Table I. Integral rate constants (equivalence based) for compounds with diverse functional groups at initial concentrations <50 ppm^a

Compound	M _w	N	10 ² k _a	Compound	M _w	n	10 ² k _a
	g/mol	eq/mol	1/min		g/mol	eq/mol	1/min
Urea	60.06	0	0.36	4-amino-pyridine	94.12	20	1.47
Oxalic acid dihydrate	126.00	2	0.38	Acetic acid	60.05	8	1.54
Nitromethane	61.04	8	0.63	Sucrose	342.29	48	1.55
Salicylate-Na salt	160.10	28	0.73	Methylphosphonic acid	96.02	8	1.56
formic acid	46.03	2	0.73	2,2'-thiodiethanol	122.18	28	1.71
Triethylamine	101.19	36	0.76	1,4-dioxane	88.11	20	1.94
DMSO	78.13	18	0.79	Ethylene glycol	62.07	10	1.95
DIMP	180.18	44	1.26	Formamide	45.04	5	2.01
Na-EDTA	372.24	39	1.34	Na-lauryl sulfate	288.38	72	2.32
4-chloropyridine HCl	150.01	21	1.43				

^aConditions: T= 100°C; [H₃PO₄]= 0.0574 M; [S₂O₈⁻²] = 0.245 N; 0.3 cm² Pt wire catalysis.

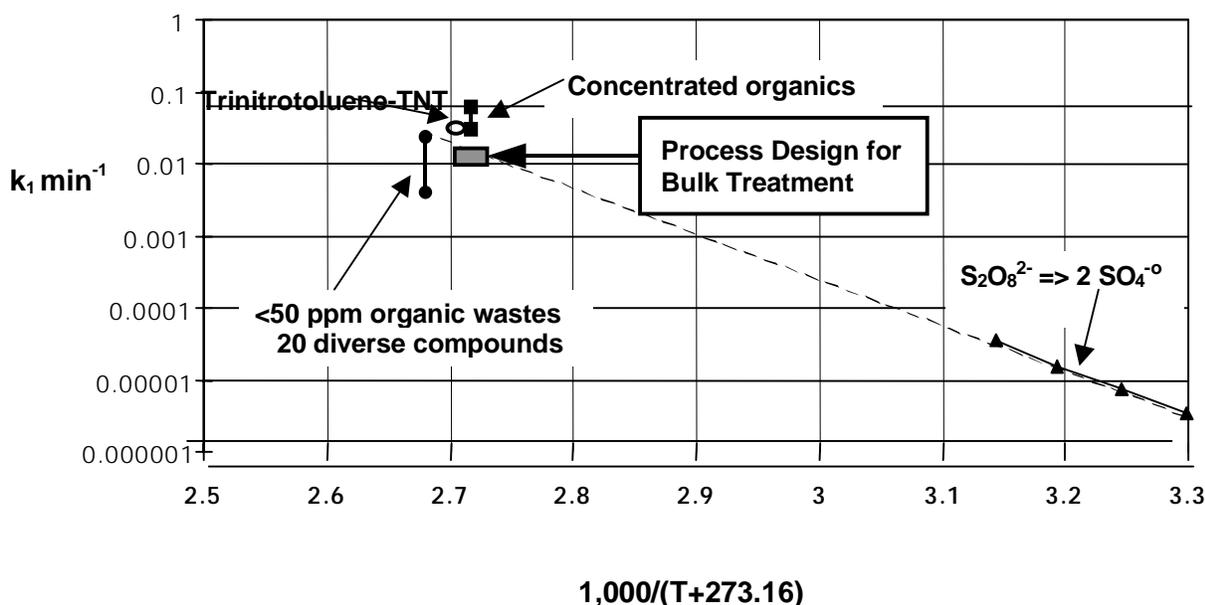


Figure 1. Oxidation rate as a function of temperature.

Phosphorus, sulfur, and amino nitrogen groups are converted to their oxyanions. Ammonium ion and perfluorinated polymers (CF_x) are not oxidized. Organic compounds are attacked preferentially to water and to functional or free chloride ions. At temperatures below 100°C, amorphous carbon, polyethylene, and polyvinyl chloride plastics are slowly attacked. The rate of oxidation (governed by rate of formation of SRA) is independent of pH above pH = 1. Basic solutions are favored for treatment of halide-rich compounds such as chlorinated solvents or PCBs, because chlorine remains in the Cl⁻ state due to the shift of the chloride-hydroxyl-radical equilibrium [4]:



The steady-state concentration and half-life of the SRA is exceedingly small and the mean-free path of the SRA is also very short. This means that the peroxydisulfate oxidant is very effective when pumped as a concentrated solution into porous media such as soils, filters, or sand—allowing the SRA to be formed in situ at the point of use. Destruction of PCBs and pesticides in soil or sand media has been demonstrated elsewhere (Farley 1995). No difference in the destruction rates of common surrogates



(such as dichloropropanol, ethylene glycol, or phenol) in well mixed solutions compared with slurried sludge, sand or clay formulations was found.

System Operation

Normally, bulk organic destruction is best pursued in a cascaded series of continuously stirred tank reactors (CSTRs). Additional peroxydisulfate may be used in the final stage as a polisher to eliminate the last traces of organic material. The resultant bisulfate or sulfate ion may be recycled to produce new oxidant by electrolysis using industrial electrolysis equipment. This recycle is not hindered by small quantities of common inorganic materials (such as nitrates chlorides, phosphates, etc.) or by small quantities of organic residuals that might be entrained in the process stream.

No unusual or expensive containment materials are required. Oxidation is best pursued in ceramic or glass-lined vessels, or in earthenware. Hydrolysis vessels are stainless steel. Electrolysis vessels are stainless steel, glass or earthenware; electrodes are graphite and platinum.

An integrated bench-scale system for the destruction of a wide range of chlorinated organic liquids and organic-contaminated sludge has been demonstrated at LLNL. Many chlorinated solvents benefit (but do not require) hydrolysis to offset difficulties presented by their high volatility at operating temperatures of 100°C. In pilot tests at LLNL, mixed-waste solvents based on 1,1,1-trichloroethane (TCA) were hydrolyzed at elevated temperatures ($\leq 150^{\circ}\text{C}$) (Figure 2). The products of hydrolysis, which are water-soluble and nonvolatile, were subsequently oxidized at ambient pressure in a three-stage CSTR system. (Figure 3).

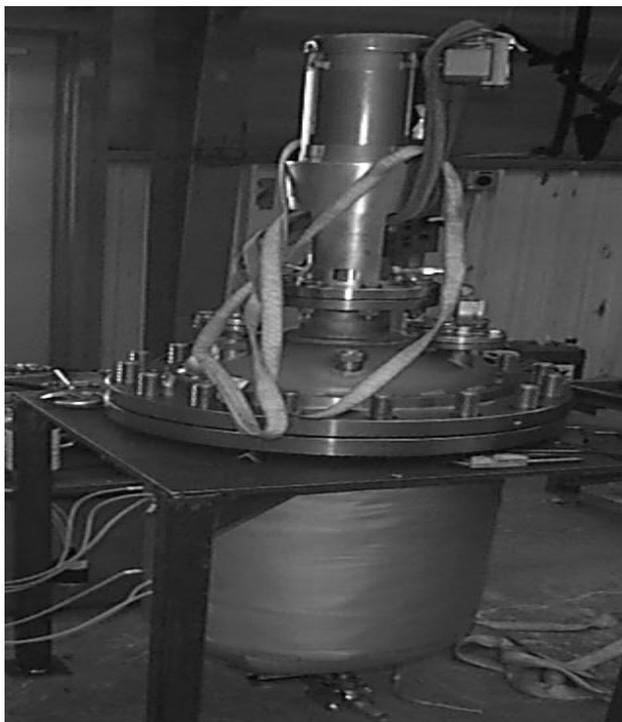


Figure 2. One of five, 2-m tall, 75-L hydrolysis (or oxidation) vessels at Lawrence Livermore National Laboratory (LLNL's) pilot-scale waste treatment facility. Rapid hydrolysis of mixed-waste chloro-solvents to produce water-soluble products was demonstrated here and in similarly scaled laboratory systems (Figure 4).



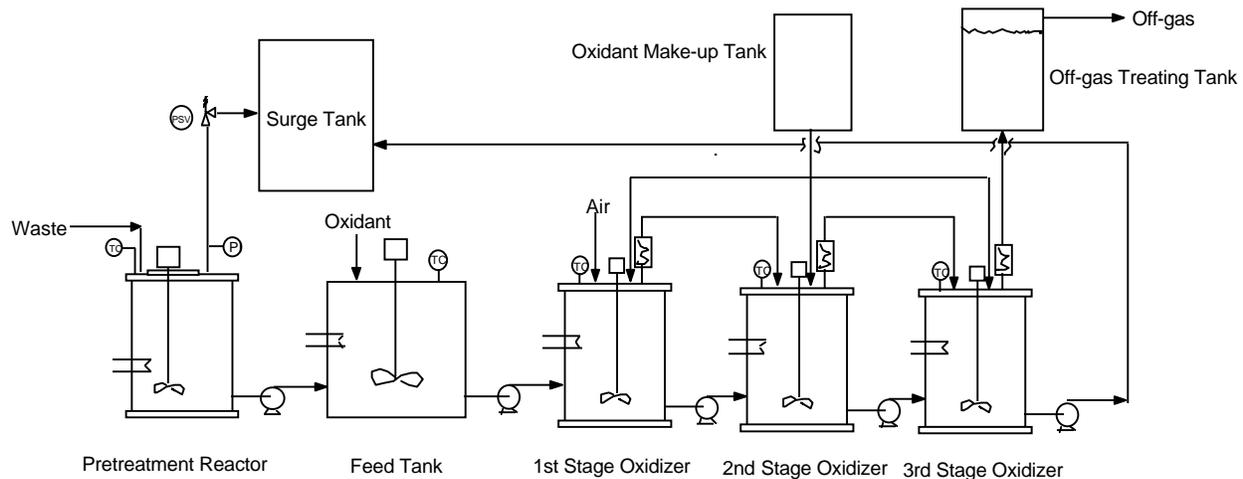


Figure 3. Schematic of pilot-scale process tested at Lawrence Livermore National Laboratory (LLNL) on wastes based on 1,1,1-trichloroethane (methyl chloroform). Prehydrolysis converts very volatile chlorinated solvents to water-soluble products, which are then oxidized at atmospheric pressure in a series of three CSTRs.



Figure 4. Pilot-scale laboratory unit used in destruction of trichloroethane (TCA) solvents, 15 kg/day. The 60-L hydrolysis vessel (left) converts TCA into water-soluble species, which are oxidized in a three-stage continuously stirred test reactor (CSTR) system (right). Data from this system are presented in Table 6.

SECTION 3

PERFORMANCE

Demonstration Plan

The integrated DCO process (including hydrolysis) was demonstrated on the pilot-plant scale (at a destruction rate of 15 kg of carbon/day), using LLNL waste streams or surrogates containing chlorinated solvents. A broad spectrum of materials has been successfully oxidized using peroxydisulfate, including: (a) acetic acid, (b) formamide, (c) ethylene glycol, (d) tributyl phosphate, (e) trialkyl amines, (f) kerosene, (g) methyl chloroform, (h) trinitrotoluene and other explosives, (i) surrogates for biological or chemical warfare agents, (j) paper and cotton, (k) PCBs, (l) pentachlorophenol, (m) ion exchange resins (DOWEX), and (n) carbon residuals found in simulated sludge. Further research is not deemed necessary before scale-up for implementation, but treatability studies should be undertaken on each candidate waste stream to ensure processability. LLNL is pursuing commercialization of the process through a collaborative effort with waste treatment vendors and end users; a process that would involve field treatability studies in parallel with technical and scientific support at LLNL, using the pilot plant units (Figures 3 and 4).

The composition of the offgas stream will depend on the particular waste being processed, but general predictions can be made. Common to all organic waste streams will be carbon dioxide; oxygen will also be produced by a minor, competing side reaction (oxidation of water). In acid solutions, some chlorine will be present in the offgas resulting from oxidation of chlorine-containing wastes; the chlorine may be neutralized by thiosulfate. The use of DCO in alkaline solutions avoids the formation of chlorine and chlorine released from organic molecule or free inorganic chloride remains as the chloride ion in solution. In cases where the oxidant is recycled by electrolysis, then oxygen, ozone, and possibly chlorine (if chloride is present) will be added to the anode offgas. In industrial electrolysis cells, the hydrogen gas is concurrently produced at the cathode; this gas may be oxidized to water (in a catalyzed bed) and the water internally recycled. Commercial catalysts are available for this purpose.

Because of the low volume of offgas (essentially only the carbon dioxide fraction and water vapor), the offgas can be captured and retained if volatile radionuclides (tritium) or heavy metals (mercury) are present in the waste. At the process operating conditions, formation of dioxins and furans in the offgas is not believed possible, and analyses to check for these materials have been negative.

Development Plan

The oxidation proceeds at a rate of about 200-kg (as carbon) per cubic meter of reaction vessel per day. This rate can be derived directly from a k_a of 0.02-0.04 min^{-1} and an input concentration of 5 N oxidant. This number can be used as a *rough estimate* for batch and CSTR scaling. Rates of destruction of solids can be lower if the reaction is transport or surface-kinetics limited, as in the case of some plastics or amorphous carbon. Performance can best be described by a series of examples:

Bulk rates for concentrated wastes. Table 2 summarizes rate data for various surrogate wastes, representing important waste streams. The percentage destroyed at the given rate is presented.

Oxidation time profiles. Table 3 follows the destruction of kerosene following introduction of the oxidant at 90°C. The data illustrate the rapid destruction of material from the initial concentration, followed by slower reaction of the very dilute solution.

Oxidation of chlorosolvents without hydrolysis. Table 4 summarizes data on treatment of chlorinated solvents in sealed vessels, without hydrolysis pretreatment. It is emphasized that chlorinated materials are readily destroyed by peroxydisulfate. Prehydrolysis avoids the requirements for pressurizing the oxidation step (with CO₂ evolution) to avoid entrainment of the volatile solvents in the CO₂ offgas.



Destruction of PCBs. Table 5 presents results of treatment of PCBs in very dilute solutions, with and without a hydrolysis pretreatment. Here, hydrolysis is not necessary as PCBs are not volatile, and therefore little is gained by the pretreatment. Pentachlorophenol is also fully oxidized in basic DCO media. Work is in progress to determine rates of destruction of high concentrations of PCBs (2% in oils).

Scale-up of hydrolysis and oxidation of methyl chloroform. In Table 6, the results of pilot-scale testing of DCO on the destruction of trichloroethane (methyl chloroform) in a two step process: base hydrolysis in a 60-L vessel, followed by oxidation in a CSTR system (consisting of three 15-L vessels). The products of hydrolysis are fully destroyed, in good agreement with a process model based on Equation 3. This work establishes that the process scales well from bench top equipment to pilot scale (i.e., 15 kg-C/day).

Table 2. Rates of oxidative destruction (scale factors) for compounds at high concentrations (bulk)

Compound	Rate, kg/m ³ -day	Percentage destroyed at rate
2,4,6-trinitrotoluene	132	>98.8
Kerosene	186	>99.97
Triethylamine	205	>98.8
Dowex	132	>99
Ethylene glycol	432	>99.93

Table 3. Oxidation of kerosene (predominately dodecane) at 90°C

Time, min	Oxidant added, Equivalents	Carbon determinations, ppm-Wt C	Residual Carbon, g-C	Destruction extent, %
0	0	59,060	3.17	0
70	1.4	1.3	0.00073	99.97
140	2.8	0.27	0.00029	99.99

Table 4. Oxidation of Chloro-solvents by peroxydisulfate in sealed vessels

Chloro-solvent	Extent of oxidation after 1 h
Perchloroethylene	0.991
Trichloroethylene	0.996
methylene chloride	0.991
Chloroform	0.967
Perchloroethylene/chloroform mixtures (50%)	0.991

Table 5. Results of Direct Chemical Oxidation (DCO) treatment of low concentrations of PCBs (45 ppm Arochlor 1242) by oxidation in basic media, and by oxidation following hydrolysis pretreatment. Analysis is by Environmental Protection Agency (EPA) method 608; Analysis by Centre Analytical, Inc.; *corresponds to limit of detection. Values are in microgram/L (ppb).

Compound	Oxidation #1: Excess oxidant, 1 M NaOH 85–95°C for 1 h Two samples		4.5 h hydrolysis, 100°C oxidation for 1 h	48 h hydrolysis, 100°C oxidation for 1 h
	monochlorobiphenyl	<0.65*	<0.5*	<0.5*
dichlorobiphenyl	<0.65*	<0.5*	<0.5*	3.47
trichlorobiphenyl	<0.65*	<0.5*	<0.5*	2.37
tetrachlorobiphenyl	<1.3*	<1.0*	<1.0*	7.08
pentachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
hexachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
heptachlorobiphenyl	<1.9*	<1.5*	<1.5*	<1.5*
octachloro-biphenyl	<1.9*	<1.5*	<1.5*	<1.5*
decachlorobiphenyl	<3.2*	<2.5*	<2.5*	<2.5*



Table 6. Experimental and theoretical destruction of waste (base-hydrolyzed trichloroethane) in three-stage continuously stirred test reactor (CSTR) T = 90°C; V = 15 liters per vessel; flow = 0.10 liter/min; process model: rate = $k_a [S_2O_8^{2-}]$

Parameter	Experimental	Process Model
Concentration of waste input	0.11 M	(0.11 M)
CSTR #1 output	0.0061 M	0.00701 M
cumulative efficiency	94.45%	93.6%
CSTR #2	0.0006M	0.0005 M
cumulative efficiency	99.46%	99.59%
CSTR #3	0.0003M	0.00003 M
cumulative efficiency	99.76%	99.97%



SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Incineration is the baseline technology for treating organic based mixed waste debris in order to meet RCRA Land Disposal Restriction (LDR) treatment standards for RCRA regulated hazardous organic constituents. However, due to regulatory and societal hurdles, as well as limitations in accommodating some problematic radionuclides, various alternatives have been proposed and developed. Technologies that have been developed to commercial scale include steam reforming, the ChemChar method, and hydrogen reduction processes. Others in development or near deployment besides DCO include Catalytic Detoxification and Acid Digestion. A brief description of these alternatives is given below.

Steam Reforming

The DOE EM-50 organization is supporting the demonstration of steam reforming of mixed wastes under contract with a commercial company. Nominal throughput of the demonstration is 90 lb/h for various low-level mixed waste surrogates. In nonradioactive applications, the steam reforming process usually involves two stages: (1) waste is pyrolyzed and volatilized by exposure to steam at elevated temperatures (300 to 800°C) and (2) volatile species are further reacted with steam at temperatures up to 1,200 °C to produce synthesis gas. However, for mixed waste treatment purposes, the primary effluent is oxidized to completion and the offgas scrubbed before discharge.

Concentrated or pure organic liquids pose no problems for steam reforming. In addition, steam reforming should be just as flexible as incineration in handling both combustible and inorganic debris. Soils and sludges may present challenging feed problems, which may be solved with modifications to existing technologies and feed equipment.

Commercialized steam reforming gasifies organic waste in a fluidized bed of sodium carbonate (or other nonreactive particulate compatible with the ultimate stabilization process) that serves as a catalyst for reforming reactions. After particulate removal, the product gases from the steam reformer flow into a flameless thermal oxidizer, which converts volatiles to water, carbon dioxide, and acid gases. An offgas cleanup system removes the acid gases as dry salts and a baghouse and high-efficiency particulate air (HEPA) filter remove particulate before discharge to the environment.

Recent test runs with simulated mixed wastes containing uranium surrogate and a PCB simulant indicated that heavy metals are retained in the first stage reactor bed and destruction and removal efficiencies (DREs) of 99.9999% have been demonstrated. Follow-on efforts include detailed design and costing for a 500-lb/h system for testing with radioactive waste. In comparison with DCO, the system is more complex, creates more emissions, and operates at higher temperatures and pressures, but is more readily applicable to shredded debris and bulk organic liquids and sludges.

ChemChar Method

In the ChemChar process, the waste materials undergo pyrolysis, partial combustion, steam reforming, and gasification in a moving reaction zone at 1,200°C. The reactions take place in a shaft furnace packed with a mixture of the waste and a triple reverse burn char. The char provides a porous adsorptive media that binds the waste, but allows passage of reaction and product gases. The process may be operated in a continuous mode by regulating the char/waste feed and the burned char in a manner to provide a stationary reaction zone. Appropriate size reduction and blending of debris waste would be required to ensure waste/char mixes are acceptable for the ChemChar process. A commercial company in California has an exclusive license to develop and market the ChemChar technology.



Hydrogen Reduction

In this process, vaporized organic wastes are mixed with hydrogen rich gas at 900°C in an electrically heated reactor. The process is well-suited for both liquid organics and aqueous wastes containing dilute organics. Because the organics must be in the vapor phase for complete hydrogenation of the waste components, organics from solid waste matrices must first be desorbed. As a consequence, typical combustible debris waste may be degraded too slowly for practical applications. Only debris waste containing readily desorbed contamination will be a good candidate for hydrogen reduction. A private company has commercialized the technology and has built systems with design capacities of 150 tons per day.

Catalytic Detoxification

This process, which is being developed with EM-50 support to a private research company, is a catalytic, aqueous process that oxidizes organic materials with internal regeneration of the oxidant. The low operational temperature (150 to 250°C) and the nature of the catalyst typically do not produce regulated gases or volatile metals in the offgas. The reagent solution (containing FeCl₃, with Pt and Ru cocatalysts) is not consumed in the reaction, readily dissolves metals, and, therefore, can accumulate toxic and radioactive metals before recovery or disposal. Oxygen present above the reagent solution supports reoxidation of the reduced ferrous ions back to ferric.



Reported destruction efficiencies range from 98.9% for PCB compounds to over 99.999% for nonchlorinated solvents. Catalytic detoxification is being developed primarily for the treatment of organic liquids. However, the process should handle some solids, sludges, and particulate if they are shredded, and suspended, slurried, or emulsified in the working fluid.

The advantage of the catalytic detoxification process is that it can aggressively digest a variety of organic waste matrices, including chlorinated compounds, while at the same time continually regenerating the oxidant. In contrast, the system is more complex than DCO, is probably more difficult to contain (requiring a tantalum-lined reaction vessel), and, due to its more aggressive operating conditions, may generate greater emission concerns.

Acid Digestion

The Acid Digestion technology is applicable to most solid and some liquid organic mixed wastes containing a variety of RCRA hazardous metals and radiological components (e.g., actinides and fission products). The category of wastes targeted by the development of this AOT is combustible job control waste containing significant quantities of Pu-238. The technology may also have some success in digesting nonvolatile organic liquids (e.g., nitromethane), including oils, though digestion may be slow. Specifically, the process can destroy the following organic materials at moderate temperatures: cellulose (paper, wood, and cotton), polyethylene, latex rubber, Tyvek®, neoprene, polyvinyl chloride, polystyrene ion exchange resins, filters, munitions, and some other plastics. Larger nonreactive inorganic matrices mixed with the above organic debris are acceptable, but will only be decontaminated in the process.

Even though treatment of halogenated organics has been shown, additional development to ensure removal of HCl from the offgas, separation of HCl from nitric acid, and elimination of the need for posttreatment is necessary. The process is not recommended for aqueous wastes containing only dilute organics and has not been demonstrated for nondebris solids, including sludges and particulate. Treatment capabilities for RCRA regulated organics has not been fully assessed.

Since surface area of the mixed waste can have a significant effect on the digestion efficiencies and rate, the Acid Digestion Process may only be applicable to specific wastes that have been sized before feeding. Continued development is required to define the acceptable size range to support practical digestion of a given waste stream. Of the processes described here, this process is probably most similar to the DCO process in capability and level of development.



Technology Applicability

DCO is capable of oxidizing nearly any organic solid or liquid contaminant under practical operating conditions ($T < 100^{\circ}\text{C}$, ambient pressure), such as:

- solvents, including chloro-solvents;
- detergents, pesticides, and chemical warfare agents;
- biologic materials,
- water-insoluble oils and greases,
- filter media, chars and tars;
- paper and cotton,
- chlorinated, sulfated, nitrated, and phosphorus-containing wastes;
- organics contaminants immobilized in organic/inorganic matrices such as soil, sands, sludge, or porous solids.

DCO is also capable of surface etching and decontamination of metal (including ferrous, brass, copper, stainless steel) ceramic, or plastic debris.

Technology Status and Maturity

Patents are pending in potentially important applications of the DCO technology: base hydrolysis followed by oxidation, treatment of PCBs, and destruction of organic materials on metal substrates.

LLNL has an operating commercialization agreement with Permafix, Inc., for treatment of certain classes of wastes. However, Permafix is currently marketing a DCO technology with little or no recognition of LLNL. LLNL is seeking to enter into coordinated demonstrations involving the use of one or more of its five pilot-scale reaction vessels, in which LLNL equipment would be operated in field treatability studies while identical equipment would be retained and operated at LLNL on surrogates to provide technical and scientific support as needed. The DCO technology is believed ready for implementation on a test basis, and requires support from an end user for limited use of pilot-scale equipment to produce operating data at a site planning for treatment of radioactive materials.



SECTION 5

COST

Cost Analysis

The cost of organic-waste destruction using the DCO technology is directly related to the carbon content, matrix of the waste stream being treated, and whether or not the expended oxidant is recycled. On a per pound of carbon basis, costs are lowest when treating oxidizable organics in a concentrated liquid form or when dispersed in an essentially nonreactive matrix such as sandy soil or sludge. Costs will be higher for heavily chlorinated wastes if the wastes are oxidized in acid media and chlorine gas is produced that has to be captured and neutralized. Also, if the waste contains a substantial amount of nonhazardous organics (such as humic acid in contaminated soils, or cotton rags or paper in undifferentiated wastes), then oxidant use and cost will be proportionately higher.

For destruction of organics, whether neat or in matrix, the cost can be estimated using the following values in Table 7.

Table 7. Direct Chemical Oxidation (DCO) cost factors and assumptions for 50 kg-C/day (waste measured in terms of weight of carbon content)

Factor	Basis	Value
1. Cost of peroxydisulfate purchased in bulk	Bulk, \$0.73/lb; 3 g-C/equivalent	\$79/kg-C
2. Equivalent weight of carbon	$C + O_2 \Rightarrow CO_2$	0.003 kg/equivalent
3. Destruction stoichiometric efficiency	Measured	80%
4. Electrolysis cell voltage	Industrial value	4 V
5. Electrolysis efficiency	Industrial	80%
6. Cost of electrical energy	\$0.06/kWh; 4V; 80% efficiency; 3-g-C/equiv	\$2.68/kg-C
7. Labor cost for destruction and recycle	\$120/day; 80% capacity factor	\$3/kg-C
8. Capital amortization	\$100,000; 6 years; 15% interest; 80% capacity factor	\$1.92/kg-C
9. Profit and General and Administrative (G&A)		30%

If the expended oxidant is not recycled, then the cost of DCO is \$79/kg of carbon content in the waste. This is calculated from the equivalent weights of sodium peroxydisulfate (119 g/equivalent) and carbon (3 g/equivalent), the bulk cost of the sodium peroxydisulfate (\$0.73/lb), and an assumed 80% stoichiometric efficiency: $\$79/\text{kg-C} = (\$0.73/454 \text{ g})(119 \text{ g}/3\text{g-C})(1/0.8)$. Purchased peroxydisulfate would be used when recycle is either too complex or too expensive to be cost-effective, such as when the concentration of organic material in the matrix is very small and the contribution of the product sulfate to secondary waste is negligible.

If the product sulfate is to be recycled to produce new oxidant, then the cost and complexity of the electrolysis plant must be considered versus the cost of new chemical. The cost of the process, including recycling is the sum of electrical energy, labor, and capital ($\$2.68 + \$3 + \$1.92$) estimated for a plant operating at 80% capacity factor and scaled for 50 kg/day, increased by 30% profit and G&A. This reduces the cost of DCO to \$9.88/kg of carbon content in the waste.

In cases where a small amount of organic material is entrained in a large amount of inorganic waste (including water), the cost benefit of recycling is likely to be very small. In cases where the organic waste is highly concentrated, recycling is necessary because chemical costs and the sulfate contribution to secondary wastes become significant.



These estimates are scoping in nature, and do not include costs of working in a nuclear environment, special costs of pretreatment, (i.e., sorting, segregating, or sizing operations, and hydrolysis), and stabilization and disposition of the final product.



SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

Major regulatory requirements, including permitting and licensing, will be necessary for implementing a production-scale DCO process at a site in the DOE complex. In summary, these requirements are as follows.

- A National Environmental Policy Act (NEPA) review for implementation at federal facilities (categorical exclusion is likely to apply for treatability studies). At DOE facilities, this includes an initial environmental checklist that is used to assist in determining if a more detailed Environmental Assessment or Environmental Impact Statement is required.
- A radioactive material license from the Nuclear Regulatory Commission (NRC) or its applicable agreement state for non-DOE facilities or for DOE facilities expected to be regulated by NRC or the agreement state.
- RCRA notifications or permit applications submitted to the regulatory agency based upon the scale and purpose of the process and the capability of the process to achieve the required treatment of LDR wastes and meet applicable LDR treatment standards.
- Toxic Substances Control Act (TSCA) waste treatment permitting, as applicable, for treatment of TSCA regulated PCB wastes that require such permitting.
- A notification to the applicable regulatory agency (state or EPA) for treatability studies.
- A variance or Determination of Equivalent Treatment to allow disposal of treated wastes and residues if specific wastes to be treated require a technology based LDR treatment standard that is not this technology.
- Waste Analysis and Treatment Plans for wastes treated by a generator per 40 CFR 262.34 or per 40 CFR 254 or 265 for wastes to be treated at permitted facilities.
- Submittal of a permit application or modification to the applicable regulatory agency (state or EPA) for review and approval of treatments that are not treatability studies. Currently, a risk assessment for emissions and effluents is required for this.
- Treatment of hazardous waste or mixed waste to dispose elsewhere than Waste Isolation Pilot Plant (WIPP) would have to meet the applicable RCRA 40 CFR 268.40 LDR treatment standards for wastewater or nonwastewater and include treatment of underlying hazardous constituents to Universal Treatment Standards (UTSs), as applicable. NRC waste form testing requirements may also need to be met for disposal in NRC licensed sites. Individual commercial and DOE disposal sites may have site specific requirements, including specific radionuclide limitations, which may affect the qualification of the final waste form. Final waste forms must meet the Waste Acceptance Criteria (WAC) for the intended disposal site. For transportation to and disposal at WIPP, final waste forms in which alpha emitting radionuclides can result in hydrogen generation must not exceed a maximum allowed wattage of heat generation or hydrogen generation rate.

Requirements specific to air emissions under the Clean Air Act (CAA) are as follows:

- An air permit/National Environmental Standards for Hazardous Air Pollutants (NESHAPS) applicability review to determine need for NESHAPS permitting or air/emissions monitoring for any operation that involves potential releases of hazardous air pollutants as particulate, gases (e.g., NO_x, HCl), or vapors (e.g., volatile organics), that may contain radionuclides or other regulated hazardous air pollutants.



- A National Ambient Air Quality Standards (NAAQS) and New Source Performance Standards (NSPS) applicability evaluation to determine the need for a Permit to Construct application or an air permit modification, as applicable.

Specific waste treatability studies will also be needed to ensure that applicable RCRA treatment standards can be met for each waste to be treated.

Other environmental areas that may require consideration by the potential end user include the following:

- Any other secondary waste stream treatment and its associated disposal requirements, for example:
 - spent prefilters and HEPA filters from offgas system,
 - scrubber solution blowdown from an offgas system,
 - miscellaneous wastes,
 - process residuals.
- National Pollutant Discharge Elimination System (NPDES) permit limits or Publicly Owned Treatment Works (POTW) limits if process cooling water effluent is released to an affected system.
- State or a locality specific requirement, e.g., citing, zoning, historic preservation, and other laws and regulations, that may require additional permits and licenses.

The AOT development and demonstration efforts conducted by the LLNL were R&D activities performed under existing air permits and NESHAPs documentation. A NESHAPs evaluation was performed. A DOE-required environmental checklist for the radioactive bench-scale treatability study was used to determine that the project met the requirements of categorical exclusion B3.6 under NEPA Regulation, 10 CFR Part 1021.400, Subpart D.

Safety, Risks, Benefits, and Community Reaction

DCO technology exhibits hazards typical of many industrial treatment and chemical synthesis operations. To its advantage, the process does not require the use of high voltage or amperage, and generates no toxic or explosive gases. However, the use of strong oxidants at slightly elevated temperatures can lead to worker safety concerns if the proper engineering and administrative controls are not established. Proper design and use of established procedures should mitigate these risks. Critical to a safe design is material selection to avoid corrosion and potential breach of the primary containment. In addition, procedures must address methods and monitoring required to avoid reaction rate excursions leading to rapid temperature and pressure increases. Feed rate control of easily oxidized materials and/or highly reactive organics is of particular concern. Aluminum, iron and zinc powders, metallic alkali metals, lithium hydride, and sodium oxide should be removed from DCO feeds, as they should from essentially all oxidizing aqueous solutions. In addition, dry sodium peroxydisulfate must be handled per the applicable safety protocol and stored separately from reducible materials, but as used, in relatively dilute aqueous solutions, and contained in ceramic, earthenware or glass-lined vessels, reactions are predictable and readily controlled. The DCO process is typically operated with acidic process solutions, but for certain applications, basic operation is desirable. For example, at elevated values of pH, iron is readily passivated, and chlorine is retained in solution as chloride ion, thus keeping it out of the vapor stream leaving the reactor(s).

Interest in alternatives to incineration derives largely from public concern for the potential stack emissions from excess air combustion systems. Concern is with the quantities of contaminants emitted. Large gas volumes could conceivably contain a significant quantity of contaminants even at very low concentrations. Releases of concern include products of incomplete combustion (PICs), products of recombination of molecular fragments and chlorination, especially dioxins and furans, and emissions of toxic metals and radionuclides. Excursions in the treatment operation are also a concern due to the potential difficulty in controlling incinerator releases to the atmosphere. Excursions may occur due to increases in organic input rates or an input of organic material with an unexpectedly high heating value. Either may cause rapid reactions and overloading of the incineration system.



Stakeholders are concerned that these problems still exist after spending millions of dollars on the design, operation, and testing of a thermal treatment unit, like incineration. They do not believe that adequate attention has been directed to the nonthermal, nonflame process such as the DCO technology. The EPA has proposed new regulations for controlling emissions from incinerators. The Maximum Achievable Control Technology requirements commonly referred to as the MACT Rule will, when promulgated, limit emissions of chlorine, particulate, volatile organic compounds, and metals. Of particular concern to DOE incinerators are the low mercury and dioxin emission standards. These new standards are based on the top performing existing incinerator systems in use today. Control technologies required for these systems may or may not be applicable to mixed waste treatment systems. EPA and state permit writers have indicated that they intend to use their Omnibus authority under RCRA to require the same level of control for all mixed waste thermal treatment systems.

The greatest concern is with particularly problematic combustible wastes (i.e., TRU, mercury, and PCB contaminated combustible debris). Methods chosen for these types of waste must ensure radiological and toxic metal containment during essentially complete oxidation. A low-temperature, low-pressure destruction technology like DCO is more likely to be accepted by the stakeholders and state regulators for the treatment of Pu-238 waste since its emissions are considerably less and more easily controlled. The MWFA Tribal and Public Involvement Resource Team initiated activities to gather stakeholder issues, needs, and concerns about alternative organic oxidation technologies. The Technical Requirements Working Group (TRWG), a stakeholder group formed to assist the MWFA, reviewed and provided recommendations on changes to the Chemical Oxidation Technology Development Requirements Document. Their comments are in the process of being reviewed and resolved.

Following are general stakeholder issues and concerns regarding high temperature treatment methods found in public reports:

- Stakeholders expressed concerns regarding the current baseline technology, incineration, to treat various mixed waste streams. These concerns range from the release of contaminants, to mechanical failure and injury. One important concern is worker safety during operation of an incinerator. That concern is due primarily to the high temperatures associated with the treatment process.
- Incinerators are becoming more complex, difficult, and expensive to permit and operate in both DOE and the private sector. Because of these combined technical and policy considerations, alternative methods are needed to oxidize organic materials in the waste. The Acid Digestion technology is an alternative. It is a moderate temperature, less complex treatment option that can destroy various types of organic materials. Stakeholders look favorably upon technologies that reduce air emissions and are less complex, thus minimizing the potential for accidents and effects on human health and the environment.



SECTION 7

LESSONS LEARNED

Technology Selection Considerations

To deploy the DCO technology for a particular organic mixed waste application, potential end users need to consider factors common to most waste treatment systems. These factors include the identification of sorting and segregating requirements to preclude feeding incompatible wastes, any pretreatment (hydrolysis) needed for intractable materials, and the design requirements for the front-end waste sizing equipment and the back-end waste handling methods. Decisions also need to be made on the cost-effectiveness of oxidant recycle for the intended feed streams.

Because the primary process hazard associated with the DCO process arises from the contact between the oxidant and reducible materials, potential end users must take care to store and handle the oxidant appropriately using the proper personal protective equipment and procedures. Tests have shown that following some simple but important constraints can safely control the process:

1. High surface area and highly reactive reducing agents such as aluminum, iron and zinc powders, metallic alkali metals, lithium hydride, and sodium oxide should be removed from DCO feeds.
2. Ceramic, earthenware or glass-lined vessels should be used for the oxidation reactors.
3. The DCO process is typically operated with acidic process solutions, but for operations with ferrous debris and chlorine bearing organic materials, operation with basic solutions is desirable.
4. The process is designed for reoxidation of the oxidant by electrolysis for recycle, but this system should be evaluated for cost-effectiveness based on the wastes to be treated and the potential complexity of recovery of the oxidant from the process residuals.

Technology Limitations and Needs for future Development

As mentioned previously, the DCO process was developed to destroy a wide variety of regulated organic materials. It is well-suited to the destruction of most liquid organics, though some may require a hydrolysis step to enhance miscibility in water and/or decrease vapor pressure. The process can also destroy cellulosic debris and dispersed organic contamination in an essentially inert inorganic matrix such as sandy soil or metallic debris, with the potential to provide excellent decontamination of most debris. However, applications to large quantities of bulk organic matter or combustible debris will require large amounts of oxidant, which will contribute to secondary wastes or require significant recycle. Incineration will probably be a more cost-effective choice for these wastes.

Though the process chemistry is relatively well-defined, operations to date have been conducted in carefully controlled laboratory conditions and operating experience is needed. It is also acknowledged that treatability studies will be required for any new waste stream. Sufficient performance data are also needed to support a RCRA permit application. In addition, the operating envelope must be better defined to support design of ancillary systems for feed sorting, segregating and sizing, and oxidant recycle and recovery systems.

Technology Selection Considerations

Potential end users and waste managers in the DOE complex need to consider many factors when selecting destruction technologies for the treatment of their organic-based mixed wastes. The primary decision involves choosing between fully developed thermal and mostly undeveloped nonthermal (or AOT) technologies. This decision is not only driven by negative stakeholder perceptions of incineration, but is largely influenced by the waste characteristics. Wastes containing particulate actinides, mercury, and/or certain volatile constituents, that may result in significant offgas treatment challenges, may be more readily treated by one of the AOT methods, such as DCO. After choosing to use a nonthermal technology, end users need to choose among the various AOTs available. Factors influencing this selection include, but are not limited to, the following:



1. The General Waste Matrix Category and Its Physical Properties

While all alternative oxidation technologies overlap in range of application somewhat, none are as broadly applicable as incineration, and each has some niche in which it is particularly effective. Some AOTs are best suited to liquid organics, while others are more amenable to solid materials such as sludge or debris. The DCO process is best suited to destroy essentially any organic contaminant dispersed in an inert matrix such as soil or water, which is not efficiently treated by incineration. The DCO process may also be an excellent choice to decontaminate largely inorganic or plastic debris. The DCO process could be used to completely destroy combustible debris, but oxidant use or recycle would have to be evaluated for cost-effectiveness against competing technologies. The matrix and form of the waste may also affect throughput, because development data indicate that some matrices, such as polyethylene and PVC, digest at a substantially lower rate than for other combustibles such as paper and cotton.

2. Waste Composition and Characteristics

DCO can be configured to destroy significant organic content in the waste feed at ambient pressure and only slightly elevated temperatures, while only etching inorganic and polymeric material. This uses the oxidant for the intended purpose, rather than depleting the process chemistry on environmentally benign substrates, while providing a thorough decontamination of debris. The ambient pressure system also makes this concept attractive for radiological applications. Debris, soil, and wastewater contaminated with listed organics or PCBs would all be candidate waste streams for this technology.

3. Secondary Waste Generation

Though the process is certainly amenable to oxidant regeneration and reuse, the cost-effectiveness of recovery must be evaluated based on the waste to be treated. For example, dilute wastewaters may be readily treated using peroxydisulfate to destroy organic constituents, but recovery of the sulfate from a dilute solution will probably cost more than the value of the replacement chemical. Conversely, treatment of concentrated organic material or complete destruction of combustible debris would use substantial quantities of oxidant, and secondary waste treatment and disposal or oxidant recycle costs could become excessive.

4. Desired Degree of Oxidation/Destruction Removal Efficiency

Data collected during development of the DCO process indicate that the degree of oxidation for some waste matrices is not as efficient compared to other AOTs, such as steam reforming. Though the regulated organic contaminants tested to date are readily destroyed, substrates including metals, ceramics, and many polymers would only be etched under normal operations. Total destruction of combustibles is theoretically possible, but may be impractical due to secondary waste and cost issues as described above. The desired degree of oxidation is dependent on the requirements imposed by the end user to support the ultimate goal of the treatment. If the requirement is to destroy all contamination of RCRA regulated organics to meet EPA land disposal restrictions, DCO may be a suitable choice. However, if wholesale destruction of combustible debris is required, incineration is almost certainly a cost-effective solution, and steam reforming may be a more effective nonflame alternative.

5. Extent of Development

DCO has only been tested at the pilot scale, and can be scaled-up directly for deployment, though operating time with complex waste matrices is necessary to better define ancillary system requirements. These tests should be designed to collect data to define the operating envelope and WAC. Other test objectives include determination of the following:

- Oxidation rate for complex matrices to determine design throughput.
- Feed size and surface area ranges needed for oxidation. This is necessary to design pretreatment and waste handling systems.



- Extent of oxidation to determine if posttreatment methods are needed and to aid in the design of process monitoring methods and stabilization of residuals.
- Determination of offgas emission compositions to design offgas cleanup and containment systems.
- Oxidant-recycle system costs to determine when such a system is most likely practical and when it is better to supply new oxidant.



APPENDIX A

REFERENCES

- Adamson, M., John F. Cooper, F. Wang, J. Farmer, K. King and R. Krueger. 1995a. Direct Chemical Oxidation: peroxydisulfate destruction of organic wastes. Paper presented at the Proceedings World Environmental Congress, International Conference and Trade Fair. P. 219; London, Ontario, September 17–22.
- Adamson, M., F. Wang, J. F. Cooper, J. Farmer, and T. Shell. 1995b. Destruction of ion exchange resins by wet oxidation and by direct chemical oxidation--a comparison study. Paper presented at the Proceedings World Environmental Congress, International Conference and Trade Fair, p. 206; London, Ontario, September 17–22.
- Adamson, M., John F. Cooper, Francis Wang, Roger Krueger, Ken King, and Joseph C. Farmer. 1995c. *Destruction of organic wastes by ammonium peroxydisulfate with electrolytic regeneration of the oxidant*. LLNL Internal Report, September 1995., UCRL-121979 Rev. 1 October 10, 1995.
- Adamson, M., John F. Cooper, Francis Wang, Roger Krueger, Ken King, Thomas Shell, and Joseph C. Farmer. *Demonstration of omnivorous nonthermal mixed waste treatment: Direct chemical oxidation using peroxydisulfate*. First Quarterly Report to Mixed Waste Focus Group, SF2-3-MW-35 October - December 1995; UCRL-ID-123193, February 1996.
- Cooper, J.F., Roger Krueger, and Joseph C. Farmer. 1995. Destruction of VX by aqueous-phase oxidation using peroxydisulfate: direct chemical oxidation. Paper presented at the Proceedings Workshop on Advances in Alternative Demilitarization Technologies, pp. 429–442; Reston, Virginia, September 25–27; published by SAIC, Aberdeen, MD).
- Cooper J.F., F. Wang, J. Farmer, R. Foreman, T. Shell, and K. King. 1995. Direct Chemical Oxidation of hazardous and mixed wastes. Paper presented at the Proceedings. of the Third Biennial Mixed Waste Symposium, American Society of Mechanical Engineers in August. Lawrence Livermore National Laboratory Report UCRL-JC-120141 March 28, 1995.
- Cooper, J.F., Francis Wang, Thomas Shell, and Ken King. *Destruction of 2,4,6-trinitrotoluene using ammonium peroxydisulfate*. LLNL Report UCRL-ID-124585, July 1996.
- Cooper, J.F., Francis Wang, Roger Krueger, and Ken King. 1997., Destruction of organic wastes with electrolytic regeneration of the oxidant. Paper presented at the Proceedings Sixth International Conference on Radioactive Waste Management and Environmental Remediation, Singapore, October 12–16, 1997, UCRL-JC--121979 Rev. 2, July 1997.
- Farley, J.A., J. Richard Pugh, John H. Grinstead, Jr., and James L. Horton.1995. Degradation of PCBs and atrazine by peroxydisulfate compounds. Paper presented at the Proceedings for the World Environmental Congress, International Conference and Trade Fair, London, Ontario, September 17.
- House, D. A., Chem. Rev. 1961 62 185.
- Minisci, F., A.C., and Giordano, C.; Acc. Chem. Res.1983 16 27.
- Peyton, G., Marine Chemistry 41 91-103 (1993).



APPENDIX B

TMS DATA ELEMENTS

This section provides cross-reference information in regards to the EM-50 Mixed Waste Focus Area contract established for development of the Direct Chemical Oxidation technology. The Department of Energy –Headquarters (DOE-HQ) Technology Management System (TMS) tracking number is provided, as well as the specific Technical Task Plan (TTP):

TMS # 109 Direct Chemical Oxidation, Alternative Oxidation Technology
TTP # SF23MW35 Direct Chemical Oxidation.



APPENDIX C

ACRONYMS

AOT	Alternative Oxidation Technology
BDAT	Best Demonstrated Available Technology
CAA	Clean Air Act
CSTR	continuously stirred tank reactor
DCO	Direct Chemical Oxidation
DOE	Department of Energy
DOE-HQ	Department of Energy Headquarters
DRE	destruction and removal efficiency
EPA	Environmental Protection Agency
G&A	General and Administrative
HEPA	high-efficiency particulate air
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
LLNL	Lawrence Livermore National Laboratory
MACT	Maximum Achievable Control Technology
MWFA	Mixed Waste Focus Area
NAAQS	National Ambient Air Quality Standards
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NPDES	National Pollutant Discharge Elimination System
NRC	Nuclear Regulatory Commission
NSPS	New Source Performance Standards
OST	Office of Science and Technology
PIC	product of incomplete combustion
POTW	publicly owned treatment work
RCRA	Resource Conservation and Recovery Act
SRA	sulfate radical anion
TMS	Technology Management System
TNT	Trinitrotoluene
TRWG	Technical Requirements Working Group
TSCA	Toxic Substances Control Act
TTP	Technical Task Plan
UTS	Universal Treatment Standard
UV	Ultraviolet (radiation)
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant

