

RECEIVED

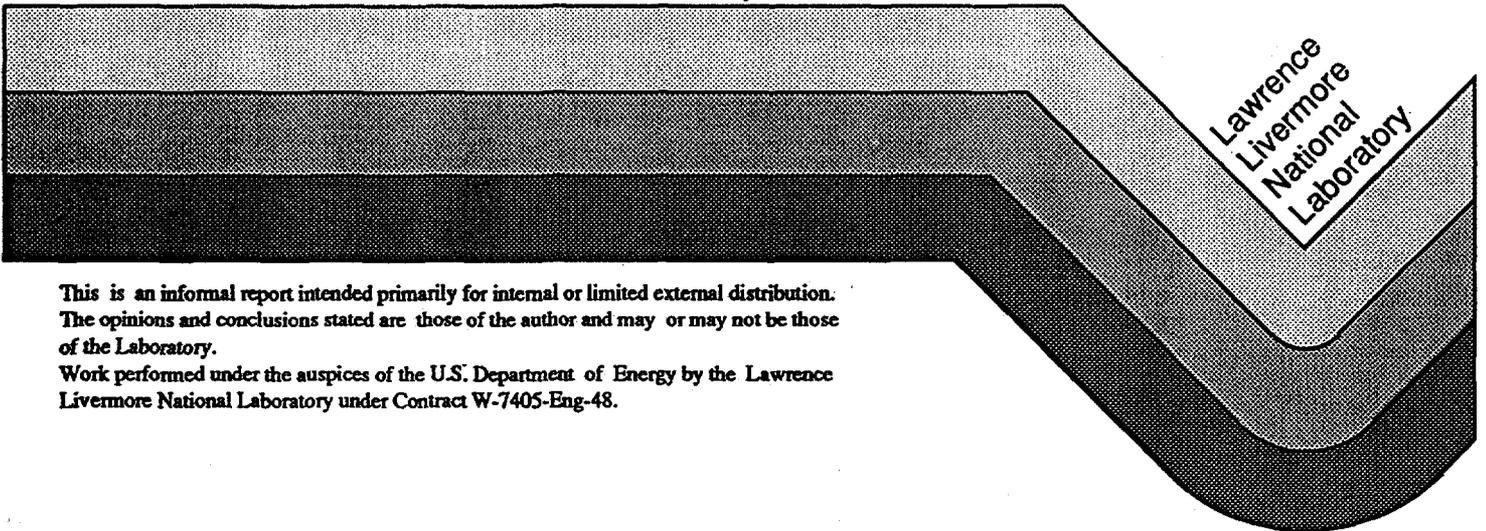
APR 05 1996

OSTI

**Demonstration of Omnivorous Non-Thermal Mixed
Waste Treatment: Direct Chemical Oxidation using
Peroxydisulfate**

John F. Cooper
Francis Wang
Roger Krueger
Ken King
Thomas Shell
Joseph C. Farmer
Martyn Adamson

February 1996



Lawrence
Livermore
National
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

MASTER

OK

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DEMONSTRATION OF OMNIVOROUS NON-THERMAL MIXED WASTE TREATMENT: Direct Chemical Oxidation using Peroxydisulfate

Progress Report: SF2-3-MW-35 October-December 1995

by

John F. Cooper, Francis Wang, Roger Krueger, Ken King, Thomas Shell,
Joseph C. Farmer and Martyn Adamson

Lawrence Livermore National Laboratory Livermore CA 94550
Tel. (510) 423-6649 FAX 422-2118 e-Mail Cooper3@LLNL.gov

January 27, 1996

Contents:

1. Introduction
 2. Technical Background
 3. Experimental system
 4. Technical Results
 - 4.1 Preliminary Plug Flow Reactor Tests (Ethylene glycol)
 - 4.2 Batch Pre-reactor Tests
 - Destruction of Kerosene
 - Destruction of Triethylamine: Nitrogen Product Species
 - Destruction of Cotton Machine Shop Rags (Cellulose; dyes; grease)
 - Tributyl Phosphate and Tributyl-phosphate/Kerosene Mixtures
 5. Conclusions
- Acknowledgments
- References
- Appendices:
- A. Work Statement for Mixed Waste Focus Project, SF2-3-MW-35
 - B. Standard Electrode Potentials of Oxidants
 - C. Historical and Modern Materials used with Peroxydisulfate Solutions.

Abstract

Direct Chemical Oxidation is an emerging "omnivorous" waste destruction technique which uses one of the strongest known oxidants (ammonium peroxydisulfate) to convert organic solids or liquids to carbon dioxide and their mineral constituents. The process operates at ambient pressure and at moderate temperatures (80-100 °C) where organic destruction is rapid without catalysts. The byproduct (ammonium sulfate) is benign and may be recycled using commercial electrolysis equipment. We have constructed and initially tested a bench-scale facility (batch pre-reactor and plug-flow reactor) which allows treatability tests on any solid or liquid organic waste surrogate, with off-gas analysis by mass spectroscopy. Shake-down tests of the plug flow reactor on model chemical ethylene glycol confirmed earlier predictive models. Pre-reactor tests on water-immiscible substances confirmed destruction of cotton rags (cellulose), kerosene, tributyl phosphate and triethylamine. The process is intended to provide an all-aqueous, ambient pressure destruction technique for difficult materials not suitable or fully accepted for conventional incineration. Such wastes include solid and liquid mixed wastes containing incinerator chars, halogenated and nitrogenated wastes, oils and greases, and chemical or biological warfare agents.

1. Introduction

This report summarizes work completed in a three-month "startup project" for the Mixed Waste Focus Area Program: "Omnivorous Waste Treatment Technologies: Oxidation using Ammonium Peroxydisulfate." The Proposed Work Statement for this project appears in Appendix A. The HQ Milestone "Assembly and preliminary Tests" has been met.

The objective of this startup phase is to provide The Mixed Waste Focus Area with a facility which would allow rigorous testing of the peroxydisulfate waste treatment process on any organic solid or liquid surrogate waste. This would allow direct comparisons with alternative aqueous-medium processes, and with thermal processes. As proposed, this facility will be used to produce chemical treatability and rate data on a wide range of "difficult" organic wastes of interest to DoE facilities, including incinerator chars and graphite, various metals; soils and clays; nitrated and chloride-containing wastes; and wastes containing rags, paper, plastics, oils, metals, etc. The subsequent work will trace reaction routes for halogenated and nitrogenated wastes.

Direct Chemical Oxidation refers to the oxidative destruction of organic substances (often called "mineralization") by aqueous solutions of peroxydisulfate ($S_2O_8^{2-}$) [1-3]. The overall configuration of a DCO waste destruction system is shown in Figure 1. Peroxydisulfate is the strongest known oxidant (other than fluorine and oxyfluorides). Appendix B compares chemical oxidants of interest in waste treatment. Solutions of $(NH_4)_2S_2O_8$ are stable at ambient temperatures for months, but become highly reactive at elevated temperatures (>80 °C) which stimulate production of the sulfate free radical, $SO_4^{\cdot-}$. This radical ($E_0 \sim 2.6$ V) is a strong charge-transfer agent in the presence of organics, and initiates a free-radical cascade involving production of OH^{\cdot} and organic free radicals. The byproduct of peroxydisulfate reactions (ammonium sulfate) can be recycled into ammonium peroxydisulfate using industrial electrolysis equipment. Many materials have proven suitable for containment of peroxydisulfate in industrial electrolysis cells and in moderate temperature ($T \sim 100$ °C) reactors [4,5,9]. Appendix C is a summary of proven materials of construction.

Because of its high oxidation potential and aggressive attack on organic materials, aqueous peroxydisulfate is used world-wide in laboratory total carbon analyzer instruments, whereby organic material is detected by oxidation down to levels of 10 ppb, followed by collection and spectroscopic determination of the evolved CO₂ [6,7]

Today, the US produces 10,000 tons/year of (NH₄)₂S₂O₈. Several thousand tons are used in the destruction of hydraulic fluids used in secondary oil recovery. Larger quantities are consumed as industrial bleaches, disinfectants, etchants, and polymerization initiators.

Ammonium persulfates have been successfully used to destroy atrazine and PCB's in clay soils, without catalysis and at ambient temperatures [12]. Thus mineralization reactions of chlorinated and nitrogenated (amino) organics occur even under ambient temperature conditions, although at reduced rates. In separate work, we have tested a process for surface decontamination employing peroxydisulfate at ambient temperature with sunlight- and transition-metal catalysis, for cleanup of toxic spills or chemical warfare agents [20]. Success in these areas suggests that ammonium peroxydisulfate can be used for *in-situ* remediation of soils, the product being the harmless ammonium sulfate (plant fertilizer). Others have used peroxydisulfate to decontaminate machinery and glove boxes and for recovery of PuO₂ [21].

Deliverables/Milestone. This 3-month task provides DoE with a fully operative test facility consisting of (1) a plug flow reactor, for continuous processing of waste surrogates under conditions of excess oxidant; (2) a batch reactor, or "pre-reactor," for oxidation of water-insoluble solids and fluids with excess oxidant, prior to injection into the PFR; and (3) a Residual Gas Analyzer employing a mass spectrometer for direct measurement of oxygen, carbon dioxide and other offgases entrained in an argon purge gas. Shake down tests of the PFR and pre-reactor have been completed using the following chemical surrogates: ethylene glycol, rags, kerosene, triethylamine, and tributyl phosphate.

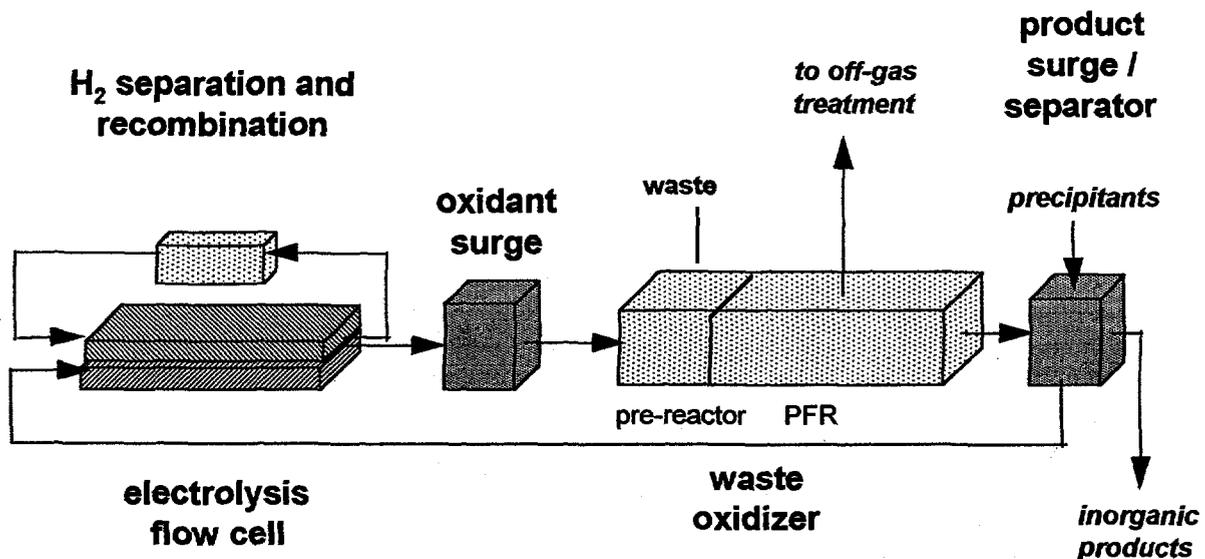


Figure 1. Overall configuration of a DCO waste destruction system using pre- and plug flow reactors.

2.0 Technical Background

This project was preceded by three internally-funded tasks: (1) show recycle feasibility of ammonium sulfate into ammonium peroxydisulfate; (2) measure first-order rate constants of 20 diverse organic materials at 50 ppm initial concentrations (to bound low-concentration reaction rates); and (3) develop an engineering model for destruction of model chemicals at high concentrations (~0.5 N) for use in scaleup. Background work is summarized below (1-3).

Industrial Production and uses of Peroxydisulfate. We tested an electrolysis cell under conditions of the Loewenstein Process, which produced concentrated ammonium peroxydisulfate as an intermediate in the industrial production of hydrogen peroxide. Peroxydisulfate was produced at current densities of 1-2 A/cm² at high efficiencies (~80%) along with lesser amounts of oxidants hydrogen peroxide and ammonium peroxymonosulfate. The Loewenstein process and two related techniques were used on an industrial scale for 60 years. Appendix C summarizes historical and modern materials used for peroxydisulfate production and high-temperature processes.

Oxidation of Surrogate Wastes at Low Concentrations. We measured destruction rates for ion exchange resin (DOWEX I-x4) and low concentrations (~50 ppm, as C) of 19 other chemical compounds bearing diverse functional groups, using a total carbon analyzer modified to generate rate data. The test compounds were chosen for their similarity with substances expected in undifferentiated wastes. Four compounds in Table 1 (MPA, DIMP, TDG, and TEA) are surrogates for products of the hydrolytic or oxidative detoxification of chemical warfare agents [14]. Low concentrations were chosen to simulate the final stages of waste destruction.

The oxidation of the organic sample was generally quenched before 100% destruction, in order to provide a ratio of extent-destruction to time-interval and, hence, an integral rate constant. Results are shown in Table 1. [3] Because of the low organic concentration, 0.3 cm² bright platinum wire catalyst was used to initiate production of SO₄^{-o} free radical. (Some TOC instruments and techniques use UV radiation or transition metal redox couples for this purpose; the Pt is not required). For each compound, we calculated the number of equivalents required for complete oxidation of one mole to carbon dioxide and (as appropriate) inorganic residuals. In most cases, a reaction time of Δt = 2.5 min allowed greater than 95% conversion of organic carbon to carbon dioxide, from which we could then estimate an integral rate constant, k_a' from a formal first order rate equation:

$$- \{ [R]_t - [R]_0 \} / \Delta t = k_a' [O] \quad (1)$$

[R]₀ and [R]_t are the initial and final normality of reductant; and [O] is the concentration of peroxydisulfate. We reduced the data to an equivalency basis, which allows more direct extrapolations to multicomponent, undifferentiated wastes. {A rate constant k_a is also be defined on the basis of molar concentrations.} For all but two compounds, measured integral rates fell into the narrow range of k_a' = 0.006- to 0.020 min⁻¹ (equivalent basis). Oxalic acid and formic acid possess carbon in the highest oxidation states tested: C(III) and C(II) respectively. The slowness of oxidation of these compounds and the small number of charge transfer steps required to produce CO₂ suggests that the last step of oxidation to CO₂ may be rate controlling. The oxidation of the triethylamine sample was slow (0.006 min⁻¹) and consistent with the finding of trialkylamines in the residues following Fe(II)-catalyzed hydrogen peroxide destruction of ion exchange resins [15,16].

Table 1. Integral first order rate constants k_a' and k_a calculated from the extent of oxidation, as measured by CO₂ evolution using a modified total carbon analyzer [7]

No.	Compound	MW	n	fc	[R] ₀	Ratio	C(th)	C(t)	Δt	E	10 ² k _a '	10 ³ k _a
		g/mol	eq/mol	g-C/g	mM	[O]/[R]	ppm	ppm	min	%	1/min	1/min
1	Urea	60.06	0	0.19	1.16	N/A	43.19	41.03	2.5	95	--	7.11
2	oxalic acid dihydrate	126.00	2	0.19	1.17	116.86	43.47	44.00	2.5	101	0.38	7.62
3	nitromethane	61.04	8	0.20	2.51	13.59	46.76	41.61	11.5	89	0.63	1.57
4	Salicylate-Na salt	160.10	28	0.53	0.36	27.14	46.81	46.17	5.5	99	0.73	3.64
5	formic acid	46.03	2	0.26	2.47	55.14	46.09	42.25	2.5	92	0.73	7.32
6	Triethylamine	101.19	36	0.71	0.14	53.62	15.80	14.70	2.5	93	0.76	2.55
7	DMSO	78.13	18	0.31	1.30	11.67	48.40	46.46	11.5	96	0.79	1.75
8	DIMP	180.18	44	0.47	0.18	34.57	23.39	23.20	2.5	99	1.26	4.02
9	Na-EDTA	372.24	39	0.32	0.22	31.25	41.71	39.67	2.5	95	1.34	6.87
10	4-chloropyridine HCL	150.01	21	0.40	0.46	28.04	43.15	39.26	2.5	91	1.43	6.80
11	4-amino-pyridine	94.12	20	0.64	0.47	28.82	44.09	42.33	2.5	96	1.47	7.34
12	acetic acid	60.05	8	0.40	1.19	28.64	44.36	44.54	2.5	100	1.54	7.72
13	sucrose	342.29	48	0.42	0.20	28.01	45.35	44.79	2.5	99	1.55	7.76
14	Methylphosphonic acid	96.02	8	0.13	1.21	28.20	22.53	22.50	2.5	100	1.56	3.90
15	2,2'-thiodiethanol	122.18	28	0.39	0.38	25.47	28.51	28.30	2.5	99	1.71	4.90
16	1,4-dioxane	88.11	20	0.55	0.63	21.73	46.79	44.84	2.5	96	1.94	7.77
17	ethylene glycol	62.07	10	0.39	1.28	21.27	47.80	44.96	2.5	94	1.95	7.79
18	formamide	45.04	5	0.27	2.52	21.68	46.90	46.47	2.5	99	2.01	8.05
19	Na-lauryl sulfate	288.38	72	0.50	0.21	17.99	47.08	44.71	2.5	95	2.32	7.75

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

^bUrea is not oxidized, but hydrolyzes at the reported rate to form NH₄⁺ and CO₂.

Key: MW, molecular weight; n, equivalents per mole; fc, weight fraction carbon; R₀, initial concentration of organic; Ratio, oxidant to reductant initial concentration; C(th) and C(t), theoretical and actual concentration destroyed at time t, respectively; Δt, reaction time; E, apparent extent of reaction at time t; k_a, mole-based integral first-order rate constant; k_a', equivalence-base integral first order rate constant.

Interpretation of results. Reactions involving S₂O₈⁻² oxidation of water or organic reducing agents are generally first order with respect to S₂O₈⁻² [4]:

$$-d [S_2O_8^{-2}] / dt = k[S_2O_8^{-2}] \quad (2)$$

The first step in peroxydisulfate oxidation involves the decomposition of $S_2O_8^{-2}$ to form the sulfate free-radical, $SO_4^{\cdot-}$ which is a fast charge-transfer agent [4,5].

The rate of decomposition of $S_2O_8^{-2}$ in pure water at moderate temperatures (30-60 °C) is accelerated (factors of 10) by the addition of oxidizable substrates, such as formate, oxalate, or alcohol. The increase of first-order rate constant upon addition of reducing agents depends on the identity of the reducing agent, but the law is independent of its concentration. The enhanced rate has been explained by the formation of organic free-radical intermediates, which accelerate the initial decomposition of the peroxydisulfate to form the sulfate free radical. As discussed by House [4], the formation of a free radical intermediate R^{\cdot} , from the action of $SO_4^{\cdot-}$ on R, leads (with the steady-state hypothesis) to a rate equation of the form

$$\begin{aligned} -d[R]/dt &= k_3 [S_2O_8^{-2}] + k_4 [R^{\cdot}] [S_2O_8^{-2}] \\ &= k_a [S_2O_8^{-2}] \end{aligned} \quad (3)$$

This equation generally fits reaction profiles at moderate concentrations of reductants. At very low concentrations (up to 10 ppm), the rate of oxidation of organic material shows a dependence on the product of reductant and oxidant concentrations [22].

Oxidation of model chemicals at high concentrations. In order to develop equations of scale, it is necessary to know the rates of *uncatalyzed* oxidation reactions in the presence of high concentrations of reducible material. These are the conditions likely to prevail in large-scale processing of undifferentiated wastes.

High concentrations (0.05-0.5 N) of model organic materials (ethylene glycol, oxalic acid, triethyl amine and ion exchange resins) were oxidized *without Pt or metal ion catalysis* in 350 ml batches in a 0.5 L reaction vessel with temperature held at points between 80 and 95°C. Of these materials, only the oxidation of the ion exchange resin Dowex I-x4 was too fast to reveal the oxidation-time profile. The full data is reported in reference [3].

A quantitative model was developed [3] and applied to the interpretation of the time dependence of the oxidation of one model compound, ethylene glycol (Fig. 2), given a kinetic model accounting for simultaneous oxidation of water and organic. The oxidation of organic to carbon dioxide follows the relation:

$$R_O - R_t = (k_a V_r G / k) t - k_a V_r G / k^2 (1 - \exp[-kt]), \quad k \equiv k_O + k_a' \quad (4)$$

k_a' is the rate constant (equivalence basis) of organic oxidation (an adjustable parameter); k_O is the equivalent rate constant for water oxidation; and $V_r G$ is the rate of addition of peroxydisulfate to the digester. The reasonable fit of equation (4) to the experimental curve indicates that early stages of oxidation of ethylene glycol to soluble intermediates is very fast compared with the rate-limiting oxidation of intermediates to carbon dioxide. Because of organic free-radical generation, the rate constant for oxidation of EG at high concentrations ($k_a' = 0.06 \text{ min}^{-1}$ at 0.5 N) is much greater than that for trace levels ($k_a' = 0.0195 \text{ min}^{-1}$ at 50 ppm).

As indicated in Figure 2, a 20% excess of peroxydisulfate was required. At the other extreme, the oxidation of triethylamine required 60% excess peroxydisulfate. These efficiencies can be improved if oxidant concentration is controlled at a fixed ratio to substrate concentration, as in a well-engineered plug-flow reactor.

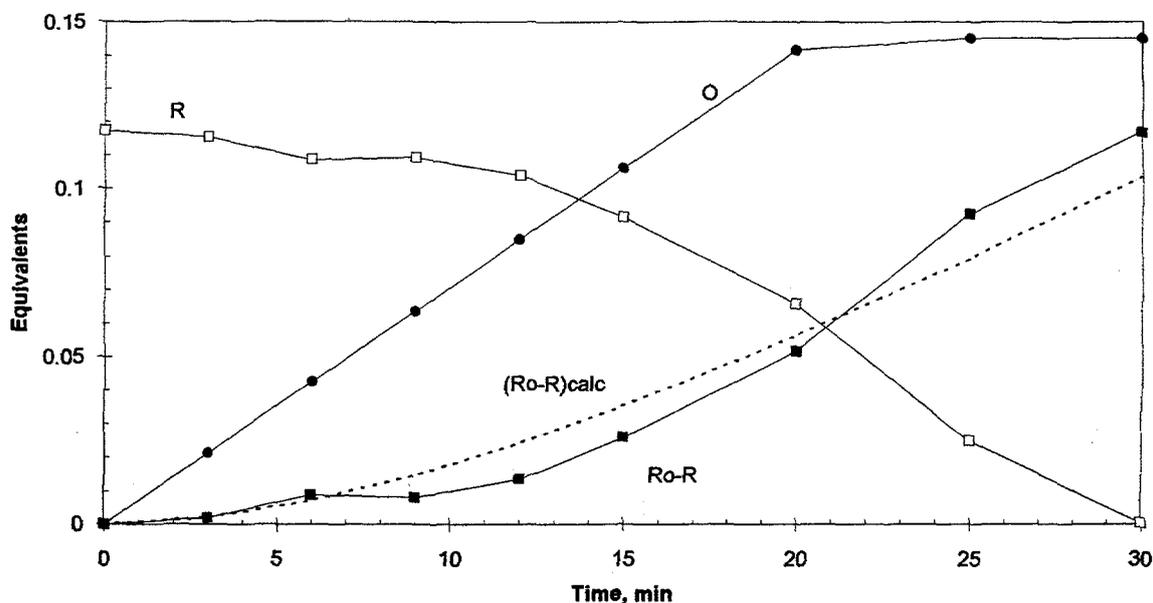


Figure 2. Oxidation of ethylene glycol using near equivalent amounts of ammonium peroxydisulfate reagent under conditions of low and constant acidity (0.10 M H_2SO_4). Calculated curve is for simultaneous water oxidation ($k_o = 0.02 \text{ min}^{-1}$) and organic oxidation ($k_a = 0.06 \text{ min}^{-1}$, adjustable parameter). This reaction used a 20% excess of oxidant.

3.0 Experimental System

The experimental system consists of two reactors: (1) a plug flow reactor, for continuous oxidation of water-miscible wastes at controlled temperature; and (2) a stirred batch reactor, for initial oxidation of solids and water-immiscible liquids to form dissolved products. The plug flow reactor (PFR) supports continuous oxidation of water-entrained waste solutions or emulsions under nearly optimum efficiencies. For solids (cotton, ion exchange resins, chars, etc.) and water immiscible substances (kerosene, tributyl-phosphate, benzene, etc.), a batch pre-reactor operating under reflux is used to liquify the wastes, prior to any injection into the PFR. In any practical application of this process, the pre-reactor and PFR would be linked together to form a single system (Figure 1) for acceptance of any solid or liquid waste.

The modular plug flow reactor consists several horizontal, heat-jacketed Pyrex tubes 25 mm in diameter and of total length 0.3-2 m. The tubes are filled with Rasching rings to minimize free movement of the reaction medium. A free surface at the top of the reaction fluid allows an overflow of argon gas, which carries gaseous reaction products from the system for RGA analysis. In preliminary tests, we used two PFR modules totaling in length 1 m and having a total reaction volume of 300 ml. (Figure 3) Table 2 gives scale parameters.

The plug-flow reactor and pre-reactor vessels were operated independently to facilitate analysis of products. Gaseous products were monitored with a residual gas analyzer utilizing a quadrupole mass spectrometer (Hiden Analytical, Warrington, UK) and continuous mobile sampling system (Turboquad, NGS Associates, Canton MA). Samples periodically withdrawn

from the reactors were analyzed by a calibrated Total Carbon Analyzer (IO Scientific, College Station TX) to determine organic and inorganic carbon content, normally to levels of 100 ppb (by weight, as C).

Scale Factor. We have estimated that a scale factor relating system reaction volume to daily throughput is 200 kg-C/day-m^3 . This number is based on the rate equation (3) using an equivalent rate constant of 0.02 min^{-1} ; an oxidant concentration of $2.5 \text{ N S}_2\text{O}_8^{2-}$; and an effective equivalent weight of waste of 3 g/equiv .

Table 2. Scale Parameters of the Plug Flow Reactor.

Parameter	Range	Comments
PFR tube length	1 m	Length altered using modular tube segments
PFR tube ID	25.4 mm	--
Reaction medium volume	300-360 ml	expandable to 500 ml per meter
Control temperature	80-100 C	precision, $\pm 1 \text{ C}$
Heat exchange temperature	to 120 C	50% ethylene glycol in water
Gas overflow	10-100 ml/min	Argon
Liquid flow	10 ml/min	Determined by residence time of 30 min/m
Throughput capability	100 g-C/day	scale factor for PFR is $200 \text{ kg-C/m}^3\text{-day}$

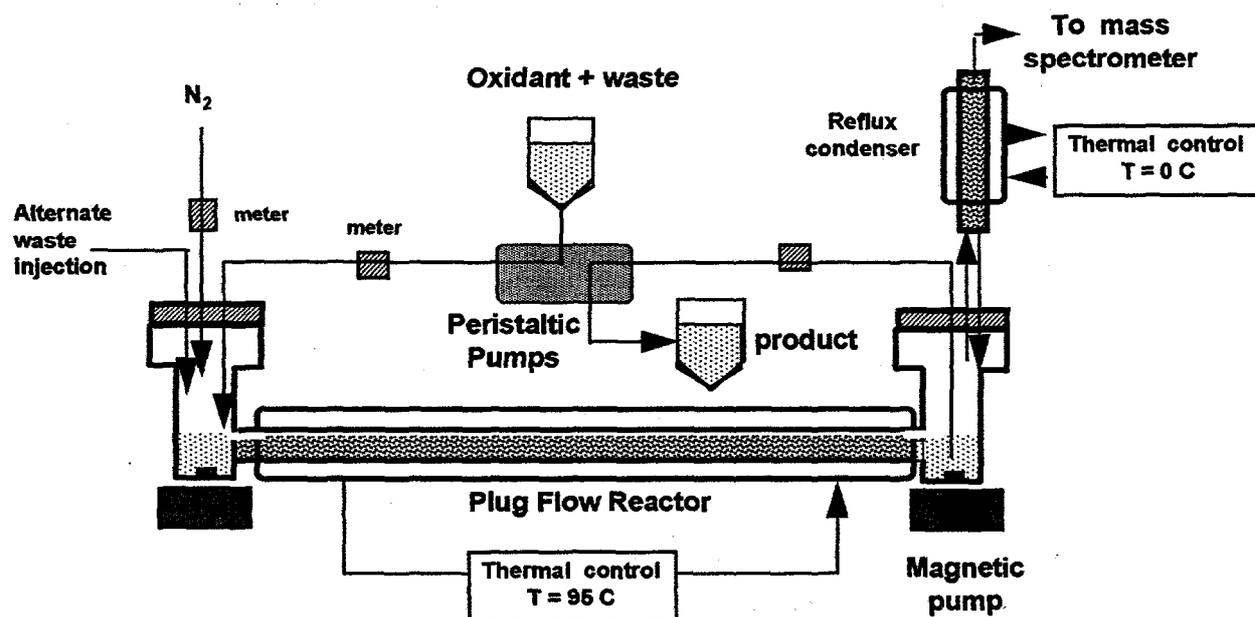
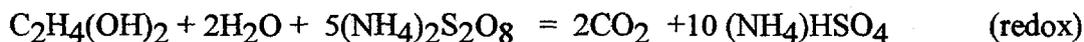


Figure 3. Experimental Configuration of the plug flow reactor.

4.0 Technical Results

4.1 Plug Flow Reactor Tests (Ethylene Glycol)

Shake-down tests were done with ethylene glycol to determine operability of the PFR and diagnostics. The partial and net reactions for ethylene glycol (EG) and peroxydisulfate are:



Since 10 equivalents of peroxydisulfate are consumed per mole of ethylene glycol, the equivalent weight of the ethylene glycol is 6.2 g/equiv. In one experiment, 200 ml of a room-temperature premixed solution of 1N $\text{C}_2\text{H}_4(\text{OH})_2 + 2\text{N } (\text{NH}_4)_2\text{S}_2\text{O}_8 + 0.1\text{M } \text{H}_2\text{SO}_4$ were added to the preheated reactor tube, and circulated continuously at 9.8 ml/min; the preheated reactor brought the temperature to 95 °C within 2-3 minutes. The time constant for residence in the reactor is only 20 minutes. Argon was passed over the free surface of the reaction medium 8 l/min and thence through a 6-inch condenser. The condenser gas was bled into the residual gas analyzer. Experimental conditions and results are summarized in Table 3.

Figure 4 and 5 give respectively the instantaneous and time-integrated signals for argon, carbon dioxide and oxygen--all measure relative to the fixed argon flow rate. A sharp peak in the carbon dioxide signal occurs after only 8 minutes, and spans only 8 minutes of time--indicating that the EG is substantially destroyed after passing through 40% of the PFR tube. We can estimate a quasi-first-order reaction rate constant from equation (3), for a 1 N $\text{C}_2\text{H}_4(\text{OH})_2$ solution and the 2N oxidant concentration:

$$k_a' \sim [\text{C}_2\text{H}_4(\text{OH})_2]/[(\text{NH}_4)_2\text{S}_2\text{O}_8] 8 \text{ min} = 0.06 \text{ min}^{-1}$$

This result is similar to the rate constant (0.06 min⁻¹) found to fit the curve for EG oxidation in Figure 2, thus confirming the operation of the PFR with a reaction scheme similar to that of a batch reactor.

There is a second smaller peak at about 25 minutes. The peak was reproduced during 2 similar runs. This peak may be the result of oxidation of EG which initially filled the exiting well (relatively cold) and thus was not fully reacted until the entire volume was pumped back to the inlet--after 20 minutes of cycling. If so, the peak is an artifact of the injection of a cold mixture of oxidant and EG into the hot reactor--and would not be seen during continuous injection of waste in the PFR.

It is also possible that the peak is due to the oxidation of organic materials leached from or resulting from the surface oxidation of the Viton tubing used to transfer (relatively cold) oxidant from the exit well to the entrance of the PFR. We note that the integral of the CO₂ curve is slightly greater (Table 3) than the actual CO₂ evolved during the oxidation of EG, although there are errors of ~1% in this numerical integration of discrete data.

Integrals of the curves in Figure 3 are shown in Figure 4. Oxidation is substantially complete after 40 minutes, with DRE >99.7% determined by analysis of the reaction medium at that time. In two additional experiments, the final efficiencies were DRE >99.93% and >99.91%. Figure 5 shows (on logarithmic scale) the signals for a probable reaction intermediate, formaldehyde, which was assumed to be the cause of the above background mass spectrometer reading at a molecular weight of 30. The ratio of formaldehyde to CO₂ was approximately 1:1000. Since formaldehyde may be an intermediate in oxidation of ethylene glycol, it is possible that a portion of it evaporated into the free overflowing argon stream along with CO₂. The argon overflow was introduced into the PFR system in order to give a time resolution to the reaction offgas of about 1 second. In a production plug flow reactor, the reductant and resultant carbon dioxide bubbles would reside within the reaction medium (or be refluxed through the reaction medium) for the liquid phase residence time--about 20 minutes--allowing trace organics to re-enter the liquid phase and become oxidized. If this is true, then less-than-100% DRE is an artifact of our diagnostic approach involving the use of a carrier gas overflow.

Table 3. Data from operation of the PFR for the destruction of ethylene glycol.

Parameter	Amount	Comments
Mass of EG in feed	1.24 g	gravimetric
Flow rate--reaction liquids	9.8 ml/min	
Flow rate--argon gas	81 ml/min	± 2%
Residence time in PFR	20 min	volume/flow rate
Reaction volume	200 ml	
Initial concentration	2:1 ratio oxidant to reductant	2N S ₂ O ₈ ²⁻ + 1N C ₂ H ₄ (OH) ₂ + 0.1M H ₂ SO ₄
Amount of EG destroyed at 40 min	1.27 +/- g	determined from numerical integration of CO ₂ curve
Destruction/removal efficiency of EG at 40 min	>99.7%	Determined by TOC analysis of liquor samples taken at 40 minutes.
Rate constant for EG destruction	0.06 min ⁻¹	determined from Eq. 3, using normalities: $k_a' = [EG]/(8 \text{ min } [Ox])$

Conclusion. The PFR efficiently destroyed the EG model chemical at a rate predicted by earlier experiments in batch reactors, with overall DRE ranging for >99.7 to >99.93 %. This was lower than the DRE found with batch reactor oxidations of EG under reflux of >99.995%. A second small wave was encountered after an interval equal to the residence time of the reaction medium in the PFR during continuous recycle of the reaction medium. This second peak is most likely an artifact of the loading of the cold reaction medium into an initially empty reaction tube,

which caused a small, initially downstream portion to remain incompletely reacted until a complete cycle had been completed (time constant, 20 min).

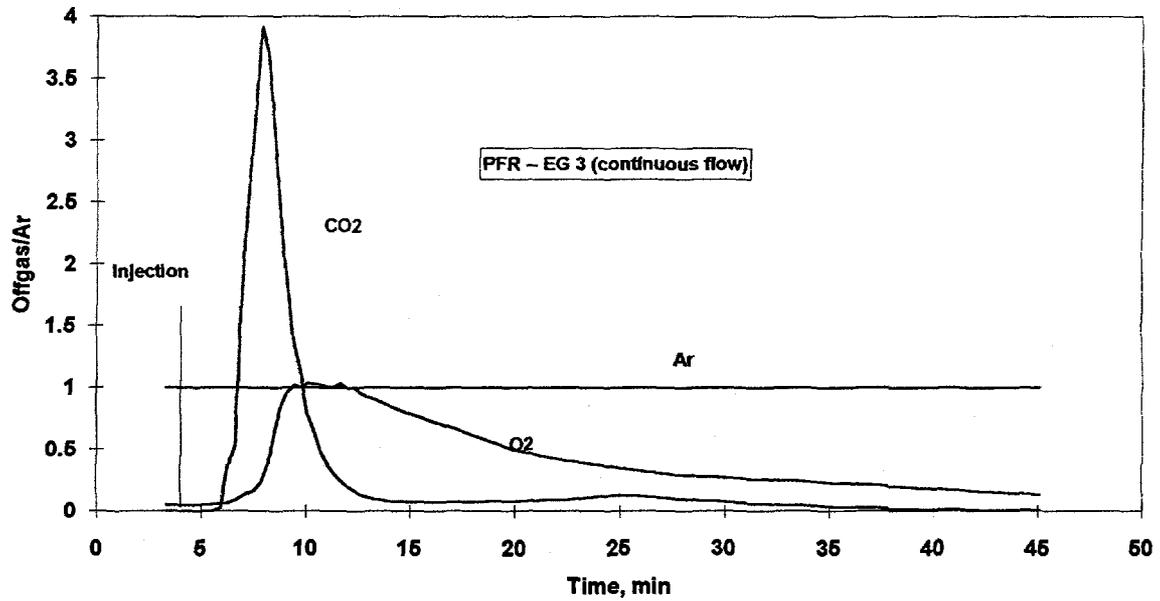


Figure 4. Rate of carbon dioxide and oxygen evolution for continuous cycling of the oxidant and reductant through the PFR, with argon gas overflow for diagnostics.

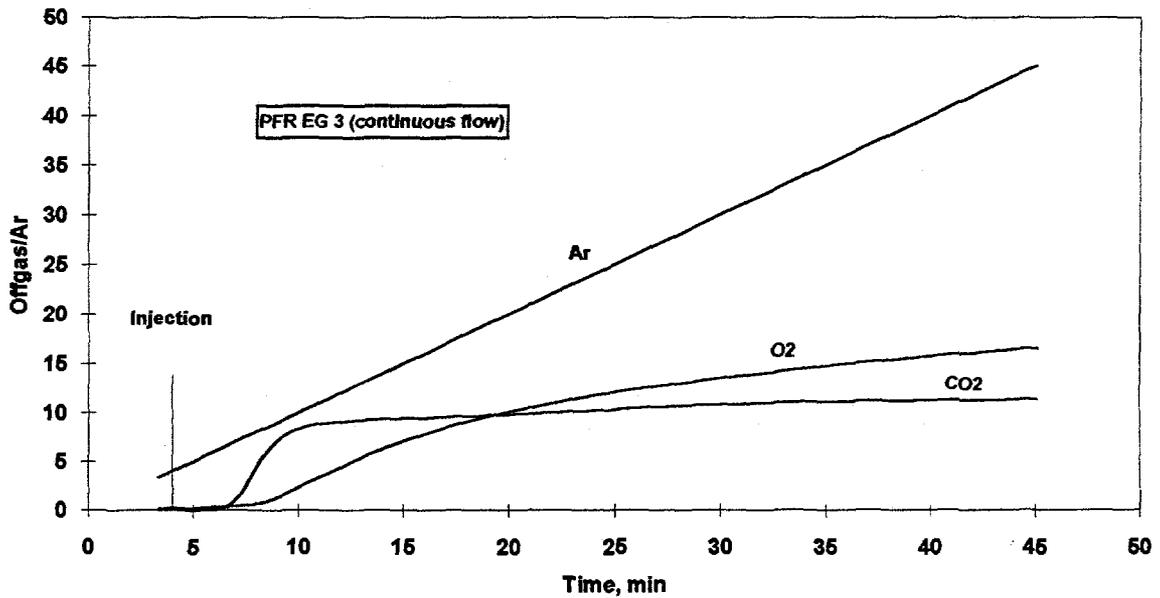


Figure 5. Integral CO₂ and O₂ production for continuous flow in the PFR, relative to argon flow.

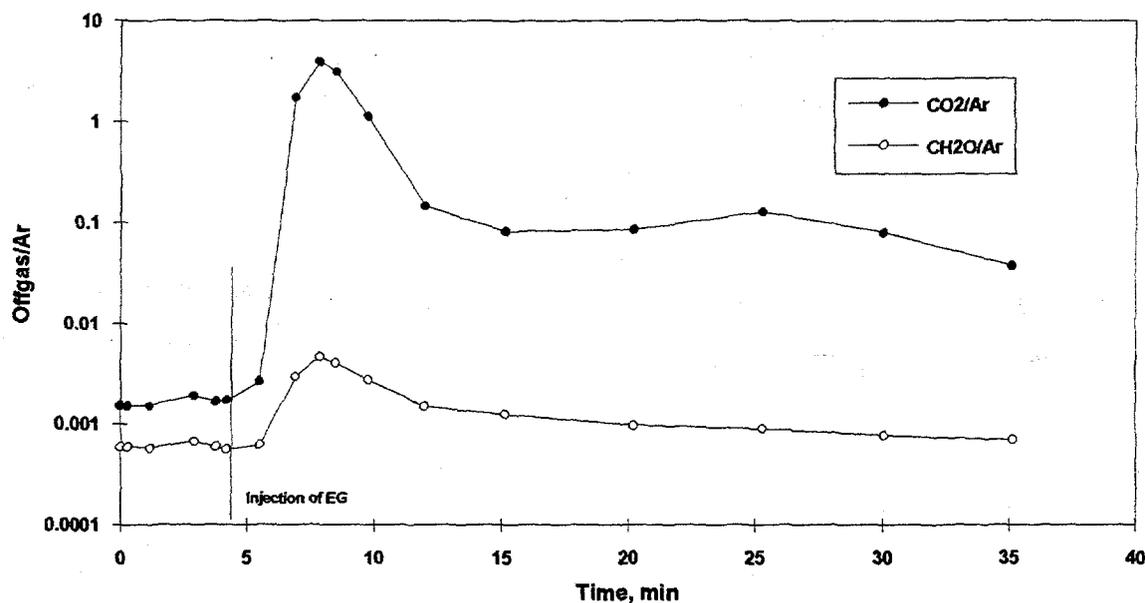


Figure 6. Comparison of carbon dioxide and mass/charge ratio 30 (formaldehyde) in off-gas during oxidation of ethylene glycol. The injection of the reaction medium occurred at 4 min. The formaldehyde signal may result from the reduced contacting and residence times of off-gas in the reaction medium, due to the use of a separate overflow phase of argon.

We found evidence of a trace off-gas constituent at molecular weight 30 g/mol, which we interpreted to be formaldehyde, a likely reaction intermediate. If this off-gas accounts for the less than perfect DRE, it is an artifact of the sampling technique which uses a continuous overflow of argon to limit residence time of carbon dioxide product in the reactor. Subsequent tests will be undertaken in the single-pass mode and without argon overflow, to more accurately measure a DRE. Any production PFR should be provided with a packed column condenser to collect and return unreacted off-gas contaminants to the reaction medium. Alternatively, the process might be operated in batch mode under reflux.

4.2 Pre-Reactor Tests

A batch pre-reactor is used for destruction of solids or water-immiscible fluids, to produce organic liquids suitable for final destruction in a PFR. In some cases, the destruction of the organic is complete in the reactor.

Destruction of Kerosene

Samples of kerosene (the predominate component of which is dodecane) were fully oxidized in well-stirred batch reactors, at $T \sim 100$ °C and without catalysis by a solution of 4 N ammonium peroxydisulfate + 0.1 M H_2SO_4 at 100 °C. Kerosene consists of alkanes (C_{10} - C_{16} ; and predominately n-dodecane) plus lesser amounts of benzene and naphthalene derivatives. Five

milliliters of kerosene were added to 50 ml of 0.1 M H₂SO₄, and the 4N peroxydisulfate solution was pumped into the vessel at a rate of 5 ml/min. After 70 minutes, the solution was examined and found to be free of any visible second phase. The total carbon analysis at this point indicated 1.30 ppm carbon remaining. After an additional 70 minutes of reaction, the total carbon analysis indicated 0.27 ppm C.

Table 4. Results for the Oxidation of Kerosene (predominately dodecane)

Time min.	Mass, grams	Total oxidant added, Equiv.	Carbon determination, ppm-wt as C	Carbon unoxidized, grams carbon	Destruction and removal extent
0	54	0	59060	3.17	0.0
70	564	1.4	1.30	0.00073	0.99977
140	1073	2.8	0.27	0.00029	0.99991

Destruction of Triethylamine: Nitrogen Product Species

Wastes containing amino groups tend to be resistant to chemical oxidation. In previous work [3], trialkyl amines were fully oxidized by ammonium peroxydisulfate at low initial concentrations (< 16 ppm; 0.14 mM; 0.005 N) in a Pt-wire catalyzed reactor at 100 °C; and in higher concentrations (0.032 N) in uncatalyzed 1-L batch reactor vessels at 95 °C. The first order rate constants in the two systems were, respectively, $k_a' = 0.0076 \text{ min}^{-1}$ and $k_a' = 0.037 \text{ min}^{-1}$. The higher rates of oxidation obtained with the higher initial concentration of organic results from the acceleration of the breakdown of peroxydisulfate into sulfate free-radicals in the presence of organic free radical intermediates.

In this work, we have determined the distribution of nitrogen products following oxidation of triethylamine by sodium peroxydisulfate. Water (100 ml) and 0.35 ml of N(C₂H₅)₃ (254 mg, 0.0025 moles) were added to a 1 L batch reactor vessel and rapidly heated to 100 C under reflux. The oxidant (3.6 N Na₂S₂O₈) was added at a rate of 2.0 ml/min. Samples were taken after 26 and 42 ml of oxidant were added. The organic fraction was destroyed to better than 98.8% in 13 minutes and to below the limit of detection (0.5 ppm, >99.97%) in 21 minutes. The samples were concentrated by precipitation of the excess sulfate by Ba(OH)₂, and then analyzed for nitrate and nitrite by solution chromatography. Summary results are given in Table 5.

Conclusions. Triethylamine can be oxidized fully by peroxydisulfate even at low concentrations, and the molar efficiency of the reaction exceeds 96% for the first 98% of the oxidation (13 minutes). Most of the nitrogen remains in the -3 oxidation state (ammonium ion), but both nitrite and nitrate are found in the final product. Most of the nitrate appears after 98% of the oxidation is complete as measured by the total carbon analysis of the medium. This means that most of the organic carbon is oxidized before the onset of any substantial nitrogen oxidation.

Table 5. Distribution of nitrogen following oxidation of triethylamine at an initial concentration of 25.1 mM (0.090 equivalents, total) by peroxydisulfate in a batch reactor.

Time min.	Oxidant added, equiv.	Total mass grams	C ppm	NO ₃ ⁻ ppm	NO ₂ ⁻ ppm	Mole-fraction N as nitrate	Mole-fraction N as nitrite	Mole-fraction N as NH ₄ ⁺ *	Mole-fraction C oxidized to CO ₂
0	0	100.3	1850	0	0	0	0	--	0
13	0.094	137	22	14	7	0.012	0.008	0.98	>0.988
21	0.151	160	0	34	10	0.035	0.014	0.95	>0.9997

*calculated from difference in total nitrogen and the sum of nitrate and nitrite products, assuming no N₂ formation.

Destruction of Cotton Machine Shop Rags (Cellulose; dyes; grease)

We undertook two preliminary batch reactor digestion's of Red Devil™ cotton machine shop rags, to estimate the rate of destruction of this cellulose-based waste in batch reactors.

The machine shop rags (dirtied with oil, and containing an aniline red dye) were cut into 0.5-1 cm² pieces. Water (100 ml) and 7.5 g of rag were added to a 1L batch reactor and heated to 100 C under reflux. 2.0 N (NH₄)₂S₂O₈ + 0.1 M H₂SO₄ was added at a rate of 10 ml/min for 75 min, with the reaction vessel stirred using a 2 cm magnetic stirring bar. A total of 7.4 g of the rag were destroyed, but 0.1 g (which became tangled on a glass thermocouple well) was in poor contact the oxidant medium and was not destroyed.

To improve contacting, the 5.0 grams of shredded cotton rag were packed into a glass tube resting in the reaction vessel containing 200 ml of water; the tube was arranged such that 2 N ammonium peroxydisulfate contacted first the cotton rags before being diluted. After 40 minutes, all cotton below the surface of the liquid had been destroyed, while cotton out of thermal contact with the reaction medium (above the liquid level) was incompletely consumed.

Conclusions. Cotton rags are rapidly destroyed by acidified ammonium peroxydisulfate without catalysis in 40-75 minutes provided the reaction medium is agitated and the cotton remains in good thermal contact with the reaction medium. Since cotton is a polysaccharide which is built up of units similar materials already quantitatively destroyed by peroxydisulfate (sucrose, alcohol, carboxylates), the problem of cotton destruction is one primarily of achieving sufficient contacting to initiate chain breaking. Mechanical means (such as high speed impellers or revolving vessels) are required to prevent the cotton fibers from floating above the surface of the reaction medium, which would prevent sufficient heating and remove them from contact with the oxidant. The uncatalyzed reaction is not limited by kinetic factors at T ~ 100 °C and ambient pressure.

Tributyl-phosphate (TBP) and Tributyl-phosphate/kerosene mixtures.

The experiments were first carried out under similar conditions as those of rag and kerosene destruction: oxidant was added to a vessel containing excess TBP such that the reductant was always present in excess. Few minutes after the addition of 4 N $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (5 mL/min), an orange-red oily liquid was formed and floated on the top of solution, which we interpreted to be the result of polymerization of free-radical intermediate oxidation products under conditions of deficit oxidant.

Since kerosene was completely destroyed under nearly identical conditions, we attempted oxidation of an equal volume mixture of TBP and kerosene. After the 0.1 M H_2SO_4 solution was heated to boil, 5 mL of the mixture was added dropwise (~ 0.15 mL/min) into the reactor while maintaining the 5.0 mL/min addition rate of peroxydisulfate solution. No orange-red oil or solid phases were formed. It is likely that the radicals formed from TBP are prevented to polymerize by reacting with either kerosene or products from the oxidation of kerosene.

In planned tests, we will add the TBP to excess peroxydisulfate, where we expect full oxidation through the gettering of organic free radical intermediates by the peroxydisulfate ion. Other organo-phosphates have been fully and rapidly oxidized by us under conditions of excess oxidant [3], including methyl-phosphonic acid and di-isopropyl-methyl-phosphonate (See Table 1).

5. Conclusions

We have completed the installation and initial shakedown tests of a facility to measure the effectiveness of uncatalyzed peroxydisulfate as an oxidant for an ambient pressure, low-temperature alternative to incineration. Preliminary tests of the plug flow reactor or supporting batch reactor confirmed system effectiveness on ethylene glycol, triethylamine, kerosene, rags, and TBP. At the suggestion of reviewers, we conducted tests on kerosene and rags in lieu of tests on chars. (Proposed DOWEX tests were completed prior to the start of this task, and have been separately published [3].) We also added tests on triethylamine to determine the fate of the amino nitrogen. Specific conclusions are as follows:

(1) Reaction rates for the oxidative destruction of 1N ethylene glycol in the PFR confirmed rate constants ($k_a' = 0.06 \text{ min}^{-1}$) obtained from curve fits to data from batch reactors obtained earlier [3]. Based on analysis of the reaction medium, destruction extents ranged from >99.7 to >99.97 after 40 minutes of operation, compared with $>99.995\%$ in batch reactions. This less-than perfect destruction extent in the PFR can be tentatively attributed to the experimental technique of adding cold reaction medium (oxidant plus EG) to an empty reaction vessel, which resulted insufficient time-at-temperature for a small initially-cold portion of the medium at the downstream end at the time of injection. Future tests will be conducted with one-pas flow-through, with destruction measured in the steady state.

(2) Continuous off-gas analysis were conducted (time resolution ~ 1 s) using a mass-spectrometer. A signal at 30 g/mole (1/1000 of the carbon dioxide) was attributed to evaporation of formaldehyde (a reaction intermediate) into the argon overflow. This signal is an artifact of the sampling technique using a rapid argon overflow (free volume), which was used to limit product gas residence time in the reactor to about 1 s, rather than the 20 minutes reaction time allowed for

the reaction medium to complete the liquid phase reaction. Loss of formaldehyde can be avoided by (1) eliminating the gas overflow and examining only the carbon dioxide emerging after 20 minutes of contacting with the oxidation medium; (2) using an efficient packed-column condenser, to return liquids to the reactor; or (3) operating the process in batch mode, with total retention of off-gas for the duration of the treatment.

(3) Tests on kerosene were conducted at the urging of INEL reviewers. Kerosene was destroyed in batch reactors to DRE of 99.991% after 140 minutes at 100 °C. The reaction was substantially complete at 70 minutes, where the DRE was 99.977%.

(4) Tests on triethylamine showed destruction >99.97% after 21 minutes at 100 °C, with the amino nitrogen being converted substantially to ammonium ion, with small amounts of nitrite and nitrate at the terminal stages of oxidation.

(5) Cotton rags (cellulose, oil and dye) were substantially (>95%) destroyed after 40 minutes, but incomplete contacting of the cotton with the reaction medium prevented measurement of a DRE.

(6) Tributyl phosphate tends to polymerize under conditions of deficient oxidant, but this tendency does not occur with equal volume mixtures of TBP and kerosene. Experiments will be repeated under conditions of excess oxidant, which were found to completely oxidize methyl phosphonic acid and di-isopropyl-methyl-phosphonate at 100 °C.

(7) At this stage, we have found no fundamental barriers which would prevent the development of an omnivorous ambient-pressure, low-temperature process for destruction of organic solids and liquids. However, the tendency for complex organic molecules to be oxidized to CO₂ by mechanisms involving small volatile organic intermediates (such as methanol or formaldehyde) suggests that some of these will be entrained in the carbon dioxide off-gas. We expect that any continuous effluent process (such as a PFR) will require the use of an off-gas reflux column to return any volatile precursors to CO₂ or other volatile constituents to the reaction medium. The process might alternatively be operated as a batch process under continuous reflux, or with temporary retention of the off-gas until complete oxidation is achieved.

Acknowledgments

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

References

1. John F. Cooper, Joseph C. Farmer, Beverly Lum and Frances Wang, "Direct Chemical Oxidation of Hazardous and Mixed Wastes," (Proceedings of the Third Biennial Mixed Waste Symposium, August 1995, Baltimore.)
2. John F. Cooper, Francis Wang, R. Krueger, J. Farmer, M. Adamson and K. King, "Direct chemical oxidation: peroxydisulfate destruction of organic wastes," (Proc. World Environmental Congress: International Conference and Trade Fair, London Ontario 17-21 September 1995).

3. John F. Cooper, Francis T. Wang, Roger Krueger, Ken King, Joseph C. Farmer and Martyn Adamson, "Destruction of organic wastes by ammonium peroxydisulfate with electrolytic regeneration of the oxidant," paper submitted to the J. Electrochem. Society, September 1995.
4. D. A. House, "Kinetics and Mechanism of oxidations by peroxydisulfate," *Chem. Rev.* **62**, 185, (1961).
5. Francesco Minisci and Attilio Citterio, "Electron-transfer processes: peroxydisulfate, a useful and versatile reagent in organic chemistry," *Acc. Chem. Res.* v. 16 27 (1983).
6. Jon M. Baldwin and Richard E. McAtee, "Determination of organic carbon in water with a silver-catalyzed peroxydisulfate wet chemical oxidation method," *Microchemical Journal*, v. 19, 179 (1974).
7. "Model 700 TOC Total Organic Carbon Users Manual, (O.I. Analytical, Inc.; Graham road at Wellborn Rd. PO Box 2980; College Station TX 77841-2980).
8. Walter C. Schumb, Charles N. Satterfield, Ralph L. Wentworth, *Hydrogen Peroxide*, (Reinhold Publishing, Inc., New York, 1955).
9. Wolfgang Thiele and Hermann Matschiner, "Zur elektrosynthese von Wasserstoffperoxid und Peroxodisulfaten, Teil I. Wasserstoffperoxid und Peroxodischwefelsauer," *Chem. Techn.* v. 29(3) p. 148 (1977).
10. "Peroxides and Peroxy Compounds, Inorganic," (*Encyclopedia of Chemical Technology*, V. 17, ed. Kirk Othmer).
11. *Uses of Persulfate* (Bulletin of FMC, Inc.; Buffalo NY; 1951; 1960).
12. J. Richard Pugh, "Degradation of PCBs and atrazine by peroxysulfate compounds (Proc. World Environmental Congress, International Conference and Trade Fair, London Ontario, Sept. 17-22, 1995).
13. Committee on Alternative Chemical Demilitarization Technologies, National Research Council, "Alternative technologies for the destruction of chemical agents and munitions", Washington DC: National Academy Press, 1993.
14. Yu-Chu Yang, "Chemical Reactions for Neutralising Chemical Warfare Agents," *Chemistry and Industry*, May 1995.
15. J. P. Wilks, and N. S. Holt, "Wet oxidation of mixed organic and inorganic radioactive sludge wastes from a water reactor," *Waste Management*, v. 10 p. 197 (1990). See also, J. P. Wilks, D. J. Holman and N. S. Holt, (*AEA Technology*), "Pilot scale demonstration of spent ion exchange resin treatment by wet oxidation," paper submitted to the 1991 Joint International Waste Management Conference.
16. T. Piccinno, A. Salluzzo, and L. Nardi, "Wet oxidation by hydrogen peroxide for the treatment of mixed radioactive and toxic organic wastes and waste waters," *Waste Management*, v. 11 125 (1991).
17. J. Balej, "Thermodynamics of reactions during the electrosynthesis of peroxodisulfates," *Electrochimica Acta* **29(9)** 1239-1242 (1984).

18. W. M. Lattimer, *The oxidation states of the elements and their potentials in aqueous solutions*, Prentice Hall, NY.
19. G. F. Potapova, O. V. Shestakova, A. I. Sorokin, and S. A. Asaturov, "Electrosynthesis of ammonium persulfate at glassy carbon anode," *Russ. Electrochemistry*, **31(5)** 477 (1995).
20. John F. Cooper, *Large-Area Decontamination and Detoxification using Peroxydisulfate with UV and Metal Ion Catalysis*, Lawrence Livermore National Laboratory US Patent Record of Invention and Disclosure IL-9853 January 1996.
21. F. D. Fisher, G. S. Barney, T. D. Cooper and M. J. Duchsherer, "Silver-catalyzed PuO₂ Dissolution with Persulfate," (Westinghouse Hanford Company Report WHC-SA-1170-FP, June 1991).
22. P. D. Goulden and D. H. J. Anthony, *Analytical Chemistry* **50(7)** 953 (1978).

Appendix A. Proposal Work Statement for Mixed Waste Focus Task

OFFICE OF TECHNOLOGY DEVELOPMENT

Part 1 Task Summary

Title: DEMONSTRATION OF OMNIVOROUS NON THERMAL MIXED WASTE:

Direct chemical oxidation using peroxydisulfate

Program Elements	NW03-COMBUSTIBLE ORGANICS
Focus Area:	(UST, D&D, Landfills, Plumes, Mixed Waste)
TTP No.:	SF-# or New
Revision:	Start at 0
Date:	
Subtask No.	(For roll-up TTP's)
Contractor:	LLNL
EM-50 Office:	(DTE, EP, PS, RD, SP, TD)
Fiscal Year:	(FY95 targeted for funding)
HQ Program Manager:	
HQ Financial Officer:	Jim Simpson
Technical Program Officer:	Richard Scott, DOE/SAN, (510) 637-1623
Principal Investigator:	John F. Cooper
Technical Program Manager:	Jesse L. Yow, Jr., LLNL (510) 422-3521
ID/IP Coordinator:	
Joint Participants:	(Other labs, industry, universities, other)
Jointly Funded Program Code:	
Primary Technology Area:	
Budget & Reporting Code:	(B&R Code) TBD
Joint Budget & Reporting Code:	(WBS) TBD

Task/Subtask Summary

Direct Chemical Oxidation (DCO) employs 100 °C, 1-Atm solutions of acidified peroxydisulfate to destroy any organic solid or liquid waste, including nitrated- and chlorinated wastes, plastics, and carbon chars. The process uses no toxic catalysts and has no unsolved corrosion problems. Secondary wastes are avoided by recycling the sulfate product into peroxydisulfate. The process combines three mature technologies: the sulfate/p peroxydisulfate recycle step [makes $(\text{NH}_4)_2\text{S}_2\text{O}_8$ from NH_4HSO_4] of the old hydrogen peroxide industry (1915-60); today's 1000 ton/y treatment of petroleum-recovery wastes by peroxydisulfate; and Total Carbon Analyzers which use this process to detect any organic substance by oxidation.

We propose to integrate the knowledge embodied in these three technologies to create an omnivorous waste treatment technology, and to demonstrate it on an engineering (bench) scale (100 A, 30 g/day level) on DOE-complex waste surrogates. In addition to broad organic solids and liquids categories, we will demonstrate destruction of (1) chlorinated/oxyhalogenated wastes

with off-gas neutralization of the chlorine and (2) nitrated wastes, with conversion to N_2O/N_2 in a modified plug-flow reactor using Cl^- -catalyzed autoreduction of hot NH_4NO_3 solutions.

The following start-up subtask ("Microscale tests," \$100 K, 3 months) was suggested by EM-50, following review of preliminary proposal which identified Task A and Task B; these tasks are included for reference, and are intended to expand tests to nitrated and chlorinated wastes.

Start-up Task: Microscale tests of DCO using a plug-flow digester. \$100K for Oct.1-Dec. 31 1995.

In accordance with DOE guidelines for a start-up three-month project (Oct-Dec, 1995; \$100 K), this will be completed by Jan 1 1996 for consideration of DCO in the directed call:

A plug-flow tube reactor will be constructed (2.5 cm diameter, 1 m long) to fully oxidize 30 g/day (as carbon) of water-entrained solid or liquid organic wastes at 100 °C, with continuous removal of product gases using a N_2 carrier stream. The off-gas will be monitored for carbon CO_2 and O_2 using (an existing) residual gas analyzer, with internal calibration of the off-gas concentrations using the N_2 feed. Acidified ammonium peroxydisulfate solution (at concentrations previously produced in LLNL electrolysis cells) will be injected with waste surrogates. In parallel with the operation of the tube flow reactor, we will conduct batch digester studies of destruction of the same wastes, for development of an engineering model describing scale-up (rates as functions of system geometry, flows, and compositions at $T = 100$ °C and 1 ATM pressure).

The plug flow tube reactor and the batch reactor will be used to destroy: (1) ethylene glycol (a chemical model); (2) TBP; (3) DOWEX resin; (4) recalcitrant carbon chars found in incinerator ash; and (5) one additional chemical solid or liquid organic waste chosen from among suggested chemicals suggested by DOE sponsors of this work.

Task A. Integration of peroxydisulfate recycle with plug-flow digester. \$381 K OE + \$60K CE

This task demonstrates an integrated system (1 kA or 0.3 kg/day) consisting of a commercial electrolysis cell, heat exchanger, and plug-flow digester, with control via LabVu/IBM486 (existing). Efficient destruction will be verified for treatment of surrogates: tributyl phosphate, Trimsol, Dowex, 5%-chlorinated wastes, charcoal filter media, kerosene, and PVC. Duration: 12 months.

Task B. Extension of the process: highly chlorinated and nitrated wastes \$248K OE + \$30K CE

This task extends the usefulness of the unit of Task A by modifications for the treatment of heavily chlorinated, oxychloride and nitrated wastes. Oxyhalide intermediate products are destroyed by organic free-radical intermediates of peroxydisulfate treatment, while evolved chlorine gas (sink for chlorine) is neutralized in conventional reverse electrolysis cells to form NaCl. Since the working chemical in DCO is ammonium peroxydisulfate, any nitrates present are destroyed by Cl^- -catalyzed autodecomposition of NH_4NO_3 to form N_2 and N_2O . (Further reduction of N_2O to N_2 uses conventional catalytic converters, not covered here). Nitrate treatment would be accomplished in the downstream portions of the plug reactor, with modifications for thermal control, diagnostics, and off-gas collection and retention. Duration, 12 months.

Appendix B. Standard Electrode Potentials of Oxidants

Table B1. Standard electrode potentials of oxidants in acid solution [17,18].

Half-reaction	E_0° , V	Comments
$O_3 + 2H^+ + 2e^- = 2H_2O + O_2$	2.07	Not stable in high conc.
$(NH_4)_2S_2O_8 + 2H^+ + 2e^- = 2(NH_4)HSO_4$	2.05	Stable at 5 N, 20 °C; non-toxic products
$Ag^{+2} + 1e^- = Ag^+ \text{ (4M HClO}_4\text{)}$	1.90	Precipitated by chloride
$Co^{+3} + 1e^- = Co^{+2}$	1.84	Toxic metal
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.78	Weak, unstable oxidant
$HClO + H^+ + 2e^- = Cl^- + H_2O$	1.49	Chlorine bleach
$KMnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$	1.49	Non-reversible
$Ce^{+4} + 1e^- = Ce^{+3} \text{ (0.5 M H}_2\text{SO}_4\text{)}$	1.45	Weak
$O_2 + 2H_2O + 4e^- = 4OH^-$	1.23	Weak unless pressurized
$Fe^{+3} = Fe^{+2} \text{ (1M HCl)}$	0.77	Weak

Appendix C. Historical and Modern Materials Used with Peroxydisulfate Solutions.

Table C1. Historical and modern materials of construction for use with peroxydisulfate solutions [4,9,19].

<i>Proven materials</i>	<i>Uses at T = 30 °C</i>	<i>Uses at T = 100 °C</i>
Pt, glassy carbon [19]	anodes	Pt wire catalysts
graphite or lead	cathodes	
porous alumina	separators	reaction vessel filters
Ta; ebonite-covered Al	conductors	
hard rubber; PTFE; PP	insulation	
lead tubing	heat exchanger	heat exchanger
glass tubing	heat exchanger	heat exchanger
HDPE, PP, TFE, Pb, etc.	storage of 4 N oxidant	
PTFE	plumbing	reaction vessel
porcelain; stoneware	cell walls; separators	filters; reaction vessel; all media
glass-lined steel	heat exchanger	reaction vessel; all media
18-8 stainless + 2.2% Mo	heat exchanger	heat exchanger; low-Cl media
Krupp V4A	heat exchanger	heat exchanger; low-Cl media
Argon, nitrogen	inert atmosphere	evaporative cooling of reaction vessel

*crucible used in total carbon analyzers [7].