CONF-9509340--1

UCRL-JC-121999
PREPRINT

Destruction of VX by Aqueous-Phase Oxidation Using Peroxydisulfate (Direct Chemical Oxidation)

RECEIVED
APR 05 1996
OSTI

by

John F. Cooper
Roger Krueger
Joseph C. Farmer

Paper prepared for submittal to *The Workshop on Advances in Alternative Demilitarization Technologies, Reston, VA., September 25-27, 1995*

October 11, 1995

Lawrence Livermore National Laboratory

MASTER

Workshop on Advances in Alternative Demilitarization Technologies
Reston, Virginia 25-27 September 1995

Destruction of VX by Aqueous-Phase Oxidation Using Peroxydisulfate (Direct Chemical Oxidation)

John F. Cooper , Roger Krüeger and Joseph C. Farmer
Lawrence Livermore National Laboratory • Livermore CA 94550

Abstract

Chemical warfare agents may be completely destroyed (i.e., converted to water, carbon dioxide and inorganic salts) by oxidation at 90-100 °C using acidified ammonium peroxydisulfate, with subsequent recycle of the ammonium sulfate byproduct. The process requires no toxic or expended catalysts and produces no secondary wastes other than the precipitated inorganic content of the agents. To determine the oxidative capability of peroxydisulfate at low reductant concentrations, we measured rate data for oxidation of twenty diverse compounds characterized by diverse functional groups. Four of these compounds have bonds which are similar to those found in VX, HD and GB. On an equivalence basis, the integral first-order rate constants for oxidation at 100 °C are 0.012 ± 0.005 min^{-1} for di-isopropyl-methyl-phosphonate, methyl phosphonic acid, triethylamine and 2,2'-thiodiethanol, at low initial concentrations of ~50 ppm (as carbon) and pH = 1.5. To provide scale-up equations for a bulk chemical agent destruction process, we measured time-dependent oxidation of bulk model chemicals at *high concentrations* (0.5 N), and developed and tested a quantitative model. A practical process for bulk VX destruction would begin with chemical detoxification of the agent by existing techniques (such as hydrolysis or mild oxidation using Oxone), followed by mineralization of the largely-detoxified products by peroxydisulfate. Secondary wastes would be avoided by use of commercially-available electrolysis equipment to regenerate the oxidant. Reagent requirements, mass balance and scale up parameters are given for VX destruction, using peroxydisulfate alone, or supplemented with hydrogen peroxide. For the use of 2.5 N peroxydisulfate as the oxidant, a 1 m^3 digester will process about 200 kg (as C) per day. The process may be extended to the total destruction of HD and the hydrolysis products of G agents.

Background

Direct Chemical Oxidation. A process called "Direct Chemical Oxidation" ("DCO") has been under current development at LLNL (1994-5) for destruction of highly toxic substances as well as the organic fraction of undifferentiated mixed waste. DCO is essentially mineralization using hot peroxydisulfate [1-3]. We have completed three primary tasks of an on-going project: (1) 2 N ammonium peroxydisulfate was generated at >80% efficiencies from ammonium sulfate solutions by electrolysis (Loewenstein process); (2) integral rates of destruction of very low initial concentrations (50 ppm, as C) of twenty diverse compounds (including surrogates for VX, GB and GD, and HD) were measured at T = 100 °C and pH = 1.5; and (3) the time-dependent oxidation of concentrated (~ 0.5 N) model chemicals using electrolytic oxidant were followed in a stirred batch reactor, from which a quantitative model was developed. Full results are reported elsewhere [3]. Ongoing work (1995) involves the construction and testing of two engineering-scale flow reactors, which will provide detailed time-dependent measures of mineralization process as well as peroxydisulfate utilitztions, heat balances, and equations of scale.

This report concerns applications of DCO to the destruction of chemical warfare agents in bulk form. In early 1993, we recommended to the Committee on Alternate Chemical Demilitarization Technologies that peroxydisulfate mineralization be evaluated as an approach to destruction of bulk chemical agents at Newport IN and Aberdeen MD [4]. Subsequently, preliminary tests by ERDEC showed total mineralization of VX and HD by peroxydisulfate at T>80 °C [5]; no attempt was reported concerning process design or optimization.

We have proposed the system configuration is shown schematically in Figure 1. Peroxydisulfate is generated in flow electrolysis cells at T = 30 °C and stored. The oxidation of waste is confined to a plug flow reactor, with subsequent precipitation of the inorganic fraction of the wastes. For reaction kinetics associated with mineralization, efficient use of reagents is generally achieved with either with a continuous plug-flow reactor or with a batch reactor.

There are unique benefits associated with this approach: (1) No dissolved catalysts are required; this obviates problems of catalyst precipitation or loss by entrainment in wastes. (2) No secondary wastes are generated, the products of the reaction being the inorganic content of the chemical agents and ammonium hydrogen sulfate, which is recycled. (Table A3) (3) The process operates at ambient pressure and at low temperatures (T < 100 °C). (4) The reagents are easily handled and are non-corrosive to common vessel materials (Table A4). (5) The electrolysis process scales to 1 mt/day, and can make use of industrial technology and commercially-available equipment.

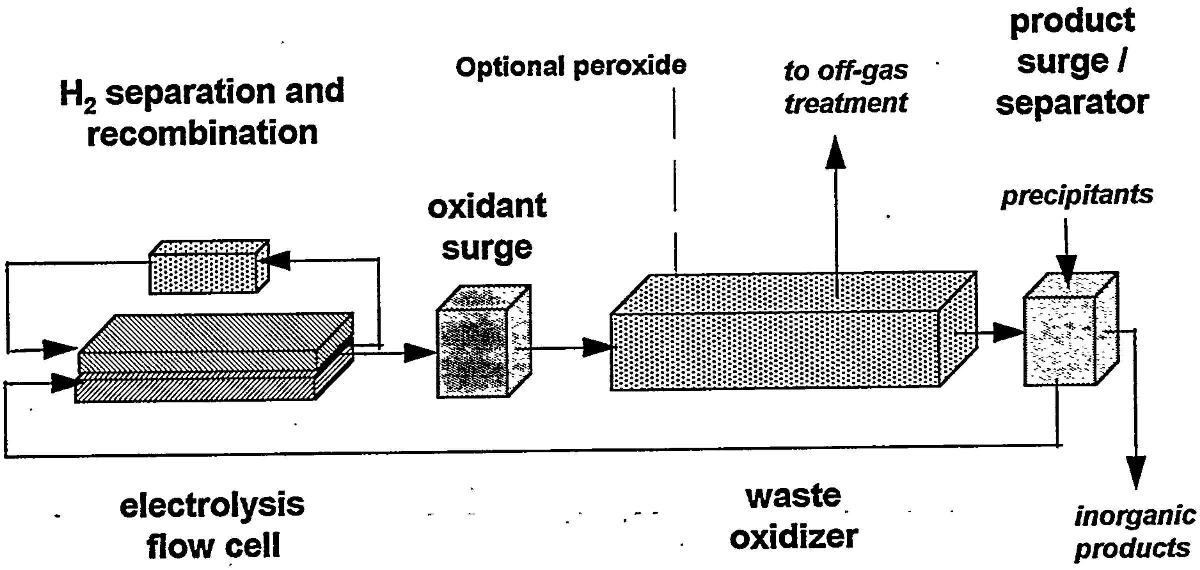

Fig. 1. The direct chemical oxidation process uses electrolysis cells to produce ammonium peroxydisulfate (T < 30 °C) , which is subsequently used in a batch- or a plug-flow reactor to fully oxidize solid or liquid organic wastes (T > 80 °C).

Peroxydisulfate use as an oxidant. Acidified ammonium peroxydisulfate is among the strongest known chemical compounds (See Table A5). Acidified peroxydisulfate is used routinely in commercial total organic carbon (TOC) analyzers [26,27]. Such analyzers detect carbon by total oxidative destruction of organic compounds. Peroxydisulfate has been used to destroy such resistant materials as PCBs and atrazine in ambient temperature soils [6]. Thousands of tons are used annually for destruction of hydraulic fluids used in enhanced oil recovery. Large quantities are produced annually for uses as bleaches (of paper and wood pulp; dyes and colorants), metal etching agents, intermediates in chemical syntheses and polymer production, and as disinfectants[24,25]. Materials attacked by hot acidified peroxydisulfate include elemental carbon, polyethylene, polyvinyl chloride, cellulose and metal carbides. Perfluorinated polymers are unreactive.

Aqueous solutions of ammonium peroxydisulfate are stable at ambient temperatures, and can be stored in polyethylene containers. The peroxydisulfate ion thermally decomposes to form $SO_4^{-\circ}$ free radicals at 80-100 °C (or at lower temperatures, upon activation by UV, radiolysis, certain metal ion redox couples, or platinum-metal catalysts). This begins a free-radical cascade resulting in OH° and intermediate organic free radicals which further accelerate the oxidant's attack on the organic substrate. Oxidation reactions of catalyzed and uncatalyzed peroxydisulfate are reviewed by House [7] and Minisci [8].

Industrial production of peroxydisulfate by electrolysis. For the first half of this century, hydrogen peroxide was produced industrially by the reaction of acidified peroxydisulfate with water, producing sulfate as a byproduct [9]. This sulfate was continuously recycled in the same plants back to peroxydisulfate by electrolysis at platinum electrodes at high current densities (0.5-2 A/cm^2). The working solutions contained sulfuric acid alone or acidified ammonium sulfate. This process produced the world's supply of hydrogen peroxide until being replaced by a non-electrolytic process in the 1960's. Abundant patent and technical literature exists concerning cell construction and operating conditions, electrochemical kinetics, and commercial uses of peroxydisulfate [7-10, 24, 25]. Large industrial sulfate-to-peroxydisulfate plants exist in the U.S. today [11], while electrolysis units are commercially available from several companies.

Oxidation of diverse compounds at low concentrations

Objectives. Despite widespread use of peroxydisulfate in total carbon analyzers, there is little generalized data on the rates of mineralization of diverse organic substances present at *low* concentrations (< 50 ppm, as C). This data is needed if we are to develop a general-purpose oxidation treatment for undifferentiated organic wastes, in the low-concentration range where collision theory predicts rates to diminish.

Technical approach and results. We measured destruction rates for ion exchange resin (DOWEX I-x4) and low concentrations (~50 ppm, as C) of chemical compounds bearing diverse functional groups, using a modified total carbon analyzer. These were chosen for their similarity with substances expected to be found in wastes, including chemical warfare agents. Low concentrations were chosen to simulate the final stages of waste destruction. The oxidation of the organic sample was generally stopped before 100% destruction, in order to provide a ratio of extent-destruction to time-interval and, hence, an integral rate constant. Partial results are shown in Table 1. [3] The oxidant was sodium peroxidisulfate (0.245 N), with pH adjusted to ~ 1.5 using phosphoric acid. Because of the low organic concentration, 0.15 cm^2 bright platinum wire catalyst was used to initiate production of $SO_4^{-\circ}$ free radical. (Some TOC instruments and techniques use UV radiation or transition metal redox couples for this purpose). For each compound, we calculated the number of equivalents required for complete oxidation of one mole to carbon dioxide and (as appropriate) sulfate, chloride, ammonium or nitrate. (In acid media, the nitrogen from alkylated amino groups are converted to ammonium ion, which is stable.) In most cases, a reaction time of $\Delta t = 2.5$ min allowed greater than 90% 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:

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

Here $[R]_o$ and $[R]_t$ are the initial and final concentrations of reductant, respectively, in units of normality (equivalents/liter); and [O] is the initial concentration of peroxydisulfate (0.245 N). Table 1 lists the compounds in ascending order of the rate of reaction (based on k_a). We reduced the data to an equivalency basis, which should allow more direct extrapolations to undifferentiated wastes. These results may also be expressed as an integral rate of production of carbon dioxide (all concentrations in molarity), recasting (1) into a form which emphasizes that we are measuring reaction rates from the appearance of the final product, yielded a molar rate constant k_a.

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 CO_2 suggests that the last step of oxidation to CO_2 may be rate controlling. The oxidation of the triethylamine sample was slow (0.006 min^{-1}) and consistent with the finding of tri-alkyl-amines in the residues following Fe(II)-catalyzed hydrogen peroxide destruction of ion exchange resins [18,19].

Four compounds in Table 1 are surrogates for products of the hydrolytic or oxidative detoxification of chemical warfare agents. (Actual agents and decomposition products were not available to us). Methyl phosphonic acid, $(CH_3)P(OH)_2O$; 2,2'-thiodiethanol, $S(CH_2CH_2OH)_2$; and Di-isopropyl-methyl-phosphonate (DIMP), $(C_3H_7O)_2P(CH_3)O$, have bond types and functional groups similar to those of hydrolyzed GB and GD, HD (Mustard), and Oxone-detoxified VX, respectively, and are commonly used as benign chemical surrogates for these materials. Oxone is a commercial bleach containing stable salts of peroxymonosulfuric acid--a decomposition product of peroxydisulfate. The test on triethylamine (TEA) was intended to simulate a portion of the VX molecule bearing an ionized alkylated amino group.

<u>Interpretation of results</u>. Reactions involving $S_2O_8^{-2}$ and water are generally first order with respect to $S_2O_8^{-2}$,

$$-d\,[S_2O_8^{-2}]/dt = k_o[S_2O_8^{-2}] \quad (3)$$

where k_o shows a linear dependence on acid concentration in mild to strong acids: $k_o = k_1 + k_2[H^+]$ [12,13]. At moderate acidity (pH > 1), water is oxidized to oxygen; above molar concentrations of acid, the peroxydisulfate may decompose to hydrogen peroxide and peroxymonosulfate (Caro's acid). A law similar to (3) holds for reactions with organic reducing agents as well, but the rate constant can be larger:

$$-d\,[R]/dt = k_a[S_2O_8^{-2}],\ k_a > k_o \quad (4)$$

The rate of reduction of $S_2O_8^{-2}$ found with pure water at moderate temperatures (30-60 °C) is accelerated (factors of 10-100) by the addition of oxidizable compounds, such as formate, oxalate, or alcohols. 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-radicals, which accelerate the initial decomposition of the peroxydisulfate. As discussed by House, the formation of a free radical intermediate R°, from the action of $SO_4^{-\circ}$ on R, leads (with the steady-state hypothesis) to a rate equation of the form

$$-d[R]/dt = k_3 [S_2O_8^{-2}] + k_4[R^\circ][S_2O_8^{-2}] \qquad (5)$$
$$= k_a [S_2O_8^{-2}]$$

Goulden [13] found that oxidation of a series of amino acids and EDTA began first order with respect to oxidant concentration, but ended first order with respect to both oxidant and organic concentrations as the organic concentration diminished to ~10 ppm.

Oxidation of model chemicals at high concentrations

Objectives. In order to develop equations of scale, it is necessary to know the rates of uncatalyzed oxidation (i.e., mineralization) reactions in the presence of high concentrations of reducible material. These are the conditions likely to prevail in large-scale processing of undifferentiated wastes or of chemical warfare tank agents. For reasons discussed above, the first order rate constant for peroxydisulfate oxidation is likely to be higher in the presence of high concentrations of organic substrate than in the low concentrations used in TOC measurements.

Technical approach and results. High concentrations (0.05-0.5 N) of model organic materials in Table 2 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. Up to 100 ml of 1.5 N oxidant solutions produced by electrolysis in our laboratory (or, in some cases, synthesized from reagent grade ammonium peroxydisulfate) were pumped steadily into the vessel at the indicated rate. Table 2 gives the initial and final concentration of reducing agent, the temperature, the reaction time t_f to achieve $[R]_f$, and the oxidant feed concentration and transfer rate. Of these materials, only the oxidation of the ion exchange resin Dowex I-x4 was too fast to reveal the oxidation-time profile.

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). The model assumes that the final step (carbon dioxide formation) is slow and determines the overall oxidation/time profile. The technical basis and derivation of the kinetic equation is given in reference [3]. The oxidation of organic to carbon dioxide follows the relation:

$$R_o - R_t = (k_a V_r G/k)\,t - k_a' V_r G/k^2 \,(1-\exp[-kt]), \qquad k \equiv k_o + k_a' \qquad (6)$$

k_a' is the rate constant (equivalence basis) of organic oxidation (an adjustable parameter); k_o is the measured rate constant for water oxidation; and V_rG is the rate of addition of peroxydisulfate to the digester (equivalents per second). The difference $(R_o - R_t)$ is the organic carbon remaining in the digester. The reasonable fit of equation (3) 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.

The curve fit to the data for ethylene glycol required adjustment of $k_{a'}$ to 0.06 min^{-1}, although the integral rate constant measured for ethylene glycol (at very low concentrations) was only 0.015 min^{-1}. The integral rate constants determined from these profiles as given in Table 2 (as k_a'') is consistently larger than those derived from the total carbon analyzer at much lower concentrations. The lower rate at lower concentrations may reflect a smaller role of organic ion intermediates in stimulating the initial decomposition of peroxydisulfate into sulfate free-radicals.

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

Oxidative detoxification of VX by peroxymonosulfate

VX may be detoxified by oxidation, using chlorine, peroxymonosulfate or hydrogen peroxide, and other oxidants[5, 14-17]. VX has been detoxified by oxidation in 50 kg batches on the pilot scale, using pH = 4 treatment with chlorine [17]. The half life of VX is 1.2 min., and destruction efficiencies to 10^8 were reported.

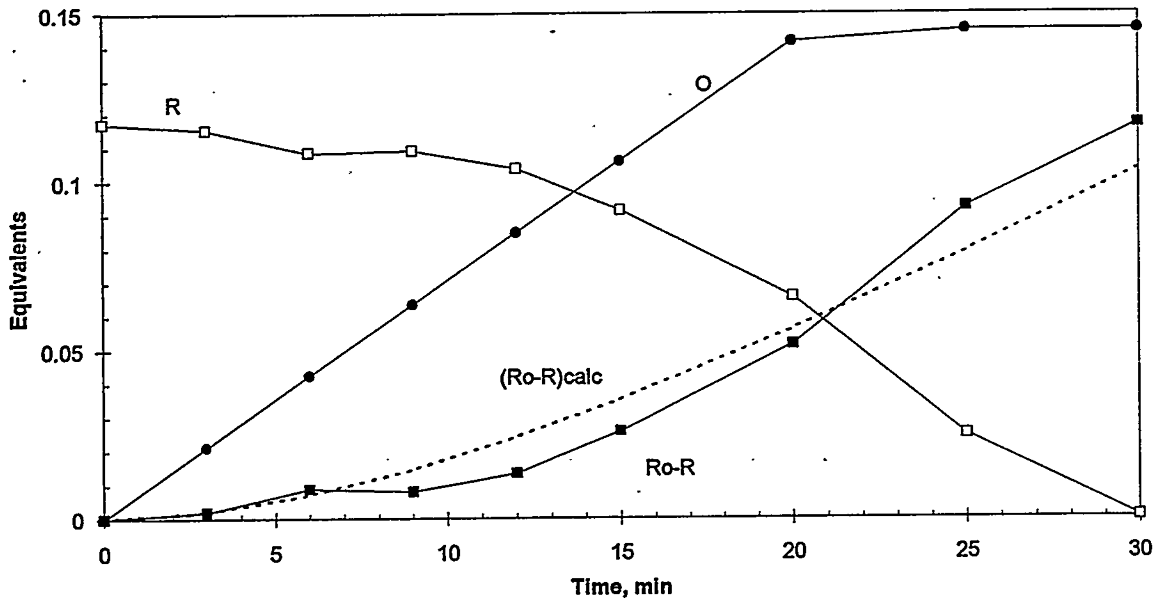

Fig. 2: Oxidation of ethylene glycol using near equivalent amounts of ammonium peroxydisulfate reagent under conditions of low and constant acidity (0.10 M H_2SO_4). Calculated curve is for simultaneous water oxidation (k_o = 0.02 min^{-1}) and organic oxidation ($k_{a'}$ = 0.06 min^{-1}, adjustable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

The process suggested here takes note of the existing process for VX decontamination. Treatment with Oxone (a commercial bleach containing stable salts of peroxymonosulfate or

Caro's acid [H_2SO_5]) effectively splits VX into non-lethal phosphonic and sulfonic acid derivatives, with a half life of 19 min at pH = 2.3 and T= 23 °C [15]. The reaction (shown in Figure 3) occurs under conditions of low pH where VX ios water soluble due to the ionization of the amino group, and consumes 6 equivalents of peroxymonosulfate per mole of VX.

Application of Direct Chemical Oxidation to the destruction of VX

Summary The approach is to completely destroy VX in four steps, in the system shown schematically in Figure 1. The steps are:

- Detoxification by peroxymonosulfate oxidation, as with Oxone;
- Complete mineralization of the detoxified agent by peroxydisulfate;
- Precipitation of excess salts using CaO; and
- Regeneration of the peroxydisulfate from the sulfate product.

The overall reaction stoichiometry of the electrolytic and oxidation steps are given in Appendix A, with reactions (Table A1) quantitative evaluation (Table A2).

(1) The VX is first detoxified at ambient temperature by treatment with the peroxymonosulfate generated *in situ* by the decomposition of peroxydisulfate at a platinum metal catalyst. This results in non-lethal phosphonic and sulfonic acid derivatives. (Figure 3).

(2) These sulfonic and phosphonic derivatives are then completely oxidized (mineralized) by 1-2.5 N $(NH_4)_2S_2O_8$ at T = 90 - 100 °C. The oxidation of detoxified VX by peroxydisulfate occurs until organic substances are converted entirely to carbon dioxide and water.

(3) The inorganic constituents of the process are precipitated by CaO as calcium phosphate and calcium sulfate, and are removed from the system. The ammonium ion is removed by partial precipitation of ammonium sulfate from chilled liquor.

(4) The remainder (acidified ammonium hydrogen sulfate) is then recycled to produce the peroxydisulfate in a closed-loop electrolysis cell purchased or leased from a vendor.

Given an overall rate constant of k_a = 0.025 min^{-1} (a conservative estimate for *high* concentrations of waste), 2.5 N oxidant, 80% mole efficiency, and an equivalent weight of about 3 g-C/equiv, a 1 m^3 digester will process about 200 kg of undifferentiated waste (as C) in one day. This preliminary estimate should be considered accurate to within a factor of two, and should apply to VX.

Discussion Peroxydisulfate rapidly decomposes to form peroxymonosulfate and thence hydrogen peroxide in hot acidic solutions. Platinum catalysts accelerates the production of peroxymonosulfuric acid (Caro's acid):

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4 \qquad (7)$$

The peroxymonosulfate [SO_5^{-2}] thus produced is used directly to decompose the VX *in lieu* of the same anion contained in Oxone. (Oxone consists of a salt of $KHSO_4$, $KHSO_5$, and K_2SO_4).

Alternative uses of peroxydisulfate in VX destruction. There are in all perhaps three ways in which peroxydisulfate technology could be used to destroy VX: (1) The destruction of VX could stop after detoxification using (locally recycled) peroxydisulfate (6 equiv/mole). (2) Peroxydisulfate could be use to mineralize VX, (74 equivalents/mole). (3) A cost-optimized combination of peroxydisulfate (10%) and hydrogen peroxide (90%) could be used to effect total destruction of VX. Scaleup data is given for each of these cases in Table A3.

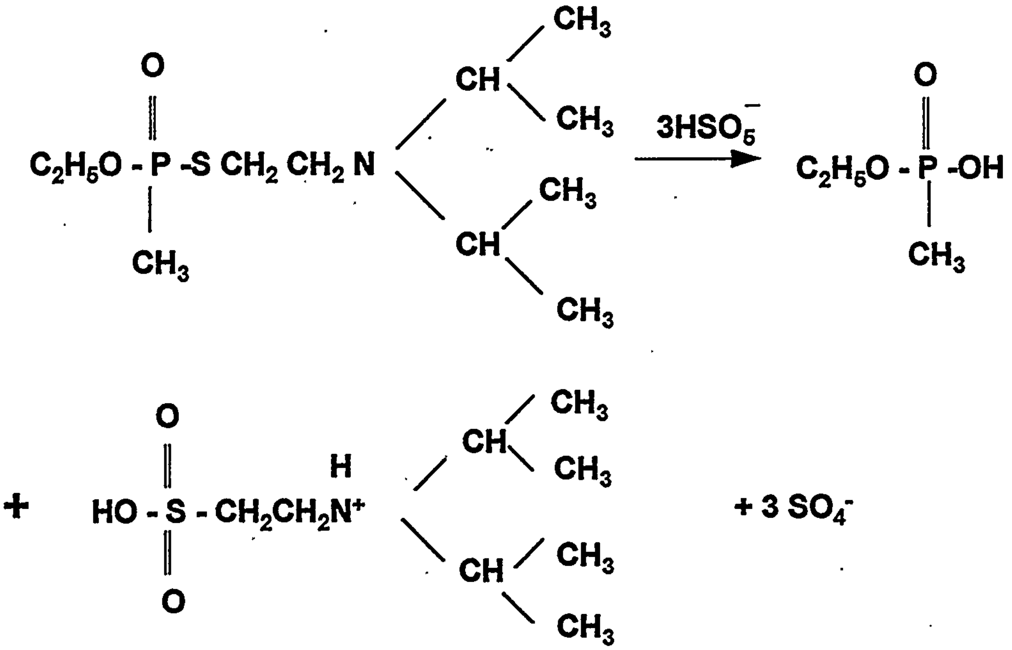

Figure 3. Detoxification of VX by peroxymonosulfate at pH =2.3 at 23 °C [15].

Conclusions

This work concludes that the rates of mineralization of VX (following detoxification by hydrolysis or oxidation) are sufficiently fast to form the basis of a practical bulk treatment technology for tank agents or for cleaning agent-contaminated munitions or equipment. While actual VX or VX oxidation or hydrolysis fragments were not available to us for test, the oxidation tests on 20 diverse compounds (including common agent surrogates DIMP, MPA, 2,2'-thiodiethanol, and tri-ethyl amine) revealed that integral rate constants were bound between narrow limits (0.006-0.020 min^{-1}) for low concentrations (<50 ppm-C). This result was not surprising, as mineralization processes depend on the rate of SO_4^{-o} free radical generation which is only indirectly dependent on the nature or concentration of the organic substrate (through organic free generation).

At the same time, high concentrations (0.5 N) were more rapidly destroyed. This is consistent with the accepted model for peroxydisulfate activation by a cascade of hydroxyl and organic free-radical intermediates [7,8]. The rates of a bulk destruction technique are projected to be about 200 kg/day (as carbon) for a 1 m^3 plug-flow or batch reactor, for high initial concentrations.

Required for applications to VX and other chemical warfare agents are (1) precipitation techniques for removing salt buildup (as Ca_2SO_4, $Ca_3(PO_4)_2$, $(NH_4)_2SO_4$ etc.); (2) integration of electrolytic and reactor subsystems; (3) reclamation of water from off-gas; and (4) certification of CO_2 off-gas purity. The fundamental advantages of direct chemical oxidation using peroxydisulfate over alternative aqueous processes derive from the unique combination: low temperature and pressure process operating in the aqueous phase; absence of requirements for toxic or consumable catalysts; grounding in mature industrial practice (electrolysis) and existing large-scale uses.

Table 1. Integral first order rate constants k_a' and k_a calculated from the extent of oxidation, as measured by CO_2 evolution using a modified total carbon analyzer [20]

No.	Compound	MW	n	fc	[R]o	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

[a] Conditions: T= 100°C ; $[H_3PO_4]$= 0.0574 M; $[S_2O_8{}^{-2}]$ = 0.245 N; 0.3 cm^2 Pt wire catalysis.

[b] Urea is not oxidized, but hydrolyzes at the reported rate to form $NH_4{}^+$ and CO_2.

Key: MW, molecular weight; n, equivalents per mole; fc, weight fraction carbon; R_0, initial concentration of organic; Ratio, oxidant to reductant concentration, initial; C(th) and C(t), theoretical and actual concentation 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.

Table 2. Summary of the oxidation experiments with model chemicals [3]

#	Compound	$[R]_0$, N	$[R]_f$, N	t_f min	Int k_a" min^{-1}	T, °C	Rate, ml/min	Oxidant[a]
1	Ethylene glycol	0.46	0.146	30	0.045	94	3	1.4 N + 2 M H_2SO_4
2	Ethylene glycol	0.23	<0.002	30	0.035	94	5	1.14 N + 2 M H_2SO_4
3	Ethylene glycol	0.39	<0.002	30	0.054	90	4.9	1.45 N $(NH_4)_2S_2O_8$ + 0.1 M H_2SO_4 [b]
4	Oxalic acid	0.048	$<5x10^{-4}$	24	0.016	80	2.8	1.14 N + 2 M H_2SO_4
5	Oxalic acid	0.048	$<2x10^{-4}$	15	0.030	88	2.8	1.14 N + 2M H_2SO_4
6	Triethylamine	0.032	$<5x10^{-4}$	12	0.037	95	3.3	1.14 N + 2 M H_2SO_4
7	Dowex I-x4	0.10	$<2x10^{-4}$	3	--	95	3.3	1.26 N + 2 M H_2SO_4

[a] Oxidant produced by electrolysis cell and determined by titration.

[b] Oxidant was reagent grade ammonium peroxydisulfate.

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. We gratefully acknowledge support by the Laboratory Directed Research and Development (LDRD) at Lawrence Livermore National Laboratory (John Holzrichter, Director). We also gratefully acknowledge ongoing support for mixed waste applications of this technology by the Department of Energy.

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. Committee on Alternative Chemical Demilitarizaton Technologies, National Research Council, "Alternative teechnologies for the destruction of chemical agents and munitions", Washington DC: National Academy Press, 1993.
5. Yu-Chu Yang, "Chemical Reactions for Neutralising Chemical Warfare Agents," *Chemistry and Industry*, May 1995.
6. 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).
7. D. A. House, "Kinetics and Mechanism of oxidations by peroxydisulfate," Chem. Rev. 62, 185, (1961).
8. Francesco Minisci and Attillio Citterio, "Electron-transfer processes: peroxydisulfate, a useful and versatile reagent in organic chemistry," Acc. Chem. Res. v. 16 27 (1983).
9. Walter C. Schumb, Charles N. Satterfield, Ralph L. Wentworh, *Hydrogen Peroxide*, (Reinhold Publishing, Inc., New York, 1955).
10. Wolfgang Thiele and Hermann Matschiner, "Zur elektrosynthese von Wasserstoffperoxid und Peroxodisulfaten, Teil I. Wasserstoffperoxid und Peroxodischwefelsauer," Chem. Techn. v. 29(3) p. 148 (1977).
11. "FMC invests in persulfates facility," (*Chemical Marketing Reporter* May 8, 1995; p. 4)

12. I. M. Kolthoff and I. K. Miller, "The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium," p. 3055 July (1951).
13. P. D. Goulden and D. H. J. Anthony, "Kinetcis of uncatalyzed peroxydisulfate oxidation of organic material in fresh water," Analytical Chemistry **50(7)** 953 (1978).
14. Harvey W. Yurow and George T. Davis, "Decontamination and disposal methods for chemical agents--a literature survey," ARCSL-TR-81080, US Army Armament Research and Development Command, Aberdeen Proving Ground, Nov. 1982.
15. Yu-Chu Yang, "Oxidative detoxification of phosphonothiolates," J. A. Chem. Soc., 112 6621 (1990).
16. Yu-Chu Yang, James A. Baker, and J. Richard Ward, "Decontamination of chemical warfare agents," Chem. Rev. 92 1729 (1992).
17. Jack H. Benson, et al., "Laboratory and pilot scale detoxification of VX in acidic media using chlorine gas," AD-780-821 Edgewood Arsenal, May 1974.
18. 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 scael demonstration of spent ion exchange resin treatment by wet oxidation," paper submitted to the 1991 Joint International Waste Management Conference.
19. 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).
20. *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).
21. G. F. Potapova, O. V. Shestakova, A. I. Sorokin, and S. A. Asaturov, "Electrosysnthesis of ammonium persulfate at glassy carbon anode," Russ. Electrochemistry, **31(5)** 477 (1995).
22. J. Balej, "Thermodynamics of reactions during the electrosynthesis of peroxodisulfphates," Electrochimica Acta **29(9)** 1239-1242 (1984).
23. W. M. Lattimer, *The oxidation states of the elements and their potentials in aqueous solutions*, Pentice Hall, NY .
24. "Peroxides and Peroxy Compounds, Inorganic," (*Encyclopedia of Chemical Technology*, V. 17, ed. Kirk Othmer).
25. *Uses of Persulfate* (Bulletin of FMC, Inc.; Buffalo NY; 1951; 1960).
26. 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).
27. "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).

Appendix
Reaction Stoichiometry for Oxidation and Electrolysis
Scale-up Estimates
Standard Potentials of Oxidation Couples

Table A1: VX Reactions with peroxydisulfate:

Oxidation half reaction (written for one VX molecule)

$$C_{11}H_{26}O_2PSNH^+ + HSO_4^- + 28\,H_2O \Rightarrow 11CO_2 + H_3PO_4 + H_2SO_4 + NH_4HSO_4 + 74\,H^+ + 74\,e^- \quad (A1)$$

Molecular weight VX = 267 g/mol; 74 equiv./mole; equivalent weight = 3.61 g/equiv.

Reduction half reaction (written for equivalent peroxydisulfate reduction)

$$74\,H^+ + 37(NH_4)_2S_2O_8 + 74\,e^- \Rightarrow 74(NH_4)HSO_4 \quad (A2)$$

Net stoichiometric redox reaction

$$C_{11}H_{26}O_2PSNH^+ + HSO_4^- + 37(NH_4)_2S_2O_8 + 28H_2O = 11CO_2 + H_3PO_4 + H_2SO_4 + 75(NH_4)HSO_4 \quad (A3)$$

Table A2. Reaction Requirements per kilogram of VX (267 g/mol; 74 equivalents/mol-VX)

Reactant	**Quantity per kg-VX**	**Comments**
Oxidation:		
VX	1.00 kg/kg-VX	--
$(NH_4)_2S_2O_8$	8.44 kg/kg-VX	Reaction A3
excess $(NH_4)_2S_2O_8$	0.91kg/kg-VX	10% inefficiency of A3; loss to O_2
Regeneration:		
$(NH_4)_2S_2O_8$	9.35 kg/kg-VX	(required reactant: A3 + loss)
$(NH_4)_2S_2O_8$	1.82 kg/kg-VX	cell losses @ 80 % coulombic efficiency
Total $(NH_4)_2S_2O_8$	11.17 kg/kg-VX	total recycle per kg-VX destroyed
Charge required	368.5 equiv/kg-VX	Equivalent weight of $(NH_4)_2S_2O_8$, 114 g/eq
Charge required	9878 AH/kg-VX	(Faraday constant, 96500 coul/eq)
Cell voltage	5 V	experimental
Energy required	49.4 kWh/kg-VX	(voltage times charge per kg-VX)
Energy cost	2.96 $/kg-VX	industrial AC electricity rate, 6 ¢/kWh

Table A3. Parameters for Detoxification/Destruction of 1091 mt of VX in one year

Parameters of scale	**$S_2O_8^{-2}$ for detox @ 6 eq/mol-VX**	**$S_2O_8^{-2}$ oxidation (sole oxidant)**	**10%$S_2O_8^{-2}$ +90%H_2O_2**
Rate of VX destruction	3000 kg/day 9.62 equivalents/s	3000 kg/day 9.62 equivalents/s	3000 kg/day 9.62 equivalents/s
Rate: $S_2O_8^{-2}$ regeneration*	0.93 equivalents/s	12.7 equivalents/s	1.27 equivalents/s
Power required for $S_2O_8^{-2}$ recycle	452 kW	6.1 MW	610 kW
Rate of use of H_2O_2 at 50% stoichiometric efficiency	--	--	17.3 equivalents/s 294 g/s (as H_2O_2)
Rate of tramp water production (for 70% feed)	--		126 g water/s (1 million gal/yr)
Total electricity use (1 year)	4.0 GWh	54 GWh	5.4 GWh
Total 70% H_2O_2 used (1 year)		--	9270 metric tonnes, as H_2O_2

*Includes consideration of total use and production efficiencies

Table A4. Historical and modern materials for use with peroxydisulfate solutions [9,10, 21]

Proven materials	**Electrolyis, T = 30 C**	**Oxidation, T = 100 C**
Electrolysis		
Pt, vitreous carbon [22]	anodes	
graphite or lead	cathodes	
porous alumina; porcelain	separators	
Ta; ebonite-covered Al	conductors	
hard rubber; PTFE; PP	insulation	
lead or glass tubing	heat exchanger	
Containment		
HDPE, PP, TFE, Pb, etc.	storage	
PTFE	plumbing	reaction vessel
porcelain; stoneware	cell walls; separators	filters; secondary containment
glass-lined steel	heat exchanger	reaction vessel; heat exchanger
18-8 stainless + 2.2% Mo	heat exchanger	heat exchanger
Krupp V4A	heat exchanger	heat exchanger

Table A5. Standard electrode potentials of oxidants in acid solution [22,23].

Half-reaction	Standard Electrode Potential, V
$O_3 + 2H^+ + 2e^- = 2H_2O + O_2$	2.07
$(NH_4)_2S_2O_8 + 2H^+ + 2e^- = 2(NH_4)HSO_4$	**2.05**
$Ag^{+2} + 1e^- = Ag^+$ $(4M\ HClO_4)$	1.90
$Co^{+3} + 1e^- = Co^{+2}$	1.84
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.78
$HClO + H^+ + 2e^- = Cl^- + H_2O$	1.49
$KMnO_4^- + 8H^+ + 5\ e^- = Mn^{+2} + 4H_2O$	1.49
$Ce^{+4} + 1e^- = Ce^{+3}$ $(0.5\ M\ H_2SO_4)$	1.45
$O_2 + 2H_2O + 4\ e^- = 4OH^-$	1.23
$Fe^{+3} = Fe^{+2}$ $(1M\ HCl)$	0.77

Technical Information Department · Lawrence Livermore National Laboratory
University of California · Livermore, California 94551