Direct Chemical Oxidation: Applications to Hazardous Waste Treatment in Demilitarization

John F. Cooper
G. Bryan Balazs
Patricia Lewis

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by

John F. Cooper, G. Bryan Balazs and Patricia Lewis
Chemistry and Materials Science Directorate, L352
Lawrence Livermore National Laboratory Livermore CA 94550
Tel. (925) 423-6649; Fax (925) 422-0049; email: Cooper3@LLNL.gov

Abstract

Several applications of Direct Chemical Oxidation (DCO) relevant to the demilitarization of munitions are reported and evaluated here. The role of low levels of transition metal catalysts on rate of oxidation of organics by peroxydisulfate was investigated, because such materials are normally present in demilitarization wastes and could conceivably alter the rate or effectiveness of DCO. It was found that the presence of transition metal ions of Fe, Co, Cu, and Mn had little or no accelerating effect. Silver alone substantially increased oxidation rate, except where segregated as AgCl by free chloride. The destruction of trace explosives on metal substrates (mild steel, copper and brass) was found to be effective in basic media, where the peroxydisulfate prevented corrosion of the base metal (anodic chemical passivation) without impeding oxidation of the organic explosive. A method of detection of completeness of reaction (based on mass-spectroscopic detection of the intermediate oxidation product, formaldehyde) was proposed. Rate data on the destruction of 2,4,6-trinitrotoluene by acidified ammonium peroxydisulfate is reported. Appended to the report is a comprehensive bibliography on DCO.

1. Background

Direct Chemical Oxidation is a low temperature (<100 °C) process for destruction of organic waste material in aqueous media. The waste may be concentrated, in dilute solutions or dispersions, or distributed within an inorganic matrix such as sludge, soil or sand. The process uses the one of the strongest known oxidants, the peroxydisulfate ion, $S_2O_8^{2-}$. The oxidation reaction is controlled by the rate of formation of the sulfate radical anion, $SO_4^{\cdot -}$, which is liberated by the decomposition of the peroxydisulfate by thermal activation, redox transition metal catalysis, or noble metals. Normally, the process operates without chemical catalysis at temperatures above 80 °C. At lower temperatures, various metals (Fe, Cu, Ag, etc.) and their redox ion couples can accelerate the formation of the radical anion and thus accelerate the oxidation of organic material.

We have tested the process through rate measurements of over 30 chemical substances, conducted studies of the process using batch, plug flow, and CSTR reactors, and scaled the process for destruction of chlorinated solvents following thermal hydrolysis (rates 10-15 kg/day). Most recently, a pilot plant has been constructed at LLNL for destruction of chlorosolvents in a system comprised of five 60-liter dual use (hydrolysis and oxidation) vessels, each capable of oxidation throughputs of about 10-15 kg/day.

The current work reported here concerns the application of the process to the destruction of energetic materials associated with demilitarization of munitions and rockets.

2. Objectives

The primary objective of this project in its first year (February - September 1998) was to determine appropriate operating conditions for oxidative destruction of small amounts of energetic materials from steel weapons casings. This work included bench scale studies and simulated process applications on a laboratory scale (grams organic in a matrix of kilograms of steel). A secondary objective was to develop test data relevant to one of the following: (1) the destruction of red and pink waters; (2) cleaning of stack gasses contaminated with TNT and related materials; and (3) removal of explosive materials from soils contaminated by open pit detonation or burning.

In a closely coordinated effort, we also sought to understand the role of low levels of catalysts known to accelerate the decomposition of peroxydisulfate into the sulfate radical anion. This is of interest in resolving two questions: (1) Can the presence of tramp ions in wastes accelerate the reaction beyond a safe rate at high temperatures of operation? (2) Might the process operating temperature be lowered below 60 °C by additions of suitable transition metal catalysts? This work was supported in part by the Mixed Waste Focus Area of EM-50.

3. Transition metal Catalysis of Oxidation Process

Experiments were conducted at the laboratory scale (1.0 liter reactor), using acidic solutions of 1.0 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 0.1 M H_2SO_4 . Catalyst ions were added in the form of the sulfate salts of the appropriate transition metal, except in the case of Ag, which was by addition of the nitrate salt. Solutions were put into lightly stoppered 250 ml glass flasks immersed in a water bath at the appropriate temperature. Four organic substrates were tested: ethylene glycol (Tables 1-4), 1,3-dichloro-2-propanol (Tables 5-6), and the hydrolysis product of 1,1,1-trichloroethane (Table 7). Initial organic loading was between 500 and 6000-ppm total carbon, and the catalyst concentrations were varied between 1 and 1000 ppm (with the exception of additional Fe tests at 5900 ppm). Additional oxidant was added after each period as noted. DRE's were measured by Total Carbon Analysis (TCA) of the solution.

3.1 Oxidation of Ethylene Glycol

Results for oxidation of ethylene glycol are shown in Tables 2-5, and Figures 1-4. The destruction and removal efficiency (DRE) after 6, 12 and 18 hours are shown, for experiments conducted at 50-, 35-, and 20 °C. We have included bar charts of this data for clarity.

Table 1. (1800 ppm carbon loading, 50 °C, three batches of oxidant). See also Figure 1.

<i>catalyst</i>	<i>DRE after 6 hrs</i>	<i>DRE after 12 hrs</i>	<i>DRE after 18 hrs</i>
none	0	87	92
10.2 ppm Cu	0	90	92
103 ppm Cu	2	89	92
9.6 ppm Co	1	85	92
105 ppm Co	6	95	97
1 ppm Ag	2	79	88
10 ppm Ag	49	93	94
104 ppm Ag	99.9	99.9+	99.9+
100 ppm Fe	1	82	90
4000 ppm Fe (mild steel)	62	93	95
99 ppm Mn	58	77	81
101 ppm Ni	2	1	72
Pt wire	0	73	85

Table 2. (1800 ppm carbon loading, 35 °C, three batches of oxidant). See also Figure 2.

<i>catalyst</i>	<i>DRE after 6 hrs</i>	<i>DRE after 12 hrs</i>	<i>DRE after 18 hrs</i>
102 ppm Ag	98.8	99.4	99.8
100 ppm Co	1.6	13	14
100 ppm Fe	0.8	13	12

Table 3. (1800 ppm carbon loading, 20 °C, three batches of oxidant). See also Figure 3.

<i>catalyst</i>	<i>DRE after 6 hrs</i>	<i>DRE after 12 hrs</i>	<i>DRE after 18 hrs</i>
100 ppm Ag	89.9	97.1	98.4
101 ppm Co	2.4	14	13
100 ppm Fe	5.5	15	14

Table 4. (1800 ppm carbon loading, 20 °C, single batch of oxidant). See Figure 4.

<i>catalyst</i>	<i>DRE after 96 hrs</i>	<i>DRE after 192 hrs</i>	<i>DRE after 744 hrs</i>
none	2.8	0.6	0
1000 ppm Cu	0	0	0
1000 ppm Co	5.0	7.8	99
1000 ppm Fe	4.4	2.2	0
10000 ppm Fe	44	82	89

Figure 1. 1800 ppm carbon loading, 50 °C, three batches of oxidant. Comparison of copper, cobalt, manganese, iron and silver catalysts.

Figure 2. 1800 ppm carbon loading, 35 °C, three batches of oxidant. Comparison of silver, cobalt and iron catalysts.

Figure 3. (1800 ppm carbon loading, 20 °C, three batches of oxidant)

Figure 4. (1800 ppm carbon loading, 20 °C, single batch of oxidant, longer runs)

3.2 Oxidation of 1,3-dichloro-2-propanol

Results for 1,3-dichloro-2-propanol are shown in Tables 5-6 and Figures 5,6. As with ethylene glycol, we have varied catalyst, catalyst loading and temperature. The differences in DRE between catalysts and the uncatalyzed reagents are unsubstantial.

Table 5. (1700 ppm 1,3-dichloro-2-propanol loading, 50 °C, three batches of oxidant). See Figure 5.

<i>catalyst</i>	<i>DRE after 6 hrs</i>	<i>DRE after 12 hrs</i>	<i>DRE after 18 hrs</i>
none	6.5	29	50
10.0 ppm Cu	6.5	29	51
102 ppm Cu	4.9	29	50
106 ppm Co	11	35	66
105 ppm Ag	7.1	29	48
4000 ppm Fe (mild steel)	17	36	39

Table 6. (1800 ppm 1,3-dichloro-2-propanol loading, 20 °C, single batch of oxidant, longer times). See Figure 6.

<i>catalyst</i>	<i>DRE after 96 hrs</i>	<i>DRE after 192 hrs</i>	<i>DRE after 744 hrs</i>
none	0.6	2.2	36
1000 ppm Cu	3.9	2.8	0
1000 ppm Co	3.9	7.8	66
1000 ppm Fe	2.8	2.2	9
10000 ppm Fe	3.9	5.0	12

Figure 5. (1700 ppm 1,3-dichloro-2-propanol loading, 50 °C, three batches of oxidant).

Figure 6. (1800 ppm 1,3-dichloro-2-propanol loading, 20 °C, single batch of oxidant, longer times)

3.3 Hydrolysis product of 1,1,1-trichloroethane

The chlorosolvent, 1,1,1-trichloroethane was hydrolyzed at $T > 100\text{ }^{\circ}\text{C}$ under pressure until conversion to acetic acid and free chloride ion. The resultant mixture was then oxidized with and without transition metal catalysts at $20\text{ }^{\circ}\text{C}$ (Table 7). Again, the catalysts had little or not effect on long term oxidation.

Table 7. Oxidation of TCE hydrolysis product: 4900-ppm organic loading, $20\text{ }^{\circ}\text{C}$, and single batch of oxidant.

<i>catalyst</i>	<i>DRE after 72 hrs</i>	<i>DRE after 144 hrs</i>	<i>DRE after 672 hrs</i>
none	2.7	3.7	10
100 ppm Fe	4.5	5.5	6.3
100 ppm Co	5.1	3.7	7.3
100 ppm Cu	4.1	5.9	4.9

3.4 Decomposition of Peroxydisulfate

The effect of selected transition metal ions on oxidation rates were determined at normal operating temperatures $80\text{ }^{\circ}\text{C}$. Measurements were made of both the instantaneous concentration of peroxydisulfate (by titration) and the conversion of organic to carbon dioxide (by on-line IR gas analysis). Ethylene glycol and the hydrolysis output of chlorosolvent hydrolysis were used as substrates; several typical transition metals were tested with each.

Ethylene Glycol. Figure 7 shows the decrease in peroxydisulfate concentration as a function of time during the oxidation of ethylene glycol (1400 ppm loading). Initial $[\text{S}_2\text{O}_8^{2-}]$ is 1.0 M, in 0.1 M H_2SO_4 . Each of the catalysts systems, except for 100 ppm Fe(II), showed some catalytic activity for the decomposition of peroxydisulfate, with the silver system being the most pronounced.

Figure 7. Transition metal ions Cu, Co and Fe slightly accelerated the reduction of peroxydisulfate in the presence of ethylene glycol at 80 °C, while 100-ppm levels of Ag substantially accelerated the oxidation. The ethylene glycol concentration was initially 1400 ppm.

Figure 8 shows the output of carbon dioxide obtained during each of seven runs, with and without the catalysts as noted, during the oxidation of ethylene glycol at 80 °C. The expected output based on the amount of ethylene glycol initially added was 420 ± 20 ml CO_2 . All of the results fall within this range, but the silver system is noticeably different, both in terms of a higher CO_2 output as well as a much steeper rise.

Figure 8. Rate of oxidation of ethylene glycol to carbon dioxide is substantially increased by the presence of the transition metal catalysts, with the effect of 102 ppm Ag being the greatest. By comparison with Figure 7, the ethylene glycol is preferentially oxidized in comparison with the oxidation of water.

Product of Hydrolysis of 1,1,1-trichloroethane. Figure 9 shows the decrease in peroxydisulfate concentration as a function of time during the oxidation of hydrolyzed 1,1,1-trichloroethane (3400 ppm loading) at 80 °C. Initial $[S_2O_8^{2-}]$ is 1.0 M, in 0.1 M H_2SO_4 . Again, these results are quantitatively similar to those obtained with ethylene glycol as the organic substrate, whereby all the catalysts showed varying activity with the exception of 100 ppm Fe(II).

Figure 10 shows the output of carbon dioxide obtained during each of seven runs, with and without the catalysts as noted, during the oxidation of hydrolysis product at 80 °C. Insufficient oxidant was intentionally added to completely oxidize the organic to carbon dioxide. The expected output based on the organic content was 420 ± 20 ml CO_2 . All of the results fall within this range except for the cobalt and silver systems. For cobalt, the accelerated loss of oxidizing power (figure 9) may have reduced the concentration of oxidant prematurely to consume all of the organic. Further loss of catalyst (with silver) may have resulted from AgCl precipitation.

Figure 9. Transition metal ions (particularly Cu and Co) accelerate the reduction of peroxydisulfate during the oxidation of hydrolyzed 1,1,1-trichloroethane (3400 ppm loading) at 80 °C. The comparatively weak effect of Ag(I) (see figures 7,8) is due to the loss of silver catalyst by precipitation of AgCl.

Figure 10. The time-dependent release of carbon dioxide (from oxidation of hydrolyzed with various the catalysts as noted, during the oxidation of hydrolysis product at 80 °C. Insufficient oxidant was intentionally added to completely oxidize the organic to carbon dioxide. The expected output based on the amount of organic added was 420 ± 20 ml CO_2 .

3.5 Conclusions of Catalyst Tests

Effect of Transition Metal Catalysts. All of the transition metals studied exhibited some effect on the rate of oxidation of the organic substrates by peroxydisulfate, although the magnitudes varied greatly. This is not surprising, as peroxydisulfate has a sufficient oxidation potential to oxidize all of the transition metals to their highest valent state, and the participation of these higher valence states in organic oxidation is well known. It was generally the case that the transition metals which exhibited the most facile organic oxidation capability (Ag(II), Co(III), Fe(III)) also exhibited the most pronounced catalytic effect in these studies. Note that this order of catalytic effectiveness is surprisingly similar to the results obtained on Mediated Electrochemical Systems. Although an all-encompassing maxim for the rate enhancements obtained with a specific catalyst is not possible, a general rule of thumb is that the effectiveness of the catalysts followed the general order $\text{Ag} \gg \text{Co} > \text{Cu, Fe} > \text{Pt}$. Individual results varied depending on the temperature regime, the organic substrate, and the matrix. This has been noted before in the literature. The above results lead to the conclusion that catalysis of organic destruction by peroxydisulfate is merely due to the formation of another, favorably solvated transition metal cation with a high oxidation potential.

Complete destruction of the organics tested was achievable with silver as a catalyst, even at 20 °C in a relatively short time, and cobalt, iron or copper showed some enhancement although a much longer time was required. This result is backed by previous literature studies as

discussed above. However, it was also noted in this current study that different organic substrates exhibited different behavior with respect to catalysis.

In all the cases studied, the enhancement of the organic destruction rate was a function of the catalyst concentration, and this is reflected in the literature as well (Eq. 4). Thus, higher rates of organic destruction can be achieved with higher catalyst concentrations. Due to the copious data available in the literature, a systematic reinvestigation of the order of the catalyst concentration on the rate equation was not attempted.

Although rate equations such as that shown in Eq. 4 would predict that destruction of organics might be faster with higher oxidant concentrations, the present work was not sufficiently detailed to either bolster or refute this statement. Additional oxidant made only a slight difference in DRE's, at least at close to ambient conditions. However, with higher organic loading it may be necessary to periodically replenish the oxidant in waste treatment systems. See also the following section regarding oxidant concentration.

During catalyzed oxidation, there is an incubation period during which the carbon content of the solutions is unchanged from the initial value. This is presumably reflective of the fact that oxidation is occurring, but has not proceeded to the stage of evolving carbon dioxide from the solution and thus the carbon content of the solution remains unchanged from the original value. This incubation period was not noticed with silver, as oxidation with this catalyst proceeded much faster than the sampling timescales at the temperatures tested.

In waste systems containing chloride ion, or containing organic chlorine, silver ion is ineffective as a catalyst. AgCl, being highly insoluble, immediately precipitates thus removing the active catalyst. Along these same lines, silver will be ineffective as a catalyst in systems where the pH is sufficiently high to result in the precipitation of silver hydroxide. In fact, this latter characteristic would presumably be extendable to all potential transition metal catalysts in systems at high pH.

Decomposition of Peroxydisulfate. As shown in Figures 7 and 9, the concentration of peroxydisulfate decreases rapidly at 80 °C due to its reduction by organic and, to a lesser extent, water. All of added transition metals tested had some effect (with the exception of low concentrations of iron), and this effect was towards an acceleration of the peroxydisulfate decomposition rate. In the case of ethylene glycol as the added organic substrate (Figure 7), silver ion showed the highest perturbation, which is expected based on the fact that silver showed the highest catalytic effect in the destruction tests. The effect of silver was not nearly as pronounced in tests where chloride ion was present (Figure 9). Based on results obtained with and without catalysts at 80 °C, peroxydisulfate does not appear to be a very aggressive oxidant at concentrations of less than about 0.3M. Catalysts did not change this cutoff value appreciably. Thus, any DCO waste treatment system would have to keep the oxidant concentration greater than 0.5M for optimal efficiency.

During the experiments, it was noted that additional heat outputs were obtained at 80 °C with the catalysts, and the amount of extra heat correlated well with the acceleration in peroxydisulfate decomposition/organic destruction (Figures 7-10). As noted in the organic destruction tests detailed in the previous section, silver exhibited the most pronounced effect. As the oxidative destruction of organics is exothermic, any organic waste treatment system using peroxydisulfate *must* take into account the extra heat output encountered when transition metal ions (especially silver) are present.

It was noted that, when treating chlorinated organics, catalysts also affected the production of chlorine gas. However, this effect appeared random; in some cases the chlorine production (observed by watching the reactor offgas trap color) was immediate and quantitative and in other cases it was minimal. Chlorine production is regulated by the pH-dependent equilibrium between Cl and OH free radicals:

Because peroxydisulfate oxidation may give rise to large changes in pH (due to formation bisulfate products, which consume H^+), part of this randomness might reflect changes in pH which were not always monitored.

4. Decontamination of Shell Casings

A series of experiments were done to determine the effectiveness of Direct Chemical Oxidation for the destruction of trace organics on shell casings consisting of mild steel or brass. In the first set of experiments detailed below, the heat rise associated with the decomposition of the oxidant (either through organic or water oxidation) was measured to determine if any unsafe thermal scenarios might be envisioned. In the second set of experiments, the relative rates of destruction of ethylene glycol vs. dissolution of mild steel were measured. These experiments were done in acid media, similar to that used in organic waste destruction.

The expected result of rapid corrosion of metals in the presence of acid led us to consider sustaining the oxidation reaction in alkaline medium, with the objective of passivating the mild steel casings while destroying any organic material present. This approach proved to be successful, and led the proposed process for cleaning demilitarized shells of the last traces of explosives or propellants. Also, the last step in organic oxidation is the conversion of formaldehyde into carbon dioxide. Detection of trace levels of formaldehyde in the off gas (by, for example, mass spectroscopy) gives an indication of ongoing and incomplete oxidation of organic explosives, while the absence of formaldehyde is an indication of complete destruction.

4.1 Thermal Safety Experiments

In the first set of experiments, hot oxidant was added to metals used in shells (including copper, brass and mild steel). One hundred and fifty (150) ml, 2.0 M $\text{Na}_2\text{S}_2\text{O}_8$, 0.1 M H_2SO_4 at 88 °C were added at time zero to 1.0 ml of EG and 10.0 g of metal in stirred, unheated plastic reactor (end weights of metal shown in legend).

Figure 11. Temperature excursions occurred following addition of hot oxidant to various metals in acidic solution. (2.0 M $\text{Na}_2\text{S}_2\text{O}_8$, 0.1 M H_2SO_4)

Figure 12. Reduction of oxidant concentration reduced temperature excursion for acidic oxidation of ethylene glycol in the presence of mild steel; the ethylene glycol was completely oxidized. 150 ml of 85 °C, 1.0 M $\text{Na}_2\text{S}_2\text{O}_8$, 0.1 M H_2SO_4 added at time zero to 1.0 ml of EG and 10.5 and 48.7 g of mild steel in stirred, unheated plastic reactor (end weights of metal shown in legend).

4.2 Oxidation of Ethylene Glycol in the Presence of Mild Steel

350 ml of 75 °C, 0.5 M $\text{Na}_2\text{S}_2\text{O}_8$, 0.1 M H_2SO_4 added 0.5 ml of EG (0.0089 moles) and 49.3 g of mild steel (0.88 moles) in stirred glass reactor; more oxidant added during course of run to bring final added oxidant concentration to 2.0 M. Ten Total Organic Carbon samples taken over course of run. Initial concentration of carbon (added as ethylene glycol) is 613 ppm.

Figure 13. Ethylene glycol was oxidized by acidified peroxydisulfate (added in discrete steps) in the presence of mild steel in a stirred glass reactor. This indicates that the oxidation of the organic is rapid compared with the oxidation of the mild steel in acidic media.

4.3 Oxidation of organic explosives and propellants on steel, copper or brass casings in alkaline solutions.

We next sought to determine whether the metal oxidation could be selectively inhibited by passivation under alkaline conditions. Here, the approach is to use the peroxydisulfate to anodically passive the metal in alkaline solutions by raising the corrosion potential into a passivating region. In Table 8, the rates of corrosion of steel, brass, copper (and of all three in electronic contact) were measured. In all cases the corrosion rates are negligible. The presence of chloride (as KCl) did not significantly increase corrosion rates, even though the chloride is a known accelerating agent for corrosion in alkaline solutions.

Finally, we conducted oxidation tests on ethylene glycol (Figure 14, 15) and on 2,4 dinitro-tolulene (DNT; a surrogate for TNT) in alkaline solutions of peroxydisulfate. In the case of the ethylene glycol, oxidation was allowed to go to completion and the pH of the solution was allowed to fall due to the conversion of peroxydisulfate to the mildly acid bisulfate (Figure 14). The pH was forced to low levels by addition of concentrated sulfuric acid (Figure 15). In both

cases, the organic was substantially destroyed without appreciable oxidation of the metal substrate. In Figure 16, DNT was also oxidized in the presence on mild steel in alkaline solution. Although insufficient oxidant was use for complete destruction of the DNT, the metal was left uncorroded.

The destruction of DNT provides the basis for cleaning trace explosives from demilitarized shells having mild steel, copper and/or brass components. The alkaline medium and oxidizing strength of the peroxydisulfate raises the corrosion potential of iron, copper and brass into a passivating level, so that consumption of the oxidant by corrosion of the metal is negligibly small. The alkaline/peroxydisulfate combination, however, is very effective for destruction of organic material and probably operates through a combination of sulfate radical anions (SO_4^-) and hydroxyl free radicals ($\text{OH}^\cdot$). Since the last step of oxidation of organic substances by peroxydisulfate involves the oxidation of formaldehyde intermediates to carbon dioxide, a sensitive test for completeness of oxidation of explosives is defined. If trace levels of formaldehyde are found in the mass spec analysis of the offgas, then oxidation of an organic is still proceeding. If pure oxygen is found to be evolved from the system, and no formaldehyde is present, then the peroxydisulfate is still present (oxidizing water) but the organic material has been completely oxidized. This can be an extremely sensitive test, limited only by the sensitivity of the mass spectrometer for a given (formaldehyde) signal in the presence of larger amounts of oxygen.

Table 8. Rates of corrosion of weapons metals in alkaline solutions of peroxydisulfate, at 85 °C and for exposure times of 1 hour.

<i>Metal</i>	<i>Solution</i>	<i>Area cm²</i>	<i>W_o g</i>	<i>ΔW, g</i>	<i>Loss rate, g/m²-h</i>
Fe (mild steel)	1 M NaOH + 0.5 M Na ₂ S ₂ O ₈	10.1	10	0.01	9.9
Cu	“	9.0	10.	<0.01	<11
Brass	“	4.5	10.0	0.01	22
Fe+Cu+brass	“	16.14	11.86	0.02	12.5
Fe	0.5 M KCl+1M NaOH+0.5 M Na ₂ S ₂ O ₈	10.0	10.0	0.06	60
Cu		9.0	10.0	0.17	189
Brass		9.5	10.	0.03	32

Figure 14. Oxidation of ethylene glycol by basic solutions of peroxydisulfate in the presence of mild steel. Complete oxidation was observed, without reduced oxidation of the iron substrate.

DCO329, 5-12-98
 350 ml of 0.5M Na₂S₂O₈ / 1.0M NaOH
 9.96 gms mild steel **, 0.5 ml EG
 Temperature 84-89 °C.

** No appreciable weight loss at end of experiment

Figure 15. Oxidation of ethylene glycol on mild steel by basic peroxydisulfate occurred without substantial oxidation of the mild steel substrate.

** 471.8 ml CO₂ theoretical so 89.2% destruction if DNT

Figure 16. Oxidation of explosive surrogate, 2,4-dinitrotoluene was found with basic oxidant and negligible weight loss of the metal substrate.

4.4 Oxidation of TNT in acidified solutions of peroxydisulfate.

Earlier, we conducted tests on the oxidation of 2,4,6-trinitrotoluene (TNT) in aqueous peroxydisulfate solutions. These results are reported here and in an internal document. TNT was destroyed in a small batch reactor, using uncatalyzed 4 N ammonium peroxydisulfate at 95 °C. The material was destroyed below limit of detection in less than 15 minutes, indicating a formal first order rate constant of 0.06 min⁻¹. A crude estimate of scaleup rates indicates a throughput of 1 tonne/m³-day.

Experimental Technique and Results. Tests were conducted on the oxidative destruction of 2,4,6-trinitrotoluene using uncatalyzed 4 N ammonium peroxydisulfate at 95 °C. A 1-L batch reactor vessel with reflux column was loaded with 100 ml of 0.1 M H₂SO₄ and preheated to 95 °C. One gram (1 g) of granular TNT was injected; the TNT immediately melted to form a dispersion of fine globules.

Using a peristaltic pump, 4N (NH₄)₂S₂O₈ was introduced at a rate of 5.5 ± 0.5 ml/minute. After 10 minutes, the TNT separate phase had vanished, and a sample was taken, chilled, and analyzed for total carbon using a calibrated TOC machine. The experiments were repeated twice, with oxidant injection terminated after 15 and 30 minutes, and residuals analyzed as before. The

peroxydisulfate concentration was determined by reduction by excess Fe(II), followed by titration with a standardized solution of 0.1 N KMnO₄. The TOC was calibrated using 25-ppm solutions of sucrose. Results are summarized in Table 9.

TNT has a molecular weight of 227.13 g/mol, a weight fraction of carbon of 0.37, and an equivalent weight of 6.31 g/equiv, based on the stoichiometry oxidation half reaction:

Initially 1 g (0.159 equivalents) were added to 100 ml of acid, thus producing a carbon concentration of 3627 ppm (as C) and a total amount of carbon of 0.37 g in the vessel. After 10 minutes, 55 ml of oxidant were added (containing 0.22 equivalents), the TNT separate phased had vanished, and analysis of the product showed 0.045 g of carbon remaining in the solution, or 87.7% destroyed--an apparent oxidant utilization of 63%. After 15 minutes of oxidation, the carbon content of the resultant liquid fell below the limit of the TOC analyzer (~0.5 ppm), or <2 ppm when corrected for dilution prior to test, with an apparent utilization of oxidant of 0.159/0.33 = 48%. This indicates that more than 99.9% of the material had been destroyed in 15 minutes at 95°C by 4 N peroxydisulfate, with a utilization of between 48 and 63%.

We can calculate a formal rate constant, based on the assumption of first-order reaction kinetics. Using concentrations expressed in equivalents, the rate constant is

$$k_a \sim (0.159 \cdot 0.877 / 0.22) / 10 = 0.06 \text{ min}^{-1}.$$

This value is in the midpoint of values measured for destruction of bulk ethylene glycol, triethylamine, oxalic acid, etc. , and supports the general model that uncatalyzed peroxydisulfate oxidation is controlled by the thermal decomposition of the oxidant to form the sulfate radical anion. The Attached chart shows the rate superimposed on data for trace-level organic compounds as well as data taken from destruction of bulk organic compounds, with rates extrapolated from rate data for formation of the free radical.

Projections of throughput. We can make a crude estimate of the throughput of a waste destruction technique, simply by scaling the rate data to a 1-m³ vessel fed with 4 N oxidant and TNT. Based on this rate, the projected throughput of the process (using 4 N ammonium peroxydisulfate, 50% utilization) is roughly 1.1 tonne/m³/day, as computed from:

$$\text{Throughput} \sim 50\% \cdot 0.06 \text{ min}^{-1} \cdot 4 \text{ equiv/L} \cdot 6.3 \text{ g/equiv} = 0.756 \text{ g-TNT/L-min}$$

Table 9. Destruction of 1 g of TNT in experiments lasting 10,15, and 30 minutes, using 4N ammonium peroxydisulfate (uncatalyzed) at 95 °C.

<i>Time min</i>	<i>oxidant added equiv</i>	<i>total weight, g</i>	<i>ppm-C determined</i>	<i>carbon remaining, g</i>	<i>Fraction C destroyed</i>
0	0	102 g	3627	0.37	(0)
10	0.22	168	269	0.045	0.877
15	0.33	201	<2*	<0.0004	>0.999
30	0.66	301	<2*	<0.0006	>0.998

*Below limit of detection, corrected for dilution of aliquot; actual measurement 0.19 ppm, 30 minutes.

Figure 17. Given are rates of destruction of 20 diverse organic substances at trace levels, TNT at bulk concentrations 1% (circle), and other test chemicals (ref [1]) are plotted against reciprocal absolute temperature. The rate of formation of the sulfate free radical from uncatalyzed thermal decomposition of peroxydisulfate are also given, supporting the theory that peroxydisulfate destruction of organic compounds is determined by the initial formation of the sulfate radical anion [4,5].

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References

1. John F. Cooper, Francis Wang, Roger Krueger, Ken King, Joseph C. Farmer, and Martyn Adamson, "Destruction of organic wastes by ammonium peroxydisulfate with electrolytic regeneration of the oxidant," UCRL-JC-121979 Rev.2 April 1996.
2. John F. Cooper, Roger Krueger and Joseph C. Farmer, "Destruction of VX by aqueous-phase oxidation using peroxydisulfate: Direct chemical oxidation," (Proc. Workshop on Advances in Alternative Demilitarization Technologies, pp. 429-442; Reston VA September 25-7 1995; published by SAIC Aberdeen, MD)
3. John F. Cooper, Francis Wang, Roger Krueger, Ken King, Thomas Shell, Joseph C. Farmer, and Martyn Adamson, "Demonstration of omnivorous non-thermal 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.
4. Beylerian, N. M. and Khachatryan, A. G., J. Chem. Soc. Perkin Trans. II 1984 1937-1941.
5. Gary R. Peyton, "The free-radical chemistry of persulfate-based total organic carbon analyzers," Marine Chemistry 41, 91-103 (1993).

Appendix: Comprehensive Bibliography of Direct Chemical Oxidation Publications from LLNL Research

1. John F. Cooper, F. Wang, J. Farmer, R. Foreman, T. Shell and K. King, "Direct Chemical Oxidation of Hazardous and Mixed Wastes" (Proc. of the Third Biennial Mixed Waste Symposium, American Society of Mechanical Engineers; Aug. 1995); Lawrence Livermore National Laboratory Report UCRL-JC-120141 March 28, 1995.
2. John F. Cooper, F. Wang, J. Farmer, M. Adamson, K. King and R. Krueger, "Direct Chemical Oxidation: Peroxydisulfate destruction of organic wastes," Proc. World

Environmental Congress, International Conference and Trade Fair, Page 219; London Ontario Sept. 17-22 1995.

3. F. Wang, J. F. Cooper, J. Farmer, M. Adamson and T. Shell, "Destruction of ion exchange resins by wet oxidation and by direct chemical oxidation--a comparison study," Proc. World Environmental Congress, International Conference and Trade Fair, p. 206; London Ontario Sept. 17-22 1995.
4. John F. Cooper, Francis 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 Journal of the Electrochemical Society, September 1995. UCRL-JC-121979 October 10, 1995.
5. John F. Cooper, Roger Krueger and Joseph C. Farmer, "Destruction of VX by aqueous-phase oxidation using peroxydisulfate: Direct chemical oxidation," (Proc. Workshop on Advances in Alternative Demilitarization Technologies, pp. 429-442; Reston VA September 25-7 1995; published by SAIC Aberdeen, MD)
6. John F. Cooper, Francis Wang, Roger Krueger, Ken King, Thomas Shell, Joseph C. Farmer, and Martyn Adamson, "Demonstration of omnivorous non-thermal 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.
7. John F. Cooper, "Large-area decontamination using Peroxydisulfate with UV and metal-ion catalysis," US Patent disclosure and record of invention, IL-9875, November 21 1995.
8. John F. Cooper (with Joseph C. Farmer, Francis T. Wang, and Martyn G. Adamson, "Alternatives to Incineration," (Proc. ASME/EPRI Radwaste Workshop, New Orleans, LA, July 24-6 1996.)
9. John F. Cooper, Francis Wang Thomas Shell, and Ken King, "Destruction of 2,4,6-trinitrotoluene using ammonium peroxydisulfate," LLNL Report UCRL-ID-124585, July 1996.
10. John F. Cooper, Francis Wang, Roger Krueger and Ken King, "Destruction of organic wastes with electrolytic regeneration of the oxidant," Proc. Sixth International Conference on Radioactive Waste Management and Environmental Remediation, Singapore October 12-16 1997. UCRL-JC--121979 rev 2 July 1997.
11. John F. Cooper, Bryan Balazs, and Pat Lewis, "Direct Chemical Oxidation: Applications to demilitarization and decontamination," UCRL-ID-130293, March 1998.
12. "Direct Chemical Oxidation: Destruction of chlorinated solvents by aqueous peroxydisulfate," Bryan Balazs, John Cooper, Peter Hsu, Pat Lewis, Martyn Adamson, poster presentation, SERDP Symposium, Washington, D.C., December 3-5, 1997.
13. "Non-thermal Organic Waste Destruction Technology Development at Lawrence Livermore National Laboratory," Bryan Balazs, presentation to Technician Affiliate Group, Clorox Co, Pleasanton, CA, Nov. 12, 1997.
14. "Process Engineering of Direct Chemical Oxidation for the Treatment of Insoluble Chlorinated Solvents in Waste Streams," Peter Hsu, John Cooper, Bryan Balazs, Pat Lewis,

- and Martyn Adamson, UCRL-JC-128142 abs., presented at AIChE Spring National Meeting, New Orleans, LA, March 8-12, 1998.
15. "Integrated Direct Chemical Oxidation System for the Non-Thermal Destruction of Chlorosolvents," Bryan Balazs, John Cooper, Peter Hsu, Pat Lewis, Joe Penland, Larry Finnie, Martyn Adamson, WM '98 Proceedings, Tucson, AZ, March 1-5, 1998, UCRL-JC-128131.
 16. "Demonstration of Omnivorous Non-thermal Mixed Waste Treatment: Direct Chemical Oxidation of Organic Solids and Liquids using Peroxydisulfate," John F. Cooper, G. Bryan Balazs, Final Report to Mixed Waste Focus Area, Oct. 1997, UCRL-ID-129826.
 17. "Destruction of organic wastes by ammonium peroxydisulfate," J. Cooper, F. Wang, B. Balazs, R. Krueger, P. Lewis, T. Shell, J. Farmer, M. Adamson, presented at AIChE Spring National Meeting (March 9-13, 1997), Houston, TX, UCRL-MI-126794.
 18. "The Effect of Trace Additives on the Efficiency of Peroxydisulfate Regeneration," Balazs, G. B., Cooper, J. F., and Shell, T.E., UCRL-JC-129827; accepted for publication in J. Appl. Electrochemistry.
 19. "Omnivorous Waste Destruction Process Using Uncatalyzed Peroxydisulfate Solutions," Cooper, J. F., Wang, F., Balazs, G. B., Shell, T., Krueger, R., Lewis, P., Adamson, M., poster presentation at WM '97 conference, Tuscon, Arizona, March 2-6, 1997, UCRL-MI-126764.
 20. John F. Cooper, G. Bryan Balazs and Patricia Lewis, "Applications of Direct Chemical Oxidation in Demilitarization," Conference on Demilitarization, Couer d'Alene, ID May 1998, UCRL-JC-130803, May 1998.
 21. Innovative Technology Summary Report, "Direct Chemical Oxidation," Department of Energy Office of Science and Technology, Report 109, Sept. 1998; published by the Mixed Waste Focus Group.
 22. John F. Cooper, G. Bryan Balazs, Patricia Lewis and Joseph C. Farmer, Direct Chemical Oxidation of Mixed or Toxic Wastes, (Proc. Advanced Research Workshop: Environmental Aspects of Converting CW Facilities to Peaceful Purpose March 10, 1999 Spiez Switzerland.)