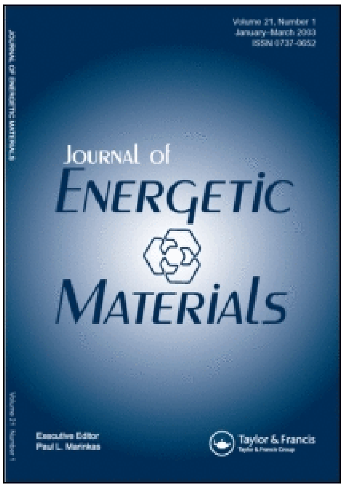

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WET AIR OXIDATION OF ENERGETICS AND CHEMICAL AGENT SURROGATES

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ABSTRACT

Wet air oxidation studies have been conducted on a number of energetic materials and wastewaters derived from energetic materials to demonstrate high destruction levels of specific energetic components. Triple-base propellant, OTTO Fuel (used as a torpedo propellant) and hydrazine-based rocket fuel were energetics of interest. Triple-base propellant contain nitrocellulose, nitroglycerin, and nitroguanidine. OTTO Fuel contains substantial amounts of propylene glycol trinitrate. Hydrazine based rocket fuel contains hydrazine and 1,1-dimethylhydrazine (asymmetrical dimethyl hydrazine or UDMH). A bench scale wet air oxidation study on alkaline hydrolyzates of triple-base propellants indicated that essentially complete destruction of the reactive nitrogen components could be achieved at an oxidation temperature of 280°C. Bench scale wet air oxidation studies on OTTO Fuel wastewaters indicated that a 99+ percent

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destruction of propylene glycol dinitrate can be achieved at an oxidation temperature of 280°C. Processing OTTO Fuel wastewaters in a continuous flow, full scale wet air oxidation unit achieved even higher destruction levels.

Bench scale wet air oxidation studies on hydrazine-based rocket fuel wastewaters indicated that a 99.8 percent destruction of hydrazine and a >99.0 percent destruction of 1,1-dimethylhydrazine can be achieved at an oxidation temperature of 280°C. Again, processing of hydrazine-based rocket fuel wastewaters in a continuous flow, full scale wet air oxidation unit achieved similar destruction levels.

The application of wet air oxidation for the destruction of chemical agents has been made by the extrapolation of data from the wet air oxidation of compounds with similar chemical structures or of surrogate compounds. Sarin and V-agents are nerve agents which have an organo-phosphorus structure similar to that of certain commonly used pesticides. Pesticides such as glyphosate and malathion, which have a similar organo-phosphorus structure, are essentially completely destroyed (>99 percent destruction) by wet air oxidation in the temperature range of 200 to 280°C.

The chemical agent surrogate, dimethyl methyl phosphonate (DMMP) was wet air oxidized at temperatures of 220 to 280°C. Alkaline hydrolyzed DMMP was wet air oxidized at 280°. All of the oxidized effluents showed a >97.5 percent destruction efficiency for the DMMP.

The blister agent, mustard (HD) is a chlorinated sulfide, bis(2-chloroethyl) sulfide. Organic sulfides such as mercaptans can be destroyed by wet air oxidation at 260 to 280°C.

It is concluded that the wet air oxidation process is a promising alternative to incineration for disposal of energetics and chemical warfare agents.

INTRODUCTION

The reactive components of energetics are generally compounds which react exothermically. Thus, the disposal of these materials must be approached with caution. The successful destruction of a solid propellant by wet air oxidation was reported in U.S. Patent 4,174,280(1). In the development work for this patent, a slurry of a double-base propellant in water was subjected to wet air oxidation in both bench scale and pilot plant studies. In the pilot plant wet air oxidation study, the propellant slurry was injected directly into the wet air oxidation reactor resulting in a controlled oxidation. This procedure maintained the propellant slurry at a safe temperature prior to wet air oxidation and prevented any denotation conditions.

More recently, it has been found that the disposal of energetics, such as triple-base propellants, can be made less hazardous if the propellant is hydrolyzed in a sodium hydroxide solution as the first step in the disposal process.

The subsequent disposal technology must then be capable of handling an aqueous slurry. The wet air oxidation technology has been successfully applied, for over thirty years, to the treatment of aqueous waste streams.

The wastewater that is produced in the handling of liquid propellants also presents unique treatment problems. Two such wastewaters, one from OTTO Fuel and one from hydrazine-based rocket fuels, have been successfully treated by wet air oxidation, both in a bench scale, batch unit and in a continuous flow, full scale system.

The wet air oxidation studies which demonstrate the destruction of the energetics as well as the treatment of the energetics containing wastewaters, are discussed below.

Chemical warfare agents such as sarin (GB) and V-agent (VX) are organophosphorus compounds. Sarin is isopropyl methyl phosphonofluoridate and VX is a phosphonothioate. The organophosphono structure is readily oxidized and hydrolyzed in the wet air oxidation process to simple phosphonic acids, i.e., methyl phosphonic acid, and to inorganic orthophosphate.

The blister agent, Mustard (HD), is bis(2-chloro ethyl) sulfide. Organic sulfides can easily be oxidized to simple sulfonic acids, i.e., methyl sulfonic acid and inorganic sulfate.

The application of wet air oxidation for the destruction of compounds which have structures similar to the chemical agents or to surrogate compounds of the chemical agents is also discussed in the following sections.

PROCESS DESCRIPTION

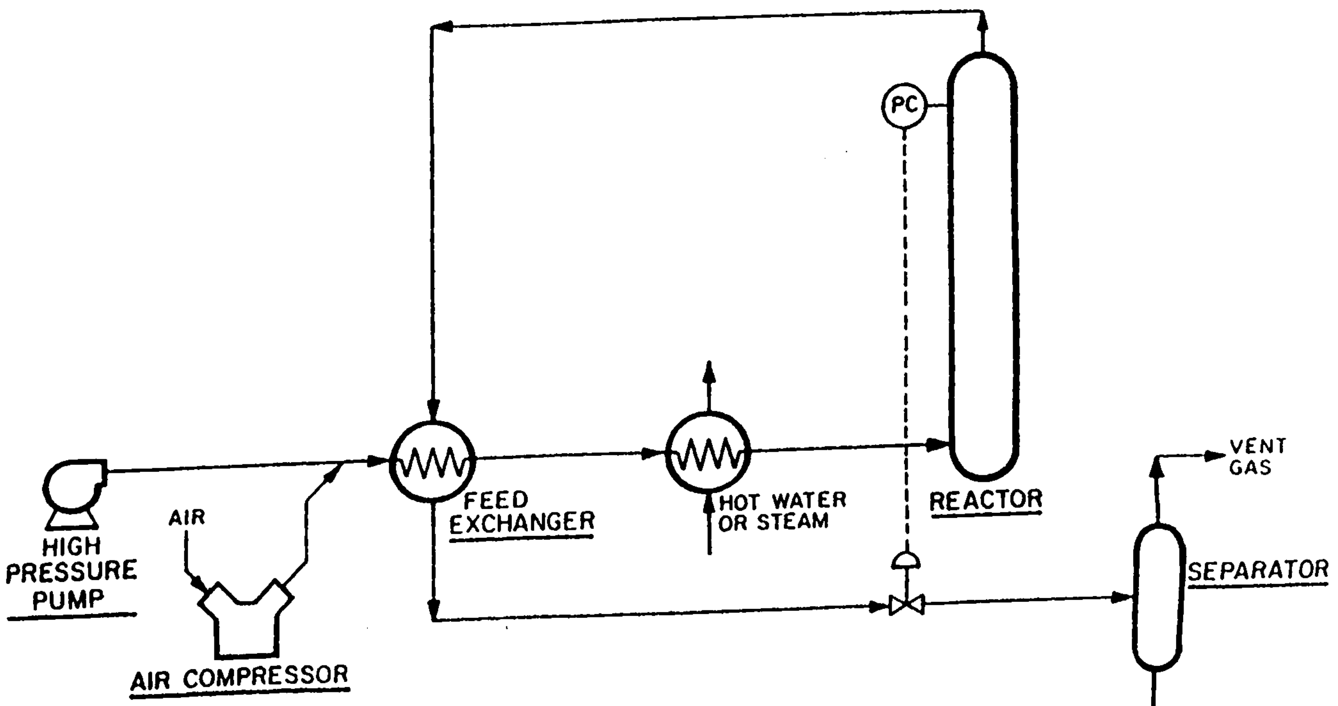
Wet air oxidation (WAO) refers to the aqueous phase oxidation of organic and inorganic materials at elevated temperatures and pressures. Oxidation takes place through a family of related oxidation and hydrolysis reactions at temperatures of 150 to 320° C (302 to 608°F) and at pressures of 2,069 to 20,690 kPa (300 to 3000 psig). The enhanced solubility of oxygen in aqueous media at elevated temperature and pressure provides a strong driving force for oxidation. The source of oxygen is compressed air or high pressure pure oxygen.

Elevated pressures are required to keep water in the liquid state. Liquid water "catalyzes" oxidation so that reactions proceed at relatively lower temperatures than would be required if the same materials were oxidized in open flame combustion. At the same time, water moderates oxidation rates providing a medium for heat transfer and removing excess heat by evaporation.

A basic flow diagram for a WAO system is shown in Figure I. In the operation of a WAO system, a stream containing oxidizable material is pumped to the system using a positive displacement, high pressure pump. The feed stream is preheated by heat exchange with hot oxidized effluent. Air or oxygen is introduced at the high pressure pump discharge or injected directly into the wet oxidation reactor. The reactor, a vertical bubble column, provides liquid retention time during which oxidation and hydrolysis reactions occur. The retention time varies from a few minutes to several hours depending on the type of wastewater

FIGURE 1

WET OXIDATION FLOW DIAGRAM



and the treatment objectives. The heat of oxidation raises the reactor temperature to the desired operating level. Injection of steam into the reactor or external heating may be necessary to maintain the operating temperature for systems not generating sufficient heat from the oxidation reactions. Hot oxidized effluent is cooled by heat exchange with the feed before pressure letdown through a control valve. Liquid and non-condensable gases are disengaged in a separator drum and discharged separately.

Wet oxidation consumes far less fuel than other forms of thermal oxidation. In incineration, for example, one must supply not only the sensible heat and heat of vaporation of the liquid, but also heat for elevating the water vapor, combustion products, and excess air to combustion temperatures of between 815 and 1110°C (1500 and 2000°F). With WAO, however, the only energy required is the difference in enthalpy between the incoming and outgoing streams. With sufficient heat transfer between incoming and outgoing streams, wet oxidation can proceed autogenously (self-sustaining, with no auxiliary fuel). For this to occur, a heat release from a chemical oxygen demand (COD) reduction of approximately 15,000 to 20,000 milligrams per liter in the waste stream is required.

The wet oxidation process is simple, exceptionally adaptable to changes and variations in feed characteristics, and can process a wide variety of oxidizable materials. The oxidation products are relatively innocuous. The primary products of oxidation are carbon dioxide and water. Sulfur is oxidized to sulfate which remains in the aqueous phase. Organic nitrogen is usually coverted to NH_3, nitrate, or nitrous oxide. SO_x or NO_x is not formed. Metals generally are coverted to their highest oxidation state and remain in the aqueous phase as dissolved or suspended solids. Organic halogens also stay in the aqueous phase and are coverted to inorganic halides. The gas discharged from a WAO unit consists mainly of spent air and CO_2 and is essentially free of any air polluting constituents.

TRIPLE-BASE PROPELLANT

Wet air oxidation was applied to the destruction of a triple-base propellant. This development work showed that high destruction efficiencies of the reactive compounds, i.e. nitrocellulose, nitroglycerin and nitroquanidine could be achieved at wet air oxidation temperatures of 280 to 320°C. A triple-based propellant identified as M31A1E1 was tested in the bench scale wet air oxidation study. The initial study was conducted with an alkaline hydrolyzate of the M31A1E1 propellant. The characterization of the alkaline hydrolyzate is shown in Table 1.

The results of the initial bench scale wet air oxidation of the hydrolyzed M31A1E1 propellant are reported in Table 2. In this study, the non-purgeable organic carbon (NPOC) analyses of the hydrolyzed propellant and wet air oxidized effluents were used to assess the destruction efficiency. Hence, destruction efficiencies of 80.3 to 86.4 percent were accomplished in these wet air oxidation tests. In evaluating these wet air oxidation results, an attempt was made to obtain a balance on the nitrogen in the feed and the nitrogen in the oxidized effluent samples. The latter forms of nitrogen include nitrate, nitrite, ammonia, and organic nitrogen as total kjeldahl nitrogen. Nitrogen balances could not be achieved (see Tables 1 and 2) in the bench scale oxidation's that used air as the source of oxygen. Apparently, all of the nitrogen in the alkaline hydrolyzed propellant did not respond to the analytical methods that were used.

TABLE 1

Characterization of Hydrolyzed M31A1E1 Propellant

Parameter	Units	Result
COD	g/l	32.3
BOD	g/l	ND
Suspended Solids	mg/l	344
Suspended Ash	mg/l	104
Total Solids	g/l	455.9
Total Ash	g/l	289.8
Total Kjeldahl Nitrogen	mg/l	1,141
Ammonia Nitrogen	mg/l	283
Nitrate Nitrogen	mg/l	2,477
Nitrite Nitrogen	mg/l	4,267
Total Nitrogen	mg/l	7,885
Nonpurgeable Organic Carbon	mg/l	13,900
pH	---	>14
Soluble Chloride	mg/l	323

ND = Not Detected

TABLE 2

Analysis of Wet Air Oxidized Effluents from the Oxidation of Alkaline Hydrolyzed M31A1E1 Propellant

Parameter	Units	280°C Oxidation Results	300°C Oxidation Results	320°C Oxidation Results
Liquid Products				
COD	g/l	12.5	12.7	9.9
BOD	g/l	ND	ND	ND
Suspended Solids	mg/l	<100	<100	<100
Suspended Ash	mg/l	<100	<100	<100
Total Solids	g/l	376.5	353.8	352.4
Total Ash	g/l	280.1	318.8	330.2
Total Kjeldahl Nitrogen	mg/l	4,147	4,662	2,114
Ammonia Nitrogen	mg/l	2,099	2,320	1,330
Nitrate Nitrogen	mg/l	2,773	2,125	2,406
Nitrite Nitrogen	mg/l	5,397	5,296	6,548
Total Nitrogen	mg/l	12,317	12,083	12,068
Nonpurgeable Organic Carbon	mg/l	2,741	4,763	1,896
pH	---	>14	13.9	13.9
Soluble Chloride	mg/l	324	192	164

OTTO FUEL WASTE WATER

OTTO Fuel was developed as a monopropellant for use in torpedo propulsion units. The reactive component of this fuel is a liquid explosive, propylene glycol dinitrate (PGDN). In an assessment of the treatment methods available for OTTO Fuel wastewaters, Sullivan, Lay and Dale(2) concluded wet air oxidation to be an energy-efficient, cost-effective method for the complete disposal of such wastes. Other treatment means considered included incineration, carbon adsorption, or solidification followed by land disposal.

As pointed out by Sullivan et. al.(2), the PGDN wastewater usually contains three layers; a top layer of oily water waste, a larger middle layer of water with some suspended and some dissolved PGDN, and a bottom layer of mostly PGDN. Our initial bench scale wet air oxidation tests were performed on the middle water layer with some of the top oily layer which easily dispersed on shaking. Bench scale wet air oxidation was conducted at 280°C for 60 minutes of a 1:1 dilution of the wastewater. An analysis of the feed and oxidized effluent is shown in Table 3. A destruction of 99+ percent of the PGDN was found based on GC/MS analysis of oxidized product and starting material using the characteristic m/e 46 ion as a basis for calculations.

TABLE 3

Bench Scale Wet Air Oxidation of OTTO Fuel Wastewater

	Feed	Oxidized Sample
Oxidation Temperature, °C	---	280
Time at Temperature, Min.	---	60
COD, g/l	44.2	7.5
COD Destruction, %	---	82.6
BOD_5, g/l	8.57	5.05
BOD_5/COD	0.19	0.67
pH	9.3	3.3
Soluble Chloride, mg/l	895	846
Soluble Fluoride, mg/l	3.3	1.4
Propylene Glycol Dinitrate Destruction, %[1]	---	99+

[1] Based on m/e 46 Ion Ratio

A full scale, continuous flow wet air oxidation of OTTO Fuel wastewater was performed at a hazardous waste treatment facility located at Casmalia Resources, Casmalia, CA. The wet air oxidation system operating conditions are shown in Table 4, as are the analyses of the feed streams and the oxidized effluent. During this testing, only the "middle" aqueous phase and "lower" PGDN phases of the OTTO Fuel wastewater were processed through the unit. The relative proportions were 38 percent aqueous phase and 62 percent PGDN phase for the particular batch treated at that time period. The PGDN phase and aqueous phase were injected directly into the wet oxidation reactor at 0.4 to 0.5 GPM along with 7.5 GPM of dilution water. In this mode of operation, the wet air oxidation reaction proceeded smoothly and the system operated without any mechanical interruptions.

TABLE 4

Full Scale Wet Air Oxidation of OTTO Fuel Wastewater

System Operating Conditions	
Oxidation Temperature	274°C (525°F)
Nominal Residence Time	75 Min.
OTTO Fuel Wastewater Flow	0.4 - 0.5 GPM
Water Flow	7.5 GPM
Compressed Air Flow Rate	175 SCFM
Reactor Pressure	1500 - 1700 psig
Residual Oxygen Concentration	2.6%

	Influent Mixture	PGDN	Oxidized Sample
COD, g/l	50.3	1,400	2.75
COD Destruction, %	---	---	94.5
BOD_5, g/l	29.9	---	1.42
pH	7.3	---	4.3
Soluble Chloride, mg/l	553	---	297
Soluble Fluoride, mg/l	<0.5	---	31.5
Freon TF, g/l	1.2	88	---
Propylene Glycol Dinitrate Destruction, %[1]	---	---	99.99

[1] Based on m/e 46 Ion Ratio

A sample of concentrated OTTO Fuel wastewater feed, in the above relative proportions, was analyzed for PGDN by GC/MS as was a sample of the oxidized effluent. Again, using the m/e 46 ion as a basis, the feed, after a thousand-fold dilution, gave 366,000 ion counts for the PGDN peak while the effluent, after a hundred-fold dilution, gave no peak in excess of 500 ion counts. Therefore, a destruction of PGDN in excess of 99.99 percent was indicated on this basis.

The presence of Freon TF (1,1,2-Trichloro-1,2,2-trifluoroethane) caused total hydrocarbon emissions in the wet air oxidation off gases of 475-550 ppm prior to carbon adsorption treatment. The presence of Freon in the OTTO Fuel wastewater has precluded the use of wet air oxidation for the treatment of this wastewater due to both high THC levels in the off gases and the possibility of corrosion caused by hydrofluoric acid. The substitution of an unfluorinated solvent for Freon in the Department of Navy cleaning procedures would circumvent these treatment deterrents.

HYDRAZINE BASED ROCKET FUEL WASTE WATER

Hydrazine-based rocket fuel wastewaters were produced in connection with the Space program centered at Vandenberg AFB, California and Cape Canaveral, Florida. The most troublesome of these wastewaters contains a mixture of hydrazine and 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH). Monomethylhydrazine (MMH) has also been mentioned as a candidate for use as a rocket fuel.

A full scale wet air oxidation of hydrazine-based rocket fuel wastewater was conducted at Casmalia Resources, Casmalia, CA. The wet air oxidation system operating conditions and results are reported in Table 5.

TABLE 5

Full Scale Wet Air Oxidation of Rocket Fuel Wastewater

System Operating Conditions	
Oxidation Temperature	271°C (520°F)
Nominal Residence Time	117 Min.
Wastewater Flow Rate	5.13 GPM
Compressed Air Flow Rate	178 SCFM
Reactor Pressure	1500-1600 psig
Residual Oxygen Concentration	3.4%

	Feed	Oxidized Sample
COD, g/l	42.13	2.54
COD Destruction, %	---	94
pH	10.4	8
Total Kjeldahl Nitrogen, mg/l	5,930	2,360
Ammonia-N, mg/l	2,680	1,876
Nitrate-N, mg/l	2.5	60.8
Nitrite-N, mg/l	<1.0	<1.0
Hydrazine, mg/l	12,700	<0.11
Hydrazine Destruction, %	---	>99.99
1,1-Dimethyl Hydrazine, mg/l	9,250	<0.70
1,1-Dimethyl Hydrazine Destruction, %	---	>99.99
N-Nitrosodimethylamine, mg/l	3	34

The wastewater feed was diluted with water prior to entering the heat exchangers of the full scale unit. Hydrazine and UDMH were analyzed as their salicylaldehyde derivatives via HPLC using the method of Abdou, Medwick and Bailey(3). Excellent removals of both hydrazine and UDMH were observed in the effluent, however, the concentration of N-nitrosodimethylamine (NNDMA) increased from 3 ppm to 34 ppm on oxidation. NNDMA was analyzed by EPA Method 607. The nitrosamine apparently is an oxidation intermediate in the wet oxidation of UDMH. The observed increase in NNDMA concentration is somewhat surprising since this compound has been shown to be oxidized in excess of 99 percent under comparable wet oxidation conditions(4).

Since NNDMA is a carcinogen, a laboratory investigation was undertaken to evaluate ways to eliminate this substance from the effluent. Alteration of reaction conditions or effluent post treatment were evaluated.

In conducting the bench scale wet air oxidation study, the handling of the hydrazine based wastewater was performed in a special laboratory where the autoclaves were filled and sealed prior to wet air oxidation. After processing, the oxidized samples were removed from the autoclave and this equipment was thoroughly cleaned. Work was performed in a fume hood by personnel equipped with the appropriate personal protective clothing.

A bench scale wet air oxidation study, conducted on actual rocket fuel wastewater, was undertaken to investigate the alteration of reaction conditions and the resulting effects on the formation of NNDMA. By reducing the pH of the feed wastewater to a pH of 2, the NNDMA concentration in the oxidized effluent could be substantially reduced. The results of this bench scale study are reported in Table 6. These results show that by reducing the pH of the feed wastewater to 2, the NNDMA concentration could be reduced to 1.1 mg/l, compared to 17.7 mg/l in the control wet air oxidation under alkaline conditions. The reduction in the pH of the feed wastewater did not effect the destruction efficiencies of the hydrazine or 1,1-dimethylhydrazine.

Attempts at reducing the concentration of NNDMA in the oxidized effluent by post treatment in a biological reactor, in the presence of powdered activated carbon, also showed positive results.

TABLE 6

Bench Scale Wet Air Oxidation of Rocket Fuel Wastewater

	Feed	Oxidized Samples	
Oxidation Temperature, °C	—	280	280
Time at Temperature, Min.	—	60	60
pH of Charge	10.4	10.4	2
pH of Effluent	—	8	1.5
COD, g/l	42.1	—	—
Oxygen Uptake, g/l	—	39.8	26.5
Hydrazine, mg/l	12,700	24	28
Hydrazine Destruction, %	—	99.8	99.8
1,1-Dimethyl Hydrazine, mg/l	9,250	<7	<7
1,1-Dimethyl Hydrazine Destruction, %	—	>99.9	>99.9
N-Nitrosodimethylamine, mg/l	3	17.7	1.1

CHEMICAL AGENT SURROGATES

The chemical warfare agents, sarin (GB) and V-agent (VX) are phosphonofluoridate and phosphonothioate compounds, respectively. The pesticide glyphosate (N-phosphono methyl glycine) has the organic phosphono structure. A solution of commercially available glyphosate was wet air oxidized in a bench scale test. The results of this oxidation study are reported in Table 7. The wet air oxidation tests were conducted at 200, 240, and 280°C utilizing a 60 minute reaction time at temperature and pure oxygen gas as the source of oxygen. The oxidation results, shown in Table 7, indicate that extensive cleavage of the carbon-phosphorus and carbon-nitrogen bonds occurred during the oxidation at 200°C. The oxidized effluent from the 200°C oxidation shows a dramatic increase in ortho-phosphate and ammonia nitrogen compared to the untreated glyphosate sample. Over 99.5 percent of the glyphosate was destroyed by wet air oxidation at 200°C. At the higher oxidation temperature of 280°C, nearly complete mineralization of the phosphorus and nitrogen was indicated along with a 99.8 percent destruction of the glyphosate.

TABLE 7

Characterization of Feed and Oxidation Products from the Oxidation of Glyphosate

Analyses	Autoclave Feed	200°C for 60 Minutes	240°C for 60 Minutes	280°C for 60 Minutes
COD, mg/l	27,500	14,400	9,300	6,900
COD Destruction, %	---	47.6	66.2	74.9
NPOC, mg/l	7,500	5,800	3,900	2,300
pH	4.89	5.85	5.49	4.49
Total Solids, mg/l	24,000	15,500	10,800	10,000
Total Ash, mg/l	6,000	5,200	4,550	5,700
Total Kjeldahl Nitrogen, mg/l	2,320	2,440	2,190	1,320
Ammonia-N, mg/l	1,157	1,871	1,739	1,463
Nitrate-N, mg/l	<0.5	1	9	87
Total Phosphorous, mg/l	2,890	2,463	2,264	2,353
Ortho-P, mg/l	14	2,277	2,120	2,226
Glyphosate, mg/l	14,600	73	66	33
Glyphosate Destruction, %	---	99.5	99.5	99.8
DIC, mg/l	<10	800	300	<1
Total Carbon in off-gas, mg/l	---	1,900	4,100	5,700
Total Nitrogen in off-gas, mg/l	---	<200	870	850

The pesticide malathion, a phosphonodithioate compound, has a phosphorus-sulfur bond similar to that found in the phosphonothioate structure of VX. A full scale, continuous flow wet air oxidation of a pesticide waste which contained malathion was conducted at the hazardous waste treatment facility located at Casmalia Resources, Casmalia, CA. The wet air oxidation unit was operated at a reactor temperature of 281°C, a reactor pressure of 1600 psig, and a waste flow of 3.3 gallons per minute. The influent wastewater contained 93.1 mg/l of malathion. The oxidized effluent contained 0.13 mg/l of malathion which indicates a 99.9 percent destruction.

The surrogate compound for sarin is dimethyl methyl phosphonate (DMMP). A bench scale wet air oxidation study was conducted on DMMP and alkaline hydrolyzed DMMP. The results from this bench scale study are reported in Table 8. These results indicate that the DMMP was essentially completely destroyed (>97.5 percent) at all conditions tested. The data also indicate that very little oxidation of the organic carbon occurred indicating that hydrolysis of the DMMP may be the mechanism of destruction.

TABLE 8

Analysis of DMMP and DMMP Wet Air Oxidized Effluents

	Autoclave Feed	Oxidized Effluents				
Oxidation Temperature, °C	---	220	240	260	280	280
Time at Temperature, Min.	---	60	60	60	60	60
NaOH added, g/l	---	0	0	0	0	16.6
COD, mg/l	14,600	13,600	13,706	13,596	13,596	12,390
NPOC, mg/l	4,929	4,270	4,889	4,393	4,024	4,165
pH	3.6	1.9	1.8	1.8	1.8	13
DMMP, mg/l	19,900	<500	<500	<500	<500	<500
% DMMP Destruction	---	>97.5	>97.5	>97.5	>97.5	>97.5

The blister agent Mustard (HD) is bis (2-chloroethyl) sulfide. Spent caustic samples from various refinery operations contain several organic sulfides as well as mercaptans and inorganic sulfides. The reduced sulfur compounds can be wet air oxidized to sulfates and sulfonic acids. An example of the wet air oxidation of refinery spent caustic is shown in Table 9. This data shows that the reduced sulfur compounds are essentially completely oxidized. The sulfide sulfur and mercaptans concentrations indicate that a >99.9 percent destruction efficiency is obtained for these substances in the wet air oxidation process.

TABLE 9

Analysis of Refinery Spent Caustic and Wet Air Oxidized Effluents

	Feed	Oxidized	Effluents
Oxidation Temperature, °C	---	260	280
Time at Temperature, Min.	---	60	60
COD, mg/l	81,300	24,200	18,000
% COD destruction	---	70.2	77.9
Total Sulfur, mg/l	7,900	9,260	8,972
Sulfide Sulfur, mg/l	5,024	<4	<4
Sulfate Sulfur, mg/l	<54	6,350	6,727
Mercaptans as Methyl, mg/l	8,680	<10	<10

CONCLUSIONS

A high degree of destruction of the reactive components of energetics can be achieved by wet air oxidation. Triple-base propellants containing nitrocellulose, nitroglycerin, and nitroguanidin can be destroyed by wet air oxidation at temperatures of 280°C to 320°. In the wet air oxidation of triple-base propellants, the propellant was initially hydrolyzed in an alkaline slurry and wet air oxidized under highly alkaline conditions. Wet air oxidation under acid conditions would yield different oxidation products.

Essentially, complete destruction of propylene glycol dinitrate, the reactive component in OTTO Fuel, can be achieved by wet air oxidation at 280°C. The immiscible OTTO Fuel must be slurried in water prior to oxidation. Care must be taken to avoid the mixture of Freon with the OTTO Fuel wastewater.

Wet air oxidation of Freon produces hydrofluoric acid which is corrosive, even to titanium materials.

Hydrazine and 1,1-dimethylhydrazine, the reactive components in rocket fuel, can be nearly completely destroyed by wet air oxidation at 280°C. The wet air oxidation reaction of 1,1-dimethylhydrazine yields trace amounts of N-nitrosodimethylamine. The amount of N-nitrosodimethylamine in the oxidized effluent can be reduced by acidification of the feed wastewater or by post treatment of the effluent.

Glyphosate and malathion, which have similar chemical structures to the nerve agents, sarin (GB) and VX, can be destroyed by wet air oxidation in the temperature range of 200 to 280°C. Dimethyl methyl phosphonate (DMMP), which is a chemical surrogate for sarin, is destroyed by wet air oxidation in the temperature range of 220 to 280°C. Alkaline hydrolyzed DMMP is destroyed in the same temperature range. Organic sulfides and disulfides, which are similar in chemical structure to the blister agent, Mustard (HD), are destroyed by wet air oxidation at temperatures of 260 and 280°C.

This work demonstrates that the wet air oxidation process can be used as an alternative to incineration for the disposal of chemical agents and energetic materials.

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