10
10/12/94 J5①

SANDIA REPORT

SAND95-8202 • UC-706

Unlimited Release

Printed November 1994

Supercritical Water Oxidation of Ammonium Picrate

C. A. LaJeunesse, B. E. Mills, B. G. Brown

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution unlimited.

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

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

This report has been reproduced from the best available copy.

Available to DOE and DOE contractors from:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge TN 37831

Prices available from (615) 576-8401

Available to the public from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

DISCLAIMER

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

SUPERCRITICAL WATER OXIDATION OF AMMONIUM PICRATE*

C. A. LaJeunesse, B. E. Mills, and B. G. Brown
Engineering for Transportation and Environment Department
Sandia National Laboratories/California

ABSTRACT

This study demonstrates the feasibility of using supercritical water oxidation to destroy ammonium picrate. Analyses of reactor effluent composition at various temperatures, residence times, and oxidant concentrations were used to design an improved reactor configuration for achieving destruction with minimum corrosion. The engineering evaluation reactor, a room-sized laboratory scale reactor, was reconfigured to incorporate this design change. Destruction of ammonium picrate with minimized corrosion was demonstrated on this reconfigured reactor. Factors that must be considered in scaling up to pilot plant size are discussed.

* This report presents the results of a project directed by the Naval Surface Warfare Center in Crane, Indiana, to assess the feasibility of using SCWO to effectively destroy ammonium picrate that is removed from Navy projectiles. The specific tasks or items to be addressed are described in DOE proposal #84930721, "Explosive D Destruction with Supercritical Water Oxidation." Mr. Keith Sims, Crane Division, Ordnance Engineering Directorate, SEA Department, was the principal contact.

ACKNOWLEDGMENTS

D. E. Meeker, T. J. Sage, and T. J. Boyd assisted in the gas analysis. C. Hays performed some of the metal analyses of effluent samples. L. G. Hoffa provided drafting assistance. Figure 5 was adapted from work by D. C. Macmillan. The scale-up estimates were adapted from work by T. N. Raber. We thank M. C. Stoddard for valuable technical discussions and support.

Contents

	Page
Introduction	7
Experimental	8
Results and Discussion	11
Scale-up Estimates	22
Summary and Conclusions	27
References	29

Illustrations

No.	Page
1. Composite layout of SCWO reactor showing both the original configuration and the modified configuration.	9
2. Liquid effluent analysis from tests using the original reactor configuration.	14
3. Liquid effluent analysis from tests using the modified reactor configuration.	19
4a. Fluid temperature as a function of position along the reactor axis.	21
4b. Calculated time as a function of position along the reactor	21
5. Reactor schematic.	24

Tables

No.	Page
1. First Test Series (Baseline Tests)	13
2. Second Test Series (Tests without Additional Oxidant)	15
3. Third Test Series (Minimal Excess Oxidant Tests)	16
4. Fourth Test Series (Reconfigured Reactor Tests)	18
5. Fifth Test Series (High Concentration Test)	20
6. Parameters used in Cost Analysis	22
7. Cost Estimate Breakdown	25

INTRODUCTION

Background

Explosives such as ammonium picrate* can be destroyed by open burning/open detonation (OB/OD) techniques or by incineration in a dedicated incinerator. OB/OD is the established technique for final disposition of conventional explosive weapons. However, regulatory agencies may eventually prohibit OB/OD, which emits particulates and suspected carcinogens into the environment. OB/OD can also produce shock waves that can be heard for large distances.

Incineration, the alternate technology for disposal of explosives, produces nitrogen oxides and is unacceptable to the public. Therefore, incineration permits, which are increasingly hard to obtain, may soon be unavailable.

Various government agencies are interested in developing alternative technologies for the final disposition of obsolete weapons and munitions. They have directed that studies be performed on alternative destruction technologies for disposition of the DoD chemical weapon inventory [1]. Among the technologies considered were molten salt, plasma arc, and supercritical water oxidation. These methods may also be applicable to the destruction of explosives.

There are over 17,000 short tons of Navy projectiles loaded with ammonium picrate in the demilitarization inventory awaiting final disposition. The Naval Surface Warfare Center in Crane, Indiana, is interested in developing alternative treatment methods for the disposition of ammonium picrate that do not have the problems of OB/OD and incineration.

Supercritical water oxidation (SCWO) is a candidate treatment method being considered by private industry, the Department of Defense (DoD), and the Department of Energy (DOE) for a variety of wastes. In addition to the destruction of ammonium picrate and chemical warfare agents, projects administered by these agencies for the disposal of military components and wastes include the development of a module to treat DOE mixed radioactive waste, the development of a SCWO reactor for disposal of obsolete rocket boosters, and the application of SCWO technology for the destruction of obsolete smokes, dyes, and pyrotechnic munitions.

SCWO for the Treatment of Wastes

Aqueous waste, typically ranging from 1-10 wt.% oxidizable material (fuel) and an oxidant (oxygen, air, or hydrogen peroxide), are pressurized and heated above the critical point of water (374°C, 22.1 MPa). The supercritical fluid is maintained at elevated temperature (typically, 550°C) for sufficient time to oxidize the fuel. Since oxidation of hydrocarbons to water and carbon dioxide is exothermic, the heat of reaction can help to maintain an elevated temperature. The heat capacity of the water moderates any tendency of the reaction to run away.

* Ammonium picrate is the ammonium salt of picric acid, 2,4,6-trinitrophenol. It is also referred to as "Explosive D". The terms are used interchangeably in this report. "The explosive" is also used in this report to denote ammonium picrate.

The oxidation products of organic species containing only carbon, hydrogen, and oxygen are straightforward. However, species with other heteroatoms may have more than one reaction path available. Molecules with nitro groups (e.g., ammonium picrate) are in a special class because they contain both fuel and oxidizer in the same molecule. They may follow different reaction paths to form different products depending on the reaction conditions.

This study demonstrates the feasibility of using supercritical water oxidation to destroy ammonium picrate. Analyses of reactor effluent composition at various temperatures, residence times, and oxidant concentrations were used to design an improved reactor configuration for achieving destruction with minimum corrosion. The engineering evaluation reactor, a room-sized laboratory scale reactor, was reconfigured to incorporate this design change. Destruction of ammonium picrate with minimized corrosion was demonstrated on this reconfigured reactor. Factors that must be considered in scaling up to pilot plant size are discussed.

EXPERIMENTAL

Materials and Handling

Ammonium picrate is bright yellow and soluble in 20°C water to 1.1 wt.%. The water solution is not explosive and toxicity is the primary safety concern [2].

Sample packets of about 50g each of crystalline powdered Explosive D were supplied by McAlester Army Ammunition Plant (MCAAP) in conventional ammunition boxes. Trained explosive handlers dissolved the powder in plastic gallon containers in an explosive handling facility. The containers were transported to the SCWO reactor site and stored in a dedicated cabinet inside an explosive cell. The reactor is located in an explosive cell and operated remotely. Since the SCWO reactor is not equipped to pump explosive slurries at high pressure, testing was limited to 1.0 wt.%. Although ammonium picrate could be fed as a more concentrated solution at higher temperatures, slurry handling methods would be necessary for explosives that are sparingly soluble in water.

The first shipment of powder, which had been reclaimed from shells, clumped and was difficult to break up. In addition to the yellow ammonium picrate, it was contaminated with an insoluble brown material. Samples were prepared from this shipment by heating water to 50°C prior to dissolution, dissolving the explosive in the water at 1.0 wt.%, and decanting the solution from the undissolved solid.

The second shipment of powder was readily soluble in hot water except for a brown suspended contaminant which was filtered prior to processing. This prevented the small nozzle used to introduce the feed into the reactor from becoming clogged.

Hydrogen peroxide was used as the oxidant in these experiments. A solution of peroxide in water was made up and the oxidant concentration was calibrated by titration for each test. To calculate oxidant required for complete destruction, the global reaction pathway was assumed to be:

in which the carbon and hydrogen are fully oxidized, the nitro nitrogens are reduced to molecular nitrogen, and the ammonium nitrogen is oxidized to molecular nitrogen. All excess oxidant concentrations are stated as if this were the sole reaction pathway. However, if the nitrogen in the nitro groups is incompletely reduced, nitrogen oxides will be produced [3].

SCWO System Design and Operation

All of the oxidation experiments were conducted in Sandia's remotely operated supercritical water oxidation flow reactor, the Engineering Evaluation Reactor (EER). An extension of Sandia's experience using a resistively heated plug flow SCWO reactor [4] and the Materials Evaluation Reactor (MER) [5-7], the EER is of modular design to facilitate testing different reactor configurations. It is also built for remote operation to perform experiments on processing hazardous materials. A schematic of the EER as configured for these experiments is shown in Figure 1.

Figure 1. Composite layout of SCWO reactor showing both the original configuration and the modified configuration (see text for modifications).

Pressurization Subsystem

The high-pressure pumps are positive displacement pumps with nitrile seals. The axial shaft is geared to an electric motor and servo-actuator for remote flow control. Peristaltic pumps insure that the high-pressure pumps are always primed. They recirculate the feed, distilled water, and oxidizer streams at several times the flow requirements of the high-pressure pumps, pressurizing the suction side to about 10 psi, regulated by an in-line relief valve.

Reactor Subsystem

The baseline EER configuration is a continuous plug flow reactor, i.e. without the section shown above the disconnect joint. The experiments described in this work prompted us to refit the reactor as shown to supply oxidant either with the fuel/water mixture at the inlet to the reactor, or after the fuel/water mixture had been heated to supercritical conditions.

The reactor is composed of sections of 9/16 inch (1.43 cm) OD, 3/16 inch (0.477 cm) ID inconel 625 tubing. Tees or crosses allow pressure and temperature measurements at various positions along the reactor; only a few positions are shown for illustration. Temperatures are measured with inconel 600 sheathed Type-K thermocouples located directly in the fluid. Watlow 375-1000 W cable heaters are wrapped around the inconel 625 tubing and are used to heat the fluid to supercritical conditions. They are controlled by monitoring reactor surface temperature to prevent overheating the tubing. The reactor has a maximum operating temperature of 650°C at an operating pressure of 34.0 MPa (5000 psi). All the experiments reported here were performed at 28.4 MPa (4000 psi). Total flow can be varied from about one ml/s to four ml/s (STP) while still maintaining good flow control.

After the reactor section, the fluid is cooled to between 50 and 100°C. The flow is then discharged through a liquid back-pressure regulator into either a liquid collection tank for subsequent analysis or into a larger tank where the gas is diverted for on-line analysis by gas chromatography (GC) or mass spectroscopy (MS).

Control Subsystem

The reactor system is controlled remotely by an operator through a graphical user interface to LabVIEW on a Macintosh Quadra 950. This program is easily modified to reflect changes to the reactor and to collect additional data. Currently, all control parameters as well as all other measured temperatures and pressures are automatically logged by the computer.

Effluent Analysis

The liquid feed and effluent, and the gaseous effluent, were subjected to several chemical analyses.

Analytical Procedures

The total organic carbon content (TOC) of both feed and effluent were measured using a Rosemount DC-190. The total destruction and removal efficiencies (DREs) for the explosive were determined from these measurements.

Corrosion is a problem when destroying energetic compounds. In order to quantify the corrosion, the metal content of the effluent was measured. The initial analysis was performed using a VG Plasma Quad inductively coupled mass spectrometer (ICP/MS) to determine all soluble corrosion products. A few subsequent analyses were performed on

a Perkin Elmer ICP/AES (atomic emission spectrometer) where we analyzed for the RCRA (Resource Conservation and Recovery Act) elements, which include the corrosion products nickel and chromium. Since the mechanism of corrosion can be related to the pH, the pH of the effluent was measured for each reactor condition. Nitrate and nitrite indicate incomplete reduction of the nitro groups of the ammonium picrate. Their concentrations were determined colorimetrically using a Model 943 Orbeco Analyzer.

Gaseous effluent composition was measured on-line using an MTI Analytical Instruments M200 gas chromatograph (GC). A quadrupole mass spectrometer was also used for gas analysis.

Experimental Accuracy

There are two sources of uncertainty in the results reported here: operational parameters (temperature, flow rates, and sample collection) and analytical measurements.

Although operation of the EER is automated, there are design limitations in its control precision. For example, temperature control at any particular location is within $\pm 5^{\circ}\text{C}$. The accuracy of the thermocouple, itself, is $\pm 2.2^{\circ}\text{C}$ or $\pm 0.75\%$ of the reading, whichever is greater.

The flow rates of the oxidizer and explosive are accurate to about 1% above 0.5 ml/s. At flow rates less than 0.5 ml/s, the amount of fluid drawn into the pumping chamber during the intake portion of the stroke has more variability. Therefore flow rates well above 0.5 ml/s were used in all the tests reported here.

Pressure fluctuations during testing are caused by: (1) pressure pulses of 25 psi from the positive displacement pump strokes, and (2) variation of ± 50 psi due to passing a two-phase mixture through the pressure regulator. Pressure is recorded by two different types of transducers, Teledyne-Taber 2205 transducers (estimated accuracy of ± 50 psi) and Paroscientific 410k-101 (estimated accuracy of ± 2 psi). The type of transducer used for any measurement is noted in the data file.

The TOC measurements are accurate to $\pm 1.7\%$ above 10 ppm. Below 6 ppm the accuracy is reduced to ± 0.1 ppm with 95% confidence. The pH electrode is calibrated with standard buffer solutions to an accuracy of better than 1%. Chromium and nickel measurements are performed in replicates for estimating errors. Nitrate and nitrite measurements are estimated to have an accuracy of 0.022 and 0.005 ppm, respectively and detection limits of 0.044 and 0.007 ppm. Detection limits by GC are better than 0.5 ppm. Accuracy is limited for these experiments by the gas sampling method, which does not sample the entire quantity of gas evolved at all pressures and includes an air component, indicating a leak in the sampling system.

RESULTS AND DISCUSSION

First Test Series: Baseline Tests

Tests were first conducted at 0.20 wt.% ammonium picrate, less than one-quarter of the room temperature solubility limit, to insure that no precipitation of explosive could occur in the reactor system. The primary goals of these tests were to: 1) gain experience at processing Explosive D, and 2) analyze how efficiently SCWO destroyed Explosive D.

Tests were first run with excess oxidant as ratioed to the oxygen demand calculated using equation 1.

Table I lists the test results along with a summary of the test conditions. It should be noted that with the fixed reactor length and flow rate used for these tests, the residence time increases at lower temperatures. The lowest temperature studied is still above the exotherm for ammonium picrate as measured with a differential scanning calorimeter at a temperature ramp rate of 10°C per minute [2].

The results are shown graphically in Figure 2 along with the results of the second test series. Although the explosive was effectively destroyed in test series I, the pH of the effluent was very low and there was chromium and nickel in the effluent. Molybdenum, tungsten, nitrate, and nitrite were also present in the effluent.

Second Test Series: Tests without Additional Oxidant

The acid formed in the first test series was clearly a result of incomplete destruction of the nitro groups from the ammonium picrate. Corrosion of the reactor material might be minimized if the nitro groups could not form acid. Therefore, tests were performed without additional oxidant. With no other source of oxidizer present, the nitro groups were the only oxidizer available. The results listed in Table II and shown graphically in Figure 2 show that the effluent pH remained nearly neutral, there was almost no chromium in the effluent, and there was almost no nickel evident at the lower temperatures.

Most of the destruction possible was completed by 453°C, where no chromium or nickel could be measured; in the absence of additional oxidant the DRE above 453°C increases only marginally with a temperature increase. Further destruction would require the addition of oxidant. However, in previous work we had noted a correlation of chromium in the effluent with excess oxidant level and pH [8]. Supplying sufficient oxidizer for destruction but not enough to cause corrosion could be accomplished in one of two ways: either the oxidant addition could be precisely balanced to ensure that all the nitro groups are used for oxidation while there is sufficient destruction, or the reactor could be modified to add oxidant only after the nitro groups are destroyed.

Third Test Series: Tests with Minimal Excess Oxidant

A series of tests was run at 464°C with different oxidant ratios to determine if, by controlling the amount of oxidant introduced with the waste feed, it is possible to achieve destruction of the organic component with reduced acid production and corrosion. The ammonium picrate concentration was fixed at 0.2%. Test conditions and results are shown in Table III and Figure 2.

DRE increased from 97.3 to 98.3% as excess oxidant was increased from a ratio of 1.10:1 to 1.61:1. Both chromium and nickel in the effluent increased with increasing excess oxidant. There is still acid formation and metal removal even at low excess oxidant concentration. Approximately 20% of the nitrogen in the feed emerged in the form of nitrate or nitrite.

In summary, comparison with the results of the first test series indicates that increasing excess oxidant several hundred percent increased DRE only 1 or 2 percent while significantly increasing the chromium content of the effluent. Nickel in the effluent is

Table I

First Test Series (Baseline Tests)*

Test Number	Temp. (°C)	Oxidizer Ratio‡	DRE (%)	pH	Cr (ppm)	Ni (ppm)
1	550	6.0	99.5	2.29	7.07 ± .04	7.44 ± .03
2	515	6.0	99.7	2.41	7.25 ± .12	7.48 ± .03
3	493	6.0	99.7	2.45	19.38 ± .19	2.76 ± .06
4	423	6.0	99.3	2.59	6.86 ± .04	7.16 ± .09
5	540	2.4	99.6	2.36	10.31 ± .10	4.69 ± .12
6	499	2.4	99.7	2.40	11.26 ± .11	3.55 ± .06
7	448	2.4	99.5	2.41	6.14 ± .03	5.91 ± .16
8	402	2.4	99.1	2.44	2.36 ± .04	8.63 ± .11

* Conditions:

Total flow rate:

1.0 - 1.5 g/sec

Oxidizer concentration:

1.5 wt.% H₂O₂

Amount processed:

~10.0 liters

Input concentration:

506 ppm TOC, approx. 0.20 wt% Exp. D

Residence time:

At the stated temperature, residence time is approx. 9 seconds at 550°C, increasing to

25 seconds at 400°C

System Pressure:

3937 - 4218 psi

‡ An oxidizer ratio of 1.0 corresponds to the stoichiometric amount of additional oxidizer for oxidation (Eq. 1). Any oxidizer ratio above 1.0 indicates excess oxidant.

Figure 2. Liquid effluent analysis from tests using the original reactor configuration. Series I: Fuel and oxidizer fed together. Series II: Fuel with no additional oxidizer. Series III: Fuels and minimal oxidant fed together.

Table II

Second Test Series (Tests without Additional Oxidant)*

Test Number	Temp. (°C)	Oxidizer Ratio‡	DRE (%)	pH	Cr (ppm)	Ni (ppm)
9	551	0	78.7	7.04	0.023 ± .014	4.96 ± .07
10	503	0	74.5	6.25	0.010 ± .007	1.20 ± .11
11	453	0	72.0	7.03	0.0†	0.0†
12	404	0	57.3	7.36	0.0†	0.08 ± .05
13	349	0	28.7	7.68	0.0†	0.04 ± .01
14	301	0	0.03	7.67	0.061 ± .003	0.01 ± .11

* Conditions:

Total flow rate:

1.0 - 1.5 g/sec

Oxidizer concentration:

0.0 wt.% H₂O₂

Amount processed:

~10.0 liters

Input concentration:

506 ppm TOC, approx. 0.20 wt% Exp. D

Residence time:

At the stated temperature, residence time is approx. 9 seconds at 550°C, increasing to 25 seconds at 400°C, and to 100 seconds at 300°C.

System Pressure:

3937 - 4218 psi

‡ An oxidizer ratio of 1.0 corresponds to the stoichometric amount of additional oxidizer for oxidation (Eq. 1). Any oxidizer ratio above 1.0 indicates excess oxidant.

† Value within error of zero.

Table III

Third Test Series (Minimal Excess Oxidant Tests)*

Test Number	Temp. (°C)	Flow Rate (g/s)	Res. Time (sec)	Oxidizer Ratio	DRE (%)	pH	Cr (ppm)	Ni (ppm)	NO ₃ (ppm)	NO ₂ (ppm)
15	464	1.10	16.1	1.10	97.3	2.80	0.44 ±.05	1.64 ±.09	326	70
16	464	1.23	14.4	1.34	97.6	2.41	1.64 ±.02	5.10 ±.24	320	14
17	464	1.36	13.0	1.61	98.3	2.45	2.00 ±.06	7.03 ±.11	362	17

* Conditons:

Oxidizer concentration:

Amount processed:

Input concentration:

System pressure:

0.25 wt% H₂O₂

~7.0 liters

605 ppm TOC (~0.20 wt.% explosive D)

3910 psi

also not adequately controlled by operating with small excess oxygen. Clearly, the approach of controlling exposure to oxygen is fruitful, but more innovative methods are necessary to minimize the formation of acid in the reactor by forcing the destruction of the nitro groups before any additional oxygen is introduced.

Fourth Test Series: Tests with Reconfigured Reactor

The reactor was reconfigured to add oxidant after the nitro groups had been destroyed. To permit the nitro groups to be fully consumed as oxidant, the ammonium picrate feed was heated to 450°C, a temperature where the first test series had indicated no nickel removal and almost as high organic oxidation as at 550°C. The additional oxidant was preheated to 425°C before injection into the 450°C waste stream to supply sufficient oxygen to complete the destruction. The waste was then either held at this temperature or heated further to accelerate the final destruction. Tests were run with this reactor configuration at 454°C, 560°C, 612°C, and 620°C.

Test conditions and results are shown in Table IV and Figure 3. Three tests were performed at a nominal reactor temperature of 454°C for comparison with the tests reported in Table III, which were performed at similar oxidant ratios and flow rates. The pH as well as the nitrate and nitrite concentration of the effluent indicates that most of the nitro groups were destroyed before the oxidant was introduced. Because the pH is near neutral, little nickel is removed from the reactor. Since the oxidant is at a similar level, the chromium depletion is comparable in both sets of tests. DRE decreased by 2 or 3 percentage points because there was little room to have significant residence time both before and after the injection of oxidant. Residence times at the same temperature were reduced by 25%. Consequently, higher temperatures were used for the next three tests. The DRE improved by about three percentage points while nitrate and nitrite ion concentration decreased.

Fifth Test Series: Higher Concentration

In the final test the concentration of the explosive feed was increased several-fold and oxidized with a large excess concentration of hydrogen peroxide to enhance the oxidation of the explosive. These tests were run with the modified reactor configuration. The primary goal of this final test series was a complete quantification of the reaction products in both the gaseous and liquid effluent streams exiting the modified reactor configuration. The test conditions and results are shown in Table V, Figure 3, and Figure 4.

The explosive was allowed to react at a temperature above 550°C before the addition of the preheated oxidant. The residue of unreacted organic material was then allowed to react further with the oxidant as it was held above 543°C for 655 cm (21.5 feet). The temperature profile of the reacting fluid is shown in Figure 4a with calculated residence times at different positions along the reactor plotted in Figure 4b. The calculated residence time after oxidant addition, was 8.7 seconds.

Although the large excess oxidant concentration improved DRE to 99.28%, the residence time above 500°C was insufficient to drive the DRE higher. There was a relatively large amount of inorganic carbon in the effluent, which was colorless and clear. We believe that DREs would be higher with longer residence times.

Table IV

Fourth Test Series (Reconfigured Reator Tests)*

Test Number	Temp. (°C)	Flow Rate (g/s)	Res. Time (sec)	Oxidizer Ratio	DRE (%)	pH	Cr (ppm)	Ni (ppm)	NO ₃ (ppm)	NO ₂ (ppm)
18	454	1.20	12.0	1.54	94.3	5.70	1.04 ± .04	0.04 ± .03	9.3	4.8
19	454	1.25	11.5	1.65	96.2	6.03	0.93 ± .09	0.02 ± .00	9.1	3.2
20	454	1.36	10.6	1.18	95.3	5.93	0.76 ± .20	0.04 ± .01	14.2	4.3
21	560	1.20	8.2	1.72	99.1	5.59	1.29 ± .09	0.02 ± .00	1.7	0.5
22	612	1.38	6.4	1.47	97.9	5.59	0.98 ± .03	0.04 ± .04	1.1	0.3
23	620	1.55	5.6	1.20	98.4	5.88	1.14 ± .02	0.04 ± .03	1.4	0.4

* Conditons:

Oxidizer concentration:

Amount processed:

Input concentration:

System pressure:

0.29 wt% (tests 18-20), 0.41 wt% (tests 21-23) H₂O₂.
 ~7.0 liters (tests 18-20), ~13.0 liters (tests 21-23)
 605 ppm TOC (tests 18-20), 576 ppm (tests 21-23)
 (~0.20 wt.% explosive D)
 3910 psi (tests 18-20), 3950 psi (tests 21-23)

Figure 3. Liquid effluent analysis from tests using the modified reactor configuration. Triangles show liquid effluent analysis from tests using modified reactor configuration, where the feed is allowed to react at high temperature before the addition of supplemental oxidizer. Series V was run at a higher fuel concentration. Test Series I through III are shown for comparison.

Table V

Fifth Test Series (High Concentration Test)*

Test Number	Temp. (°C)	Flow Rate (g/s)	Res. Time (sec)	Oxidizer Ratio	DRE (%)	pH	Cr (ppm)	Ni (ppm)	NO ₃ (ppm)	NO ₂ (ppm)
24	‡	1.08	‡	5.83	99.3	6.51	1.15	.05	1.8	0.7

* Conditons:

Oxidizer concentration:

4.0 WT% H₂O₂.

Amount processed:

~7.0 liters

Input concentration:

2329 ppm TOC, approx. 1.0 wt% Exp. D

System pressure:

4180 psi

Temperature profile

See Figure 4a

Residence time

See Figure 4b

Other effluent values:

Effluent TC

78.94 ppm C

Effluent TIC

71.24 ppm C

Effluent TOC

7.70 ppm C

‡ See Figure 4.

Figure 4a. Fluid temperatures as a function of position along the reactor axis.

Figure 4b. Calculated time as a function of position along the reactor.

The gaseous effluent was analyzed by gas chromatography. Most of the effluent was H₂O, CO₂, N₂, and O₂, the expected species. However, a small amount of N₂O was also detected. Most of the carbon content of the feed emerges as carbon dioxide, with a small amount appearing as TIC and TOC in the liquid effluent (less than 3.4%). Most of the nitrogen was converted to molecular nitrogen leaving the resultant liquid effluent at pH 6.51 and with only traces of nitrate and nitrite.

SCALE-UP ESTIMATES

The modified reactor configuration developed for this work can be scaled up to pilot plant size by extrapolation from a study done for the U. S. Army Armament Research, Development & Engineering Center (ARDEC) for a 1000 gallon per day reactor operating at 5 wt.% organic loading [9]. Some assumptions, given in Table VI, are necessary for a meaningful assessment of utility and capital equipment cost.

Approximately 400 lbs of explosive can be destroyed per day with a flow rate of 1000 gallons per day at 5 wt.% loading. Daily throughput and waste loading values are a reasonable extrapolation from bench scale size and data. The 50 gallons per hr flow rate and 1000 gallons per day throughput assume 20 hours per day of operation. More research is needed to specify residence time and excess oxygen capacity accurately. These parameters originate from requirements on allowable fluid discharge and treatment options which depend on reactor siting and local regulations. For calculation purposes, a residence time of 15 seconds at 550°C with 100% excess oxidant is specified. Sample #21 analysis indicates that these conditions will provide a DRE of greater than 99.1%.

Table VI

Parameters Used in Cost Analysis

Description	Parameter
Daily throughput	1000 gallons
Waste loading	5 wt. %
Flow rate	50 gallons/hr
System pressure	4000 psi
Residence time	15 seconds at 550°C
Heated components	inconel 625
Excess oxygen capacity	100%

A major component, control schematic, for the pilot scale reactor is shown in Figure 5. It consists of a feed preparation subsystem, oxidant addition subsystem, high-pressure pumping subsystem, reactor/heater subsystem, high-pressure gas/liquid/letdown subsystem, and effluent collection, purification, and recirculation subsystem. For the pilot plant, the explosive is heated and allowed to oxidize to equilibrium before additional oxidant injection to reduce corrosion.

Plant Operation

Based on an economic trade-off analysis, air is the preferred oxidant [9]. Oxygen or peroxide may alternatively be used. Peroxide is significantly more expensive than either oxygen or air. Air is more capital intensive than oxygen but the up front cost is negated over time by the operational raw material cost of oxygen. It is, however, more hazardous to operate a high pressure system with oxygen. Weighing these trade-offs, air is used as the oxidant for a capital equipment cost estimate.

To begin operation, air is compressed and metered into the reactor and separator to the desired system pressure. After system pressure is established, air flow rate is set, and system pressure is maintained by the combination of the pressure transducer and valve attached to the gas effluent line of the separator.

Deionized water is then pumped by a positive displacement high-pressure pump into the reactor at the desired flow rate. This will cause the control system to make adjustments in the letdown valve systems. Feedback between the flow monitor and control valve on the compressor line are used to adjust air flow rate.

The temperature profile in the reactor is then established by radiatively or resistively heating the inconel tubing while flowing distilled water and air. After the desired temperature profile is established with pure water and air, diluted explosive is directed to the first reactor section (top reactor section) where it is heated to 550°C before it arrives at the air injection point. The fluid mixture is allowed to react for a further 15 seconds after air injection.

The effluent is brought to ambient temperature by chilled water in the heat exchanger before the gravity separator. Liquid, gas, and any residual solids that migrate through the reactor sections are separated by gravity in the final subsystem. The primary effluents from the system are water and non-polluting gas, but provision is made to analyze the liquid and gaseous effluent. The effluent may contain ppm quantities of chromium and nickel. These should not be reintroduced into the reactor. The liquid effluent is treated using a reverse osmosis effluent treatment system.

Capital and Utility Cost

A materials list with associated cost by subsystem is included as Table VII. The cost was calculated by requesting quotations from vendors based on preliminary design and specification, and then increased by 20%. Approximately 39% of the cost is due to the reactor. Approximately 47% of the cost of the liquid/gas/solid separation and letdown system is due to the analyzers. Provision in capital cost is made for both an on-line gas chromatograph and an on-line TOC analyzer.

Figure 5. Reactor schematic.

Table VII
Cost Estimate Breakdown

<i>Mix & feed subsystem</i>	<i>Cost (\$)</i>
Low pressure pumps	5600
High pressure pumps	22500
Stroke control	3600
Pulsation damper	3600
Tanks	9600
Screw feed	6000
Mixers	4000
Valves/rupture disks	11400
Transducers/indicators	17200
<u>Tubing/fittings</u>	<u>7000</u>
Total	90500
 <i>Air compressor subsystem</i>	 <i>Cost (\$)</i>
Air compressor	10000
Pressure tank	14500
Valves/rupture disks	4500
Transducers/indicators	3900
<u>Tubing/fittings</u>	<u>2600</u>
Total	35500
 <i>Reactor/heater subsystem</i>	 <i>Cost (\$)</i>
Reactor with heater	180000
Valving/regulators/rupture disks	27500
Filters/transducers/indicators	16700
<u>Tubing/fittings</u>	<u>13000</u>
Total	237200
 <i>Liquid/gas/solid separation subsystem</i>	 <i>Cost (\$)</i>
Heat Exchanger/recirculation line	38400
Vessels	48600
Recirculation pump	1800
Valves/regulators/rupture disks	23900
Filters	1000
TOC analyzer	48000
Gas analyzer	60000
Transducers/indicators	5000
<u>Tubing/fittings</u>	<u>4800</u>
Total	231500
 <i>Miscellaneous equipment</i>	 20000
Grand Total (rounded)	615000

Included as miscellaneous equipment is a house air system (to drive valves), and a chiller to recirculate the coolant. Not included is the cost of the water purifier should it be required.

Oxidant requirements are small, minimizing capital equipment costs and the intensifying (pressurization) costs of air. An estimate of operational cost is obtained by noting that 1000 gallons of water must be raised from ambient conditions (20°C, 1 atm) to supercritical conditions (550°C, ~270 atm). The energy needed is approximately 3350 kw-hr. A reasonable cost for electricity at a government installation is about \$0.04/kw-hr giving a daily operational cost of \$134/day.

Heat transfer losses are small for a well insulated system and compensated by the heat of combustion released by the explosive. The operational cost can be reduced by recovering energy from the treated fluid stream; sensible heat of the treated fluid stream may be used to preheat the feed stream before introduction into the reactor. However, this increases the complexity in system design and introduces the risk of fouling the heat transfer surfaces of another exchanger. It may be possible to reduce the cost further by balancing the heat released from the oxidation of the explosive with the energy needed to raise the feed to supercritical conditions.

Control

All pressure transducers, thermocouples, flow monitors, TOC equipment, gas monitoring equipment, and liquid levels, are monitored by computer for data acquisition and control. Remote control is exercised by electric, pneumatic, or electropneumatic means, as appropriate. Pressure transducers and thermocouples can be located throughout the system for both monitoring and control. Due to the heat of oxidation, external electrical power to the reactor heaters can be reduced by local temperature controllers based on local temperature measurements rather than only with foreknowledge of the feed composition.

Initially, pure water is flowing into the reactor during start-up. After start-up, control is automatic. Air is metered into the reactor with local feedback or local control (LC), and continuously adjusted based on on-line measurement of TOC and oxygen concentration in the effluent. On-line corrosion measurements may also be used for control as well as monitoring. Feed flow rate is determined by the speed of the high-pressure pump motor, which is adjusted electrically through a servo-mechanism and computer interface, similar to the EER. All flow control valves are adjusted electrically or pneumatically, and interfaced to an appropriate flow meter or pressure transducer. Compensation for variations in flow rate occurs automatically.

Trace unreacted organic remains in the effluent holding tank. Water is produced as an end product and will need to be discharged from the system. However, this is a small percentage of the total throughput; the bulk of the water is recirculated. Water is analyzed before discharge from the system.

Tanks are sized to permit a day's operation without recirculation or disposal of the liquid effluent. A 500-gallon mixing tank is assumed; two batches of explosive must be mixed per day to meet the 1000 gpd flow rate. This preparation scheme was assumed for cost analysis only. A final preparation scheme is a system and interface issue with base personnel. For example, perhaps a continuous mixing scheme would be preferred.

System pressure is maintained at the separator by the free surface in the separator (gas bubble). A servo-controlled flow control valve and pressure transducer maintain target pressure. A letdown valve (LDV) controls liquid level in the separator metering effluent into the dissolved gas separation tank and into the effluent holding tank. Reaction temperature is controlled locally by temperature controllers interfaced to thermocouples placed in the reacting medium as appropriate.

Safety

During normal operation, all solenoid valves are actuated at the control console; all air-operated valve/solenoid valve combinations have a logic structure so they are normally closed except for emergency depressurization valves connected to an emergency vent vessel (not shown), which have a normally open logic structure. In an accident scenario, power is interrupted to the control console(s), initiating the following automatic and simultaneous actions: 1) the power is shut to the heaters, 2) the high-pressure pump(s) are turned off, 3) water, waste, and air flow rates are interrupted, and 4) depressurization lines are opened. Loss of electrical power or house air also depressurizes the system due to this logic structure. The system will be mechanically-safed from overpressurization by relief devices. The equipment reflecting these features, but not redundant equipment, for example, a back-up compressor, is included in the cost estimate.

To summarize, abnormal conditions that would initiate the emergency shut-down are: 1) loss of electrical power, 2) loss of pneumatic power, 3) overpressurization and, 4) increase in temperature beyond material specification.

SUMMARY AND CONCLUSIONS

Ammonium picrate can be destroyed using supercritical water oxidation. With the proper design of a reactor system, this destruction can be achieved without producing unacceptable byproducts of oxidation or corrosion.

Explosive D was oxidized in a SCWO environment using two different methods. In the conventional method, the explosive and oxidant are pressurized, mixed, heated to supercritical conditions, and allowed to react at an elevated temperature. In the modified method, the explosive is heated above 450°C and allowed to react before additional oxidant is injected into the waste stream at a temperature above 425°C.

If the oxidant and explosive are mixed before heating, the effluent contains nitric acid liberated as the carbon in the ammonium picrate reacts with the added oxidant. When the explosive is heated to reaction temperature before oxidant injection, the nitro groups on the ammonium picrate are consumed as they oxidize the carbon in the compound. Reduction of acid in the supercritical water stream minimizes the amount of nickel removed from the reactor alloy material.

Nitrogen oxides are normally seen in the effluent when explosives are processed using SCWO. No criteria pollutants were produced from the modified reactor configuration. Gases analyzed were: NO, NO₂, N₂O, N₂, CO, CO₂, H₂O, and O₂. Only N₂O (nitrous oxide), a nontoxic unregulated gas, and components of air (CO₂, H₂O, O₂, N₂, and Ar) were detected.

At 560°C with an excess oxidant concentration of 72%, the explosive and partial oxidation products were destroyed to a minimum of 99.1% DRE in 8.7 seconds with the modified reactor configuration.

An estimate of capital equipment cost, engineering design configuration, and operational cost, for a 1000 gpd prototype unit was provided. The capital equipment cost is about \$615k with utility costs of about \$134 per day. A detailed engineering and construction cost estimate is beyond the scope of this report, however, experience and cost surveys indicate that capital equipment cost is only one-half to one-third of total construction cost.

The experimental results provide a guide to the design of SCWO equipment by indicating trends in the trade-offs between destruction efficiency, residence time, reaction temperature, and reactor configuration.

To reduce the risk of scaling to a pilot plant size the following work is recommended:

- 1) Explosive D should be destroyed at increased concentrations of 5 wt.%.
- 2) A specific site for a reactor should be determined. Discharge requirements can then be determined with the appropriate regulatory agencies. From discharge requirements, performance requirements can be generated. Tests can then be performed to destroy the explosive meeting these performance requirements. The residence time before and after oxidant injection must be determined through experiment and modeling to meet the performance requirements.
- 3) The bench-scale SCWO reactor should be run for several days simulating a production run. Issues of operational reliability, such as slow fouling of the heat transfer surface, can then be addressed.

REFERENCES

- [1] Alternative Technologies for the Destruction of Chemical Agents and Munitions, National Academy Press, Washington, D. C., 1993.
- [2] DOE Explosive Safety Manual, U. S. Dept. of Energy, DOE/EVO6194.
- [3] D. M. Harradine, S. J. Buelow, P. C. Dell'Orco, R. B. Dyer, B. R. Foy, J. M. Robinson, J. A. Sanchez, and T. Spontarelli, "Oxidation Chemistry of Energetic Materials in Supercritical Water," *Hazardous Waste & Hazardous Materials*, Vol. 10, Number 2, 1993.
- [4] T. T. Bramlette, B. E. Mills, K. R. Hencken, M. E. Brynildson, S. C. Johnston, J. M. Hruby, H. C. Feemster, B. C. Odegard, and M. Modell, "Destruction of DOE/DP Surrogate Wastes with Supercritical Water Oxidation Technology," SAND90-8229, Nov., 1990.
- [5] S. F. Rice, R. R. Steeper, and C. A. LaJeunesse, "Destruction of Representative Navy Wastes Using Supercritical Water Oxidation," SAND94-8203, Oct., 1993.
- [6] S. F. Rice, C. A. LaJeunesse, R. G. Hanush, J. D. Aiken, S. C. Johnston, "Supercritical Water Oxidation of Colored Smokes, Dyes, and Pyrotechnic Compositions," SAND94-8209, January, 1994.
- [7] C. A. LaJeunesse, S. F. Rice, J. J. Bartel, M. Kelley, C. A. Seibel, L. G. Hoffa, T. F. Eklund, and B. C. Odegard, "A Supercritical Water Oxidation Reactor: The Material Evaluations Reactor (MER)," AIChE Spring National Meeting, New Orleans, La., March, 1992.
- [8] C. A. LaJeunesse and S. F. Rice, "Corrosion and Salt Deposition Issues in a Supercritical Water Oxidation Reactor," First International Conference on Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, Canada, June, 1994.
- [9] C. A. LaJeunesse, J. P. Chan, T. N. Raber, D. C. Macmillan, S. F. Rice, and K. L. Tschritter, "Supercritical Water Oxidation of Colored Smokes, Dyes, and Pyrotechnic Compositions, Final Report: Pilot Plant Conceptual Design," SAND94-8202, Nov., 1993.

UNLIMITED RELEASE
INITIAL DISTRIBUTION

Office of Technology Development
U.S. Dept. of Energy
Attn: Jaffer Mohiddin, EM 552
Trevion II
12800 Middlebrook Rd.
Germantwon, MD 20874

Office of Technology Development
U.S. Dept. of Energy
Attn: K. Hain, EM 50
Trevion II
12800 Middlebrook Rd.
Germantwon, MD 20874

Keith Sims (10)
Ordnance Engineering
Naval Surface Warfare Center
Crane, IN 47522

Mr. Dan Burch
Ordnance Engineering
Sea Department, Code 4022
Naval Surface Warfare Center
Crane, Indiana 47522

James Q. Wheeler
Chief, Demil Technology Office
U.S. Army Defense Ammunition Center
and School
Attn: SMCAC-TD
Savanna, IL 61074-9639

Crane Robinson (10)
U.S. Army Armament Research
and Development & Engineering Center
SMCAR-AES-P, Bldg 321
Picatinny Arsenal, NJ 07806-5000

Curtis Anderson
U.S. Army Armament Research
and Development & Engineering Center
SMCAR-AES-P, Bldg 321
Picatinny Arsenal, NJ 07806-5000

MS0726 J. B. Woodard, 6600
MS9001 J. C. Crawford, 8000
Attn: D.L. Crawford, 8900
E.E. Ives, 5200
M.E. John, 8100
L. A. West, 8600
R.C. Wayne, 8700

MS9213 S.C. Johnston, 8103
MS9053 T. Bramlette, 8106
MS9103 K. Wally, 8111
MS9031 N. French, 8113
MS9031 J. Swearengen, 8113
MS9410 K.L. Tschritter, 8113
MS9054 W.J. McLean, 8300
MS9056 G. Fisk, 8355
MS9052 D.R. Hardesty, 8361
MS9052 S. Rice, 8361
MS9052 R. Steeper, 8361
MS9053 R. W. Carling, 8362
MS9053 C. Hartwig, 8366
MS9105 L.A. Hiles, 8400
MS9101 W.C. Peila, 8411
MS9406 J. P. Chan, 8412
MS9406 H. Hirano, 8412
MS9406 C. LaJeunesse, 8412 (25)
MS9406 M.C. Stoddard, 8412 (25)
MS9407 B.G. Brown, 8414
MS9101 J.P. Damico, 8313
MS9407 E.T. Cull, 8415
MS9404 B.E. Mills, 8713 (25)
MS9404 V. Odegard, 8714
MS9404 J. Wang, 8713
MS0860 W.K. Tucker, 9122
MS9022 Mail Distribution Team,
8533-1, for OSTI (10)
MS9022 Mail Distribution Team,
8533-1/Technical Library,
MS0899, 13414
MS0899 Technical Library, 13414, (4)
MS9018 Central Technical Files,
8523-2, (3)