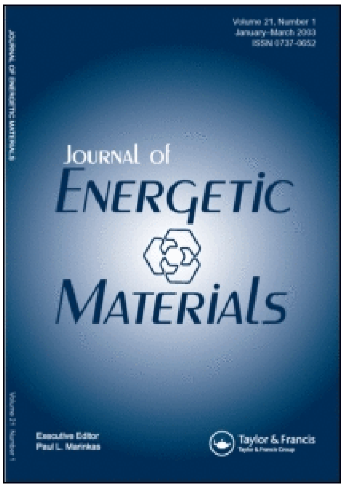

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Supercritical water oxidation of chemical agents, and solid propellants

M. H. Spritzer[a]; D. A. Hazlebeck[a]; K. W. Downey[a]
[a] 3550 General Atomics Ct., San Diego, California

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SUPERCRITICAL WATER OXIDATION OF CHEMICAL AGENTS, AND SOLID PROPELLANTS

M. H. Spritzer, D. A. Hazlebeck, and K. W. Downey; 3550 General Atomics Ct.,
San Diego, California 92121-1194

ABSTRACT

Supercritical water oxidation (SCWO), also referred to as hydrothermal oxidation (HTO), is a developing technology for the destruction of hazardous and nonhazardous wastes. SCWO destroys combustible materials using an oxidant in water at temperatures in the range of 350°C (662°F) to 600°C (1112°F) and pressures of 17 MPa (2500 psi) or greater. General Atomics and its subcontractors are currently conducting two comprehensive research and demonstration programs geared toward the destruction of Department of Defense (DoD) wastes utilizing SCWO technology. Wastes of primary interest include chemical agents and solid propellants. Technical challenges, particularly corrosion and solids handling, were overcome, and the destruction of chemical agents and solid propellants was demonstrated on a bench scale. SCWO results for chemical agents show destruction and removal efficiencies for GB, VX, and mustard agents to be in excess of 99.9999%, limited only by detection capability. SCWO results for hydrolyzed Class 1.1 solid propellant show destruction and removal efficiencies for total organic carbon (TOC) of >99.9%.

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Design and fabrication of a transportable SCWO pilot plant for chemical warfare agents, propellants and other DoD hazardous wastes and a prototype HTO system for solid rocket propellant disposal are complete and demonstration testing is underway.

INTRODUCTION

Supercritical water oxidation (SCWO), also referred to as hydrothermal oxidation (HTO), is a developing technology for the destruction of hazardous and nonhazardous wastes. Relative to standard incineration technologies, it offers the advantages of lower temperature oxidation, enhanced process stability, negligible NO_X and SO_X production, negligible air-borne particulates, and complete containment of all effluents[1]. SCWO destroys combustible materials using an oxidant in water at temperatures in the range of 350°C (662°F) to 600°C (1112°F) and pressures of 17 MPa (2500 psi) or greater. Figure 1 illustrates a simplified SCWO block flow diagram. Oxidation is often accomplished under near-homogenous, single-phase conditions which provide excellent mixing and high mass and heat transfer rates. High destruction efficiencies are achieved in relatively small reactor volumes. Typical products from a SCWO process include carbon dioxide, water, nitrogen, metal oxides, and inorganic salts. The oxidation process is performed in a completely enclosed system, permitting containment of toxic and hazardous feed materials, and holdup and analysis of SCWO products prior to controlled discharge to the environment.

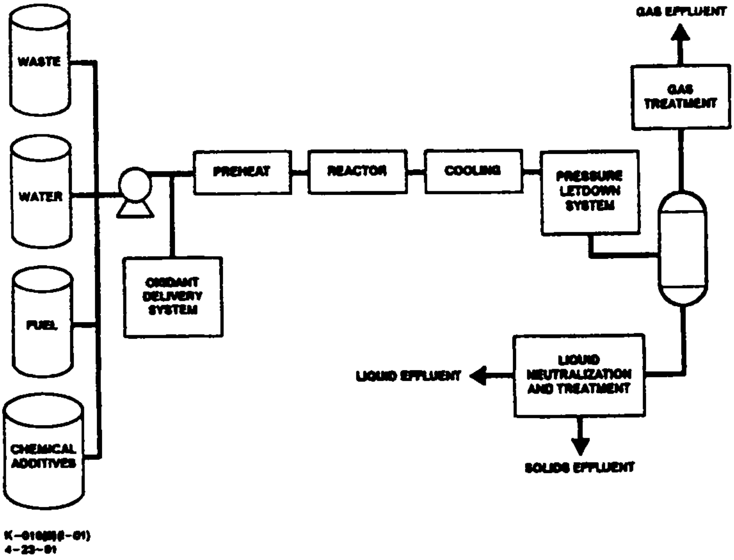

Figure 1. Simplified SCWO block flow diagram

General Atomics (GA) and its subcontractors are currently conducting two comprehensive research and demonstration programs geared toward the destruction of Department of Defense (DoD) hazardous wastes. The first program, performed for the Advanced Research Projects Agency (ARPA), involves the destruction of chemical agents, solid propellants, and other DoD hazardous wastes. The second program, performed for the U.S. Air Force, involves the destruction of Hazard Class 1.1 solid propellant removed from rocket motor casings.

Both the ARPA and Air Force programs required significant research efforts to provide sufficient data for pilot plant design. Numerous research areas were investigated, including corrosion[2-5], kinetics[4-10], hydrolysis[10-12], catalysis[9,11,13,14], solids handling[15,16], and chemical agent and solid propellant destruction verification/tests[2-5,10,11]. Only the chemical agent and solid propellant destruction data, generated under the two programs, are discussed herein.

SCWO OF CHEMICAL AGENTS

The primary focus of the ARPA SCWO program, from both a research and design standpoint, was the processing of the nerve agents GB and VX, and the blister agent mustard. To ensure a comprehensive, workable pilot plant design, it was imperative that laboratory-scale SCWO testing of actual chemical agents be conducted. (None had been performed prior to this program.) Chemical agent testing was performed at the facilities of IIT Research Institute (IITRI), a facility approved by the U.S. Army for the handling of chemical surety materials. Testing was performed in three discreet phases for GB, VX and mustard to provide sufficient time for changeover of equipment and agent monitors, validation of analytical techniques[17-19], and agent deliveries from the Army.

Agent testing was performed in a bench-scale test rig specifically designed for testing at IITRI. The rig was made as compact as possible to allow insertion into an IITRI test hood. The hood provided a ventilated, protected workspace for agent testing. Figure 2 shows a photograph of the rig inserted in the IITRI agent test hood. The major features of the test rig included: storage

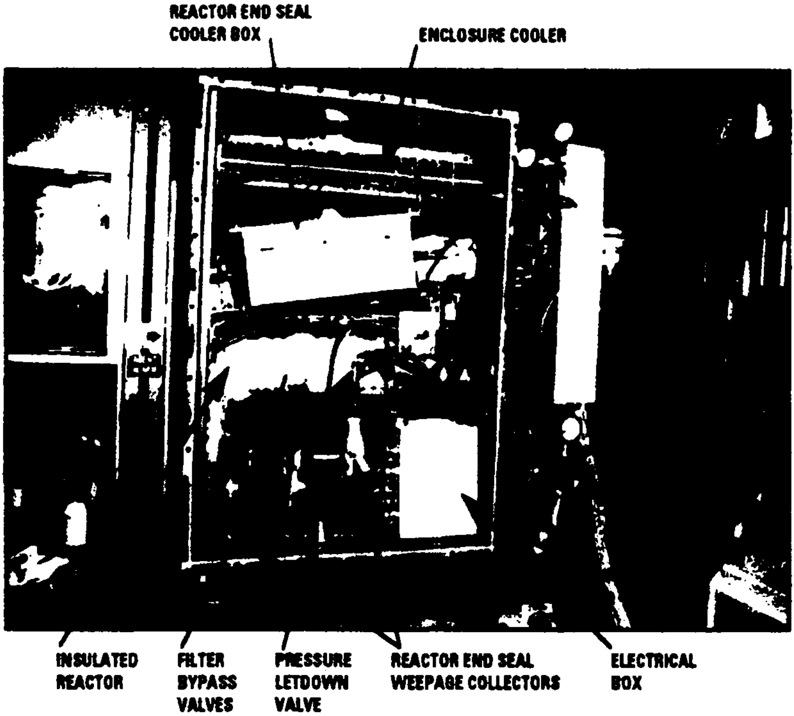

Figure 2 SCWO test rig for chemical agents

reservoirs for oxidant (H_2O_2) and water mixtures, a high pressure pump, an 8.5-ft long, 3/4" O.D., heated reactor lined with either platinum (for GB and VX testing) or titanium (for mustard testing), slip-on heaters in two independently controlled temperature zones, cooled reactor end fittings with O-ring seals, pressure monitors at both ends of the reactor, numerous external thermocouples positioned axially along the entire reactor length, a pressure letdown valve to control the system operating pressure, liquid effluent collectors, a sealable, reinforced stainless steel enclosure capable of containing a worst-case system depressurization, and a data acquisition and control system.

Corrosion testing identified platinum as the optimum material of construction for SCWO processing of GB and VX agents[4,5]. A platinum-lined Hastelloy C276 reactor was therefore used for the GB and VX test series. For processing of mustard agent, titanium was identified as the best material of construction, again as a thin liner within a Hastelloy C276 pressure bearing wall[4,5].

Prior to the start of agent testing, a test program was completed using chemical agent simulants in order to verify SCWO test rig capabilities. Tests were performed at temperatures of 450 to 550°C and flow rates of up to 100 ml/min. All tests were performed at a pressure of approximately 4000 psi. Agent simulants used were diethylmethylphosphonate (DEMP, GB and VX simulant), diisopropylethylamine (DIEA, VX simulant), and thiodiglycol (TDG, mustard simulant). Target simulant feed concentrations were 1 wt%.

GB Agent Testing.

Following successful completion of the Preoperational Test for agent operations, an Army requirement, and the receipt of final Army approvals, GB agent testing commenced on May 10, 1993. All tests were performed at GB concentrations of approximately 1 wt% with 100% excess oxygen. Table 1 presents the GB test matrix .

TABLE 1. GB AGENT TEST MATRIX

Test No.	Pressure (psig)	Temperature (°C)	Total Flow Rate (ml/min)	Residence Time (sec)	Test Duration (min)
1	4000	550	50.5	16	42
2	4000	450	39.4	29	15
3	4000	550	50.5	16	54
4	4000	450	43.4	26	71
5	4000	500	46.4	20	58

Gas and liquid samples were collected and analyzed throughout the test series. No agent was detected in any liquid samples, signifying a Destruction and Removal Efficiency (DRE) in excess of 99.99999%. [Higher DREs may have been achieved, but a DRE of 99.99999% is the maximum that can be measured given an influent agent concentration of 10,000 ppm (1 wt%) and the ~1 ppb detection limit for GB in liquid samples.] Additionally, no agent above the allowable exposure limit (AEL) was found in the gaseous effluent samples as analyzed on-line by a Minicams analyzer.

After the gaseous and liquid effluent samples were confirmed to be agent free, they were shipped to the Institute of Gas Technology (IGT) and the University of Texas Balcones Research Center (UTBRC), respectively, for further analysis. Gas samples were found to contain oxygen, nitrogen, argon, carbon dioxide, and trace amounts of methane. Liquid samples showed essentially quantitative conversion of the GB agent to complete oxidation products, i.e., HF and H_3PO_4. Small amounts (<400 ppm) of methyl phosphonic acid and acetone were detected in the 450°C samples, with significantly less detected in the 500 and 550°C samples. Table 2 shows the analytical results for the GB test series.

TABLE 2. ANALYTICAL RESULTS FOR GB AGENT TESTING[20,21]

			Reaction Temperature		
	Component	Unit of Measure	450°C	500°C	550°C
Liquid Analysis	Fluoride	ppm	1431	1719	1216
	Phosphate	ppm	6524	7785	5683
	MPA	ppm	122	83	48
	Acetone	ppm	385	106	<2
Gaseous Analysis	CO	vppm	BDL[22]	BDL	BDL
	H_2	vppm	BDL	BDL	BDL
	Methane	vppm		300	100

VX Agent Testing.

VX agent testing commenced on June 29, 1993. Six separate tests were performed, investigating temperatures of 450 to 550°C (see Table 3). As with the GB test series, all tests were performed at agent concentrations of approximately 1 wt% with 100% excess oxygen. Typically, four liquid and two gas samples were taken for each test. Additionally, 4-5 Minicams analyses of the gaseous effluent were performed during the course of testing. No agent was detected in any liquid samples, signifying a DRE in excess of 99.99999%. [Higher DREs may have been achieved, but a DRE of 99.99999% is the maximum that can be measured given an influent agent concentration of 10,000 ppm (1 wt%) and the ~1 ppb detection limit for VX in liquid samples.] No agent above the AEL for VX was detected during on-line Minicams analysis of the SCWO gaseous effluent.

TABLE 3. VX AGENT TEST MATRIX

Test No.	Pressure (psig)	Temperature (°C)	Total Flow Rate (ml/min)	Residence Time (sec)	Test Duration (min)
1	4000	500	50.5	18	68
2	4000	450	39.4	29	45
3	4000	500	50.5	18	93
4	4000	550	49.5	16	44
5	4000	450	39.4	29	56
6	4000	550	50.5	16	48

Gas and liquid samples were sent to IGT and UTBRC, respectively, for further analysis following verification by IITRI personnel of the absence of detectable agent. The VX agent was essentially quantitatively converted during testing to sulfuric and phosphoric acid. Small quantities of transformation products such as acetic acid and acetone were observed. Gas analyses showed the presence of N_2O and very low concentrations of NO_x and SO_x. The results of gas and liquid analyses are summarized in Table 4.

TABLE 4. ANALYTICAL RESULTS FOR VX AGENT TESTING[20,21]

	Component	Unit of Measure	Reaction Temperature 450°C	500°C	550°C
Liquid Analysis	Acetate	ppm	83	446	160
	Phosphate	ppm	3507	3069	3862
	Sulfate	ppm	3474	3013	3812
	Acetone	ppm	22	3	7
	Ammonia	ppm	0	8	0
Gaseous Analysis	CO	vppm	BDL[22]	BDL	BDL
	H_2	vppm	BDL	BDL	BDL
	N_2O	vppm	3000	3500	3700
	NO_X	vppm	<2	<3	4
	SO_X	vppm	4	<4	2

Mustard Agent Testing.

Unlike GB and VX, mustard agent has a low solubility in water. GB and VX agents were mixed with the water/oxidizer solution in line just upstream of the reactor. They readily went into solution to yield a uniform, miscible solution. Because of its low solubility, mustard agent would yield a two-phase mixture upon feed to the SCWO reactor if fed in the same manner as the VX and GB agents. The two phase mixture could present operational and performance difficulties in the compact test rig. Therefore, steps were taken to solubilize the mustard agent by hydrolyzing in hot water, thereby producing a safe, uniform feed for SCWO testing. A small test sample (2 g) was mixed with water in a 10 wt % solution and heated. The mixture initially showed distinct water and mustard agent phases, but after heating to 80-90°C for 7 minutes, it showed a single, clear, uniform phase. A hydrolysis apparatus was assembled to allow controlled hydrolysis of larger samples[10]. The results of hydrolysis testing showed that mustard agent hydrolysis in water can be completed within approximately five minutes at 80 to 100°C, if suitably agitated. Hydrolysis at 60°C requires approximately 4 times longer. Following hydrolysis, the solution was cooled and stored for later SCWO use.

Mustard agent testing began on April 5, 1994. Five separate tests were performed, investigating temperatures of 450 to 550°C (see Table 5). As with the prior agent testing, all tests were performed at agent concentrations of approximately 1 wt% with 100% excess oxygen. Typically, four liquid and two

TABLE 5. MUSTARD AGENT TEST MATRIX

Test No.	Pressure (psig)	Temperature (°C)	Total Flow Rate (ml/min)	Residence Time (sec)	Test Duration (min)
1	4000	450	33.3	34	55
2	4000	450	31.3	37	55
3	4000	550	aborted	aborted	aborted
4	4000	500-525	30	34	92
5	4000	500	32.5	28	47
6	4000	500	31.5	29	47

gas samples were taken for each test. Additionally, multiple Minicams analyses of the gaseous effluent were performed during the course of testing.

No agent was detected in any liquid samples, signifying a DRE in excess of 99.9999%. [Higher DREs may have been achieved, but a DRE of 99.9999% is the maximum that can be measured given an influent agent concentration of 10,000 ppm (1 wt%) and the ~10 ppb detection limit for mustard agent in liquid samples.] Also, except for Run 3 & 4, where a system upset resulted in agent contamination of the effluent collection lines, no readings above the mustard agent AEL of 0.003 mg/m^3 were detected. (During Run 3, an equipment malfunction necessitated test termination. Residual feed material was flushed at reduced pressure and temperature through the reactor into the effluent collection lines, thus contaminating them. This was not discovered until after the start of Run 4.)

Gas and liquid samples were sent to IGT and UTBRC for further analysis. The results are listed below in Table 6. The data for runs performed at the same

TABLE 6. ANALYTICAL RESULTS FOR MUSTARD AGENT TESTING[21,23,24]

	Component	Unit of Measure	Reaction Temperature 450°C	500°C	525°C
Liquid Analysis	Acetate	ppm	597	47	<1
	Formate	ppm	211	16	<1
	Sulfate	ppm	6008	5336	3105
Gaseous Analysis	CO	mole%	14.5	1.4	0.17
	H_2	vppm	3000	BDL[22]	BDL
	C_2H_4	vppm	700	BDL	BDL
	SO_X	vppm	2133	1098	2600

temperature have been combined and averaged. Low levels (≤600 ppm) of the intermediate transformation products acetic and formic acids were observed at 450°C, with less observed at 500°C, and none observed at ~525°C. Relatively high concentrations of CO were observed at lower temperatures, decreasing to less than 2000 ppm at 525°C. Higher operating temperatures will even further reduce observed CO levels.

SO_x levels of 1000 to 2600 ppm were observed during testing. A major factor contributing to these relatively high levels is thought to be poor mixing/mass transport limitations caused by the low flow rates and short lengths of the test system. Even so, the sulfur present in the observed SO_x represented only about 2% of the available sulfur, the remaining having been fully converted to sulfate. The pilot plant reactor, designed to provide much better mixing and more flexibility in operational capabilities, should yield significantly lower SO_x levels.

SCWO OF SOLID PROPELLANT

The Air Force is developing an end-to-end process for demilitarizing Class 1.1 solid rocket propellant: cryogenic washout to remove and size reduce the propellant, base hydrolysis to inert the propellant, and SCWO to destroy the hydrolysis products in an environmentally sound manner.

The development work is focused on the Minuteman II Stage III motor containing CYH and DDP composite modified double base (CMDB) propellants. CYH contains nitroglycerin (NG), nitrocellulose (NC), and HMX explosive, as well as ammonium perchlorate (AP), and aluminum metal. The composition of CYH propellant is given in Table 7. DDP is similar except it does not contain HMX.

TABLE 7. COMPOSITION OF CYH PROPELLANT[12]

Constituent	Weight (%)
Nitroglycerin	29.6
2-Nitrodiphenylamine	1.0
Nitrocellulose	21.6
Cyclotetramethylenetetranitramine (HMX)	10.8
Aluminum	19.8
Ammonium Perchlorate (AP)	10.8
Resorcinol	1.1
Triacetin	5.3

Pretreatment is often useful to condition the feed prior to its introduction to the SCWO system. Hydrolysis is an attractive pretreatment process for solid propellant because it enhances the safety of the downstream processes by eliminating the explosion hazard.

Extensive laboratory and bench-scale hydrolysis test were performed at Thiokol using aqueous sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), and concentrated aqueous nitric acid (HNO_3)[12]. Tests were performed to (1) determine the hydrolysis rate with each reactant versus temperature, (2) determine propellant particle size and concentration effects, (3) determine heat of hydrolysis, (4) establish important scale-up factors, and (5) characterize process safety. Three series of tests were performed. The original set of experiments were done on a small scale (0.030 to 10 grams of propellant) with laboratory glassware. Later experiments involved the hydrolysis of larger amounts of propellant (200 grams), again using laboratory glassware. The last set of experiments were accomplished with a small-scale glass reactor (4 liters) with up to 900 grams of propellant per run. A significant amount of literature review and chemical reaction analysis were also performed.

The general results from the hydrolysis experiments were:

- All three reagents can effectively hydrolyze NG and NC.
- HMX can be hydrolyzed by NaOH and HN_4OH, but not by HNO_3.
- For NaOH, hydrolysis can be violently exothermic (Al-water reaction), and control of NaOH concentration is vital. A solid residue (hydrated Al) remains at low NaOH concentration, and HMX hydrolysis is suppressed at high NaOH concentration. Hydrolysis time ~24 hr.

- For NH_4OH, hydrolysis is not significantly exothermic (suppressed Al-water reaction), and rate is strongly dependent on temperature and NH_4OH concentration. Bubbling NH_3 gas through solution improves rate of hydrolysis. Hydrolysis time ~24 to 48 hr.

- For HNO_3, NG and NC are rapidly hydrolyzed (30 minutes), with significant heat generation and NO_X production. This process appears difficult to scale up.

- AP can be easily extracted from CYH/DDP in water, although some NG is extracted with the AP.

Additional results for NH_4OH hydrolysis were:

- NH_4OH hydrolysis tends to be the safest most controllable method, avoids salts precipitation during SCWO, and produces far less salts in the effluent than NaOH.

- HMX hydrolysis is very slow, but improves significantly when NH_3 is bubbled through solution, and with dilution following NG/NC hydrolysis.

- Hydrolysis is limited by low solubility of NH_3 at elevated temperatures and ambient pressure.

- Hydrolysis products include glycerol, ammonium acetate, ammonium formate, ammonium oxalate, ammonium nitrate, ammonium nitrite, ammonium perchlorate, and hydrated alumina (solid).

Based on these results, NH_4OH hydrolysis has been selected as the safest, most controllable, and most compatible method with SCWO. The use of ammonium hydroxide instead of sodium hydroxide or nitric acid improves the safety and control of the hydrolysis process, and avoids salts precipitation during SCWO and the creation of excess salts (in the form of sodium carbonate).

Laboratory and bench-scale SCWO test were performed using sodium hydroxide and ammonium hydroxide hydrolyzed propellant[11]. One of the bench-scale test rigs is shown in Figure 3. Table 8 shows the results for hydrolyzed propellant indicating destruction of nearly all total organic carbon (TOC) at temperatures of about 500 C (932 F) with relatively short residence times of about 10 seconds. The reaction rates were most likely accelerated by the presence of nitrates and nitrites in the feed material. In prior tests, these oxidants were found to increase the oxidation rates for many compounds. Generally, the reaction rates for NH_4OH hydrolyzed propellant were greater than for NaOH hydrolyzed propellant. For NH_4OH hydrolyzed propellant, the TOC was 99.9% (the limit of measurement accuracy) at temperatures from 450 to 476 C. In all tests, the aluminum in the hydrolyzed propellant (approximately 20 wt% of the propellant) was readily transported through the system and separated from the clean effluent solution.

Figure 3. Hazard Class 1.1 solid rocket motor propellant bench-scale HTO test rig

TABLE 8 RESULTS OF HYDROLYZED SOLID PROPELLANT HTO TESTS

Test No.	Hydrolysis Agent	Pressure [Mpa (psig)]	Temperature [C (F)]	Flow Rate [ml/s (gal/hr)]	TOC Removal (%)
1	NaOH	27.6 (4000)	498 (928)	0.58 (0.55)	99.7
2	NaOH	27.6 (4000)	472 (881)	0.58 (0.55)	98.6
3	NaOH	27.6 (4000)	450 (842)	0.58 (0.55)	90.9
4	NaOH	27.6 (4000)	449 (840)	0.58 (0.55)	95.5
5	NaOH	27.6 (4000)	418 (784)	0.58 (0.55)	87.1
6	NaOH	27.6 (4000)	418 (784)	0.58 (0.55)	86.8
7	NaOH	27.6 (4000)	395 (743)	0.58 (0.55)	74.6
8	NH40H	27.6 (4000)	476 (889)	0.58 (0.55)	>99.9
9	NH40H	27.6 (4000)	476 (889)	0.58 (0.55)	>99.9
10	NH40H	27.6 (4000)	450 (842)	0.58 (0.55)	74.5
11	NH40H	27.6 (4000)	450 (842)	0.58 (0.55)	72.8
12	NH40H	27.6 (4000)	424 (795)	0.58 (0.55)	61.0
13	NH40H	27.6 (4000)	424 (795)	0.58 (0.55)	58.3
14	NH40H	27.6 (4000)	450 (842)	0.58 (0.55)	68.7
15	NH40H	27.6 (4000)	450 (842)	0.58 (0.55)	67.3
16	NH40H	27.6 (4000)	525 (977)	0.58 (0.55)	>99.9
17	NaOH	27.6 (4000)	450 (842)	1.17 (1.11)	87.8
18	NaOH	27.6 (4000)	450 (842)	1.25 (1.19)	99.2
19	NH40H	27.6 (4000)	450 (842)	1.13 (1.08)	>99.9
20	NH40H	27.6 (4000)	550 (1022)	1.00 (0.95)	>99.9

ARPA AND AIR FORCE PILOT-SCALE SYSTEMS

The ARPA HTO pilot plant is designed to provide a transportable pilot-scale demonstration unit of HTO for extremely hazardous wastes such as chemical warfare agents, as well as solid propellants and other DoD hazardous wastes. The system is designed to provide a very flexible test bed. The maximum operating pressure and temperature are 4500 psi and 650°C. It has a nominal flow rate of 1 gallon per minute with a typical feed concentration of 5 wt% organics and up to 12 wt% inert solids.

Figure 4 is an illustration of the skids included in the ARPA transportable SCWO system. There are five skids–feed skid, mix skid, reactor skid, liquid effluent skid, and gas effluent skid. Figure 5 is a photograph of the system as currently installed at GA.

In addition, both an air compressor and a liquid oxygen system are available. The control system is configured to allow the testing of different modes of operation and control.

All of the high pressure equipment other than the oxygen supply system and the high-pressure water pump are contained on the reactor skid. There are numerous flanges in the lined system to allow installation of instruments and special test equipment. The system can be operated with or without heat recovery and with or without preheaters. The reactor skid is enclosed with

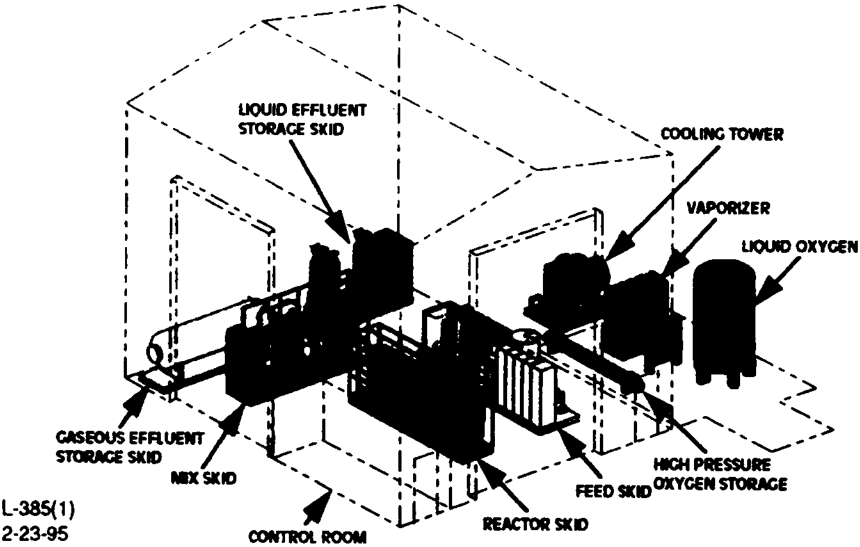

Figure 4. HTO test facility at GA

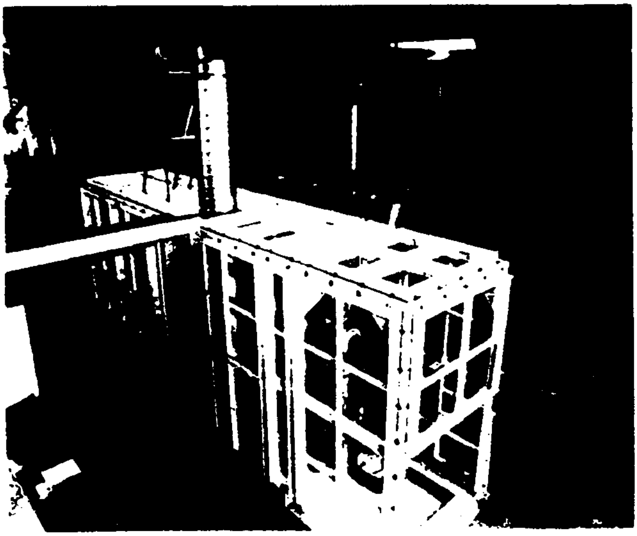

Figure 5. Picture of HTO test facility at GA

polycarbonate shielding to provide personnel protection from all high pressure components and to contain the effluent in the event of a system rupture prior to discharge to the facility ventilation system.

The transportable ARPA pilot plant is currently undergoing shakedown testing in preparation for an extensive test program to be performed at GA using waste simulants. Testing to date has been limited to ethanol in water with air as the oxidant at temperatures up to 600°C. The performance characteristics so far have been as predicted. Following the completion of the test program at GA, the pilot plant will be moved to a DoD test site for further testing using actual hazardous wastes.

For the Air Force program, the prototype hydrolysis and HTO systems are installed at a Thiokol site near Brigham City, Utah and are currently undergoing testing. Figure 6 is an illustration of the prototype hydrolysis system. Propellant hydrolysis is performed remotely once a batch of size-reduced propellant is transported from the propellant removal system. Hydrolysis is performed in the 2000-gal stainless steel transport hydrolysis container (THC) which is used to collect the propellant removed by cryogenic washout. The THC and transporter are shown in Figure 7.

The hydrolysis system utilizes hot water combined with ammonia gas to hydrolyze the granular propellant. The extent of decomposition is of secondary importance as long as the explosive constituents are inerted. The aluminum is

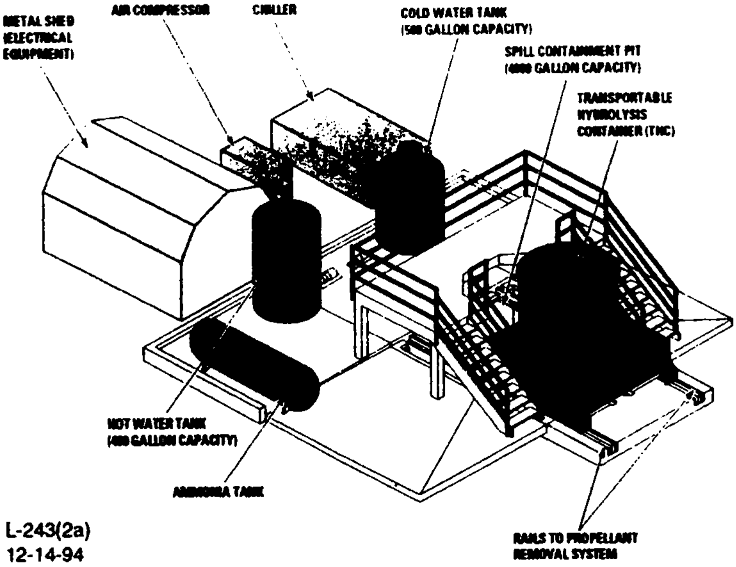

Figure 6. Hydrolysis equipment arrangement

Figure 7. Transport hydrolysis container (THC) mounted on remotely controlled transporter

slowly converted to aluminum oxide but not at fast enough rate to affect the hydrolysis solution temperature. A photograph of the hydrolysis system with THC in place is shown in Figure 8.

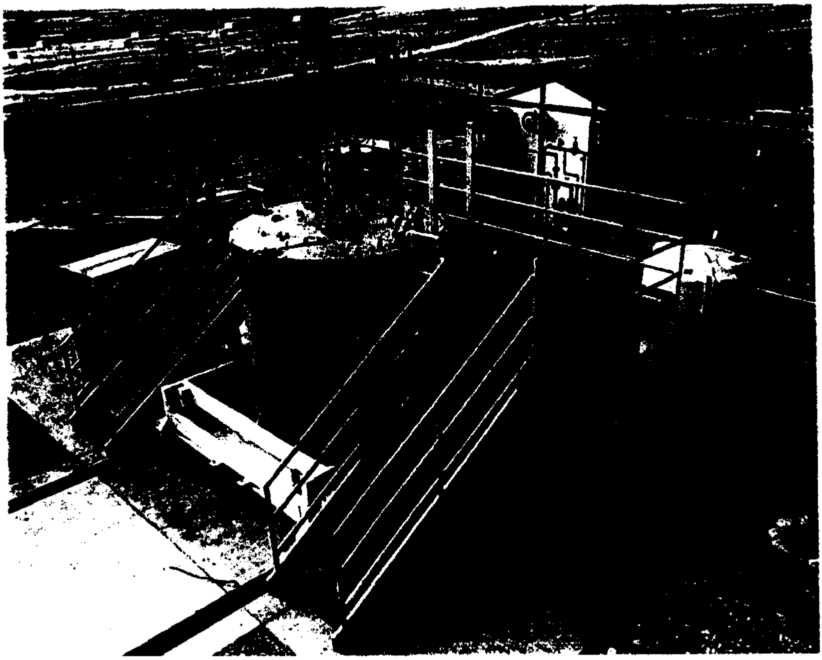

Figure 8. Hydrolysis system equipment

The Air Force prototype HTO system installed at Thiokol is currently undergoing testing with hydrolyzed CYH propellant. The system is designed to provide a very flexible test bed. The maximum operating pressure and temperature are 4500 psi and 650°C. It has a nominal flow rate of 0.42 gallons per minute with a typical feed concentration of 5 wt% organics and 3 wt% inert solids.

Fig. 9 is an illustration of the Air Force prototype SCWO system. Fig. 10 is a photograph of the prototype plant as installed in Utah. The prototype system consist of an array of water, feed storage, mix and effluent storage tanks and other auxiliary equipment surrounding the reactor skid. A vendor supplied liquid oxygen system is also provided.

All of the high pressure equipment other than those associated with the oxygen supply system are contained on the reactor skid. Like the ARPA system, there are numerous flanges in the lined piping to allow installation of instruments and special test equipment. The reactor skid is enclosed with polycarbonate shielding to provide personnel protection from all high pressure components.

A RCRA RD&D permit has been obtained for the Air Force system at Thiokol.

The Air Force Prototype HTO system was recently operated for 24 hrs continuously, during which hydrolyzed propellant was fed to the system for approximately 18 hrs. The hydrolyzed propellant feed was approximately 1 wt% (much lower than system design range due to the limited amount of propellant available at the time from the propellant removal system). The operating pressure was approximately 3900 psi. The reactor temperature was varied from 425°C to 510°C. The flow as varied from 0.27 gpm to 0.30 gpm.

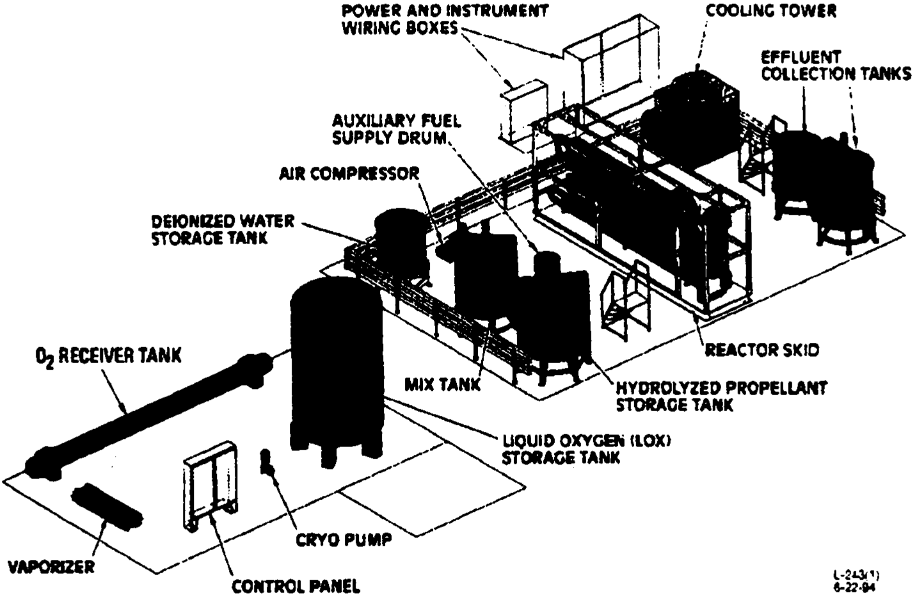

Figure 9. Layout of prototype HTO system for the U. S. Air Force

Figure 10. U. S. Air Force prototype HTO plant and liquid oxygen system

Seventeen liquid samples were taken over the test period and analyzed. The organic carbon was destroyed to below the detection limit (1 ppm) for all samples except for those taken with a reactor temperature of 425°C. This corresponds to a DRE for total organic carbon of >99.9%. At 425°C, the DRE for total organic carbon was 96%. The only constituent (other than water) in the liquid effluent was 2.2 to 2.6% ammonia. Ammonia was expected to be present in the effluent from this test because it is mineralized by utilizing higher temperatures (550-625°C) or by processing feed streams with higher concentrations of hydrolyzed propellant which have sufficient nitrites and nitrates present to react with the ammonia. The solid and gas samples from this test are currently being analyzed.

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20. DRE of >99.99999% achieved for all test samples.

21. Effluent data are averaged for multiple runs performed at the same temperature.

22. Below detection limit.

23. DRE of >99.9999% achieved for all test samples.

24. Several unknown, nonagent peaks of ~50-100 ppm each were detected.