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MASTER

DESTRUCTION OF EXPLOSIVES AND ROCKET FUELS BY SUPERCRITICAL WATER OXIDATION

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ABSTRACT

The destruction of energetic materials, including propellants, explosives and pyrotechnics (PEPs) by oxidation in supercritical water is described. The focus is on the chemistry of the process. The destruction efficiencies and products of reaction contained in the aqueous and gaseous effluents of several representative PEPs are reported.

INTRODUCTION

Traditional methods for disposing of PEPs have been open burning or open detonation (OB/OD); however, regulatory agencies are likely to prohibit OB/OD because of the uncontrolled air emissions and soil contaminations. Likewise, controlled incineration carries a liability for air pollution because large quantities of NO_x are produced in the conventional combustion chemistry of PEPs. Soil and ground water have already been contaminated with PEPs through normal operations at manufacturing plants and military bases. Incineration can be used for decontamination of these soils, with the associated liability for air pollution, but few satisfactory and economic methods exist for ground water decontamination. A clear need exists for improved disposal and destruction methods.

The principle of supercritical water oxidation (SCWO) has been successfully demonstrated. High destruction and removal efficiencies (DREs) have been reported for a broad range of common solid and liquid wastes, including difficult examples such as chlorinated aromatic solvents.[1-3] These same studies have indicated that the major reaction products were water, carbon dioxide, and inorganic salts. The general approach is to mix the waste with an oxidant (oxygen, air, or hydrogen peroxide) in water at pressures and temperatures above the critical point (374 °C and 22.13 MPa). Under these conditions, water is a fluid with densities high enough that reasonable process throughput can be achieved, but its transport properties are like those of a gas, allowing rapid chemical reaction. Supercritical water (SCW) is a unique solvent medium in which oxidation can take place at lower temperatures than incineration, thus limiting the production of NO_x and char. The reaction is entirely enclosed in a pressure vessel at concentrations low enough that the heat of reaction is absorbed by the solvent. As a result the temperature can be maintained at any desired level (typically in the range 400-650 °C). Oxidation occurs rapidly, on the time scale of seconds to minutes, and produces simple products (ideally CO_2, H_2O, and N_2).

A great range of scale appears to be possible for supercritical water oxidation plants. Standard pressure-vessel technology can be used to provide small mobile units or permanent medium-sized surface installations for processing of laboratory or manufacturing wastes. Plants with very large capacities have also been proposed, in which a cylindrical heat exchanger and reaction vessel are placed in the ground by use of oil-field drilling and well-completion technology. Operation of a SCWO unit for the treatment of explosive wastes would need to be controlled remotely. The details for full scale operation (site preparation, facility needs, utilities) will depend on the waste being treated and the particular design of the reactor (i.e., tube, vessel, in-ground, etc.). A more complete description of the operation of full-scale SCWO units, including materials throughput, mass balances, and equipment design, can be found in several reports.[4]

Compared to other available technologies, supercritical water oxidation is applicable to a broader range of waste types. It can be used to treat pure organics, contaminated soils and water, sludges, and some inorganics. At present, public concern should not delay obtaining operating permits. The complexity of the technology is comparable to incineration so that with proper engineering and process controls, qualified technicians should be able to be operate and maintain an SCWO unit.

Incineration is a non-specific alternate method for destroying organic materials. Incineration can be operated at a relatively low cost, but requirements for extensive emission controls and difficulties associated with obtaining permits can negate potential advantages. Supercritical water oxidation takes place at a much lower temperature (about 500 °C) than incineration and in a completely contained system. Almost no oxides of nitrogen are expected at these low temperatures, and the effluent is completely contained and controlled. Supercritical water oxidation can be applied to water containing 20% or less organic waste. By comparison, incineration is not as cost effective at these concentrations. Cost estimates for developing technologies, such as SCWO at full scale, are inherently uncertain and should be considered cautiously. The cost of SCWO of wastes has been estimated in several studies.[3,4] For treating a ton of dry organic material, the costs are estimated to be between $300 and $600 per ton depending on the size of the SCWO treatment unit.[4] Other methods under development that may apply to explosive wastes include oxidation by hydrogen peroxide and/or ozone with UV radiation, electrochemical oxidation, and oxidation in molten salts. In two-phase systems such as these, concentration gradients across phase boundaries and mass transfer of oxygen limit the rate and extent to which compounds can be completely destroyed. A supercritical fluid is single phase making complete mixing possible; thus, reaction rates are not diffusion limited. A preliminary cost comparison of these oxidation processes prepared by the Energy and Environmental Analysis Group at Los Alamos National Laboratory estimates the costs for the UV processes for contaminated water are 10 to 100 times less per gallon of water than for SCWO. However, these technologies are limited to low (<1000 ppm) organic concentrations. Concentrated wastes would need to be diluted. In addition, these methods usually require special pretreatment of the waste water, thereby increasing costs.

The Environmental Protection Agency (EPA) has informally stated that supercritical water oxidation is not considered to be incineration, thus it will probably be permitted under Part X. If supercritical water oxidation units become an integral part of a manufacturing process, the EPA will not consider the unit to be a treatment facility, implying that waste water and air discharge permits are sufficient. In a demonstration of SCWO technology in New York State, the MODAR corporation obtained a permit under the New York State Environmental Conservation Law, and approval from the EPA to treat polychlorinatedbiphenyls (PCBs). The waste analysis plan and trial test plan were developed to comply with the Resource Conservation and Recovery Act (RCRA) regulations. A second demonstration by MODAR at a chemical plant in Pennsylvania did not require similar permits since PCBs were not being treated and the effluent was sent to the plant's water treatment facility.

This work seeks to examine the behavior of energetic substrates, including Ammonium perchlorate (AP), Cyclotrimethylene trinitramine (RDX), Cyclotetramethylene tetranitramine (HMX), Nitroguanidine (NQ), Nitromethane (NM) Pentaerythritol tetranitrate (PETN) and 2,4,6-Trinitrotoluene (TNT) under conditions of SCWO to provide the DREs of the substrates, to determine the optimum conditions for maximizing the DREs, and to ensure safe operation. Products of destruction are identified and measured. Experimental results are evaluated to determine whether the reaction products are environmentally acceptable. Corrosion studies are underway to determine the suitability of various reactor materials. In addition, safety studies are in progress to determine the detonation sensitivity characteristics of PEPs in supercritical water systems.

EXPERIMENTAL APPROACH

This section describes the reactors used to destroy high energy materials through SCWO processes, and the analytical methods used to measure product species. The specific experimental conditions under which the destruction measurements were performed will be presented in the results and discussion section.

Bench-scale linear flow reactors have been developed to destroy explosives in supercritical water. A schematic of a linear flow reactor is shown in Figure 1. Solutions of oxidizer and/or explosive are introduced at high pressure into the reactor by constant flow, high performance liquid chromatography pumps (LDC Analytical, Constametric 3200). The explosives are typically in water at less than half their solubility limit or decomposed in water as the result of prior hydrolysis reactions. Check valves are placed in each line to prevent back streaming in case of pump failure. Fuel and oxidizer are either premixed before being pumped or are introduced separately. In either case, mixing is completed before reaching the heated section of the reactor. The central core of the reactor is heated to a controlled temperature by six heaters in parallel consisting of hollow brass tubes wrapped with MgO_2 insulated nichrome wire. The temperature is maintained by regulating the current through the heating wire with Omega CN9000 series microprocessor temperature controllers. The temperature of each of these heaters can be varied independently; however, for all experiments described in this report the temperature of each heated section was kept the same. The temperature is monitored with six K-type (chromel-nickel), sheathed thermocouples in close proximity to the reactor core. A water-cooled heat exchanger at the exit cools the reacted mixture to room temperature. The cooled effluent is passed through a 7 μm filter for removal of any particulate matter before reducing the pressure to ambient with a let-down valve. Gas and liquid effluents at ambient temperature and pressure then enter a gas-liquid separator.

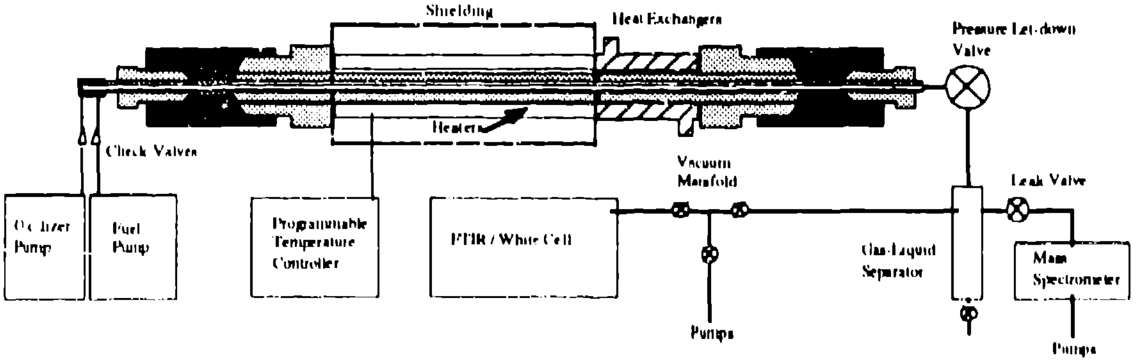

Figure 1. Schematic of linear flow reactor coupled to the gas-liquid separator and pumping manifold and pathways to various gaseous analysis.

The high temperature portion of one of our linear reactors is constructed out of C-276, a nickel alloy. The C-276 alloy was chosen because of its known strength and resistance to corrosion at high temperatures. Even so, under some reaction conditions we have seen considerable corrosion. To overcome this problem, a second reactor was constructed containing a 316 stainless steel sheath with a gold liner. A seal was made with the gold liner by flaring one end of the gold tube and compressing it between tapered high pressure fittings. The liner is open at the exit of the reactor, creating a static supercritical region between the liner and stainless core. The gold liner protects all high temperature sections of the reactor. All "taper seal" high pressure fittings, and most other components obtained from High Pressure Equipment Co., are manufactured from 316 stainless steel and rated to a minimum of 4080 atm. The C-276 reactor core is 64 inches long by 0.083 in. inside diameter (id), and the gold-lined stainless steel reactor is 55 in. x 0.103 in. These dimensions provide a heated volume of 5.7 ml and 7.4 ml, respectively. Using an empirical equation of state for supercritical water[5] we estimate a residence time of 5-150 seconds, depending on flow rate (typically 1-8 grams/min) and temperature (400-600 °C) with a pressure of 340 atm.

We have developed a variety of analytical approaches to quantifying residual energetics and products of reaction in the aqueous and gaseous reactor effluents. The gaseous effluent is primarily analyzed using Fourier-Transform Infrared (FTIR) Spectroscopy. A procedure was developed to quantify the concentration of CO_2 and N_2O (the primary gas phase products) produced using a 1 m path length cell. Calibration curves for CO_2 and N_2O were obtained by measuring the fraction of infrared light absorbed by a series of known concentrations of CO_2 or N_2O in the range expected to be produced in SCWO reactions. The dependence on concentration of the integrated absorbance of each of the two major CO_2 IR absorptions (asymmetric OCO stretch, 2350 cm^{-1} and OCO bend, 630 cm^{-1}) was nonlinear, exhibiting distinctive saturation behavior over the range of pressures (concentrations) from 0.1 to 10 torr, a consequence of the narrow linewidths of the ro-vibrational line and the limited (0.5 cm^{-1}) resolution of the FTIR. The resulting calibration data were fit to a saturation function, $y=a(1-e^{-bP})+cP$ where P is the partial pressure of the absorbing gas. This technique enabled us to measure the gas pressure with a relative standard deviation of 3%. A UTI quadrupole mass spectrometer is also used for detection of H_2, N_2, and O_2. Gaseous products are sampled on-line through a leak valve. To obtain a steady leak rate, a constant backing pressure of sample plus He buffer gas (600 torr total) was maintained. The pressure in the quadrupole region was typically in the 10^{-5} torr range. Calibration of this technique has so far proved difficult due to constantly changing backgrounds.

Analyses in the liquid phase included metals, total organic carbon (TOC), total inorganic carbon (TIC), inorganic anions and the substrate energetics. Metals analyses for Cr, Ni, Fe, Mo and Au are performed on a Perkin-Elmer inductively coupled plasma spectrophotometer (ICP) using indium as an internal standard. Total organic carbon (TOC) and total inorganic carbon (TIC) are analyzed using a Rosemount Dohrmann Model DC-190 Carbon Analyzer. Calibrations are performed with each set of samples using different concentrations of standardized potassium acid phthalate solution. Inorganic anions, particularly nitrate, nitrite and chloride, are analyzed with a Dionex 4500i Series Ion Chromatograph using a Dionex IonPac AS4A column with an eluent consisting of 1.5 mM $NaHCO_3$ and 2.2 mM Na_2CO_3. In most cases conductivity detection is used, but a UV/Visible detector set at 215 nm is used for low levels of nitrate and nitrite. Trace amounts of TNT, PETN, HMX, NQ, and RDX are analyzed by reverse phase liquid chromatography on the Dionex 4500i. The liquid chromatograph uses a Waters 490E Programmable Multiwavelength Detector that allows for simultaneous, multiwavelength detection. This feature is particularly useful if interferences are present, since interferences usually give different signals at different wavelengths. All these compounds are analyzed using a 150 mm x 2.1 mm id C8 narrow-bore column that is slightly heated for temperature stability.

RESULTS AND DISCUSSION

SCWO Reactions of energetics below solubility limits. Most of our effort has focused on reactions of solutions having concentrations less than half of their room temperature solubilities. The destruction efficiencies for the SCWO of five explosive compounds, PETN, HMX, RDX, TNT, and NQ are given in Table I. These reactions were run at high temperatures (near 600 °C) and with a large excess of oxidant.

TABLE I. Destruction Efficiencies for Energetics Below Water Solubility Limits[a]

Substrate	PETN	HMX	RDX	TNT	NQ
Initial conc. (ppm)	3.8	2.6	35.2	65.5	1700.
Destruction efficiency	>0.9825	>0.9900	>0.9992	>0.9998	>0.9999

[a]Conditions: 600 °C, 5500 psi; excess H_2O_2; 11 s residence time; gold-lined reactor.

The initial concentrations of the explosives were kept at less than half their room temperature solubilities to prevent precipitation and accumulation of explosive material in the feed lines leading to the reactor. Hydrogen peroxide was used as the oxidizer and was mixed with the feedstock containing explosives before the fluids were heated. In all cases the oxidizer was in 30-fold excess of the stoichiometry required to convert the explosive to CO_2, H_2O and N_2. The experimental conditions for each of these explosives were nearly identical, with pressures of 340 atm, reactor temperatures of 600 °C and residence times of 11 seconds. The reactions were primarily run in the gold-lined reactor to minimize the heterogeneous chemistry that might occur at the reactor walls. The only compound for which any reactor dependent chemistry has been observed is AP. No significant difference in DREs and products chemistry was observed for reactions of TNT, HMX, and RDX in the C-276 and the gold-lined reactors. We conclude from these observations that reactions with the C-276 and stainless 316 walls must not be significant for these energetic materials. For these "extreme" conditions, the aqueous effluent contained no detectable amounts of explosives. The detection limit of the HPLC/UV-vis analysis ranges from 20 to 50 parts per billion (ppb) depending on the compound. Consequently the measured destruction efficiencies represent lower limits defined by the low starting concentrations and the detection limits.

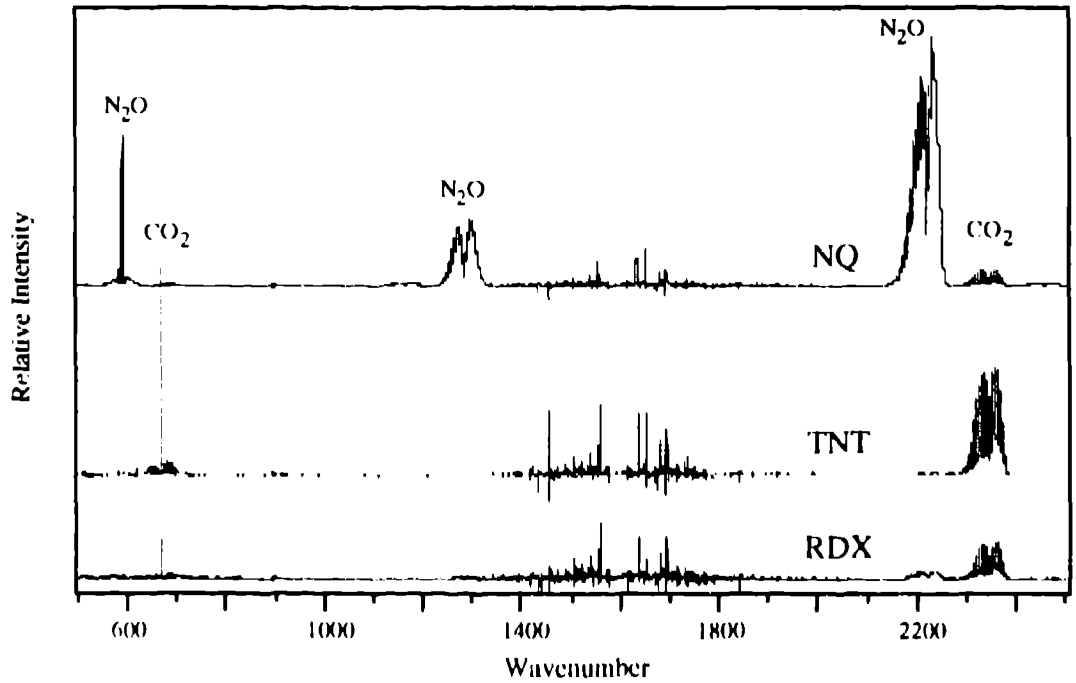

Figure 2. FTIR spectra of the reaction products of SCWO of TNT, NQ and RDX.

Gaseous and liquid effluents from these reactions have been analyzed to determine the products of reaction. Typical FTIR spectra for TNT, NQ and RDX are shown in Figure 2. It is clear from these analyses that the extreme conditions of high temperature and excess oxidant produce only CO_2 and N_2O in the gaseous effluent. Other possible products such as CO, CH_4, NO and NO_2

are not detected and are therefore below parts per million (ppm) levels (generally below 0.1% of the starting C and N). Additional products that are likely to be produced in these reactions but which cannot be quantified by FTIR include N_2, O_2 (no infrared active vibrations) and H_2O (swamped by large water background absorption).

The reactor effluents have been analyzed for carbon content and the results are summarized in Table II. The final two columns list the percentage of the starting C that is observed in the aqueous effluent (as organic and inorganic C) and as CO_2 in the gaseous effluent. For PETN and HMX, both the TIC and TOC quantities are below detection limits (0.1 ppm). Detectable quantities of organic carbon were found for RDX, TNT and NQ. Since in all of these cases the substrate is destroyed to levels well below the detection limits of the HPLC analysis (10 ppb) and since no volatile organics were observed in the FTIR analyses, the observed organics must be nonvolatile reaction products such as formate or acetate. For the TNT reactions, greater than 98% of the C was detected as CO_2, with the remainder detected as involatile organics in solution. The only substrate to give significant TIC (carbonate or bicarbonate) quantities is NQ. In this case, 83% of the C is detected as CO_3^{2-} or HCO_3^- while 15% is detected as gaseous CO_2, accounting for most of the C.

TABLE II. Analysis of Carbon Products in Effluent Streams for SCWO of Energetics[a]

Substrate	$[C]_i$ [b](ppm)	TIC (ppm)[c]	TOC (ppm)[c]	$\% C_{aqueous}$	$\% C_{CO_2}$
PETN	2	[d]	[d]	[d]	81
HMX	2	[d]	[d]	[d]	87
TNT	24	0.2	1.7	8	98
RDX	5.7	<0.1	<0.1	<4	98
NQ	195	152	10	83	21

[a] Conditions: 600 °C, 5500 psi; excess H_2O_2; 11 s residence time; gold-lined reactor; [b] Initial carbon concentration.; [c] TIC, Total inorganic carbon, TOC, Total organic carbon; [d] Since starting concentrations of PETN and HMX are ~2-3ppm, the analyses for TOC and TIC are below detectable limits;

Reactor effluents have also been analyzed for nitrogen content and the results are summarized in Table III. For PETN, HMX, and RDX, some N_2O was observed in the FTIR spectra, but quantitative analysis showed the amounts to be less than 0.5% of the initial N. With excess oxidant, significant amounts of nitrite and nitrate were observed for all substrates except NQ. Most of the detected N from NQ was determined to be N_2O. Trinitrotoluene (TNT) produced the greatest fraction (65%) of NO_x^-.

TABLE III. Analysis of Nitrogen Products in Effluent Streams for SCWO of Energetics[a]

Substrate	PETN	HMX	RDX	TNT	NQ
$\% NO_3^-$	18.7	12.4	10.1	36.6	0.03
$\% NO_2^-$	6.0	5.3	14.1	28.5	0.04
$\% N_2O$	[b]	[b]	[b]	4.0	35

[a] Conditions: 600 °C, 5500 psi; excess H_2O_2; 11 s residence time; gold-lined reactor. [b] Less than 0.5%.

In all cases examined so far, a large fraction of the initial nitrogen remains undetected by our current analytical techniques. We have recently interfaced a mass spectrometer to the gas-liquid separator on the gold-lined reactor which enables us to obtain on-line analyses of the effluent gases. We have observed formation of N_2 in the SCWO oxidation of TNT. However, we have not yet worked out the calibration protocol for making these analyses quantitative.

Effects of temperatue and oxidant concentration on SCWO of TNT. A large number of experiments has been conducted on TNT to determine the SCWO chemistry as a function of reaction temperature and oxidant concentration. In all cases, the TNT was destroyed to below detectable limits of ~10 ppb, yielding a destruction efficiency of greater than 99.98%. The product analysis results are summarized in Table IV. The NO_2^- and NO_3^- values are listed as a percentage of the starting nitrogen concentration. Similarly, the TIC and TOC values are listed as a percentage of the starting carbon concentration. The ratio of H_2O_2 to TNT represents a stoichiometric ratio based on complete reaction of TNT with H_2O_2 to form CO_2, H_2O, and N_2. The most efficient conversion of TNT to CO_2, as determined by FTIR analysis of the gas production and by the TIC and TOC analyses of the aqueous effluents, occurs at the highest temperature (600 °C) and the highest H_2O_2 concentration. These conditions also yielded the highest concentrations of NO_2^- and NO_3^-. In general, at lower temperatures and lower ratios of H_2O_2:TNT, less NO_2^- and NO_3^- are observed. While these conditions do not compromise the destruction efficiency of TNT, they tend to leave more carbon in the aqueous effluent. Much of this carbon appears as carbonate, however, which can be removed by lowering the pH. The best conditions for the destruction of TNT and any organic byproducts with minimum NO_2^- and NO_3^- formation appear to be 600 °C and a 1:1 stoichiometric ratio of H_2O_2:TNT.

TABLE IV: TNT SCWO products as a function of temperature and H_2O_2 concentration

Temp (°C)	H_2O_2:TNT[a]	%NO_2^-	%NO_3^-	Total %NO_x^-	%TIC	%TOC	%Total C
400	20:1	11	30	41	4	18	22
500	0:1	18	0	18	14	28	42
500	20:1	26	51	77	4	11	15
600	0:1	18	0	18	12	34	46
600	1:1	11	6	17	15	0	15
600	2:1	6	6	12	14	0	14
600	5:1	33	38	71	9	0	9
600	20:1	25	49	74	4	0	4

[a] Stoichiometric ratio

Reactions of Ammonium Perchlorate (AP). The chemistry of AP is unique and consequently is discussed separately. Because of corrosion problems, most AP SCWO reactions were performed in the gold-lined reactor. Some results in the C-276 reactor are included for comparison. Sodium hydroxide was always added to the AP solutions in a 1:1 stoichiometry to ensure a net pH balance. This is particularly important for the gold-lined reactor, where the presence of a high Cl^- ion concentration together with a low pH and highly oxidizing conditions may result in the oxidation of the gold liner to $AuCl_4^-$.

Data for the dependence of destruction efficiencies and reaction products on temperature are summarized in Table V. The products containing Cl and N are given as a percentage of the initial Cl and N concentration, respectively. At temperatures lower than 400 °C, no decomposition of the ammonium perchlorate is observed. Most of the ammonia and all the perchlorate are recovered. The small ammonia loss is most likely due to the evolution of ammonia gas from the feed solution and effluent. The AP begins to react at 450 °C and is completely destroyed (99.6%) at 600 °C. Almost all the chlorine from the perchlorate appears in the effluent as sodium chloride (NaCl). Although salt solubility decreases in supercritical water, the sodium chloride product remains in solution at low concentrations or temperatures. However, when the concentration and/or temperature are raised, the Cl mass balance is degraded, probably due to precipitation of Cl^- salts in the reactor. We have found that our mass balances improve when the reactor is cooled and flushed between runs and the 'flush' solutions are included in the analysis. With this procedure a burst of Cl^- is generally observed in the first or second flush sample as the reactor is cooled. The liquid effluent also contains a small amount (<2%) of nitrogen as nitrite (NO_2^-) and nitrate (NO_3^-). The mass spectra indicated that both nitrous oxide (N_2O) and oxygen (O_2) are produced. The amount of N_2O produced was quantified using the FTIR/White cell and appears to increase with increasing temperature and AP concentration. Most of the N was not detected (for the best case, 600 °C, only 25% is detected) and likely occurs as N_2. The FTIR and mass spectrometric analyses of the gaseous effluent did not detect the presence of chlorine (Cl_2), nitrosyl chloride (NOCl), or nitrogen dioxide (NO_2).

TABLE V. AP SCWO Products as a Function of Temperature[a]

T (°C)	% ClO_4^-	% Cl^-	% NO_2^-	% NO_3^-	% N_2O	%NH_4^+
400	100	0.0	0.3	0.0	0.0	95.0
450	95.5	6.9	0.8	0.3	1.3	85
500	46.0	16.0	0.0	2.0	13.6	40.0
550	3.5	17.0	0.0	2.0	23.1	0.0
600	0.4	5.0	0.2	0.2	23.3	0.0

[a]Conditions: 0.1 M AP; equimolar NaOH; residence time varied from 11 - 52 s (600 - 400 °C); flush between runs not analyzed; gold-lined reactor.

Previous studies of the thermal decomposition of solid ammonium perchlorate show that a variety of products is possible.[6] Below 300 °C, the equation

$$4\ NH_4ClO_4 \rightarrow 2\ Cl_2 + 3\ O_2 + 8\ H_2O + 2\ N_2O$$

represents the majority of the products. At higher temperatures more nitric oxide (NO) is produced. Between 350 °C and 450 °C gas analysis of the products of thermal decomposition gives

$$10\ NH_4ClO_4 \rightarrow 2.5\ Cl_2 + 6.4\ O_2 + 18.8\ H_2O + 2\ N_2O + 2.5\ NOCl + HClO_4 + 1.5\ HCl + 1.75\ N_2.$$

Thus the decomposition of AP in supercritical water avoids the formation of the hazardous products (Cl_2, NOCl) formed in thermal decomposition.

Above 450 °C, ammonium perchlorate detonates. The possibility of explosive energy release was investigated. Concentrated solutions of ammonium perchlorate (1.0 M, 122 g/L) were rapidly heated to temperatures over 600 °C at pressures near 340 atm in a small batch reactor. Neither pressure nor temperature transients indicative of rapid energy release was observed. These results indicate SCWO is, therefore, more controlled, i.e., safer than thermal decomposition.

Reactor Corrosion. Corrosion of metals and alloys at high temperature and pressure is an important issue for applying supercritical fluid technology to the treatment of hazardous wastes. Corrosion may in fact be a cost-limiting factor for the scale-up to large SCWO facilities. Corrosion is inherently electrochemical in nature. An understanding of the oxidation-reduction reaction chemistry in supercritical environments is essential for eventual control of these corrosion processes. The most corrosive substance we have run to date is ammonium perchlorate. When running AP in the C-276 alloy reactor corrosion was a problem as we first noted by the dark-colored effluent. Analyses are presented in Table VI. Most corrosion products formed insoluble salts in supercritical water. While it was generally possible to flush the insoluble salts out of the reactor during the cool-down phase, the reactor eventually plugged and could not be reopened. The gold-lined reactor was built to avoid these corrosion problems.

TABLE VI. Corrosion Products for SCWO of Ammonium Perchlorate

Reactor	Au (ppm)	Cr (ppm)	Fe (ppm)	Mo (ppm)	Ni (ppm)
C-276 reactor	---	130.00	---	54.00	39.00
Gold lined Stainless reactor (acidic)	1622.00	3.36	65.38	---	55.04
Gold lined Stainless reactor (alkaline)	0	0.99	0.99	---	3.73

We have run AP in the gold-lined reactor in both alkaline and acidic solutions. Significant corrosion is observed in acidic solutions of AP. At low pH, the oxidation of gold, $Au^0 \rightarrow Au^{+3} + 3e^-$ is activated. The oxidant could be NO_3^- produced in the decomposition of AP or the perchlorate itself. The gold complexes with chloride ion and is dissolved into solution as $AuCl_4^-$. These reactions are analogous to the well known dissolution of gold in aqua regia. By raising the pH, this corrosion pathway is blocked as shown in Table VI. What little corrosion we do see probably occurred on exposed, hot stainless portions of the reactor. In contrast with AP, other explosives have exhibited very little corrosivity.

CONCLUSIONS

In general, the chemistry of oxidation of energetic materials in supercritical water is very similar to that found previously for other classes of organics. We have established conditions for which the hydrocarbon elements of all the energetic compounds investigated thus far are completely oxidized to CO_2 and H_2O. The temperature, residence time and oxidant concentration necessary to achieve complete oxidation vary, depending on the nature of the energetic material. Our results indicate that complete oxidation is always achievable using excess oxidant and operating the linear reactor at 600 °C (11 s residence time). Reasonable carbon balances are obtained for all the energetic materials investigated under these conditions, including PETN, HMX, TNT, RDX, and NQ. Most of the carbon is detected as CO_2, with some small fraction remaining in solution as inorganic carbon (CO_3^{2-} or HCO_3^-). The exception is NQ, which produces large quantities of inorganic carbon. The conditions that produce these results were deliberately "extreme" to ensure complete oxidation. We have not adequately explored the dependence of the chemistry on oxidant concentration and temperature to determine optimum conditions. Minimization of oxidant concentration is important since the oxidant represents a large fraction of the process cost and if present in excess may enhance corrosion or cause the formation of undesirable products. Furthermore, we have very little data for one variable, the reactor residence time. Less "extreme" conditions (e.g., lower temperatures and 1:1 oxidant stoichiometries) may be sufficient to achieve complete oxidation given longer residence times. Without added oxidant, products of incomplete oxidation were often observed, including CO, CH_4 and HCN.

The nitrogen chemistry of energetics is considerably more complicated, varying widely depending on the nature of the starting material. The nitrogen is always distributed among a group of products, N_2, N_2O, NO_2^- and NO_3^-, having formal oxidation states of N varying from 3- to 6+. Quantitative data have been obtained for all products except N_2. The latter is implicated as the major N product in many of the reactions by elimination of other possible products. Qualitative data (Mass Spectroscopy and Gas Chromatography) indicate N_2 production in the case of NM, NQ and TNT. No obvious correlation exists between the nitrogen content or the type of nitrogen groups (e.g., NO_2 or NH_2 groups) of a particular energetic material and the distribution of nitrogen products (N_2, N_2O, NO_2^- and NO_3^-). It is possible, however, to vary the distribution of products in the different oxidation states by varying the temperature and the oxidant concentration.

The clearest example of this tunability is NO_x^- production in the reactions of TNT. When a large excess of oxidant is employed at 600 °C, a significant fraction of the initial N (74%) is converted to NO_x^-. This fraction is much less (12%) for a small (5-fold) excess of oxidant and yet complete oxidation of the carbon still occurs. The same trend is observed for the oxidation of RDX with excess H_2O_2 (10% NO_3^-) and with oxygen balance (no NO_3^-). These results indicate that significant control over the oxidation chemistry is possible through the precise tuning of reaction parameters.

The destruction chemistry of AP in SCWO is unique among the energetic materials since AP has no carbon, and is a strong oxidant. The chemistry is best described by the following equation:

$$NH_4ClO_4 + NaOH \rightarrow NaCl + 2.5\ H_2O + 0.4\ N_2 + 0.1\ N_2O + 1.2\ O_2.$$

Conditions have been determined for which 99.6% of the ClO_4^- is destroyed. The Cl is converted to Cl^-, formally reduced from 7^+ to 1^-, and excess oxygen is produced in the reaction. Further evidence for the highly oxidizing nature of this reaction is provided by the strong oxidative corrosion of the C-276 and 316 stainless reactors. The addition of reducing equivalents, in the form of a fuel such as a hydrocarbon, may improve the destruction of AP as well as reduce the reactor corrosion. The nitrogen is distributed between N_2 and N_2O, with no formation of higher oxides or NOx^-. In contrast to thermal decomposition of solid AP, no harmful products such as Cl_2 or NOCl are formed in the SCWO reactions.

A critical issue for practical application of an SCWO process to the treatment of energetic materials is reactor wear caused by corrosion. Corrosion of the C-276 reactor by most of the energetic materials does not appear to be a problem. The exception is AP, which caused severe corrosion of the C-276 and 316 stainless reactors. For laboratory scale reactors, this problem has been solved by the use of a gold liner in the SCW region, which reduces corrosion to acceptable levels.

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