

Sandia Combustion Research

Technical Review



Destruction of Hazardous Munitions by Supercritical Water Oxidation

Supercritical water oxidation has the potential to be an affordable and environmentally friendly way to dispose of a variety of hazardous obsolete munitions including military dyes and an assortment of pyrotechnics such as colored smokes and flares. The results from feasibility testing of dyes and pyrotechnics in the CRF's Materials Evaluation Reactor illustrate this potential by determining suitable operating conditions and identifying large-scale system design strategies.

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The U. S. military stockpile has large quantities of obsolete munitions awaiting disposal. Although suitable means for the safe dismantlement of much of this stockpile have been identified, there are still quantities of specialty materials for which existing methods have been deemed inappropriate from an environmental standpoint. Among these munitions are colored spotting dyes and pyrotechnic colored smoke compositions. In open air burn or incineration treatment processes these materials produce large quantities of toxic, and possibly carcinogenic, gases and particulate matter.

The U. S. Army Armament Research, Development, and Engineering Center (ARDEC) is interested in developing alternative treatment methods for the final disposal of these materials that do not have the problems of open air burning or incineration. Consequently, a series of tests was undertaken at the Combustion Research Facility to assess the feasibility of using supercritical water oxidation (SCWO) to effectively destroy the organic dyes in these munitions. We have processed four dyes in the CRF's SCWO flow reactor, evaluated experimental destruction efficiencies as a function of temperature, and identified several operational considerations for pilot plant scale-up.

Supercritical water oxidation is conceptually simple. Aqueous waste, typically ranging from 1-10 wt% oxidizable material, is

pressurized and heated to supercritical conditions (above 374°C and 22.1 MPa) where it can function as a fuel in an oxidation reaction. An oxidizer is added and the elevated temperature of the mix, typically at 550°C, is maintained primarily by the excess heat of reaction. Given adequate reaction time, the waste-fuel is converted to relatively innocuous products; organic carbon in the feed emerges as CO₂, nitrogen is converted to N₂, and metals, heteroatoms, and halides appear in the effluent as inorganic salts and acids. The results from these dye processing tests provide a guide to the design of SCWO equipment by establishing the reaction conditions necessary to effectively destroy the dyes. Process difficulties can be identified so that they can be addressed prior to designing and building a prototype reactor.

The SCWO Materials Evaluation Reactor is constructed from Inconel 625 and is approximately 750 cm long. It is designed to maintain isothermal conditions over a length of 490 cm following mixing of the reactants and afford experimental residence times from 0.15 to 20 s.

Testing was done in one of two different modes with one used for temperature-dependent measurements conducted on the orange dye only. The second method was instituted as a result of the dye pyrolysis and charring that occurred using the first method. The principal difference between the two methods is that in first experimental strategy, the reactants are preheated separately, prior to mixing, while in the second strategy the

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reactants are mixed first and then heated. The procedure was as follows: 1) a solution of the dye was prepared in water at a nominal concentration of 0.5 wt%, 2) the solution was pressurized to 27.2 MPa (4000 psi) and heated to temperature in a series of tube furnaces, 3) in a parallel line, a solution of 5 wt% hydrogen peroxide in water was pressurized and brought to reaction temperature (when the peroxide was heated to above 400°C, it rapidly decomposed to molecular oxygen and water), 4) these two solutions were mixed at known flow rates, temperature, and pressure and allowed to react in a fixed length of tubing, 5) the mixture was then cooled rapidly and diverted to the sample collection vessel for liquid effluent analysis. The procedure for the second method is identical to the first except the two solutions were mixed before heating rather than heated separately.

Orange G dye, $\text{Na}_2(\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2)$ was processed in the flow reactor at constant flow rate and oxidizer concentration; only temperature was varied. The samples were analyzed for input and effluent total organic carbon (TOC). The results are presented in Table 1. At temperatures above 550°C the orange dye is destroyed effectively. The TOC that remains in the effluent at these temperatures is probably composed of relatively stable low molecular weight organic species such as methanol, formic acid, and formaldehyde or single ring aromatics such as phenol. Carbonaceous deposits were formed in the dye feed line due to pyrolysis in the absence of oxygen.

Using the second method, the dyes are destroyed to >99% without the pyrolysis problems. Analysis of the primary hazardous components, the specific dye molecules, using spectrophotometry indicated that all dyes, except the green dye, are destroyed below the detection limit of the technique, 0.5 ppm. The pale yellow appearance present in the effluent from green-dye processing is probably chromate ion from mild corrosion of the reactor.

Although at temperatures above 550°C the dyes and partial oxidation products were destroyed to a minimum of 99.5% DRE in 10 seconds, destruction of the toxic components of the dyes resulted in plugging and fouling of the reactor and general (leaching) corrosion

from the reactor tubing. When the organic dye was heated above 350°C before introduction of oxidant, it pyrolyzed, adhered and fouled the reactor until flow restriction became serious. We did not find a method to remove the pyrolytic material other than a mechanical honing operation. Mixing the oxidant with the waste prior to heating eliminated the carbonaceous deposits, but produced "sticky" salts that agglomerated on the walls of the reactor vessel until a shut-down was initiated by a rise in pressure upstream of the plug. Examination indicated that this material was anhydrous sodium sulfate, Na_2SO_4 .

This feasibility study has led to the development of a new reactor design now being developed at Sandia in conjunction with GenCorp Aerojet and Foster Wheeler Development Corporation that is likely to eliminate the salt deposition and corrosion problems encountered in these initial tests.

Table 1. Destruction Efficiencies for Orange Dye.

Analytical Method:	Total Organic Carbon
Oxidizer:	5 wt% hydrogen peroxide
Flow Rate:	0.75 g/sec
Amount Processed:	5.7 liters
Input Concentration:	2140 ppm TOC, 0.5 wt% dye
Appearance:	dark orange

T(°C)	TOC (ppm)	Residence Time (s)	DRE %	Appearance
556	3.35	7.4	99.69	colorless
553	3.39	7.4	99.68	colorless
542	4.51	7.6	99.58	colorless
520	21.4	8.1	98.00	pale yellow
506	180	8.5	83.1	brown
484	247	9.2	76.9	brown/solids

Table 2. Destruction Efficiencies for Four Dyes.

Oxidizer:	5 wt% hydrogen peroxide
Flow Rate:	0.6 g/sec
Amount Processed:	3.7-7.5 liters/dye
Input Concentration:	~ 0.25 wt% dye
Temperature	560°C

Sample	TOC _o (ppm)	TOC _i (ppm)	DRE	Appearance
Orange	2.36	780	99.69	colorless
Red	4.11	936	99.56	colorless
Blue	3.74	1232	99.69	colorless
Green	2.65	819	99.67	yellow

This work was supported by the U.S. Army Armament Research Development and Engineering Center at Picatinny Arsenal.