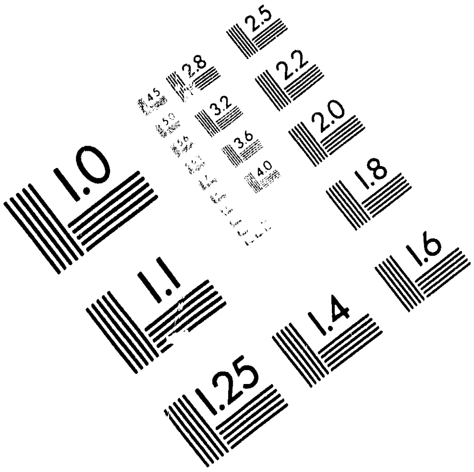

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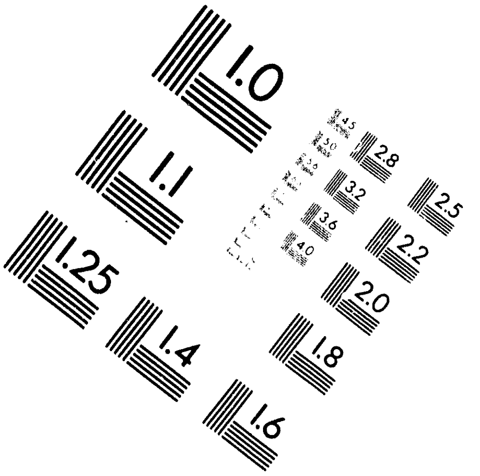

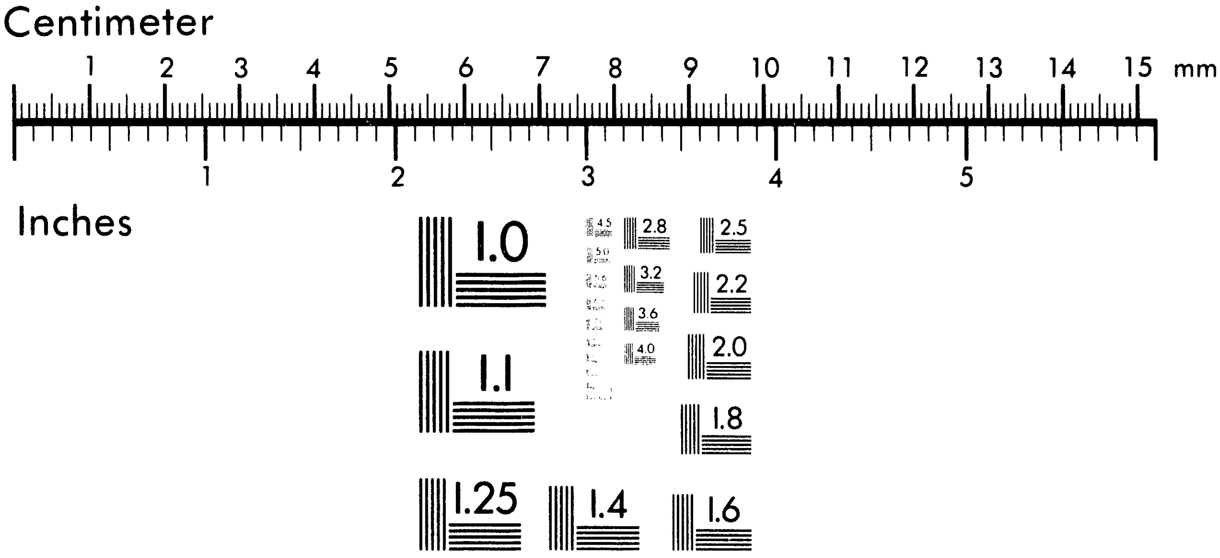

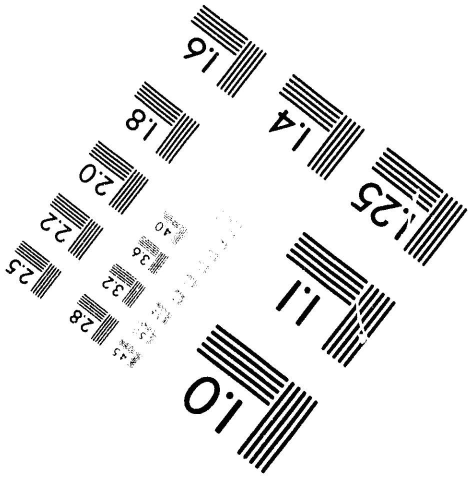

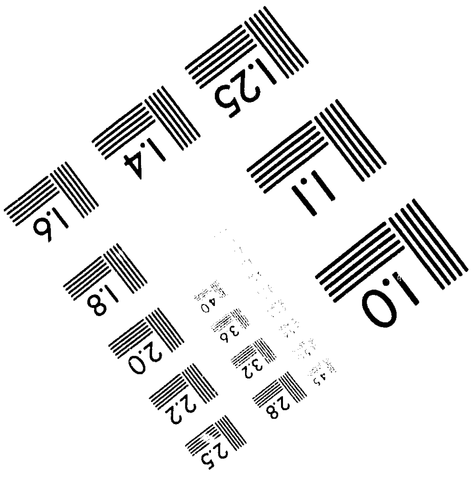

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SUPERCRITICAL WATER OXIDATION OF COLORED SMOKE, DYE, AND PYROTECHNIC COMPOSITIONS*

Phase I Final Report

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ABSTRACT

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 considerable quantities of specialty materials for which existing methods have been deemed inappropriate from an environmental standpoint. Among these munitions are colored spotting dyes and a wide assortment of pyrotechnics, including colored smokes and flares. In open 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 at Picatinny Arsenal, NJ is interested in developing a method of treatment that will dispose of these munitions without the difficulties identified above. This report examines the feasibility of supercritical water oxidation, an emerging waste treatment technology, to process these materials. Four colored dyes and one pyrotechnic smoke composition were processed in a flow reactor, and the effluent was analyzed to determine the effectiveness of the processing. The tests showed that all of these materials could by oxidized to much less hazardous compounds in less than 10 seconds with a destruction and removal efficiency (DRE) typically > 99.5%. Two technical issues were identified as needing more attention in Phase II of this project: formation of sulfate and chloride salt deposits within the flow reactor and corrosion of the materials of construction. Based on the tests reported here this technology shows much promise, and its implementation for the treatment of military dyes, and at least some pyrotechnic compositions, is feasible. Recommendations for further testing and system development for Phase II of this project are included.

* This work was supported by the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ and the DoD office of Munitions Memorandum of Understanding with Sandia.

INTRODUCTION

The existing U.S. military stockpile contains large quantities of colored smoke, spotting dye, and pyrotechnic munitions. For many years, these munitions have been stored in magazines at various locations within the continental United States awaiting completion of their life-cycle. In 1991, colored smokes and dyes accounted for 2.9% of the total inventory of 205,000 short tons. Pyrotechnics accounted for 1.4%. Thus, compositions containing colored smokes, spotting dyes, and pyrotechnics account for about 8,000 short tons of the demilitarization stockpile. This inventory has continued to increase since 1991. The chemical compositions of these munitions include toxic organic dyes, inorganic salts, metallic salts, and heavy metals. The open air burning of these munitions produces poisonous gases that are detrimental to human health and harmful to the environment. Consequently, in August of 1980, the Office of the Surgeon General issued a moratorium prohibiting the open burning of colored smoke, dye, and pyrotechnic munitions.

Prior efforts to incinerate colored smoke, dye, and pyrotechnic compositions in modified deactivation and fluidized bed furnaces produced toxic emissions containing polycyclic aromatic hydrocarbons and large quantities of particulate matter (approximately 50% by weight of initial feed). The particulate matter serves to "lock up" incinerators and causes severe plugging of the pollution abatement equipment. These difficulties force an incineration system to be shut down for costly and lengthy maintenance before being reactivated. Earlier tests have indicated that existing pollution abatement process equipment is inadequate in its ability to capture the heavy metal particulate matter generated from the incineration of these materials and is consequently incapable of meeting RCRA permit requirements for particulate standards. In addition, tests conducted on the incineration of pyrotechnic materials indicated that the high temperatures generated during combustion would destroy the combustion chamber of the furnace. Consequently, conventional incineration coupled with existing pollution abatement technology is essentially incapable of treating a majority of the colored smoke, dye, and pyrotechnic munitions that are currently in the demilitarization inventory.

Supercritical water oxidation (SCWO) is an alternative rapidly developing hazardous waste treatment method that has attracted the interest of both private industry and government agencies including the Department of Defense (DoD) and the Department of Energy (DOE). In addition to the destruction of smoke, dye, and pyrotechnic compounds, projects administered by these agencies for the disposal of military components and wastes using SCWO technology include the development of a pretreatment module for the DOE Hanford mixed waste site, the development of a SCWO reactor to destroy chemical warfare agents, and the application of SCWO technology for the safe disposal of obsolete rocket boosters.

SCWO is conceptually simple. Aqueous waste, typically ranging from 1-10 wt% oxidizable material, is pressurized and heated to conditions above the critical point of water (374 °C, 22.1 MPa) where it can function as a fuel in an oxidation reaction. An oxidizer is added either to the cold feed or to a preheated feed. The elevated temperature of the mix is maintained primarily by the excess heat of reaction, and, given adequate reaction time, the waste-fuel is converted to innocuous materials. Organic carbon in the feed emerges as CO_2, nitrogen is converted to N_2, and metals, heteroatoms, and halides appear in the effluent as inorganic salts and acids.

The U. S. Army Armament Research, Development and Engineering Center (ARDEC) has established a program at Sandia to assess the feasibility of SCWO as a treatment technology for colored smokes, dyes, and pyrotechnics. If feasibility is indicated, Sandia is to design a 1000 gallon/day SCWO production prototype reactor and then to build and test the reactor at the McAlester Army Ammunition Plant (MCAAP).

ARDEC's program at Sandia for developing this reactor includes three Phases. Phase I has the goal of assessing the feasibility of destroying the military waste. Phase II and Phase III have the goals of designing and building the prototype reactor. We are currently in transition from Phase I to Phase II. This report presents the complete results of Phase I. Five compounds, four dyes and one pyrotechnic composition, have been destroyed successfully with Sandia's SCWO bench reactor. A pilot plant conceptual design has been finished, documented, and delivered to ARDEC.[1] Contractor bids to build the reactor according to Sandia's specifications for Phases II and III have been received and are being evaluated.

The primary goal of the Phase I experimental effort was to identify the range of temperatures over which the smoke, dye, and pyrotechnics oxidize with reasonable efficiency, identify any compounds that are difficult to oxidize, and record any process difficulties encountered in destroying the compounds. These results provide a guide to the design of SCWO equipment for the pilot plant by indicating the operational trends and problems of destroying these specific munitions slated for disposal.

EXPERIMENTAL MATERIALS, SYSTEMS, AND PROCEDURES

Materials

Dyes

Samples of four dyes, identified here as Red, Orange, Green, and Blue, were received by Sandia from MCAAP in conventional ammunition boxes. The red, green, and orange samples were very finely divided powders. The blue dye was a hard solid mass that was difficult to break up into granular material. All dye samples were entirely and rapidly soluble in water at the 0.25 - 1.0 wt% concentration used in these tests. The solutions produced were intensely colored and odorless.

The most accurate available support documentation was provided by ARDEC. Unfortunately, this documentation often contained conflicting, incomplete, and outdated information, dating as far back as 1946. Based on a careful examination of the documentation, our best estimate of the chemical formulas of the dyes is given as follows:

Table 1
Composition of Spotting Dyes

1) Orange dye:	$Na_2(C_{16}H_{10}N_2O_7S_2)$	(100%)
2) Red dye:	$Na_2(C_{18}H_{13}N_3O_8S_2)$	(80%)
	$Na_3(C_{16}H_9N_4O_9S_2)$	(20%)
3) Green Dye (Type I):	$Na_3(C_{16}H_9N_4O_9S_2)$	(80%)
	$Na(C_{27}H_{31}N_{2}0_{6}S_2)$	(20%)
4) Green Dye (Type II):	$Na_3(C_{16}H_9N_4O_9S_2)$	(80%)
	$Ca(C_{27}H_{31}N_2O_7S_2)_2 + 10H_{2}0$	(20%)
5) Blue Dye (Type I):	$Na(C_{27}H_{31}N_{2}0_{6}S_2)$	(30%)
	$Na(C_{37}H_{36}N_3O_6S_2)$	(20%)
	$C_{12}H_{22}O_{11}$	(50%)
6) Blue Dye (Type II):	$Ca(C_{27}H_{31}N_2O_7S_2)_2 + 10H_{2}0$	(30%)
	$Na(C_{37}H_{36}N_3O_6S_2)$	(20%)
	$C_{12}H_{22}O_{11}$	(50%)

From the documentation it was not possible to determine if the green and blue dyes contained calcium or sodium as the cation. Compositions are therefore listed above for both calcium-containing (Type II) and non-calcium-containing dyes (Type I).

Pyrotechnic

Six gallons of pyrotechnic labeled "Pyrotechnic Composition Smoke Green" were received from Pine Bluff Arsenal in conventional carboys. The pyrotechnic was received as an aqueous slurry. The accompanying documentation indicated that these samples were mixed at a concentration of one pound of dry mix to one gallon of water. This documentation supplied by Pine Bluff was very complete and an accurate assessment of the original composition could be made with confidence (see Table 2).

Unlike the dyes discussed above, which are salts of organic acids and soluble in water, the dyes in the pyrotechnic are insoluble and form a dark green slurry with particulates that partially settle to the bottom. Some of the particles remained suspended and were barely visible by the naked eye. Microscopic examination indicated roughly spherical particles having diameters between 5 and 10 microns, as shown in Figure 1.

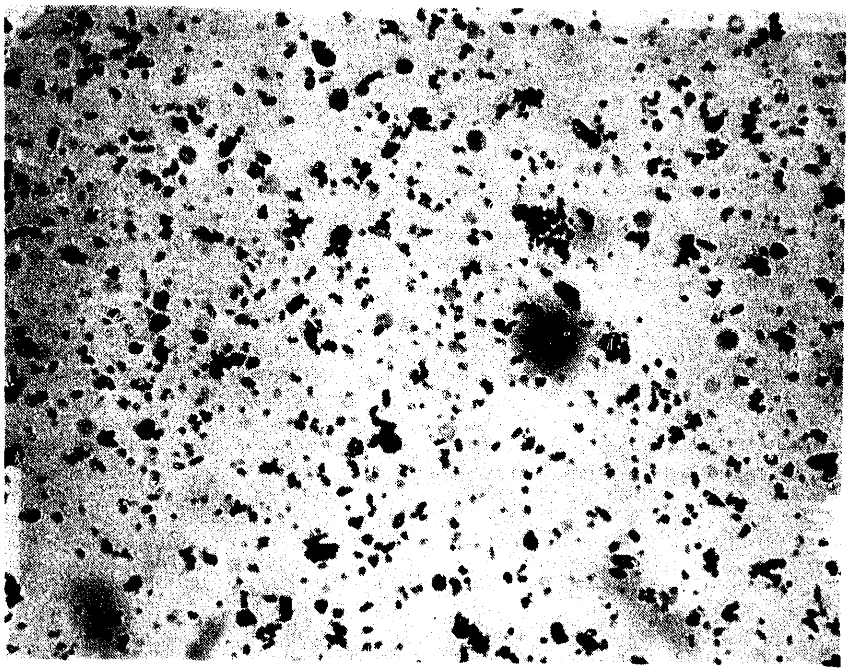

Figure 1: Optical micrograph of the pyrotechnic composition "Smoke Green". Scale = 500X.

Table 2
Pyrotechnic Composition

$KClO_3$	(31.5%)	Potassium Chlorate
$C_{12}H_{22}O_{11}$	(18%)	Lactose
$MgCO_3$	(3.5%)	Magnesium Carbonate
$C_{24}H_{12}O$	(4.7%)	Dye, Vat Yellow #4, MIL-D-50029B Indanthrene Golden Yellow
$C_{17}H_{10}O$	(9.4%)	Dye, Benzanthone, MIL-D-50074D
$C_{28}H_{21}O_2N_2$	(32.9%)	Dye, Solvent Green #3, MIL-D-3277E 1,4 -di-p-tolidinoanthraquinone

The magnesium carbonate and the three dye constituents of the pyrotechnic are insoluble in water.

Handling

Test material was prepared in a fume hood equipped with a HEPA filter by dissolving the dyes into water, or in the case of the smoke, by dilution. Deionized water was used for all tests. Feed preparations were contained in high density polyethylene jugs.

Material Safety Data Sheets on the dyes indicated that these materials are most hazardous in powder form. This derives from inhalation and from skin contact with the fine dust. The dyes are best handled with protective gloves in relatively dilute water solution, making them well suited for destruction with SCWO.

The pyrotechnic was delivered to Sandia's explosive handling facility. As shipped, it was designated as a Class 1.3 explosive. As received, the material was an 11% solution/suspension in water. Due to dilution below 33 wt%, the primary hazard, if any, was considered to be that associated with the solvent, water in this case, and not the explosive in accordance with the DOE Explosive Safety Manual.[2] Special procedures permitted it to be handled and stored at Sandia's SCWO reactor site.

Apparatus and Procedures

All of the oxidation experiments were conducted in Sandia's supercritical water oxidation flow reactor, referred to as the Materials Evaluation Reactor (MER). This equipment is designed to mix two separate flows at a known temperature and known flowrate, and to keep this mixture at a fixed temperature. A schematic of the MER is shown in Figure 2.

The reactor has a maximum operating temperature of 650°C and a maximum operating pressure of 51.0 MPa (7500 psi). Flowrate can be varied from about 1.5 ml/s (ambient condition feed, 25°C) to 0.2 ml/s and still maintain good flow control. The feed and oxidizer heater sections are two parallel lines heated using a series of Marshall tube furnaces with combined power of 4500 W on each line. These furnaces are individually controlled with Omega process controllers. The reactor section is heated with six Watlow 375 W cable heaters which are needed to maintain isothermal conditions along the reactor. The high-temperature portions of the system are made of 9/16" (1.43 cm) OD - 3/16" (0.477 cm) ID inconel 625 tubing with inconel 625 high-pressure fittings as unions. The temperature of the feed, oxidizer, and reacting fluid is measured with inconel 600 sheathed Type-K thermocouples located directly in the fluid. The reaction is quenched with two simple counterflow heat exchangers.

Testing was done in one of two different modes: Method A and Method B, described below. Method A was used for the initial temperature-dependent measurements conducted on the orange dye only. Method B was instituted as a result of the dye pyrolysis and charring that occurred using Method A. The principal difference between the two Methods is that in Method A the ingredients are preheated separately, prior to mixing, while in Method B the ingredients are mixed first and then heated.

Method A

1) A solution of the dye in deionized water is prepared at a nominal concentration of 0.5 wt%.

2) The solution is pressurized to approximately 27.2 MPa (4000 psi) and is heated to temperature in the series of tube furnaces (feed heaters).

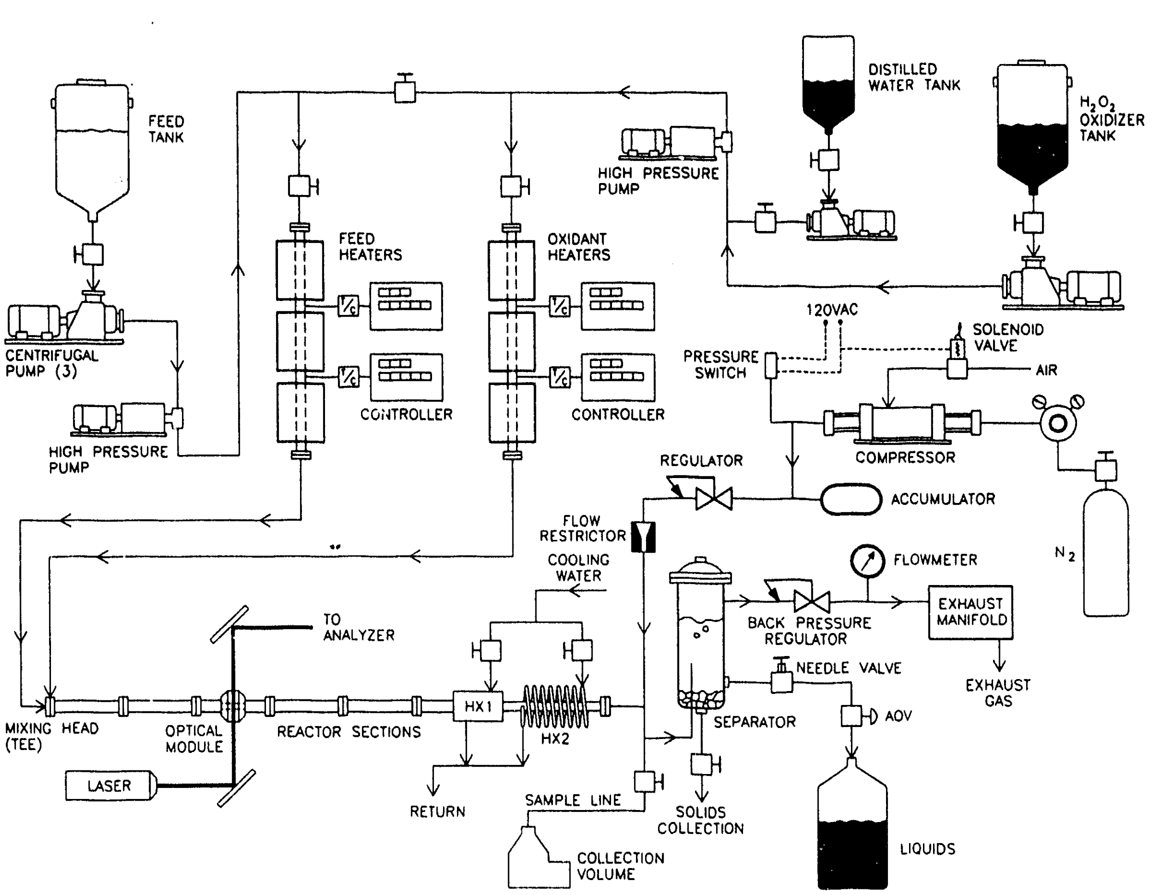

Figure 2: Schematic diagram of Sandia's SCWO Materials Evaluation Reactor. The overall system is composed of five main subsystems or modules: Pumping and Pressurization, Heating, Reactor, Cooldown and Separation, and Pressure Regulation. Each subsystem can be modified easily without affecting the operation of another subsystem. Note that the feed and oxidizer may be preheated separately or together depending on the configuration of the valves supplying the preheat system.

3) In a parallel line, a solution of 5 wt% hydrogen peroxide in deionized water is pressurized and brought to reaction temperature. When the peroxide is heated to above 400°C it rapidly decomposes to molecular oxygen and water.

4) These two solutions are mixed at known flow rates, temperature, and pressure at a pipe-tee (mixing head), and allowed to react together in a fixed length of tubing.

5) The mixture is cooled rapidly and diverted to the sample collection vessel for liquid effluent analysis.

Method B

1) A solution of the dye or pyrotechnic and deionized water is prepared at a nominal concentration of 0.5 wt% respectively.

2) The feed solution is pressurized to approximately 27.2 MPa (4000 psi) along with a solution of 5 wt% hydrogen peroxide and deionized water.

3) The two solutions are then mixed at known flow rates at a pipe-tee before heating.

4) The mixture is heated in the feed heater line only and allowed to react with a known fluid temperature profile.

5) The mixture is rapidly cooled and diverted to the sample collection volume before the separator for liquid effluent analysis.

Depending on the objectives of the tests, the input solution and the effluent samples were analyzed for destruction and removal efficiencies (DRE's). Some samples were also examined for purgeable and extractable organics, metals, salts, and chloride and chlorate ions.

A more detailed description of the reactor capabilities and its operation is given elsewhere.[3]

Analytical Procedures

The DRE's for the dyes were determined by analyzing the feed and effluent for Total Organic Carbon (TOC) and for the concentration of the principal organic component, the dye itself, using scanning ultraviolet spectrophotometry. Scanning ultraviolet spectrophotometry was not done on the pyrotechnic sample.

TOC was analyzed by an Astro Inc. 2001 TOC analyzer at Sandia. This equipment works on the principle of chemical oxidation of the sample at 50°C by persulfate ion in the presence of ultraviolet light. The CO_2 produced is sparged from the solution and carried to a carbon dioxide analyzer. The signal from the analyzer is integrated and scaled relative to calibration samples. As a result, the effluent analysis may include not only the primary component, the dye or pyrotechnic, but any carbon-containing compounds that were not fully converted to CO_2 during processing. Total organic carbon can be directly related to the chemical oxygen demand, a value that is important in determining effluent suitability for discharge to the environment.

Analysis of the primary hazardous component, the dye itself, was conducted by Alpha Chemical and Biomedical Laboratories (ABCL), in Petaluma, CA, an analytical lab specializing in custom procedures. The method chosen was scanning visible/ultraviolet spectrophotometry. In this technique, a dye reference solution was prepared and the ultraviolet/visible spectrum was scanned to determine the absorption maximum for each dye. This sample was diluted to give concentrations of 0.5, 1.0, 1.5, and 3.0 ppm, and a curve of concentration versus absorbance at the UV maximum of each dye was constructed. The relative absorbance of the process effluent was then obtained and related to the concentration curve to obtain the concentration of dye in the effluent.

The destruction removal efficiency, DRE, is defined for our experiments as

$$\mathrm{DRE} = (\mathrm{TOC_{in}}/2 - \mathrm{TOC_{eff}})/(\mathrm{TOC_{in}}/2) \times 100 \qquad (1)$$

where $\mathrm{TOC_{in}}$ is the organic concentration of the feed and $\mathrm{TOC_{eff}}$ is the organic concentration of the effluent. The input concentration is divided by 2 because the oxidant and feed flowrates are equal (see the description of Method B). Comparison of DRE's are therefore based on total flowrate. DRE, based on the concentration of the dye itself from the ACBL tests, is similarly calculated, but the concentration of dye is substituted for TOC concentration.

Clayton Environmental Consultants, in Pleasanton, CA, analyzed an orange dye effluent sample from a Method B test for purgeable organics, extractable organics, and for nine metals in accordance with EPA 624, EPA 625, and EPA 200.7 procedures.

Metals in the effluent of the pyrotechnic were analyzed by spectrophotometric techniques using a Model 943 Orbeco analyzer. This equipment works by adding a reagent to the sample and recording the intensity of UV light passing through the resultant mixture. This intensity is then compared to a preestablished calibration curve for the particular metal of interest. Sulfate ion concentration was also determined this way. Sodium, potassium, and chloride ion concentration were determined by specific ion electrode; pH of the pyrotechnic effluent was also determined by a standard pH electrode. Specific ion electrodes record the emf between two electrodes developed by the electrostatic interaction of ions in an electrolyte. This emf is converted by a calibrated microprocessor to ppm concentration units. Chlorate ion concentration was measured using indirect iodometric titration.[4]

Experimental Accuracy

There are two main catagories of error that contribute to the overall accuracy of the experimental results presented in this report. Within these two main catagories there are several specific sources. One catagory involves equipment operation parameters such as temperature, flow rates, and sample collection techniques. The other is associated with precision and accuracy of the analytical methods used.

Operation of the MER is mostly automated, but there are design limitations governing the precision of its control. The isothermal section of the reactor is controlled in sections. The heat loss within one section is not perfectly uniform, but the heat addition method is fairly constant over each two-foot section. As a result, there is some variation over the length of the "isothermal" section of the reactor. Typically, this variation is ± 8°C from the average value. The accuracy of the thermocouples is ± 2.2°C or ± 0.75% of the reading, whichever is greater.

The flow rates of the oxidizer and waste are accurate to about 1% above 0.25 ml/s. At flow rates less than 0.25 ml/s, pulsing of the high pressure pumps begins to introduce some error in determining the flow due to leakage in the air driver section of the pumps. As a result, the accuracy in the flow rate, and therefore accuracy of the calculated residence times, degrades to ± 10% at low flow rates. For the test results presented here, the flow rates were always well above 0.25g/s.

Fluctuations in pressure during a test originate from two sources: (1) manual adjustment of the liquid level that can induce a pressure change of about ± 75 psi, and, (2) variations in inert gas flowrate that can induce a pressure fluctuation of about ± 25 psi. During sample collection, manual adjustment of the separator liquid level was not done, eliminating the first source of uncertainty. However, the second source of pressure variation, inert gas flowrate, could not be eliminated. Inert gas (either argon or nitrogen) was introduced by the compressor for safety reasons; the inert gas diluted excess oxygen preventing a build-up of pure oxygen in the separator region. Hence the pressure may fluctuate ± 25 psi during sample collection.

Additionally, pressure may fluctuate due to plugging of the reactor. Plugging, discussed in detail in the next section, is the agglomeration of inorganic salts or charred organic material to the reactor walls. Plugging may be intermittent or gradually escalating. In general, samples for DRE analysis are not taken during an escalation of system pressure.

Pressure is recorded by two different types of transducers, Teledyne-Taber 2205 transducers having an estimated accuracy of about ± 50 psi and Paroscientific 410k-101 having an estimated accuracy of ± 2 psi. All the Teledyne-Taber transducers are interfaced to a PC and any plots reported are done from Teledyne-Taber output.

Accuracy of the analytical methods is also an important consideration. The TOC measurements, done at Sandia using standard commercial equipment, are accurate to ± 2% full scale, except on the 0 - 10 ppm scale where the accuracy is reduced to ± 5 %. Chromium, nickel, and sulfate measurements done at Sandia are estimated to have an error less than ± 3%, ± 1.2%, and ± 1.7%, respectively. Only hexavalent chromium concentration is analyzed by the Orbeco spectrophotometric method. Chromium in the effluent in other oxidation states is not detected. Specific ion electrodes are calibrated by standard solutions. Accuracy is estimated to be ± 2%. Chlorate accuracy is limited by the accuracy that the titration can be performed and the background dissolved oxygen which in our case was about $\pm 1\times10^{-4}$ mole/liter (8 ppm).

For the scanning UV analysis performed by ACBL, the maximum standard error with 2σ confidence (95%) is estimated to be ± 0.17 ppm over the calibrated range of 0 to 3.0 ppm.

As discussed in the next section, no purgeable or extractable organics were found within the list specified by EPA 624 and 625. Detection limits are 40 ppb. Metals analysis by

Clayton is accurate to ± 1.3% for chromium concentration and to ± 0.03% for nickel concentration. Clayton analyzed for total chromium concentration.

RESULTS AND DISCUSSION

Orange Dye, Method A

Tests were conducted on the orange dye using Method A. Orange dye 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 TOC. The results are presented in Table 3.

Table 3
Destruction Efficiencies (based on TOC) for Orange Dye

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

Sample #	Temperature (°C)	TOC (ppm)	Residence Time (seconds)	Destruction Efficiency	Appearance
1	556	3.35	7.4	99.69	colorless
2	553	3.39	7.4	99.68	colorless
3	542	4.51	7.6	99.58	colorless
4	520	21.4	8.1	98.00	pale yellow
5	506	180	8.5	83.1	brown
6	484	247	9.2	76.9	brown/solids

Analysis of the primary hazardous component, the orange dye itself, results in the destruction efficiencies reported in Table 4. Calibration curves and details of the sample analysis are included in Appendix A. The orange dye is destroyed to at least 99.9% at all experimental conditions. Note that in Appendix A p.6 that the feed material is reported to be only 593 ppm instead of the 5000 ppm (0.5%) that was prepared (2100 ppm TOC). The ACBL system was set up to detect in the 0 - 3 ppm range and was not designed to extrapolate to large values and as a result is not likely to be very accurate.

Table 4
Destruction Efficiencies (Based on Spectrophotometry) for Orange Dye

Sample #	Temperature (°C)	Concentration (ppm)	Destruction Efficiency
1	556	<.5	>99.98
2	553	<.5	>99.98
3	542	<.5	>99.98
4	520	<.5	>99.98
5	506	0.9	99.96
6	484	2.2	99.91

At temperatures above 550 °C the orange dye is destroyed effectively. The total organic carbon that remains in the effluent at these temperatures is probably low molecular weight more stable organic species such as methanol, formic acid, and formaldehyde or single ring aromatics such as phenol.

These tests concluded with a shut down of the reactor that was the result of an overpressurization at the inlet section. It was determined upon cooling and dismantling that a plug of carbonaceous deposit had formed in the second and third heater sections. This deposit is the result of pyrolysis of the dye in the absence of oxidizer, producing a char that adheres to the reactor walls. These results indicate that thermal decomposition of the dye begins to occur near 350 °C, if no oxidizer is present. A slow, but steady, build up of this char will eventually clog a tubular reactor. These products cannot be removed from the reactor wall unless a mechanical honing operation is performed.

All dyes, Method B

In an attempt to avoid the reactor plugging and sample charring observed with test Method A, Method B was adopted for subsequent tests. Using Method B, all four dyes were run at the same conditions to generate large samples for complete effluent analysis. These conditions were chosen to produce high DREs. Samples were evaluated for TOC, dye concentration, metals, and salts at Sandia. The analysis of the primary hazardous component, the dye itself, was again done by ACBL Laboratories. Clayton Environmental Consultants of California also analyzed the orange dye for EPA 624 purgeable organics, EPA 625 extractable organics, and for nine metals in compliance with EPA 200.7 guidelines. The TOC results and reaction conditions are presented in Table 5.

Table 5
Destruction Efficiencies (based on TOC) for Four Dyes.

Oxidizer:	5 wt% hydrogen peroxide.
Flow Rate:	0.6 g/sec
Amount Processed:	3.7-7.5 liters.
Input Concentration:	Approximately 0.25 wt%.

Sample	Temperature (°C)	TOC$_{eff}$ (ppm)	TOC$_{in}$ (ppm)	Destruction Efficiency	Effluent Appearance
Orange	565	2.36	780	99.69%	colorless
Red	560	4.11	936	99.56%	colorless
Blue	565	3.74	1232	99.69%	colorless
Green	561	2.65	819	99.67%	pale yellow

Residence times at the reported temperature for the different tests are approximately 10 seconds. This residence time is approximate since density, and therefore flow velocity, vary as the fluid reaches the maximum temperature.

The residence time, as a function of position in the flow reactor are shown in Figures 3 and 4. In Figure 3, the fluid temperature is shown as a function of axial distance along the reactor. Knowing the density as a function of pressure and temperature, the residence time is estimated in Figure 4 by integrating the velocity from one experimental temperature point to the next. Approximately 10 seconds of residence time occurs at a temperature of 560°C. Additionally, about 5 seconds of residence time occurs between 480°C to 560°C. There is probably some contribution to the overall oxidation reaction occurring in the lower temperature region.

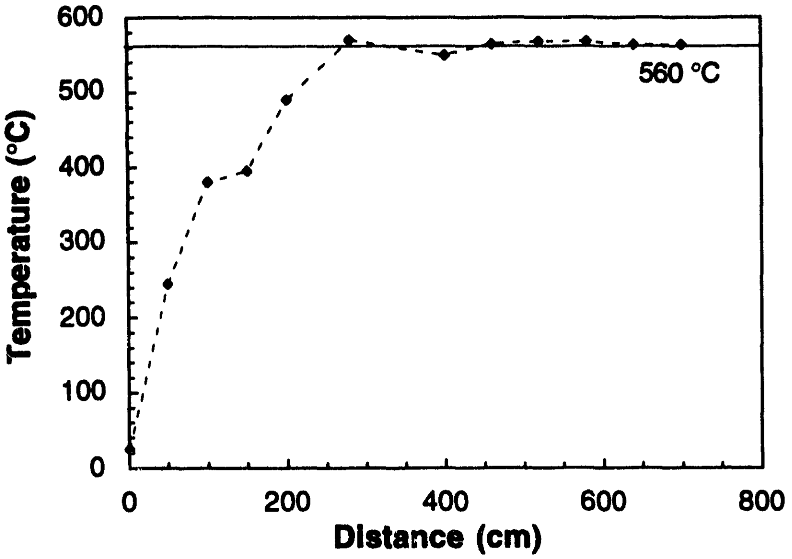

Figure 3: Fluid temperature as a function position along the reactor axis.

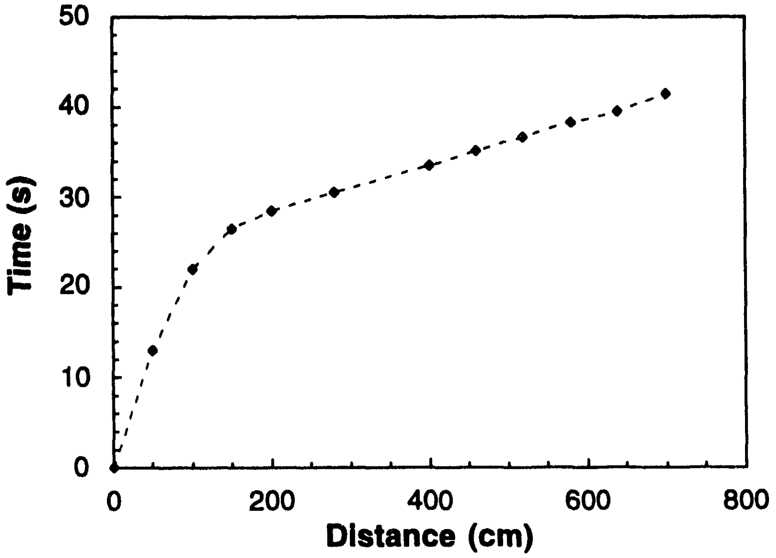

Figure 4: Estimated time as a function position along the reactor.

At maximum process temperatures of 560°C using Method B, the dyes are destroyed to >99% without the pyrolysis problems discovered in Method A. Analysis of the primary hazardous components, the specific dye molecules, by ACBL using the same scanning ultraviolet spectrophotometric technique indicates that all dyes, except the green dye, are destroyed to below the detection limit of the technique, 0.5 ppm. The amount of green dye found in the sample was 2.6 ppm and is believed to be in error due to the interference of products from mild corrosion of the reactor. The pale yellow appearance present in the effluent is probably chromate ion, which could be affecting the results.

When operating using Method B, the processing tests were terminated due to plugging within the flow reactor. White salt deposits built up in the preheat section of the reactor and in the case of the red, green, and orange dye, resulted in complete plugging. In the case of the blue dye, a pressure drop developed between the pumps and the effluent pressure letdown valve, but did not cause catastrophic plugging over four or more hours of operation. Figures 5 and 6 show how the pressure builds up with time for the red and blue dyes. Subsequent analysis of the white powder that was removed from the reactor after cooldown indicated it was anhydrous sodium sulfate that was precipitated homogeneously from the fluid as it was heated.

The sulfur in the organic dyes is oxidized under these conditions to form sulfate ion. Because these dyes are principally sodium salts of organic acids, the sulfate is balanced by the sodium counter ion forming sodium sulfate and by H^+ forming sulfuric acid. In general, the Na^+ content of the dyes is insufficient to balance the sulfate product completely and as a result the effluents are acidic. Some sulfate remains in the reactor as Na_2SO_4 and the rest emerges in the effluent as H_2SO_4.

Analysis of the effluent by specific ion electrode indicated that approximately 97% of the initial sodium remained in the reactor. As discussed in detail in the pilot plant conceptual design report,[1] sodium sulfate is a salt that precipitates out of the single dense gas supercritical water phase and adheres to the reactor walls. Complete plugging eventually occurred with the red dye at 1.8 hours.

Process flow analyses[1] indicate that after oxidation, the salt loading for the orange, green, and red dye, is approximately 30% of the initial feed concentration, whereas for the blue dye, it was 5%. These differences in concentration explain the lack of catastrophic plugging over the 4+ hours of operation with the blue dye.

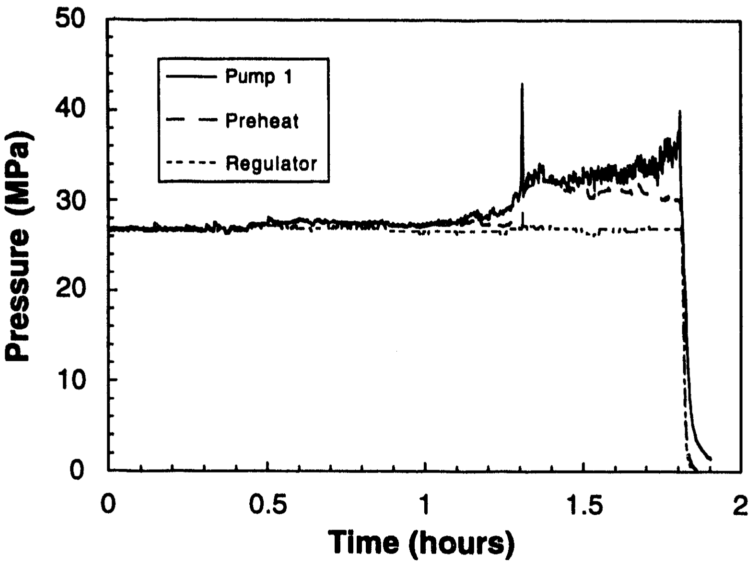

Figure 5. Pressure traces for the red dye. The pressure upstream of the plug escalates to 44 MPa at 1.3 hours but rapidly decreases a short time thereafter. Presumably, the salt bridge forming the plug could not support the pressure. However, gradual escalation continues until the test is terminated.

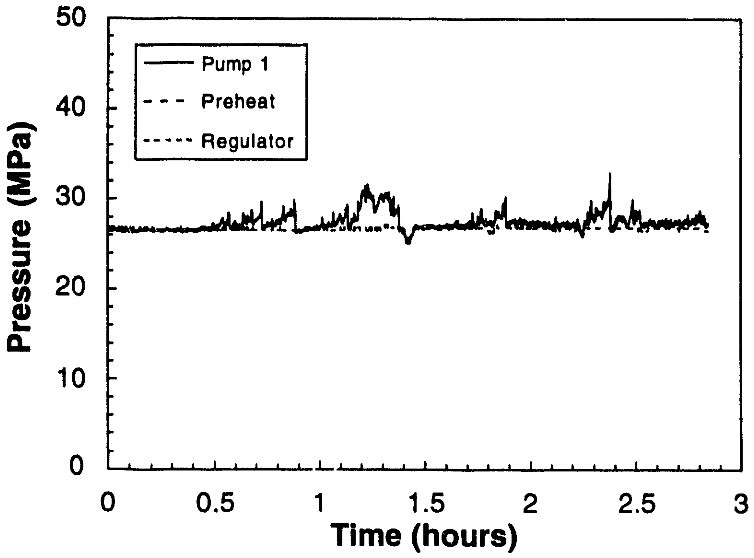

Figure 6. Pressure traces for the blue dye. Although plugging is evident, pressure escalation is not seen.

Solutions to the salt plugging problem are discussed in detail in the pilot plant conceptual design report. Briefly, these methods are: (1) a tubular configured reactor can be periodically flushed with 300°C water to remove any salt build-up; (2) the salt can be prevented from contacting the walls of a tubular reactor by a transpirationally-induced boundary layer of subcritical fluid; and (3) oxidation can occur in a broader, vertically oriented reactor and the salt can be separated by gravity.

In addition, work with "sticky" salts, indicates that it is possible to keep such salts in solution during oxidation of the organic material by increasing the operating pressure. This has been demonstrated on the MER with NaCl. In Figure 7, the effluent concentration of Na^+ is plotted as a function of temperature at two different MER system pressures. At 420°C and 28.6 MPa (4200 psi), the Na^+ concentration begins to drop from 2000 ppm to 50 ppm at 500°C. At 49.7 MPa (7300 psi), this drop begins at 500°C, and even at 550°C the Na^+ concentration has only decreased to 800 ppm. Presumably, increasing the pressure further or operating below 500°C would keep the salt in solution during destruction of organic solutions with Na^+ and Cl^- constituents.

We have found that there is a similar effect on Na_2SO_4 solubility upon changing operating pressure from 25 MPa to 50 MPa, but this effect is not as dramatic as for NaCl and may not be an effective method at 550 °C for Na_2SO_4. These results are shown in Figure 8.

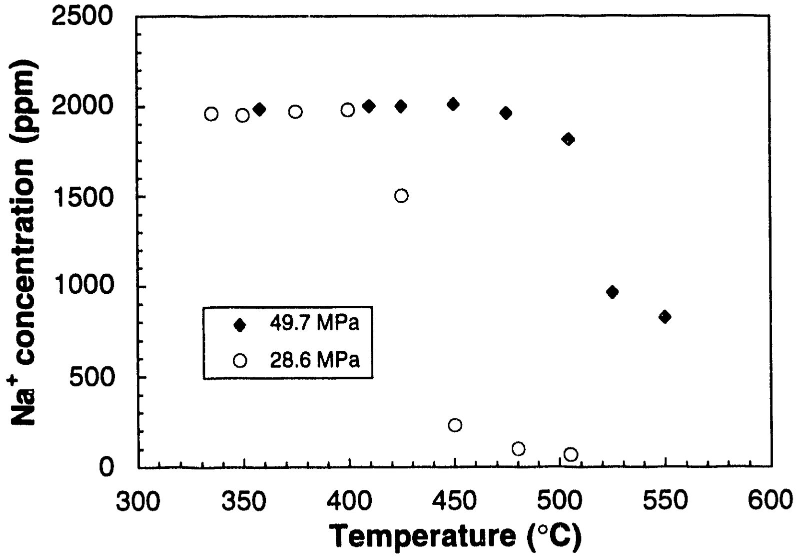

Figure 7. Na^+ concentration emerging from the reactor at 28.6 MPa (4200 psi) and 49.7 MPa (7300 psi) from 0.5 wt% NaCl feed solution .

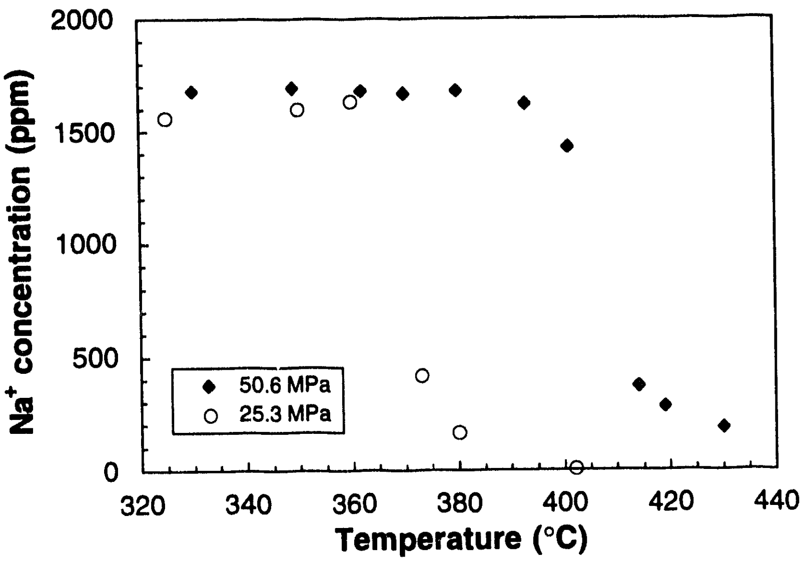

Figure 8. Na^+ concentration emerging from the reactor at 25.3 MPa (4200 psi) and 50.6 MPa (7300 psi) from a 0.5 wt% Na_2SO_4 feed solution.

Sewer Discharge Analysis/Reactor Corrosion Concerns

A wastewater quality analysis was done on the orange dye effluent by Clayton Environmental Consultants of California. Both EPA 624 Purgeable Organics and EPA 625 Extractable Organics were done resulting in no detectable amounts of these organic compounds. Nine metals were analyzed in accordance with EPA 200.7 with two appearing at levels slightly higher than would be permissible for Sandia to discharge to the City of Livermore sewer. Nickel was at 1.1 ppm (0.61 permissible) and chromium was at 1.2 ppm (0.62 permissible). The complete analysis is contained in Appendix B.

As discussed in the pilot plant conceptual design report, the processed effluent is expected to be polished by a water purifier, such as an ion exchange column, and then recirculated as feedwater (and not discharged to the environment). This is one of the advantages of this technology over competitive technologies for the destruction of military spotting dyes and pyrotechnic smokes - any undestroyed organic remains in the recirculating water and is not discharged to the environment.

Appearance of metals in the effluent is primarily a corrosion concern. Pretreatment with caustic soda, NaOH, is expected to reduce the concentration of metals in the effluent. Resolution of the corrosion issue is planned in Phase II of the program.

It is possible from the bench scale data, to estimate the corrosion rate of the pilot plant reactor having a throughput of 1000 gal/day. In order to do this a number of assumptions must be made, as discussed below.

Assumptions

1. The corrosion rate is independent of initial dye concentration. Experimentally, the initial dye concentration was 0.25 wt%. The design requirement is 5 wt% for the pilot plant. The effect of dye concentration on corrosion rate will be studied in Phase II.

2. Corrosion is uniform over the hottest sections of the reactor. Investigation of positional corrosion on feeds other than the dyes indicates that corrosion is highly positional.[5] Figure 9 and 10 show that it is also radially nonuniform. In the figures, a portion of the reactor in the feed heater that operates at a skin temperature of about 650°C is shown, after dismantling and sectioning. The micrographs indicate about 4 mils attack that is not circumferentially uniform. Unfortunately, it is difficult to correlate this corrosion with the above analysis because this section was exposed to many feedstocks and operating conditions; it has an integrated history of corrosion. It illustrates that corrosion can easily be nonuniform.

3. The current corrosion rate is independent of the integrated history of reactor operation of several hundred hours with a variety of feed streams.

4. The corrosion rate does not depend on oxidant.

5. The concentration of chromium in the effluent of a larger scale system will also be 1 ppm. A similarly scaled system at 1000 gallons/day would have an inside surface to volume ratio 5 times less than the test reactor used here. It is likey that the decreased amount of exposed inner surface of the reactor will result in lower corrosion rates.

Estimation of Corrosion Rate

Assume that the chromium content of the effluent pilot plant tube is 1.0 ppm. Assume further that material leached of its chromium has no structural value. The corrosion rate, r, can be expressed as a linear dimension of reactor wall lost per unit volume processed, such that

$$r = V_v/A = m_c/(\phi\rho)A. \qquad (2)$$

Here V_v is the volumetric corrosion rate of the reactor - it has the units of volume of metal per unit volume of effluent, A is the surface area of the reactor exposed to contact with the reacting fluid, m_c is the mass of chromium removed from the wall per unit volume effluent (assumed 1.0 mg/l), ρ is the specific gravity of inconel 625, 8.2 g/cm^3, and ϕ is the mass fraction of chromium in inconel, $\phi = 21.5\%$.

In the pilot plant design, the ID of the tubular configuration is 3.411 cm (1.343 inch). The reactor section that is maintained at a temperature in excess of 550 °C is approximately 12.7 meters in length. If we assume that the removal of chromium occurs uniformly over this

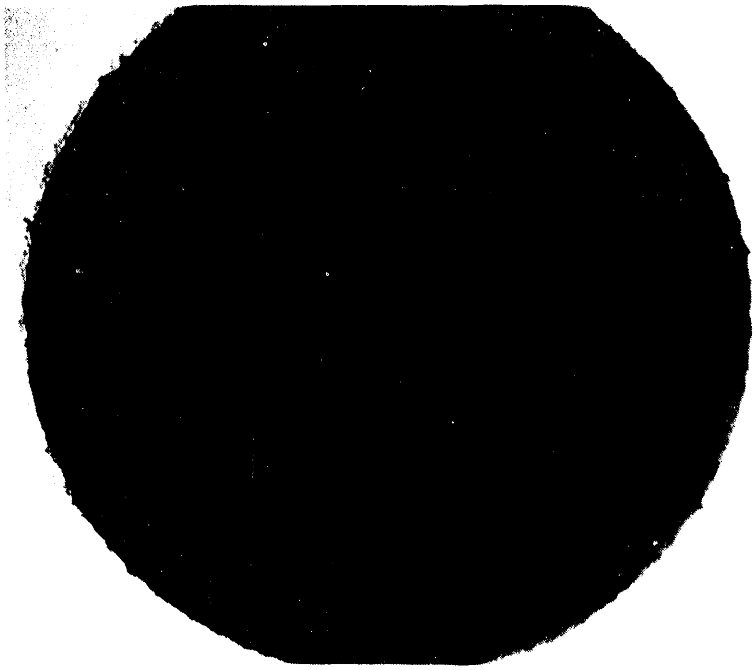

Figure 9. Micrograph of a section of the MER tubing. Scale = 20x.

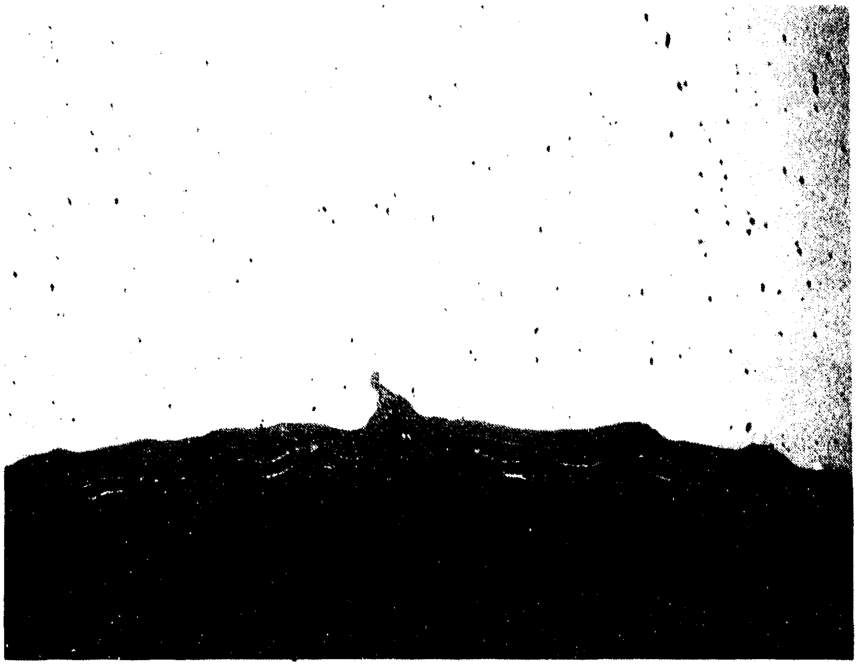

Figure 10. Enlargement of Figure 9. Scale = 100x.

surface, then A in Eq. 2 is 1.36 m^2. Substituting this value for the area into Eq. 1 yields the material removal rate, $r = 4.27 \times 10^{-11}$ cm/l = 6.3×10^{-5} mils/gallon.

This corrosion rate is large and would result in 23 mils of reactor destroyed in one year at 1000 gallon/day throughput. This is about 20 times the corrosion rate in typical steam generators, for example. However, the primary function of a steam generator is to transfer energy - wall thicknesses are minimized as much as possible. The primary function of the tubular reactor is to provide a containment where the destruction of waste can proceed, therefore a corrosion rate of 20 mils/year may not be unacceptable. However, it is our judgment that it is excessive.

It is unknown at this time whether the bulk of the corrosion occurs at a particular temperature and solution composition, or if it is more or less uniformly distributed as the flow composition evolves along the length of the reactor (as assumed for illustrative purposes in the description above).

A series of tests were done to begin to develop an understanding of the corrosion phenomena at different conditions: (a) with pure deionized water; (b) with pure deionized water with 5 wt% hydrogen peroxide concentration; (c) and with pure deionized water at 10 wt% hydrogen peroxide concentration. No chromium was evident in the effluent, down to a detection limit of 0.1 ppm with pure water as the feed. However, at 5 wt% approximately 2 ppm of chromium appeared in the effluent and at 10 wt%, the concentration of chromium increased to 4 ppm. Nickel was not detectable in the effluent whereas molybdenum was detectable at concentrations of 0.7 ppm for the 10 wt% solution of peroxide.

Pyrotechnic: Results and Discussion Using Test Method B

The pyrotechnic was run at the same conditions, 560°C and 27.2 MPa (4000 psi) using Method B. Table 6 summarizes the results.

It is important to note that there is a significant inconsistency between the calculated composition of the pyrotechnic slurry and the values measured in Table 6. As shipped, the composition of the smoke slurry was 1.0 lb added to 1 gallon of water . This slurry was diluted by precisely a factor of twenty to produce a slurry with 0.535 wt% of pyrotechnic material. Based on the known composition and formulas of the organic materials in the slurry, this slurry should contain 0.248 wt% (2480 ppm) TOC, implying the original undiluted slurry at 1lb in 1 gallon contains 210.5 g TOC added to 1 gallon of water. The observed value from our analysis of the diluted sample was 310 ppm, a factor of eight less organic than the feed should contain.

Our initial suspicion was that the samples, as shipped, had not been properly prepared and that they were much more dilute than indicated by Pine Bluff Arsenal's documentation. If this were the case, all of the components of the pyrotechnic should be too dilute. The calculated concentration of potassium ion in the 20x diluted feed is 538.4 ppm and the measured value was 539 (see Table 6). This clearly shows that at least the correct amount of pyrotechnic was initially added to the slurries and that Pine Bluff had not erred.

Another possibility is that the chlorate ion in the slurry had oxidized the organic dyes during storage. The calculated amount of chlorate ion in the slurry, as shipped, is approximately 0.275 mole/liter. The observed value of 0.29 mole/liter is in good agreement and indicates that all of the chlorate is still present as chlorate and had not reacted.

Another possible explanation for the measured low carbon content of the feed material is that the feed slurry was not well mixed when diluted at Sandia, and that the insoluble dye powders had settled to the bottom of the shipping container. This would produce proper values for the soluble material such as $KClO_3$, but poor values for organic carbon. Because of this concern, the TOC analysis was repeated on a very well-mixed sample taken directly from the original shipping container. A TOC value of 7140 was obtained. The calculated value for the feed is 49600 ppm. Even if mixing was incomplete the soluble organic carbon from the lactose alone would produce a value of 8100 ppm.

We do observe that the insoluble dye powder in the analytical sample is effectively oxidized by the TOC analyzer. This was easily determined by the visual appearance of the input and effluent to the analytical system. The particulate green dye could be seen in the sample as a fine gray/green powder, but the effluent from the analyzer after oxidizing the slurry was perfectly clear. The time evolution of the analyzer signal during an analytical run appeared normal, also indicating complete oxidation of all the organic carbon in the sample. The inorganic carbon in the sample gave a value near that expected for the $MgCO_3$.

At this time we have no explanation for the lack of agreement between the calculated composition of the smoke slurry and the TOC values obtained for the feed. Additional analytical work is needed to solve this inconsistency. Here we report the DRE on the organic component of the smoke based only on the measured carbon in the feed and not on the assumed concentration based on the documentation provided and the known sample dilution.

Discussion

Like the dyes, the pyrotechnic was effectively destroyed under the experimental conditions employed. A reduced concentration of pyrotechnic was used, 0.5 wt%, due to the large expected corrosion. As anticipated, high corrosion rates were observed. The 10 ppm chromium detected in the effluent is 10 times the concentration of chromium that was measured in the effluent from the orange dye processing. Although there are still some problems associated with an accurate description of the chemical composition of the pyrotechnic, the destruction of the organic material was very effective, as was the destruction of the ClO_3^- ion.

Table 6
Summary of experimental conditions and effluent analysis.

Oxidizer:	5 wt% hydrogen peroxide.
Flow Rate:	0.6 g/sec.
Amount Processed:	2 liters.
Input Concentration:	0.5% total pyrotechnic by weight 310.0 ppm TOC (measured)
Appearance:	dark green.
Residence time at 560°C:	approximately 10 seconds.

Parameter	Result
Temperature (°C)	560°C
TOC_{out}(ppm)	1.38
TOC_{in}(ppm)	310.0
DRE	99.1
Nickel(ppm)	n.d.
Chromium(ppm)	10.0
Appearance	intense yellow
pH_{in}	7.56
pH_{eff}	3.50
K^{+}_{in} (ppm)	539.0
K^{+}_{eff} (ppm)	42.0
Cl^{-}_{in} (ppm)	16.7
Cl^{-}_{eff} ppm)	73.1
Na^{+}_{in} (ppm)	4.4
Na^{+}_{eff} (ppm)	0.2
$SO_4^{2-}{}_{in}$ (ppm)	n.d.
$SO_4^{2-}{}_{eff}$ (ppm)	n.d.
$ClO_3^{-}{}_{in}$ (ppm)	1250
$ClO_3^{-}{}_{eff}$ (ppm)	<8

n.d. - none detected

At a peak reactor temperature of 560°C, the effluent was collected for approximately two hours without an escalation of system pressure as occurred for the dyes. However, note the small amount of potassium or chloride in the effluent, indicating that salt was accumulating in the reactor. Presumably plugging did not occur because of the reduced initial concentration of the pyrotechnic in the feed stream. Increased concentrations of the pyrotechnic or process times would probably have resulted in plugging by potassium chloride, KCl. Potassium ion concentration in the effluent is less than 8% of the initial feed concentration. Based on the results we estimate that the accumulating potassium chloride or other potassium salts in the reactor will eventually cause a plug as in the dye experiments.

SUMMARY AND CONCLUSIONS

At temperatures above 550°C the dyes, pyrotechnic, and partial oxidation products were destroyed to a minimum of 99.1% DRE in 10 seconds. Any surviving organic carbon remained in the effluent and could have been recirculated as new feed and not discharged to the environment.

Destruction of the toxic components of the dyes resulted in plugging and fouling of the reactor and preferential leaching of chromium from the reactor tubing. When the organic dye was heated above 350°C before introduction of oxidant, it pyrolized, 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 this problem.

Destruction of the organic component of the dyes 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 annhydrous sodium sulfate, Na_2SO_4.

When processing the green smoke pyrotechnic, destruction of the organic component did not conclude with a shut-down of the reactor due to escalating pressure, although potassium salts were accumulating in the reactor. There is little doubt that deposits in the form of potassium chloride accumulated and would have plugged the reactor given sufficient time. Sufficient time was not allotted due to the bright yellow color of the effluent - a color indicative of dissolved chromium in the form of chromate ion.

As discussed in detail in the pilot plant conceptual design, plugs can be cleared "on-line" by lowering the temperature to 300-380°C where the solubility of Na_2SO_4 in water increases from 0.5 wt% at 380 °C to 20 wt% at 350 °C. However, this would be a cyclic operation that may have to occur every 10 minutes at the pilot plant target concentration of 5 wt% feed.

Leaching corrosion occurred during destruction of the dye and pyrotechnic. Neither effluent could have been discharged to the City of Livermore sewer due to chromium concentration in the effluent (1.1 ppm). The concentration of chromium in the pyrotechnic effluent was ten times that in the dye effluent. It is unknown how much of the corrosion problem is due to excess oxidizer. A minimum of 100% excess oxygen was used for all tests. It appears from tests with just hydrogen peroxide and no organic that hydrogen peroxide alone can leach chromium from the reactor.

RECOMMENDATIONS

The principal result of Phase I of this technology development and implementation project was a demonstration that SCWO technology destroys the hazardous organic and inorganic constituents of the dyes and pyrotechnic. We have identified the range of temperatures that the smoke and dyes oxidize with good efficiency and have highlighted process difficulties encountered in destroying the compounds. In addition, this report contains information to be used to identify and develop design parameters.

To overcome the plugging problems experienced in these tests, we propose four design options. These are:

1. Process the material in a reactor configured vertically rather than in a horizontal tube, so that salt formed in the vessel is continuously removed. MODAR, a private company developing SCWO for general application to waste treatment, has patented a reactor design that operates on this principle.[6]

2. Employ a double-walled reactor where the reacting waste is isolated from the outer walls of the reactor by an active boundary layer. In this design, a transpiration tube inner wall, which allows flow of clean supercritical water through microscopic holes, separates the pressure-containing outer thick jacket from the reacting fluid. The boundary layer that is formed on the inside of the inner wall prevents salt deposits from attaching to the surface or corrosive fluid from making contact with the tubing. Aerojet Corporation has invented and developed this technology for applications in cooling parts of rocket motors.

3. Use a tubular configured reactor where the pressure is raised to 2 to 5 times the critical pressure to increase salt solubility at supercritical temperatures.

4. Develop an operational scheme where a number of input tubes feed one reactor. As one tube begins to become restricted, the feed is switched to the next tube and the deposits are removed from the first by isolation, cooling, and rinsing. A manifold of feed tubes is cycled.

To alleviate corrosion, the munition should be treated with caustic soda for design choices (1), (3), and (4), whereas corrosion should be minimal for design choice 2).

Resolution of the issues raised in this report, and in the conceptual design report, will occur simultaneously with design and construction of the production prototype, in accordance with the existing program management plan (PMP).

This series of experiments has identified two technical barriers that must be overcome: system plugging due to inorganic salts and corrosion of the reactor walls. There are a variety of possible solutions to these problems, only some of which are mentioned in this report. It is likely that other ideas will be generated by Sandia and others working in this technology over the next year. Phase II of this project will serve to determine which methods will best suit the immediate problem of salt deposition during dye processing. The corrosion problem has not been as well characterized and will need further study before the severity of this concern is quantified.

These Phase I tests have shown that SCWO exhibits a potential for destroying military smokes, dyes, and pyrotechnics. The development of large-scale equipment for the demilitarization of these munitions using SCWO is feasible. Because there are currently no other hazardous material treatment methods that show promise for handling these materials in an environmentally secure manner, it is appropriate to proceed with evaluation and development of SCWO technology for these special demilitarization purposes.

To have confidence that the pilot plant will work as intended at MCAAP (that is, to eliminate the risk of plugging by insoluble salts) all the design options should be experimentally evaluated prior to commitment to a final design. Contractors capable of supplying equipment that meets our specifications for the different design options above need to be identified. This equipment should then be evaluated based on characteristics of the materials to be processed in this program. Concurrently, one of Sandia's SCWO process facilities should be modified to operate to 100 MPa (5 times the critical pressure of water) and the destruction of the dyes and pyrotechnic evaluated at these pressures.

One design should then be chosen for pilot plant scale-up. The experimental tasks would then be to: (1) destroy all dyes and pyrotechnic at concentrations of 5 wt%, (2) evaluate the composition of the gaseous effluent, (3) evaluate liquid and solid effluent for TOC concentration, purgeable and extractable and other organics as specified by the Oklahoma State Department of Health, and for metals, and (4) neutralize the wastes and reevaluate all effluents.

Acknowledgment

Valuable discussions with Steve Buelow and his team (LANL) and with Dave Hazlebeck and his team (General Atomics) influenced our research into "sticky" salts. The authors thank Crane Robinson of ARDEC for his assistance in directing the development of this project and for his technical support. This work was supported by the U.S. Army Armament Research, Development, and Engineering Center and the Memorandum of Understanding between the Department of Defense and the Department of Energy for the Conduct of a Cooperative Research and Development Program.

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Appendix A

The UV analysis of the residual dyes is contained in this appendix. The following mapping between ACBL samples in the appendix and results in the report will facilitate understanding:

ACBL sample #	Report Sample #
4676	Table 2, #1
4677	Table 2, #2
4679	Table 2, #3
4680	Table 2, #4
4681	Table 2, #5
4682	Table 2, #6
4667	Table 3, orange
4668	Table 3, red
4669	Table 3, green
4670	Table 3, blue

ALPHA CHEMICAL & BIOMEDICAL LABORATORIES, Inc.

Joe E. Hodgkins, Ph.D.
Director

March 9, 1993

COMBUSTION RESEARCH FACILITY
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REPORT
UV ANALYSIS OF RESIDUAL DYES

<u>Sample Identification</u>:

ACBL Sample # 4659 : Standard #1, 0.1073 g "orange" in 100 ml.
\# 4660 : Standard #2, 1.00 ml of Std. #1 in 100 ml.
\# 4661 : Standard #3, 0.09549 g "red" in 100 ml.
\# 4662 : Standard #4, 1.00 ml #3 in 100 ml.
\# 4663 : Standard #5, 0.1001 g "green" in 100 ml.
\# 4664 : Standard #6, 1.00 ml #5 in 100 ml.
\# 4665 : Standard #7, 0.1031 g "blue" in 100 ml.
\# 4666 : Standard #8, 1.00 ml #7 in 100 ml.
\# 4667 - 4670: Test Process Samples # 9, 10, 11, 12.
\# 4671 - 4674: Pure Dyes # 13, 14, 15, 16. HOLD.
\# 4675 : Process Input Sample # 17.
\# 4676 - 4682: Process Output Samples # 18-24.

Received in Lab : 02/19/93.

<u>Analysis</u>:

Individual reference solutions of four dyes (orange, red, green and blue) were supplied by the client (ACBL Samples # 4659-4666). The ultraviolet spectrum of each was measured and the UV maximum of each dye determined to be 475, 525, 420 and 625 nm, respectively. The reference solutions (# 4660, # 4662, # 4664 and # 4666) were diluted to give concentrations 0.5, 1.0, 1.5 and 3.0 ppm, and the UV spectrum of each solution was measured. Calibration graphs were constructed and a detection limit study for each 0.5 ppm standard was carried out.

Dye Calibration Graphs and Detection Limit Studies:

1. ORANGE DYE: UV at 475 nm

LEVEL	CONCENTRATION	ABSORBANCE
1	0.0 ppm	0.000
2	0.5 ppm	0.0170
3	1.0 ppm	0.032
4	1.5 ppm	0.050
5	3.1 ppm	0.101

Correlation coefficient = 0.999

ORANGE DYE DETECTION LIMIT STUDY (concentration = 0.5 ppm)

RUN	ABSORBANCE
1	0.016
2	0.019
3	0.017
4	0.016
5	0.020
6	0.017
7	0.016

AVERAGE ABSORBANCE = 0.0170

RSD = 9.4%

2. RED DYE: UV at 525 nm

LEVEL	CONCENTRATION	ABSORBANCE
1	0.0 ppm	0.000
2	0.5 ppm	0.0126
3	1.0 ppm	0.023
4	1.5 ppm	0.033
5	3.0 ppm	0.066

Correlation coefficient = 0.997.

RED DYE DETECTION LIMIT STUDY (0.5 ppm)

RUN	ABSORBANCE
1	0.013
2	0.012
3	0.011
4	0.014
5	0.013
6	0.013
7	0.012

AVERAGE ABSORBANCE = 0.0126

RSD = 7.7%.

3. GREEN DYE: UV at 420 nm

LEVEL	CONCENTRATION	ABSORBANCE
1	0.0 ppm	0.000
2	0.5 ppm	0.0126
3	1.0 ppm	0.026
4	1.5 ppm	0.036
5	3.1 ppm	0.069

Correlation coefficient = 0.996

GREEN DYE DETECTION LIMIT STUDY (0.5 ppm)

RUN	ABSORBANCE
1	0.000
2	0.013
3	0.013
4	0.013
5	0.012
6	0.012
7	0.013

AVERAGE ABSORBANCE = 0.0126.

RSD = 4.2%.

4. BLUE DYE: UV at 625 nm

LEVEL	CONCENTRATION	ABSORBANCE
1	0.0 ppm	0.000
2	0.5 ppm	0.0203
3	1.0 ppm	0.041
4	1.5 ppm	0.050
5	3.1 ppm	0.105

Correlation coefficient = 0.994

BLUE DYE DETECTION LIMIT STUDY (0.5 ppm)

RUN	ABSORBANCE
1	0.019
2	0.023
3	0.020
4	0.019
5	0.020
6	0.021
7	0.020

AVERAGE ABSORBANCE = 0.0203

RSD = 6.8%

Analysis of Test Process Samples:

ACBL SAMPLE #	SANDIA #	TYPE of DYE	FOUND, ppm
4667	9	ORANGE	< 0.5
4668	10	RED	< 0.5
4669	11	GREEN	2.6
4670	12	BLUE	< 0.5

Analysis of Process Samples for "Orange" Dye:

ACBL SAMPLE #	SANDIA #	TYPE of DYE	FOUND, ppm
4675	17	ORANGE	**593**
4676	18	ORANGE	< 0.5
4677	19	ORANGE	< 0.5
4678	20	ORANGE	< 0.5
4679	21	ORANGE	< 0.5
4680	22	ORANGE	< 0.5
4681	23	ORANGE	**0.9**
4682	24	ORANGE	**2.2**

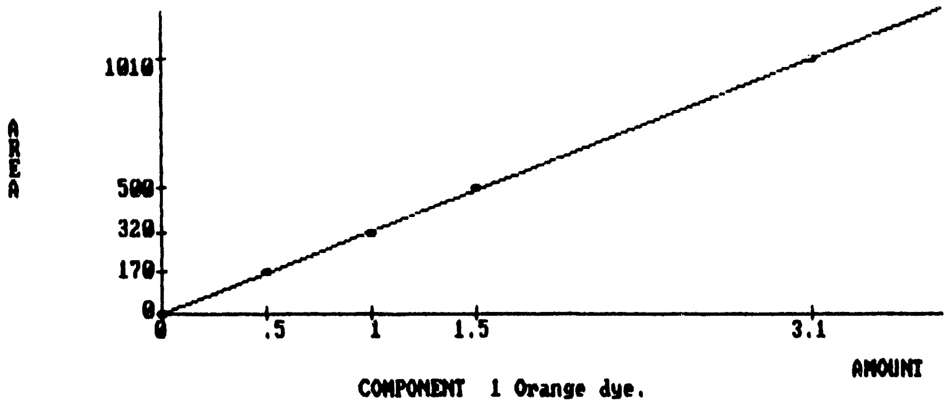
Detection Limit = 0.5 ppm.

J. Ackrell, Ph.D.
Analytical Director

Enclosures (Dye calibration graphs)
SANDIA.RPT

```
Method recorded in file:  D:4660.MET
```

```
                    Method 4660
      Sample Orange dye by UV at 475 nm.
                   Operator JA
                Run date 03/05/93
          Printed on 03-05-1993 AT 05:40:25
      -----------------------------------------
```



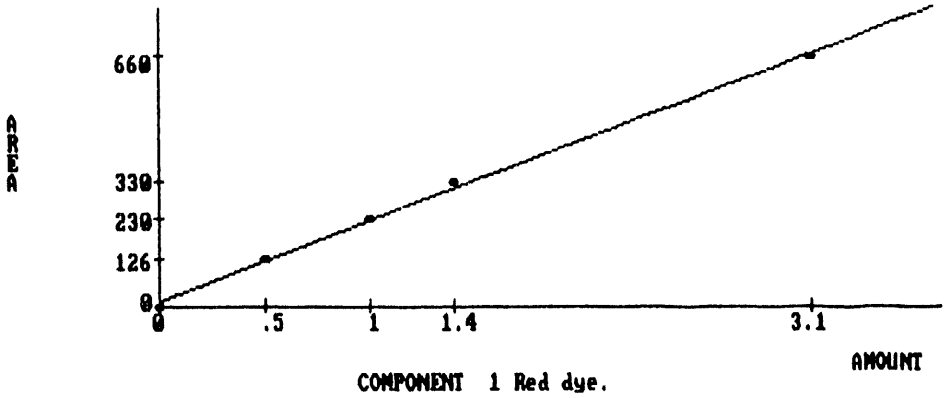
```
                Component  1  Orange dye.

            LEVEL     AMOUNT          AREA
            -----   ----------     ----------
              1        0.0000             0
              2        0.5000           170
              3        1.0000           320
              4        1.5000           500
              5        3.1000          1010

                                                                    STANDARD
                                                  CORRELATION       ERROR OF
       Y =      SLOPE     *     X    +  INTERCEPT COEFFICIENT       ESTIMATE
 -------------------------------------------------  -----------     --------
  AREA   = 3.2569D+02 * AMOUNT + 2.6605D+00            0.9997          5.997
 AMOUNT  = 3.0695D-03 *  AREA  +-7.8018D-03            0.9997          0.018
```

```
Method recorded in file:  D:4662.MET
```

```
                          Method 4662
                Sample Red dye by UV at 525 nm.
                          Operator JA
                       Run date 03/05/93
               Printed on 03-05-1993 AT 05:41:54
               ---------------------------------
```



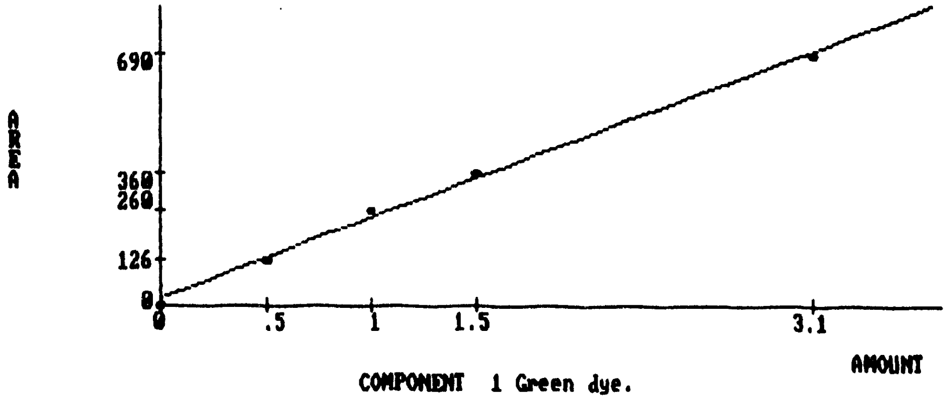
```
                      Component  1  Red dye.

                 LEVEL    AMOUNT        AREA
                 -----  ----------  ----------
                   1      0.0000           0
                   2      0.5000         126
                   3      1.0000         230
                   4      1.4000         330
                   5      3.1000         660

                                                                   STANDARD
                                                   CORRELATION     ERROR OF
      Y =      SLOPE     *     X    +   INTERCEPT  COEFFICIENT     ESTIMATE
------------------------------------------------   -----------     --------
  AREA   = 2.1100D+02 * AMOUNT + 1.6004D+01             0.9971       12.110
 AMOUNT  = 4.7256D-03 *  AREA  +-7.2123D-02             0.9971        0.057
```

```
Method recorded in file:  D:4664.MET
```

```
                    Method 4664
      Sample Green dye by UV at 420 nm.
                   Operator JA
                Run date 03/05/93
        Printed on 03-05-1993 AT 05:34:05
      -----------------------------------------
```



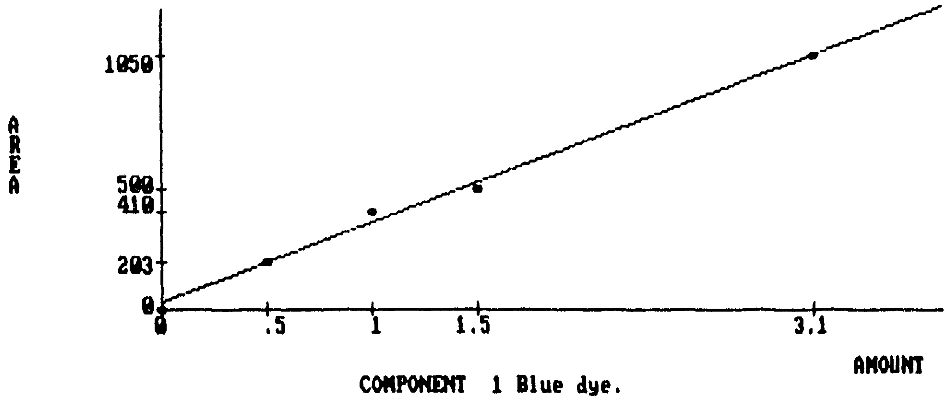
```
                 Component  1  Green dye.

              LEVEL     AMOUNT          AREA
              -----   -----------   -----------
                1        0.0000             0
                2        0.5000           126
                3        1.0000           260
                4        1.5000           360
                5        3.1000           690

                                                                    STANDARD
                                                   CORRELATION      ERROR OF
     Y =      SLOPE    *      X     +   INTERCEPT  COEFFICIENT      ESTIMATE
 ----------------------------------------------   -------------    --------
  AREA   = 2.2055D+02 * AMOUNT  + 1.8128D+01          0.9962          14.499
 AMOUNT  = 4.5169D-03 *  AREA   +-7.7251D-02          0.9962           0.066
```

```
Method recorded in file:  D:4666.MET
```

```
              Method 4666
Sample Blue dye by UV at 625 nm.
              Operator JA
           Run date 03/05/93
Printed on 03-05-1993 AT 05:37:13
-----------------------------------------
```



```
                      Component  1  Blue dye.

                   LEVEL    AMOUNT        AREA
                   -----  ----------   ----------
                     1      0.0000             0
                     2      0.5000           203
                     3      1.0000           410
                     4      1.5000           500
                     5      3.1000          1050

                                                                  STANDARD
                                                 CORRELATION      ERROR OF
     Y =      SLOPE     *     X     +  INTERCEPT  COEFFICIENT     ESTIMATE
-------------------------------------------------  -------------  --------
  AREA   = 3.3127D+02 * AMOUNT + 2.8450D+01          0.9935        28.597
 AMOUNT  = 2.9990D-03 *  AREA  +-7.7354D-02          0.9935         0.086
```

Appendix B

The analysis on the orange dye by Clayton Environmental Consultants is contained in this appendix.

Western Operations

1252 Quarry Lane
P.O. Box 9019
Pleasanton, CA 94566
(510) 426-2600
Fax (510) 426-0106

Clayton
ENVIRONMENTAL
CONSULTANTS

May 13, 1993

Mr. Ken Nunez
SANDIA NATIONAL LABORATORIES
Division 8542
P.O. Box 969
Livermore, CA 94551-0969

Client Ref. LB-6193
Clayton Project No. 93050.86

Dear Mr. Nunez:

Attached is our analytical laboratory report for the samples received on May 10, 1993. Results for metals and EPA method 624 were verbally reported on May 12, 1993. A copy of the Chain-of-Custody form acknowledging receipt of these samples is attached.

Please note that any unused portion of the samples will be disposed of 30 days after the date of this report, unless you have requested otherwise.

We appreciate the opportunity to be of assistance to you. If you have any questions, please contact Suzanne Silvera, Client Services Supervisor, at (510) 426-2657.

Sincerely,

Ronald H. Peters, CIH
Director, Laboratory Services
Western Operations

RHP/caa
Attachments

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	A01292	Date Sampled:	05/10/93
Lab Number:	9305086-01B	Date Received:	05/10/93
Sample Matrix/Media:	WASTEWATER	Date Analyzed:	05/10/93
Analytical Method:	EPA 624		

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
<u>Purgeable Organics</u>			
Benzene	71-43-2	ND	5
Bromodichloromethane	75-27-4	ND	5
Bromoform	75-25-2	ND	5
Bromomethane	74-83-9	ND	5
Carbon tetrachloride	56-23-5	ND	5
Chlorobenzene	108-90-7	ND	5
Chloroethane	75-00-3	ND	5
2-Chloroethylvinyl ether	110-75-8	ND	5
Chloroform	67-66-3	ND	5
Chloromethane	74-87-3	ND	5
Dibromochloromethane	124-48-1	ND	5
1,2-Dichlorobenzene	95-50-1	ND	5
1,3-Dichlorobenzene	541-73-1	ND	5
1,4-Dichlorobenzene	106-46-7	ND	5
1,1-Dichloroethane	75-34-3	ND	5
1,2-Dichloroethane	107-06-2	ND	5
1,1-Dichloroethene	75-35-4	ND	5
cis-1,2-Dichloroethene	156-59-2	ND	5
trans-1,2-Dichloroethene	156-60-5	ND	5
1,2-Dichloropropane	78-87-5	ND	5
cis-1,3-Dichloropropene	10061-01-5	ND	5
trans-1,3-Dichloropropene	10061-02-6	ND	5
Ethylbenzene	100-41-4	ND	5
Freon 113	76-13-1	ND	5
Methylene chloride	75-09-2	ND	5
1,1,2,2-Tetrachloroethane	79-34-5	ND	5
Tetrachloroethene	127-18-4	ND	5
Toluene	108-88-3	ND	5
1,1,1-Trichloroethane	71-55-6	ND	5
1,1,2-Trichloroethane	79-00-5	ND	5
Trichloroethene	79-01-6	ND	5
Trichlorofluoromethane	75-69-4	ND	5
Vinyl chloride	75-01-4	ND	5
o-Xylene	95-47-6	ND	5

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	A01292	Date Sampled:	05/10/93
Lab Number:	9305086-01B	Date Received:	05/10/93
Sample Matrix/Media:	WASTEWATER	Date Analyzed:	05/10/93
Analytical Method:	EPA 624		

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
Purgeable Organics (continued)			
p,m-Xylenes	--	ND	5
Surrogates		**Recovery (%)**	**QC Limits (%)**
Bromofluorobenzene	460-00-4	101	86 - 115
1,2-Dichloroethane-d4	17060-07-0	94	76 - 114
Toluene-d8	2037-26-5	98	88 - 110

ND: Not detected at or above limit of detection
--: Information not available or not applicable

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	METHOD BLANK	Date Sampled:	--
Lab Number:	9305086-02A	Date Received:	--
Sample Matrix/Media:	WASTEWATER	Date Analyzed:	05/10/93
Analytical Method:	EPA 624		

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
<u>Purgeable Organics</u>			
Benzene	71-43-2	ND	5
Bromodichloromethane	75-27-4	ND	5
Bromoform	75-25-2	ND	5
Bromomethane	74-83-9	ND	5
Carbon tetrachloride	56-23-5	ND	5
Chlorobenzene	108-90-7	ND	5
Chloroethane	75-00-3	ND	5
2-Chloroethylvinyl ether	110-75-8	ND	5
Chloroform	67-66-3	ND	5
Chloromethane	74-87-3	ND	5
Dibromochloromethane	124-48-1	ND	5
1,2-Dichlorobenzene	95-50-1	ND	5
1,3-Dichlorobenzene	541-73-1	ND	5
1,4-Dichlorobenzene	106-46-7	ND	5
1,1-Dichloroethane	75-34-3	ND	5
1,2-Dichloroethane	107-06-2	ND	5
1,1-Dichloroethene	75-35-4	ND	5
cis-1,2-Dichloroethene	156-59-2	ND	5
trans-1,2-Dichloroethene	156-60-5	ND	5
1,2-Dichloropropane	78-87-5	ND	5
cis-1,3-Dichloropropene	10061-01-5	ND	5
trans-1,3-Dichloropropene	10061-02-6	ND	5
Ethylbenzene	100-41-4	ND	5
Freon 113	76-13-1	ND	5
Methylene chloride	75-09-2	ND	5
1,1,2,2-Tetrachloroethane	79-34-5	ND	5
Tetrachloroethene	127-18-4	ND	5
Toluene	108-88-3	ND	5
1,1,1-Trichloroethane	71-55-6	ND	5
1,1,2-Trichloroethane	79-00-5	ND	5
Trichloroethene	79-01-6	ND	5
Trichlorofluoromethane	75-69-4	ND	5
Vinyl chloride	75-01-4	ND	5
o-Xylene	95-47-6	ND	5

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	METHOD BLANK	Date Sampled:	--
Lab Number:	9305086-02A	Date Received:	--
Sample Matrix/Media:	WASTEWATER	Date Analyzed:	05/10/93
Analytical Method:	EPA 624		

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
Purgeable Organics (continued)			
p,m-Xylenes	--	ND	5
Surrogates		**Recovery (%)**	**QC Limits (%)**
Bromofluorobenzene	460-00-4	90	86 - 115
1,2-Dichloroethane-d4	17060-07-0	112	76 - 114
Toluene-d8	2037-26-5	91	88 - 110

ND: Not detected at or above limit of detection
--: Information not available or not applicable

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification: A01292
Lab Number: 9305086-01D
Sample Matrix/Media: WASTEWATER
Extraction Method: EPA 625
Analytical Method: EPA 625

Date Sampled: 05/10/93
Date Received: 05/10/93
Date Extracted: 05/10/93
Date Analyzed: 05/11/93

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
Acid Extractables			
4-Chloro-3-methylphenol	59-50-7	ND	5
2-Chlorophenol	95-57-8	ND	5
2,4-Dichlorophenol	120-83-2	ND	5
2,4-Dimethylphenol	105-67-9	ND	5
2,4-Dinitrophenol	51-28-5	ND	20
2-Methyl-4,6-dinitrophenol	534-52-1	ND	20
2-Nitrophenol	88-75-5	ND	5
4-Nitrophenol	100-02-7	ND	20
Pentachlorophenol	87-86-5	ND	20
Phenol	108-95-2	ND	5
2,4,6-Trichlorophenol	88-06-2	ND	5
Base/Neutral Extractables			
Acenaphthene	83-32-9	ND	5
Acenaphthylene	208-96-8	ND	5
Anthracene	120-12-7	ND	5
Benzidine	92-87-5	ND	30
Benzo(a)anthracene	56-55-3	ND	5
Benzo(b)fluoranthene	205-99-2	ND	5
Benzo(k)fluoranthene	207-08-9	ND	5
Benzo(ghi)perylene	191-24-2	ND	5
Benzo(a)pyrene	50-32-8	ND	5
Benzyl butyl phthalate	85-68-7	ND	5
Bis(2-chloroethoxy)methane	111-91-1	ND	5
Bis(2-chloroethyl)ether	111-44-4	ND	5
Bis(2-chloroisopropyl)ether	108-60-1	ND	5
Bis(2-ethylhexyl)phthalate	117-81-7	ND	10
4-Bromophenyl phenyl ether	101-55-3	ND	5
2-Chloronaphthalene	91-58-7	ND	5
4-Chlorophenyl phenyl ether	7005-72-3	ND	5
Chrysene	218-01-9	ND	5
Dibenzo(a,h)anthracene	53-70-3	ND	5
Dibenzofuran	132-64-9	ND	5
Di-n-butylphthalate	84-74-2	ND	5
1,2-Dichlorobenzene	95-50-1	ND	5

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification: A01292
Lab Number: 9305086-01D
Sample Matrix/Media: WASTEWATER
Extraction Method: EPA 625
Analytical Method: EPA 625

Date Sampled: 05/10/93
Date Received: 05/10/93
Date Extracted: 05/10/93
Date Analyzed: 05/11/93

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
Base/Neutral Extractables (continued)			
1,3-Dichlorobenzene	541-73-1	ND	5
1,4-Dichlorobenzene	106-46-7	ND	5
3,3'-Dichlorobenzidine	91-94-1	ND	40
Diethylphthalate	84-66-2	ND	5
Dimethylphthalate	131-11-3	ND	10
2,4-Dinitrotoluene	121-14-2	ND	5
2,6-Dinitrotoluene	606-20-2	ND	5
Di-n-octylphthalate	117-84-0	ND	5
Fluoranthene	206-44-0	ND	5
Fluorene	86-73-7	ND	5
Hexachlorobenzene	118-74-1	ND	5
Hexachlorobutadiene	87-68-3	ND	5
Hexachlorocyclopentadiene	77-47-4	ND	5
Hexachloroethane	67-72-1	ND	5
Indeno(1,2,3-cd)pyrene	193-39-5	ND	5
Isophorone	78-59-1	ND	5
Naphthalene	91-20-3	ND	5
Nitrobenzene	98-95-3	ND	5
N-Nitrosodiphenylamine	86-30-6	ND	5
N-Nitrosodi-n-propylamine	621-64-7	ND	5
Phenanthrene	85-01-8	ND	5
Pyrene	129-00-0	ND	5
1,2,4-Trichlorobenzene	120-82-1	ND	5
Surrogates		**Recovery (%)**	**QC Limits (%)**
2-Fluorobiphenyl	321-60-8	82	43 - 116
2-Fluorophenol	367-12-4	65	21 - 100
Nitrobenzene-d5	4165-60-0	86	35 - 114
Phenol-d5	4165-62-2	50	10 - 94
Terphenyl-d14	98904-43-9	97	33 - 141
2,4,6-Tribromophenol	118-79-6	84	10 - 123

ND: Not detected at or above limit of detection
--: Information not available or not applicable

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification: METHOD BLANK
Lab Number: 9305086-02A
Sample Matrix/Media: WASTEWATER
Extraction Method: EPA 625
Analytical Method: EPA 625

Date Sampled: --
Date Received: --
Date Extracted: 05/10/93
Date Analyzed: 05/11/93

Analyte	CAS #	Concentration (ug/L)	Limit of Detection (ug/L)
Acid Extractables			
4-Chloro-3-methylphenol	59-50-7	ND	5
2-Chlorophenol	95-57-8	ND	5
2,4-Dichlorophenol	120-83-2	ND	5
2,4-Dimethylphenol	105-67-9	ND	5
2,4-Dinitrophenol	51-28-5	ND	20
2-Methyl-4,6-dinitrophenol	534-52-1	ND	20
2-Nitrophenol	88-75-5	ND	5
4-Nitrophenol	100-02-7	ND	20
Pentachlorophenol	87-86-5	ND	20
Phenol	108-95-2	ND	5
2,4,6-Trichlorophenol	88-06-2	ND	5
Base/Neutral Extractables			
Acenaphthene	83-32-9	ND	5
Acenaphthylene	208-96-8	ND	5
Anthracene	120-12-7	ND	5
Benzidine	92-87-5	ND	30
Benzo(a)anthracene	56-55-3	ND	5
Benzo(b)fluoranthene	205-99-2	ND	5
Benzo(k)fluoranthene	207-08-9	ND	5
Benzo(ghi)perylene	191-24-2	ND	5
Benzo(a)pyrene	50-32-8	ND	5
Benzyl butyl phthalate	85-68-7	ND	5
Bis(2-chloroethoxy)methane	111-91-1	ND	5
Bis(2-chloroethyl)ether	111-44-4	ND	5
Bis(2-chloroisopropyl)ether	108-60-1	ND	5
Bis(2-ethylhexyl)phthalate	117-81-7	ND	10
4-Bromophenyl phenyl ether	101-55-3	ND	5
2-Chloronaphthalene	91-58-7	ND	5
4-Chlorophenyl phenyl ether	7005-72-3	ND	5
Chrysene	218-01-9	ND	5
Dibenzo(a,h)anthracene	53-70-3	ND	5
Dibenzofuran	132-64-9	ND	5
Di-n-butylphthalate	84-74-2	ND	5
1,2-Dichlorobenzene	95-50-1	ND	5

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	**METHOD BLANK**	**Date Sampled:**	**--**
Lab Number:	**9305086-02A**	**Date Received:**	**--**
Sample Matrix/Media:	**WASTEWATER**	**Date Extracted:**	**05/10/93**
Extraction Method:	**EPA 625**	**Date Analyzed:**	**05/11/93**
Analytical Method:	**EPA 625**		

Analyte	**CAS #**	**Concentration (ug/L)**	**Limit of Detection (ug/L)**
Base/Neutral Extractables (continued)			
1,3-Dichlorobenzene	541-73-1	ND	5
1,4-Dichlorobenzene	106-46-7	ND	5
3,3'-Dichlorobenzidine	91-94-1	ND	40
Diethylphthalate	84-66-2	ND	5
Dimethylphthalate	131-11-3	ND	10
2,4-Dinitrotoluene	121-14-2	ND	5
2,6-Dinitrotoluene	606-20-2	ND	5
Di-n-octylphthalate	117-84-0	ND	5
Fluoranthene	206-44-0	ND	5
Fluorene	86-73-7	ND	5
Hexachlorobenzene	118-74-1	ND	5
Hexachlorobutadiene	87-68-3	ND	5
Hexachlorocyclopentadiene	77-47-4	ND	5
Hexachloroethane	67-72-1	ND	5
Indeno(1,2,3-cd)pyrene	193-39-5	ND	5
Isophorone	78-59-1	ND	5
Naphthalene	91-20-3	ND	5
Nitrobenzene	98-95-3	ND	5
N-Nitrosodiphenylamine	86-30-6	ND	5
N-Nitrosodi-n-propylamine	621-64-7	ND	5
Phenanthrene	85-01-8	ND	5
Pyrene	129-00-0	ND	5
1,2,4-Trichlorobenzene	120-82-1	ND	5
Surrogates		**Recovery (%)**	**QC Limits (%)**
2-Fluorobiphenyl	321-60-8	64	43 - 116
2-Fluorophenol	367-12-4	61	21 - 100
Nitrobenzene-d5	4165-60-0	79	35 - 114
Phenol-d5	4165-62-2	47	10 - 94
Terphenyl-d14	98904-43-9	101	33 - 141
2,4,6-Tribromophenol	118-79-6	81	10 - 123

ND: Not detected at or above limit of detection
--: Information not available or not applicable

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification: A01292
Lab Number: 9305086-01
Sample Matrix/Media: WASTEWATER

Date Sampled: 05/10/93
Date Received: 05/10/93

Analyte	Concentration	Detection Limit	Units	Date Prepared	Date Analyzed	Prep Method	Analysis Method
Arsenic	<0.05	0.05	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Cadmium	0.025	0.005	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Chromium	1.2	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Copper	0.11	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Lead	<0.05	0.05	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Mercury	<0.0005	0.0005	mg/L	05/11/93	05/11/93	EPA 245.2	EPA 245.2
Nickel	1.1	0.02	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Silver	0.02	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Zinc	0.02	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7

ND	Not detected at or above limit of detection
<	Not detected at or above limit of detection
—	Information not available or not applicable

Results of Analysis
for
Sandia National Laboratories

Client Reference: LB-6193
Clayton Project No. 93050.86

Sample Identification:	METHOD BLANK	**Date Sampled:**	—
Lab Number:	9305086-02	**Date Received:**	—
Sample Matrix/Media:	WASTEWATER		

Analyte	Concentration	Detection Limit	Units	Date Prepared	Date Analyzed	Prep Method	Analysis Method
Arsenic	<0.05	0.05	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Cadmium	<0.005	0.005	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Chromium	<0.01	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Copper	<0.01	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Lead	<0.05	0.05	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Mercury	<0.0005	0.0005	mg/L	05/11/93	05/11/93	EPA 245.2	EPA 245.2
Nickel	<0.02	0.02	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Silver	<0.01	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7
Zinc	<0.01	0.01	mg/L	05/10/93	05/11/93	EPA 200.7	EPA 200.7

ND — Not detected at or above limit of detection
< — Not detected at or above limit of detection
— — Information not available or not applicable

Quality Assurance Results Summary
for
Clayton Project No. 93059.86

Clayton Lab Number: 9305076-01A
Ext./Prep. Method:
Date: / /
Analyst:
Std. Source: M930305-01W
Sample Matrix/Media: WATER

Analytical Method: EPA624 8240
Instrument ID: G2831
Date: 05/10/93
Time: 19:36
Analyst: AC
Units: UG/L

Analyte	Sample Result	Spike Level	Matrix Spike Result	MS Recovery (%)	Matrix Spike Duplicate Result	MSD Recovery (%)	Average Recovery (% R)	LCL (% R)	UCL (% R)	RPD (%)	UCL (%RPD)
1,1-DICHLOROETHENE	ND	50.0	44.6	89	49.2	98	94	61	145	9.9	14
BENZENE	ND	50.0	51.7	103	52.1	104	104	76	127	0.8	11
CHLOROBENZENE	ND	50.0	47.7	95	50.3	101	98	75	130	5.4	13
TOLUENE	ND	50.0	44.9	90	50.8	102	96	76	125	12	13
TRICHLOROETHENE	ND	50.0	48.3	97	49.0	98	97	71	120	1.4	14

LCS = Laboratory Control Sample
ND = Not detected at or above limit of detection

LCL = Lower Control Limit

UCL = Upper Control Limit
SOR = Spike out of range due to high sample concentration.

Quality Assurance Results Summary
for
Clayton Project No. 93050.86

Clayton Lab Number:	9305076-MB	Analytical Method:	EPA625 8270
Ext./Prep. Method:	EPA 3510	Instrument ID:	05624
Date:	05/10/93	Date:	05/11/93
Analyst:	HYT	Time:	20:39
Std. Source:	E930413-01W	Analyst:	AC
Sample Matrix/Media:	WATER	Units:	UG/L

Analyte	Sample Result	Spike Level	Matrix Spike Result	MS Recovery (%)	Matrix Spike Duplicate Result	MSD Recovery (%)	Average Recovery (% R)	LCL (% R)	UCL (% R)	RPD (%)	UCL (%RPD)
1,2,4-Trichlorobenzene	ND	100	87.0	87	92.0	92	90	39	98	5.6	28
1,4-Dichlorobenzene	ND	100	74.0	74	77.0	77	76	36	97	4.0	28
2,4-Dinitrotoluene	ND	100	83.0	83	89.0	89	86	24	96	7.0	38
2-Chlorophenol	ND	100	73.0	73	76.0	76	75	27	123	4.0	40
4-Chloro-m-cresol	ND	100	75.0	75	77.0	77	76	23	97	2.6	42
4-Nitrophenol	ND	100	24.0	24	25.0	25	25	10	80	4.1	50
Acenaphthene	ND	100	75.0	75	81.0	81	78	46	118	7.7	31
N-Nitrosodipropylamine	ND	100	80.0	80	84.0	84	82	41	116	4.9	38
Pentachlorophenol	ND	100	63.0	63	75.0	75	69	9	103	17	50
Phenol	ND	100	35.0	35	37.0	37	36	12	89	5.6	42
Pyrene	ND	100	76.0	76	77.0	77	77	26	127	1.3	31

LCS = Laboratory Control Sample

ND = Not detected at or above limit of detection

LCL = Lower Control Limit

UCL = Upper Control Limit

SOR = Spike out of range due to high sample concentration.

Quality Assurance Results Summary
for
Clayton Project No. 93050.86

Clayton Lab Number:	9305071-02D	Analytical Method:	EPA200 7
Ext./Prep. Method:	EPA200 7	Instrument ID:	03891
Date:	05/10/93	Date:	05/11/93
Analyst:	JSL	Time:	21:11
Std. Source:	VHG21599	Analyst:	JSL
Sample Matrix/Media:	WATER	Units:	MG/L

Analyte	Sample Result	Spike Level	Matrix Spike Result	MS Recovery (%)	Matrix Spike Duplicate Result	MSD Recovery (%)	Average Recovery (% R)	LCL (% R)	UCL (% R)	RPD (%)	UCL (%RPD)
ANTIMONY	ND	2.00	1.93	97	1.93	97	97	81	115	0.0	20
ARSENIC	ND	2.00	1.97	99	1.95	98	98	60	130	1.0	20
CADMIUM	ND	2.00	1.92	96	1.92	96	96	79	114	0.0	20
CALCIUM	110	2.00	107	SOR	109	SOR	SOR	66	131	1.9	20
CHROMIUM	ND	2.00	1.87	94	1.89	95	94	75	120	1.1	20
COPPER	ND	2.00	1.95	98	1.97	99	98	80	114	1.0	20
LEAD	ND	2.00	1.89	95	1.91	96	95	81	116	1.1	20
MAGNESIUM	160	2.00	162	SOR	164	SOR	SOR	70	127	1.2	20
MANGANESE	0.740	2.00	2.65	96	2.68	97	96	82	118	1.1	20
NICKEL	0.0300	2.00	1.89	93	1.91	94	94	74	117	1.1	20
POTASSIUM	5.00	20.0	24.2	96	24.5	98	97	85	114	1.2	20
SILVER	ND	2.00	1.95	98	1.96	98	98	74	123	0.5	20
SODIUM	84.0	2.00	86.1	SOR	87.1	SOR	SOR	60	123	1.2	20
ZINC	1.00	2.00	2.94	97	2.97	99	98	67	127	1.0	20

LCS = Laboratory Control Sample
ND = Not detected at or above limit of detection

LCL = Lower Control Limit

UCL = Upper Control Limit
SOR = Spike out of range due to high sample concentration.

Quality Assurance Results Summary
for
Clayton Project No. 93058.86

Clayton Lab Number: 9305086-01A
Ext./Prep. Method: EPA245 2
Date: 05/11/93
Analyst: JSL
Std. Source: A93030301W
Sample Matrix/Media: WATER

Analytical Method: EPA245 2
Instrument ID: 05583
Date: 05/11/93
Time: 11:11
Analyst: JSL
Units: MG/L

Analyte	Sample Result	Spike Level	Matrix Spike Result	MS Recovery (%)	Matrix Spike Duplicate Result	MSD Recovery (%)	Average Recovery (% R)	LCL (% R)	UCL (% R)	RPD (%)	UCL (%RPD)
MERCURY	ND	0.0100	0.0106	106	0.0103	103	105	67	124	2.9	20

LCS = Laboratory Control Sample
ND = Not detected at or above limit of detection

LCL = Lower Control Limit

UCL = Upper Control Limit
SOR = Spike out of range due to high sample concentration.

CHAIN OF CUSTODY RECORD AND ANALYTIC INSTRUCTIONS

9205086

Page 1 of 1

Sample ID	Location	S. Time	S. Date	Sample Mat'l	Analyze For	Method	# of Cont	Initials	Comments
A01242	922/120	0800	930510	WASTEWATER	As, Cd, Cu, Cr, Pb, Hg, Ni, Ag, Zn		1L	KN	pH<2; HNO3
A0 1292	↓	↓	↓	↓	VOLATILE ORGANICS	624	2 VOA's	KN	pH<2; HCL
A0 1292	↓	↓	↓	↓	EXTRACTABLES	625	2×1L	KN	
		LAST	ITEM						
									THESE SAMPLES
				48 HR. T-A-T					FOR ORG.
									8446
									KN

Tamper resistant seals in place ([✓ yes] / no)

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Project Name or ID No: LB-6193
Sampler(s) Signature: Ken Nuñez
Sandia Contact Name: KEN NUÑEZ
Sandia Phone Number: (510) 294-1386
Date Sample shipped: 5/10/93

Sample Released By: Ken Nuñez
Date Sample Released: 5/10/93
Courier Name: KEN NUÑEZ
Received by Lab Personnel:
Date and Time Received: 5/10/93 1:00PM

Laboratory Name, Address, Phone:
CLAYTON ENVIRONMENTAL
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PLEASANTON, CA 94566
(510) ~~2~~ 426-2600

1. Specify analytical method used and detection limits
2. Specify date
3. Notify Sandia of anomalies or problems
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5. Tamper resistant seals are in place (yes/no)

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