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# BIODEGRADATION OF HT AGENT FROM AN ASSEMBLED CHEMICAL WEAPONS ASSESSMENT (ACWA) PROJECTILE WASHOUT STUDY

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In this study, HT agent, removed from a chemical round similar to the current stockpile stored at Pueblo Chemical Depot, was neutralized and the hydrolysate treated in a laboratory scale Immobilized Cell Bioreactor (ICB). This study was designed as a first attempt to gather biotreatability data on neutralized HT agent from a projectile washout study. Previous studies have demonstrated treatability of HD agent from ton containers and washout studies but not the less refined "HT" agent. The neutralized HT agent was found to be treatable using an ICB reactor. Total organics removal, using HD agent from projectiles and ton containers, was less complete than previously studied. However, Schedule-2 removal efficiency was comparable to previous studies. The treatment of an off-spec batch of HT hydrolysate was more problematic in that it increased culture salt concentrations above an estimated optimal level and decreased total organics removal.

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# PREFACE

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# BIODEGRADATION OF HT AGENT FROM AN ASSEMBLED CHEMICAL WEAPONS ASSESSMENT (ACWA) PROJECTILE WASHOUT STUDY

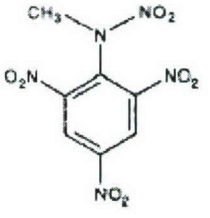
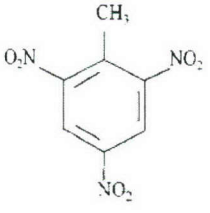
## 1. INTRODUCTION

The Assembled Chemical Weapons Assessment (ACWA) Program[1] was established in 1996, by public laws 104-208, 105-261, and 106-79. To address public concerns over safe destruction of the U.S. chemical weapon stockpile; the ACWA program was tasked to identify two or more viable alternatives technologies to the "baseline" destruction method of incineration. Neutralization followed by biodegradation was one technology to be successfully demonstrated[2,3] in a pilot facility at the U.S. Army Edgewood Chemical and Biological Center (ECBC) APG, MD. A successful Engineering Design Study (EDS) followed the demonstration and the Neutralization/Biodegradation process was subsequently approved for destruction of assembled chemical weapons stored at the Pueblo Chemical Depot (PCD).

During the initial laboratory[4,5] and subsequent pilot-scale studies hydrolyzed mustard taken from ton storage containers and tetrytol from storage was used to simulate the agent and explosive fills of the M60 chemical round. Presently, rocket cutting and washout engineering studies continue at Deseret Chemical Activity (DCA), Utah in preparation for eventual destruction of the chemical rounds. Concern has risen over the possible effect undissolved heel and aluminum hydroxide found in a portion of the chemicals munitions may have on the biotreatability of these neutralized agents. Also, a portion of the chemical round stockpile at PCD also contains the less refined, and less studied agent "HT". Laboratory studies are ongoing to assess the biotreatability of hydrolyzed HT (hHT) and hHT containing aluminum hydroxide. This follow-on laboratory study uses hHT removed during rocket cutting and washout testing on actual chemical rounds stored at DCA. These follow-on studies are being conducted to gain additional data on the treatability of the contents of the actual chemical rounds stored at PCD and to further identify design requirements that may be specific to treatments of the PWS components. The PCD stockpile contains mostly HD agent in rockets and mortars. A smaller portion of the stocks contains a less pure mixture of mustard (HD) and T (bis 2-2-chloroethylthioethyl ether). These rounds also contain the explosive tetrytol, which is a mixture of Tetryl and trinitrotoluene (TNT). The agents and explosives found in the PCB stockpile, along with their quantities are shown in Table 1.

In addition to the treatability of the different mustard agents, variations on the general treatment theme are being addressed. As a result of aging, the agent cavities of the munitions may also contain a solid sludge-like material commonly referred to as "heel". Laboratory studies conducted at ECBC in 2002[6] compared the effect that this heel material may have on degradability of the hydrolyzed mustard and discovered no significant difference in treatability of mustard removed during PWS with or without heel.

Table 1. Agents and Energetics in Pueblo Chemical Munitions Stockpile.

| Component | Chemical Structure or Formula | Total Quantity (Metric tons) |
|---|---|---|
| **AGENTS** | | |
| **HD** (distilled $\beta,\beta$-dichloroethyl-sulfide, ~89% purity) | $ClCH_2CH_2SCH_2CH_2Cl$ | 2,350 |
| **HT**: mixture of<br>~67% HD<br>~22% T ( bis 2-2-chlorethyl-thioethylether)<br>~ 11% impurities (i.e., other organo-sulfur compounds) | $ClCH_2CH_2SCH_2CH_2Cl$ (HD)<br>$(ClCH_2CH_2SCH_2CH_2)_2O$ (T) | 54 |
| **EXPLOSIVES** | | |
| **Tetrytol**: mixture of<br>~70% tetryl (2,4,6-trinitrophenyl-methylnitramine) |  | 101 |
| ~30% TNT (2,4,6-trinitrotoluene) |  | |
| **Tetryl** (2,4,6-trinitrophenyl-methylnitramine) | (see above) | 6 |

Sources: Adapted from U.S. Army, 1997; NRC, 2001.

This laboratory study intended to measure the treatability of HT and compare the treatability of an off-spec batch of hydrolyzed HT that was produced during an equipment malfunction to treatability of an on-spec batch. This study will also measure the effect if any, of the addition of aluminum hydroxide to the bioreactor feed. The Aluminum hydroxide added to the feed is to simulate aluminum hydroxide from burster charges that may be in portions of the explosive hydrolysate. The major components of the PWS HD and HT hydrolysates are presented in Table 2.

Table 2. HD and HT Test Batch Composition.

| Component | HT Batch 11 | HT Batch 12 | HD |
|---|---|---|---|
| Batch ID | | | PBHY25DO2BX |
| **HT breakdown products, mg/L** | | | |
| Thiodiglycol (TDG) | 15,210 | 4,502 | 17,537 |
| TOH | 4,402 | 100 JU | |
| QOH | 1,189 | 454 | |
| Thiox | 696.8 | 336.6 | |
| Dithiane | 139.4 | 138.6 | 2,093 |
| **Organic content** | | | |
| Chemical oxygen demand (COD), mg/L | 51,800 | 15,200 | 43,100 |
| Total organic carbon (TOC), mg/L | 11,325 | 3,230 | 8,120 |
| % TOC as TDG | | | 84.9 |
| COD:TOC ratio | 4.57 | 4.71 | 5.31 |
| Inorganics, mg/L | | | |
| Chloride | 8,490 | 1,020 | |
| Sulfate | 42 | 38 | 84 |
| Sulfur | | | 6,010 |
| Solids | | | |
| Total solids (TS) | 29,600 | 25,300 | |
| Total dissolved solids (TDS) | 27,400 | 20,000 | 28,000 |
| Total suspended solids (TSS) | 184 | 117 | 1,000 |
| pH, pH units | 12.82 | 13.31 | 13.0 |
| Specific gravity, g/mL | 1.01 | 1.12 | 1.03 |
| Volatile organic compounds (VOCs), mg/L | | | |
| 1,2-Dichloroethane | 70 | 6.2 | |
| Vinyl chloride | 0.51 | 0.49 | |
| Metals, mg/L | | | |
| Aluminum | 2.5 | 5.4 | 1.99 |
| Arsenic | .96 | .96 | 0.579 |
| Barium | .42 | .42 | 0.033 |
| Cadmium | .45 | .45 | 3.2 |
| Calcium | 7.8 | 6.3 | 10.9 |
| Chloride | 8490 | 1020 | 10,800 |
| Chromium | .52 | .52 | 0.281 |
| Copper | 1.2 | 1.2 | 3.63 |
| Iron | 81 | 61 | 520 |
| Lead | 6.6 | 4.5 | 3.69 |
| Magnesium | 9.7 | 2.7 | 5.74 |
| Manganese | 0.27 | 0.29 | 3.08 |
| Mercury | .33 | .33 | 0.013 |
| Molybdenum | .47 | .47 | 0.065 |
| Nickel | .45 | .45 | 0.330 |
| Phosphorus | 600 | 610 | 0.456 |
| Potassium | 13 | 12 | 15.2 |
| Silver | .5 | .5 | 5.73 |
| Sodium | 11,000 | 8,400 | 10,630 |
| Zinc | 1.0 | 0.62 | 3.59 |

Scope and Objectives.

The objective of this study was to measure the treatability of the PWS-generated HT hydrolysate in laboratory-scale ICBs. Two ICBs were operated, monitored, and sampled over a 5- to 8-month period (including startup). The two ICBs were operated in parallel, both initially receiving the same HT/tetrytol hydrolysate. Later in the test the feed to one ICB was spiked with aluminum hydroxide to simulate the dissolved aluminum that may be present in the energetics hydrolysate at PCD.

Specific objectives of the test include:

- Confirm the ability of the laboratory-scale ICBs to effectively treat the PWS-generated HT hydrolysate at hydraulic residence times (HRTs) that are representative of full-scale design by assessing the following parameters:
  - Organic removal efficiency
  - Elimination of thiodiglycol and other target organics in the HT hydrolysate
  - Assess the impact of aluminum hydroxide in the energetics hydrolysate on ICB performance.
  - Characterize ICB liquid effluents.

## 2. MATERIALS AND METHODS

### 2.1 HT Hydrolysate.

The HT hydrolysate used for this test was produced from the water hydrolysis of drained agent and heel material removed from 4.2-inch HT mortars as part of the PWS study. It was produced in a stirred tank reactor at a nominal HT loading of 3.8 weight %, with a reaction time of approximately 2 hr and at reaction temperature of 90°. The HT hydrolysate batch used in this test was characterized for the major constituents shown in Table 2.

### 2.2 Tetrytol Hydrolysate.

Tetrytol hydrolysate was prepared at ECBC for this test by caustic hydrolysis of tetrytol at a nominal tetrytol loading of 6.67% (wt/vol) at 90 °C for at least 8 hr. Samples of the tetrytol hydrolysate were analyzed for energetics, metals, mercury, anions, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs). The energetics and breakdown products were of principle interest. None of the energetics was detected in the hydrolyzed samples. Analysis for energetics was difficult due to interferences in the sample matrix.

## 2.3 Laboratory-Scale ICBs.

Two laboratory-scale ICBs were operated in parallel at ambient room temperature. One ICB (ICB 1) received PWS HT batch 11 hydrolysate, tetrytol hydrolysate, and nutrients. This system was designated ICB 1. The second ICB, designated ICB 2, received essentially the same feed with the only difference being that the PWS HT hydrolysate was from batch 12 during the second and third steady state test period. Both ICBs received Aluminum hydroxide during the third steady state. Two ICBs were used to allow one (ICB 1) to act as a control for testing the effect of the off-spec batch 12 hydrolysate and as a baseline when aluminum hydroxide was eventually added to both reactors.

Each ICB consisted of two 1-liter glass cylinders (designated Cell A and Cell B) connected in series as illustrated in Figure 1 and pictured in Figure 2. Each cylinder measured 30.5 cm in length and 6.5 cm in diameter. The two cells in series were designed to simulate the first two cells of the full-scale ICB.

Each cell had three ports for circulating air and liquids. The port at the bottom of the cell was used to supply aeration through a sintered glass disk. Ports for feed and effluent circulation were located 4.0 cm and 19.5 cm above the sintered glass disk. The open top of the cells was sealed with a rubber stopper with holes drilled for pH and dissolved oxygen probes, an exhaust hose, and recirculating loop.

Each cell was packed with media to support the biomass. The support media consists of 2-$cm^3$ expanded polyurethane foam cubes coated with activated carbon and cylindrical polypropylene spacers to promote good liquid and gas circulation. The initial working liquid volume of each cell was approximately 630 mL, for a total of 1.26 L per ICB. The ICBs were seeded with activated sludge from the City of Baltimore Back River Wastewater Treatment plant (BRWTP). All systems were operated at ambient room temperature (23 to 25 °C). Because the biodegradation of TDG produces sulfuric acid, pH control is essential. A pH controller was used to maintain the pH within the ICBs at the design pH of 6.5 to 7.5 by addition of a 0.9 molar solution of $NaHCO_3$.

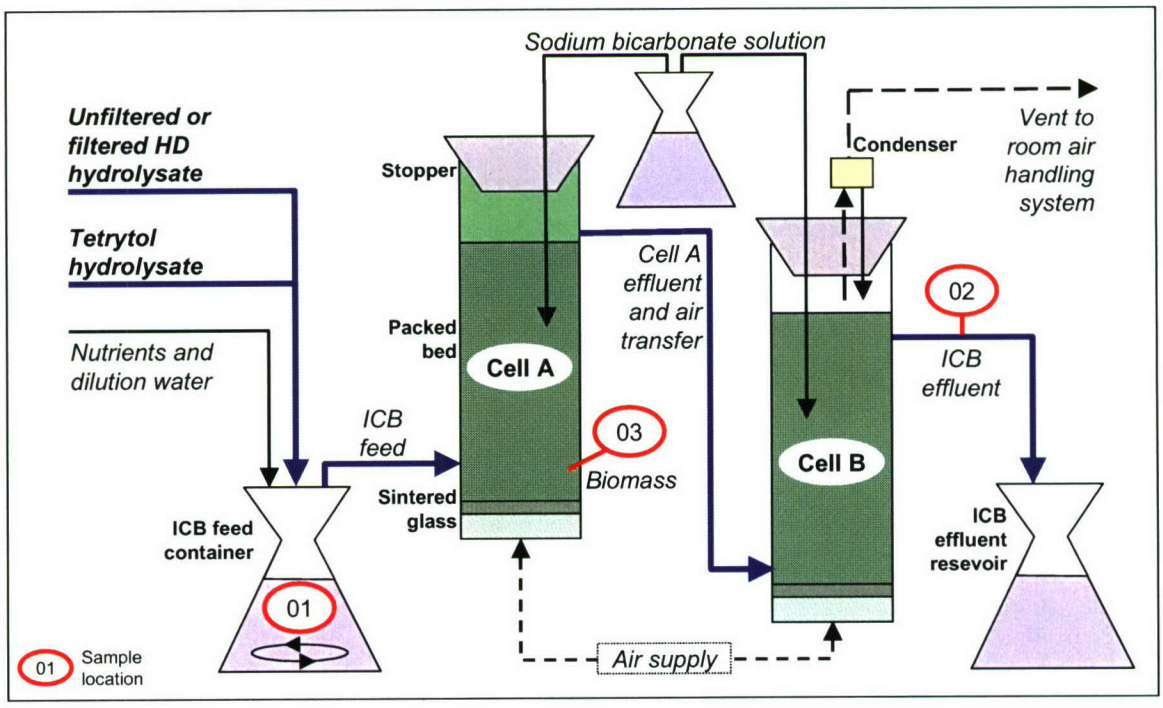



Figure 1. PWS HD and HT/Tetrytol ICB Flow Diagram.

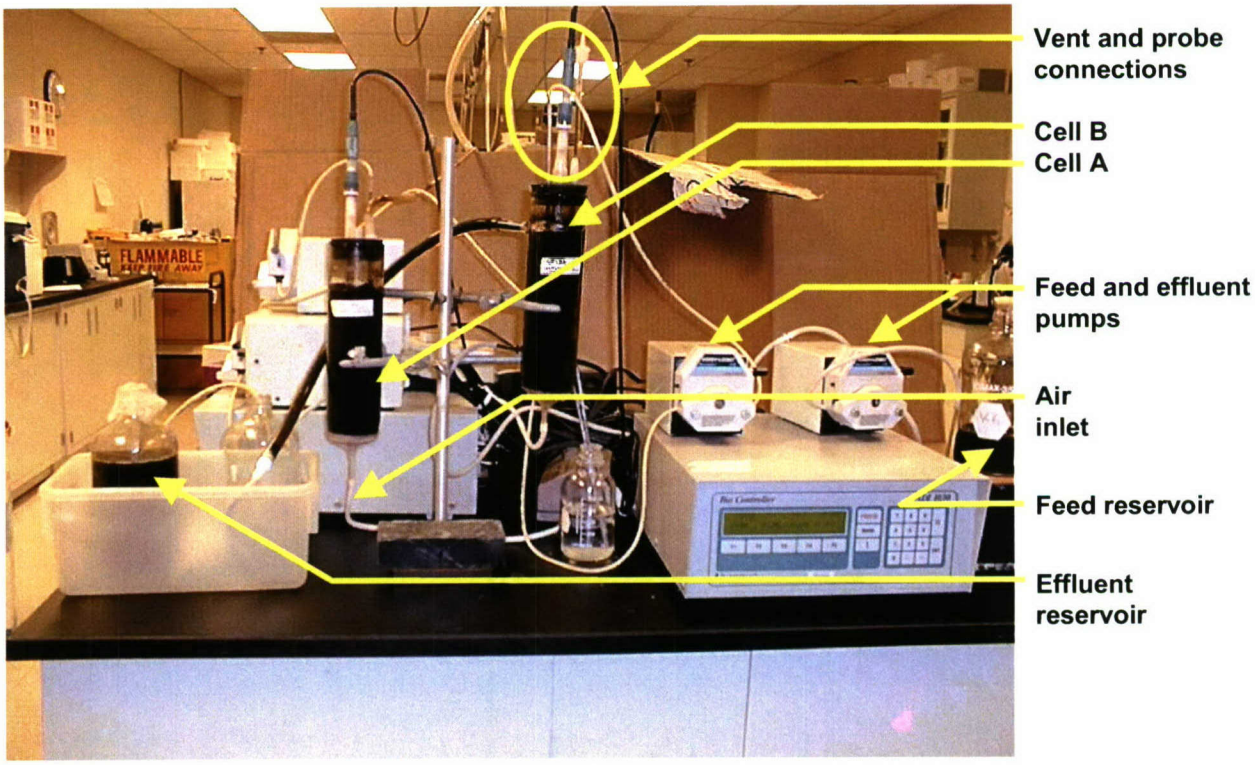



Figure 2. PWS HT/Tetrytol Hydrolysate ICB at ECBC.

2.4 Feed Preparation.

HT hydrolysate from PWS batches 11 and 12 were received for this study in 20-liter drums from DCA. Before preparation of the feed, the 20-L hydrolysate container was shaken vigorously for 5 minutes to suspend the hydrolysate-undissolved solids. A portion of the HT hydrolysate was removed immediately after shaking and used directly in the preparation of the biofeed. Initially batch-11 hydrolysate was used for both ICBs until ICB 2 was switched to batch 12. Typical feed recipe is listed in Table 3.

Table 3. ICB Feed Recipe (per 1 L of Feed).

| Item | Batch 11 | Batch12 | Unit |
|---|---|---|---|
| HD hydrolysate (3.8 wt%) | 300 | 975 | mL |
| Tetrytol hydrolysate (6.67 wt/vol%) | 15 | 15 | mL |
| $NH_4Cl$ | 1.25 | 1.25 | G |
| Potassium Phosphate Di-basic ($K_2HPO_3$) | 0.25 | 0.25 | G |
| Sulfur-free Wolin Salts | 10 | 10 | mL |
| Tap water to volume | ~685 | 0 | mL |
| Final volume | 1000 | 1000 | mL |

Sulfur-free Wolin salts were added to the feed to supply necessary micronutrients. The ingredients for sulfur-free wolin salts are listed in Table 4.

Table 4. Wolin Salts Recipe.

| Compound | Wt. Per Liter (gm) |
|---|---|
| Nitrilotriacetic acid | 3.00 |
| NaOH | Enough to allow Nitrilotriacetic acid to dissolve |
| $MgCl_2$ $4H_2O$ | 6.95 |
| $MnCl_2$ | 0.66 |
| $FeCl_2$ | 0.23 |
| $CaCl_2$ $2H_2O$ | 0.07 |
| $CoCl_2$ $6H_2O$ | 0.10 |
| $ZnCl_2$ | 0.06 |
| $H_3BO_3$ | 0.02 |
| $Na_2MoO_2$ $2H_2O$ | 0.01 |
| $CuCl_2$ $2H_2O$ | 0.01 |

## 2.5 ICB Test Plan.

The operation of the laboratory ICBs is divided into the four phases described below.

### 2.5.1 Startup and Acclimation.

The first phase consists of seeding the ICBs with activated sludge from the BRWTP and acclimatizing the biomass to the Batch 11 hydrolysate feed. During this time, the hydraulic residence time of the ICBs will be 5-days. The hHT feed concentration will be gradually increased until the target biofeed concentration has been reached.

Typically, biomass growth in response to food availability is represented by an increase in COD consumption (reduction in the effluent COD level) over a 24-hr period. As the rate of COD consumption increases, concentration of the biofeed will be stepped up. The goal of the acclimation period is to gradually increase the concentration of active biomass while preventing the accumulation of biodegradable COD in the ICB. Organic removal efficiencies of 80 to 90% were achieved in previous testing with HD hydrolysate made from HD from ton containers. Past results indicate that the acclimation phase could last about 45 days, however, period of 60 days has been allotted to this phase.

### 2.5.2 Steady-State Phase 1: Steady State with Batch 11 Hydrolysate Feed.

Once fully acclimated to the Batch 11 hydrolysate feed and at the target HRT, the first steady-state phase of the test will begin. During this phase the ICBs will continue to be monitored as before, but the ICB effluents will undergo more extensive analyses to validate performance. The target HRT in the ICBs will be maintained for at least 45 days exclusive of upsets. A period of 60 days has been allotted to this phase.

### 2.5.3 Steady-State Phase 2: Steady State Comparing Batch 11 and Batch 12 Hydrolysate.

At the end of steady-state phase 1, the ICBs will transition into steady-state phase 2. In this phase ICB 1 will continue to receive Batch 11 hydrolysate feed while ICB 2 will receive the off-spec Batch 12 hydrolysate. Some acclimation of the biomass in ICB 2 may be required with the change in feed. This will involve lowering the hHT feed concentration for a few days, as dictated by ICB performance, and re-acquiring the target concentration. Once ICB 2 has acclimated to the new feed, both ICBs will again be operated for 60 days at the target HRT exclusive of upsets.

### 2.5.4 Steady-State Phase 3: Steady State with Batch 11 and Batch 12 Hydrolysate Feed with Aluminum Hydroxide.

At the end of steady-state phase 2, the ICBs will transition into steady-state phase 3. Each ICB will continue to receive its steady state 2 feed with aluminum hydroxide added. As before, some acclimation of the biomass may be required with the change in feed. Once acclimated to the new feeds, the ICBs will be operated for 60 days at the target HRT exclusive of upsets.

A summary of the test phases is shown in Table 5.

Table 5. Summary of Test Phases

| Phase | ICB feed | | Duration |
|---|---|---|---|
| | ICB 1 | ICB 2 | |
| Startup and acclimation | Batch 11 hydrolysate feed | | 30 to 60 days |
| Steady-state phase 1 | Batch 11 and 11 hydrolysate feed | | 60 days |
| Steady-state phase 2 | Batch 11 hydrolysate feed | Batch 12 hydrolysate feed | 60 days |
| Steady-state phase 3 | Batch 11 hydrolysate feed w/aluminum hydroxide | Batch 12 hydrolysate feed w/ aluminum hydroxide | 60 days |
| | | Total duration | 210 to 240 days |

2.6 Sampling and Analysis.

Sampling of the ICB feeds, contents, and effluents occurred in two stages. The first stage was the ramp-up period in which only in-house process monitoring parameters were measured. In-house measurements included bench-top analysis for chemical characteristics using a Hach[8] kit. Standard methods for wastewater analysis were used for feed and effluent solids measurement. In-house process monitoring included the following analyses:

- COD, Hach method 8000, Reactor digestion method[8]
- Ammonia ($NH_3$), Hach method 10030, Salicylate method ($NH_3$-N)8
- Phosphate ($PO_4$), Hach method 8178 (orthophosphate) amino acid method 8
- Total suspended solids (TSS), Method 2540 D *
- Volatile suspended solids (VSS), Method 2540 E *
- Total dissolved solids (TDS), Method 2540 C

* - From standard methods for examination of water and wastewater 18th, ed., 1992[9]

Process monitoring sampling occurred frequently during ramp-up due to the need to closely monitor the biomass response to frequent changes in ICB feed strength. COD was one of the more important monitoring parameters since it is the easiest method for measuring the concentration of organic compounds. COD is a good and quick indicator of feed consumption and excess food accumulation within the ICB.

Steady state sampling occurred after the ramp-up period was completed. The steady state period started when the ICB feed reached the test design strength of 300 ml (full strength hHT for batch 12) HT hydrolysate per liter of feed at a 5-day HRT. Steady state sampling included the process monitoring analyses mentioned above as well as additional feed and effluent characterization analyses, which included the following parameters:

- Volatile Organic Chemicals (VOC)
- Semi-Volatile Organic Chemicals (SVOC)
- Thiodiglycol (TDG)

- Metals and mercury
- Anions
- Toxicity characteristics leaching procedure (TCLP) analysis of solids

# 3. RESULTS

## 3.1 Chemical Oxygen Demand.

COD is a measure of the chemically oxidizable compounds in an aqueous sample. COD was one of the major process parameters used to measure the overall system effectiveness in treating the combined HT/tetrytol hydrolysates. The major sources of COD in the feed are TDG and other organic hydrolysis products. Because COD analysis is inexpensive, has a quick turn-around time, and it can be done as a process monitoring sample, it was used as a primary indicator of the biomass health and performance throughout the test. TDG analysis of steady state samples was also performed; the results are presented later in this report.

After the initial batch operating period, the initial feed strength in continuous mode was $1/8^{th}$ the design strength. The feed strength was adjusted as the biomass grew and became acclimated to the feed, as indicated by COD removal. The feed strength was ramped-up in response to COD removal. The COD concentration was routinely measured in the feed, in Cell A, and in the effluent of each ICB. COD input and output values are represented in Figure 3 below.

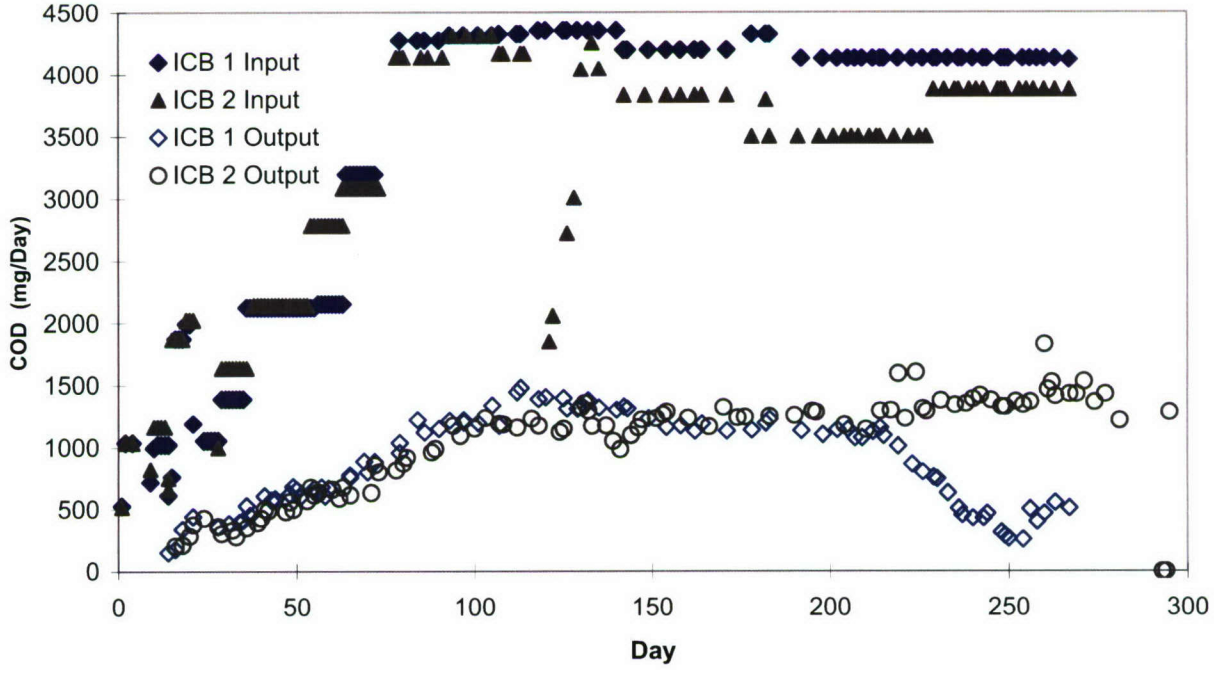



Figure 3. COD Input and Output Values Calculated during the Study.

Generally, A COD removal efficiency greater than 85 percent on a consistent basis indicates that the culture is ready for an increase in feed strength. However, it is also important to monitor COD levels in all cells of the ICB. There is a threshold concentration above which the organics in a feed can become inhibitory to the biomass.

The COD removal efficiency was calculated as follows:

$$COD_{REMOVAL\ EFF},\ \% = [(COD_{input},\ mg/Day - COD_{output},\ mg/Day)/\ COD_{input},\ mg/Day]*100$$

That level has not been well established for this hydrolysate feed. In past experience with the pilot-scale reactor, the COD in the first cell was generally below 4000 mg/L. This level became a benchmark for possible signs of trouble early in this lab-scale test. During ramp-up, the feed was stopped on occasion due to higher than expected COD levels in Cell 1A. Later in the test, the COD was allowed to increase to above 5000 mg/L with no apparent detrimental effects on the overall COD removal efficiency of the ICB.

During the course of the study the COD removal efficiencies of the two cultures diverged. Initially this occurred during the second steady-state period when the ICB 2 removal efficiency decreased with the switch to hHT batch 12, the off-spec batch. A further divergence occurred during the third steady state period as Aluminum hydroxide was added to the feed streams. ICB 1 efficiency improved with the added aluminum hydroxide while ICB 2 continued to decline. ICB COD removal efficiency during the study is represented in Figure 4.

## 3.2 Nutrient Levels, pH, and Other Process Monitoring.

Nutrient levels were analyzed as part of the routine process monitoring. Nitrogen levels were monitored as nitrogen-ammonia. Phosphorus was monitored as phosphate. Nitrogen and phosphate levels were in an optimum range for biodegradation of this type. The pH in each cell of the ICBs was controlled through the biocontrollers. The pH of each reactor was set to 7.5 and maintained with 0.9N sodium bicarbonate solution. The pH readings were monitored daily and recorded during ramp-up and steady state sampling events. The pH readings of all feeds and ICB cells were fairly stable and trend less. The ICBs were operated in a temperature-controlled environment. ICB temperatures were 22-24 oC throughout the test. Air was supplied at a rate of 500 ml/min. from the house compressed air system. Nutrient levels, air supply, pH and temperature were kept optimal for the study. Nutrients or process controls were never an issue during the study.

COD has normally been used to indicate overall system performance and infer TDG removal. COD is also used to compare performance of a control system versus the treatment. COD summaries of the two ICBs are presented in Tables 6 and 7.

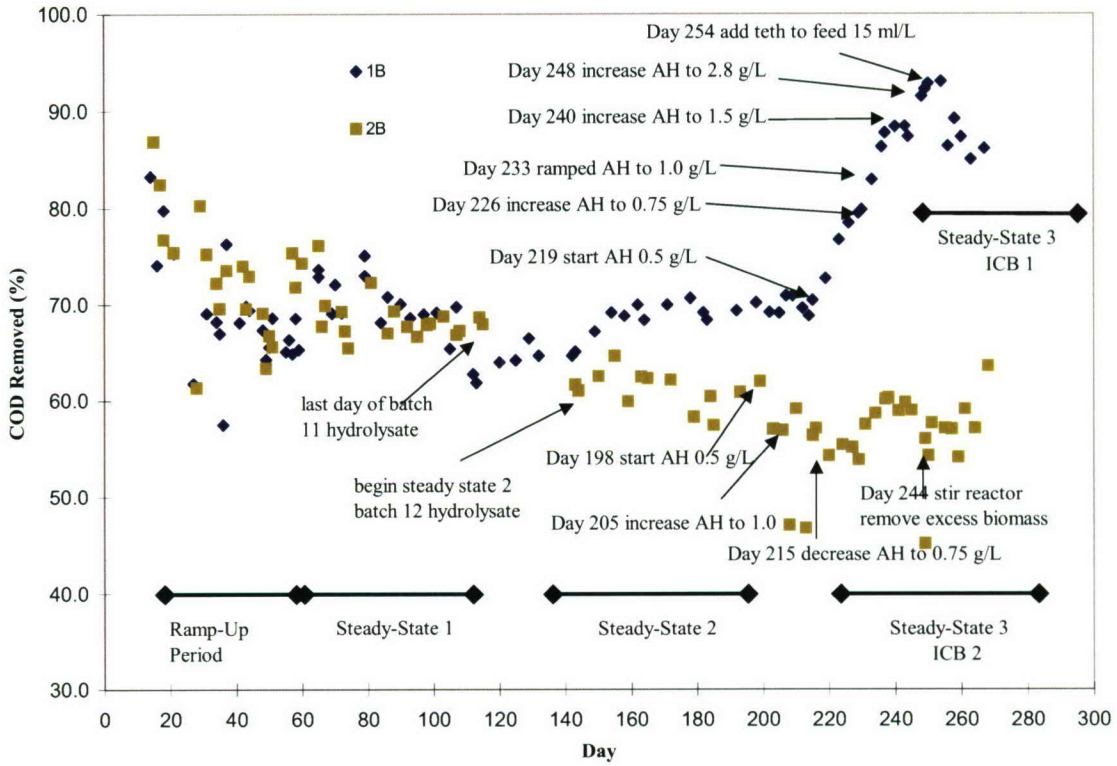



Figure 4. COD Removal across ICBs 1 and 2 during the Study Period.

Table 6. COD Summaries for HT-ICB 1 after the Ramp-Up Period.

| | Feed COD (mg/L) | COD input (mg/Day) | Effluent COD (mg/L) | COD Output (mg/Day) | COD Removal (%) | COD consumption (mg/Day) |
|---|---|---|---|---|---|---|
| **mean** | 16846 | 4215 | 4567 | 980 | 74 | 3233 |
| **min** | 15740 | 4120 | 1200 | 258 | 62 | 2848 |
| **max** | 18220 | 4355 | 6880 | 1479 | 93 | 3871 |
| **std-d** | 591 | 93 | 1673 | 365 | 9 | 306 |
| **count** | 39 | 63 | 64 | 62 | 62 | 62.0 |

Table 7. COD Summaries for HT-ICB 2 after the Ramp-Up Period.

| | Feed COD (mg/L) | COD Input (mg/Day) | Effluent COD (mg/L) | COD Output (mg/Day) | COD removal (%) | COD Consumption (mg/Day) |
|---|---|---|---|---|---|---|
| **mean** | 15178 | 3794 | 5930 | 1281 | 60 | 2484 |
| **min** | 7410 | 1853 | 4470 | 961 | 45 | 558 |
| **max** | 18100 | 4310 | 8500 | 1828 | 73 | 3176 |
| **std-d** | 2085 | 455 | 710 | 151 | 6 | 500 |
| **count** | 42 | 42 | 67 | 54 | 54 | 61 |

3.3 Thiodiglycol and Breakdown Products.

Thiodiglycol is the principle organic compound, and the only Chemical Weapons Convention Schedule-2 compound in the HT hydrolysate. Once the ICB biomasses reached steady state the ICB biofeeds and effluents were sampled three times per 4-L feed batch. Field duplicates and effluent composite samples were also taken during the steady state period. Results of these analyses of the field samples listed in Table 8 and 9.

Table 8. Results of Analysis for Thiodiglycol and HT Breakdown Products in ICB 1.

| | ICB 1 Feed | | | | | ICB 1 Effluent | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample Date | Dith (ug/ml) | QOH (ug/ml) | TDG (ug/ml) | TOH (ug/ml) | Thiox (ug/ml) | Dith (ug/ml) | QOH (ug/ml) | TDG (ug/ml) | TOH (ug/ml) | Thiox (ug/ml) |
| 6/3 | 28.5 | 95.7 | 1265 | NA | 81.8 | 0.153 | <0.1 | 0.67 | NA | 8.58 |
| 6/12 | 50.9 | 190 | 2419 | NA | 166 | <0.1 | 2.05 | 2.45 | NA | 14.8 |
| 6/26 | 43.1 | 188 | 2294 | NA | 146 | <1.00 | <1.00 | <1.00 | NA | 10.8 |
| 7/9 | 59.8 | 191 | 2364 | NA | 159 | <1.00 | <1.00 | 2.35 | NA | 6.15 |
| 7/14 | 28.3 | 99.2 | 1336 | NA | 79.9 | <1.00 | <1.00 | 2.47 | NA | 5.02 |
| 7/18 | 43.0 | 218 | 2782 | NA | 154 | <1.00 | <1.00 | 3.05 | NA | 4.16 |
| 7/24 | 86.7 | 277 | 3635 | NA | 251 | <1.00 | <1.00 | 3.26 | NA | 5.44 |
| 7/29 | 66.2 | 281 | 3841 | NA | 212 | <1.00 | <1.00 | 2.13 | NA | 8.61 |
| 7/31 | 90.2 | 292 | 3816 | NA | 241 | <1.00 | <1.00 | 2.91 | NA | 8.35 |
| 8/5 | 125 | 384 | 4919 | NA | 324 | <1.00 | <1.00 | 1.92 | NA | 6.12 |
| 8/7 | 129 | 406 | 5189 | NA | 360 | <1.00 | <1.00 | 1.26 | NA | 7.02 |
| 8/14 | 110 | 395 | 5030 | NA | 369 | <1.00 | <1.00 | <1.00 | NA | 12.9 |
| 8/19 | 108 | 390 | 4931 | NA | 297 | <1.00 | <1.00 | <1.00 | NA | 11.5 |
| 8/26 | 120 | 364 | 4574 | NA | 310 | <1.00 | <1.00 | <1.00 | NA | 11.2 |
| 8/27 | 128 | 480 | 5200 | NA | 305 | <1.00 | <1.00 | <1.00 | NA | 10.8 |
| 9/3 | 6.54 | 20.1 | | NA | 6.57 | <1.00 | <1.00 | <1.00 | NA | 6.04 |
| 9/4 | 101 | 382 | 4551 | NA | 317 | <1.00 | <1.00 | <1.00 | NA | 4.48 |
| 9/11 | 93.4 | 366 | 4738 | 1689 | 301 | 57.3 | <2 | <2 | <2 | 7.03 |
| 9/11 | 103 | 370 | 4780 | 1709 | 304 | 60.2 | <2 | <2 | <2 | 7.17 |
| 10/8 | 132 | 352 | 4745 | 1688 | 330 | 58.1 | <2 | <2 | 9.16 | 17.0 |
| 10/23 | 121 | 392 | 5001 | 1692 | 336 | <2 | <2 | <2 | <2 | 20 |
| 10/24 | 120 | 364 | 4806 | 1654 | 331 | <2 | <2 | <2 | <2 | 20.0 |
| 11/13 | 113 | 422 | 4962 | 1708 | 386 | <2 | <2 | 16.4 | <2 | 34.3 |
| 11/25 | 133 | 410 | 5242 | 1845 | 366 | <2 | <2 | <2 | <2 | 16 |
| 12/1 | 132 | 367 | 4892 | 1695 | 331 | <2 | <2 | <2 | <2 | 14.5 |
| 1/21 | 134 | 394 | 4975 | 1808 | 323 | <2 | <2 | <2 | <2 | 11.3 |
| 2/5 | 122 | 370 | 4839 | 1731 | 314 | <2 | <2 | <2 | <2 | 10.1 |
| 2/12 | 130 | 362 | 4779 | 1663 | 340 | 2.22 | <2 | <2 | 4.65 | 15.9 |
| 2/24 | 126 | 375 | 4752 | 1734 | 322 | <2 | <2 | <2 | 24.6 | 5.04 |
| 3/3 | 136 | 387 | 4991 | 1821 | 368 | <2 | 5.81 | <2 | 29.7 | 5.45 |

Detection limit in ICB effluents is 1-2 mg/L

During the ramp-up and Steady-State 1 period, the feed to both reactors was made from the batch 11 hHT. Feed thiodiglycol and HT breakdown products for ICB 2 are listed in Table 9.

Table 9. Results of Thiodiglycol and HT Breakdown Products Analysis in ICB 2.

| | ICB 2 Feed | | | | | ICB 2 Effluent | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample Data | Dith (ug/ml) | QOH (ug/ml) | TDG (ug/ml) | TOH (ug/ml) | Thio (ug/ml) | Dith (ug/ml) | QOH (ug/ml) | TDG (ug/ml) | TOH (ug/ml) | Thio (ug/ml) |
| 6/3 | 28.5 | 95.7 | 1265 | NA | 81.8 | <0.1 | <0.1 | 0.850 | NA | 8.42 |
| 6/12 | 50.9 | 190 | 2419 | NA | 166 | <0.1 | 1.17 | 2.7 | NA | 14.9 |
| 6/26 | 43.1 | 188 | 2294 | NA | 146 | <1.00 | <1.00 | <1.00 | NA | 9.81 |
| 7/9 | 59.8 | 191 | 2364 | NA | 159 | 2.51 | <1.00 | 1.75 | NA | 6.22 |
| 7/14 | 28.3 | 99.2 | 1336 | NA | 79.9 | <1.00 | <1.00 | 2.15 | NA | 4.08 |
| 7/18 | 43.0 | 218 | 2782 | NA | 154 | <1.00 | <1.00 | 2.44 | NA | 3.61 |
| 7/24 | 86.7 | 277 | 3635 | NA | 251 | <1.00 | <1.00 | 2.57 | NA | 3.89 |
| 7/29 | 66.2 | 281 | 3841 | NA | 212 | <1.00 | <1.00 | 2.19 | NA | 8.13 |
| 7/31 | 90.2 | 292 | 3816 | NA | 241 | <1.00 | <1.00 | 1.8 | NA | 5.66 |
| 8/5 | 125 | 384 | 4919 | NA | 324 | <1.00 | <1.00 | 2.24 | NA | 6.18 |
| 8/7 | 112 | 391 | 5126 | NA | 331 | <1.00 | <1.00 | <1.00 | NA | 9.62 |
| 8/14 | 116 | 368 | 4808 | NA | 307 | <1 | <1 | <1 | NA | 11.2 |
| 8/19 | 108 | 376 | 4734 | NA | 296 | <1.00 | <1.00 | <1.00 | NA | 7.42 |
| 8/26 | 119 | 363 | 4516 | NA | 295 | <1 | <1 | <1 | NA | 18.8 |
| 8/27 | 130 | 392 | 5023 | NA | 358 | <1.00 | <1.00 | <1.00 | NA | 18.6 |
| 9/3 | 3.85 | 13.6 | | NA | 17.2 | <1.00 | <1.00 | <1.00 | NA | 17.1 |
| 9/4 | 120 | 416 | 4662 | NA | 332 | <1.00 | <1.00 | <1.00 | NA | 18.4 |
| 9/11 | 101 | 374 | 4811 | 1740 | 301 | 55.7 | <2 | <2 | <2 | 7.39 |
| 9/11 | 94.7 | 386 | 4856 | 1752 | 334 | 57.1 | <2 | <2 | <2 | 7.75 |
| 10/8 | 150 | 304 | 4305 | 1679 | 328 | 5.63 | <2 | <2 | 7.21 | 11.4 |
| 10/23 | 138 | 328 | 4279 | 1677 | 340 | <2 | <2 | <2 | <2 | 12.6 |
| 10/24 | 87.2 | 107 | 4319 | 1680 | 115 | <2 | <2 | <2 | <2 | 12.1 |
| 11/13 | 122 | 319 | 4101 | 1667 | 326 | <2 | <2 | <2 | <2 | 6.75 |
| 11/25 | 147 | 303 | 4197 | 1636 | 341 | <2 | <2 | <2 | <2 | 8.03 |
| 12/1 | 146 | 302 | 4099 | 1636 | 326 | <2 | <2 | <2 | <2 | 6.42 |
| 1/21 | 150 | 310 | 3835 | 1625 | 331 | <2 | <2 | <2 | <2 | 4.34 |
| 1/21 | 148 | 309 | 4056 | 1679 | 325 | <2 | <2 | <2 | <2 | 6.64 |
| 2/5 | 148 | 290 | 4038 | 1625 | 347 | <2 | <2 | <2 | <2 | 3.92 |
| 2/13 | 152 | 301 | 4054 | 1653 | 318 | <2 | <2 | <2 | <2 | 20.2 |
| 2/24 | 155 | 325 | 4176 | 1678 | 366 | <2 | <2 | <2 | <2 | 5.39 |

Detection limit in ICB effluents is 1-2 mg/L

Summaries of the TDG input, output and consumption values are presented in Table 10. Findings of BDL are treated as zero statistically.

Table 10. Summary of Thiodiglycol Values Measured in HT-ICB 1 and HT-ICB 2 during combined Steady-State Periods.

| | HT-ICB 1 | | | HT-ICB 2 | | |
|---|---|---|---|---|---|---|
| | **Feed TDG mg/L** | **Effluent TDG (mg/L)** | **TDG Consumed (mg/day/L)** | **Feed TDG (mg/L)** | **Effluent TDG (mg/L)** | **TDG Consumed (mg/day/L)** |
| **Mean** | 4747.3 | 1.2 | 941.7 | 4356.8 | 0.4 | 864.37 |
| **Min** | 3635 | 0.0 | 721.2 | 3635.0 | 0.0 | 721.23 |
| **Max** | 5242.0 | 16.4 | 1036.8 | 5126.0 | 2.6 | 1016.55 |
| **Std-d** | 482.5 | 3.4 | 95.1 | 432.1 | 0.9 | 85.55 |
| **Count** | 23 | 24 | 23 | 23 | 24 | 23 |

3.4 Volatile Organic Compounds.

ICB feeds and effluents were analyzed for VOCs as part of overall system performance and possibly consideration during future washout studies, system design and permitting. Quantitation and identification of VOC compounds can be difficult due to the poor matrix spike recoveries and separation of analytes within the sample matrix. Therefore, numerous qualifiers are routinely attached to s specific analyte value. Compounds that were not detected have been removed from the lists shown. Positive results for analytes of interest are listed in table 11 and 12 below. Total VOCs decreased by more than an order of magnitude across both ICBs. Chloromethane was the most abundant VOC is both ICB effluents.

Table 11. Positive Results of VOCs in ICB 1.

| Analyte | ICB 1 Feed (ug/L) | Qualifier | ICB 1 Effluent (ug/L) | Qualifier |
|---|---|---|---|---|
| **1,2-Dichloroethane** | 197 | J* | | |
| **1,2-Dichloropropane** | | | 1 | J* |
| **Acetaldehyde** | | | 67 | JN* |
| **Acetone** | 435 | J* | | |
| **bis(2-Chloroethyl) ether** | 115 | JN* | | |
| **Bromomethane** | | | 80 | J |
| **Chloroform** | 33 | JD* | 22 | JD |
| **Chloroethane** | | | 0.9 | JD |
| **Chloromethane** | 3811 | J* | 140 | J* |
| **Hexanal** | | | 23 | JN* |
| **Methylene chloride** | 18 | J* | 10 | JB* |
| **Unknown** | 130 | J | 11 | J |
| **Total VOC's** | **4738** | | **355** | |

J- Estimated value; concentration is below limit of quantitation.
D- Result was obtained from analysis of a dilution.
N- Tentatively identified compound.
*- Indicates a calculated average of multiple positive results.

3.5 Semi-Volatile Organic Compounds.

Bio feeds and effluents were analyzed for Semi-volatile Organic Compounds (SVOCs). There were more tentatively identified compounds with estimated quantitation the compounds of certain identity and quantity. The complete listing of positive results for the ICBs is listed in Appendices A and B.

Only bis (2-chloroethly) ether was positively identified and quantified. Total SVOCs were approximately 0.5 g/L in ICB 1 Biofeed and 1 g/L in the Biofeed for ICB 2. Based on the data each ICB was able to reduce SVOCs by more than a factor of 10, but not eliminate. The concentration of SVOCs in ICB 2 feed and effluents was approximately 2 times higher than the Feeds and Effluents of ICB 1.

3.6 Metals.

Metals were characterized for purposes of potential regulatory and permitting requirements. The metals content was trend less throughout the study. The most noteworthy metals data are aluminum and sodium. Aluminum hydroxide was added to the feed of both ICBs at different concentrations. Biofeed samples for ICB 1 were not analyzed for aluminum during the third steady state. Aluminum was monitored in ICB 2 third steady state. Aluminum was not as concentrated in the effluent since once introduced the aluminum settled to the bottom of the ICB.

Table 12. Positive Results For VOCs in ICB 2.

| Analyte | ICB 2 Feed (ug/L) | Qualifier | ICB 2 Effluent (ug/L) | Qualifier |
|---|---|---|---|---|
| **1,2-Dichloroethane** | 197 | J* | | |
| **1,2-Dichloropropane** | | | 1 | J* |
| **Acetone** | 435 | J* | | |
| **Acetaldehyde** | | | 67 | JN* |
| **bis(2-Chloroethyl) ether** | 115 | JN* | | |
| **Bromomethane** | | | 80 | J |
| **Chloroethane** | | | 1 | JD |
| **Chloroform** | 33 | JD* | 22 | JD |
| **Chloromethane** | 3811 | J* | 140 | J* |
| **Hexanal** | | | 23 | JN* |
| **Methylene chloride** | 18 | J* | 10 | JB* |
| **Unknown** | 130 | J | 11 | J |
| **Total VOC's** | **4738** | | **356** | |

J- Estimated value; concentration is below limit of quantitation.
D- Result was obtained from analysis of a dilution.
N- tentatively identified compound.

3.7 Sodium.

Sodium is introduced into the process as sodium hydroxide during the neutralization step. As mentioned previously, the biofeed identified as batch 12 was from an off-spec production run of HT hydrolysate. During the neutralization process a recipe specifying particular volumes of HT agent from the washout and 6 percent sodium hydroxide. This recipe was followed in the batch 12 production, however a malfunction limited the amount of HT added. The normal allotment of NaOH was added. Therefore there was a greater than designed ratio of NaOH to HT in the batch 12 hydrolysate. Subsequently batch-12 hydrolysate was used at full strength when preparing the ICB 2 biofeed for this study to maintain comparable TDG loading in each ICB. Hydrolysate from batch-11 hydrolysate is diluted to 200ml/L when used for preparing biofeed. Therefore the sodium content in ICB 2 increased proportional to the increase in the feed during steady state two and three of this study. The increase in sodium in ICB 2 is represented in figure 5.

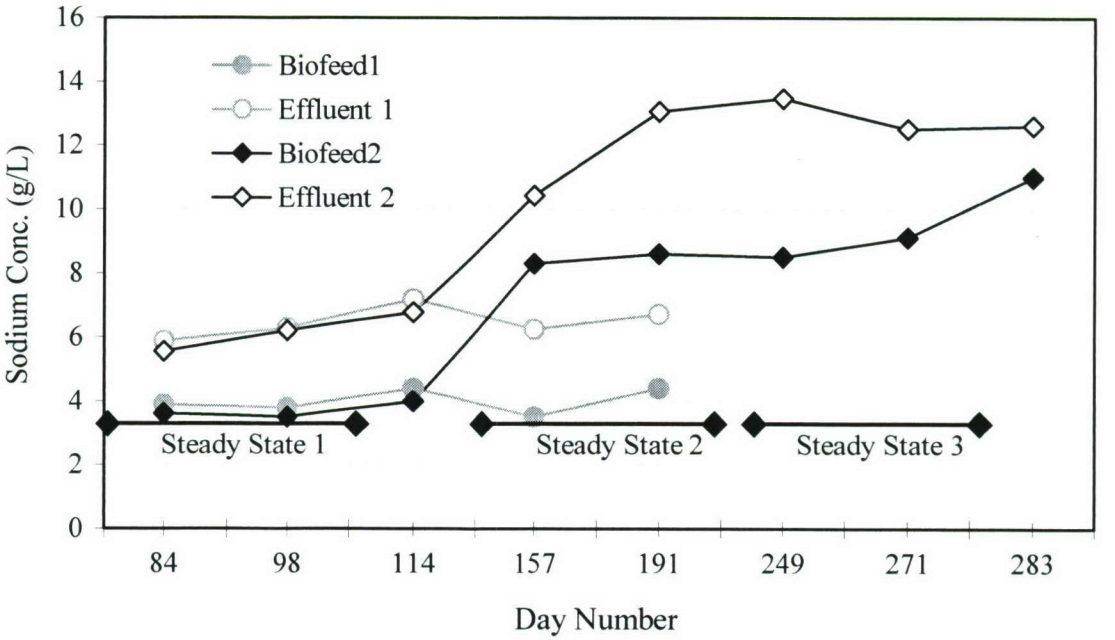



Figure 5. Chart of Sodium Concentration in ICBs during Study

The increase in sodium concentration coincided with a decrease in COD removal efficiency.

3.8 Toxic Characteristic Leachate Procedure.

The Toxic Characteristics Leachate Procedure was conducted on the ICB biomass at the end of the study to satisfy waste characterization and potential regulatory requirements for final biomass disposal. The solid biomass removed from the ICB at the end of the study was analyzed for the following compounds:

| | | |
|---|---|---|
| Arsenic | 2-Methylphenol | 1,4-Dichlorobenzene |
| Barium | 4-Methylphenol | 2-Butanone |
| Cadmium | Hexachlorobenzene | Benzene |
| Chromium | Hexachlorobutadiene | Carbon tetrachloride |
| Lead | Hexachloroethane | Chlorobenzene |
| Mercury | Mercury | Chloroform |
| Selenium | Nitrobenzene | Tetrachloroethene |
| Silver | Pentachlorophenol | Trichloroethene |
| 2,4,5-Trichlorophenol | Pyridine | |
| 2,4,6-Trichlorophenol | 1,1-Dichloroethene | |
| 2,4-Dinitrotoluene | 1,2-Dichloroethane | |

Table 13. Positive Results for TCLP Analysis of ICB Solids.

| Compound | ICB 1 (mg/L) | Qualifier | ICB 2 (mg/L) | Qualifier |
|---|---|---|---|---|
| Chromium | 0.005 | JB | 0.014 | JB |
| Lead | | | 0.16 | |
| Mercury | | | 0.0015 | |
| Silver | | | 0.019 | B |

3.9 Solids.

Solids are measured routinely as a process-monitoring sample. The buildup of biomass in an ICB is often difficult to measure as compared to a traditional stirred tank reactor. Solids going into and coming out of the reactor were measured. Feed solids were measured prior to the addition of Aluminum Hydroxide. Throughout the study the suspended solids exiting ICB 2 were much lower than ICB 1. This may be a result of the decreased COD consumption that was taking place in ICB 2 versus the higher performing ICB 1. Total dissolved solids (TDS) increased across the ICBs due to the addition of Sodium Bicarbonate for pH control. TDS values were considerably higher after the switch to hHT batch 12 in ICB 2. Batch 12 of the hHT had a considerably higher NaOH to TDG ratio than batch 11. As solids must be further processed downstream for water recycling and land-filling of the dried biomass, lower quantities of solids exiting the reactor are preferred. Excessive build-up of solids within the reactor can also produce aeration and flow problems that can cause poor performance. Excessive solids build-up is a parameter that is monitored occasionally to head off problems or understand why a reactor may be performing poorly. Excessive or sudden sloughing of biomass is also an indication that there may be a problem within the reactor. Summaries for the ICB solids measured during the study are presented in Table 14.

Table 14. Summary of the Solids Measurements Taken during the Study.

| **Parameter** | **ICB 1 Feed** | | | **ICB 1 Effluent** | | |
|---|---|---|---|---|---|---|
| | TSS | VSS | TDS | TSS | VSS | TDS |
| Mean | 168 | 73 | 8777 | 348 | 240 | 16489 |
| Min. | 26 | 12 | 723 | 33 | 5 | 10622 |
| Max. | 421 | 252 | 12590 | 2010 | 1550 | 21824 |
| Std-D | 117 | 71 | 3329 | 447 | 357 | 4383 |
| | | | | | | |
| | **ICB 2 Feed** | | | **ICB 2 Effluent** | | |
| | TSS | VSS | TDS | TSS | VSS | TDS |
| Mean | 171 | 51 | 11878 | 100 | 61 | 20322 |
| Min. | 20 | 10 | 4687 | 39 | 11 | 10023 |
| Max. | 525 | 132 | 25926 | 231 | 163 | 39766 |
| Std-D | 184 | 43 | 6106 | 51 | 46 | 10230 |

# 4. CONCLUSIONS

Chemical Oxygen Demand (COD) and Thiodiglycol (TDG) removal are the primary methods for assessing performance. The data presented are a good representation of the bioreactors ability to degrade the HT hydrolysate processed during projectile washout studies at Desert Chemical Activity, Utah.

Thiodiglycol removal across each of the ICB reactors has been good. TDG was initially detected in the effluents of each of the reactors during the ramp-up period. Once at steady-state there has been only one instance of TDG in effluent samples. That was HT-ICB 2 effluent from the first sample taken after reaching steady state at the design feed level and a 5-day hydraulic residence time (hrt). Since that sample, there have been no positive results for TDG in the effluents from any of the steady state periods. The TDG data is presented in Table 15 of the results section and again here.

Table 15. Summary of Thiodiglycol Values Measured in HT-ICB 1 and HT-ICB 2.

| | HT-ICB 1 | | | HT-ICB 2 | | |
|---|---|---|---|---|---|---|
| | **Feed TDG mg/L** | **Effluent TDG (mg/L)** | **TDG Consumed (mg/day/L)** | **Feed TDG (mg/L)** | **Effluent TDG (mg/L)** | **TDG Consumed (mg/day/L)** |
| **Mean** | 4810 | 1.8 | 1021 | 4539 | <1 | 945 |
| **Min** | 4551 | 0 | 948 | 3835 | 0 | 799 |
| **Max** | 5200 | 16.4 | 1083 | 5126 | 2.24 | 1068 |
| **Std-d** | 175 | 4.9 | 29 | 1200 | 1.2 | 134.7 |
| **Count** | 10 | 11 | 11 | 11 | 11 | 11 |

These TDG results indicate that the neutralization/biodegradation treatment previously demonstrated using higher quality mustard (HD) agent from ton containers works well on HD agent and now on the less pure HT agent from the aging weaponized stockpile at Pueblo Chemical Depot. Concerns about the treatability of weaponized Mustard agents using the process of neutralization followed by biodegradation are now, for the most part answered. The fill material in these systems can be effectively treated with this system.

This study has also demonstrated that the Aluminum Hydroxide (AH) that may be present in the explosive hydrolysate does not appear to interfere with the treatability of the HT hydrolysate. It is curious however, that on addition of the AH to the ICB 1 feed the COD removal dramatically increased as the effluent COD decreased. We speculate that the AH may supply a micronutrient missing from those supplied in the biofeed. It may also be possible that the AH in the feed binds with some of the non-degradable compounds making them transparent to effluent COD analysis, or they may become bound to the AH and have settled to the bottom of the ICB where they may continue to accumulate. However, upon addition of the AH to the feed, the feed COD does not decrease.

Throughout the course of the study ICB 2 did not remove COD as effectively as ICB 1. In the second steady state, ICB 2 was switched to batch 12 of the HT hydrolysate. An equipment malfunction during the hydrolysis process produced an off-spec batch of hydrolysate. This batch had a lower TDG concentration than a normal batch but contained the equivalent amount of NaOH normally used to stop the neutralization reaction. Therefore the TDG to NaOH ratio of this batch was much lower. This type of off-spec batch production may occur occasionally during full-scale operations, therefore the test was scheduled to determine if the bioreactor could handle this hydrolysate. To keep the TDG at the design strength the hHT was not diluted 300 ml/L as with a normal feed batch, but instead was used a full strength. Therefore the NaOH content of the hydrolysate was not diluted but instead feed to the bioreactor. The ICB culture seemed to handle this feed, except for a short upset caused by the high pH of the feed. Since the TDG:NaOH ratio was decreased, the culture was unable to produce sufficient acid from breakdown of the TDG to counteract the caustic load. Treatment of the biofeed with HCl to lower the pH to 11.0 was sufficient to keep the pH in balance with the existing pH control system. The culture acclimated to the increased salt content, was able to consume the TDG load, but was unable to remove the COD as efficiently as did ICB 1 that was given the on-spec feed through out the study.

To answer the question, can the ICB culture handle the off-spec hydrolysate? The answer is yes. There was no TDG detected in the ICB 2 culture effluent.

ICB 2 did not respond to the addition of AH as did ICB 1. Perhaps in part due to the additional salt in the feed. On addition of AH to 1.0 g/L, COD removal decreased and effluent COD increased. ICB 2 AH concentration was reduced to 0.75 g/L and the third steady state period proceeded at the 0.75 g/L level. The addition of the AH to the biofeed produced reactions by the cultures in opposite directions. Perhaps the combination of off-spec hydrolysate and high AH loading should be avoided during full-scale operations whenever possible. Figure 4, COD removal is presented again below to allow following of the batch 12 and AH addition to the ICB feeds.

Solids accumulation in the ICBs continues to be a concern. Solids did seem to accumulate in ICB 2 to the point of causing anaerobic conditions. As long as the ICB performs well, the observation of channeling is ignored. When performance drops, concerns over plugging begin. Visual observation of the culture will be difficult in a scaled-up system. When ICB 2 was not performing as well as hoped, approx. 200 mL of concentrated biomass was removed from each cell. It is difficult to tell is this helped the performance of ICB 2. By the third steady state ICB 1 also appeared visually clogged, but since it was performing well, no biomass was removed.

4.1 Comparison to Previous Studies.

Previous studies using neutralization/biodegradation to degrade hydrolyzed mustard agents include the ACWA Demonstration and Engineering Studies were conducted using 1000-gallon pilot ICB system and two previous laboratory studies using the 1-liter reactors. These studies have been previously discussed[3]. The performance of the lab scale reactors at breaking down the once thought "more difficult" weaponized mustard agents are always of interest to ACWA and the technology providers. Tables 12 below compares TDG and COD performance values from Pilot and PWS ICBs in the studies conducted to date.

Input and output values have been normalized to performance per liter of reactor volume for direct value comparison. Performances of the ICBs in studies after Demo 1 indicate comparable TDG removal capabilities. Performance differs in COD removal efficiency across the reactors. It should be noted that studies involving HT hydrolysate contain test treatments that differ across the study period and COD removal response to treatment varied during the study. For instance, this table does not clearly show the greatly improved COD removal efficiency of HTPWS-ICB 1 after addition of AH.

It is clear that the COD input load to the reactors was much greater during the HTPWS study. Since the % TDG as COD values are lower in the HT biofeed, a higher COD load was added to provide comparable TDG input values. Hence, even though COD removal efficiency was lower during HTPWS study, TDG removal from HT biofeeds was similar to that of HD biofeeds.

Table 16. Comparisons of COD and TDG Performance Values from HD and HT Pilot and PWS Studies.

| Test ICB | COD Input (mg/Day/L) | COD Output (mg/Day L) | % COD Removal Efficiency | TDG Input (mg/Day/L | TDG Consumption (mg/Day/L) |
|---|---|---|---|---|---|
| **PWS HT ICB 1** | 3512 | 817 | 74 | 942 | 941.7 |
| **PWS HT ICB 2** | 3162 | 1067 | 60 | 864.4 | 864.37 |
| **PWS ICB 1 Unfiltered HD hydrolysate** | 2375 | 349 | 85.5 | 1141 | 1128 |
| **PWS ICB 2 (Filtered HD hydrolysate)** | 2411 | 350 | 85.6 | 1092 | 1084 |
| **Demo I Pilot ICB** | 1298 | 115 | 91.1 | 612 | 612 |
| **EDS Pilot ICB** | 2266 | 217 | 90.4 | 1069 | 1069 |

4.2 Summary of Stated Objectives.

From the Introduction sections, the test objectives included:

- Confirm the ability of the laboratory-scale ICBs to effectively treat the PWS-generated HT hydrolysate at hydraulic residence times (HRTs) that are representative of full-scale design by assessing the following parameters:
  - Organic removal efficiency
  - Elimination of thiodiglycol and other target organics in the HT hydrolysate
  - Assess the impact of aluminum hydroxide in the energetic hydrolysate on ICB performance.

- Characterize ICB liquid effluents

The ICBs demonstrated the ability to degrade TDG produced during neutralization of HT agent PWS solutions at a level approximately that of previous studies conducted using HD hydrolysates. Total organic removal was not as efficient as seen in HD-ICB studies. This is assumed to be in part to the impurities in the HT that may not be biodegradable and to the different chemistry of the HT and HT hydrolysate. However, COD net removal by wt., per unit reactor volume, is comparable, although slightly lower, to previous studies on treatability of hydrolyzed HD feeds in ICB reactors.

While TDG was eliminated for the most part by the ICB, another breakdown product, 1,4-Thioxane was not. Thioxane was the only other major breakdown product of the neutralization process to be routinely present in the effluent stream. As a note, Thioxane was also present in effluent samples from previous studies.

The effect of Aluminum hydroxide added to the feed may be still inconclusive. When added to the reactor processing on-spec hydrolysate, the COD removal improved. When added to the reactor processing off-spec hydrolysate, the COD removal decreased. Even though aluminum hydroxide addition affected COD removal efficiencies in both reactors, TDG removal rates were unchanged. Removal of the other breakdown product, 1,4-thioxane, appeared to be unaffected. Aluminum hydroxide may present other handling problems. In this study the AH was added exogenously in a granular form that was undissolved and quickly settled to the bottom of any container. Movement of this material in solution continuously presented a problem. Samples of the liquid containing the AH were not representative and feed a uniform solution containing AH was nearly impossible. Perhaps AH that is produced in the neutralization process may be of a finer particle size, if not, handling may be an issue.

Sampling and analysis for complete characterization of bioreactor effluents has been completed. In general the shear number of low level compounds present in hydrolysate and biofeed samples complicated the analysis for many components. There were frequently interferences, calibration issues, and compounds of interest found in laboratory

and trip blanks. Additionally, since this was a small-scale laboratory study the volume of sample requested for particular analyses was not available. Availability of HT and Tetrytol hydrolysate was limited due to regulatory and programmatic limitations.

As of 1 March 2004, the studies described in this report will be transitioned to the PMACWA prime contractor for the PCD disposal site contractor Bechtel Corp*. Battelle**, a subsidiary of Bechtel, will conduct continued lab and engineering development studies. These continued studies and engineering would be incorporated into full-scale planning for the eventual destruction facility planned for PCD.

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** Battelle Memorial Institute, Columbus, Ohio

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APPENDIX A

POSITIVE RESULTS OF SVOC ANALYSIS FOR ICB 1 BIOFEED AND EFFLUENT

J- Estimated value; concentration is below limit of quantitation.
D- Result was obtained from analysis of a dilution.
N- Tentatively identified compound.
*- Indicates a calculated average of multiple positive results.

| Method | Analyte | Result | Qualifie | avg. result | Units |
|---|---|---|---|---|---|
| SVOC (3.8% HT Mod) | 2,2'-(ethylenedithio)diethanol | | JN | 68500 | ug/l |
| SVOC (3.8% HT Mod) | 2,4-Dinitrophenol | 320 | J | | ug/l |
| SVOC (3.8% HT Mod) | bis(2-Chloroethyl)ether | | J | 9020 | ug/l |
| SVOC (3.8% HT Mod) | Diphenyl Oxide | 3500 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Docosane | 3900 | JN | | ug/l |
| SVOC (3.8% HT Mod) | TETRACOSANE | 8500 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Unknown | | J | 113611 | ug/l |
| SVOC (3.8% HT Mod) | Unknown (RT 27.19 min) | | J | 61267 | ug/l |
| SVOC (3.8% HT Mod) | Unknown Alcohol (RT 21.66) | | J | 185833 | ug/l |
| SVOC (3.8% HT Mod) | Unknown Alkane | | J | 5722 | ug/l |
| SVOC (3.8% HT Mod) | Unknown organic acid | 4500 | J | | ug/l |
| | | | | 464673 | ug/l |
| | | | | | |
| | | | | | |
| SVOC | [1,4,5]OXADITHIEPANE | | JN | 129 | ug/l |
| SVOC | 1,2,5,6-Tetrathiocyclooctane | | JN | 628 | ug/l |
| SVOC | 1,4-OXATHIANE, 4-OXIDE | | JN | 13066 | ug/l |
| SVOC | 2(3H)-Benzothiazolimine, 3-methyl- | 890 | JN | | ug/l |
| SVOC | Acetic acid, mercapto-, methyl ester | 560 | JN | | ug/l |
| SVOC | Benzene, 1-bromo-2-fluoro- | 760 | JN | | ug/l |
| SVOC | bis(2-Chloroethyl)ether | | J | 66 | ug/l |
| SVOC | Bis(2-ethylhexyl)phthalate | 24 | J | | ug/l |
| SVOC | Dimethyl-cyano-phosphine | 550 | JN | | ug/l |
| SVOC | Dithiane isomer | 170 | J | | ug/l |
| SVOC | Hexadecenoic acid, Z-11- | | JN | 95 | ug/l |
| SVOC | Naphtho[2,3-b]thiophene, 4,9-dimethyl- | 650 | JN | | ug/l |
| SVOC | Oxirane, 2,3-dimethyl-, cis- | 450 | JN | | ug/l |
| SVOC | Unknown | | J | 748 | ug/l |
| SVOC | unknown (RT 9.82 min) | | J | 371 | ug/l |
| SVOC | Unknown Alkane (RT 23.06 min) | 99 | J | | ug/l |
| SVOC | Unknown Organic Acid (RT 22.66 min) | 94 | J | | ug/l |
| | | | | 19349 | ug/l |

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# APPENDIX B

## POSITIVE RESULTS OF SVOC ANALYSIS FOR ICB 2 BIOFEED AND EFFLUENT

| Method | Analyte | Result | Qualifier | avg | Units |
|---|---|---|---|---|---|
| SVOC (3.8% HT Mod) | 1-(2-Hydroxyethylthio)-2-(vinylthio)ethane | 2300 | JN | | ug/l |
| SVOC (3.8% HT Mod) | 1,1'-Biphenyl]-4,4'-diamine, 3,3'-dimethyl- | 30000 | JN | | ug/l |
| SVOC (3.8% HT Mod) | 1,4-Dithiane-1-oxide | | JN | 2250 | ug/l |
| SVOC (3.8% HT Mod) | 1H-1,2,3-Triazole, 4-methyl-5-(3-methyl-5-isoxazol | 39000 | JN | | ug/l |
| SVOC (3.8% HT Mod) | 2,2'-(ethylenedithio)diethanol | | JN | 580000 | ug/l |
| SVOC (3.8% HT Mod) | 2-Pentanethiol | 6000 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Benzene, 1-bromo-2-fluoro- | 34000 | JN | | ug/l |
| SVOC (3.8% HT Mod) | bis(2-Chloroethyl)ether | | | 7742.86 | ug/l |
| SVOC (3.8% HT Mod) | Bis(2-ethylhexyl)phthalate | 3000 | J | | ug/l |
| SVOC (3.8% HT Mod) | Diphenyl Oxide | 3900 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Docosane | | JN | 5250 | ug/l |
| SVOC (3.8% HT Mod) | Ethanol, 2,2'-[1,2-ethanediylbis(thio)]bis- | 55000 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Pentacosane | 8200 | JN | | ug/l |
| SVOC (3.8% HT Mod) | TETRACOSANE | 8200 | JN | | ug/l |
| SVOC (3.8% HT Mod) | TRICOSANE | 7500 | JN | | ug/l |
| SVOC (3.8% HT Mod) | Unknown Alcohols | | J | 134900 | ug/l |
| SVOC (3.8% HT Mod) | Unknown Alkanes | | J | 62970 | ug/l |
| | | | | 990212.9 | |
| | | | | | |
| SVOC | [1,1'-Biphenyl]-4,4'-diamine, 3,3'-dimethyl- | 730 | JN | | ug/l |
| SVOC | [1,4,5]OXADITHIEPANE | | JN | 133.4 | ug/l |
| SVOC | 1-(2-Hydroxyethylthio)-2-(vinylthi | | JN | 356.7 | ug/l |
| SVOC | 1,2,5,6-Tetrathiocyclooctane | | JN | 280.0 | ug/l |
| SVOC | 1,4-DIOXANE | | JN | 110.0 | ug/l |
| SVOC | 1,4-Dithiane-1-oxide | | JN | 3995.0 | ug/l |
| SVOC | 1,4-OXATHIANE, 4-OXIDE | | JN | 5187.5 | ug/l |
| SVOC | 1-Nitro-2-propanol | 260 | JN | | ug/l |
| SVOC | 2(3H)-Benzothiazolimine, 3-methyl- | 900 | JN | | ug/l |
| SVOC | 2,2'-(ethylenedithio)diethanol | 520 | JN | | ug/l |
| SVOC | 4,4'-Difluorobiphenyl | 73 | JN | | ug/l |
| SVOC | Benzene, 1-bromo-2-fluoro- | 800 | JN | | ug/l |
| SVOC | bis(2-Chloroethyl)ether | | J | 51.9 | ug/l |
| SVOC | Dimethyl-cyano-phosphine | 650 | JN | | ug/l |
| SVOC | Dithiane isomer | 220 | J | | ug/l |
| SVOC | Hexadecanoic acid | 120 | JN | | ug/l |
| SVOC | N,N-Diisopropylformamide | 40 | JN | | ug/l |
| SVOC | NITRIC ACID, ETHYL ESTER | | JN | 905.0 | ug/l |
| SVOC | Oxirane, 2,3-dimethyl-, cis- | 420 | JN | | ug/l |
| SVOC | Thiirane | 100 | JN | | ug/l |
| SVOC | Unknown | | J | 7889.7 | ug/l |
| SVOC | Unknown (RT 9.52 min) | | J | 54.0 | ug/l |
| SVOC | UNKNOWN ALCOHOL (RT 6.48 min) | 48 | J | | ug/l |
| SVOC | UNKNOWN ORGANIC ACID (RT 24.12 min) | 220 | J | | ug/l |
| SVOC | UNKNOWN ORGANIC ACID (RT 7.58 min) | 3400 | J | | ug/l |
| | | | | 26734.1 | |

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APPENDIX C

POSITIVE RESULTS FOR METALS OF INTEREST IN ICB 1 FEED AND EFFLUENT

| Analyte | Result | Qualifier | Result | Qualifier |
|---|---|---|---|---|
| | ug/L | | | |
| Aluminum | 433.33 | * | 292.5 | * |
| Barium | | | 45.04 | * |
| Cadmium | | | 3.9 | J |
| Calcium | 11650 | * | 11700 | * |
| Chromium | 205 | J* | 35 | J |
| Cobalt | 372 | J* | 192.4 | * |
| Copper | | | 116.06 | * |
| Iron | 9800 | D* | 3124 | * |
| Lead | 1250 | * | 216 | J* |
| Magnesium | 11320 | D* | 10884 | * |
| Manganese | 1700 | * | 1051.8 | * |
| Mercury | | | 2.09 | J* |
| Molybdenum | | | 73.62 | J* |
| Nickel | | | 14.4 | J* |
| Phosphorus | 43800 | D* | 33100 | * |
| Potassium | 113600 | D* | 114200 | * |
| Silicon | 10540 | * | | |
| Sodium | 4100000 | D* | 6426000 | * |
| Sulfur | 2040000 | D* | | |
| Thorium | 110 | J | | |
| Titanium | 546 | * | | |
| Zinc | 470 | * | 484.2 | * |
| | 6345686 | | 6601535 | |

J- Estimated value; concentration is below limit of quantitation.
D- Result was obtained from analysis of a dilution.
N- tentatively identified compound.
*- Indicates a calculated average of multiple positive results.

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APPENDIX D

POSITIVE RESULTS FOR METALS OF INTEREST FOR ICB 2 FEEDS AND EFFLUENT

| | Feed | | Effluent | |
|---|---|---|---|---|
| Analyte | Result | Qualifier | Result | Qualifier |
| | (ug/L) | | (ug/L) | |
| Aluminum | 8414 | D* | 597 | * |
| Arsenic | | | 117 | J |
| Barium | | | 29 | J* |
| Bismuth | 305 | JB* | | |
| Cadmium | | | 7 | J* |
| Calcium | 8263 | D* | 8643 | * |
| Chromium | 270 | J* | 31 | J* |
| Cobalt | 293 | J* | 133 | * |
| Copper | 783 | J* | 95 | * |
| Iron | 17475 | * | 3060 | * |
| Lead | 2431 | * | 294 | * |
| Magnesium | 6725 | D* | 9045 | J* |
| Manganese | 18766 | D* | 878 | * |
| Mercury | | | 4 | * |
| Molybdenum | | | 72 | B* |
| Nickel | | | 23 | J* |
| Phosphorus | 390000 | D* | 31463 | * |
| Potassium | 98375 | D* | 133875 | * |
| Silicon | 13838 | D* | | |
| Silver | 580 | | 54 | J |
| Sodium | 7075000 | D* | 10042500 | * |
| Sulfur | 2285000 | D* | | |
| Thorium | 88 | JB* | | |
| Titanium | 426 | * | | |
| Vanadium | | | 24.4 | JB |
| Zinc | 536 | * | 272 | * |
| Total Metals | 9927568 | | 10231215 | |

J- Estimated value; concentration is below limit of quantitation.
D- Result was obtained from analysis of a dilution.
N- Tentatively identified compound.
*- indicated a calculated average of multiple positive results.

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