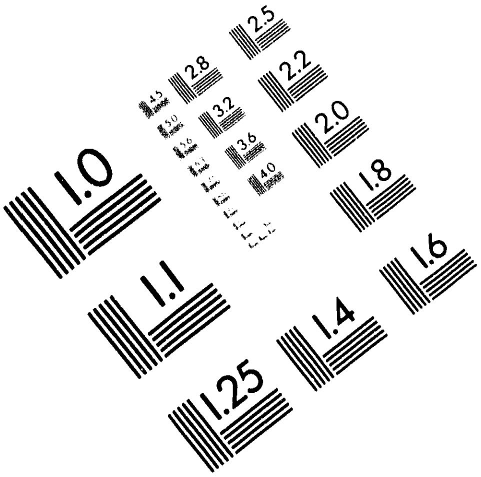
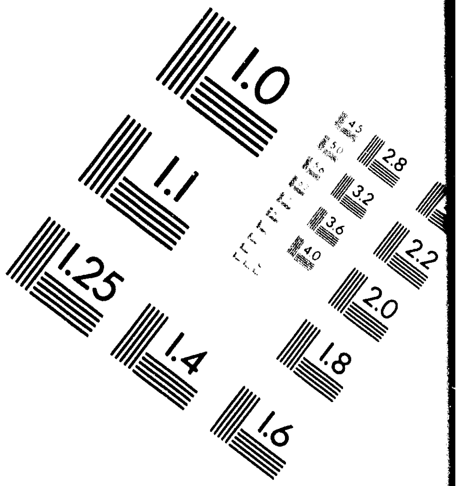
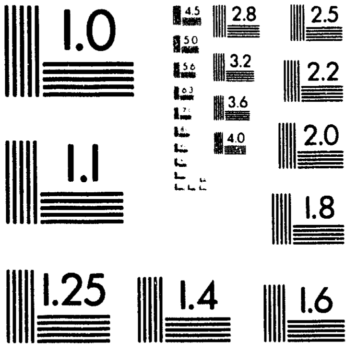
AIIM

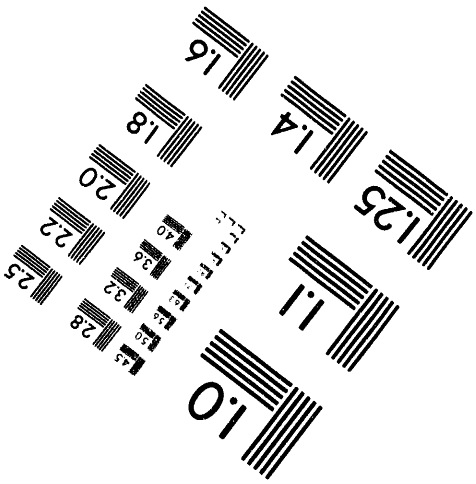
Association for Information and Image Management

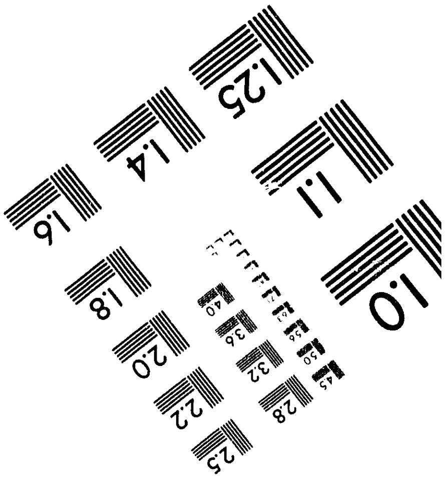
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202











MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

EGG-WTD-11271

Supercritical Water Oxidation Test Bed Effluent Treatment Study

C. M. Barnes

Published April 1994

Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Office of Environmental Restoration and Waste Management
Under DOE Idaho Operations Office
Contract DE-AC07-76ID01570

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SUPERCRITICAL WATER OXIDATION TEST BED EFFLUENT TREATMENT STUDY

Prepared by

C M Barnes
4-25-94

C. M. Barnes, Senior Engineering Specialist
Chemical and Process Engineering
Date

Reviewed by

Carolyn Shapiro
4-25-94

C. Shapiro, Engineering Specialist
Mechanical Engineering and Design
Date

Approved by

4-26-94

T. R. Charlton, Project Manager
Waste Technology Development
Date

ABSTRACT

This report presents effluent treatment options for a 50 gph Supercritical Water Test Unit. Effluent compositions are calculated for eight simulated waste streams, using different assumed cases. Variations in effluent composition with different reactor designs and operating schemes are discussed. Requirements for final effluent compositions are briefly reviewed. A comparison is made of two general schemes. The first is one in which the effluent is cooled and effluent treatment is primarily done in the liquid phase. In the second scheme, most treatment is performed with the effluent in the gas phase. Several unit operations are also discussed, including neutralization, mercury removal, and evaporation.

SUMMARY AND RECOMMENDATIONS

The U.S Department of Energy (DOE) is evaluating Supercritical Water Oxidation (SCWO) as a means to treat mixed hazardous and radioactive wastes currently stored or generated at various DOE sites. A 50 gph test bed is currently being designed that will provide evaluation data for SCWO technology. The test bed will have the flexibility to test multiple SCWO reactor designs, and will contain all feed, effluent and support systems required in a SCWO process.

Effluent treatment from the supercritical water reactor is required in order to comply with environmental regulations, to enable the test bed to operate under Idaho National Engineering Laboratory (INEL) permits and to permit disposal of wastes from the tests.

The test bed will need flexibility to handle 10 simulated wastes that vary widely in form, composition and heating value, to interface with different reactor designs that potentially operate at different temperatures and have different means of heat transfer, and also to handle a wide range of oxygen flow rates. This flexibility sets demands on the effluent treatment system because of the wide range of effluent flowrates, the range of compositions of reactor effluent, and the different types of hazardous materials that are expected in the effluents of the different waste series.

Air pollution standards set requirements for different types of effluent treatment. The very low emission limits on hazardous materials such as arsenic compounds set standards for solids removal equipment from the gaseous effluent. The form of mercury in the effluent from Test Series 1 is not certain, and removal of mercury vapor from offgas and mercury compounds from liquid effluent may be required. Several of the organic feed liquids (e.g., benzene, methanol, and tributyl phosphate) have low air emission limits and will require a means of removal for cases of incomplete oxidation in the supercritical reactor. While high destruction efficiency is expected, the scope of testing includes determining operating limits or other cases where oxidation may be incomplete. A removal efficiency of 99% of the HCl generated in Test Series 4 is required, based on maximum TRIM®SOL in the feed, to meet the air emission limit. Other acid-gases, and aqueous acids and bases formed in the process will also require neutralization.

Mercury can be removed from the gaseous effluent by adsorption on activated carbon. Impregnation of the carbon with sulfur enhances removal efficiency. An activated carbon bed in the gaseous effluent line can provide removal of other air pollutants as well, both hazardous metal solids and organic vapors. Removal of mercury from the liquid effluent can be accomplished through ion exchange or precipitation.

Of the commonly used neutralization agents, sodium hydroxide is favored because of its solubility, the solubilities of neutralization products, and the amount of reagent required. Ammonia also shows advantages, but would require additional equipment to recover the excess ammonia needed to ensure complete neutralization.

The specific requirements for waste minimization of the test bed operation need further investigation. Liquid and solid wastes from many of the test series are not expected to be hazardous, although waste minimization may still be desirable. Evaporation offers a versatile and well-proven means to achieve a large reduction in waste volume. Of the many types of evaporators available two types are most applicable for the test bed. A pot, kettle, or pan evaporator is a single vessel design that would likely operate in a batch or semibatch mode. A forced circulation evaporator can generally achieve higher concentrations of solids in the bottoms product while minimizing scaling and deposition.

Conventional SCWO effluent treatment systems cool the effluent through heat exchange or quench prior to depressurization. This results in a partially condensed fluid, which, when acid gases are present, is highly corrosive. For a SCWO unit treating mixed waste, effluent treatment would then be needed for both gaseous and liquid phases. If condensation can be avoided by minimizing effluent cooling and depressurizing in low velocity control valves, effluent treatment would be simpler, more able to separate radionuclides from salt wastes, and very likely more economical in both operating and capital costs. However, because of concerns of corrosion and plugging of these control valves, it is recommended that such a system be designed and tested.

CONTENTS

TABLES

ACRONYMS

DOE	U.S. Department of Energy
INEL	Idaho National Engineering Laboratory
LHV	lower heating value
PWA	process waste assessment
RCRA	Resource Conservation and Recovery Act
SCWO	Supercritical Water Oxidation

SUPERCRITICAL WATER OXIDATION TEST BED EFFLUENT TREATMENT STUDY

1. INTRODUCTION

The U.S Department of Energy (DOE) is evaluating Supercritical Water Oxidation (SCWO) as a means to treat mixed hazardous and radioactive wastes, currently stored or generated at various DOE sites. A 50 gph test bed is currently being designed, which will provide evaluation data for SCWO technology. The test bed will have the flexibility to test multiple SCWO reactor designs, and will contain all feed, effluent and support systems required in a SCWO process.

Effluent treatment from the Supercritical Water Reactor is required in order to comply with environmental regulations, to enable the test bed to operate under Idaho National Engineering Laboratory (INEL) permits, and to allow disposal of wastes from the tests.

The purposes of this report is to: (a) provide definition of the effluent, (b) to determine and propose alternative treatment schemes, and (c) to provide an evaluation of treatment alternatives at a general level. More detailed evaluations and selection of the test bed effluent treatment system will be done by the Test Bed Design team.

2. REACTOR EFFLUENT COMPOSITION

The reactor effluent composition will depend on:

- The composition of simulated waste being tested
- The concentration of waste in water being fed to the reactor
- The type and amount of oxidizer used
- The efficiency of organic destruction in the reactor
- The amount of corrosion in the reactor
- The type and amount, if any, of neutralization agents added in or upstream of reactor.

Ten simulated DOE wastes have been defined for testing in the test bed.[1] Eight of these 10, Series 1 through 8, have been given priority, and serve as the design basis for the test bed.[2] The eight wastes include organic liquids and solids, with Resource Conservation and Recovery Act (RCRA)-hazardous metals, surrogate radionuclides, and nonhazardous salts added. All of the simulated test wastes are mixtures of components. Actual tests may depart from these definitions, both in preliminary tests in which feed compositions are simplified, or in later tests to determine effects of waste stream variability.

The test bed design will be reviewed for its capability to treat Test Series 9, which is a halogenated solvents waste. Test Series 10 is a waste sludge, and modifications would be expected to be required in the test bed to handle the high inorganic solids content of this waste.

One set of feed and effluent compositions is given in Appendix A, Table 3 (feed) and Table 4 (effluent). These compositions are based on: (a) the eight waste series as defined in Reference 2, (b) a concentration of waste in water corresponding to a heating value of 1500 Btu/lb, (c) oxygen of three times the stoichiometric requirement, (d) complete organic destruction, (e) no corrosion products in the reactor, and (f) no neutralization. The effluent compositions given in Table 4 of Appendix A, represent one set of limiting cases, and also a basis for recalculating compositions for departures from the above assumptions.

Flows and compositions of other cases also need to be considered in the design of an effluent treatment system. The amount of waste in water will vary with reactor design, and over the course of testing a given waste series. To estimate the effect of this variation, effluent compositions were calculated for different cases of methanol and oxygen concentrations and are given in Table 1.

To enable calculation of other cases of reactor effluent, the heating values of the test waste series are given in Table 1 of Appendix A, and the stoichiometry of oxidation reactions of test waste components is given in Table 2 of Appendix A.

Heating values (LHV) of individual components not shown in Appendix A, Table 1, are found in Table 2.

Table 1. Effect of waste and oxygen concentrations on effluent composition.

Methanol, wt% of water plus waste	Oxygen, % of stoichiometric	Effluent rates, lb/hr			
		Water	CO_2	O_2	Total
3.3 (300 Btu/lb)	105	418.2	18.8	1.0	438.0
3.3	200	418.2	18.8	20.5	457.5
3.3	300	418.2	18.8	41.0	478.0
9.9 (900 Btu/lb)	105	421.4	56.4	3.1	480.9
9.9	200	421.4	56.4	61.6	539.4
9.9	300	421.4	56.4	123.2	601.0
16.5 (1500 Btu/lb)	105	424.6	94.1	5.1	523.8
16.5	200	424.6	94.1	102.7	621.4
16.5	300	424.6	94.1	205.4	724.1

Table 2. LHV of individual components.

Methanol	9,078 Btu/lb
Acetone	12,513 Btu/lb
Polyethylene	18,650 Btu/lb
Polyvinyl chloride	7,920 Btu/lb
Cellulose	7,500 Btu/lb
Ethylene glycol	7,784 Btu/lb

The heating values vary slightly with temperature. Heating values of benzene, methanol, acetone and ethylene glycol were calculated at 600°C, and found to be within 0.6% of standard values, which are at 298 K.

It is expected that different reactor designs and reactor/preheater configurations will differ in the maximum heating value that can be tolerated, and hence in the effluent composition. If a preheater heated waste and water to 400°C and due to materials, the reactor temperature was limited to 650°C, the feed would be limited to about 420 Btu/lb, or 2.4% benzene in water. For this case, the exothermic heat of reaction is equivalent to that needed to heat the feed from 400 to 650°C. If, for the same reactor, heat given off by the reaction is used to heat feeds from ambient temperature to 400°C, the amount of waste can be increased to 8.6 to 10% benzene (1500 to 1720 Btu/lb). The lower value corresponds to stoichiometric oxygen and the higher to three times stoichiometric.

A platelet reactor is expected to be capable of a reactor outlet temperature higher than 650°C. Heat released from the oxidation of 4% benzene in water would be equivalent to raising the temperature of the total feed from 400° to 800°C. Some increase in waste concentration for the platelet reactor is possible by feeding low temperature water to the porous wall reactor. However, since neither the inlet temperature needed to sustain oxidation, nor the maximum outlet temperature is known with certainty, the maximum concentration of waste to water for the platelet reactor will need to be determined by testing.

A neutralization agent for reactor effluent has not been selected, and it is possible that different ones could be used in different tests. The following are neutralization reactions for caustic, ammonia, and calcium hydroxide:

$$NaOH + HCl = NaCl + H_2O$$
$$NH_3 + HCl = NH_4Cl$$
$$Ca(OH)_2 + 2\ HCl = CaCl_2 + 2\ H_2O$$

Products of neutralization of SO_2 may be sulfates, sulfites, hydrogen sulfates, or hydrogen sulfites, depending on temperature, pH and amount of base added.

Table 3 shows the effluent for Test Series 3, 4, and 8, neutralized with 120% of stoichiometric 20% caustic, and using the same assumptions as Appendix A, Table 4.

Table 3. Effluent for Test Series 3, 4, and 8 based on neutralization with caustic, lb/hr.

	Series 3	Series 4	Series 8
H_2O	414.0	440.0	469.0
CO_2	140.2	104.7	101.2
O_2	258.1	216.2	225.1
N_2	—	0.35	—
Other			
Sm_2O_3	—	0.145	—
Na_2O	—	0.28	—
K_2O	—	0.11	—
CaO	—	0.09	—
Fe_2O_3	—	0.012	—
ZnO	—	0.005	-
NaCl	3.1	7.7	—
Na_2SO_3	—	1.6	—
Na_3PO_4	—	—	12.7
NaOH	0.42	1.3	1.9

3. EFFLUENT STANDARDS

A very brief review of regulatory standards for expected wastes was made in order to better determine effluent treatment alternatives. This review is not intended to be a process waste assessment (PWA) as required by EG&G Company Procedure 8.1.

Liquid and solid effluents will be subject to disposal regulations contained in the RCRA, due to RCRA-hazardous components purposely added to feeds, and possibly products of corrosion or byproducts of oxidation. Air emissions will be subject to Idaho air pollution control rules.

Table 4 shows concentrations of contaminants that cause the waste to be classified as hazardous under RCRA. Only those contaminants are listed that are expected to be present in waste from the test bed.

It should be noted that hazardous waste is not expected to be produced for every test waste. Whether hazardous waste results from tests of Series 1 (in regard to benzene), 9, and 10 depends on the destruction efficiency achieved in the reactor. Tests with reactors constructed of a high-chromium alloy may result in chromium in the waste of Series 3, 4, 5, 8, 9, and 10 as a result of corrosion.

Possible air pollutants in SCWO gaseous effluent are given in Appendix B, which also presents estimates of a worst case effluent composition. As for the liquid effluents, not all air pollutants are expected for every test waste. Pollutants that are those most likely to be present in one or more tests are given in Table 5.

Table 4. RCRA concentration of contaminants for the toxicity characteristic.

EPA hazardous waste number	Contaminant	Regulatory level mg/L	Test Series which may contain contaminant
D004	Arsenic	5.0	2
D005	Barium	100.0	2
D018	Benzene	0.5	1
D006	Cadmium	1.0	2
D019	CCl_4	0.5	9, 10
D007	Chromium	5.0	2, possibly others
D030	1,1-Dichloroethene	0.7	9, 10
D008	Lead	5.0	2
D009	Mercury	0.2	1
D010	Selenium	1.0	2
D011	Silver	5.0	2
D039	Tetrachloroethylene	0.7	9

Table 5. Pollutants likely to be present in one or more tests.

Substance	IDAPA emission limit lb/hr	Circumstances of highest emissions
Ammonia	1.2	Series 5, low temperature
Biphenyl	0.1	Series 1, low conversion
Dibutyl phosphate	0.573	Series 8, low conversion
Diethanolamine	1.0	Series 5, low conversion
Ethanolamine	0.533	Series 5, low conversion
Hydrogen chloride	0.05	Series 4, incomplete neutralization
Mercury	0.001–0.007[a]	Series 1
Methyl alcohol	2.6	Series 2, low conversion
P_2O_5	0.067	Series 8, poor solids separation
Tributyl phosphate	0.167	Series 8, low conversion
Arsenic compounds	0.0000015	Series 2
Benzene	0.0008	Series 1, less than 99.993% destruction
Cd & compounds	0.0018	Series 2
CCl_4	0.00044	Series 9 and 10, low conversion
Tetrachloroethylene	0.013	Series 9, low conversion

---

a. Emission limit depends on form of mercury.

The above standards set requirements for different types of effluent treatment. The very low emission limits on hazardous materials (e.g., arsenic compounds), set standards for solids removal equipment from the gaseous effluent. The form of mercury in the effluent from Case 1 is not certain, and removal of mercury vapor from offgas and mercury compounds from liquid effluent may be required. Several of the organic feed liquids such as benzene, methanol and tributyl phosphate, have low emission limits, and will require a means of removal for cases of incomplete oxidation in the supercritical reactor. A removal efficiency of 99% of the HCl generated in Series 4 is required, based on maximum TRIM®SOL in the feed, to meet the emission limit. Other acid gases, and aqueous acids and bases formed in the process will also require neutralization.

The following air pollutant emission standards set requirements for treatment of any gaseous waste released to the atmosphere:

- Removal of mercury
- Removal of solid pollutants (e.g., As and Cd compounds and PO_5)

- Removal of organic compounds (e.g., benzene, methanol and ethanolamine)
- Removal of acidic and alkaline gases (e.g., HCl and NH_3).

RCRA regulations also set requirements for effluent treatment. Neutralization will succeed in rendering corrosive waste into nonhazardous waste for all test series but 1, 2, 9, and 10, assuming no RCRA-hazardous metals in the effluent as a result of corrosion. Cases 1, 9, and 10 contain toxic organics as defined by RCRA. Although the solubilities of these compounds in water are "low", they are still orders of magnitude higher than the RCRA limit (see Table 6).

Thus for Test Series 1 containing benzene, the destruction efficiency will need to be greater than 99.999% to ensure the effluent water is not hazardous because of residual benzene in solution. This cannot be guaranteed for the test bed, since one goal of the unit is to define an envelope of operating conditions where this level of destruction is obtained. Therefore, for some tests, the waste will likely be hazardous. The same is true for series 9 and 10.

A more thorough review of waste treatment in light of environmental waste minimization criteria needs to be performed. If reactors are tested, which are constructed of alloys containing chromium, hazardous waste could be minimized either by evaporation of the effluent to a small volume of solids or sludge, or by ion exchange to remove chromium. Removal of residual organics from liquid effluent is another means of hazardous waste minimization, either through recycle to the SCWO reactor or a separate treatment method. The major alternatives for treatment are air or steam stripping, and ozone/hydrogen peroxide/UV oxidation.

Table 6. Solubilities in water.

Compound	Solubility in water mg/l	RCRA limit mg/l
Benzene	1,720	0.5
1,1-Dichloroethylene	210	0.7
Tetrachloroethylene	400	0.7

4. ALTERNATIVE TREATMENT SYSTEMS

Existing SCWO pilot plants process effluent by first cooling, then depressurizing, and then, if needed, further processing gaseous and liquid effluent. Advantages of this general scheme are that energy can potentially be recovered from the high pressure fluid, it is amenable to oxygen and/or carbon dioxide recovery, and some equipment is of reduced size due to higher pressure compared to alternate schemes.

As the supercritical fluid is cooled, it's density gradually increases and water condenses. If the effluent was 100% water, a theoretical case, the density would increase 10-15 times and the fluid would become liquid without going through a phase boundary. In the real case with oxygen and CO_2 present, the fluid will become mixed phase as it is cooled. As the fluid is cooled to and below the critical temperature, for effluents containing HCl, the initial liquid condensate will be very concentrated in acid and hence very corrosive. If cooling is done by quench water, liquid is introduced into the system and the volume of liquid effluent increases by a factor of three or higher, which will increase the cost for the system.

After cooling, the fluid is depressurized. Part of the condensed water, the amount depending on the temperature to which the fluid was cooled, will revaporize as the pressure is let down. Vaporization can damage the let-down valves because of cavitation and erosion.

Several advantages could result from an alternate system, in which cooling prior to pressure let down is minimized in order to avoid condensation:

- Avoiding the liquid phase will avoid electrochemical corrosion in the effluent cooler, and possibly also the let-down valves.
- In the gas phase, virtually all solids are in the solid phase and can be separated by gas-solid separation techniques. Separation becomes more difficult in a liquid in which many solids dissolve in part or in whole.
- Acid gases, with no liquid water present, are noncorrosive, and can be removed in separate operations from removal of solid radionuclides. This may permit a good separation between radionuclide solids and neutralization salts, which make solidification difficult. Once water condenses, however, both acid gases and radionuclides can dissolve into the aqueous phase.
- Little or no equipment may be needed to treat liquid effluent.
- Compared to the conventional system, which uses energy to first condense and then revaporize the water in the effluent in an evaporator, less energy is required.
- The high temperature, low pressure effluent is similar to off-gas from many other oxidation technologies, and treatment technology is well established.

Based on steam properties only, it's estimated that the effluent could be cooled to about 450°C and then depressurized without any condensation. With oxygen and CO_2 in the effluent, cooling to a lower temperature prior to depressurization may be possible. Following depressurization to about 240 psia, solids would be separated using conventional gas-solid separation techniques. If radionuclides were present, they would be expected to be removed with the solids, thereby separating them from salts that result from later neutralization.

Acid gases (e.g., HCl) could then be removed by several techniques. The gas containing HCl is still hot enough to allow efficient operation of a spray drier, which would cool the gas, remove HCl, and result in a dry salt waste and an offgas of oxygen and carbon dioxide. Other well-proven methods could also be used, (e.g., packed-bed scrubbers, tray scrubbers, fluidized bed scrubbers, venturi scrubbers, or spray towers). Mercury would likely need to be removed prior to acid-gas scrubbing, in order to avoid contaminating the salt waste with a RCRA-hazardous metal.

The major uncertainty in a gas phase effluent treatment system is whether valves exist which are capable of operating at high temperature with both acid gases and particulate, and without internal condensation. Condensation can likely be avoided by a low velocity control valve that forces the fluid to follow a tortuous path of right angle turns. Severe service valves of this type are manufactured by Control Components, Inc., and have been used in high pressure stream production and also in many applications in the oil and gas industry.

5. MERCURY REMOVAL

The forms of mercury that will be in the effluent cannot be determined with certainty. When Modar tested a mercury containing feed in SCWO, they used mercury chloride in the feed and found mercury, assumed as the chloride, in the effluent. It was concluded that most of the mercury deposited since it was found in water and acid rinses. Mercury was not detected in the gaseous effluent. Based on municipal waste incinerators, mercury can be in offgas as chloride, oxide, or elemental mercury. Elemental mercury is sufficiently volatile that treatment of the offgas must be done for air pollution control.

5.1 Mercury Removal from Gaseous Effluent

Based on a very brief review of the literature, the best method of mercury removal appears to be activated carbon adsorption. Most experience with mercury removal in gas streams comes from municipal waste incinerators, and mostly from Europe. Three methods are used:

1. Sodium sulfide injection
2. Activated carbon injection
3. Activated carbon beds.

The injection methods require a fabric filter, which is not planned for the test bed. There are other less-developed methods (e.g., selenium filters and scrubbing with cupric chloride). These offer no apparent advantage over the simple carbon bed.

A carbon bed has the advantage of being a well-developed, simple technology. It also would provide purification of the offgas for a variety of contaminants besides mercury, namely heavy metals, acid gases, and organics. If sized for only mercury removal, it would likely become loaded very quickly for upset cases of low conversion. Activated carbon impregnated with sulfur has been found to more effective than nonimpregnated carbon for adsorbing elemental mercury.[3]

For the SCWO test bed, if the gas is not saturated with water, moisture condensation will not occur in the carbon bed. Particulate removal should be done upstream of the bed to prevent the bed from plugging. Another advantage of using activated carbon for mercury removal is that the carbon will also remove other RCRA-hazardous and heavy metals as well as organics.

Air Pollution Control in Thermal Treatment, EGG-WTD-10038[4] lists the following suppliers of activated carbon for heavy metals (presumably including mercury):

CSC (919) 923-2911
P.O. Box 3
Bath, NC 27808

7. EVAPORATION

Table 8 shows estimates of the amount of solids in test bed effluent, based on neutralization with 20% caustic, and material balances using 1500 Btu/lb feed. It should be recognized that actual effluents will have lower solids concentrations than shown in Table 8 because of quench water and lower organic feed contents.

From the above concentrations, a large volume reduction in waste is possible by evaporating water from the liquid effluent. Evaporators have been widely used in the nuclear industry for this purpose. However, assuming no hazardous organics or corrosion products, waste in most test series will not be hazardous, and benefits of volume reduction may be outweighed by the energy cost of an evaporator.

Evaporators can experience operational problems due to scaling, foaming, and entrainment, particularly for feeds of widely varying composition. Upstream filtration, chemical inhibitors, and proper selection of materials are needed to avoid corrosion. If used, chemical inhibitors would need to be nonhazardous.

Measures to limit scaling, which impedes heat transfer should also be considered. External rather than internal heating would allow heat transfer to the dilute feed rather than the concentrated liquid in the evaporator, thus reducing scale. Adding seed crystals as nuclei for precipitation is another method for limiting scaling.

Vapor-liquid separation devices at the vapor outlet improve disentrainment of liquid. These devices include: (a) disengagement chambers, (b) beds of packing, (c) cyclones, (d) baffles, and (e) demisters.

Table 8. Amount of solids present in test bed effluent.

	Solids produced lb/hr	Solids concentration wt%	RCRA-hazardous
Series 1	0.04	0.01	Yes
Series 2	2.08	0.50	Yes
Series 3	3.1	0.67	No
Series 4	9.94	2.10	No
Series 5	3.82	0.92	No
Series 6	1.73	0.46	No
Series 7	1.59	0.38	No
Series 8	12.7	2.7	No

There are a large variety of evaporator designs. The majority utilize steam and are not readily adaptable to electric heating. Two common designs that can be used with electric heating are the pot, kettle, or pan evaporator and the forced circulation evaporator. Pot, kettle, or pan evaporators are single vessels, almost always operated in a batch or semibatch mode. Heat transfer and evaporation occur inside a vessel that is externally heated by a jacket or internally heated by a heating coil. Advantages of this design include its simplicity, low expense and space requirements compared to other designs, and, in some designs, the ability to easily remove and clean the heating coils. The major disadvantage is that, with the heating coils inside the vessel, deposition and fouling may be high.

Forced circulation evaporators can achieve higher concentrations of solids. Force circulation improves heat transfer as well as minimizing scaling and deposition. The mechanical energy may be from pumps or scrapers for deposition control. The heat transfer unit is usually separate from the evaporation and separation chamber.

8. REFERENCES

1. C. M. Barnes, *Mixed Waste Survey for the Supercritical Water Oxidation Program*, EGG-WTD-10984, November 1993, Appendix D.

2. C. Barnes, K. Garcia, R. Mizia, C. Shapiro, J. Svoboda, G. Thurston, *Supercritical Water Oxidation Test Bed Functional and Operational Requirements*, F/OR-232, February 1994.

3. AirTECH News, July 1993, p. 98. Contact Brian Gullett of EPA at (919) 541-1534 for more information on mercury removal with sulfur impregnated carbon.

4. G. L. Anderson, "Air Pollution Control in Thermal Treatment Systems," EGG-WTD-10038, May 1991

5. D. O. Reimann, "Mercury Output from Garbage Incineration," *Waste Management & Research 4*, 1986, pp 45-56.

6. T. G. Brna, J. D. Kilgroe, "The Impact of Particulate Emissions Control on the Control of Other MWC Emissions," *J. Air Waste Management Association 40*, September 1990, pp. 1324-1330.

Appendix A

Calculation of Feed and Effluent Compositions for Eight Test Waste Cases

EG&G Idaho, Inc.
FORM EGG-2631#
(Rev. 01-92)

Project File Number	WTD-3YH061-074-HW
EDF Serial Number	ID121217/0015
Functional File Number	

ENGINEERING DESIGN FILE

Project/Task	Supercritical Water Oxidation Hazardous Waste Pilot Plant		
Subtask	Feed and Effluent Composition	EDF Page	1 of 9

TITLE: CALCULATION OF FEED AND EFFLUENT COMPOSITIONS FOR EIGHT TEST WASTE CASES

SUMMARY: EDF ID121217/11, "Hazardous Waste Pilot Plant Test Waste Definition", defines compositions of eight simulated wastes. This EDF contains summaries of calcuations of the feed and effluent compositions for a 50 GPH SCWO test unit. The following tables are attached:

1. Heating values for the test wastes, and the basis for these values
2. Stoichiometry of reactions for the components of the test wastes
3. Summary of feed rates, including waste, water and oxygen, for the eight test series
4. Summary of effluent rates for the eight test series.

All calculations of feed and effluent rates are based on the water plus waste feed having a heating value (LHV) of 1500 Btu/lb, and using three times the stoichiometry requirement of oxygen.

Distribution (complete package): C. M. Barnes, J. M. Beller, T. R. Charlton, K. M. Garcia, R. W. Marshall, Jr., W. C. Reed, C. Shapiro, H. Welland

Distribution (summary page only): J. J. McCarthy

Author Dept. C. M. Barnes B820 C M Barnes 3-24-94	Reviewed Date D. M. Ginosar 3/24/94 D. M. Ginosar	Approved Date T. R. Charlton 3-24-94
	EG&G Review Date	EG&G Approval Date

TABLE 1

HEATING VALUES OF TEST SERIES

Series	Heating Value, Btu/lb	Basis
1	17,450	Benzene
2	10,800	50% Methanol, 50% Acetone
3	9,500	60% cellulose, 35% polyethylene, 5% PVC; heating values for these estimated
4	15,000	Rounded from value given in Report DOE/ID/12915-FIN for TRIMSOL
5	9,800	50% ethylene glycol (7800 Btu/lb), 15% ethanolamines (approx. 10,000 Btu/lb) 15% motor oil (est. 19,000 Btu/lb)
6	14,090	Carbon
7	17,860	Trimethylbenzene
8	15,670	Heating values for TBP and DBP estimated to be 12,200 and 11,600 Btu/lb respectively, and of diluent to be 19,200 Btu/lb

TABLE 2

STOICHIOMETRY OF OXIDATION REACTIONS OF TEST WASTE COMPONENTS

Test Series 1

(benzene)	$C_6H_6 + 7.5\ O_2 \dashrightarrow 6\ CO_2 + 3\ H_2O$
(biphenyl)	$C_{12}H_{10} + 14.5\ O_2 \dashrightarrow 12\ CO_2 + 5\ H_2O$
(diphenylamine)	$C_{12}H_{11}N + 14.75\ O_2 \dashrightarrow 12\ CO_2 + 5.5\ H_2O + 0.5\ N_2$
(phenol)	$C_6H_6O + 7\ O_2 \dashrightarrow 6\ CO_2 + 3\ H_2O$
(diphenyl mercury)	$C_{12}H_{10}Hg + 14.5\ O_2 \dashrightarrow 12\ CO_2 + 5\ H_2O + Hg$

Assumptions:

1. Complete oxidation
2. Elemental mercury is formed rather than oxides

Table 2 continued

Test Series 2

(methanol) $CH_4O + 1.5\ O_2 \text{ ---> } CO_2 + 2\ H_2O$
(acetone) $C_3H_6O + 4\ O_2 \text{ ---> } 3\ CO_2 + 3\ H_2O$

$Ba(C_2H_3O_2)_2 + 4\ O_2 \text{ ---> } BaO + 4\ CO_2 + 3\ H_2O$
$Cd(C_2H_3O_2)_2 + 4\ O_2 \text{ ---> } CdO + 4\ CO_2 + 3\ H_2O$
$Cr(C_2H_3O_2)_3 \cdot H_2O + 6\ O_2 \text{ ---> } 0.5\ Cr_2O_3 + 6\ CO_2 + 5.5\ H_2O$
$Pb(C_2H_3O_2)_2 + 4\ O_2 \text{ ---> } PbO + 4\ CO_2 + 3\ H_2O$
$Ag(C_2H_3O_2) + 2\ O_2 \text{ ---> } AgO + 2\ CO_2 + 1.5\ H_2O$
$Nd(C_2H_3O_2)_3 \cdot H_2O + 6\ O_2 \text{ ---> } 0.5\ Nd_2O_3 + 6\ CO_2 + 5.5\ H_2O$
$Sm(C_2H_3O_2)_3 \cdot 3H_2O + 6\ O_2 \text{ ---> } 0.5\ Sm_2O_3 + 6\ CO_2 + 7.5\ H_2O$
$Eu(C_2H_3O_2)_3 + 6\ O_2 \text{ ---> } 0.5\ Eu_2O_3 + 6\ CO_2 + 4.5\ H_2O$

Assumptions:

1. Complete oxidation of methanol, acetone and acetates
2. Metals in acetates will form oxides
3. As_2O_3 and SeO_2 will not react

Test Series 3

(PVC) $(C_2H_3Cl)_n + 2.5n\ O_2 \text{ ---> } n[2\ CO_2 + HCl + H_2O]$
(polyethylene) $(CH_2)_n + 1.5n\ O_2 \text{ ---> } n[CO_2 + H_2O]$
(cellulose) $(C_6H_{10}O_5)_n + 6n\ O_2 \text{ ---> } n[6\ CO_2 + 5\ H_2O]$

Assumptions

1. Complete oxidation
2. All components except polyethylene and PVC can be represented by cellulose.

Table 2 continued

Test Series 4

(Trimsol) $C_{20}H_{37.5}O_{1.65}Cl_{1.1}S_{0.11}N_{0.22} + 28.385\ O_2 \dashrightarrow 20\ CO_2 + 18.2\ H_2O + 0.105\ N_2 + 0.11\ SO_2 + 1.1\ HCl$

$Na + 0.25\ O_2 \dashrightarrow 0.5\ Na_2O$
$Ca + 0.5\ O_2 \dashrightarrow CaO$
$K + 0.25\ O_2 \dashrightarrow 0.5\ K_2O$

$Zn(C_2H_3O_2)_2 + 4\ O_2 \dashrightarrow ZnO + 4\ CO_2 + 3\ H_2O$
$Fe(C_2H_3O_2)_2 \cdot 4H_2O + 4.25\ O_2 \dashrightarrow 0.5\ Fe_2O_3 + 4\ CO_2 + 7\ H_2O$

Assumptions

1. Complete oxidation
2. Trimsol formula is estimated based on elemental analysis and typical petroleum oil carbon number
3. Na, Ca, K which are contained in Trimsol produce respective oxides
4. S in Trimsol goes to SO_2; N to N_2
5. Zn and Fe go to oxides as shown above

Test Series 5

(ethylene glycol)	$C_2H_6O_2 + 2.5\ O_2 \dashrightarrow 2\ CO_2 + 3\ H_2O$
(MEA)	$C_2H_7ON + 3.25\ O_2 \dashrightarrow 2\ CO_2 + 3.5\ H_2O + 0.5\ N_2$
(DEA)	$C_4H_{11}O_2N + 5.75\ O_2 \dashrightarrow 4\ CO_2 + 5.5\ H_2O + 0.5\ N_2$
(TEA)	$C_6H_{15}O_3N + 8.25\ O_2 \dashrightarrow 6\ CO_2 + 7.5\ H_2O + 0.5\ N_2$
(motor oil)	$C_{18}H_{38} + 27.5\ O_2 \dashrightarrow 18\ CO_2 + 19\ H_2O$
(boric acid)	$H_3BO_3 \dashrightarrow 0.5\ B_2O_3 + 1.5\ H_2O$
(PCB)	$C_{12}H_6Cl_4 + 12.5\ O_2 \dashrightarrow 12\ CO_2 + H_2O + 4\ HCl$

Assumptions

1. Complete oxidation
2. Motor oil assumed to be as given above
3. Boric acid assumed, at supercritical conditions, to decompose to boric oxide and water
4. Motor oil typically has Mg, Zn, Ca, and S; it is assumed these are present as sulfates and undergo no reaction

Table 2 continued

Test Series 6

$C + O_2 \text{---}> CO_2$
$Al(C_2H_3O_2)_3 + 6\ O_2 \text{---}> 0.5\ Al_2O_3 + 6\ CO_2 + 4.5\ H_2O$
$Ca(C_2H_3O_2)_2 + 4\ O_2 \text{---}> CaO + 4\ CO_2 + 3\ H_2O$
$Fe(C_2H_3O_2)_2{\cdot}4H_2O + 4.25\ O_2 \text{---}> 0.5\ Fe_2O_3 + 4\ CO_2 + 7\ H_2O$
$Ni(C_2H_3O_2)_2 + 4\ O_2 \text{---}> NiO + 4\ CO_2 + 3\ H_2O$
$K(C_2H_3O_2) + 2\ O_2 \text{---}> 0.5\ K_2O + 2\ CO_2 + 1.5\ H_2O$
$Si(C_2H_3O_2)_4 + 8\ O_2 \text{---}> SiO_2 + 8\ CO_2 + 6\ H_2O$

Assumptions

1. Complete oxidation
2. NaF, $NaHSO_4$, and Na_2SO_4 do not undergo reaction
3. Metals (as acetates) for oxides

Test Series 7

(trimethylbenzene) $C_9H_{12} + 12\ O_2 \text{---}> 9\ CO_2 + 6\ H_2O$
$C_{14}H_{26}O_7SNa + 18.25\ O_2 \text{---}> 14\ CO_2 + 13\ H_2O + SO_2 + 0.5\ Na_2O$
$C_{20}H_{38}O_7SNa + 27.25\ O_2 \text{---}> 20\ CO_2 + 19\ H_2O + SO_2 + 0.5\ Na_2O$
$C_{20}H_{41}O_5 + 27.75\ O_2 \text{---}> 20\ CO_2 + 20.5\ H_2O$

Assumptions

1. Complete Oxidation
2. Composition based on Atomlight formulation, Instagel expected to be similar
3. 20% of Atomlight composition unknown, know composition prorated

Test Series 8

$(C_4H_9)_3PO_4 + 18\ O_2 \text{---}> 12\ CO_2 + H_3PO_4 + 12\ H_2O$
$(C_4H_9)_2HPO_4 + 12\ O_2 \text{---}> 8\ CO_2 + H_3PO_4 + 8\ H_2O$
$C_{12}H_{26} + 18.5\ O_2 \text{---}> 12\ CO_2 + 13\ H_2O$

Assumptions

1. Complete Oxidation
2. C_{10}-C_{14} diluent taken to be all C_{12}

TABLE 3

FEED SUMMARY, LB/HR

	Series 1	Series 2	Series 3	Series 4
(Dilution, % Waste)	(8.6)	(14.25)	(15.75)	(10)
H_2O	380.7	357.2	350.9	374.9
O_2	327.2	315.0	387.1	324.3
Other				
Benzene	28.6			
Diphenyl	5.4			
Diphenylamine	0.9			
Phenol	0.9			
Diphenyl Hg	0.072			
CH_3OH		27.9		
CH_3COCH_3		27.9		
As_2O_3		0.235		
$Ba(C_2H_3O_2)_2$		0.331		
$Cd(C_2H_3O_2)_2$		0.365		
$Cr(C_2H_3O_2)_3 \cdot H_2O$		0.85		
$Pb(C_2H_3O_2)_2$		0.28		
SeO_2		0.25		
$Ag(C_2H_3O_2)$		0.275		
$Nd(C_2H_3O_2)_3 \cdot H_2O$		0.42		
$Sm(C_2H_3O_2)_3 \cdot 3H_2O$		0.23		0.32
$Eu(C_2H_3O_2)_3$		0.39		
Polyvinylchloride			3.3	
Polyethylene			23.0	
Cellulose			39.3	
Trimsol				41.7 (Note 3)
$Fe(C_2H_3O_2)_2 \cdot 4H_2O$				0.02
$Zn(C_2H_3O_2)_2$				0.01

Basis and Assumptions:

1. 50 GPH waste + water, 1500 Btu/lb, 3 times stoichiometric O_2
2. For series 3, all components except PVC and PE represented by cellulose
3. Formula for TRIMSOL assumed to be $C_{20}H_{37.5}O_{1.65}Cl_{1.1}S_{0.11}N_{0.22}$ plus 5000 ppm Na, 1800 ppm Ca, 1800 ppm K

TABLE 3 continued

FEED SUMMARY, LB/HR

	Series 5	Series 6	Series 7	Series 8
(Dilution, % Waste)	(15.3)	(10.7)	(8.4)	(9.6)
H_2O	352.8	371.9	381.5	376.5
O_2	322.6	364.4	312.5	337.5
Other				
$C_{12}H_6Cl_4$ (PCB)	0.032			
H_3BO_3	3.2			
$HOCH_2CH_2OH$	31.9			
MEA	6.37			
DEA	6.37			
TEA	6.37			
Motor Oil*	9.6			
$MgSO_4$*	0.08			
$ZnSO_4$*	0.03			
$CaSO_4$*	0.1			
$Al(C_2H_3O_2)_3$		1.7		
$Ca(C_2H_3O_2)_2$		0.11		
NaF		0.01		
$Fe(C_2H_3O_2)_2{\cdot}4H_2O$		0.59		
$Ni(C_2H_3O_2)_2$		0.08		
$K(C_2H_3O_2)$		0.07		
$Si(C_2H_3O_2)_4$		0.25		
$NaHSO_4$		0.59		
Na_2SO_4		0.31		
Carbon		44.6		
Trimethylbenzene			28	
Sodium diamyl sulfsuccinate			1.4	
Sodium dioctyl sulfsuccinate			2.8	
Polyoxyethylenelauryl ether			2.8	
Tributyl Phosphate				18
Dibutyl Phosphate				2
$C_{12}H_{26}$				20

* contained in motor oil, which is represented as $C_{18}H_{38}$

TABLE 4

EFFLUENT SUMMARY, LB/HR

	Series 1	Series 2	Series 3	Series 4	Series 5
H_2O	404.7	415.1	403.1	413.9	413.3
CO_2	118.0	104.1	140.2	104.7	106.5
O_2	218.1	210.0	258.1	216.2	215.0
N_2	0.07			0.35	2.9
HCl			1.9	4.77	0.015
SO_2				0.84	
H_3PO_4					
Other					
Hg	0.04				
As_2O_3		0.235			
BaO		0.2			
CdO		0.205			
Cr_2O_3		0.258			
PbO		0.201			
SeO_2		0.251			
Ag_2O		0.209			
Nd_2O_3		0.202			
Eu_2O_3		0.211			
Sm_2O_3		0.105		0.145	
Na_2O				0.28	
K_2O				0.11	
CaO				0.09	
Fe_2O_3				0.012	
ZnO				0.005	
B_2O_3					3.59
$MgSO_4$					0.08
$ZnSO_4$					0.03
$CaSO_4$					0.1

TABLE 4 continued

EFFLUENT SUMMARY, LB/HR

	Series 6	Series 7	Series 8
H_2O	373.0	412.5	420.3
CO_2	166.9	107.1	101.2
O_2	243.0	208.4	225.1
N_2			
HCl			
SO_2		0.065	
H_3PO_4			7.57
Other			
Al_2O_3	0.43		
CaO	0.04		
NaF	0.01		
Fe_2O_3	0.19		
NiO	0.04		
K_2O	0.06		
SiO_2	0.06		
$NaHSO_4$	0.59		
Na_2SO_4	0.31		
Na_2O		0.31	

Assumptions and basis

1. No neutralization of effluent
2. Metals in feed acetates oxidize to oxides
3. Metals in feed sulfates or bisulfates pass through the reactor without reaction
4. Sulfur in TRIMSOL forms SO_2 in reactor
5. Boric acid dehydrates to boric oxide
6. TBP, DBP yield phosphoric acid
7. Sulfur in series 7, scintillation fluid, forms SO_2 in reactor

Appendix B

Test Bed Worst Case Air Emissions

EG&G Idaho, Inc.
FORM EGG-2631#
(Rev. 01-92)

Project File Number	WTD-3YH061-074-HW
EDF Serial Number	ID121217/0016
Functional File Number	

ENGINEERING DESIGN FILE

Project/Task	Supercritical Water Oxidation Hazardous Waste Pilot Plant		
Subtask	Test Bed Worst Case Air Emissions	EDF Page	1 of 3

TITLE: TEST BED WORST CASE AIR EMISSIONS

SUMMARY: The list of air pollutants in Idaho's proposed Air Pollution Control Rules, IDAPA 16.01.01, were reviewed to identify possible air pollutants from the Supercritical Water Oxidation (SCWO) Test Bed. From thes, a preliminary "worst case" scenario was determined in order to identify air pollution control requirements.

Table 1 contains a list of possible air pollutants in test bed effluent. The pollutants fit into five catagories - the volatile RCRA-hazardous metal mercury; nonvolatile solids; organic liquids; gases including H_2S, NH_3, AsH_3, NO, and HCl; and sulfuric acid.

The presence of pollutants of these catagories set requirements for corresponding treatment of effluent:

1. Mercury removal
2. Solids removal
3. Destruction or organics from incomplete oxidation
4. Neutralization/removal of acid gases, acids and ammonia

The probability of forming arsine is very low because of the high level of oxygen present. Also, NO will certainly fall below the 6 lb/hr EL since, based on SCWO experience only traces of NO_x forms, and for the waste series with the most nitrogen, only 3.6 lb/hr of nitrogen will be in the effluent.

The worst case for mercury and organics removal will be Test Waste Series 1, and a worst case effluent composition is given in Table 2. To achieve a mercury emission rate of less than 0.003 lb/hr, and assuming worst case conditions, 93% removal of Hg would be required. The worst case for HCl removal is Series 4, TRIMSOL, and 99% removal is required to meet the EL of 0.05 lb/hr.

Distribution (complete package):	C. M. Barnes, J. M. Beller, T. R. Charlton, K. M. Garcia, R. W. Marshall, Jr., W. C. Reed, C. Shapiro, H. Welland
Distribution (summary page only):	J. J. McCarthy

Author Dept. C. M. Barnes B820 C M Barnes 3-24-94	Reviewed. Date D.M. Ginosar 3/24/94 D. M. Ginosar	Approved Date 3/24/94 T. R. Charlton
	EG&G Review Date	EG&G Approval Date

TABLE 1

POSSIBLE AIR POLLUTANTS IN SCWO EFFLUENT

Noncarcinogen

Byproducts of incomplete oxidation

- Acetic acid
- Ammonia
- Arsine
- Dichlorethane
- Dichloroethylene
- Ethylene dichloride
- Formic acid
- Hydrogen sulfide
- Nitrous oxide
- Toluene
- Trichloroethylene

Directly added to feed

- Acetone
- Biphenyl
- Chromium compounds
- Dibutyl phosphate
- Diethanolamine
- Ethanolamine
- Mercury and Hg compounds
- Methyl alcohol
- Phenol
- Selenium and Se compounds
- Silver compounds
- NaOH
- Tributyl phosphate

Oxidation Products

- Boron oxide
- Calcium carbonate
- Calcium hydroxide
- Calcium oxide
- Calcium silicate
- Calcium sulfate
- Hydrogen chloride
- Phosphorus pentoxide
- Sulphuric acid
- Zinc chloride
- Zinc oxide

Carcinogen

Byproducts of incomplete oxidation

- Carbon tetrachloride
- Chloroform
- Chloromethane
- 1,1 Dichlorethylene
- 1,2 Dichlorethylene
- Dichlormethane
- Formaldehyde
- 1,1,2,2 Tetrachloroethane
- Tetrachloroethylene
- Trichloroethylene
- Vinyl Chloride

Directly added to feed

- Arsenic compounds
- Benzene
- Cadmium and Cd compounds

Oxidation Products

TABLE 2

WORST CASE EFFLUENT COMPOSITION

Basis:

8.6 weight% benzene in water
3 times stoichiometric O_2
Maximum benzene case based on no oxidation
Minimum benzene case based on 99.99% destruction efficiency
Assume all O_2 and CO_2 in gaseous phase at final letdown
Water calculated from partial pressure at 35°C and total pressure of 15 psia

Compositional range: (lb/hr)

	Minimum	Maximum	
Benzene	0.0036	35.5	
O_2	218	327	
CO_2	120.2	0	
H_2O	6.5	7.5	(this should be updated according to latest conditions of pressure letdown)
Hg	0	0.0406	

Required organic destruction for EL of 0.0008 lb/hr benzene:

(35.5-0.0008)/35.5 = 99.998%

Required Hg removal for EL of 0.003 lb/hr:

(0.0406-0.003)/0.0406 = 92.7%

DATE
FILMED
9/1/94

END