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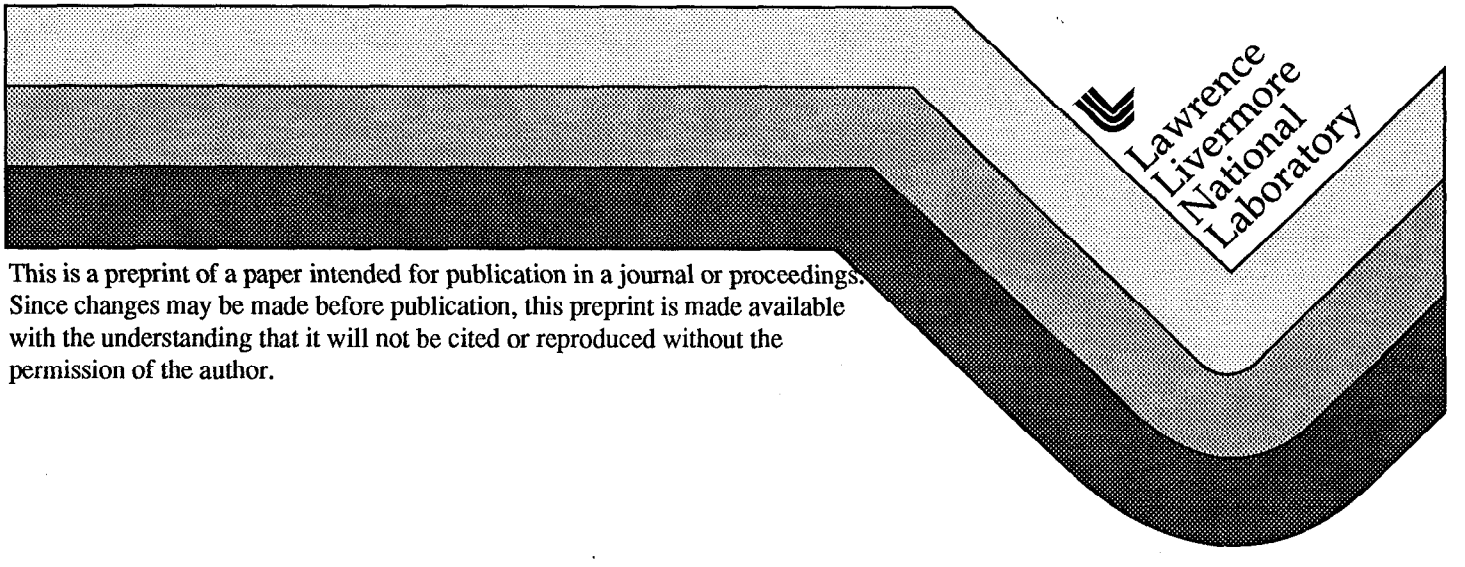

# Molten Salt Oxidation for Treating Low-level Mixed Wastes

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## ABSTRACT

MSO is a promising alternative to incineration for the treatment of a variety of organic wastes. Lawrence Livermore National Laboratory (LLNL) has prepared a facility (please see the photo attached) in which an integrated pilot-scale MSO treatment system is being tested and demonstrated. The system consists of a MSO vessel with a dedicated off-gas treatment system, a salt recycle system, feed preparation equipment, and a ceramic final waste forms immobilization system. The MSO/off-gas system has been operational since December 1997. The salt recycle system and the ceramic final forms immobilization became operational in May and August 1998, respectively. We have tested the MSO facility with various organic feeds, including chlorinated solvents; tributyl phosphate/kerosene, PCB-contaminated waste oils & solvents, booties, plastic pellets, ion exchange resins, activated carbon, radioactive-spiked organics, and well-characterized low-level liquid mixed wastes. MSO is a versatile technology for hazardous waste treatment and may be a solution to many waste disposal problems. In this paper we will present our operational experience with MSO and also discuss its process capabilities as well as performance data with different feeds.

## INTRODUCTION

MSO is a robust thermal treatment process used to oxidatively destroy the organic constituents of mixed and hazardous wastes. It accomplishes this as follows: 1) by injection of organic-based wastes beneath a bed of molten carbonate salt at 900-950 C in an Inconel 600 vessel, 2) by catalytic oxidation of organic constituents to inorganic products (H2O, CO2, etc), 3) by neutralization of acid gases such as HCL in the bed, and 4) by periodic discharge of the salt for disposal or for processing and recycle. The molten salt, usually sodium carbonate, has several functions: 1) it acts as a dispersion medium both for the waste being processed and the process air, 2) it catalyses, and hence accelerates, the oxidation reactions, 3) it enhances completion of the chemical reactions by providing intimate physical contact between the reactants and a stable heat transfer medium that resists thermal surges, 4) it helps retain soot and char in the melt for more complete reaction, and 5) it retains most of the ash, radionuclides, and other noncombustible material associated with the waste in the salt bed.

An integrated MSO facility, as shown in the photo, has been installed at Lawrence Livermore National Laboratory. The facility has been operational since December 1997 and is capable of processing at a maximum organic feed rate of 5-7 kg/hr.

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## SYSTEM DESCRIPTION

The integrated MSO system, shown in Figure 1, consists of several subsystems. It includes a reaction vessel (or processor), an off-gas treatment system, a salt recycle system, feed preparation equipment, and a ceramic final waste forms immobilization system. The feed preparation area includes a limited capability for waste receiving, for separating solids and liquids, and for reducing the size of soft solid wastes such as paper, rags, gloves, booties, etc. The waste is fed to the reaction vessel along with oxidant air using a top-feed injection system designed for solid and liquid waste streams at throughputs up to 7 kg/hr for chlorinated solvents. Product off-gas exiting the vessel is then treated in the off-gas system to remove entrained salt particulates, water vapor, and traces of gas species such as CO and NOx (NOx represents a mixture of various oxides of nitrogen). As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed which necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, the removed spent salt would create a large secondary waste stream without further treatment. A salt recycle system is needed to segregate these materials to minimize the amount of secondary waste, and to reduce the consumption of fresh salt. The segregated inorganic residues are then incorporated into a ceramic for final disposal. Detailed description of the integrated system is given elsewhere [1,2].

## CURRENT STAGE OF DEVELOPMENT

### MSO Processor

There are several new features being demonstrated in the facility. With regard to the MSO processor, they are:

a. A special lance (or injector) is used to inject the organic feed and oxidant air into the bottom of the molten salt bed in the processor vessel. The injector is a specialized item. The design being used here has evolved from previous designs used at LLNL and is being demonstrated here for the first time.

b. When the processor is being operated, gases resulting from the oxidation of the organic feed material, plus remaining excess air, exit the processor through the off gas piping. This gas flow can carry salt particles, which result from the turbulence in the salt bed plus salt vapor resulting from the vapor pressure of salt at operating temperatures. We have implemented methods to minimize transport of salt particles out of the MSO processor into the off gas piping.

c. We have also implemented new methods to minimize the plugging that can occur due the presence of salt in the off gas piping. This salt has two sources: one source is the carry-over of salt particulate (or salt spray) into the off gas piping, the other is condensation of salt vapor as it reaches lower temperatures in the off gas piping.

Several features of the MSO processor involve existing, or "off-the-shelf", technology. These include:

a. The use of Inconel 600 for the reactor vessel. LLNL has used this material in Molten Salt processors before [3].

b.The off gas system includes a high temperature ceramic filter. While not used before in a Molten Salt Oxidation system to our knowledge, this is commercially available technology.

c. The salt will be removed from the processor while molten by use of a drain pipe. During normal operation, the drain pipe is kept well below the salt melting temperature and is plugged with solid salt. To drain the vessel, the drain pipe is heated to above the salt

melting temperature, and the plug melts out. The use of a salt freeze plug in a drain pipe like this has been used at LLNL before.

### Salt Recycle

There are several new features being demonstrated in the facility. With regard to salt recycle, they are:

a. The salt will be drained out of the processor into a freeze pan. This will form a block of frozen salt about 5 inches thick. This system will demonstrate the handling and size reduction of this salt.

b. The aqueous chemical process used in salt recycle was developed at laboratory scale. This facility demonstrates it at pilot-plant scale. The process is carried out as follows. Salt removed from the MSO processor is dissolved into water. Most metal species precipitate as metal oxides/hydroxides due to their low solubilities in alkaline solutions. A reducing agent, dithionite, is used for further removal of chromate and some radionuclides from the salt solution. A filter with small pore size filter media is used to capture the precipitants. An ion exchange column is used for removing soluble radionuclides that may remain in the solution after chemical precipitation and filtering. After precipitation and filtering, a clean salt solution remains. If this solution has a high carbonate content, it is dried in a spray dryer and then reused in the MSO processor. If the salt solution has a low carbonate content (and therefore a high chloride content), it is discharged as waste whose metal content is below the RCRA hazardous waste characteristic levels.

Several aspects of the salt recycle system are existing technology ("off the shelf"). These include:

a. The dissolution and chemical precipitation tanks and their associated mixers, heaters, pumps, and piping.
b. Reagent feed methods.
c. Filtration of salt brine slurry.
c. Solids crushing and conveying equipment.
d. Spray drying of salt brine.

## RESULTS OF THE DEMONSTRATION

### 1.0 Organics Tested in the MSO/Off-gas System

The pilot-scale MSO/Off-gas system was successfully started up in December 1997. The system had been tested with various liquid feeds including simple organics, organics containing heteroatoms (Cl, F, N, O,P,S), surrogate feeds, and LLNL real wastes. The system was also tested with several solids such as ion exchange resin, plastic, rubber, and activated carbon.

#### 1.1. Simple Organics

Organic comprised of C and H atoms was used in the beginning to verify the hydraulic of liquid delivery to the MSO vessel. Toluene and mineral oil were chosen for their viscosities. It was expected that viscosities of most of surrogate and real wastes would be in between viscosities of toluene and mineral oil. Some runs were also conducted in which the toluene feed was labeled with small quantities of C-14. By simultaneously following the carbon tracer build-up in the off-gas and in the salt charge, valuable information was obtained about the carbon mass balance and the kinetics of carbon exchange.

#### 1.2. Organics Containing Heteroatoms

Many organics which contain heteroatoms Cl,F,N,O,P,S were tested in the system. Cl,F,P, and S convert into sodium salt and stay in the vessel while oxygen and nitrogen exit the vessel as O2, N2, and NOx. These organics included trichloroethylene, tetrachloroethylene, trichloroethane, carbon tetrachloride, freon, nitromethane, pyridine, urea, alcohol, ethylene glycol, tributyl phosphate, and dimethyl sulfoxide.

1.3. Solids

Ion exchange resin beads, ABS plastic pellets, shredded rubber booties, and granular activated carbon were fed by a vibratory feed to the MSO vessel for a limited demonstration.

1.4. Surrogate Wastes

Surrogate wastes which mimed waste streams LLW-008 and LLW-009 at LLNL were demonstrated. These surrogates were spiked with uranium nitrate for radioactivity. 2,4 Dichlorophenol, a strong precursor to dioxins and furans was used in one of the surrogate feeds. Tributyl phosphate in kerosene, a widely used extractant in nuclear material processing, was also demonstrated.

1.5. Treatability Study

Two real waste streams, LLW-008 and LLW-009, were used for the treatability study. LLW-008 is chlorinated solvent with traces of metals and low-level of radionuclides such as uranium and tritium. LLW-009 is waste equipment oil contaminated with about 1600 ppm of PCB with traces of metals and radionuclides.

2.0 Each Component in the MSO/Off-gas System Works

The MSO/off-gas system consists of many components. Some of them are off-the shelf items and some of them were custom-made. Each component works well as designed. The salt brush, installed in the air-cooled jacket, was able to push condensed salt into the MSO vessel and avoid salt buildup in the off-gas system. The GSS filter, made of 0.5 microns ceramic filter element, can stand high-temperature operation and remove fine salt particles from the off-gas stream. The condenser, operated at 5 C, removed most of moisture from the off-gas stream. The catalytic converter also achieved very good efficiency. It reduced 95% of NOx and 99% of CO in the off-gas. The off-gas leaving the system was essentially dust-free and very clean. The salt drain pipe is an innovative design, the first of its kind. It has successfully drained the spent salt out of the MSO vessel six times in the FY98.

Corrosion of the MSO vessel was manageable. The vessel was inspected and found only corroded by 0.004 inches after 150 hrs at operable temperature (>900°C). At this rate, the vessel can operate for 9000 hours before a replacement vessel is needed. The corrosion products, chromium, nickel and iron, stayed in the salt and were removed in the salt recycle system.

3.0 Excellent Process Efficiency Achieved With Liquid Organic Wastes

Over 20 different liquid organic feeds were tested in the MSO/off-gas system from December 1997 to September 1998. During each MSO run, organic feed rate, oxidant air, and temperature were carefully controlled. Important parameters such as pressure, pressure drop, off-gas flow rate, off-gas composition were monitored closely. Testing with various organic feeds has confirmed function of each component in the system.

Destruction and removal efficiency (DRE) of greater than 99.999% has been achieved. Section 4 and section 5 briefly described two significant MSO runs.

## 4.0 Surrogate Feed of Waste Stream LLW-009

### 4.1 Description of the Feed

PCB-contaminated organic exists in several DOE sites and presents a difficult problem due to the lack of efficient treatment technology. Incineration can destroy PCB but it generates toxic off-gas species such dioxins and furans. The ETDP MSO team in FY98 performed a MSO demonstration for treating uranium & 2,4 dichlorophenol-spiked organic. 2,4-Dichlorophenol, a strong precursor to dioxins and furans and easier than PCB to procure commercially, was chosen for the study. Uranyl nitrate, a natural uranium salt, was spiked into the organic feed for its radioactivity. The surrogate feed for the demonstration had the following formulation: Carbon tetrachloride, 4.0 wt.%; 1,1,1- trichloroethane, 4 .0 wt.%; 2,4- dichlorophenol, 1.0 wt.%, Uranyl nitrate, 0.5 wt.%, Ethylene glycol, 46.5 wt.%, and Ethanol, 45.0 wt.%. Carbon tetrachloride and 1,1,1- trichloroethane are common RCRA solvents in wastes. Uranyl nitrate and 2,4- dichlorophenol were fed in diluent streams composed primarily of ethylene glycol and ethanol for miscibility. The organic was stored in a 5-gallon feed container and delivered to the MSO vessel by a PD pump in the feed station.

### 4.2 The Run Procedure

The surrogate feed was delivered to MSO vessel at 2.2 kgs/hr and 3.3 kgs/hr for superficial velocities of 1 ft/s and 1.5 ft/s, respectively. 250 liters/min and 375 liters/min of oxidant air, representing 30% excess air for complete oxidation of organics, were fed into the vessel. Temperature of the salt (sodium carbonate) was controlled at 950°C. Off-gas quality was monitored by off-gas analyzers during the course of the demonstration. Off-gas sample was collected and sent to the Environmental Laboratory in E&ES for analysis of POHCs (principle organic hazardous compounds), dioxins, furans, and total organics. run lasted for 3.25 hrs. Overall, 8.7 kg of surrogate waste was fed into the MSO vessel.

### 4.3. Results

Table 1 shows off-gas composition during the feed. Table 2 shows the POHCs in the feed and in the off-gas. A blank gas sample was also collected for reference.

Table 1. Off-gas analyzer readings

| | Off-gas Species, ppm or % | | | | | |
|---|---|---|---|---|---|---|
| Time, hrs | THC, ppm* | NOx, ppm | CO, ppm | $CO_2$, % | $O_2$, % | Vs, ft/s |
| 0 | 0.0 | 43 | 3.2 | 0.09 | 21.20 | 1.0 |
| 0.75 | 0.5 | 103 | 10.8 | 8.13 | 10.4 | 1.0 |
| 1.25 | 0.0 | 50.5 | 11.3 | 8.16 | 10.3 | 1.0 |
| 1.75 | 0.0 | 40.5 | 11.4 | 8.24 | 10.13 | 1.0 |
| 2.75 | 0.0 | 42.8 | 10.8 | 8.47 | 9.89 | 1.5 |
| 3.25 | 0.0 | 44.2 | 10.6 | 8.5 | 9.72 | 1.5 |

* Detection limit of THC analyzer is 0.01 ppm. It drifted down to less than 0 ppm during the course of the experiment.

Table 1 shows that off-gas quality was very good with less than 10 ppm of CO and less than 110 ppm of NOx leaving the MSO vessel, respectively. CO and NOx levels in the off-gas were further reduced to undetectable levels in the catalytic converter. Other organic PICs (products of incomplete combustion) in the off-gas were not detectable. Table 1 also indicates that operating at higher flow velocity of 1.5 ft/s would not adversely affect the off-gas quality.

Table 2 shows that DREs of the MSO process for major organics in the feed were very high, greater than 99.999%. Testing performed with the bench scale MSO unit in 1994 at Oak Ridge National Laboratory had similar results [4]. Dioxins and furans in the off-gas were not detectable.

## 5.0 Waste Stream LLW-008

A treatability study was conducted in August 1998 to demonstrate the MSO process for the treatment of real waste streams. LLW-008 was one of two LLNL waste streams chosen for the study.

### 5.1. Description of the Run

LLW-008 contains mostly 1,1,1 trichloroethane with traces of metals and low-level radionuclides. The feed was delivered to MSO vessel at 2.31 kgs/hr along with 275 liters/min oxidant air. Temperature of the salt (sodium carbonate) was controlled at 950°C. Best Environmental, Inc., a certified off-gas sampling firm, was contracted for handling off-gas sample collection and analysis. Off-gas quality was monitored with off-gas analyzers during the course of the demonstration. Concentrations of total hydrocarbon (THC), CO, and NOx in the off-gas were below 1.0 ppm, 20 ppm, and 200 ppm, respectively. These species were further treated in the catalytic converter to undetectable levels. The demonstration lasted for 16 hrs. Overall, 37 kgs of waste was fed into the MSO vessel.

### 5.2. Mass Balance

Table 3 shows the mass balance for MSO demonstration with this waste stream. Only organic material with concentration greater than 1 gram/liter is included in the calculation. Excess oxidant air and purge air were provided to ensure complete oxidation and to avoid plugging of the downcomer and several process instruments. The mass balance calculation assume complete oxidation, and several off-gas species CO, THC, and NOx are not included due to their extremely low concentrations (ppm).

Figure 2 shows the integrated mass flowsheet for the waste stream. It includes waste feed rate and oxidant air into the MSO vessel, amount of water required for the salt recycle system, and ceramic powder for the ceramic final forms. There are three product streams from the flowsheet. The off-gas stream consists of CO2, O2, N2 and is vent to a facility stack. The brine solution from the salt recycle system contains sodium chloride, sodium fluoride, water. The third stream is stabilized ceramic pellets. For a waste fed to the MSO at 2.31 kgs/hr (2 liters/hr), the product streams are 0.5 kgs/hr (0.13 liters/hr) of ceramic pellets and 10 liters/hr of clean brine solution. The clean brine solution is not longer hazardous since its metal contents are below the RCRA limits after the salt recycle process.

## 6.0 Promising Results from Organic Solids Testing

Four organic solids, ABS pellets, Amberlite ion exchange resin, shredded booties, and granular activated carbon, were tested in FY98 and the result were quite promising. Total hydrocarbon (THC) and CO concentrations in the off-gas from testing with ABS plastic pellets, Amberlite ion exchange resin, and shredded booties were less than 5.0 ppm and 40 ppm, respectively. This is an indication of good process efficiency. Large excess oxidant air was provided for these runs to overcome the feedrate fluctuation from the vibratory feeder.

A demonstration for treating activated carbon, a commonly used adsorbent in industry, was also performed. A granular activated carbon, 8 to 14 mesh size, was used as the surrogate feed. The activated carbon was fed for 4 hours at 1.5 kgs/hr followed by a 9 hours of air purge. Composition of off-gas was closely monitored with off-gas analyzers. Molten salt samples were taken during the course of demonstration and were sent for carbon analysis. It was found that carbon conversion reached about 80% at 4th hour of the run and low overall carbon conversion during the course of carbon feed. However, air purge after the feed stopped enhanced the carbon conversion greatly. Carbon analysis on salt samples taken after air purge for 2 hours and 9 hours showed that carbon conversion improved to 94% and almost 100%, respectively.

## 7.0 Salt Recycle System Works

Salt recycle is an important element of the integrated MSO system. It was developed based on extensive small-scale laboratory experiments to prove the concept with the subsequent scale-up to the pilot system as part of integrate MSO facility. The salt recycle process separates metals, mineral residues, and radionuclides from spent salt generated by the MSO process. It includes salt size reduction with a grinder, salt dissolution in water, precipitation, chemical reduction, filtration, pH adjustments, ion exchange, and drying. Each component in the salt recycle system works as designed.

## 8.0 Six Batches of Spent Salt Processed in the Salt Recycle System

The salt recycle system has successfully treated six batches of spent salt generated from the MSO vessel in FY98. For spent salts with high carbonate contents (SR1, SR2, SR3, SR5, SR6), it removed ash, metals, and radionuclides from the salts and returned 95% of the salt for reuse. For spent salts with low carbonate content (SR4), it removed ash, metals, and radionuclides from the salts and generated clean brine (sodium chloride) solution which is not considered hazardous.

Table 4 shows the cations (excluding sodium and potassium) and radionuclide (uranium) in the starting spent salt and clean salt after the salt recycle. Concentrations of Cr, Ni, and U in the starting spent salt were over 100 ppm. Salt recycle successfully reduced Cr, Ni, and U to 0.45 ppm, 2 ppm, and 0.1 ppm, respectively.

## 9.0 Ceramic Final Forms

Ceramic final forms are another important element in the integrated MSO system. It receives wet residues (metals, mineral residues, radionuclides) from the salt recycle system and processes the waste into stabilized pellets. As shown in the Figure 2, 0.13 liters of pellets would be produced for 2 liters of chlorinated solvent. This system is currently undergoing pre-operational shakedown and testing. All the major equipment items in the Ceramic Final Forms area are operational.

## TREATMENT OF PCB-CONTAMINATED ORGANICS

PCB-contaminated organic wastes are difficult to treat by incineration due to the formation of dioxins and furans, cancer-causing agents, at incineration temperatures, which are typically above 1200°C. To show that MSO is an efficient alternative to treat these wastes, we demonstrated the MSO system in August 1998 with LLNL real waste stream LLW-009 which contained about 1600 ppm PCB. The main objective of the experiments was to show that dioxin and furan emissions from the system were below the proposed regulatory limit of 100 pg/m$^3$ gas as 2,3,7,8-tetrachlorodibenzo-para-dioxin equivalents or toxic equivalence quotient.

### Waste Stream Descriptions

The PCB-contaminated waste was delivered to the MSO facility from the Waste Management Division of LLNL in a five-gallon container. The waste was sampled and sent for analysis. Table 5 shows the composition of the waste. Toluene was used as a diluent to reduce viscosity of the waste for the ease of feed delivery. The waste contains mostly hydraulic oil with over 1000 ppm PCB and traces of metals and radionuclides.

### Procedure

The waste was fed into the MSO system at 1.1 kg/hr along with 30% excess air for 13 hours. The molten salt bed, containing 160-kg sodium carbonated, was controlled at 950°C during the course of the demonstration. The GSS (gas/solid separation) filter was backflashed with compressed air periodically to prevent excessive buildup of salt cake in the filter element. CO2, O2, CO, NOx, Sox in the off-gas were continuously monitored with off-gas analyzers. Sampling was conducted from the sampling ports located on the inlet and outlet of the GSS filter and from the catalytic converter outlet. The sampling ports were located to meet the 8-duct diameter downstream and 2-duct diameter upstream from any points of flow disturbance criteria. Best Environmental, Inc. handled the off-gas sampling operation during the demonstration. All the collected samples were sent to EPA-certified laboratories for analysis of semivolatile organic species such as dioxins, furans, and PCB, volatile organics, particulates, gross alpha, gross beta, and HCl.

### Results

Figure 3 shows the off-gas composition during the feed. It indicates that off-gas quality was very good with less than 5 ppm of THC, less than 20 ppm of CO and SOx, and less than 50 ppm of NOx leaving the MSO vessel, respectively. These were from the readings of the off-gas analyzers which monitored the off-gas quality. NOx, THC, and CO in the off-gas were further treated in the catalytic converter before venting to the facility stack.

Table 6 shows that feed rates and emission rates of POHCs, total dioxins and furans, volatile organics, total semivolatile organics, particulate, gross alpha, gross beta, and HCl. The destruction efficiency of the POHCs in the feed with MSO process was greater than 99.99%.

Table 7 lists the emission rates of each dioxin and furan, the toxicity equivalent factor (TEF), and its toxic equivalence quotient (TEQ). Total TEQs of dioxins and furans in the GSS filter inlet and the catalytic converter outlet were 38.743 pg/m3 and 9.338 pg/m3, respectively. These numbers are less than 100 pg/m$^3$, the EPA proposed regulatory limits.

## CONCLUSIONS

An integrated MSO pilot scale facility has been built and operational since December 1997. The integrated MSO facility costs about $3M to build. The MSO/off-gas system (without salt recycle system and final forms immobilization system) cost $1.5M. The facility has been demonstrated with over 20 surrogates and real waste streams. Chlorinated solvents and PCB-contaminated oils, two difficult waste streams at LLNL, were successfully treated in the facility last August with good results. The MSO technology is ready to be fielded and implemented in different superfund sites and DOE mixed waste sites containing appropriate wastes.

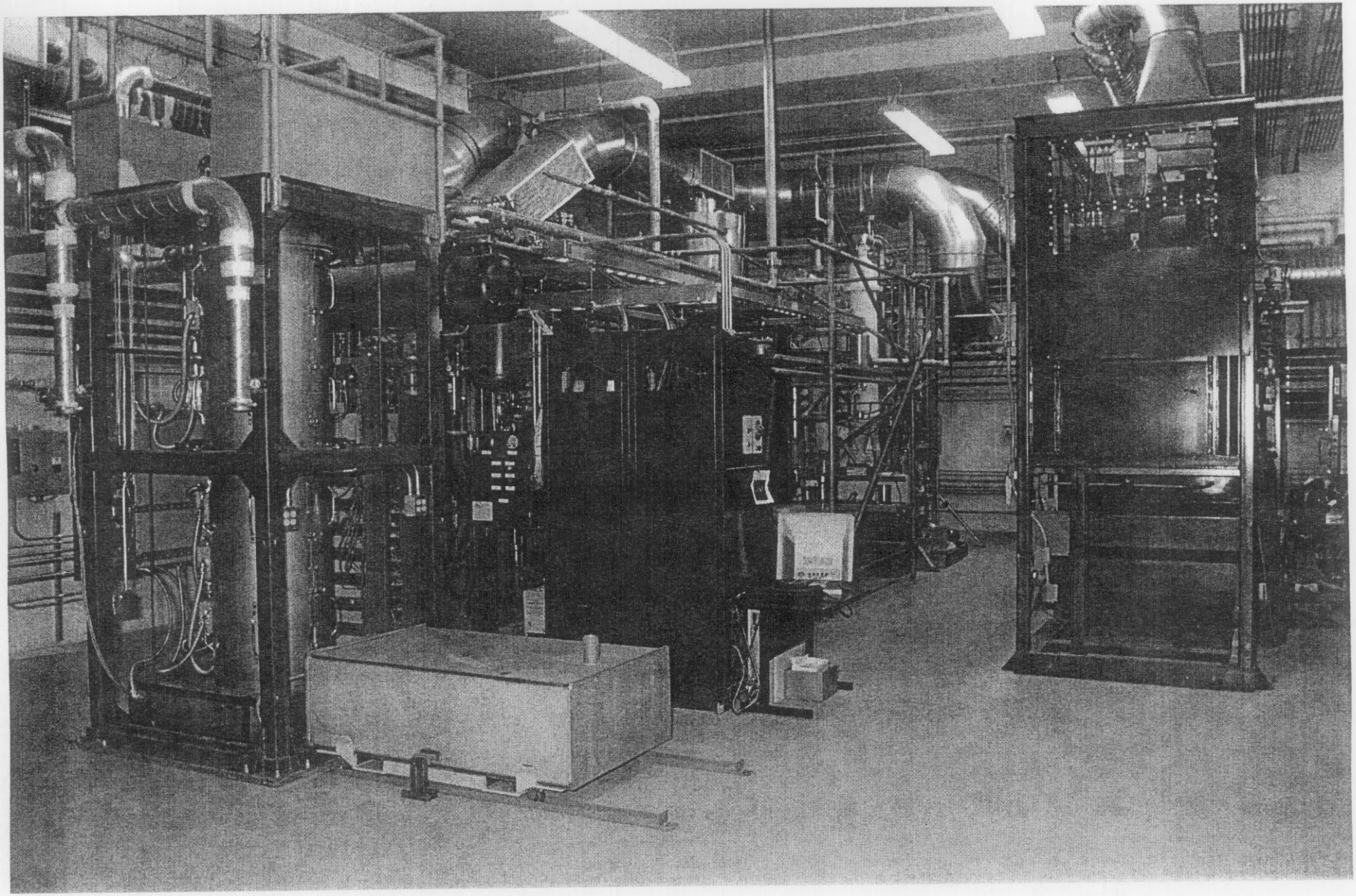
References

1. Martyn G. Adamson, Peter C. Hsu, David L. Hipple, Kenneth G. Foster, Timothy D. Ford, and Robert W. Hopper, "Organic Waste Processing using Molten Salt Oxidation," UCRL-JC-129946, presented at 1998 Euchem Conference on Molten Salt Oxidation, France, June 1998

2. Peter C. Hsu, David Hipple, Dwight Squire, Erica von Holtz, Robert Hopper, and Martyn Adamson, "Integrated Demonstration of Molten Salt Oxidation with Salt Recycle for Mixed Waste Treatment," UCRL-JC-128143, Proceedings of Waste Management '98, Tucson, AZ, March 1998

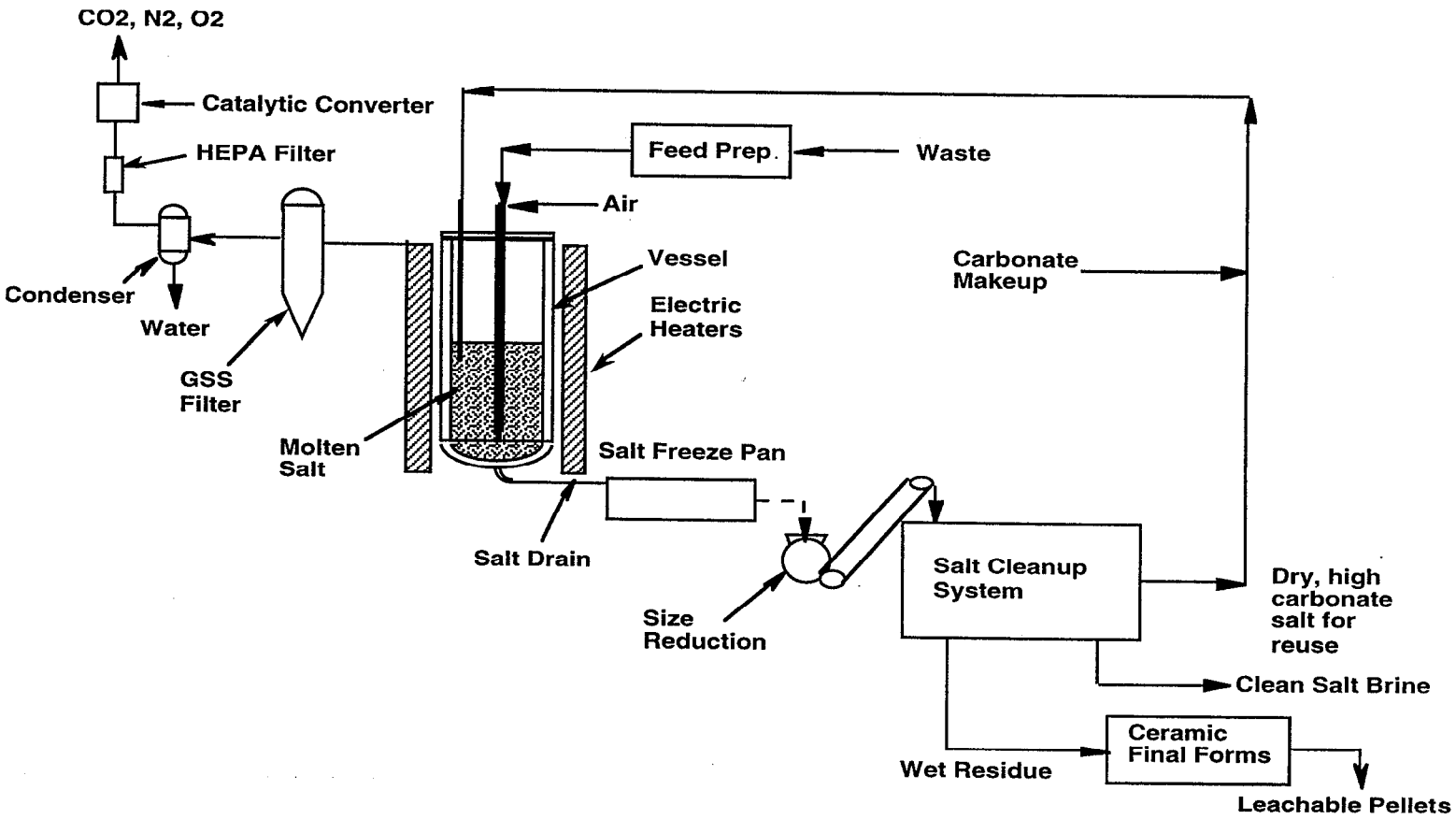
3. D. W. Stevens, W. A. Brummond, D. L. Grimmett, J. C. Newcomb, K. T. Chiang, and R. L. Gay, "Microstructure and Kinetics of Hot Corrosion for a Nickel Alloy ikn Molten Salt," UCRL-JC-126053, December 1996.

4. J.C. Rudolph, P.A. Hass, J.T. Bell, S.M. Crosley, Cl. Calhoun, Jr., A.H. Gorin, and L.E. Nulf, "Molten Salt Oxidation of Chloro-organic Compounds: Experimental Results for Products Gas Compositions and Final Forms Studies," ORNL/TM-129412, Oak Ridge National Laboratory, April 1995



MSO Facility

# Fig. 1 Integrated MSO System



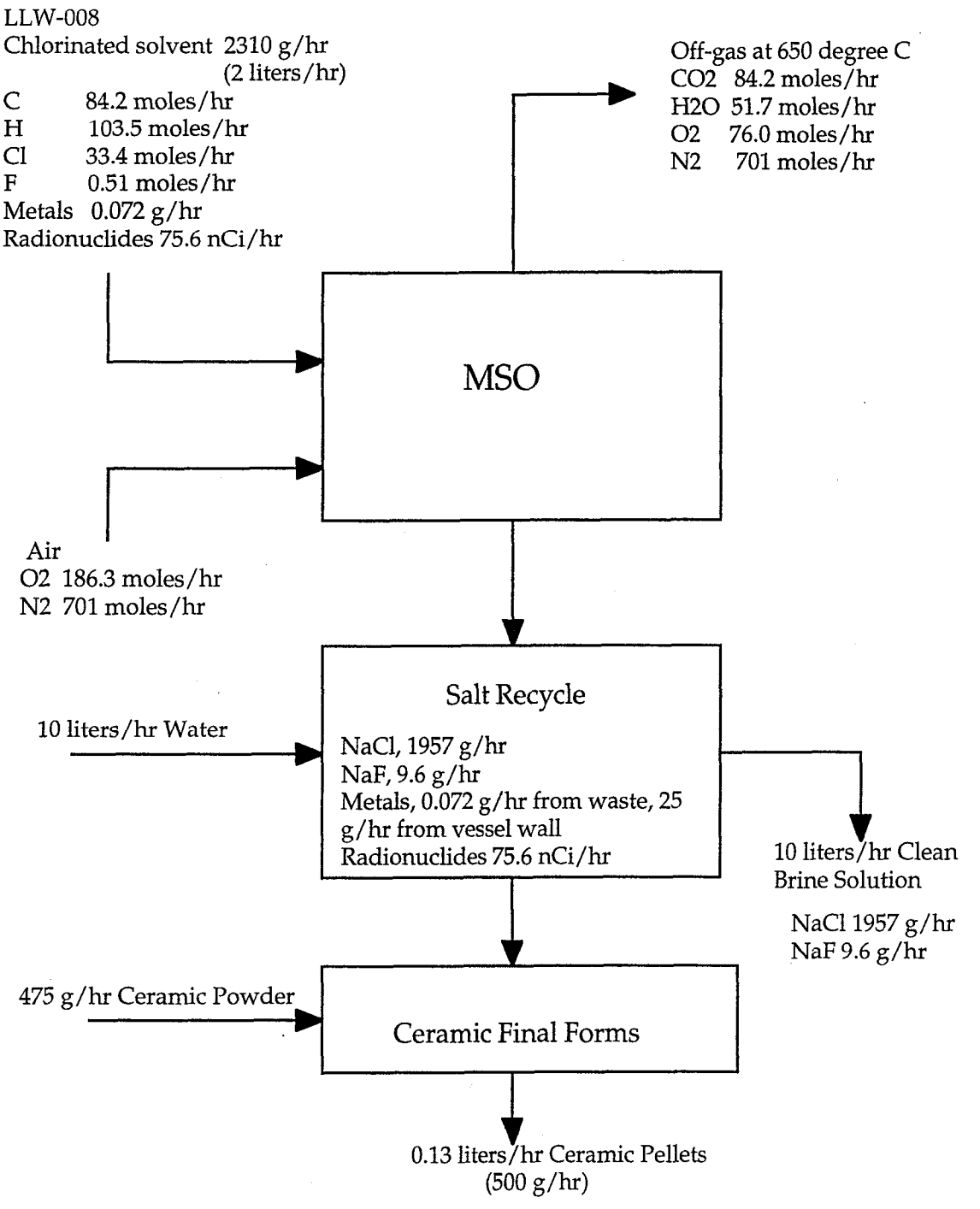
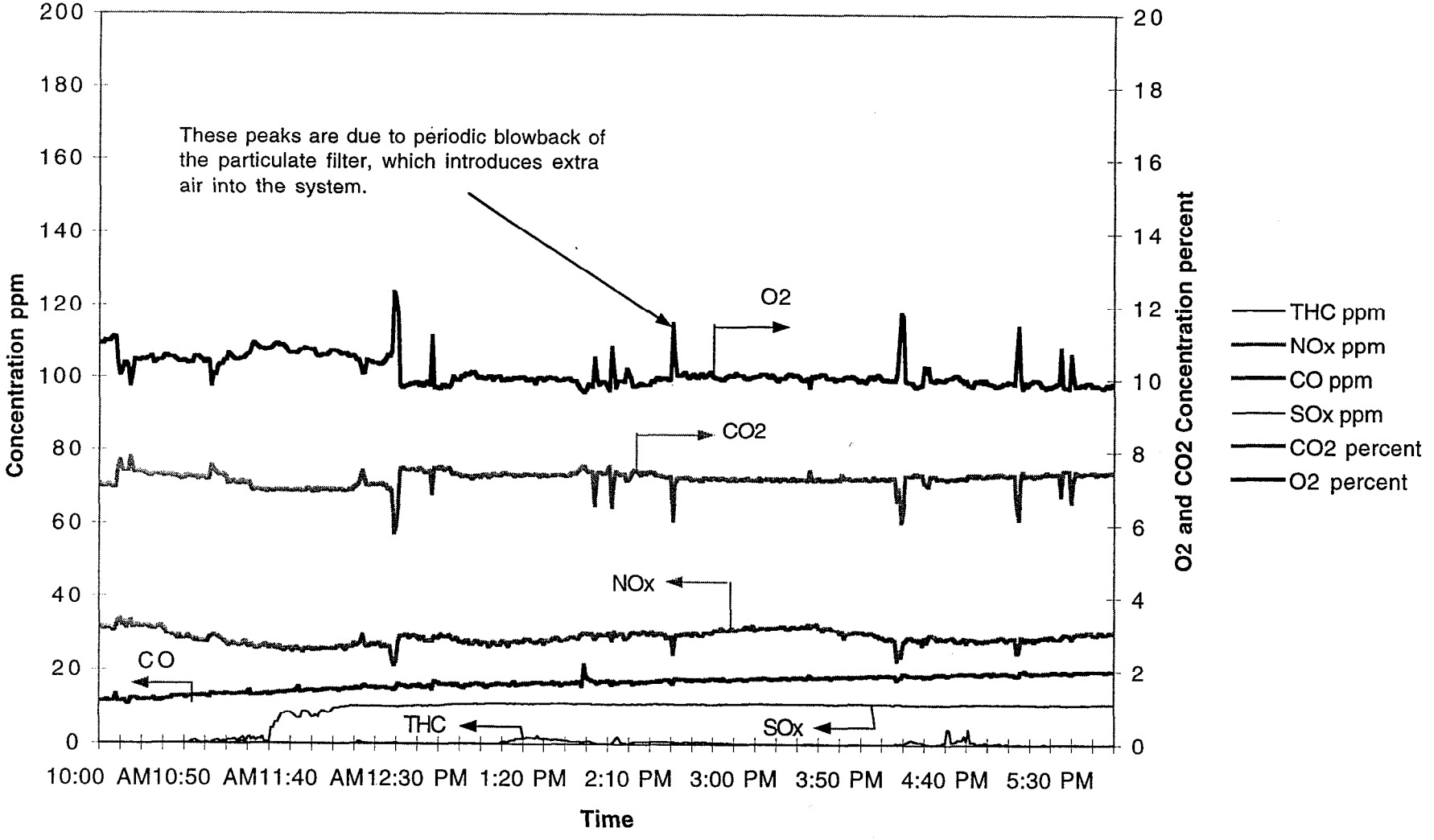



Fig. 2 MSO Flow balance for feed stream LLW-008 (Chlorinated Solvents)

## Fig. 3 Off-gas Composition During MSO Demonstration With PCB-Contaminated Oil



| Table 2 | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Destruction and Removal Efficicency for the MSO Demonstration** | | | | | | | |
| **with Uranium & 2,4-Dichlorophenol- spiked Organics** | | | | | | | |
| | | | | | PCH, 10/2/98 | | |
| Conditions: 950 C, 30% excess air | | | | | | | |
| Component | In the feed, g/min | | In the off-gas, g/min | | DRE, %, minimum | | ORNL Test |
| | 1 ft/s | 1.5 ft/s | 1 ft/s | 1.5 ft/s | 1 ft/s | 1.5 ft/s | 1.5 ft/s |
| Ethylene Glycol | 16.633 | 24.950 | 1.44E-06 | 1.01E-06 | 99.999991 | 99.999996 | N/A |
| Ethanol | 16.267 | 24.400 | 1.44E-06 | 1.01E-06 | 99.999991 | 99.999996 | N/A |
| CCl4 | 1.192 | 1.788 | 1.44E-06 | 1.01E-06 | 99.999879 | 99.999943 | 99.999988 |
| MCM | 1.450 | 2.175 | 1.44E-06 | 1.01E-06 | 99.999901 | 99.999954 | 99.999985 |
| 2,4-dichloropheno | 0.367 | 0.550 | 1.44E-06 | 1.01E-06 | 99.999607 | 99.999816 | 99.998283 |
| Total | 35.908 | 53.863 | | | | | |
| Dioxins & Furans were not detectable. | | | | | | | |
| Other organic PICs (products of incomplete combustion) were not detectable. | | | | | | | |
| **DRE = (1- organic in the off-gas/organic fed to the MSO vessel)*100%** | | | | | | | |
| Note: GC/MS was used for off-gas sample analysis. | | | | | | | |
| | GC/MS Detection limit is 25 nanogram. | | | | | | |

## Table 3

## Mass Balance for MSO Demo with LLW-008 (Chlorinated Solvent)

### Feeds Into the MSO Process

**Organic**

| Component | Formula | Mass flow, g/hr | MW | Molar flow, moles/hr | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Component | C | H | Cl | F |
| Dichloroethylene | C2H2Cl2 | 22.6400 | 96.84 | 0.2338 | 0.46758 | 0.46758 | 0.46758 | |
| Freon | C2Cl3F3 | 31.6500 | 187.38 | 0.1689 | 0.33782 | 0.50672 | 0.50672 | 0.50672 |
| Tetrachloroethane | C2H2Cl4 | 45.0400 | 167.85 | 0.2683 | 0.53667 | 0.53667 | 1.07334 | |
| Toluene | C7H8 | 814.4700 | 92.14 | 8.8395 | 61.87638 | 70.71587 | | |
| Trichloroethane | C2H3Cl3 | 1384.7900 | 133.41 | 10.3800 | 20.75991 | 31.13987 | 31.13987 | |
| Trichloroethylene | C2HCl3 | 11.3200 | 131.39 | 0.0862 | 0.17231 | 0.08616 | 0.25847 | |
| Total | | 2309.9100 | | 19.97663 | 84.15067 | 103.45286 | 33.44598 | 0.50672 |

**Air**

| Component | Formula | Mass flow, g/hr | MW | Molar flow, moles/hr | | |
|---|---|---|---|---|---|---|
| | | | | Component | O2 | N2 |
| Process Air | O2/N2, 21/79 | 15157.143 | 28.840 | 525.560 | 110.368 | 415.192 |
| Excess air to the salt | | 6062.857 | 28.840 | 210.224 | 44.147 | 166.077 |
| Purge air to the vessel | | 4370.940 | 28.840 | 151.558 | 31.827 | 119.731 |
| | | | Total | 887.342 | 186.342 | 701.000 |

### Components to the Off-gas System

| Component | Formula | Molar flow moles/hr | Composition % |
|---|---|---|---|
| Carbon Dioxide | CO2 | 84.151 | 9.218 |
| Water | H2O | 51.726 | 5.666 |
| Oxygen | O2 | 75.974 | 8.323 |
| Nitrogen | N2 | 701.000 | 76.792 |
| Total | | 912.851 | |

Notes: CO and NOx and total hydrocarbon in the off-gas leaving the catalytic converter were not detectable

| Table 4 Key Cations in SR4 Salt | | | |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | Starting spent salt | Final clean salt * | Limits |
| | Conc. in ppm | Conc. in ppm | |
| | | | |
| Cations | | | |
| | | | |
| Ag | ND | ND | 6 |
| As | ND | ND | 100 |
| Ba | 3 | 1.1 | 150 |
| Be | ND | ND | 0.28 |
| Cd | 3 | 1.5 | 3.8 |
| Co | 1 | ND | 800 |
| Cr | 820 | 0.45 | 17 |
| Cu | 1 | 0.5 | 250 |
| Mo | 2 | 2 | 3500 |
| Hg | ND | ND | 0.5 |
| Ni | 100 | 2 | 100 |
| Pb | 7 | ND | 7.4 |
| Sb | 10 | ND | 42 |
| Se | ND | ND | 3.2 |
| Tl | ND | ND | 1.6 |
| V | ND | ND | 4.6 |
| Zn | 2 | ND | 106 |
| | | | |
| U | 200 | 0.1 | |
| * after ion exchange process | | | |

Table 5. Composition of the PCB-Contaminated Waste

| | |
|---|---|
| chloroform (g/L) | ND |
| 1,1-dichloroethane (g/L) | ND |
| 1,2-dichloroethane (g/L) | ND |
| 1,1-dichloroethene (g/L) | ND |
| dichloromethane (g/L) | ND |
| tetrachloroethane (g/L) | ND |
| dichloroethene | 1.429 |
| trichloroethene (g/L) | ND |
| 1,1,2-trichloro, 1,2,2 trfluoroethane (g/l) | 11.772 |
| methylchloroform (g/L) | 9.249 |
| Sb (mg/L) | ND |
| Ba (mg/L) | 2.186 |
| Be (mg/L) | ND |
| Cd (mg/L) | ND |
| Cr (mg/L) | 0.320 |
| Co (mg/L) | ND |
| Cu (mg/L) | 1.429 |
| Pb (mg/L) | 6.222 |
| Mo (mg/L) | 0.252 |
| Ni (mg/L) | ND |
| K (mg/L) | ND |
| Ag (mg/L) | 0.059 |
| U (mg/L) | 9.670 |
| V (mg/L) | ND |
| Zn (mg/L) | 1.934 |
| Hg (mg/L) | 0.294 |
| hydraulic oil, g/L | 725.225 |
| Toluene as a diluent, g/L | 136.6366 |
| PCB, mg/L | 1317.598 |
| Gross Alpha (nCi/L) | 6.559 |
| Gross Beta (nCi/L) | 0.715 |
| (Tritium (nCi/L)) | 31.952 |
| Total treated Volume (Liters) | 16.65 |
| grams | 14350.00 |
| Total Radioactivity, nCi | 653.1 |
| mCi | 0.0006531 |

Table 6. Feed and Emission Data for PCB-Contaminated Oil

| Species | Feed Rate | | | Emission Rate | | Destruction Efficiency, % |
|---|---|---|---|---|---|---|
| 1,1,1 trichloroethane | 0.168 | g/min | < | 2.91E-07 | g/min | 99.99982679 |
| 1,1-dichloroethene | 0.025 | g/min | < | 1.017E-06 | g/min | 99.995932 |
| Freon 113 | 0.213 | g/min | < | 4.151E-06 | g/min | 99.99805117 |
| Toluene | 2.78 | g/min | < | 1.069E-06 | g/min | 99.99996155 |
| Total PCB | 0.0233 | g/min | < | 4.14E-08 | g/min | 99.99982232 |
| Hydraulic Oil | 14.93 | g/min | | | | |
| | | | | | | |
| Total Dioxins/Furans | | | | 9.83E-11 | g/min | |
| VOST Volatiles | | | | 0.00001789 | g/min | |
| Total Semivolatiles | | | | 0.00009728 | g/min | |
| Particultes | | | | 0.000227 | g/hr | |
| HCl | | | | 0.0015 | g/hr | |

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Table 7. Results for Dioxins and Furan Emissions

| Species | TEF | @ GSS Filter Outlet, pg/m3 | TEQ pg/m3 | @ Catalytic Converter Outlet, pg/m3 | TEQ pg/m3 |
|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 1 | 22.301 | 22.301 | 7.506 | 7.506 |
| TCDF | 0.1 | 78.954 | 7.895 | 3.503 | 0.350 |
| PeCDF | 0.05 | 50.310 | 2.516 | 5.505 | 0.275 |
| HxCDF | 0.1 | 12.521 | 1.252 | 1.426 | 0.143 |
| HpCDF | 0.01 | 4.204 | 0.042 | 1.051 | 0.011 |
| OCDF | 0.001 | 2.742 | 0.003 | 1.776 | 0.002 |
| PeCDD | 0.5 | 8.527 | 4.264 | 1.877 | 0.939 |
| HxCDD | 0.1 | 3.593 | 0.359 | 1.001 | 0.100 |
| HpCDD | 0.01 | 4.684 | 0.047 | 1.101 | 0.011 |
| OCDD | 0.001 | 64.379 | 0.064 | 2.352 | 0.002 |
| | | Total TEQ | 38.743 | | 9.338 |

Note: The oxygen concentration in the off-gas was 10.1 vol.%. Volume of off-gas sample collected was about 4 $m^3$.