

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.

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 NO_x (NO_x 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 [1,2,3].

EXPERIMENTS AND DEMONSTRATION RESULTS

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.

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.

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 NO_x. These organics included trichloroethylene,

tetrachloroethylene, trichloroethane, carbon tetrachloride, freon, nitromethane, pyridine, urea, alcohol, ethylene glycol, tributyl phosphate, and dimethyl sulfoxide.

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.

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.

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.

Results of the Demonstration in the MSO-off-gas System [4]

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 NO_x 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.

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.

Results of the Demonstration with Organic Liquid Feeds

Table 1 lists the surrogated organic liquids chosen for the demonstration. 950°C and 30% excess air were used for these runs, unless noted otherwise. Each run lasted at least one hour or longer to assure a steady state operation. Salt temperature, organic and air feed rates and vessel pressure were carefully controlled. Concentrations of CO₂, O₂, NO_x, CO, THC, and SO_x were monitored continuously with off-gas analyzers. Table 2 shows the off-gas compositions from the ethylene glycol run at three salt temperatures, 900°C, 925°C, and 950°C. CO and NO_x concentrations in the off-gas were very low. It seems that, above 900°C, the effect of temperature on the off-gas quality was very small. However, it is desirable to maintain the temperature of sodium carbonate above 900°C (50°C above its melting point) in order to avoid plugging of the injector tip.

Table 1 Run Conditions

No.	Organic Liquids	Run Conditions
1	Toluene (50%), Mineral oil (50%)	950°C, 1.2 kg/hr
2	Ethylene glycol	900°C, 925°C, 950°C, 2.6 kg/hr
3	Ethylene glycol	950°C, varying % excess air, 2.6 kg/hr
4	Toluene	950°C, varying % excess air, 1.2 kg/hr
5	Pyridine/Toluene	950°C, 1.25 kg/hr
6	NM/Ethylene Glycol	950°C, 2.23 kg/hr
7	Urea/EtOH/Propanol	950°C, 1.41 kg/hr
8	TMP/DMSO/Toluene	950°C, 1.32 kg/hr
9	Freon 113/DMSO/Toluene	950°C, 1.44 kg/hr
10	DMSO/TCE/Toluene	950°C, 1.98 kg/hr
11	TBP/Kerosene	950°C, 1.18 kg/hr

Notes:

1. NM- nitromethane; EtOH- ethyl alcohol; □DMSO- Dimethyl sulfoxide; Freon 113- 1,1,2-Trichlo-1,2,2-trifluoroethane; TCE- 1,1,1- Trichloethylene; TBP- Tributyl phosphate
2. 30% excess process air was used for these runs.

Table 2 Effect of Temperature on the Ethylene Glycol Run

Off-gas Species	Off-gas Composition at various temp		
	900°C	925°C	950°C
CO ₂ , %	8.70	8.66	8.96
O ₂ , %	10.50	10.42	10.30
CO, ppm	13.1	7.5	9.2
NO _x , ppm	8.7	11.0	8.4
THC	N/A	N/A	N/A

Note: during the time of run, the THC analyzer was being serviced and therefore was not available.

For any oxidation process, excess oxygen/air is needed to maintain a good process efficiency. Higher excess air dilutes CO₂ and increases O₂ concentration in the off-gas. It also increases off-gas flow. Tables 3 shows the off-gas compositions for the MSO demonstration with toluene at various % excess air. It shows that the off-gas qualities were not affected by the % excess air. It is desirable to run the MSO process with at least 10% excess air or higher to overcome the fluctuation of organic feed rate.

Table 3 Effect of % Excess Air for the Toluene Run

Off-gas Species	Off-gas Composition at various excess air		
	10%	30%	60%
CO ₂ , %	10.5	8.9	7.3
O ₂ , %	7.8	9.9	11.8
CO, ppm	6.2	4.5	5.0
NO _x , ppm	115	97	68
THC	0.6	0.5	0.85

Notes: 1. feed rate of toluene was 1.2 kg/hr,
2. salt temperature at 950 C.

Treatment of several organic liquids (runs 5 to 11 in table 1) containing chlorine, fluorine, nitrogen, sulfur, and phosphorous was demonstrated in the MSO process vessel in FY98. Pyridine, nitromethane, and urea consist of carbon, hydrogen, and nitrogen. Most of the organic nitrogen in the feed during the oxidation process converts into molecular nitrogen (N_2), leaves the molten salt bed, and goes to the off-gas system. Some of the organic nitrogen combines with oxygen and forms NO_x . NO_x is a toxic gas species and need to be abated to below 300 ppm in the off-gas stream with a NO_x abatement equipment. The catalytic converter installed in the off-gas system utilizes ammonia injection plus catalyst is designed to remove 90% of NO_x in the off-gas system. Table 4 shows the off-gas composition for the feed containing pyridine. The NO_x concentrations in the off-gas stream were recorded before and after the catalytic converter. The catalytic converter installed in the system was able to reduce the NO_x levels in the off-gas stream by 94%, exceeding the design value (90%).

Table 4 Off-gas Composition for Feed of Toluene/Pyridine

Time, hrs	Off-gas Species, ppm or %					
	THC, ppm*	NO_x , ppm	CO, ppm	CO_2 , %	O_2 , %	V_s , ft/s
0.3	0.61	967 (50)	10.7	9.9	11.1	1.0
0.8	1.1	1195 (50)	9.7	8.8	10.8	1.0
1.3	1.2	1371 (50)	10.0	8.6	10.5	1.0
1.7	1.3	1370 (50)	10.3	8.4	10.6	1.0

The conversion of organic nitrogen in the feed to NO_x depends on the source of organic nitrogen and oxidation temperature. Incineration would generate higher level of NO_x than molten salt oxidation because incinerators operate at several hundred degree higher than 950°C , a typical MSO temperature for waste treatment. Pruneda et.al.[5] reported that less than 1% of organic nitrogen converted into NO_x at 750°C for the destruction of energetic materials. Table 5 shows the degrees of conversion of pyridine, nitromethane, and urea at 950°C along with several explosives at 750°C .

Table 5 Conversion of Organic Nitrogen into NO_x in the Molten Salt

Feed material	Reaction Temperature	% N to NO _x
Pyridine/Toluene	950°C	44.0
Nitromethane/Ethylene Glycol	950°C	34.0
Urea/EtOH/Propanol	950°C	31.0
Explosives from ref. 4		
RDX	750°C	0.05
HMX	750°C	0.11
TNT	750°C	0.45
Comp-B	750°C	0.09
LX-10	750°C	0.019
LX-16	750°C	0.14
LX-17	750°C	0.20
PBX 9404	750°C	0.25

Notes:

RDX- hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine; TNT-2,4,6-trinitrotoluene; Comp-B-(RDX/TNT); LX-10- (HMX/Viton); LX-16- PETN/FPC 461); LX-17- (TATB/Kel F); PBX-9404- (HMX/CEF/Nitrocellulose); PETN- 2,2-bisnitoxymethyl-1,3-propanediol dinitrate; TATB- 2,4,6-trinitro-1,3,5-benzentriamine.

One of the features of the MSO process is its ability to retain halides, sulfur, and phosphorous. They stay in the molten sodium carbonate salt bed as sodium halide, sodium sulfate, and sodium phosphate. For the test series II, the following organics containing fluorine, chlorine, sulfur, and phosphorous were tested: Freon 113 (fluorine, chlorine), DMSO (sulfur), TCE (chlorine), TBP (phosphorous). These organics were diluted with toluene and fed into the MSO process vessel at 950°C with 30% excess process air. The off-gas quality from these testing was very good. Table 6 shows the off-gas quality for the testing. The THC levels in the off-gas were very low, an indication of good process efficiency. SO_x in the off-gas was not detectable for each run since all the organic sulfur was converted into sodium sulfate and stayed in the salt bed.

Table 6 Off-gas Composition for the MSO Runs with Halides, Sulfur, and Phosphorous-containing Feeds (please refer to run numbers in table 1)

Off-gas Species	Off-gas Composition for MSO Runs			
	8	9	10	11
CO ₂ , %	8.8	9.2	13.8	7.7
O ₂ , %	10.1	9.8	8.3	10.1
CO, ppm	11.6	9.4	11.1	12.3
NO _x , ppm	56.6	60.7	29.9	36.0
SO _x	0.0	0.0	0.0	0.0
THC	0.0	0.64	0.02	0.12

Note: 4-TMP/DMSO/Toluene; 5- Freon 113/DMSO/Toluene; 6-DMSO/TCE/Toluene; 7- TBP/Kerosene. * 20% excess process air was used for run 10, 30% excess process air for runs 8,9,11.

Results of the Demonstration with Solid Feeds

Surrogate materials including ABS plastic pellets, shredded booties and gloves, ion exchange resin (Amberlite), and activated carbon were demonstrated. Salt containing ash was drained from the MSO vessel and sent to the salt recycle system after the demonstration. Table 7 shows the run conditions. The solid feeds were fed to the MSO vessel with a vibratory feeder and an eductor and carried into the molten salt bed by the compressed air. A large excess of process air was provided for these runs to overcome the feedrate fluctuation from the vibratory feeder. A larger size of ABS pellet (3.0 to 5.5 mm) was also tested but the off-gas quality was not good, probably because the increased resident time of the pellet in the molten salt bed to complete the oxidation process. It was found that solid particles less than 3.0 mm can be effectively treated by the MSO process if sufficient excess air is provided. The off-gas composition for these runs are shown in the Table 8.

Table 7 Run Conditions

No.	Feeds	Run Conditions
1	ABS pellets (2.5 mm)	950°C, 1.45 kg/hr, 58% excess air
2	Shredded booties	950°C, 1.88 kg/hr, 65% excess air
3	Ion exchange resin (Amberlite) (0.2 to 1.0 mm)	950°C, 3.0 kg/hr, 40% excess air
4	Activated Carbon (1.2 to 2.4 mm)	950°C, 1.45 kg/hr, 30% excess air

Table 8 Off-gas Composition for the Solid Feeds

Off-gas Species	Run Numbers			
	1	2	3	4
CO ₂ , %	9.4	8.4	12.9	8.2
O ₂ , %	9.3	11.2	6.2	12.2
CO, ppm	18.6	154	17	326
NO _x , ppm	306	6.9	150	112
SO _x	0.0	0.0	0.0	0.0
THC	2.0	1.0	0.4	1.15

The values in the Table 8 were taken from the off-gas analyzer readings at steady feed rate, they varied when the feed rate fluctuated and may reach as high as 80 ppm for THC, and 400 ppm for NO_x and CO, respectively. Figure 2 shows the off-gas composition for the MSO run with ion exchange resin. The spikes were the result of feed rate variation. Although it is desirable to have a solid feeder which can deliver a constant feed to the MSO vessel, the feed rate variation can be overcome with a large excess of process air. The higher levels of NO_x, CO, and ThC in the off-gas system can be further reduced in the catalytic converter before venting to the facility stack. Effort is underway to find an alternative means to feed solids to the MSO vessel, including finding a different type of solid feeder and suspend solid particles in a slurry using water or organic liquid as a carrier. This option will be further studied in FY99.

The MSO demonstration with activated carbon was based on the collaboration between the MSO team and the Defense Programs at LLNL. 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. A more detailed description can be found elsewhere [6].

Results of the Demonstration with Spiked Organic Liquids

Some surrogate organic liquids were spiked with low-level radioactive materials such as uranium. The compositions of surrogate materials mimicked the some of the waste streams at LLNL. A surrogate organic, toluene, was traced with a small quantity of C-14 labelled organics in order to establish accurate mass balances for carbon. Tables 9&10 show the run conditions for test series IV and off-gas compositions, respectively.

Table 9 Run Conditions for Test Series IV

No.	Feeds	Run Conditions
1	C-14 Labeled Toluene	950°C, 1.3 kg/hr, 30% excess air
2A, 2B	MCM/Toluene kg/hr,	900°C (A) & 950°C (B), 2.4 30% excess air
3	Uranyl Nitrate & 2,4 Dichlorophenol in EtOH/MCM/Toluene/Mineral oil	950°C, 1.2 kg/hr, 30% excess air
4	Perchlor	910°C, 8.2 kg/hr, 30% excess air
5	Uranyl nitrate & 2,4-Dichlorophenol in EtOH/MCM/CCl ₄ /EG	950°C, 2.2 & 3.3 kg/hr, 30% excess air

Table 10 Off-gas Composition for the Radioactive-spiked Organic Liquids

Off-gas Species	Run Numbers					
	1	2A	2B	3	4*	5
CO ₂ , %	10.3	11.1	11.2	7.8	16.0	8.2
O ₂ , %	7.8	10.0	9.6	10.1	14.3	10.3
CO, ppm	10.7	9.5	9.5	10.8	6200	11.3
NO _x , ppm	45	131	114	125	19.3	50.5
SO _x	0.0	0.2	0.2	0.0	0.0	0.0
THC	0.04	0.23	0.28	0.0	1.0	0.0

Note: at 8.2 kg/hr of Perchlor

C-14 Labeled Toluene Experiment

Carbon in the feed is expected to exchange with carbon of the carbonate salt during the oxidation process, however no experimental data was available. Therefore, in Run 1 of this test series, toluene was spiked and labeled with C-14 to 9.9 modern (or 9.9x10⁻¹² fraction C-14 in carbon) and fed into the MSO process vessel in order to determine carbon exchange in the MSO process. C-14-labeled toluene was fed into the molten salt bed at 950 C for 2.83 hours followed by a 4-hr gas purge (9.0% CO₂ in air). Samples including organic feed, off-gas, and salt were taken before the run, during the run, and during the gas purge. These samples were sent to the Center for Accelerator Mass Spectrometry (CAMS) at LLNL for the analysis of C-14. Table 11 and Fig. 3 show the activity of the samples during the run. C-14-labeled toluene was fed into the MSO vessel at 21 g/min with 30% excess process air. The values in the parentheses were the percentages of C-14 fed to the MSO vessel that exchanged with the carbon atom of the carbonate molecule in the molten salt. Table 11 shows that most of C-14 fed into the MSO vessel went through carbon exchange and stayed in the salt. The percentages of the exchange were 75.3%, 77.3%, and 73.9% after 1.0 hr, 2 hrs, and 2.83 hrs, respectively. These values are very close and are well within the margin of errors in sampling and analysis. The activity of C-14 in both molten salt samples and off-gas samples increased with time, which indicates that a much longer run time is needed before a true steady state can be reached.

The feed was stopped after 2.83 hours and then was followed by a gas purge at 215 liters/min for 4 hours. The purge gas consisted of 9.0 mol% CO₂ which is a typical CO₂ composition in the off-gas. Gas purging slowly decreased the C-14 activity in the molten salt. Table 11 shows that the C-14 activity decreased from 1.3158 moderns to 1.0883

moderns after 4 hours of gas purge. Based on these results, it would clearly need much longer than 4 hours to completely purge and exchange the C-14 in the molten salt. The C-14 activity in the off-gas during the feed and the gas purge depends on the C-14 activity in the melt. Table 11 and Fig. 3 also show that the activities of C-14 in the salt and in the off-gas are almost equal, indicating that gaseous CO₂ and the carbonate salt are in thermodynamic equilibrium.

The C-14 labeled experiment has provided new and valuable technical data for the MSO process.

Table 11 C-14 level in the C-14 Labeled Toluene Run

Time, hour	C-14 in the samples, modern	
	Molten Salt Sample	Off-gas Sample
Organic Feed (9.9 modern of C-14 in the feed)		
0 (before the feed)	0.0189	0.0075
0.5	---	0.2285
1.0	0.4712 (75.3%)	0.4688
1.5	---	0.7256
2.0	0.9717 (77.3%)	0.9748
2.5	---	1.2312
2.83	1.3158 (73.9%)	1.3062
Purge Period (Organic feed terminated)		
0 (before the purge)	1.3158 (73.9%)	
0.67	---	1.3015
1.0	1.2380 (69.5%)	---
1.42	---	1.2144
2.0	1.1920 (66.9)	1.1848
2.75	---	1.1564
3.0	1.1471 (64.4%)	---
3.42	---	1.0961
4.0	1.0883 (61.1%)	1.0684

Note: The salt sample collected in the GSS filter after the run was 0.3542 modern.

MCM/Toluene and Perchlor Experiments

There are 4500 gallons of organic liquid wastes in the LLNL waste inventory, and most of them are chlorinated solvents (LLW-008). Over 90% of the chlorinated waste consists of MCM. One of the runs in the test series was to simulate the composition of LLW-008 waste in order to understand the feed containing mostly MCM. The salt, consisted of sodium carbonate and potassium carbonate, has lower melting point which allowed the MSO vessel to operate at lower temperature. The off-gas qualities for the MCM run at both 900°C (run 2A) and 950°C (run 2B) were very good, as shown in the Table 10. Operating at lower temperature with chlorinated solvents is desirable because as chloride builds up in the melt, the salt becomes more volatile. Operating at lower temperature not only reduces metal corrosion but also depresses sodium chloride volatilization into the off-gas system.

Perchloroethylene, "Perchlor", consists of 85% chlorine and was chosen to build up chloride content in the molten salt. Perchlor was fed into the MSO vessel with 30% excess air at higher feed rates than most of organic feeds. The salt temperature was kept at 910°C for the run in order to reduce salt volatility. As shown in the Table 10, the THC level in the off-gas was only 1 ppm, an acceptable value despite the high CO concentration observed. The high CO concentration in the off-gas is typical at high chloride loading in the melt. The CO in the off-gas was further treated in the catalytic converter before venting through the facility stack. After the run, the high chloride salt was drained out and sent to the salt recycle system for processing.

Uranyl Nitrate and 2,4-dichlorophenol spiked organics (runs 3 and 5)

PCB-contaminated liquid organic waste exists in several DOE sites and presents a difficult problem due to the lack of an efficient treatment technology. Incineration can destroy PCB but it generates toxic off-gas species such as dioxins and furans. A PCB-contaminated liquid waste stream, one of the difficult wastes in the LLNL waste inventory, was chosen as one of the treatability study samples. A feed containing uranium and 2,4-dichlorophenol (a PCB surrogate as a recognized precursor to the formation of dioxins/furans) was demonstrated in the MSO vessel at 950 C before the real PCB-contaminated waste was introduced.

In run 3, uranyl nitrate and 2,4-dichlorophenol were dissolved in ethanol and mixed with MCM, mineral oil and toluene in the feed container. Although it mimicked the composition of PCB-contaminated waste, phase separation occurred due to immiscibility of ethanol and mineral oil. It was fed to the MSO vessel for two hours before the injector experienced a minor plugging. Pure ethanol was subsequently introduced to clear up the plugging. The off-gas quality for this run was very good.

In run 5, the surrogate waste used for the demonstration had the following formulation: Carbon tetrachloride, 4.0 wt.%; 1,1,1- trichloroethane (MCM), 4.0 wt.%, 2,4-dichlorophenol, 1.0 wt.%, uranyl nitrate, 0.5 wt.%, ethylene glycol, 46.5 wt.%, 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 surrogate feed was delivered to the 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, with 30% excess process air. Off-gas quality was monitored by off-gas analyzers during the course of the demonstration. Sample gas was also collected and sent to the Environmental Laboratory in E&ES for analysis of POHCs (principal organic hazardous compounds), dioxins, furans, and total organics. The surrogate was fed for 3.25 hrs. The system reached steady state in 30 minutes. Overall, 8.7 kg of surrogate waste was fed into the MSO vessel.

Table 12 shows the off-gas composition during the feed. Table 13 shows the POHCs in the feed and in the off-gas. A blank gas sample was also collected for reference.

Table 12 Off-gas analyzer readings

Time, hrs	Off-gas Species, ppm or %					
	THC, ppm*	NO _x , 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 12 shows that off-gas quality was very good with less than 10 ppm of CO and less than 110 ppm of NO_x leaving the MSO vessel, respectively. CO and NO_x levels in the off-gas were further reduced to undetectable level in the catalytic converter. Other organic PICs (products of incomplete combustion) in the off-gas were not detectable. It also indicates that operating at the higher flow velocity of 1.5 ft/s would not adversely affect the off-gas quality.

Table 13 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 yielded similar results [7]. Dioxins and furans in the off-gas were not detectable.

Results of MSO Demonstration With Real Wastes (Treatability Study)

Description

Two real waste specimens were chosen for the MSO treatability study in FY98. These specimens were received from the Hazardous Waste Management Division at LLNL (waste stream numbers LLW-008 and LLW-009). The first specimen (RTS #1) was chlorinated solvent and consisted of mainly 1,1,1-trichloroethane (MCM) with traces of metals and low-level of radionuclides. The second specimen (RTS#2) was PCB-contaminated waste. Table 14 shows the composition of these two specimens. Treatment of five gallons of each specimen was successfully demonstrated in the MSO process vessel in August 1998. Off-gas was monitored continuously by off-gas analyzers installed in the off-gas system during the course of the demonstration. In addition to the continuous off-gas monitoring, a comprehensive gas sampling was performed per EPA methods and handled by the Best Environmental, Inc., a certified firm. Gas sampling was conducted from the sampling ports located on the 1.375" i.d. inlet and outlet of the GSS filter and from the catalytic converter 4" i.d. outlet stack venting emission from the MSO process. The sampling ports were located to meet EPA criteria (8-duct diameter downstream and 2 duct diameter upstream from any points of flow disturbance). The source test methods and test locations used for each waste feed are summarized in Table 15.

Table 14**Real Test Specimens for MSO Treatability Study in FY 98**

	<i>RTS #1</i> <i>Chlorosolvent</i> LL-W008	<i>RTS #2</i> <i>Oil/PCB</i> LL-W009
chloroform (g/L)	0.1	ND
1,1-dichloroethane (g/L)	0.5	ND
1,2-dichloroethane (g/L)	0.5	ND
1,1-dichloroethene (g/L)	20	ND
dichloromethane (g/L)	1.4	ND
tetrachloroethane (g/L)	40	ND
toluene (g/L)	0.1	2.9
dichloroethene	ND	1.7
trichloroethene (g/L)	10	ND
1,1,2-trichloro, 1,2,2 trfluoroethane (g/l)	28	14
methylchloroform (g/L)	1226.25	11
Sb (mg/L)	0	ND
Ba (mg/L)	1.5	2.6
Be (mg/L)	8.2	ND
Cd (mg/L)	0	ND
Cr (mg/L)	1.3	0.38
Co (mg/L)	0.2	ND
Cu (mg/L)	11	1.7
Pb (mg/L)	11	7.4
Mo (mg/L)	2.5	0.3
Ni (mg/L)	2	ND
K (mg/L)	4	ND
Ag (mg/L)	0.3	0.07
U (mg/L)	20	11.5
V (mg/L)	3.1	ND
Zn (mg/L)	5.3	2.3
Hg (mg/L)	0.04	0.35
hydraulic oil, (g/L)	None	862.5
PCB, mg/L	None	1567
Gross Alpha (nCi/L)	7.26	7.8
Gross Beta (nCi/L)	11.4	0.85
(Tritium (nCi/L))	33.1	38

Table 15 Test Methods and Locations for the Treatability Study

<u>Test Location</u>	<u>Parameters</u>	<u>Test Methods</u>	<u>Runs</u>	<u>Duration, min.</u>
GSS Filter Outlet	Filtable Particulate	EPA Method 17	3	60
	Radionuclides	EPA Method 114	3	60
	Volatiles (VOST)	EPA Method 30	9	20
	HCl	EPA Method 50	3	60
	DSCFM	EPA Method 1-4	3	60
GSS Filter Inlet	Dioxins/Furan, PCB*	EPA Method 23	3	180
	Semi-Volatiles (MM5)	EPA Method 10	3	180
Catalytic Converter Outlet	Dioxins/Furan, PCB*	EPA Method 23	1	180
	Semi-Volatiles (MM5)	EPA Method 10	1	180
	Volatiles (VOST)	EPA Method 30	3	20
	Radionuclides	EPA Method 114	1	60

* PCB only for RTS#2.

Results of MSO Demonstration with Chlorinated Solvent (LLW-008)

The specimen was sampled and transferred from the waste container to the feed tank. Toluene was then added to the feed container under mixing to prevent the phase separation during the feed to the MSO vessel. The waste liquid was pumped into the MSO vessel at 2.5 kg/hr for 14 hours with 30% excess process air. The longer run was chosen to meet the time requirement for gas sampling. Table 16 shows the off-gas composition at steady state for both RTS#1 and RTS#2. Concentrations of CO and THC in the off-gas for RTS#1 were 15.6 ppm and 0.2 ppm, respectively, which were much less than 100 ppm for CO and 20 ppm for THC, the standards for mixed waste incinerators [8].

Table 16 Off-gas Composition for RTS#1 and RTS#2

Off-gas Species	Run Numbers	
	RTS#1	RTS#2
CO ₂ , %	8.1	7.3
O ₂ , %	12.0	10.1
CO, ppm	10.2	15.6
NO _x , ppm	56.4	27.3
SO _x	0.0	0.0
THC	0.2	0.0

* The numbers were taken directly from the readings of the off-gas analyzers.

Table 17 shows feed rates to the MSO vessel and emission rates and DREs for principal organic hazardous constituents (POHCs) along with total dioxin/furan, volatile organics, semi-volatile organic, particulate, gross alpha, gross beta, tritium and HCl in the off-gas. There were six POHCs in the RTS#1 feed: MCM, 1,1-dichloroethene, tetrachloroethene, trichloroethene, trichloro-trifluoroethane, and toluene. The DREs for these six POHCs were greater 99.999%, an indication of excellent process efficiency for the demonstration. The particulate emission rate was 0.00011 lbs/hr at average off-gas flow rate of 13.8 dscfm (dry standard cubic ft per min) or 0.00006 g/ft³. This is much less than the particulate loading of 0.08 g/ft³, the standard for mixed waste incinerators. The low particulate loading in the MSO off-gas system is not surprising because the GSS filter can effectively remove most particles from the gas stream. Table 17 also shows that the molten salt retained and trapped gross alpha and gross beta very well. The percentages of gross alpha and gross beta which was fed into the MSO vessel going into the off-gas were 0.32% and 0.12%, respectively. HCl level in the off-gas was less than 0.0016 g/hr, which indicated that most of the chlorine in the feed (about 50 wt.% of the liquid feed or 21 g/min of chlorine) has been converted into sodium chloride as expected and stayed in the salt bed. Sodium chloride is ten times more volatile than sodium carbonate and its vapor would carry over to the off-gas system. The concentration of sodium chloride vapor at 950°C is 0.014 g/ft³ [9]. Most of the sodium chloride vapor condensed in the air-cooled jacket of the off-gas system and was pushed back to the MSO vessel by the salt brush. Some of it may end up in the salt trap and GSS filter. After the run, a salt sample was taken from the MSO vessel and analyzed for its chloride content; the sodium chloride composition after feeding chlorinated solvent for 14 hours was found to be 30 wt.%.

In addition to analyzing the off-gas for the feed compounds, EPA method 10 and method were used to determine the emissions of semi-volatile organics (boiling point >100°C)

and volatile organics boiling point <100 C), respectively. Table 4 and Table 6 in the Appendix 2 show the emissions of each individual semi-volatile organic and volatile organic for RTS#1. Total emissions of the semi-volatile organics from RTS#1 was less than 91.376 ug/min and total emissions of volatile organics was less than 31.568 ug/min, respectively.

Table 17 Feed Rates, Emission Rates, and DREs for RTS#1

<u>Test Parameter</u>	<u>Feed Rate to the MSO Vessel</u>	<u>Emission Rate</u>	<u>DRE %</u>
MCM	24.98 g/min	<0.542 ug/min	>99.999998
1,1-dichloroethene	0.41 g/min	1.067 ug/min	99.99974
Tetrachloroethene	0.81 g/min	<0.175 ug/min	>99.999978
Trichloroethene	0.20 g/min	<0.197 ug/min	>99.99998
Trichloro-trifluoroethane	0.57 g/min	<4.372 ug/min	>99.999233
Toluene	14.69 g/min	3.775 ug/min	99.999974
Total PCB	None	None	N.A.
Total Dioxin/Furan	None	56.061 pg/min	N.A.
VOST Volatiles	N.A.	<31.568 ug/min	N.A.
Semi-volatiles	N.A.	<91.376 ug/min	N.A.
Particulate	N.A.	0.00011lbs/hr	N.A.
Gross Alpha	9,000 pCi/hr	28.55 pCi/hr	N.A.
Gross Beta	14,100 pCi/hr	16.73 pCi/hr	N.A.
Tritium	41,070 pCi/hr	` ` ` ` ` 7688 pCi/hr	N.A.
HCl	N.A.	<0.0016 g/hr	N.A.

Dioxins and furans are a group of related compounds which are suspected of having harmful effects in humans. Laboratory tests have shown that 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-para-dioxin), one of most toxic compounds in the group, can cause cancer and toxic effects in laboratory animals. Hence their emissions from a thermal treatment process are subjected to strict regulations. EPA proposed that the regulatory limit for dioxin and furan emissions from hazardous waste treatment systems be 100 pg/m³ toxic equivalence quotient (TEQ). The toxic equivalence factor (TEF) of a particular dioxin or furan is defined as the ratio of its toxicity to the toxicity of 2,3,7,8-TCDD, which has a TEF of 1.

Table 18 shows the results of dioxin and furan emissions. Gas samples were taken from the GSS filter inlet and the outlet of the catalytic converter. The table shows the emission rate and concentration of each individual dioxin and furan and its TEF and TEQ. TEQ is the concentration of each individual dioxin and furan multiplied by its TEF. As shown in the table, the total dioxin and furan emissions from the GSS filter inlet and the catalytic

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converter outlet were 18.534 pg/m^3 TEQ and 17.093 pg/m^3 TEQ, respectively. These emissions are well below the EPA proposed regulatory limit of 100 pg/m^3 .

Table 18 Results for Dioxin and Furan Emissions for RTS#1

<u>Species</u>	<u>TEF</u>	<u>@ GSS Filter</u> <u>Inlet, pg/min</u>	<u>@ GSS Filter</u> <u>Inlet, pg/m3</u>	<u>TEQ</u> <u>pg/m3</u>	<u>@ Catalytic</u> <u>Converter</u> <u>Outlet, pg/min</u>	<u>@ Catalytic</u> <u>Converter</u> <u>Outlet, pg/m3</u>	<u>TEQ</u> <u>pg/m3</u>
2,3,7,8-TCDD	1	4.941	12.973	12.973	5.108	10.941	10.941
TCDF	0.1	4.033	10.583	1.058	5.325	11.407	1.141
PeCDF	0.05	7.318	19.214	0.961	10.216	21.882	1.094
HxCDF	0.1	2.359	6.201	0.620	2.391	5.121	0.512
HpCDF	0.01	0.772	2.034	0.020	1.195	2.561	0.026
OCDF	0.001	1.536	4.047	0.004	0.967	2.072	0.002
PeCDD	0.5	1.921	5.048	2.524	2.934	6.285	3.143
HxCDD	0.1	0.892	2.351	0.235	0.880	1.886	0.189
HpCDD	0.01	2.219	5.854	0.059	1.087	2.328	0.023
OCDD	0.001	30.07	79.599	0.080	10.542	22.581	0.023
		56.061	147.904	18.534	40.645	87.064	17.093

Results of MSO Demonstration with PCB-Contaminated Organics (LLW-009)

PCB-contaminated wastes are difficult to treat by incineration due to the formation of dioxins and furans, cancer-causing agents, at the incineration temperature, which is typically above 1500°C. To demonstrate MSO is an efficient alternative to treat these wastes, 5 gallons of a PCB-contaminated waste specimen (RTS#2) was fed into the process vessel as part of the treatability study. 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/m³ gas as 2,3,7,8-tetrachlorodibenzo-para-dioxin equivalents or toxic equivalence quotient.

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 17 shows the composition of the waste. Toluene was used as a diluent to reduce the viscosity of the waste for the ease of feed delivery. The waste, containing mostly hydraulic oil with over 1000 ppm PCB and traces of metals and radionuclides 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 carbonate, was controlled at 950° during the course of the demonstration. The GSS (gas/solid separation) filter was backflushed with compressed air periodically to prevent excessive buildup of salt cake in the filter element. CO₂, O₂, CO, NO_x, SO_x 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.

The off-gas quality, as shown in Table 16, was very good with less than 50 ppm NO_x, less than 20 ppm CO, and nondetectable THC in the off-gas. Table 19 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 efficiencies of the POHCs were greater than 99.99%.

Table 19 Feed Rates, Emission Rates, and DREs for RTS#2

<u>Test Parameter</u>	<u>Feed Rate to the MSO Vessel</u>	<u>Emission Rate</u>	<u>DRE %</u>
MCM	0.168 g/min	<0.291 ug/min	>99.999827
1,1-dichloroethene	0.025 g/min	1.073 ug/min	99.99571
Tetrachloroethene	N.A.	<0.166 ug/min	N.A.
Trichloroethene	N.A.	<0.187 ug/min	N.A.
Trichloro-trifluoroethane	0.213 g/min	<4.151 ug/min	>99.99805
Toluene	2.78 g/min	1.069 ug/min	99.999962
Total PCB	0.0233 g/min	<0.0414 ug/min	>99.99982
Hydraulic oil	14.98 g/min	N.A.	N.A.
Total Dioxin/Furan	None	108.86 pg/min	N.A.
VOST Volatiles	N.A.	<17.82 ug/min	N.A.
Semi-volatiles	N.A.	<95.854 ug/min	N.A.
Particulate	N.A.	0.000034 lbs/hr	N.A.
Gross Alpha	8,140 pCi/hr	15.53 pCi/hr	N.A.
Gross Beta	890 pCi/hr	0.961 pCi/hr	N.A.
Tritium	39,700 pCi/hr	3,564,582 pCi/hr	N.A.
HCl	N.A.	<0.0015 g/hr	N.A.

Table 20 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 values are again below 100 pg/m³, the EPA proposed regulatory limits.

Table 20 Results for Dioxins and Furan Emissions

Species	TEF	@ GSS Filter Inlet, pg/m ³	TEQ pg/m ³	@ Catalytic Converter Outlet, pg/m ³	TEQ pg/m ³
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 m³.

COST ANALYSIS

Ecology and Environment, Inc. was contracted by the DOE Oakland Operations Office to prepare an innovative technology summary report for the molten salt oxidation project [10]. The report includes a cost analysis for various feeds. The capital cost for a three vessels system with salt recycle and ceramic final forms was estimated at 3.3 millions. Without salt recycle and ceramic final form, the capital cost drops to 1.8 millions. Unit costs for several feeds are listed Table 21.

Table 21 Unit Cost for various Radioactive Feeds Based on 3 Vessel System

<u>Feeds</u>	<u>MSO ^(a)</u>	<u>Incineration</u>
Halogenated organic liquid	32	338 ^(b)
Non-halogenated organic liquid	27	20 ^(b)
<u>Ion Exchange resins</u>	<u>44</u>	<u>N/A</u>

(a) 3 vessel system, plus operating cost

(b) estimates from LLNL-WM

CONCLUSION

An integrated MSO pilot scale facility has been built and operational since December 1997. The facility has been demonstrated with over 20 surrogates and real waste streams. Chlorinated solvents and PCB-contaminated oils, two of 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 with MSO treatable wastes.

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Fig. 1 Integrated MSO System

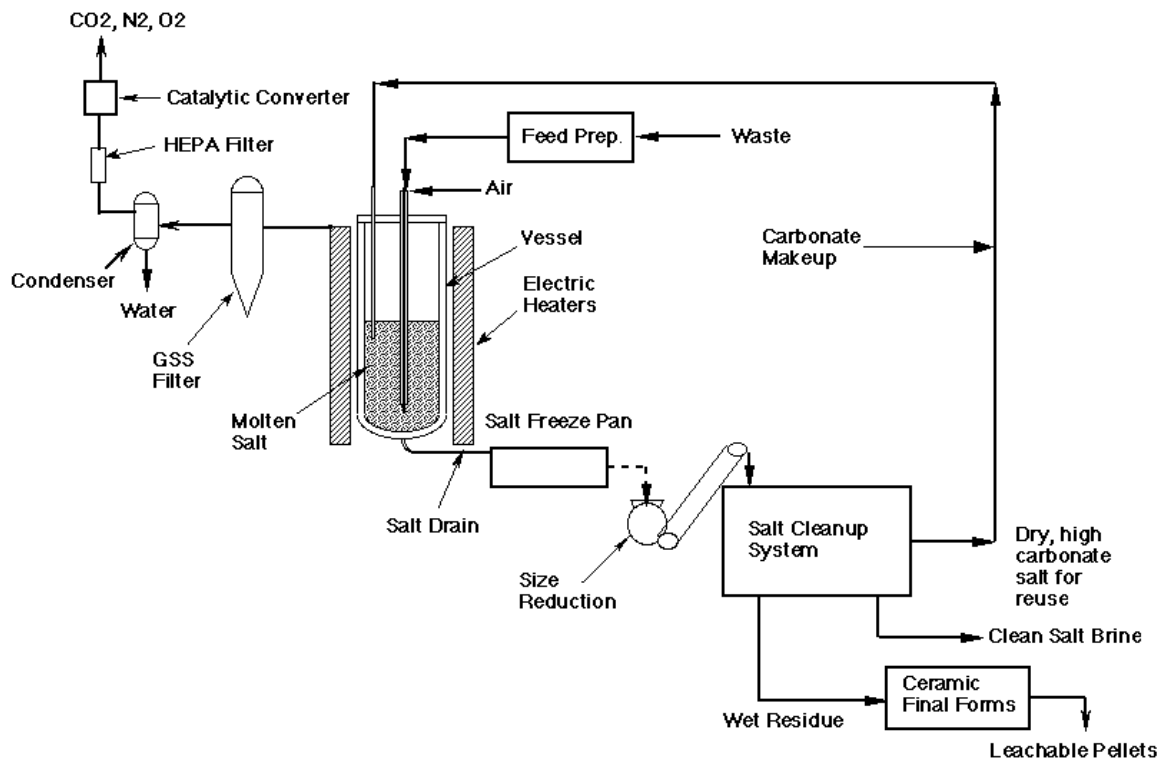


Fig. 2: 3 kg/hr Ion Exchange resin (Amberlite), salt at 950 C

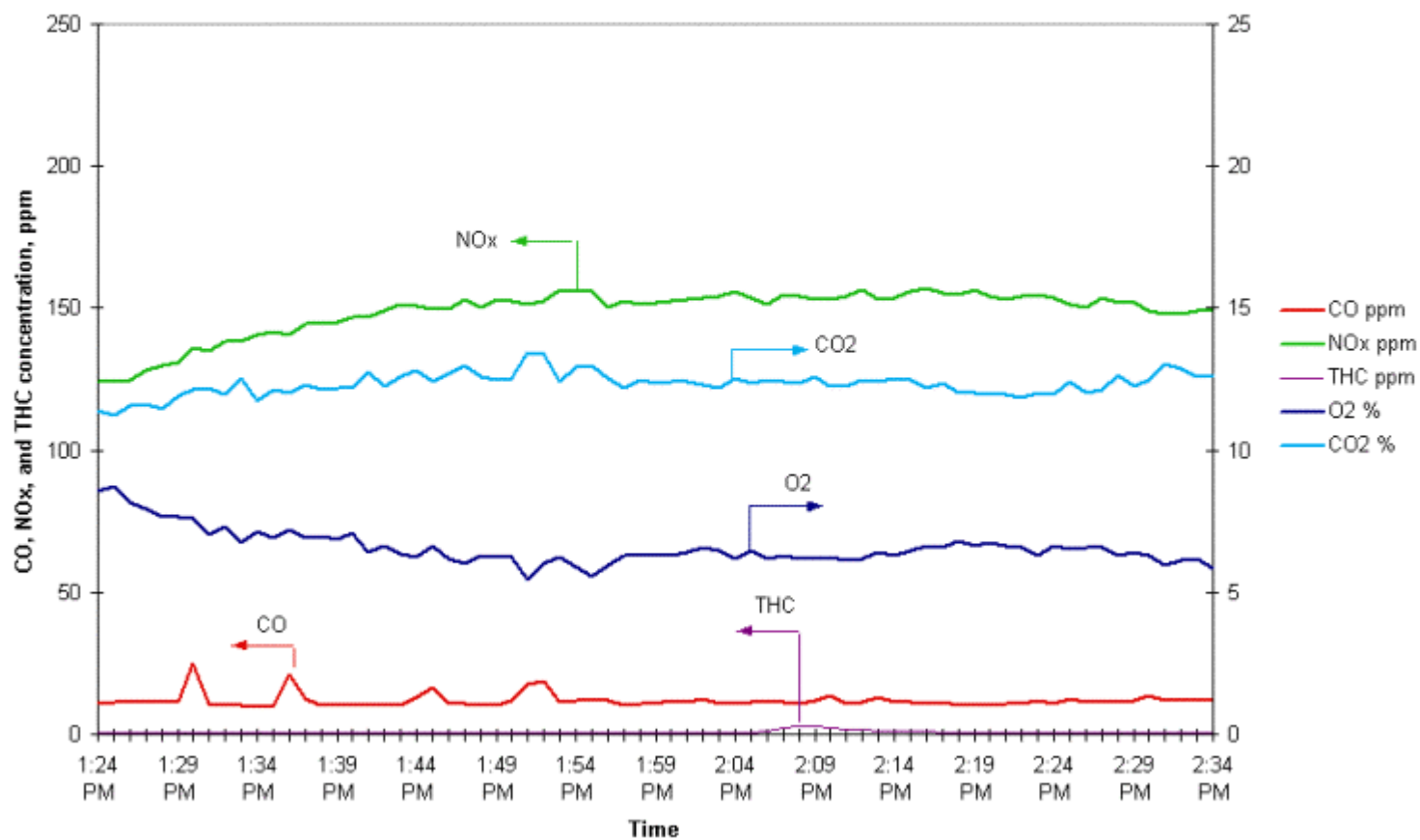


Fig. 3: C-14 Activity in Salt & Off-gas

