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MOLTEN SALT OXIDATION OF MIXED WASTES:
PRELIMINARY BENCH-SCALE EXPERIMENTS WITHOUT RADIOACTIVITY

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ABSTRACT

Molten salt oxidation (MSO) is a process in which organic wastes are oxidized by sparging them with air through a bed of molten sodium carbonate (bp = 851°C) at $\geq 900^\circ\text{C}$. This process is readily applicable to the mixed waste because acidic products from Cl, S, P, etc., in the waste, along with most metals and most radionuclides, are retained within the melt as oxides or salts. Rockwell International has studied the application of MSO to various wastes,¹ including some mixed waste.⁵ A unit used by Rockwell to study the mixed waste treatment is presently in use at Oak Ridge National Laboratory (ORNL).

ORNL's studies to date have concentrated on chemical flowsheet questions. Concerns that were studied included carbon monoxide (CO) emissions, NO_x emissions, and metal retention under a variety of conditions. Initial experiments show that CO emissions increase with increasing NaCl content in the melt, increasing temperature, and increasing airflow. Carbon monoxide content is especially high (> 2000 ppm) with high chlorine content ($> 10\%$). Thermal NO_x emissions are relatively low (< 5 ppm) at temperatures $< 1000^\circ\text{C}$. However, most (85—100%) of the nitrogen in the feed as organic nitrate or amine was released as NO_x . The metal contents of the melt and of knockout pot samples of condensed salt show high volatilities of Cs as CsCl. Average condensed salt concentrations were 60% for barium and 100% for strontium and cobalt. The cerium disappeared — perhaps from deposition on the alumina reactor walls.

1. INTRODUCTION

Molten salt oxidation (MSO) has been selected as a promising alternative to incineration for treatment of some U.S. Department of Energy (DOE) mixed wastes. Mixed wastes are defined as those wastes that contain both radioactive components, which are regulated by the Atomic Energy Legislation, and hazardous waste components, which are regulated under the Resource Conservation and Recovery Act (RCRA). The Oak Ridge National Laboratory (ORNL) has installed and operated a bench-scale MSO apparatus to obtain experimental information needed before the design and construction of an MSO pilot plant.

This paper reports the initial ORNL results from operation of the bench-scale MSO system. The primary objective of these studies was to obtain experimental information for MSO chemical flowsheet questions. The apparatus and operating conditions were those

developed and used for MSO studies by Rockwell International Corp. Organic liquids were used to simulate the waste feeds. Metal salts were added to the organic liquids or to the molten salt. The compositions of the exit gases, the melt samples, and the condensed solids were determined.

2. DESCRIPTION AND ORIGIN OF MOLTEN SALT OXIDATION OF WASTES

The MSO process for treatment of wastes is to react the waste and an excess of air by injecting them into a molten salt. The primary salt feed to the melt is Na_2CO_3 . The melt will contain NaCl , Na_2SO_4 , other sodium salts, and other metal compounds from the reaction products of the waste feed. Other metal carbonates may be added to lower the salt melting point.

The molten sodium carbonate has several important characteristics: (1) it is stable, nontoxic, and compatible with the CO_2 and H_2O products; (2) it reacts with acidic products, such as HCl or Cl_2 from organic chlorine compounds, SO_2 , P_2O_5 , etc., to form sodium salts that remain in the melt; and (3) it is an excellent heat transfer medium and heat sink. The sodium carbonate acts as a catalyst or reactant, and the destruction efficiencies for toxic organics are as good (high) in molten salt at 900 to 1000°C as those for simple incineration at much higher temperatures.¹

One important characteristic of MSO as a waste treatment is the good retention of metals as oxides or salts in the salt residues. The entrained or condensed solids in the cooled off-gases are easily collected and discharged as a residue by bag filters. Acid gases react with Na_2CO_3 in the melt and are retained as the sodium salts. The MSO treatment results in efficient destruction of waste constituents to yield salt residues and off-gases that can be discharged without scrubbing and without any aqueous scrubber residues.

The efficient collection of metallic salts and ash in the salt residues is both an advantage and limitation for MSO treatment of mixed wastes. The MSO treatment is not suitable for high contents of ash or noncombustible solids in the waste feed; excessive amounts of the carbonate salt would be removed as residues in order to remove these solids. High concentrations of elements that form acid gases when wastes are reacted with oxygen (Cl, F, S, P, etc.) convert large amounts of Na_2CO_3 to the corresponding sodium salts. The same amounts of sodium salts are formed in the scrubbers for incinerators.

Whether the salt residues or the scrubber slurries are preferred for conversion to final waste forms is not obvious.

Molten salt oxidation for treatment of hazardous wastes was developed by Rockwell International in the 1970s and 1980s.¹⁻⁴ Molten salt technology was initially developed for other nonwaste applications in nuclear fuel cycles. One of the first tests with radioactive wastes was for solid transuranic wastes.³ The MSO treatment was also tested for both liquid and solid chemical wastes.¹ Destruction efficiencies were determined for chemical warfare agents, pesticides, and a number of toxic chemicals.² At that time, MSO was less developed than conventional incineration, and the advantages of MSO were not important enough to lead to commercial applications.

The inherent MSO advantages of high destruction efficiencies and no aqueous scrubber effluents are important for treatment of mixed wastes. Several assessment studies have concluded that MSO is one of the most promising and the most completely demonstrated alternatives to incineration for mixed wastes. The operation of an MSO bench-scale system and an MSO pilot plant at Oak Ridge is part of a DOE program to apply MSO to mixed wastes.

3. BENCH-SCALE MSO APPARATUS

The bench-scale apparatus (Figs. 1 and 2) consists of a 6-in.-diam, 3-ft-deep alumina crucible which is filled with salt to a depth of 6 to 8 in. (liquid level). This crucible is further contained within an Inconel 600 vessel as a secondary containment. The feed (waste) material is injected through the top of the vessel. It is pumped down the inner of two concentric Inconel 600 tubes ($\frac{1}{4}$ in. and $\frac{1}{2}$ in., respectively) along with a dispersing gas (either N_2 or air). Oxidizing air is fed through the outer tube. These tubes are enclosed in an 1½-in.-diam alumina pipe termed a "downcomer." The Inconel tubes end ~10 in. from the crucible bottom (above the level of the stagnant salt), and the downcomer carries the feed and gases into the salt (it extends to within 1 in. of the crucible bottom). The off-gases from the oxidation process pass through a knockout drum where condensed and entrained particles collected. The gases then proceed through a prefilter and HEPA filter before entering the plant stack ventilation system.

The controlled variables in the system are the furnace temperatures, feed material, feed rate, air and dispersing gas rates and pressures, dispersing gas composition (N_2 or

Fig. 1. The schematic equipment diagram for a bench-scale MSO apparatus.

Fig. 2. A photograph of the bench-scale MSO equipment at ORNL.

air), and salt composition. Measurements are taken for the salt bath and other temperatures, for various pressures, and for analyses of off-gas compositions (for a gas sample taken after the prefilter).

The off-gas is analyzed for five components: oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HCs), and NO_x . The oxygen and CO_2 measurements are taken primarily to allow a mass balance on the overall system. The CO measurements are taken to determine both the oxidation potential of the system as well as the typical CO concentrations that can be expected under various conditions. There will be CO and NO_x concentration limitations for the off-gas of a waste treatment plant. The HC analyzer shows whether relatively large quantities of unburned organic material (>5 ppm) escape reaction. This measurement is not precise enough for determining the destruction efficiencies (DREs) for the organic waste. The O_2 is detected by its paramagnetism. The CO and CO_2 analyzers both detect the characteristic infrared spectra of these gases. The HC analyzer works on the principle of flame ionization of the hydrocarbon by hydrogen in a blanket of air. The NO_x analyzer functions by first converting all of the NO_x to NO and then passing the sample into a chamber with ozone where the following reaction occurs:

The intensity of light emitted by the de-excitation of the NO_2 molecules provides an accurate measure of the NO_x concentration.

The instrumentation for off-gas analyses was calibrated before each test using three standard gas mixtures and pure air or nitrogen from cylinders to set the zero and span values.

4. TEST CONDITIONS

Two sets of initial tests were completed. The first set was designed to determine CO and NO_x emissions as functions of feed material, temperature, and salt composition. The conditions tested were:

feed materials:	dodecane, 5.5 wt % Adogen ^a in dodecane, 1.9 and 3.7 wt % nitrobenzene/dodecane;
furnace setpoints:	900, 940, 980°C; and

salt composition: Na_2CO_3 , 10 mol % $\text{NaCl}/\text{Na}_2\text{CO}_3$, 20 mol %
 $\text{NaCl}/\text{Na}_2\text{CO}_3$.

Feed, air, and dispersing gas rates were kept constant during most of the testing. Standard rates were:

feed rate: 2.8 mL/min,

airflow: 2.15 scfm, and

N_2 (dispersing) flow: 0.5 scfm.

The second set of tests was designed to obtain information regarding the retention of metals within the salt matrix, as well as to obtain further information on CO formation. Initially, the metals were to be injected into the molten salt as salts dissolved in glacial acetic acid. Difficulties with the injection system (see Sect. 8) forced the metals (in salt form) to be introduced directly into the molten salt as solids.

The feed materials and standard rates as well as other conditions are given below.

dodecane: 1.4, 2.2, and 2.8 mL/min;

ethanol: 4.4 mL/min;
 33 vol % H_2O in ethanol at 6.6 mL/min,

temperatures: 940—980°C;

airflow: 1.25 to 2.5 scfm;

dispersing flow: air 0.05 to 0.35 scfm, N_2 0.1 to 0.9 scfm; and

salt compositions: 3 mol % NaCl in Na_2CO_3 ; 20 mol % NaCl in Na_2CO_3

(both with additions of 0.2 mol % of CsCl and 0.1 mol % each of SrCO_3 , $\text{Ce}(\text{SO}_4)_2$, CoCO_3 , BaO).

In addition to the tests run with salt, there were four short tests run without any salt present — two at startup and two between the tests with salt charges. The first set was a checkout and was run at low temperatures. The second set was run at conditions similar to those used during the first set of salt runs. For details of the steady-state operating conditions and results, see Table 1.

^aA tertiary amine with an approximate formula of $(\text{C}_9\text{H}_{19})_3 \text{N}$.

Table 1. Operating conditions and steady-state results for MSO tests 1 to 17

Operating conditions (values are only entered if different from preceding conditions)										Steady-state results					Notes
Run	Salt comp.	Feed material	Feed flow (mL/min)	Air/N ₂	Inj. flow (scfm)	Inj. P (psig)	Airflow (scfm)	Air P (psig)	Temp. (°C)	O ₂ (%)	CO ₂ (%)	CO (ppm)	NO _x (ppm)	HC (ppm)	
1	None	None Dodecane		N ₂	0.5	58	1.7	8.3	789	15.50	0.00	0	0	2	> indicates a value above range of the low-level CO analyzer, or beyond the range of the HC analyzer
			2.4						839	10.40	2.65	0	1	5	
			3.6						880	8.00	4.20	0	0.7	4	
			3.2						877	8.51	3.95	0	0.8	3	
2			2.4		0.35			8.8	431	15.42	0.00	>4400	2	>2000	
									544	11.07	3.40	0	0.7	33*	
			3.0						769	11.04	3.45	0	0.7	21	
			3.6						855	9.60	4.40	0	1.4	19	
3	Na ₂ CO ₃		2.4		0.5	18		8.8	943	11.10	4.50	175	30*	1	
			2.8						963	10.09	4.60	180	2.6	2	
									959	10.06	4.60	145	2.8	2	
									935	10.14	4.40	75	1.6	5	
									922	10.15	4.50	50	1.3	4	
									954	10.13	4.70	100	1.8	4	
4									946	10.32	4.50	145	3.4	1	
5									947	9.80	4.10	105	5.4	0	
									946	9.90	4.10	160	4.7	0	
									947	10.20	4.30	60	4.1	0	
									947	14.30	4.30	0	3.2	1	
									948	10.30	4.40	60	3.5	0	
									922	10.23	4.20	5	2	0	
									901	10.08	4.40	0	1.4	1	
									932	10.01	4.50	10	1.7	1	
6		1.9% C ₈ H ₁₇ NO ₂ 5.5% adogen Dodecane 5.5% adogen 1.9% C ₈ H ₁₇ NO ₂		Air N ₂	0.2 0.5	100 13			931	10.10	4.50	0	9.3	0	*During test 6, air P was noted as above normal but was not recorded. Airflow was lowered to keep overall airflow consistent with previous tests
									934	10.23	4.40	0	90	0	
									934	10.20	4.40	0	80	0	
									935	10.10	4.50	0	7.6	0	
									964	10.13	4.60	0	4.3	0	
									968	10.11	4.50	0	81.5	0	
									968	10.18	4.40	0	91.6	0	

∞

Table 1 (cont.)

Operating conditions (values are only entered if different from preceding conditions)									Steady-state results						Notes
Run	Salt comp.	Feed material	Feed flow (mL/min)	Air/N ₂	Inj. flow (scfm)	Inj. P (psig)	Airflow (scfm)	Air P (psig)	Temp. (°C)	O ₂ (%)	CO ₂ (%)	CO (ppm)	NO _x (ppm)	HC (ppm)	
7	Na ₂ CO ₃	Dodecane	2.8	N ₂	0.5	18	1.58	9.8	901	9.87	4.40	0	15.5*	0	
			2.1						896	11.70	3.35	0	12*	0	
			1.7						889	12.73	2.65	0	8.4*	0	
			1.4						884	13.53	2.15	0	6.5	0	
			2.8						901	9.80	4.80	0	5.7	0	
		1.9% C ₆ H ₅ NO ₂ 5.5% adogen 3.7% C ₆ H ₅ NO ₂							904	9.85	4.80	0	87.5	1	
									904	9.81	4.80	0	82.8	1	
									931	9.83	4.80	0	186	1	
			2.1						924	11.67	3.50	15	134	1	
			1.4						912	13.69	2.25	65	89.2	1	
	10% NaCl	Dodecane							906	13.48	2.10	30	61.8*	1	
			2.8						928	9.73	4.80	0	40.1*	1	
							1.6	11	922	10.19	4.30	1730	11.5	1	
							916	11.95	3.00	2750	6.8	1			
			2.1				906	13.71	1.75	>4600	4.7	3			
		3.7% C ₆ H ₅ NO ₂	1.4				918	10.18	4.20	1620	5.7	2			
			2.8				954	10.19	4.40	2000	4.4	1			
							957	10.28	4.20	1580	120	1			
8	20% NaCl	Dodecane		Air	0.25 0.18 0.5	100	1.7	8	888	10.31	4.20	810	170*	0	
									888	14.72	4.20	365	64*	0	
									876	14.59	4.40	1030	39*	1	
									881	10.77	4.20	2490	31.8*	5	
							947		10.80	4.20	>4000	12	4		
							959		7.03	5.70	50	11	1		
							960		9.13	4.50	>3150	8.4	2		
9	None		2.8	N ₂		40	1.7	8.8	981	8.73	3.85	0	1.7	2	
			2.1						926	10.39	2.85	0	1.1	3	
			1.4						867	11.91	1.80	0	0.8	2	
			2.1				1.3	4.5	970	7.35	4.10	0	1.4	3	
10		5.5% adogen Dodecane	2.8		0.35		1.7	8.8	957	10.14	4.40	0	13.2	0	
									955	10.14	4.30	0	87.4	1	
									988	10.16	4.40	0	13.9	2	
			2.1						978	11.88	3.25	0	10.3	1	
			1.4						953	13.65	2.05	0	6.6	1	
			2.1				1.3	4.8	974	9.00	4.30	0	13.5	1	
			2.8				988	6.75	5.80	0	19.9	1			
							1.7	1005	12.40	5.70	0	33.2	2		
								986	14.51	4.20	0	13.2	1		
			2.3					960	15.70	3.45	0	10.6	1		

Table 1 (cont.)

Operating conditions (values are only entered if different from preceding conditions)										Steady-state results					Notes			
Run	Salt comp.	Feed material	Feed flow (mL/min)	Air/N ₂	Inj. flow (scfm)	Inj. P (psig)	Airflow (scfm)	Air P (psig)	Temp. (°C)	O ₂ (%)	CO ₂ (%)	CO (ppm)	NO _x (ppm)	HC (ppm)				
11	Na ₂ CO ₃	Acetic acid	6.5	N ₂	0.5	20	1.7	8.7	915	10.76	6.50	225	0.5	1	Injector began plugging causing fuel spurts into salt and fluctuating CO and HC readings			
		0.25 M CsCl	7						927	9.52	7.90	1160	0.6	2				
		0.25 M SrCl ₂	7						908	10.42	7.40	880	2.1	83				
		Dodecane	2.8				1.78	8.6	932	9.68	5.60	0	8	1				
12	3% NaCl ^a		2.2	Air	0.26	100	1.7	8.9	928	13.83	4.90	225	2.6	1	0.1% each of CsCl, SrCO ₃ , BaCl ₂ , CoCO ₃ , and Ce(SO ₄) ₂ in salt for tests 12–17			
				N ₂	0.5	20			916	15.54	3.85	600	4.1	2				
			2.8	Air	0.26	100	915	10.86	3.90	1250	8	4						
							927	9.22	5.10	265	2.6	3						
							928	13.60	5.10	10	9	0						
											11.5							
13		5.5% adogen Dodecane	2.2 1.4	N ₂	0.5	20	1.72	8.3	925	13.69	5.00	70	81 ^a	N/A ^a	^a HC analyzer down for tests 12–17			
									932	9.05	5.20	10	15.3	N/A				
				Air	0.20	100			932	9.05	5.20	0	92.6	N/A				
									932	13.51	5.10	10	105.2	N/A				
									932	13.42	5.20	5	32.5 ^a	N/A				
									922	15.11	4.00	25	11.4 ^a	N/A				
									901	17.31	2.40	940	2.5	N/A				
						1.3	4.5	908	15.98	3.30	330	3.1	N/A					
						2.8 2.2	N ₂	0.5	70 18			962	13.44	5.10		145	37 ^a	N/A
												953	15.15	3.70		1430	10.2 ^a	N/A
			960	13.01	5.20							0	10.9 ^a	N/A				
			963	14.00	4.60							565	8.0 ^a	N/A				
961	14.38	4.30	810	7.4	N/A													
959	14.47	4.20	940	6.5	N/A													
956	14.83	3.95	1210	5.8	N/A													
967	13.33	5.10	205	6.6	N/A													
957	14.96	3.75	1380	5.5	N/A													
947	9.86	3.45	2970	5.4	N/A													
2.8									953	10.24	4.10	1340	4.9	N/A				
									958	8.52	4.90	690	5.6	N/A				
									966	7.01	5.70	5	7	N/A				
									962	10.84	4.00	1980	4.9	N/A				
									967	9.10	5.10	570	5.3	N/A				

Table 1 (cont.)

Operating conditions (values are only entered if different from preceding conditions)										Steady-state results					Notes
Run	Salt comp.	Feed material	Feed flow (mL/min)	Air/N ₂	Inj. flow (scfm)	Inj. P (psig)	Airflow (scfm)	Air P (psig)	Temp. (°C)	O ₂ (%)	CO ₂ (%)	CO (ppm)	NO _x (ppm)	HC (ppm)	
15		Ethanol Dodecane	4.4 2.8	Air N ₂	0.95	100	1.7	8.8	964	9.31	5.00	980	7.2*	N/A	*Atomizing airflow was set to keep CO ₂ values constant
					0.12				958	8.21	4.10	2480	4.7	N/A	
					0.5		1.48	~7	969	10.65	5.80	120	7.7	N/A	
					0.85		1.25		973	7.56	5.80	10	13.8	N/A	
					0.2—0.5*				972	4.34	5.80	1490	9.4	N/A	
					0.2		1.7	9.8	974	12.14	5.90	0	8.9	N/A	
									972	13.54	4.90	390	10.3	N/A	
									958	14.20	4.50	235	6.8	N/A	
					0.5				957	10.06	4.50	2180	4.4	N/A	
									963	9.61	4.70	880	11.7	N/A	
16	19.4% Na		2.2 2.8	Air N ₂ Air	0.2 0.5	100	1.7	8.6	921	13.61	5.20	640	198*	N/A	
									924	9.23	4.90	2270	28*	N/A	
									917	11.04	3.65	>3600	16*	N/A	
					0.2				914	15.32	3.85	2250	6.6	N/A	
									925	13.47	5.30	740	16.1	N/A	
					0.05		1.9	11	927	13.57	5.20	0	243	N/A	
					0.1		1.83	10	926	13.58	5.20	295	118*	N/A	
									924	13.45	5.20	60	32	N/A	
					0.2		1.75	9	927	13.58	5.20	0	15	N/A	
17	19.4% Na	Dodecane 33% H ₂ O/EtOH Dodecane	2.8 6.6 7 7.5 8 3 2.5	Air N ₂ Air	0.2 0.5	100	1.67 ^f	10 ^f	916	13.75	5.10	0	420*	N/A	^f High pressure due to outer tube plugging
									923	9.40	4.80	1800	69*	N/A	
									908	13.68	2.55	>4200	29*	N/A	
									912	9.64	4.40	>5600	13*	N/A	
					0.2				914	13.98	4.60	>3200	9	N/A	
									916	13.52	4.90	>3150	8	N/A	
									921	12.99	5.40	2950	7	N/A	
									926	12.21	6.10	350	4.9	N/A	
									928	13.12	4.90	0	22.9*	N/A	
									926	14.49	4.20	430	10.3	N/A	

5. OFF-GAS CONCENTRATIONS OF NITROGEN OXIDES (NO_x)

While large emissions of nitrogen oxides are probably not acceptable, the NO_x limits for an MSO treatment of mixed wastes have not been specified. The NO_x measurements for our operation of the bench-scale MSO system are reported to provide a basis for judging the need for limiting or controlling NO_x emissions.

Two sources of NO_x emissions are commonly recognized: the nitrogen compounds in the feed and the reaction of N₂ and O₂ (usually as air) to form the NO_x compounds. The steady state emissions from our MSO studies show both of these sources. Our results also show significant unsteady state effects that indicate the molten salt is a reservoir of varying concentrations of nitrogen compounds. These results seem to indicate reversible reactions of the following type:

Other reactions can be written that include other nitrogen oxides, oxygen, and CO in addition to the compounds in the reaction listed. The important concept is that the melt can accumulate nitrogen compounds when the CO₂ or CO concentrations are low and release nitrogen oxides when the CO₂ or CO concentrations are higher.

The effects of organic nitrogen compounds in the feed were studied using dodecane feeds containing nitrobenzene or a tertiary amine [Adogen 364HP, approximately (C₉H₁₉)₃N] (Table 1). For both compounds, the off-gas NO_x concentrations increased by amounts equivalent to 80 to 100% of the nitrogen in the feed. The same result was observed for three melt temperatures, two nitrobenzene concentrations in the feed, 0, 10, or 20 mol % NaCl in the melt, or for one test with nitrobenzene and no salt (Fig. 3). For the molten salt tests, the exit gas concentrations of NO_x approached steady state much more slowly than did the concentrations of O₂, CO₂, and CO. These slow approaches to steady state agree with the salt reservoir effect from nitrogen compounds in the salt.

Because of the slow release of NO_x from nitrogen compounds in the melt, the exit NO_x concentrations for dodecane feed tended to decrease slowly for several hours of operation. Steady state was approached much more rapidly for high NO_x concentrations with the nitrobenzene or amine in the feed. The NO_x concentrations increased with temperature for dodecane feed, but there was little temperature dependence for the feeds

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Fig. 3. Exit NO_x concentrations for molten salt oxidation of dodecane.

containing nitrobenzene or amine (Fig. 3). The ranges of most steady state values were as follows:

dodecane at 900°C	1 to 5 ppm NO _x ,
dodecane at 970°C	3 to 10 ppm NO _x ,
1.9 wt % nitrobenzene, all temperatures	90 ppm NO _x ,
5.5 wt % Adogen amine, all temperatures	82 ppm NO _x , and
3.7 wt % nitrobenzene, all temperatures	170 ppm NO _x .

The calculated NO_x concentrations for the three feeds containing nitrogen compounds are 98, 86, and 191 ppm. The exit NO_x was 89 to 95% of the nitrogen in the feed liquids. If the NO_x concentrations observed for dodecane feed only were subtracted, then about 90% of the feed nitrogen appeared as NO_x in the exit gases.

Two tests were made using dodecane feed without salt to measure the exit gas concentrations for comparison with the results reported for three salt compositions. The "melt" thermocouple temperatures were from 860 to 1010°C. The NO_x concentrations show little or no effect from the absence of salt. The NO_x concentrations for pure dodecane feed were <5 ppm for <950°C and increased with temperature to 33 ppm at 1005°C. A test with 5.5 wt % tertiary amine in dodecane showed about 90% of the feed nitrogen as NO_x.

6. OFF-GAS CONCENTRATIONS OF CARBON MONOXIDE (CO)

The CO measurements obtained during the first several sets of experiments are probably the results of greatest interest and are the most difficult to fully explain. The first notable result is that no CO is formed when fuel and air are fed with no salt present in the reactor. These experiments took place under very similar conditions to those used for runs with salt present.

Unlike runs without salt, the runs containing salt produced significant quantities of CO under many conditions. The CO production showed definite trends with respect to the following five variables: (1) increases with increasing chloride content in the melt; (2) increases with increasing temperature; (3) increases with increasing airflow (provided

that airflow is well above stoichiometric, >150%); (4) increases when dispersing gas is switched from air to N₂; and (5) increases with decreasing feed rate.

Figure 4 shows CO production as a function of both chloride content and temperature. Table 1 gives more complete data on CO emissions for each test (see note at bottom of table regarding CO emissions >3150ppm). Figure 5 shows the effects of switching the dispersing gas from air to N₂ as well as effects of the gas flow rate.

Because of such a large effect on CO in small concentrations (10–20 mol %), it appears likely that NaCl acts as a catalyst for the production of CO. One set of reactions that has been proposed is:

Very little data have been found regarding the formation of NaOCl; it is, therefore, difficult to estimate the kinetics or equilibrium for reaction (3). The sodium hypochlorite would not have to be present in high concentration to have a noticeable effect since it would be consumed quickly in the presence of carbon [reaction (4)].

The reaction

could be an explanation as to why there is CO produced with salt present and none when it is not. A temperature increase would increase the rate of reactions (4) and (5) to make them better competitors to the most prevalent reaction (6):

Any CO that is produced by reactions (4) and (5) will be partially oxidized when it contacts O₂ at a high temperature.

An increase in airflow would decrease the amount of time for this reaction to take place

OTHER CONDITIONS INCLUDE:

N_2 DISPERSING GAS: 0.5 scfm

DODECANE FEED: 2.8 mL/min

AIRFLOW: 2.1-2.2 scfm

* BOTH HAVE 0.1 mol EACH OF Cs, Sr, Co, Ce, AND Ba AND 0.2 mol SO_4

Fig. 4. CO concentration vs temperature and salt composition.

OTHER CONDITIONS INCLUDE:

TEMPERATURE: 951-966 °C

DODECANE FLOW: 2.2 mL/min

SALT COMPOSITION: 3 mol % NaCl w/METALS

Fig. 5. CO concentration vs airflow rate.

while not significantly affecting the forward reaction in reactions (4) and (5) (since reactants are in solution).

The decrease in CO emissions observed when the N₂ dispersing gas is replaced by air most likely occurs because of better mixing of the oxygen molecules with the hydrocarbon fuel. This enables reaction (6) to take place before the carbon has an opportunity to react with the salt.

By far, the most difficult effect to explain, even hypothetically, is the increase in CO formation with decreasing feed rates. One would usually assume that since decreasing feed rate (while keeping airflows constant) increases the excess air percentage, as well as the residence time, the CO formation would decrease [by reactions (6) and (7)]. However, the exact opposite is observed in every case.

7. BEHAVIOR OF METALS IN AN MSO SYSTEM

Many different metals may be in the waste feed to an MSO waste treatment process since metals are common radioactive (Cs, Sr, Co, U, Th, Pu) and RCRA (Ba, Cd, Cr, As, Pb, Hg, Ag) components. The retention of metals in the melt and their collection as condensed solids in a filter are important to the design and operation of MSO waste treatment processes. Metals that are not completely collected and removed as waste salt or as filter solids will be troublesome or will require pretreatments or other special procedures.

One early set of ORNL MSO studies determined the behavior of five metals by chemical analyses of samples of melt and condensed solids. While chemical analyses are in some ways less sensitive and less convenient than analyses using radioactive tracers, the tests were done without need of the reviews and improved procedures necessary for radioactivity. The basic concept was to charge known amounts of metal salts into the MSO reactor, operate at a selected set of conditions, and sample the melt and condensed solids from the off-gas system. A single charge of salt was used with 7 periods of operation during a 12-d period. The primary test variables were:

metals: Cs, Ce, Co, Ba, Sr;

furnace temperatures: 940°C, 980°C;

melt composition: ≤3 mol % NaCl, 20 mol % NaCl; and

feed organic: dodecane, acetic acid, ethanol-33 v/o H₂O
(to give a higher H₂O concentration in the exit gas).

Our attempts to feed the metals as solutions in acetic acid were discontinued because of severe plugging of the feed injector. The startup with pure acetic acid showed no problems. The feeding of 0.1 mol of CsCl in 0.4 L of acetic acid was completed, but the feed injector required frequent rod-outs to prevent excessive feed pressures. Only half of a SrCl₂ feed was completed and was ended when almost continuous rod-outs became necessary. Dodecane was fed for a short period with no pressure buildup. When a barium acetate solution was started, the injector plugged completely with the rod-out being frozen in a stationary position. Inspection of the injector after removal showed severe scaling. It appears that the liquids probably evaporate in the dispersion N₂ to deposit the dissolved salts as scale on the injector walls. Measurements with a thermocouple in place of the rod-out wire show temperatures of 120 to 300°C about 15 cm above the injector tip with normal gas and feed flows. These are high enough for complete evaporation of dodecane or acetic acid but should not cause thermal decomposition. This injector design was used for a slurry of iron filings in oil at Energy Technology Engineering Center but is probably not suitable for dissolved, nonvolatile solids.

After the feed of solutions was ended, the tests to study the behavior of metals were continued by adding 0.1 mol of each of the five metals as dry solids compounds mixed with larger amounts of Na₂CO₃ and NaCl. The solids were charged to the melt and mixed by air sparge. The remaining test operation was with liquid feeds only, no dissolved solids. Mechanical operation of the equipment was good for the remaining six periods of operation.

The mixed solids added to 6.3 kg of Na₂CO₃ contained:

<u>Compound</u>	<u>Weight (g)</u>	<u>Mole</u>
CsCl	16.82	0.1
BaCl ₂ ·2H ₂ O	24.42	0.1
CoCO ₃	11.90	0.1
Ce(SO ₄) ₂	33.28	0.1
SrCO ₃	14.76	0.1
NaCl	116.9	2.0
Na ₂ CO ₃	186.5	1.76
Total	404.6	

The test conditions were daytime operation and overnight shutdowns. Melt and knockout pot samples were taken before startup and after shutdown each day. The operating conditions were:

<u>Mol % NaCl in melt</u>	<u>Number of days</u>	<u>Feed</u>	<u>Furnace temp. (°C)</u>
3	2	Dodecane	940
3	1	Dodecane	980
3	1	Ethanol-water	980
19.4	1	Dodecane	940
19.4	1	Ethanol-water	940

The results for chlorine analyses show good qualitative and quantitative agreements with the expected values. The first melt samples after additions show agreement with the calculated values as follows:

<u>Method of chloride additions</u>	<u>Calculated concentration (10³ ppm)</u>	<u>Analyses (10³ ppm)</u>
Feed of dissolved salts	1	0.94
Na ₂ CO ₃ -NaCl-metal salt solids	13	13, 12, 9.6, 11, 8.6
NaCl	81	34, 77, 73

The solids collected in the knockout pot show high chloride concentrations in agreement with the vapor pressure of NaCl as compared to that of Na₂CO₃. The chloride analyses were:

<u>Melt (10³ ppm)</u>	<u>Knockout pot (10³ ppm)</u>
13, 12, 9.6, 11, 8.6	114, 104, 66, 114, 84
34, 77, 73	260, 233

The amounts and concentrations of the condensed solids are in reasonable agreement with amounts calculated using the vapor pressure of NaCl. The calculations for a typical run would be as follows (for tests MSO-12 through MSO-17):

average melt concentration of C_N, mol fraction;

average exit gas flow of 330 L/min at the melt temperature;

average time of gas flow of 270 min;

vapor pressure of NaCl of about 3 mm Hg at 930°C;

$(330)(270)(3.0/760)(C_N) = 350 C_N$ L NaCl vapor at temperature $79 C_N$ L NaCl vapor at 273 K;

about 70 g mol of melt, 70 C_N g mol of NaCl in melt;

$(79 C_N/22.4)(100/70 C_N) = 5.0\%$ NaCl vaporized per run;

for tests 12, 13, 14, 15, about 5 g NaCl per run; and

for tests 16 and 17, about 40 g NaCl per run.

Based on knockout pot sample analyses and the vapor pressure of NaCl, the condensed solids are calculated to be about 40 g each for tests 12 through 15, and about 100 g each for tests 16 and 17, or 360 g total.

The solids deposited are a total of: knockout pot — about 60 g; wall deposits of 500 cm² and 3 mm deep — about 300 g; total condensed solids of 360 g. A charge material balance is as follows:

total melt solids charged	7514 g
total melt dumped	6515 g
volatile content of solids charged (experimentally determined by small-scale tests) ~5 wt % of Na ₂ CO ₃)	<u>330 g</u>
weight loss including deposited solids	669 g

All of these numbers have large possible errors or uncertainties. Together, they seem to show a preferential carryover of NaCl from the melt to the off-gas system in agreement with the vapor pressure of NaCl at the melt temperature.

The losses of cesium from the melt and the amounts of cesium in the condensed solids can be compared with the vapor pressure of CsCl at the melt temperatures. Using the same calculation procedure shown for NaCl, the calculated vaporizations would be:

average melt concentration of C_C , mol fraction;

vapor pressure of CsCl is about 18 cm Hg at 930°C;

$(330)(270)(18/760) C_C = 2100 C_C$ L CsCl vapor at melt temperature;

480 C_C L CsCl vapor at 273 K;

70 C_C g mol of CsCl in melt; and

$$(480 C_C / 22.4)(100 / 70 C_C) = 31\% \text{ Cs volatilized per run.}$$

The observed changes in melt concentration show:

for tests 13, 14, and 15, $(3100/3300)^{0.33} = 0.86$, or 14% loss per test; and

for tests 16 and 17, $(880/2100)^{0.5} = 0.65$, or 35% loss per test.

The knockout pot concentrations for tests 14 or 15 check as follows:

$$(24,000/1,000,000)(40 \text{ g}) = 0.96 \text{ g Cs in condensed solids; and}$$

$$(2,000/1,000,000)(6500) = 14 \text{ g Cs in the melt.}$$

About 7% of Cs in the melt appeared in the condensed solids. The 40 g of condensed solids might be too low since tests 14 and 15 were at higher melt temperatures.

The knockout pot concentrations for tests 16 or 17 include:

$$(31,000/1,000,000)(100 \text{ g}) = 3.1 \text{ g Cs in condensed solids;}$$

about 9 g of Cs in the melt; and

about 34% of Cs in the melt appeared in the condensed solids.

These results appear to show good agreement with the calculated vapor pressure of CsCl when the melt was 19 mol % NaCl and lower than calculated volatilities when the melt was 3 mol % NaCl. These results could be explained by a major fraction of the cesium being in a less-volatile form (perhaps Cs_2CO_3) when the melt chloride concentration is low.

The other metal concentrations were as follows:

<u>Metal</u>	<u>Calculated addition</u> <u>(ppm)</u>	<u>Melt concentrations</u> <u>(ppm)</u>	<u>Knockout pot concentration</u> <u>(ppm)</u>
Ba	2100	2200 to 1800	520 to 1700
Sr	1900	1500 to 1300	3100 to 540
Co	870	530 to 390	480 to 170 ^a
Ce	2050	<20 to 37 ^b	<20 ^a

^aFirst knockout pot sample after solids addition showed higher Co and Ce ... perhaps from entrainment of dust during addition of solids.

^bOne high value of 280 ppm Ce.

Analyses of samples from the salt dumped at the end of these tests and from deposits on the off-gas lines showed metal concentrations in good agreement with these test concentrations.

An ethanol-water feed was used during test 17 to give higher H_2O concentrations in the exit gases. The presence of water vapor favors higher concentrations of more volatile $\text{Ba}(\text{OH})_2$ or $\text{Sr}(\text{OH})_2$ as compared to oxides or carbonates. The one result for this condition shows lower Ba and Sr concentrations in the condensed solids and no significant effects on the Cs or Cl concentration.

In summary, the analyses of melt and knockout pot samples show the behavior expected from the volatilities of the components. The knockout pot samples may contain both solids from condensed vapors and entrained melt droplets but should show high concentrations of volatile compounds as compared to the melt. The results and their explanations include the following:

1. Since NaCl is more volatile than Na_2CO_3 , the knockout pot samples show much higher chloride concentrations than the melt. The knockout pot chloride concentrations were 10 times higher for 3 mol % NaCl in the melt and 3 times higher for 19 mol % NaCl in the melt.
2. The melt chloride concentrations showed small decreases with time in agreement with loss of volatile chlorides.
3. The knockout pot cesium concentrations were mostly 10 to 20 times larger than the melt concentrations; this difference would be expected for volatile CsCl. The melt cesium concentrations decreased steadily with about one-fourth of the initial concentration at the end of the tests.
4. The cesium concentrations in condensed solids agreed with calculations using the vapor pressure of CsCl for 19 mol % NaCl in the melt but were lower than the calculated concentrations for 3 mol % NaCl in the melt.
5. The knockout pot barium concentrations averaged about 60% of the melt concentrations. This agrees with BaCl_2 being less volatile than NaCl but does not indicate the volatility of barium for a pure Na_2CO_3 melt.
6. The knockout pot strontium and cobalt concentrations were variable but averaged about the same as the melt concentrations.
7. The cerium disappeared with only concentrations near the detection limits for

nearly all samples. This may indicate a rapid and nearly complete deposition of cerium compounds on the alumina walls.

8. Overall, the results show that volatilization is very important, but the entrainment also contributes to the carryover.

8. LIMITED RESULTS ON MSO EQUIPMENT PERFORMANCE

The overall performance of the MSO unit has been favorable. Broken down-comers or crucibles, two problems which have been experienced in the past, have not been encountered. The fuel/air injection system performs adequately with a liquid feed, but difficulty was encountered when solutions of acetic acid containing metal salts were employed. It is believed that the acetic acid was vaporized before reaching the bottom of the injector, and hard, crystalline deposits were formed inside. A "rod-out" bar, which runs the length of the injector, became firmly wedged and could not be moved. The off-gas system also develops two types of deposits of condensed salt in the piping between the MSO reactor and the knockout pot. The first is formed by depositions of solid particles formed in the gas and results in fine particles that are easily removed. The second occurs through condensation of liquid melt on the walls and freezing to form the hard deposits. By midway through the second set of tests, the amount of these deposits had increased to a level that required the rod-out bar in the off-gas system to be removed and a large drill bit on a metal rod to be inserted to clear the off-gas line. Very little salt appears to reach the filter system because the pressure differential has not increased noticeably over the duration of these tests.

In summary, the system operates well when used with organic liquid feeds, but a new feeding system will be required if solutions, sludges, slurries (unless easily suspended), or solids are to be tested.

9. FUTURE PLANS

The studies reported here are part of a proposed DOE program to develop the molten salt oxidation process for treatment of mixed wastes. The development studies at

Lawrence Livermore National Laboratory ORNL were planned to determine the information needed to justify and design MSO pilot plants at LLNL and Oak Ridge.

The ORNL development studies were assigned specific responsibilities for determining the MSO process performance and off-gas compositions. These included measurements of destruction efficiencies for three toxic organics, of Products of Incomplete Combustion (PICs), and of CO and NO_x concentrations in the off-gas. Control procedures to limit CO and NO_x concentrations may be necessary. Future ORNL studies will also address the loss of metals or radionuclides to the off-gas by entrainment or volatility.

The studies reported here were completed with preliminary funding. Whether the experimental program is continued as planned depends on the approval of continued funding.

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