THERMAL DESTRUCTION OF HIGHLY CHLORINATED MIXED WASTES WITHOUT GENERATING CORROSIVE OFF-GASES USING MOLTEN SALT OXIDATION (1,2)

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ABSTRACT
A pilot-scale MSO (Molten Salt Oxidation) system was used to process 45-gallons of a halogenated mixed waste that is difficult to treat with other thermal systems. The mixed waste was a halogenated solvent that consisted mostly of methylchloroform. The 80 weight percent of waste consisting of highly corrosive chlorine was captured in the first process vessel as sodium chloride. The sodium chloride leached chrome from that process vessel and the solidified salt exhibited the toxicity characteristic for chrome as measured by TCLP (Toxicity Characteristic Leaching Procedure) testing. The operating ranges for parameters such as salt bed temperature, off-gas temperature, and feed rate that enable sustained operation were identified. At feed rates below the sustainable limit, both processing capacity and maintenance requirements increased with feed rate. Design and operational modifications to increase the sustainable feed rate limit and reduce maintenance requirements reduced both salt carryover and volumetric gas flows.

INTRODUCTION
The MSO process treats and stabilizes a wide variety of wastes, especially organic liquids that are either corrosive or contain halogens. Unlike other thermal treatment technologies corrosive gases, such as hydrogen chloride, never leave the initial process vessel. The resulting clean off-gas reduces the size, complexity, and capital cost of the off-gas cleaning equipment, a major contributor to capital and operating costs in most thermal systems.

LLNL (Lawrence Livermore National Laboratory) demonstrated that the MSO process transformed a variety of organic wastes into carbon dioxide and water with most destruction efficiencies greater than 99.9999%, and all greater than 99.99%, with no detectable concentrations of dioxins [LLNL 1998a, 1998b]. The work described here determined operating conditions for sustained processing of one mixed waste consisting primarily of liquid methylchloroform. The liquid waste was classified as an orphan waste
with no identified options for commercial processing and disposal because of the high chloride content.

The MSO process has several unique characteristics. The MSO system operates at temperatures lower than flame combustion temperatures, which minimizes emissions of radioactive materials. The large thermal mass of a molten salt bed provides a stable heat-transfer medium, which resists thermal surges, ensures temperature uniformity, and tolerates rapid process fluctuations better than conventional thermal systems. Flameouts are completely avoided since MSO is a non-flame process that proceeds by catalytic liquid-phase oxidation reactions.

MSO's advantages over incineration include: 1) stability - the large thermal mass of molten salt tolerates rapid process fluctuation; 2) minimal off-gas - no supplemental fuel that produces additional off-gas is required to sustain a flame; and 3) simplified off gas control - acid off-gases are "scrubbed" by alkali salts eliminating the need for a wet off-gas scrubbing system. Only simple filters are needed to remove entrained salts that exit with the off-gas.

The MSO process destroys both toxic and non-toxic organics and traps potential acid gas formers, including halogens and phosphorous, in an inert salt bed. The MSO product is a highly stable salt cake, which, if necessary, can be further treated to meet regulatory standards for disposal. The byproduct gas is relatively free of toxic materials. When sodium carbonate is used in the initial salt bed, heteroatoms, such as sulfur or chlorine, react with the carbonate salt to produce sulfate or chloride salts, respectively, which become part of the salt matrix.

The MSO system for this work was also used by LLNL (LLNL 1998a, 1998b). This MSO system injects material containing organics near the bottom of a bed of molten sodium carbonate. Air is injected along with the feed material to drive the feed material into the salt bed. The chlorinated waste reacts with the molten salt and oxygen in the process vessel according to the following equation:

\[\text{C}_n\text{H}_b\text{Cl}_c + \frac{c}{2}\text{Na}_2\text{CO}_3 + \frac{a+(b-c)}{4}\text{O}_2 \rightarrow \frac{(a+c/2)}{2}\text{CO}_2 + \frac{b}{2}\text{H}_2\text{O} + c\text{NaCl}\]

Other non-volatile, inorganic constituents, including heavy metals and radionuclides, are captured in the salt.

High chloride wastes processed in the MSO system produce a minimum of off-gas but rapidly exhaust the bed by converting all of the initial carbonate salt into a chloride salt. To extend the bed life, we examined system operations at higher chloride loadings of the salt bed, up to 60% by weight, whereas previous work generally limited chloride loadings to less than 30% by weight (LLNL 1998a, 1998b).

At higher chloride loadings, the carryover of sodium chloride salt with the gas exiting the reactor increases. The chloride can exit the reactor as either particulate salt or as salt vapors. Either the particulate salt or condensing salt vapors can plug the off-gas line.
 exiting the reactor as well as filters that remove the salt from the off-gas. The operating ranges for parameters such as salt bed temperature, off-gas temperature, feed rate and other parameters expected to result in stable and sustained operation with minimal plugging of off-gas lines and particulate filters have been identified here.

**MSO SYSTEM**

The equipment used in the MSO system is described briefly in this section. For a more complete description of this equipment, refer to papers by Hsu et al. (LLNL 1998a, 1998b).

The MSO equipment is shown in Figure 1. The MSO process vessel, a vertical cylinder with a long, slender, accordion-like feed injection lance visible above, is shown in the left side of the figure. The vessel is encased in electric heaters that maintain the bed of molten salt between 850ºC and 950ºC. The process vessel was operated slightly below atmospheric pressure, at pressures in the range of a few inches of water vacuum. The process vessel was manufactured from Inconel 600, which contains approximately 15% chrome by weight.

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**Fig. 1. Process Vessel and Salt Removal Box**
Impurities in the vessel off-gas were removed by a three stage off-gas purification system. The three stages are 1) coarse particulate removal, 2) fine particulate removal, and 3) carbon monoxide and fumes conversion. The process vessel and all three stages of the off-gas purification system are shown in the process flow diagram included as Figure 2. Only one process vessel, Chamber A in the figure, was used for this work.

The first off-gas purification stage, coarse particulate removal, consists of an air cooled heat exchanger, a salt trap, and a GSS (Gas Solids Separation) filter, all at least partially visible in Figure 1. The air-cooled heat exchanger is a horizontal double-walled pipe that runs between the reactor vessel on the left to just above the small salt trap shown in the right front side of the figure. The custom-designed GSS filter, a ceramic cartridge filter, is a tall vertical cylinder partially visible toward the back of the figure just to the right of the small control panel between the process vessel and the salt trap. Pall Filter supplied the GSS filter. The GSS filter is immediately downstream of the salt trap as shown in the process flow diagram, Figure 2. The air cooled heat exchanger cools the off-gas to condense salt vapors.

A reciprocating brush, which was custom built by LLNL, clears salt from the 3½ inch off-gas line exiting the process vessel and the inner-most surface of the double-pipe air-cooled heat exchanger. The end of the rectangular box enclosing the salt brush is shown at the far right of Figure 1, just to the right of where the horizontal air-cooled heat exchanger ends and where the off-gas flow is directed vertically down towards the salt trap. The brush removes salt from the pipe surface and pushes the salt back into the process vessel on the forward stroke and into the salt trap on the reverse stroke. Salt is removed periodically from the GSS filter by back pulsing with compressed air. Salt from both the GSS filter and the salt trap exits the system through double dump valves that empty into salt collection canisters. The square, double-dump valve mounted underneath the salt trap is visible in Figure 1.

Fine solids, less than 0.5 microns in diameter, are removed in the second stage of the off-gas treatment system. The off-gas passes from the ceramic filter in the first stage to a HEPA filter in the second stage. The HEPA filter is not shown in Figure 1.

Carbon monoxide and trace hydrocarbons are destroyed in the third stage of the off-gas treatment system. The off-gas passes from the second stage HEPA filter through a preheater in the third stage and into a catalytic converter, which destroys the carbon monoxide and trace hydrocarbons. At higher CO concentrations in the off-gas stream, cooling air mixes with the off-gas before the mixture is preheated and passed across the catalyst. The catalytic converter was supplied by On-Demand Environmental Systems.
Fig. 2. Process Flow Diagram for Molten Salt Oxidation
Monitoring and Sampling
System performance was tracked by periodically logging system temperatures, pressures, gas flows, and concentrations of carbon monoxide and of carbon dioxide. Carbon monoxide and carbon dioxide were both measured with Horiba infrared analyzers, which were calibrated daily. Salt samples were taken of two spent salt beds and analyzed for chloride and chrome content by an EPA approved laboratory.

Salt chloride loading was estimated from the total amount of waste fed by assuming that all chlorine fed to the reactor was captured in the salt bed. This assumption was checked for Batch 1, where the estimated chloride loading of 40% was in reasonable agreement with the laboratory’s reported value of 30%.

Waste
The mixed waste processed was a spent methylchloroform solvent provided by DOE-Oakland from LLNL. Other chlorinated hydrocarbon solvents were present, but at trace concentrations. The waste was 80% by weight chlorine. Chromium was present at 1.3 mg/L, below the regulatory limit for a characteristic waste. The activity of the liquid was low, on the order of 10 nCi/L of gross alpha and gross beta, and 33 nCi/L of tritium.

The liquid waste was screened and then pumped into the process vessel with a peristaltic pump capable of delivering 10-120 ml/min against back pressures of up to 100 psi. Non-linear pump curves of flow rate vs. rpm were reproducible to within 20%. Nominal flow rates were estimated from the pump rpm setting using the pump curve. Total waste volume fed was measured daily by inserting a rod into the 55-gallon drum to measure the liquid level. The total waste feed was calculated as the product of the waste volume fed and the density of the waste, 1.3 gm/l.

Operation
About 180 kg of powdered sodium carbonate was charged in three portions to the process vessel. Each portion was melted with electric heaters before the next portion was added. Once all salt had been added and bed temperatures were within 50ºC of the set point, liquid feed was initiated and salt bed temperatures rose rapidly to the set point. The catalyst in the catalytic converter was preheated to its 260ºC set point prior to initiating feed.

The total MSO air feed, which consists of driver and oxidation air flows, was within the operating range shown in Table I. Driver air flows were sufficient to drive a slug of liquid feed quickly through the injection tube and into the molten salt bed. Oxidant air flows were adjusted to maintain total MSO air feed within the ranges shown in the table. The set point for total MSO air flow within the operating range was calculated from the feed rate and the desired combustion stoichiometry. Cooling air flows for the catalytic converter were adjusted to keep the temperature of the catalyst bed less than 430ºC.
Table I. Operating Ranges for Molten Salt Oxidation System

<table>
<thead>
<tr>
<th>Operating Variable</th>
<th>Range Tested</th>
<th>Stable Operating Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate (kg/hr)</td>
<td>0.5 - 8</td>
<td>0.5 – 4</td>
</tr>
<tr>
<td>Total MSO Air Feed (slpm)</td>
<td>80-160</td>
<td>80-130</td>
</tr>
<tr>
<td>Salt Bed Temp (ºC)</td>
<td>890 - 950</td>
<td>890-950 (1)</td>
</tr>
<tr>
<td>MSO Exit Gas Temp (ºC)</td>
<td>600 - 910</td>
<td>&lt;700</td>
</tr>
<tr>
<td>GSS Filter dP (in. w.c.)</td>
<td>1 – 15</td>
<td>&lt; 8</td>
</tr>
<tr>
<td>Converter Cooling Air Feed</td>
<td>0 – 75</td>
<td>0 – 75</td>
</tr>
<tr>
<td>CO Before Converter</td>
<td>0 – 10,000</td>
<td>100</td>
</tr>
<tr>
<td>CO After Converter</td>
<td>5 – 2,150</td>
<td>&lt; 50</td>
</tr>
</tbody>
</table>

(1) Stable feed rate decreases at higher temperatures.

During operation, salt particulates collect or condense within the off-gas line and the off-gas line must be periodically cleaned. When processing wastes, such as those containing chlorine that form salts with lower boiling points than sodium carbonate, the off-gas line is normally cleaned every time the salt bed is drained. Particulate and condensing salt also eventually blinds the GSS filter elements, which then must be removed, cleaned and replaced.

For sustained operations, minimum goals were set for salt bed life and cleaning frequency for the off-gas line and the GSS filter. These goals included:

1) at least 60% by weight chloride loading of the salt bed during a batch,
2) off-gas line cleaning frequency of less than one per salt batch, and
3) GSS filter element cleaning frequency of less than one per salt batch.

When processing wastes consisting largely of chlorine, the economics of MSO treatment are extremely sensitive to the chloride loading of the bed. The amount of waste processed per salt batch is directly proportional to the chloride loading. If all carbonate salts are converted to chloride salts the maximum amount of waste chlorine that can be processed through a bed initially containing 180 kg of sodium carbonate is 120 kg, or 150 kg of methylchloroform. The minimum economical loading of the salt bed is approximately 60% by weight chloride, which would allow the processing per batch of 72 kg of waste chlorine, or 90 kg of methylchloroform. To eliminate the need for a scrubber in the off-gas train, and to reduce plugging of the off-gas line and GSS filter, the maximum chloride loading for the salt bed was set at 90% by weight.

The maximum chloride loading of the bed also corresponds to the minimum quantity of residual salt requiring disposal, which is 1.3 kg NaCl per kg of RTS#1 waste. As the residual MSO salts are dry, the MSO system produces less mass requiring disposal than gas-phase thermal systems, such as conventional incinerators. Such gas-phase thermal systems capture the hydrogen chloride emitted in the off-gas in a liquid scrubber and then dispose of the wet scrubber salts.
The MSO system is a batch system. Each batch consisted of at least two daily feed runs of two to six hours duration. The minimum time to drain spent salt between batches and then add and melt fresh salt is about 12 hours. During this time no waste is processed. At a waste processing rate of 4 kg/hr the bed will be 60% loaded with chloride after about 22 hours of processing and the equipment utilization factor will be 65%, or 22 hours out of a 34 hour cycle.

Cleaning of the off-gas line or replacement of the GSS filter elements between batches, while the spent salt is draining and the fresh salt is melting, will not reduce the equipment utilization factor. Therefore both an off-gas line cleaning and a filter element replacement frequency of less than one per salt batch are satisfactory. Once removed from service, the GSS filter elements are cleaned by soaking in water, then dried and reused.

RESULTS AND DISCUSSION

The results of each salt batch are shown in Table II. Batch 1, operated at the highest average feed rate, was terminated after the off-gas line plugged. Batch 2 was also started at a high feed rate. Three hours into Batch 2 the off-gas line plugged and the feed rate for the remainder of the run was reduced.

To reduce the amount of salt carryover from the reactor, the third batch was run with stoichiometric total MSO feed air. The stoichiometric feed air is the minimum air required to convert all carbon and hydrogen in the feed to carbon dioxide and water within the MSO process vessel. All other batches were run with air approximately 20% in excess of the stoichiometric requirement.

When fed stoichiometric air, the system performed well and stably during Batch 3, and achieved the longest run and highest chloride loading for any of the batches. Batch 3, with the longest operating run of 20 hours, had a total batch time of 32 hours, or a projected equipment utilization factor for continuous operation of 60%. Carbon monoxide levels exiting the process vessel were high, approaching the lower explosive limit.

Table II. Batch Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Operating Period (Hours)</th>
<th>Total Feed Kg</th>
<th>Op. Hours</th>
<th>Avg. Feed Rate Kg/Hr</th>
<th>Wt Percent Salt Cl Loading</th>
<th>Kg Residual Salt / Kg Feed</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 – 9</td>
<td>51</td>
<td>9</td>
<td>6</td>
<td>40</td>
<td>3</td>
<td>Salt plug at end of run</td>
</tr>
<tr>
<td>2</td>
<td>9 – 24</td>
<td>37</td>
<td>15</td>
<td>2</td>
<td>30</td>
<td>5</td>
<td>Salt plug 3 hours into run</td>
</tr>
<tr>
<td>3</td>
<td>24 – 44</td>
<td>83</td>
<td>20</td>
<td>4</td>
<td>60</td>
<td>2</td>
<td>Stoichiometric air</td>
</tr>
<tr>
<td>4</td>
<td>44 – 49</td>
<td>8</td>
<td>5</td>
<td>2</td>
<td>30</td>
<td>5</td>
<td>High Injection Temp.</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION
Except for one brief exceedance, the catalytic converter was able to reduce the CO concentrations of around 10,000 ppm exiting the MSO vessel during Batch 3 to less than 100 ppm before exhausting the off-gas to the MWF ventilation system. The brief exceedance occurred during start-up of a daily run and was quickly corrected by increasing the power to the preheater for the catalytic converter. CO concentrations exiting the MSO vessel were much lower, generally less than 100 ppm, for all other batches.

Batch 4 was prematurely stopped after 9 hours of operation. At the end of Batch 3, the liquid injection tube in the feed lance had plugged and the tube had been shortened. The shortened tube injected the liquid for Batch 4 above the heat sink, within an insulated section of the injection lance. The resulting high temperatures at the new, insulated, injection point quickly corroded away the surrounding sections of the lance and terminated the batch.

Except for one brief spike, CO concentrations entering the catalytic converter during Batch 4 were less than 1,000 ppm. The initial nominal feed rate for Batch 4 was less than half that for Batch 3. As nominal feed rates were increased during Batch 4, CO concentrations entering the catalytic converter remained at least 10 times less than the range of 10,000 ppm observed during Batch 3.

**Chloride Loading**

Table II shows that chloride salt loadings for the four batches varied from 30 to 60% of the theoretical limit. Batch 3 achieved the target loading of at least 60%.

**Off-Gas Line Cleaning Frequency**

Salt carried out of the process vessel with the off-gas twice plugged the off-gas exit line within a few inches of the exit from the process vessel. The off-gas line plugged at the end of Batch 1 and again at the beginning of Batch 2. The feed rates each time the off-gas line plugged were greater than 4 kg/hr. Plugging of off-gas lines was not observed at feed rates lower than 4 kg/hr.

The plugs first became evident when the salt brush failed to fully extend into the process vessel. After full extension of the brush was blocked, the cleanout port on the opposite side of the process vessel was opened. A hard, annular salt plug with a cylindrical opening that still allowed gas flow was clearly visible through the cleanout port each time the brush was blocked. The annular salt plugs, with an outer diameter of 3½ inches and thickness varying from ½ to 1½ inches, were then drilled and sanded out. The open annular spaces in the salt plug allowed sufficient gas flow that minimal changes in system pressure were evident when the salt plugs were removed.

The four batches demonstrated that cleaning of the off-gas line between batches will keep the off-gas line sufficiently clear to process an entire batch without reducing the available operating time for the MSO equipment.
GSS Filter Cleaning Frequency
Just as salt carried out of the process vessel twice plugged the off-gas exit line, the salt also plugged the ceramic elements in the GSS filters. The filter elements first plugged at the end of Batch 1. After an additional 37 hours of operation, the elements plugged again at the end of Batch 4.

The ceramic filters are declared plugged when backflushing overnight with air fails to reduce the pressure drop through the elements to less than the maximum acceptable pressure drop, 8 in. w.c. (water column), at an off-gas flow of 15-20 scfm measured downstream of the HEPA filter. Note in Figure 3 that during Batch 4, which begins at 44 hours, the pressure drop across the GSS filter rises rapidly to unacceptable levels. As Batch 4 progressed, the total MSO air input increased (measured upstream of the GSS filter) and the off-gas system heated up, as shown by the increase in GSS filter entering gas temperature. The increases in air input and gas temperature shown in Figure 4 for Batch 4 corresponded to increases in nominal feed flow rate. Conditions during the shakedown run, Batch 1, which occurred during the first nine operating hours, are not shown in Figures 3 and 4.

As gas flowrates through, and pressure drops across, the GSS filter elements remained acceptable for all of at least two batches, batches 2 and 3, the service life of the filters was demonstrated to be acceptable to support a feed rate of 4 kg/hr.

Residual Salts
Table II shows that the mass of raw residual salts requiring disposal after processing through the MSO system ranged from two to five times the mass of waste processed. The mass of raw residual salts per pound of waste processed is directly related to the chloride loading, which was discussed above. For Batch 3, the amount of raw residual requiring disposal after processing is twice the mass of waste processed.

Table III shows that raw residual salts from the MSO process exceed the toxicity characteristic (TCLP) limit for chromium and must be treated to reduce chromium leaching prior to disposal. The chromium leached out of the Inconel 600 process vessel into the salt and turned all four batches of salt, plus that from the processing of ethylene glycol, green. Green is the color of chromium (III) oxide.

More leachable chromium was found in the salt after treating the high chlorine RTS#1 waste than after treating ethylene glycol. Even when treating ethylene glycol, which left the salt as the less corrosive sodium carbonate, the residual salt still failed the TCLP (Toxicity Characteristic Leaching Procedure) test.

As the MSO residual salts exceeded the TCLP limit, the residuals must be stabilized prior to land disposal. Stabilization of the chromium in the residual, to reduce the leaching below the toxicity characteristic limit, will increase the mass requiring disposal. The established methods for stabilizing chromium in salts increase the mass of the waste by about four fold. Thus this MSO system, including conventional waste stabilization, will likely produce at least 8 kg of waste suitable for disposal for every kilogram of waste processed.
Fig. 3. GSS Filter Performance

Fig. 4. MSO Vessel Exit Gas Temperature
Table III. Leaching of Chromium from Residual Salts

<table>
<thead>
<tr>
<th>Residual Salt</th>
<th>Feed Chlorine Concentration (g/kg)</th>
<th>Salt Chlorine Concentration (mg/kg)</th>
<th>Salt TCLP Chromium Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>0</td>
<td>&lt;2</td>
<td>19.2</td>
</tr>
<tr>
<td>RTS#1 (Batch 1)</td>
<td>800</td>
<td>282,000</td>
<td>105</td>
</tr>
<tr>
<td>TCLP Maximum Limit</td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

**Recommended Operating Parameters**

The total cost of processing waste with the MSO system includes capital, operating and disposal costs for treatment residues. Disposal costs are always reduced by increasing the chloride loading of the salt bed. As long as salt plugging of the off-gas line and ceramic filter is avoided, capital and operating costs are also reduced by increasing the chloride loading for a given feed rate.

The operational limit on chloride loading of the salt bed is a complex function of several interrelated operating parameters. These parameters, shown in Table IV, include feed rate, total MSO air feed into the process vessel, the MSO exit gas temperature, and the GSS entering gas temperature.

Table IV. Stable Ranges for Operating Parameters

<table>
<thead>
<tr>
<th>Operating Parameter</th>
<th>Stable Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate (kg/ hr)</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Total Air Feed (1.2 X stoichiometric) (slpm)</td>
<td>&lt; 130</td>
</tr>
<tr>
<td>MSO Exit Gas Temperature (ºC)</td>
<td>&lt; 700</td>
</tr>
<tr>
<td>GSS Entering Gas Temp. (ºC)</td>
<td>&lt; 180</td>
</tr>
</tbody>
</table>

When the bed was fresh and contained mostly sodium carbonate, the maximum demonstrated stable feed rate for the highly chlorinated feed was about 4 kg/hr. At higher feed rates, salt plugs closed the off-gas lines within a few hours of operation.

After the feed rate, the temperature of the gas exiting the MSO vessel is the most critical for controlling plugging of the off-gas line. Figure 5 shows that the temperature of the off-gas generally increased from 600ºC to 800ºC after feed was initiated. No plugging of the off-gas line was observed when the off-gas temperature was kept below 700ºC. Presumably below this temperature, too little salt is carried out as a vapor to condense and plug the off-gas line. Carryover of salt particulate into the off-gas line may also contribute to plugging, especially at high air feed rates. The MSO exit gas temperature and the total MSO air feed are related as increasing the total air feed into the process vessel also raises the temperature of the gas exiting the process vessel.
Similar to plugging of the off-gas line, the temperature of the gas entering the GSS filter is a critical determinant of GSS filter plugging. Above about 180°C the salt crystals in the gas entering the GSS filter, or already lodged in the filter, may soften and irreversibly plug the filter pores. The best evidence for plugging by salt softening is the higher permanent pressure drop observed across the filter after runs of three hours or more when the gas temperature entering the GSS filter exceeded 180°C. The longest demonstrated operating time between cleanings for the GSS filter was 35 hours, or less than one filter element cleaning per salt batch, an acceptable cleaning frequency.

Other observations suggest that salt carryover is primarily a maintenance problem as long as the frequency for cleaning either the off-gas line or replacing the GSS filter element is less than once per batch. These other observations include first, an apparent consistency between the observed and theoretical relationship between pressure drop and gas velocity and second, carryover of at most a few percent of the 720 kg of salt charged to 4 batches during 50 hours of operation.

The observed pressure drop, which tripled from 5 to 15 inches of water as the total MSO air input nearly doubled, is consistent with the increase predicted based on gas velocity alone. The increase in pressure drop through a porous filter increases approximately as the gas velocity squared. The tripling in pressure drop corresponding to a doubling in total MSO air flow during Batch 4 is evident in Figure 4. Batch 4 starts at 4 hours of operation.

In the range of 5 kg of salt was collected from off-gas line plugs, the salt trap, and the GSS filter during 50 hours of operation. This small quantity of salt demonstrates that at most a few percent of the 720 kg of the salt initially charged to the vessel carried over into the off-gas. As increases in gas velocity account for observed increases in pressure drop and the rate of salt carryover was low, increases in feed rate will increase system capacity until maintenance related to salt carryover must be conducted during, rather than at the end, of a batch.

With two exceptions, the carbon monoxide concentrations in the gas entering the catalytic converter were less than 100 ppm. 100 ppm is the maximum allowable concentration for discharge of CO from the building stack. The first exception was operational anomalies. Operational anomalies included brief spikes of CO to concentrations of 2,000 ppm or less, presumably due to the sudden introduction of slugs of liquid feed into the process vessel by the peristaltic pump. Another operational anomaly was failure to heat the off-gas entering the catalytic converter to the minimum temperature as current to the preheater was set too low. The second exception was Batch 3. For Batch 3 the air feed into the process vessel was reduced to the stoichiometric amount and the CO concentration entering the catalytic converter was stable in the range of 10,000 ppm.

As concentrations of CO exiting the CO converter remained less than 100 ppm throughout Batch 3, the catalytic converter performed satisfactorily. Both pre-heating of the gas entering the converter and cooling air to limit the temperature of the gas exiting
the converter were essential to the proper operation of the converter at CO concentrations in the range of 10,000 ppm.

When operating with excess air, the catalytic converter’s function is limited to backing up the MSO system. This backup function is to reduce brief spikes of CO above 100 ppm from the MSO process vessel, such as spikes that result from the sudden introduction of slugs of liquid feed into the process vessel.

### Design and Operational Improvements

The MSO system operated for brief periods at feed rates at least twice the maximum sustainable feed rate. Above the maximum sustainable feed rate, either the off-gas lines must be cleaned or the GSS filter elements must be replaced before the desired batch chloride loading is reached.

These constraints on maximum feed rate can be relieved by modifying either the design or operating parameters of the MSO system. The objective of the modifications would be to reduce the salt carryover or the volumetric gas flow rate to reduce system maintenance requirements.

A simple reduction in the operating temperature of the salt bed to the range of 850 - 900°C would reduce both the salt carryover and the volumetric gas flow rate. Previous work by LLNL (LLNL 1998a, 1998b) suggests that destruction and removal efficiencies would still be adequate at these lower temperatures. There is adequate capacity in the existing catalytic converter to destroy any additional carbon monoxide produced at lower salt bed temperatures.

Another approach is to reduce the temperature of the off-gas exiting the vessel by turning off the upper heaters or cooling the upper sections. During one run, turning off the upper two of the seven heater sections reduced the off-gas exit temperature by at least 50°C.

Additional cooling of the off-gas before it reaches the GSS filter will reduce the operating temperature of the filter. An off-gas heat exchanger with greater cooling capacity than the existing air-cooled model may enable the GSS filter to operate below the salt plugging temperature at higher waste feed rates.

Substituting pure oxygen for the oxidation air would reduce total gas flows by several-fold, with an even greater reduction in pressure drop across the existing GSS filter. Cooling of the process vessel would be required to remove the heat of reaction currently removed by the inert nitrogen in the air. An evaluation of the potential for operation with pure oxygen to increase the rate of corrosion of the process vessel would also be required.

As in Batch 3, volumetric gas flows can be reduced by supplying less total MSO air feed. The air feed would be set to the minimum required to keep carbon monoxide concentrations and the lower explosive limit below safety limits.
CONCLUSION

The single-vessel MSO system supplied by LLNL is suitable for processing one to two 55-gallon drums per week of orphan mixed wastes, especially wastes containing halogens, sulfur, and phosphorous. The system proved to be especially appropriate for processing such wastes that also contain chromium and other RCRA metals. At feed rates below the limit for sustained operations, both system capacity and maintenance requirements increase with feed rate. System capacity could be doubled with minor design modifications and refinements in the operating settings to reduce salt carryover from the MSO process vessel.

References
