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TREATMENT OF WASTE BY THE MOLTEN SALT OXIDATION PROCESS AT THE OAK RIDGE NATIONAL LABORATORY*

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ABSTRACT

The Molten Salt Oxidation (MSO) process has been under development by the Energy Technology Engineering Center (ETEC) to treat hazardous, radioactive, and mixed waste. Testing of the system was done on a number of wastes to demonstrate the technical feasibility of the process. This testing included simulated intermediate level waste (ILW) from the Oak Ridge National Laboratory. The intermediate level waste stream consisted of a slurry of concentrated aqueous solutions of sodium hydroxide and sodium nitrate, with a small amount of miscellaneous combustible components (PVC, TBP, kerosene, and ion exchange resins). The purpose of these tests was to evaluate the destruction of the organics, evaporation of the water, and conversion of the hazardous salts (hydroxide and nitrate) to non-hazardous sodium carbonate. Results of the tests are discussed and analyzed, and the possibilities of applying the MSO process to different waste streams at ORNL in the future are explored.

INTRODUCTION

The MSO process is a thermal treatment technology developed to treat a variety of hazardous, radioactive, and mixed waste. The basic concept of the MSO process is the introduction of waste and air into a bed of molten salt (usually Na_2CO_3) at a temperature of $\sim 900°C$ at which organic waste will be oxidized and acid gases, metals, and radionuclides are expected to be retained in the salt.

In the mid-to-late seventies, several waste streams were produced at Oak Ridge during reprocessing of the breeder reactor fuel. One of the wastes was an ILW which consisted of a slurry of concentrated aqueous solution of sodium hydroxide and sodium nitrate with a small amount of miscellaneous combustible components (PVC, TBP, kerosene, and ion exchange resins). The purposes of using the molten salt oxidation process to treat this type of waste were to convert the ILW into a solid waste stream with the organics destroyed and into a vapor stream consisting of water evaporated from the waste. The solid waste stream would then be put into a suitable form for final disposal. The vapor stream would be routed to an off-gas treatment system.

The molten salt oxidation process has previously been studied for the disposal of organic wastes with the result being that organic materials are totally destroyed in the oxidizer. Even the presence of concentrated alkali salts in the waste does not hinder performance, because this merely becomes a part of the molten salt bath. However, the disposal of an aqueous waste stream has not been previously demonstrated. Thus, the main purpose of this experiment was to determine the percentage of water in the waste stream that can be safely injected into the bed of molten salt.

BACKGROUND

Rockwell International has conducted a number of experimental and theoretical studies on the molten salt process and has advocated the Molten Salt Oxidation process for waste treatment. There initial studies focused mainly on the properties and chemistry of molten salts. These studies included evaluation of the thermodynamic and transport properties of molten salts, the interaction of molten salts with molten metals, and the behavior of molten salts under high pressure.

Later, the MSO process was researched using a variety of waste streams. These tests demonstrated excellent destruction and removal efficiencies. The testing was discontinued when it appeared that incineration was to be the acceptable technology for thermal treatment. However, due to more recant technical and regulatory difficulties with incineration, MSO is once again emerging as a promising technology with significant advantages relative to incineration.

The basic concept of MSO is to introduce waste and air into a bed of molten salt (usually Na_2CO_3) at a temperature of $\sim 900°C$ at which the organics are oxidized and acid gases, metals, and radionuclides are retained in the salt. The "spent" salt can be removed for reprocessing and recycling, or for some final treatment for disposal. The MSO process basically is a combination of chemical and thermal treatment. The use of a molten salt medium provides several advantages over a purely combustion technique. The molten salt: (1) acts as a dispersing medium for both the waste being processed and the air used in the processing; (2) acts as catalyst for the oxidation reactions and accelerates the destruction of organic material; (3) enhances completeness of the chemical reactions by providing better contact over a relatively long time period and provides a stable heat transfer medium that resists thermal surges; (4) neutralizes and retains acid gases; (5) helps retain soot and chars in the melt for more complete reaction; and (6) retains the ash and other inorganic material associated with the waste. These characteristics enable (1) more complete destruction because of the catalytic effect of the salt, a longer residence time, and more intimate contact with the caustic molten salt; (2) excellent capture of heavy metals and radionuclides because of wetting, encapsulation, and chemical reaction with the salt melt; (3) reaction and neutralization of acidic products such as HCl, HF, SO_2, and P_2O_5; and (4) reduced off-gas flow.

EXPERIMENTAL

The objectives of the ILW treatment by the MSO process were: (1) to demonstrate the feasibility of molten salt oxidation for disposal of simulated ILW, (2) to demonstrate destruction of the organic material in the waste, (3) to determine the volume reduction after processing, and (4) to determine operating conditions which minimize off-gas pollutants.

The composition of the non-radioactive portion of a typical ILW stream given in Table 1 was provided by Oak Ridge National Laboratory (ORNL). The aqueous waste stream consisted mainly of a slurry of concentrated solutions of sodium hydroxide (4M NaOH) and sodium nitrate (4M $NaNO_3$) with a small amount of miscellaneous combustible components such as polyvinylchloride (PVC), tributylphosphate (TBP), kerosene and ion exchange resins. Because this waste stream had little heat content, a fuel was also added. This fuel provide the heat necessary to vaporize the water and to make up process heat losses.

Table 1. Composition of simulated intermediate level waste

Component	Volume (%)
Polyvinyl chloride	2.90
30% TBP-NPH	2.40
Ion exchange resin	
Dowex 50	0.94
Dowex 1	0.64
4 M NaOH 4 M $NaNO_3$	93.30

In the MSO unit, the waste and air was added in such a manner that any gas formed during the oxidation process was forced to pass trough the melt before release.

The bench-scale unit used in these tests (Fig. 1) was designed and constructed at Rockwell's Santa Susana field laboratory. Approximately 5.4 kg of molten salt were contained in a 152-mm-ID x 914-mm-high alumina tube mounted in a type 321 stainless steel vessel. This stainless steel vessel was inserted into a 203-mm-ID electric furnace, and the entire unit was housed within a walk-in hood.

Feeding of the slurry was accomplished with a Masterflex 7016 peristalic pump. The slurry flowed from the stainless steel beaker through 5-mm-ID Viton tubing to a 6.4-mm stainless steel manifold and into a liquid injector. The liquid injector consisted of three concentric stainless steel tubes. The liquid feed slurry passed down the center tube and out through a 2-mm hole. Carbon dioxide for cooling could be added at an adjustable distance from the bottom of the middle annulus and return up through the same annulus. The combustion air was added through the outside annulus and was directed at the liquid stream through four 1.8-mm jets. A thermocouple was inserted down the carbon dioxide annulus in order to give a measure of the approximate temperature of the interior of the injector.

The tip of the injector could be adjusted to different heights above the bottom of the alumina tube. Satisfactory operation was generally obtained when this height was 560 cm.

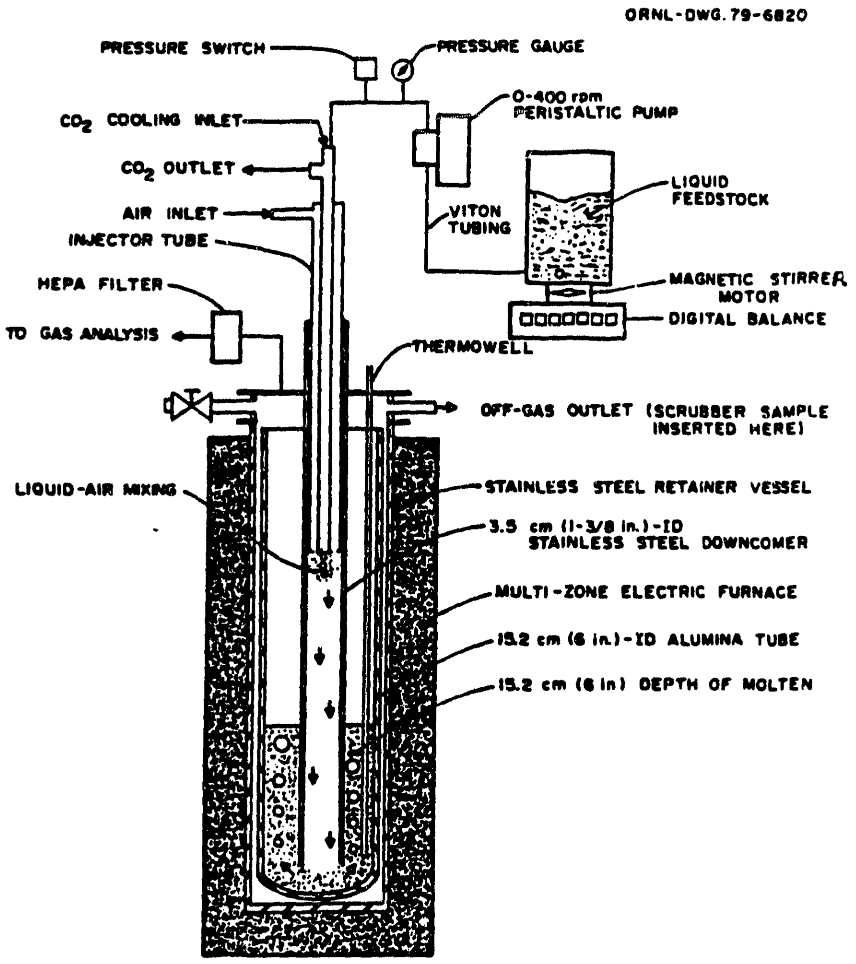

Fig. 1. Laboratory molten salt unit with liquid feed.

RESULTS AND ANALYSES

Because water and molten salt may interact violently under some conditions and because the wastes contained a strong oxidizer (spent $NaNO_3$), a series of tests were required to determine if such a material could be treated safely. A test program was performed that consisted of: (1) oxidation of fuel-water mixtures, (2) oxidation of fuel-water-salt mixtures, and (3) oxidation of the simulated intermediate level waste slurry. The base test conditions for this program are given in Table 2. Sodium chloride was added to the melt to approximate the steady-state chloride content from combustion of PVC, and methanol was used as the supplementary fuel. A temperature of 900°C was selected because volatilization of NaCl becomes excessive at higher temperatures. The superficial gas velocity of 0.3 m/s is the normal operating condition in the bench-scale oxidizer.

Table 2. Base test conditions

Salt composition	95 wt % Na_2CO_3 5 wt % NaCL
Temperature	900°C
Superficial gas velocity through the salt vessel	0.3 m/s
Fuel	Methanol
Excess air	25%
Methanol feed rate	11.4 g/min
Waste feed rate	Variable

Because the waste stream had little heating content, fuel was added to provide the heat necessary to vaporize the water and to make up process heat losses. Methanol was chosen as the fuel because it is highly miscible with water and with concentrated aqueous solutions. A 60:40 ratio of H_2O:CH_3OH (wt%) proved to provide smooth operation.

In order to determine the effects of dissolved salts in the feedstock on MSO operation, a series of tests was run in which the salt concentrations were gradually increased to the design point of 4M NaOH and 4M $NaNO_3$. A summary of the tests is given in Table 3.

Table 3. Oxidation of methanol-water-salt mixture

Test	H_2O (wt %)	CH_3OH (wt %)	NaOH (wt %)	$NaNO_3$ (wt %)	Feed rate (g/min)	Test duration (min)	Excess air (%)	MSO operation
1	51.6	40.0	8.4 (4M)	0.0	29.3	95	21	Smooth
2	51.9	34.6	8.8 (4M)	4.7 (1M)	31.7	87	29	Smooth
3	49.2	32.8	8.7 (4M)	9.3 (2M)	41.0	130	6	Smooth
4	44.1	29.4	8.5 (4M)	18.9 (4M)	35.6	140	36	Smooth

The addition of salts in the methanol-water mixture did not hinder the operation, indeed, it may have helped smooth the operation. The water:methanol weight ratio used in test 2, 3, and 4 was found to be satisfactory.

The results from the water-methanol-only test indicated that a small amount of the steam (from the water in the feed) reacts with the carbonate to form hydroxide. In tests in which the hydroxide was present in the feed, the hydroxide content in the melt increased. When hydroxide is present in the feedstock, the CO_2 from combustion must both convert the feed hydroxide to carbonate and suppress the formation of hydroxide from the reaction of steam with Na_2CO_3.

The last test in Table 3 (test No. 4) was of longer duration (140 min) than the others and used 4M NaOH and 4M $NaNO_3$ in the feed stock. The results of this test are plotted in Fig. 2 to determine the rate of hydroxide buildup with time. The conversion of hydroxide to carbonate was essentially constant at 72%.

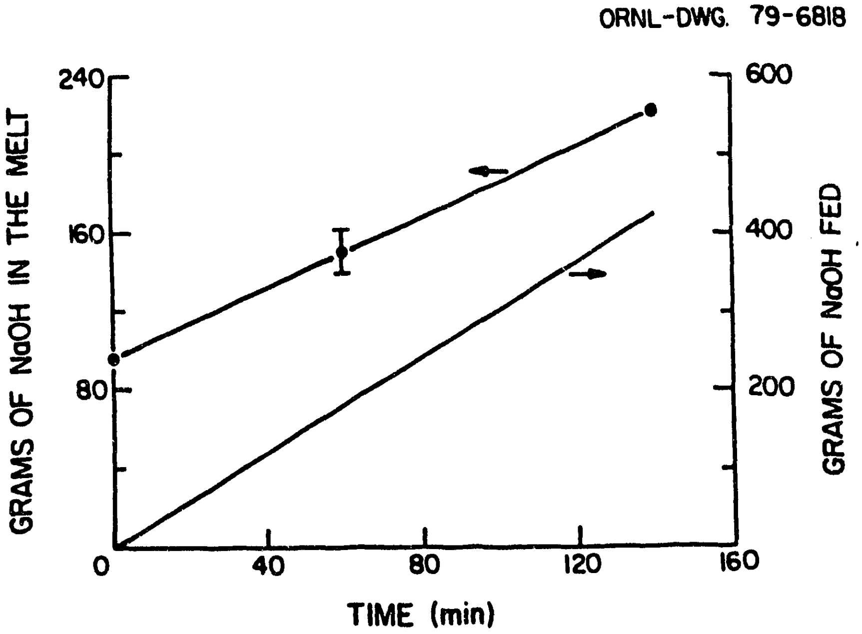

Fig. 2. Increase in melt sodium hydroxide content vs time during combustion of 4M NaOH - 4M $NaNO_3$ -CH_3OH.

The composition of feedstock used in the test of simulated ILW is given in Table 4. This detail is provided here to clarify the volume percentage originally specified (see Table 1).

Table 4. Composition of the simulated ILW feedstock

Component	Weight(%)
Intermediate level waste	
NaOH	8.27
$NaNO_3$	17.59
H_2O	43.02
PVC	0.68
TBP	0.38
Kerosene	0.73
Dowex 50	0.44
Dowex 1	0.16
Fuel	
CH_3OH	28.74
Total	100.00

A summary of the test using ILW slurry is given in Table 5. The test was run for 150 min with the melt temperature at 939°C. The operation was smooth and concentrations of CO and unburned hydrocarbons in the off-gas were less than 200 ppm (the limit of detectability). The total NO_x concentration was 8400 ppm, with 6400 ppm of NO. The particulate loading was 0.98 g/m^3 (presumably due to the volatility of unreacted sodium hydroxide).

Table 5. Oxidation of the simulated ILW slurry

Injector tip temperature, °C	208 ± 5
Melt temperature, °C	939
ILW - CH_3OH feed rate, g/min	39 ± 5
Oxidation air feed rate, slpm at 21.1°C, 0.101 MPa	765±05
Percent excess air	27 ± 16
Test duration, min	150
System operation	Smooth
Off-gas composition	
N_2, %	82.0
O_2 (+ Ar), %	8.1
CO_2, %	10.2
CO, ppm	<200
Unburned hydrocarbons, ppm	<200
Total NO_x , ppm	8400
NO, ppm	6400
Particulates, g/m^3	0.98

The initial and final melt compositions are given in Table 6. The final melt composition indicates that some of the NaCl volatilized out of the melt during the oxidation process. The NaOH concentration increased from 0.92 wt% to 2.75 wt%. This corresponds to 72% conversion of the hydroxide to carbonate.

Table 6. Change in the melt composition during oxidation of simulated ILW slurry

Melt Composition	Initial	Final
Na_2CO_3, wt%	91.5	90.6
NaCl, wt%	5.93	4.11
NaOH, wt%	0.92	2.75
C, ppm	10	40
N, ppm	70	290
Melt bed, total mass, g	5000	5900
Total NaOH fed,		418
Melt NaOH increase, g		116
NaOH to Na_2CO_3 conversion,%		72

The low carbon content increase in the melt indicates nearly complete combustion of the feed stock carbon and conversion to gases. The low nitrogen concentration in the melt indicates that virtually all of the $NaNO_3$ was decomposed.

The ability of the MSO system to destroy the organic material in the feedstock was checked by using benzene scrubbers to scrub organic phosphorus from potentially unburned TBP in the off-gas. The results of this scrubbing are summarized in Table 7. The total phosphorous concentration in the off-gas was 0.023 mg/m^3. This corresponds to 99.99% destruction of the organic phosphorus in the feedstock.

Table 7. Destruction of organic phosphorus during oxidation of the simulated intermediate level waste slurry

Total organic phosphorous fed while scrubbing, g	2.04 (as P)
Total off-gas produced while scrubbing, m^3	9.562
Percent of off-gas scrubbed	5.45
Phosphorus collected in first benzene scrubber,[a] g	6×10^{-6}
Phosphorus collected in second benzene scrubber, g	6×10^{-6}
Total phosphorous concentration in off-gas,[b] mg/m^3	0.023
Percent destruction of organic phosphorus, %	99.99

[a] The particulate sample upstream of the first scrubber contained 0.2×10^{-6} g of organic phosphorus and 0.5×10^{-6} g of inorganic phosphorus.

[b] Based on gas saturated with H_2O at 21°C [about 1% H_2O (g)].

A summary of the volume reduction is given in Table 8. An initial volume of 100 cc of ILW would have a final volume of 18 cc of Na_2CO_3-NaOH-NaCl salt. This corresponds to a volume reduction factor of 5.6.

Table 8. Volume reduction of ILW

Initial volume	93.30 cm^3
4 M NaOH	
4 M $NaNO_3$	
PVC	2.90
TBP	0.72
Kerosene	1.68
Dowex 50	0.94
Dowex 1	0.46
Total	100.00 cm^3
Final volume	
Na_2CO_3-NaOH-NaCl salt	18.00 cm^3
3-5 wt% NaCl	
5-10 wt% NaOH	
85-92 wt% Na_2CO_3	

$$\text{Volume reduction factor} = \frac{\text{initial volume}}{\text{final volume}} = 5.6$$

The volume reduction was calculated on the basis of the following data and assumptions:

1. All of the $NaNO_3$ is converted into Na_2CO_3.
2. All of the chlorine in PVC is converted into NaCl.
3. The NaOH provides sodium for the formation of NaCl from PVC.
   Seventy-two percent of the reminder of the NaOH is converted into Na_2CO_3. The other 28% remains as NaOH.
4. The density of the solid salt is 2.15 g/cc (measured in the laboratory).
5. The water in the feedstock is converted into steam.
6. All of the organics are oxidized.

The composition of the final salt was approximately 3-5 wt% NaCl, 5-10 wt% NaOH, and 85-92 wt% Na_2CO_3.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

This experiment demonstrated the feasibility of the MSO concept on a laboratory scale using simulant wastes. However, the concept still requires significant development to verify removal efficiencies, demonstrate the salt reprocessing technology, and to resolve the engineering issues associated with materials and scale-up to pilot-plant and production size.

A variety of wastes are believed to be treatable by the MSO process. These include: high-heating value liquids contaminated with radioactive waste (solvents, oils, PCB contaminated oils, etc.), low-heating value liquids (high chlorine and other high halogen content organic liquids), pesticides, herbicides, PCBs, chemical warfare agents, infectious wastes, aqueous sludges containing heavy metals and organics, combustible solids (hood waste, PCB-contaminated felt gaskets, HEPA filters, liquid filters, ion exchange beds/resins etc.), and others.

The molten salt technology can also be used as a secondary treatment system in conjunction with a primary system (e.g., incineration, pyrolysis). For this use, the input into the MSO system would be the off-gas from the primary system. The MSO system would act as both a secondary treatment system and an acid gas scrubber. As with other secondary treatment systems, to meet particulate emission standards MSO would require a particulate removal system in the form of a bag house and HEPA filters.

Further bench-scale testing is recommended in these areas:

1. Testing of different auxiliary fuels such as propane for controlling and maintaining the desired temperatures and for minimizing the operating costs.

2. Tests on chlorinated solvents. Particular emphasis should be placed on measuring the effect of the product NaCl on the salt matrix and on any incomplete or unusual oxidation products in the off-gas stream.

3. Tests on surrogate wastes. A series of tests should be performed utilizing simulated mixed waste containing transition elements and/or rare earths as stand-ins for actinides. The fate

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3. Tests on surrogate wastes. A series of tests should be performed utilizing simulated mixed waste containing transition elements and/or rare earths as stand-ins for actinides. The fate of these elements would be determined.

4. Tests on mixed wastes. These tests would be used to evaluate the performance of the equipment, the methods of measurements, adequacy of procedures, and the results for several DOE/Oak Ridge mixed wastes having different compositions.

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