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OVERVIEW OF ADVANCED TECHNOLOGIES FOR STABILIZATION OF 238PU-CONTAMINATED WASTE

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Author(s):

Kevin B. Ramsey, NMT-9
Elizabeth M. Foltyn, NMT-9
J. Mark Heslop, Indian Head Division
Naval Surface Warfare Center

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OVERVIEW OF ADVANCED TECHNOLOGIES FOR STABILIZATION OF ^{238}PU-CONTAMINATED WASTE

Kevin B. Ramsey and Elizabeth M. Foltyn
Los Alamos National Laboratory
P.O. Box 1663, MS-E502
Los Alamos, NM 87545
(505) 665-0024 and 665-0162

J. Mark Heslop
Indian Head Division, Naval Surface Warfare Center
101 Strauss Avenue
Indian Head, MD 20640
(301) 743-4365

Abstract

This paper presents an overview of potential technologies for stabilization of ^{238}Pu-contaminated waste. Los Alamos National Laboratory (LANL) has processed $^{238}PuO_2$ fuel into heat sources for space and terrestrial uses for the past several decades. The 88-year half-life of ^{238}Pu and thermal power of approximately 0.6 watts/gram make this isotope ideal for missions requiring many years of dependable service in inaccessible locations. However, the same characteristic which makes ^{238}Pu attractive for heat source applications, the high Curie content (17 Ci/gram versus 0.06 Ci/gram for ^{239}Pu), makes disposal of ^{238}Pu-contaminated waste difficult. Specifically, the thermal load limit on drums destined for transport to the Waste Isolation Pilot Plant (WIPP), 0.23 gram per drum for combustible waste, is impossible to meet for nearly all ^{238}Pu-contaminated glovebox waste. Use of advanced waste treatment technologies including Molten Salt Oxidation (MSO) and aqueous chemical separation will eliminate the combustible matrix from ^{238}Pu-contaminated waste and recover kilogram quantities of $^{238}PuO_2$ from the waste stream. A conceptual design of these advanced waste treatment technologies will be presented.

INTRODUCTION

Los Alamos National Laboratory (LANL) has processed $^{238}PuO_2$ fuel into heat sources for space and terrestrial uses for the past several decades. The 88-year half-life of ^{238}Pu and thermal power of approximately 0.6 watts/gram make this isotope ideal for missions requiring many years of dependable service in inaccessible locations. However, the same characteristic which makes ^{238}Pu attractive for heat source applications, the high Curie content (17 Ci/gram versus 0.06 Ci/gram for ^{239}Pu), makes disposal of ^{238}Pu-contaminated waste difficult. Specifically, the thermal load limit on drums destined for transport to the Waste Isolation Pilot Plant (WIPP), 0.23 gram per drum for combustible waste (DOE 1996), is impossible to meet for nearly all ^{238}Pu-contaminated glovebox waste.

No treatment options exist at LANL for converting ^{238}Pu-contaminated combustible waste to a noncombustible waste form. According to the LANL Ten-Year-Plan (TYP), the baseline process for ^{238}Pu-contaminated combustible waste disposal is to load TRU (transuranic) waste drums with a maximum of 0.23 gram ^{238}Pu and subsequently ship the drums to WIPP for disposal. The Los Alamos legacy ^{238}Pu-contaminated combustible waste inventory includes some waste drums that would have to be repackaged to meet the current WIPP Waste Acceptance Criteria (WAC). For example, the contents of one such drum would have to be separated into 10 or more drums in order to meet the current WIPP WAC. There are other waste items which are so high in ^{238}Pu content that they are thermally decomposed for safe on-site storage at the LANL Plutonium Facility, where they are generated, but cannot be packaged into drums for storage at the LANL Waste Storage Facility. One of these items, if packaged into 55-gallon drums, would have to be separated into >100 drums to meet current WIPP WAC; for comparison, if packaging was restricted by waste volume, eight such items would constitute one drum. Some increases may be made in the WIPP WAC with further testing of hydrogen gas generation from combustible waste or by the use of hydrogen gas getters or improvements in waste packaging, but it is unlikely that significant relief will be obtained. Analyses below show the unacceptably high number of waste drums, with concomitant high disposition cost, which would result from shipping ^{238}Pu-contaminated combustible waste to WIPP.

This paper describes a conceptual design that offers a solution to the problem of safe disposition of ^{238}Pu-contaminated waste. Implementation of the design will ensure that WIPP can accept ^{238}Pu-contaminated waste at the lowest required cost. Specifically, this paper outlines the implementation of Molten Salt Oxidation (MSO) and aqueous chemical separation methods for the stabilization of combustible waste and subsequent recovery of ^{238}Pu. The process flow diagram for the MSO and Pu aqueous recovery is shown in Figure 1. In the MSO process, a molten alkali salt (e.g., sodium carbonate) serves as a catalyst for the conversion of hydrogenous material (e.g., combustible waste) and oxygen (O_2) to water (H_2O) and carbon dioxide (CO_2). Acidic species such as fluorine, chlorine, bromine, iodine, sulfur, phosphorous, and arsenic in the organic waste react with the molten salt to form the corresponding neutralized salts, NaF, NaCl, NaBr, NaI, Na_2SO_4, Na_3PO_4, and $NaAsO_2$ or Na_3AsO_4. Plutonium and other metals (e.g., U, Fe, Al, Pb, etc.) in the organic waste react with the molten salt and oxygen to form metal oxides. These metal oxides are commonly referred to as "ash." An ash content of less than 20 percent by weight must be maintained to preserve the fluidity of the salt melt. In addition, the concentration of sodium salts formed as a result of the acid neutralization reaction must be limited to less than 85 percent by weight to prevent an eventual loss of the acid gas removal capability. Because the ash and sodium salts are products of the overall oxidation reaction, the concentration of these products will increase in the molten salt as a function of the quantity of waste processed. Therefore, periodic disposal of the "spent" salt is required to maintain continuous operation of the MSO reactor. As shown in Figure 1, the use of aqueous separation methods will allow for removal of ^{238}Pu from the spent salt and recycle of sodium carbonate (Na_2CO_3) for MSO processing.

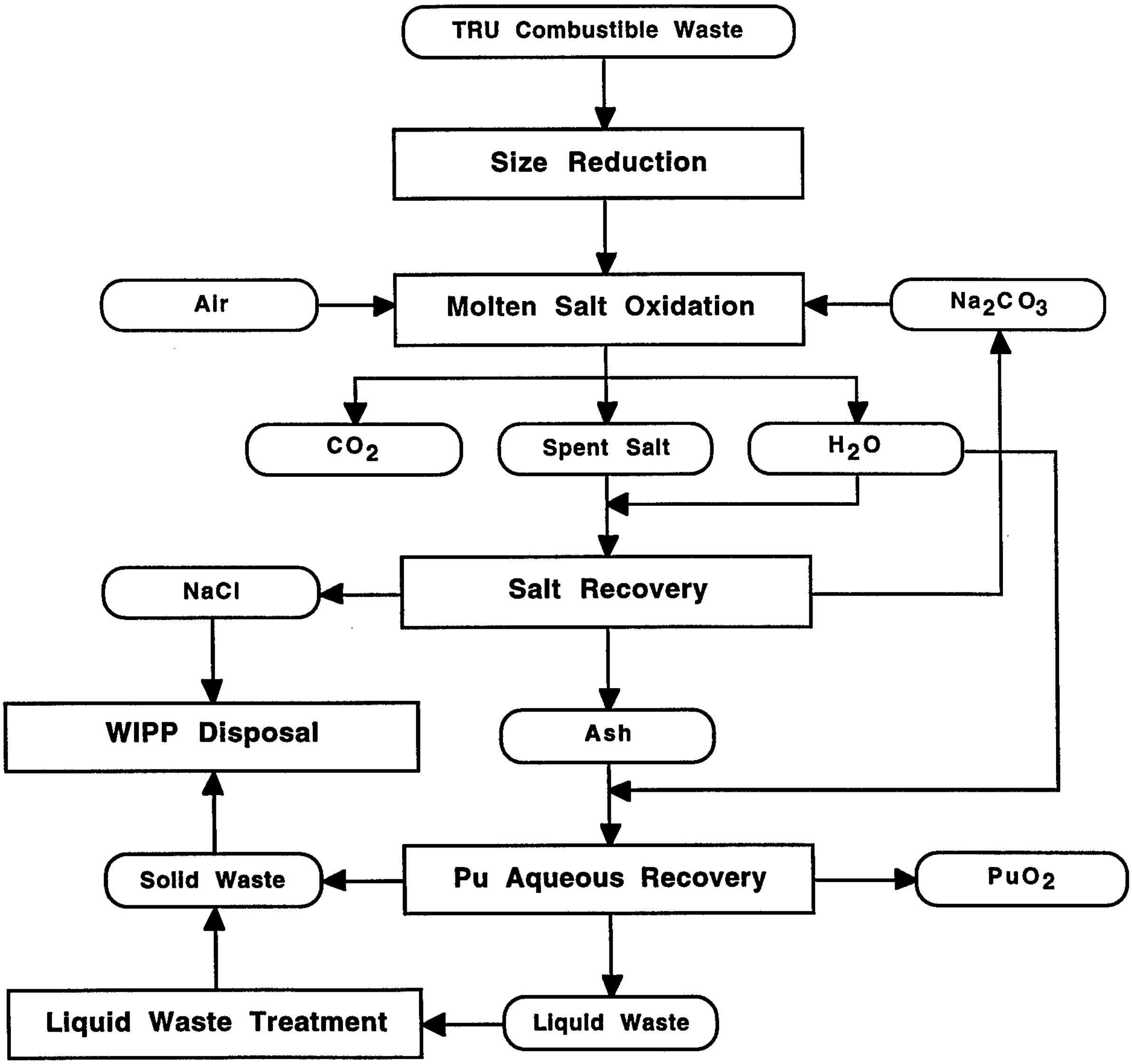

FIGURE 1. Process Flow Diagram for MSO and Aqueous Separation Processes.

BACKGROUND

Rockwell International initiated the development of MSO technology in the early 1970s. In the early 1990s, Oak Ridge National Laboratory applied MSO technology to the treatment of Resource Conservation and Recovery Act (RCRA) wastes. Recently, the Naval Surface Warfare Center, Indian Head Division, has applied MSO technology to the treatment of energetic waste materials.

Rockwell International

Rockwell International (RI) developed the MSO process in the 1970s and early 1980s for treating hazardous and radioactive wastes. Additional tests were conducted in 1992 to demonstrate the ability of MSO to destroy a diverse set of mixed wastes. Results for various waste treatment tests are described below.

Non-hazardous Waste

RI developed and operated a pilot-scale MSO reactor as part of the Atomic International Division's Molten Salt Test Facility (Grantham et al. 1976). RI operated the reactor for a period of five years. Candidate feed material consisted of combustible solid waste with a composition of 33% paper, 20% Kimwipes, 32% polyethylene, 8% polyvinyl chloride, and 7% rubber by weight. Before the solid waste was injected into a molten salt containing 90% Na_2CO_3 and 10% Na_2SO_4 by weight, the feed was reduced in size to ≤ 1.27 cm in diameter. The dimensions of the reactor outside diameter and height were 1.2 m and 3.7 m, respectively. Operating temperatures ranged from 1063 K to 1293 K. A salt bed depth of approximately 1 m allowed the reactor to destroy combustible feed at a rate of 50 kg/hr to 70 kg/hr. Off-gas emissions for HCl, SO_2, CO, hydrocarbons, and NO_X were <5 ppm, <2 ppm, <0.1%, <0.1%, and 30–500 ppm, respectively.

Hazardous Waste

RI has used a bench-scale MSO process to destroy chemical warfare agents (VX, GB, mustard), halogenated solvents (trichloroethane, chloroform), pesticides (malathion, DDT), herbicides (2,4-D), and polychlorinated biphenyl (PCB) compounds (Dustin et al. 1977 and Yosim et al. 1980). Feed materials including solids, liquids, and slurries were injected into a Na_2CO_3 molten salt at a rate of 0.25 to 1 kg/hr using a screw feeder transport system, peristaltic pump, or slurry pump, respectively. Test results for organic destruction efficiency are listed in Table 1.

TABLE 1. Destruction Efficiency for MSO Processing of Hazardous Waste.

WASTE	TEMPERATURE (K)	DESTRUCTION EFFICIENCY (%)
VX ($C_{11}H_{26}O_2PSN$)	1203	>99.99999
GB ($C_4H_{10}O_2PF$)	1198	>99.999999
Mustard ($C_4H_8C1_2S$)	1198	>99.99998
Trichloroethane (CH_3CCl_3)	1113	>99.999
Chloroform ($CHCl_3$)	1091	>99.999
Malathion ($C_{10}H_{19}O_6PS_2$)	1173	>99.99
DDT ($C_{14}H_9Cl_5$)	1173	>99.99
2,4-D	1103	>99.98
PCB	973 - 1253	>99.9999

Mixed Waste

RI has used a bench-scale MSO process to oxidize ~189 liters of waste oils, ranging from hydraulic oil to 140 weight gear oil as well as multiphase mixtures of organic degreasers, solvents, and alcohols (Darnell et al. 1993). These wastes were slightly contaminated with Cs-137 and Co-60. Test results indicated 99.9999% of the organic material was destroyed at a temperature of 1173 K. The melt retention was 85% and 99% for Cs-137 and Co-60, respectively.

Pu-contaminated Waste

RI has destroyed Pu-contaminated combustible waste using a bench-scale MSO process (Grantham et al. 1976). The waste stream was generated by mixing aqueous solutions of plutonium nitrate, chloride, and sulfate with a combustible waste composed of paper, plastic (80% polyethylene, 20% polyvinylchloride by weight), and rubber (50% surgeons gloves, and 50% black rubber gloves by weight). Waste material with a Pu concentration of 0.009% to 0.11% by weight was injected into the MSO reactor at a rate of 0.170 kg/hr to 0.190 kg/hr. The molten salt was composed of 90% Na_2CO_3 and 10% Na_2SO_4 by weight. Test results indicated >99.999% of the organic material was destroyed at an average operating temperature of 1162 K.

For the purpose of reducing waste disposal costs, RI developed a method for recovering plutonium from the spent salt (Grantham et al. 1976). Specifically, the alkali salts (i.e., Na_2CO_3 and NaCl) were separated from the Pu-rich insoluble ash using aqueous recovery techniques. The salt was dissolved in water and subsequently filtered to yield a Pu-rich insoluble residue and a Pu-lean filtrate containing the soluble alkali salts. Chemical analysis of the filtrate and residue indicated 99% of the plutonium was contained in the insoluble residue.

In addition to plutonium recovery, RI developed a method for salt recycle (McKenzie et al. 1975). Specifically, a process was developed for recovering Na_2CO_3, Na_2SO_4 and NaCl from a molten salt with an initial composition of 90% Na_2CO_3 and 10% Na_2SO_4 by weight. In the salt recycle process, the Na_2CO_3 and Na_2SO_4 salts were recycled to the MSO reactor, and the NaCl was sent to waste disposal. For the aqueous separation process, the spent salt was refluxed for two hours in water and subsequently filtered to separate the insoluble ash fraction from the filtrate containing the soluble sodium carbonate, sodium chloride, and sodium sulfate salts. The Na_2CO_3 and Na_2SO_4 salts were separated from the soluble NaCl salt using evaporative and vacuum crystallization. The recycled salt consisted of 80% Na_2CO_3, 12% Na_2SO_4, and 8% NaCl by weight. The discarded solid fraction consisted of 96% NaCl, 4% Na_2CO_3, and 0.2% Na_2SO_4.

Oak Ridge National Laboratory

Oak Ridge National Laboratory (ORNL) has used a MSO reactor similar to the RI bench-scale design to destroy combustible waste composed of chloroform, 1,1,1-trichloroethane (TCA), 2,4-dichlorophenol, ethanol, and ethylene glycol (Rudolph et al. 1995). Waste material was feed into a Na_2CO_3 molten salt at a rate of 0.4kg/hr to 0.9 kg/hr. Operating temperatures ranged from 1219 K to 1224 K. A >99.9999% destruction efficiency was achieved for chloroform and TCA. Dioxin and furan emissions for the treatment of 2,4-dichlorophenol were below the EPA regulatory limit.

Naval Surface Warfare Center, Indian Head Division

Naval Surface Warfare Center (NSWC), Indian Head Division, has used MSO technology to destroy energetic and inert waste materials. In April 1997, NSWC initiated a program to demonstrate the feasibility of using the MSO process to destroy composite and double base propellants, oils, carbohydrates, paints, cellulose, solvents, and diesel fuel. The theoretical elemental composition for the propellants is listed in Table 2. Preliminary off-gas emissions data for the treatment of the composite and double base propellant is shown in Table 3 and Table 4, respectively. The elemental analysis of the diesel fuel is listed in Table 2. The preliminary off-gas emissions data for the treatment of the diesel fuel is shown in Table 5. The test results indicate that MSO is a viable process for oxidizing energetic material.

TABLE 2. Elemental Composition for Energetic Material and Diesel Fuel.

WASTE	OXYGEN (%)	CARBON (%)	HYDROGEN (%)	NITROGEN (%)	CHLORINE (%)
Composite Propellant	47.8	11.1	4.4	11.6	25.2
Double Base Propellant	58.89	24.16	2.90	14.05	-
Diesel Fuel	1.34	87.25	12.66	-	-

TABLE 3. Off-gas Analysis for MSO Processing of Composite Propellant.

FEED RATE (kg/hr)	CO (ppm)	HYDROCARBON (ppm)
0.227[*]	27.88	0.00
0.454[*]	182.94	0.00
0.681[*]	282.29	0.00
0.908[#]	51.31	0.20
1.135[#]	323.21	0.44
1.362[#]	601.65	1.09
1.816	528.08	2.97
2.270	136.97	3.37

[*] Same air flow rate.
[#] Same air flow rate.

TABLE 4. Off-gas Analysis for MSO Processing of Double Base Propellant.

FEED RATE (kg/hr)	CO (ppm)	HYDROCARBON (ppm)
0.341[*]	85.72	0.00
0.454[*]	132.19	0.00
0.568[*]	238.05	0.00
0.681[*]	266.49	0.00
0.795	109.08	0.00
0.908	215.86	0.00

[*] Same air flow rate.

TABLE 5. Off-gas Analysis for MSO Processing of Diesel Fuel.

FEED RATE (kg/hr)	CO (ppm)	NO_X (ppm)	HYDROCARBON (ppm)
0.186	9.95	18.69	2.48
0.200	12.55	17.55	2.72
0.200	0.21	16.80	2.64
0.223	37.25	25.56	2.75
0.245	51.50	29.41	2.83
0.254	90.72	35.12	3.04
0.313	302.99	37.08	3.19
0.377	374.98	54.14	3.28
0.418	605.78	66.21	3.36
0.400	525.87	71.54	3.66
0.400	392.94	75.24	3.37
0.454	699.14	94.48	4.24

METHODOLOGY

Molten salt oxidation will be used to oxidize the organic component of the ^{238}Pu-contaminated waste. ^{238}Pu and Na_2CO_3 will be recovered from the spent salt using aqueous separation technology. The specific steps of the MSO and aqueous separation processes are described below.

MSO

For the first step in the MSO process, solid organic waste is reduced in size to less than 3 mm in diameter using a shredder, hammermill, or cryogenic crushing device. Following size reduction, the solid feed is transferred into a high-velocity air stream using a screw feeder transport system. The waste-air mixture is injected into the Na_2CO_3 molten salt at a rate of 50 to 70 liters per minute via an injector tube and downcomer. The products of the oxidation reaction, CO_2, steam, and excess air, exit the reactor via the off-gas outlet. Off-gases from the reactor are routed through a water- or air-cooled heat exchanger to prevent degradation of the HEPA filtration system. Entrained or condensed salts in the off-gases are subsequently collected in bag filters. In the final step of the process, the off-gases are routed to the HEPA filtration system for particulate removal and subsequently released to the environment.

Aqueous Recovery

The spent salt is transferred to the aqueous chemical separation process for recovery of Na_2CO_3 and ^{238}Pu. The alkali salt, Na_2CO_3, is separated from other sodium salts (e.g., NaCl) using a fractional crystallization process. ^{238}Pu is separated from impurities (e.g., Si, Fe, Cr, Al, Ni, P, ^{234}U, etc.) using ion exchange and oxalate precipitation methods. Effluent from the liquid waste treatment process and sodium salts (e.g., NaCl) are grouted for WIPP disposal.

SCOPE

Potential sources of ^{238}Pu-contaminated combustible waste for MSO processing include cellulose rags, pyrolyzed cellulose rags, and plastics (i.e., polyethylene and polyvinyl chloride). Kilogram quantities (100 - 500 kg) of these combustible waste items were generated as a result of fabricating ^{238}Pu heat sources for the Cassini mission. For the scope of this analysis, legacy waste includes combustible waste generated prior to FY98 and also waste that will be generated during a two year period from FY98 to FY99. Mission waste includes combustible waste that will be generated during FY00. The legacy waste items are primarily stored at the LANL Waste Storage Facility and LANL Plutonium Facility. We estimate that, by the end of FY99, the legacy waste inventory will include ~1840 kg of combustible waste containing ~1.3 kg of ^{238}Pu. By the end of FY00, mission waste will include ~200 kg of combustible waste containing ~0.1 kg of ^{238}Pu.

RESULTS

The use of MSO and aqueous separation technologies to stabilize ^{238}Pu-contaminated waste will achieve several benefits for waste disposal operations at LANL. The specific benefits for the waste disposal operations are described below.

Baseline Processing

Using the baseline disposal method as described in the LANL TYP, the processing of 2040 kg of combustible waste (legacy and mission) containing a total of 1.4 kg of ^{238}Pu will generate ~6087 TRU drums for WIPP disposal.

MSO Processing

The implementation of MSO technology at LANL will reduce the volume of combustible waste matrices and convert the combustible waste stream to a noncombustible waste stream (i.e., spent salt). The conversion of the combustible waste matrix to a noncombustible waste matrix will allow the TRU waste drum to contain up to 6 grams of ^{238}Pu (DOE 1996). This increase in Pu concentration (i.e., 0.23 gram to 6 grams) per waste drum will result in substantial cost savings for LANL waste disposal operations. Material balance calculations indicate that MSO processing of 2040 kg of combustible waste (legacy and mission) containing a total of 1.4 kg of ^{238}Pu will generate ~233 TRU drums for WIPP disposal. Thus, MSO processing will achieve a greater than twenty-fold decrease in the number of TRU drums for WIPP disposal.

MSO/Aqueous Recovery

The implementation of an integrated processing operation including MSO waste treatment and aqueous chemical separation at the LANL Plutonium Facility will further reduce the cost of waste disposal operations. Specifically, the use of aqueous separation methods will allow for spent salt recycle and recovery of ~1.4 kg of ^{238}Pu.

CONCLUSIONS

RI, ORNL, and NSWC have demonstrated the ability of the MSO process to destroy hazardous and mixed combustible wastes including chemical warfare agents, combustible solids, halogenated solvents, polychlorinated biphenyls, propellants, and Pu-contaminated solids.

The use of MSO technology and aqueous chemical separation methods to stabilize ^{238}Pu-contaminated waste at LANL will result in significant cost savings over the baseline method of TRU waste disposal. MSO processing will reduce the volume of waste and convert the combustible waste matrix to a noncombustible waste matrix (i.e., spent salt). Treatment of the spent salt using fractional crystallization, ion exchange, and oxalate precipitation will allow for recycle of the spent salt and recovery of ^{238}Pu.

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