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## Treatment of Plutonium Process Residues by Molten Salt Oxidation

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### ABSTRACT

Molten Salt Oxidation (MSO) is a thermal process that can remove more than 99.999% of the organic matrix from combustible  $^{238}\text{Pu}$  material. Plutonium processing residues are injected into a molten salt bed with an excess of air. The salt (sodium carbonate) functions as a catalyst for the conversion of the organic material to carbon dioxide and water. Reactive 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,  $\text{NaF}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_3\text{PO}_4$  and  $\text{NaAsO}_2$  or  $\text{Na}_3\text{AsO}_4$ . Plutonium and other metals react with the molten salt and air to form metal salts or oxides. Saturated salt will be recycled and aqueous chemical separation will be used to recover the  $^{238}\text{Pu}$ . The Los Alamos National Laboratory system, which is currently in the conceptual design stage, will be scaled down from current systems for use inside a glovebox.

### INTRODUCTION

Plutonium-238 is an excellent radioisotope for space and terrestrial heat source applications because of its 87.7 year half-life, oxide stability, minimal shielding requirements, and thermal power. It has a power density of approximately 0.6 watts per gram.  $^{238}\text{Pu}$  is used as a general purpose heat source (GPHS) for radioisotope thermoelectric generators (RTG) and radioisotopic heater units (RHU). RTGs have been utilized for more than thirty years to enable spacecraft to operate in areas where solar power isn't feasible. Heat is generated by the natural radioactive decay of plutonium and is converted into electricity by thermoelectric converters. RHUs are used to keep spacecraft instrumentation warm and within designed temperature limits.

The same quality that makes  $^{238}\text{Pu}$  attractive for heat source applications, a specific activity of 17 curies per gram, makes disposal of  $^{238}\text{Pu}$ -contaminated waste difficult. Almost all  $^{238}\text{Pu}$  waste is transuranic (TRU) waste because it has an atomic number higher than uranium, a half-life greater than twenty years and its activity is normally greater than 100 nanocuries per gram. The only current disposal path for TRU waste is the Waste Isolation Pilot Plant (WIPP). The thermal load limit for combustible TRU waste destined for WIPP disposal is 0.26 grams per drum (1). It is almost impossible to meet this limit for combustible residues generated by  $^{238}\text{Pu}$  operations. The combustibles consist of common materials, such as cheesecloth wipes, tygon<sup>TM</sup> tubing, gloves, high density polyethylene bottles, and PVC bagout bags, which are contaminated with residual quantities of  $^{238}\text{Pu}$ . If these process residues are not treated, the waste must be packaged to meet the WIPP thermal load limit. This would create large volumes of waste that would require preparation and certification to meet the stringent WIPP waste acceptance criteria and incur high disposition costs. Molten Salt Oxidation will remove the combustible matrix from the  $^{238}\text{Pu}$  process residues. The salt will be recycled and  $^{238}\text{Pu}$  will be recovered by aqueous processing. Since the WIPP thermal load limit for non-combustible TRU waste is 6.0 grams of  $^{238}\text{Pu}$  per drum, the treatment and plutonium recovery will greatly reduce the volume of waste that must be sent to WIPP.

## DISCUSSION

Molten Salt Oxidation (MSO) is a mature technology, which has been extensively studied and evaluated in pilot and full-scale systems. Although MSO has successfully treated a variety of waste streams during the last three decades, incineration was usually a more practical alternative. However, incineration is no longer the preferred alternative because of stakeholder concerns and permitting processes. MSO, which is a thermal flameless treatment technology, is now a viable technology for the treatment of organic materials.

### Process

The MSO process flow diagram is shown in Figure 1. Solid material requires a size reduction pretreatment step to reduce the material to a diameter of less than 0.62 centimeters. The material is injected into the molten salt with a high velocity air stream via an injector tube and downcomer. A molten alkali salt, usually sodium carbonate, serves as a catalyst for the conversion of organic material and oxygen to water and carbon dioxide. The reaction takes place at slightly above ambient pressure and at temperatures ranging from 900°C to 1000°C. The system is preheated and the temperature can be maintained by controlling the feed rate, which controls the heat supplied to the system by the oxidation of the organic materials.

Reactive 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<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub> and NaAsO<sub>2</sub> or Na<sub>3</sub>AsO<sub>4</sub>. Plutonium and other metals react with the molten salt and air to form metal salts or oxides. These metal oxides and salts are commonly referred to as "ash." An ash content of less than 20 wt % must be maintained to preserve the fluidity of the salt melt. The concentration of sodium salts formed as a result of the acid neutralization reaction must be limited to less than 85 wt % to prevent an eventual loss of the acid removal capability. Since 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 for continuous operation of the MSO reactor.

The first step of the salt recovery process is removal of the spent salt from the MSO reactor and dissolution in an aqueous media. The aqueous solution is filtered to separate the sodium carbonate and sodium chloride from the insoluble ash. The sodium carbonate is separated from the sodium chloride by evaporative crystallization. The purified sodium carbonate is dried and returned to the MSO reactor.

<sup>238</sup>Pu will be separated from the spent salt using conventional chemical separation methods (i.e. ion exchange and precipitation). The <sup>238</sup>Pu aqueous recovery process is shown in Figure 2. The first step of the recovery process is the reduction of the ash residue to a particle size of less than 1 micron. The pulverized feed is then dissolved in an aqueous nitric and hydrofluoric acid solution. After dissolution, the oxidation state of <sup>238</sup>Pu is adjusted using reducing and oxidizing reagents. The Pu-rich solution is transferred to the anion exchange process for removal of impurity metals (e.g., Si, Fe, Cr, Al, Ni, P, <sup>234</sup>U, etc.). <sup>238</sup>Pu is removed from the eluate stream using oxalate precipitation. Calcination of the plutonium oxalate yields <sup>238</sup>PuO<sub>2</sub>. A residual quantity of <sup>238</sup>Pu remains in the effluent stream from the anion exchange process. The remaining <sup>238</sup>Pu is removed from the effluent stream via hydroxide precipitation. The hydroxide precipitate is calcined and transferred to interim storage or grouted for final TRU waste disposition. The filtrate from the hydroxide precipitation is transferred to the LANL Radioactive Liquid Waste Treatment Facility for final processing.

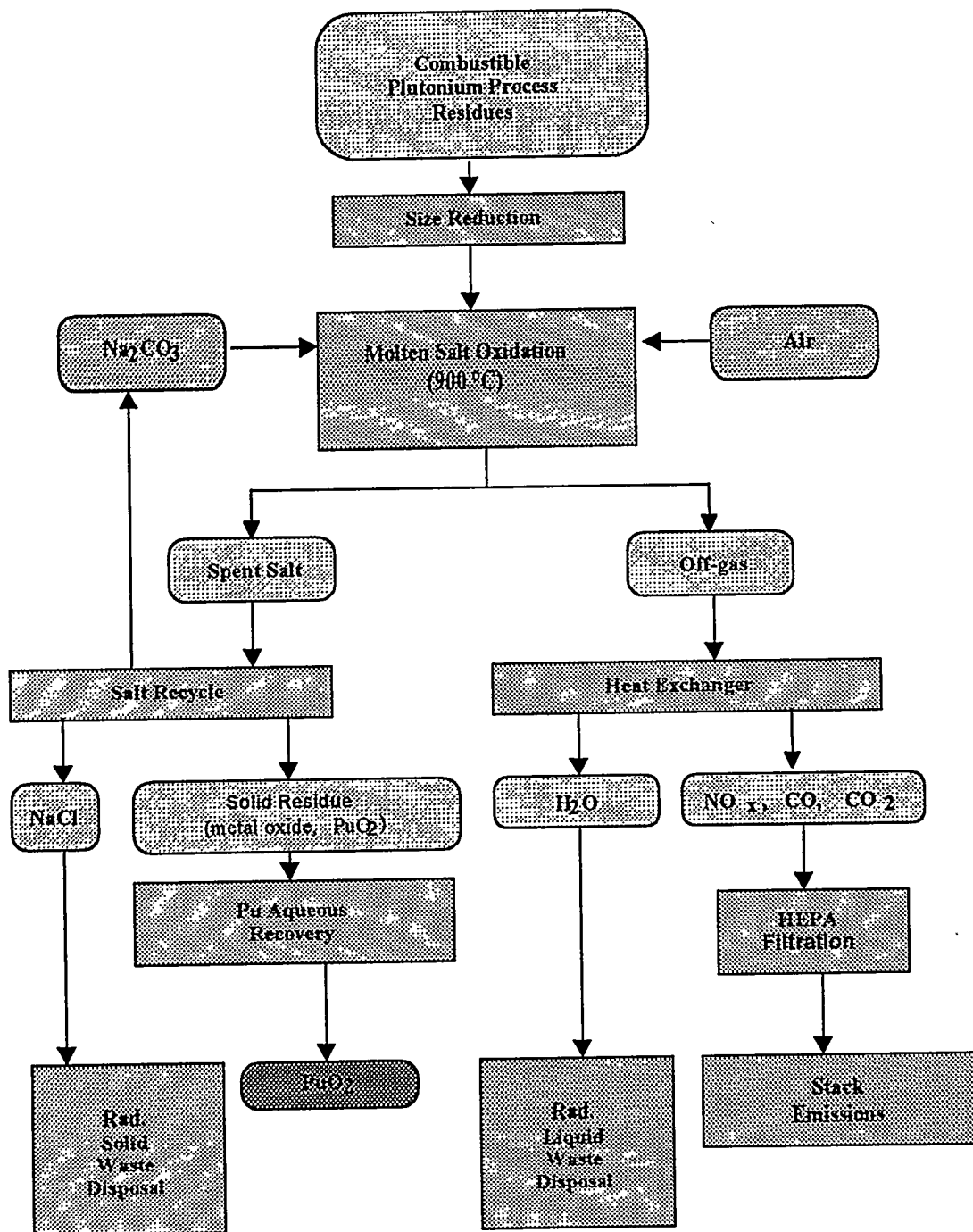


Figure 1. MSO Process Flow Diagram

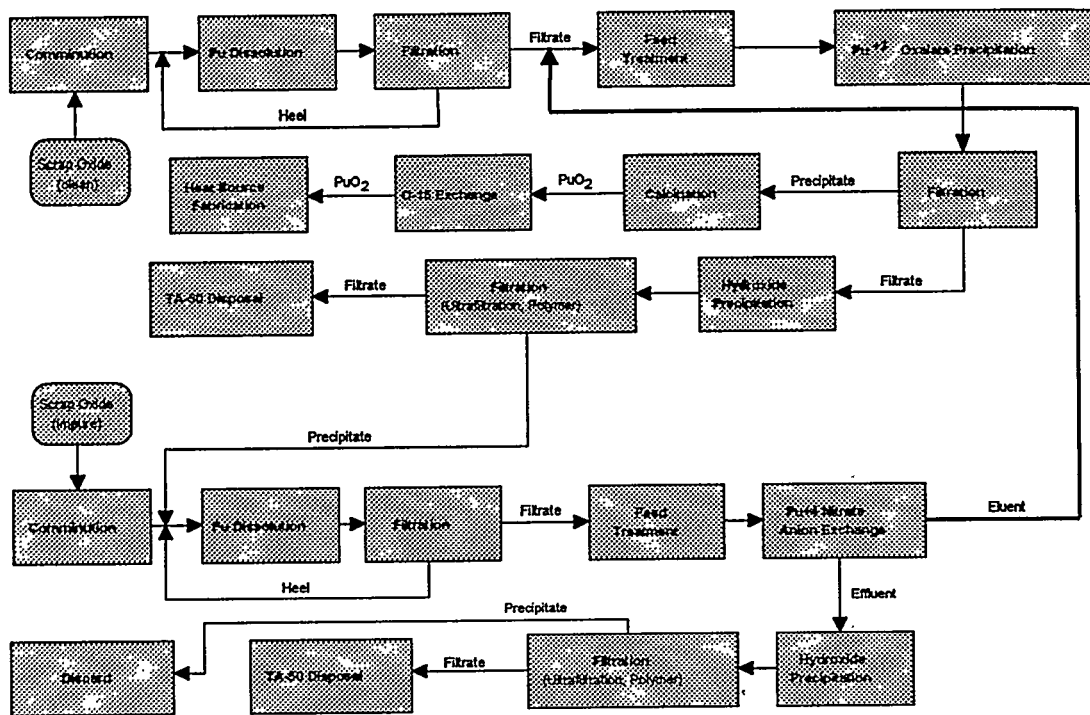


Figure 2. Process Flow Diagram for LANL Pu-238 Recovery Operation

## Background

Much of today's molten salt oxidation technology is the result of work at the Energy Technology Engineering Center in the 1970's by Atomics International (then a division of Rockwell International, now Rocketdyne Propulsion and Power a part of the Boeing Company) in Canoga Park, CA. Atomics International investigations were performed as bench scale, pilot scale and full-scale tests using molten salts initially to scrub sulfur oxides from coal combustion flue gases, and subsequently as a catalyst for coal gasification studies. This work branched into experimentation with the molten salt oxidation processes for a host of applications including destruction of hazardous chemical wastes, poison gases, pesticides, destruction of Polychlorinated Biphenyl's (PCBs) and as a recovery technique for metals including silver, antimony, aluminum and tin. These studies and tests did not result in deployment of the technology, however, because at the time, the alternative treatment method, hazardous waste incineration, was less expensive.

Lawrence Livermore National Laboratory (LLNL) has used MSO to treat organic wastes and energetic materials. LLNL has built an integrated pilot-scale MSO treatment system, which includes a MSO process vessel with dedicated off-gas treatment, a salt recycle system, feed preparation equipment, and equipment for preparing ceramic final waste forms (2).

Oak Ridge National Laboratory (ORNL) used bench-scale MSO technology to destroy hazardous wastes composed of chloroform, 1,1,1- trichloroethane (TCA) and 2,4 -dichlorophenol, ethanol and ethylene glycol(3). A destruction efficiency greater than 99.9999% was achieved for chloroform and TCA. Dioxin and furan emissions for the treatment of 2,4 -dichlorophenol were less than the EPA regulatory limits.

The Naval Surface Warfare Center (NSWC) Indian Head Division has used MSO 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. Test results for energetics destruction indicated off-gas emissions for carbon monoxide and hydrocarbons were <400 ppm and <5 ppm, respectively. These results indicate that MSO is a viable process for oxidizing energetic material.

### Treatment of Plutonium Contaminated Waste

Atomics International (AI) developed a bench-top process in the mid-1970's that was used with plutonium-contaminated combustible wastes. More than 99.9% of the plutonium was retained in the salt melt during treatment. The residual plutonium was captured as particulate in the prefilter to the off-gas cleanup and filtration system. The AI tests showed less than 0.0001 % of the plutonium was found in the off-gas condensate or on the HEPA filter (4). The AI system used a sodium carbonate/sodium sulfate molten salt mixture. In the AI system, shredded waste was fed with air to the bottom of molten salt oxidation unit. The process gases exited via an off-gas line to a water trap and gases were then routed through a heat exchanger system where they were cooled and passed through HEPA filters and exhausted to the atmosphere. The feed system tested surrogate waste material of paper (Kleenex™, Kimwipes™ and magazines), plastics (polyethylene and PVC) and rubber (surgeons gloves) with a variable speed feeder system and variable air-feed flow. The tests were run with actual plutonium contaminated waste with a concentration of  $9 \times 10^{-5}$  g/g and  $1.1 \times 10^{-3}$  g/g simulating actual TRU waste. Aqueous recovery techniques were used to recover plutonium from the spent salt.

### Molten Salt Oxidation at LANL

MSO appears to be a viable technology for the treatment of LANL's  $^{238}\text{Pu}$ -contaminated combustible process residues, which consist of cheesecloth wipes, pyrolysis residue, tygon™ tubing, gloves, polypropylene and high-density polyethylene bottles, and polyvinylchloride bagout bags. A surrogate study will soon be completed at the NSWC-Indian Head Division facility. The study will also supply material for salt recovery.

LANL's size reduction and MSO processes will have to be contained inside two gloveboxes. This will limit personnel exposure, but it will restrict the space available for process equipment. The glovebox line is shown in Figure 3. The size reduction process will operate in a double-sided glovebox equipped with six workstations. The size reduction glovebox will be connected directly to the facility dropbox and the MSO process glovebox will be the third glovebox in the line. The MSO process will operate in a double-side glovebox equipped with eight workstations.

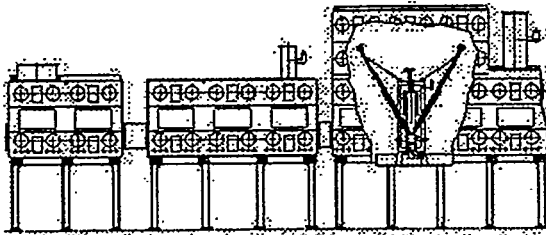


Figure 3. MSO Glovebox Line



Alternatives are currently being evaluated for the size reduction process. A vendor search is currently being conducted to find a granulation system that will fit inside a glovebox and also reduce the combustible materials to the 0.63 centimeter diameter required for the MSO system. Cryogrinding was used to produce the material for NSWC surrogate study.

LANL requires a MSO system that can process 2 kilograms of material per hour and still operate in a glovebox environment. The Molten Salt Oxidation Corporation TransOx™ system, which is shown in Figure 4, will meet the glovebox site restrictions and process throughput requirements. The TransOx™ system is an automated system that includes the following features: internal heating by electrodes, an Inconel 600 reaction vessel, multi-zone cooling to maintain a protective surface layer of salt on the vessel wall during operations at temperatures in excess of 900°C, an on-demand phase change valve for draining spent salt (5). The protective "skull" layer of salt is particularly important since it serves as buffer between the molten salt and the Inconel 600 on the reactor walls. This will minimize corrosion, leaching of chromium from the vessel walls, and extend the reactor life.

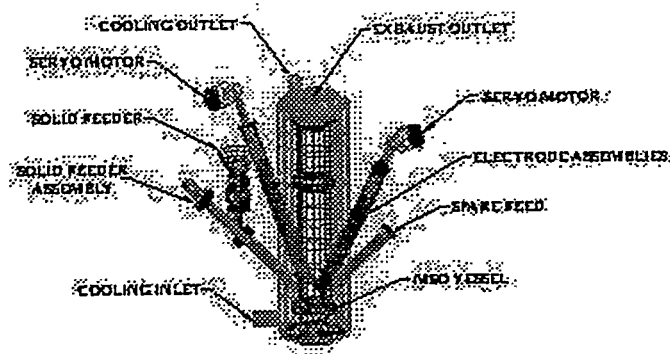


Figure 4. MSO Corporation TransOx™ System

## CONCLUSION

Molten salt oxidation appears to be a viable alternative for treating <sup>238</sup>Pu-contaminated combustibles. MSO is a mature technology without the regulatory concerns of other technologies, such as incineration. The process has moderate pretreatment and post-treatment requirements. The MSO system meets glovebox size and operating restrictions while maintaining an acceptable throughput. MSO will also minimize the volume of TRU waste that will require disposal after treatment and the treated residues are compatible with the plutonium recovery process.

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