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APPLICATION OF MOLTEN SALT OXIDATION FOR THE MINIMIZATION AND RECOVERY OF PLUTONIUM-238 CONTAMINATED WASTES

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ABSTRACT

This paper presents the technical and economic feasibility of molten salt oxidation technology as a volume reduction and recovery process for ^{238}Pu contaminated waste. Combustible low-level waste material contaminated with ^{238}Pu residue is destroyed by oxidation in a 900°C molten salt reaction vessel. The combustible waste is destroyed creating carbon dioxide and steam and a small amount of ash and insoluble ^{238}Pu in the spent salt. The valuable ^{238}Pu is recycled using aqueous recovery techniques. Experimental test results for this technology indicate a plutonium recovery efficiency of 99%. Molten salt oxidization stabilizes the waste converting it to a non-combustible waste. Thus installation and use of molten salt oxidation technology will substantially reduce the volume of ^{238}Pu contaminated waste. Cost-effectiveness evaluations of molten salt oxidation indicate a significant cost savings when compared to the present plans to package, or re-package, certify and transport these wastes to the Waste Isolation Pilot Plant for permanent disposal. Clear and distinct cost advantages exist for MSO when the monetary value of the recovered ^{238}Pu is considered.

INTRODUCTION

Plutonium-238 is a radioactive material that alpha decays with an 88 year half-life. In doing so it gives off thermal energy and thus ^{238}Pu is used to fabricate general purpose heat sources (GPHS) or radioisotope thermoelectric generators or RTG's. Plutonium-238 oxide has been used as an excellent heat and thermal-electric energy source in space for over thirty years.

The ^{238}Pu oxide is fabricated into cylindrical pellets typically having a height and diameter of three centimeters and weigh 150 grams. A heat source this size has a power output of about 60 watts. The heat can then be converted into electricity through thermal–electric converters that power instruments onboard the spacecraft [1]. Unlike a conventional battery, which relies on chemical action, the heat source can last up to 30 years.

The Los Alamos National Laboratory Plutonium Facility has processed $^{238}PuO_2$ heat sources for the past couple decades and as a result has generated ^{238}Pu contaminated wastes which is characterized as transuranic (TRU) waste.

TRANSURANIC WASTE

Radioactive waste that contains alpha particle emitting elements of atomic number greater than 92 and a half-life of greater than 20 years are called transuranic waste or simply TRU waste. Since all plutonium isotopes are alpha emitters of atomic number 94 with half-lives longer than 20 years they are considered TRU waste. TRU materials by definition have an activity of more than 100 nCi/g and at Los Alamos National Laboratory examples include contaminated equipment, rags, paper, and protective clothing and other waste produced from routine Laboratory operations.

A large portion of the waste is considered combustible waste in the form of paper towels, Kimwipes™, and cotton rags containing fine plutonium residue leftover from production facility clean-up. The TRU waste must be disposed of, and current plans call for it to be transported to the permanent underground repository known as Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. Drums of ^{238}Pu contaminated waste must be prepared, packaged, certified and transported to WIPP following strict requirements on container contents.

Presently, requirements allow no more than 0.26 grams of ^{238}Pu per drum. The Los Alamos National Laboratory inventory of 55-gallon drums includes many drums that are over this limit and thus they will have to be repackaged to meet the WIPP waste acceptance criteria. In some cases, the contents of one such drum will have to be repackaged into ten or more drums.

MOLTEN SALT OXIDATION

Molten Salt Oxidation (MSO) is proposed as a ^{238}Pu waste treatment technology that should be developed for volume reduction and recovery of ^{238}Pu and as an alternative to the transport and permanent disposal of ^{238}Pu waste to the WIPP repository.

Molten Salt Oxidation technology has been around for the last twenty five to thirty years and has been extensively studied and evaluated in pilot and full-scale systems. The primary salt of interest to this technology is sodium carbonate, Na_2CO_3, commonly known as soda ash, with a long history of use as an industrial product.

History and Study of Molten Salt Oxidation

Much of today's knowledge of the molten salt oxidation technology can be credited to the 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 on the molten salt oxidation processes for a host of applications including as a means of destroying 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 never reached full maturation of the technology however, because at the time, the alternative treatment method, namely hazardous waste incineration, was less expensive.

Basic Description of the Molten Salt Oxidation Technology

Molten Salt Oxidation (MSO) uses a flameless reaction to oxidize organic wastes. The reaction takes place in a molten pool of salt, usually sodium carbonate, at slightly above atmospheric pressure and at temperatures ranging from 900°C to 1000°C. Molten salt in a reaction vessel acts as a heat transfer and reaction media for wastes that are injected along with air[2]. The waste material and air are injected into the molten salt vessel causing mixing and complete oxidation of the waste. Gases generated are the result of organics reacting with oxygen producing carbon dioxide and water in the form of steam, nitrogen and any unreacted oxygen. The combustible waste is consumed in the salt melt, while the inorganics, neutralized salt and undissolved inert impurities are retained in the melt. When the concentration of undissolved impurities reaches about 20 weight percent, the spent salt is drained off and fresh salt is added to the system. The system is preheated electrically and once up to temperature, the temperature is controlled by the feed rate of the waste and air that serve as a heat source for the melt. Spent salt contains impurities, typically reaction products including sodium chloride, halide salts and ash which are disposed of as waste salt. The spent salt, a salt-ash impurity mixture, can be disposed in metal containers, which solidify and are then placed in 55-gallon drums. If there is anything in the waste salt worth recovering, the salt can be processed (dissolved in water using filtration) to separate insolubles for recovery, and then the carbonate fraction can be reused.

Treatment of Plutonium Contaminated Waste

The Molten Salt Oxidation process has been successfully demonstrated to reduce the weight and volume of plutonium contaminated TRU waste. Atomics International (AI) developed in the mid-1970's a bench-top process that was used with plutonium-contaminated combustible wastes. The AI system showed that greater than 99.9% of the plutonium was retained in the salt melt during treatment. The small amount of plutonium that was not retained in the melt (<0.1%) was captured as particulate in the prefilter to the off-gas clean-up and filtration system. The AI tests showed less than 10^{-4} % of the plutonium was found in the off-gas condensate or on the HEPA filter[3]. The AI system used molten salt consisting of natural inexpensive sodium carbonate and about 10 wt. % sodium sulfate. In the MSO 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 flow air-feed. The tests ran with actual plutonium contaminated waste of a concentration of 9×10^{-5} g/g and 1.1×10^{-3} g/g simulating actual TRU waste. Greater than 99.9% of the plutonium was retained in the melt in all tests.

Tests were also performed to show that plutonium could be recovered from the spent salt using aqueous recovery techniques.

The spent salt, sodium carbonate with sodium sulfate and sodium chloride was dissolved in water and filtered. It was found that 98% of the plutonium in the spent salt mixture was recovered using acid leaching. This plutonium was later purified using solvent extraction and ion exchange techniques. These tests were performed in glove-boxes in a bench scale configuration. The system was sized to process 0.2 kg/hr. From the success of these bench-scale tests AI built a pilot plant called the Molten Salt Test Facility (MSTF) where 50 kg/hr treatment tests (without plutonium) were performed. The results obtained with the MSTF were consistent with the bench-scale test confirming the MSO process as an effective volume reduction method. The AI data showed a volume reduction factor of 57 when plutonium recovery was used.

Recent Interest In MSO

Since the AI tests in the 1970's other organizations have performed similar confirmatory studies of the MSO technology. Recently, molten salt has gained renewed interest. One reason is that the U.S. EPA regulations for incinerators are now extremely rigorous. Public resistance to hazardous waste incineration has grown so strong that even when trial burn and operating permits are issued to owners of incinerators rarely are they fully licensed and operated. Thus, hazardous waste incineration has become a non-option in the 1990's. For the opposite reason, interest in molten salt oxidation is growing since the technology results in no hazardous off-gases or air emissions.

Oak Ridge National Laboratory (ORNL) reported in 1995 on use of bench-scale MSO technology to destroy hazardous wastes composed of chloroform, 111 trichlorethane (TCA) and 2,4 dichlorophenol[4]. Lawrence Livermore National Laboratory (LLNL) has used a pilot-scale MSO processing unit to destroy organic solvents including mineral oil and toluene[5].

The Naval Surface Warfare Center (NSWC) is actively examining the use of MSO technology at its Indian Head Division. In recent tests performed in 1997, they have confirmed the feasibility of using MSO to destroy propellants, oils, paints and cellulose materials. Their results have been so encouraging that the Indian Head Division has collaborated with a newly formed consortium known as Molten Salt Oxidation Corporation for the design of a prototype waste destruction system known as the TransOx™ process. The V2 design is a completely automated system that provides advanced features including the following: 1) a capability for processing greater than 2 kg bulk feed/hr, 2) internal heating by electrodes, 3) an Inconel 600 reaction vessel, 4) multi-zone cooling to maintain a protective surface layer of salt on the vessel wall during operations at temperatures in excess of 900°C and, 5) an on demand phase change valve for draining spent salt.[6]

Presently, a technical exchange and research project has been undertaken between LANL Nuclear Materials Technology (NMT) Division's Power Source Technology Group and NSWC Indian Head division. Surrogate wastes representative of LANL's ^{238}Pu combustible wastes will be oxidized at the Indian Head prototype MSO waste destruction system. This will provide additional confirmatory information on the effectiveness of MSO as volume reduction technique at LANL.

CONCLUSION

Serious consideration should be given to the implementation of Molten Salt Oxidation as a process to recover highly valuable ^{238}Pu from LANL TRU wastes. Clear and distinct cost advantages exist for MSO when compared to the costs for disposal of ^{238}Pu contaminated wastes. The implementation of MSO processing at the LANL Plutonium Facility can substantially reduce the volume of combustible transuranic waste for WIPP disposal.

When compared to the present plans to package, or re-package and ship these wastes to WIPP, the MSO process offers convincing benefits including the following:

- it eliminates the technical challenge of meeting the WIPP requirements for no more than 0.26 grams of ^{238}Pu contents per drum

- eliminates the need to ship to WIPP more than 7500 kg of bulk combustible waste containing a mass of almost 3 kg of ^{238}Pu
- this 7500 kg bulk legacy waste represents approximately 8500 drums that no longer have to be certified, or repackaged and shipped
- avoiding this re-characterization, certification and repackaging effort provides a tremendous cost savings easily in excess of 50 million dollars
- a viable process exists to recover from existing bulk legacy waste over 2 kg of highly valuable ^{238}Pu that otherwise is destined for disposal
- recovering plutonium eliminates combustible waste disposal problems for future ^{238}Pu heat source production activities eliminating the difficulties in shipping to WIPP

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