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POLYETHYLENE ENCAPSULATION OF MOLTEN SALT OXIDATION MIXED LOW-LEVEL RADIOACTIVE SALT RESIDUES*

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ABSTRACT

A limited scope treatability study was conducted for polyethylene encapsulation of salt residues generated by a Molten Salt Oxidation (MSO) technology demonstration at the Energy Technology Engineering Center (ETEC), operated by Rockwell International for the U.S. Department of Energy (DOE). During 1992 and 1993, ETEC performed a demonstration with a prototype MSO unit and treated approximately 50 gallons of mixed waste comprised of radioactively contaminated oils produced by hot cell operations. A sample of the mixed waste contaminated spent salt was used during the BNL polyethylene encapsulation treatability study. A nominal waste loading of 50 wt% was successfully processed and waste form test specimens were made for Toxicity Characteristic Leaching Procedure (TCLP) testing. The encapsulated product was compared with base-line TCLP results for total chromium and was found to be well within allowable EPA guidelines.

INTRODUCTION

Molten Salt Oxidation (MSO) is being investigated by the U.S. Department of Energy (DOE) Office of Environmental Management (EM) as an alternative treatment technology to incineration for mixed low-level radioactive wastes. In addition, MSO has also shown potential application for treatment of secondary wastes or for off gases from other thermal treatment technologies. Approximately 10% of mixed low-level radioactive waste at the ten largest DOE sites (12.8 million kg) is amenable to treatment by MSO.[1]

The MSO process utilizes a molten salt bed maintained at 900° - 1000°C to chemically and thermally destroy organic wastes through oxidation and neutralization. The salt bed, typically sodium carbonate, retains most of the ash, radionuclides, and other noncombustible materials from the waste feed stream. However, following the effective life of the salt bed, stabilization of the residual salt may be required prior to disposal. The quantity of salt requiring disposal depends on whether the melt from the MSO reactor vessel has been recycled and returned to the MSO salt bed. MSO residuals from the treatment of mixed waste contain radionuclides, and may contain toxic metals arising from corrosion products or waste contents. For this reason, or because some of the mixed waste may be listed, the residue from MSO treatment may require disposition as a mixed waste.

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Polyethylene encapsulation, which has been extensively studied at the Brookhaven National Laboratory (BNL) Environmental & Waste Technology Center (EWTC), is a robust stabilization technology applicable to a wide range of waste types including radioactive, hazardous and mixed wastes. In the polyethylene process, waste material is mixed with molten polyethylene and allowed to cool resulting in solid monolithic waste forms. BNL conducted a preliminary treatability study with a sample of the Rockwell MSO waste salt to determine the effectiveness of the polyethylene encapsulation process with this waste stream. An optimization of all operating and processing parameters was not made, but a nominal waste loading was selected and processed based on salt encapsulation experience at BNL. Waste form test specimens were prepared for Toxicity Characteristic Leaching Procedure (TCLP) testing, and were compared with base-line TCLP results of untreated salts.

MOLTEN SALT OXIDATION PROCESS

Pioneering work in molten salt technologies stems from work conducted by Rockwell International for the Atomic Energy Commission in the 1950's for nuclear fuel processing (molten fluorides). Initial research with molten sodium carbonate began with experiments to scrub sulfur dioxide from flue gas and as a catalyst for coal gasification. It was observed during these studies that complete oxidation of organic materials could be accomplished in molten salt. Rockwell pursued the development and testing of MSO as a treatment for hazardous organic wastes into the early 1980's, however, the widespread implementation of incineration resulted in a lack of commercial interest in alternative technologies. In 1992, after a decade of inactivity in the development of MSO, ETEC conducted a successful MSO treatability study for DOE. Currently, ETEC, Lawrence Livermore National Laboratory (LLNL) and Oak Ridge National Laboratory (ORNL) are investigating the use of MSO as an alternative to incineration for mixed wastes.

MSO is a combined chemical and thermal waste treatment technology that utilizes a molten salt bed maintained at 900° - 1000°C within a containment vessel. A combination of waste, air or oxygen, and make-up salt, when required, are then added to the vessel. The salt bed is normally sodium carbonate, but may be a salt mixture of sodium carbonate and other salts, like potassium carbonate. Organic waste is oxidized within the bed with the heat of oxidation functioning to maintain the molten state of the salt. The sodium carbonate (Na_2CO_3) bed neutralizes acid precursors thereby minimizing acid gas emissions. Sodium chloride is produced in-situ as a product of acid gas neutralization. The key advantages of the MSO process are inherent in the characteristics of the molten salt bed. For example, the bed enhances chemical treatment by catalyzing the oxidation reactions resulting in accelerated destruction of organic material. The bed enhances thermal treatment by providing a stable heat transfer medium that is resistant to thermal surges. The salt bed retains most of the ash, non-combustible material and radionuclides from the waste feed stream.

The steady-state operation of the MSO process requires a melt overflow stream which continuously purges ash and sodium chloride (NaCl). An equivalent amount of fresh sodium carbonate is used as make-up. Purging/make-up prevents exhausting the sodium carbonate which

is needed to react with chloride to prevent acid gas production. Dissolved impurities are primarily salts such as sodium chloride, sulfate or phosphate. Undissolved impurities include various metal oxides and silicates. The discharged salt/ash stream is a waste that will ultimately require final disposal. The volume of the waste requiring disposal can be reduced if a recycle option is introduced which separates the unspent sodium carbonate. However, this complicates the MSO process design since the separation steps must be specifically designed for the impurities and characteristics of the waste feed.

POLYETHYLENE ENCAPSULATION PROCESS

Polyethylene encapsulation is a solidification technology for waste stabilization prior to disposal. Polyethylene was identified as a leading solidification candidate in the early 1980's during a BNL survey of potential binder agents conducted as part of the Waste Form Development / Test Program, sponsored by the U.S. Department of Energy's Low-Level Waste Management Program[2,3]. Selection criteria were based on considerations such as compatibility with waste, material properties, solidification efficiency, ease of processing and economic feasibility. Since that time, BNL has conducted thorough research and development in polyethylene encapsulation and has expanded the process to be applicable to low-level radioactive, hazardous and mixed wastes. The polyethylene encapsulation process has developed from proof-of-principle, through bench-scale testing with a wide range of waste types to a full-scale technology demonstration that was conducted in September 1994.

The BNL polyethylene encapsulation process utilizes a versatile single-screw plastics extruder. In this process, dry waste and polyethylene (pellets) are proportionally metered to the extruder operating above the melting point of polyethylene, usually between 120° - 160°C. The waste and polyethylene are homogeneously mixed within the extruder then discharged to a waste form container. The benefit of polyethylene encapsulation is that simple cooling of the well-mixed, extruded melt results in the formation of a solid monolithic waste form. Solidification is guaranteed and is independent of the chemical nature of the waste material. This expands waste stream compatibility since constituents present in the waste will not affect the solidification chemistry and variations or changes in the waste stream composition over time will not require process modifications.

WASTE DESCRIPTION

During 1992 and 1993, ETEC performed a treatability study with a prototype MSO unit, destroying 50 gallons of mixed waste comprised of radioactively contaminated oils produced during the operation and decommissioning of a hot cell. Roughly 120 lbs. of salt waste requiring disposal was generated during the demonstration. The waste contains very low levels of radioactivity and is considered Class A waste (lowest activity category) under guidelines established by the Nuclear Regulatory Commission. It is comprised of over 90% sodium carbonate with the balance of material consisting of chlorides, sulfates and/or silicates.[4] Roughly half of this salt is a non-RCRA waste, the other half consists of samples containing various levels of TCLP metals above the RCRA limits. A sample of this waste was selected, based on maximum metals content, and was received at BNL for a preliminary treatability study to examine the feasibility of using the polyethylene encapsulation process for treatment of MSO salt wastes.

The waste was characterized and prepared by ETEC prior to shipping. The concentrations of metals in the salt waste, shown in Table I, were determined by acid dissolution and Inductively Coupled Plasma (ICP) spectroscopy. The metal in greatest concentration was chromium at 3800 ppm. For this reason, chromium was selected to be monitored during leach testing of waste forms generated by the polyethylene encapsulation process. The extent of radioactivity in the waste was determined by Gamma Spectroscopy. The radioactive isotopes in the MSO waste salt are shown in Table II with their respective radioactivity levels, expressed as pCi/g.

Table I. Metal Concentrations in the MSO Waste Salt

Element	Concentration (ppm)
Barium (Ba)	860
Chromium (Cr)	3800
Cobalt (Co)	57
Nickel (Ni)	27
Cadmium (Cd)	< 9
Lead (Pb)	< 40
Copper (Cu)	11
Iron (Fe)	24

Preparation of the MSO salt waste was conducted by ETEC to produce a sample that is amenable to extrusion. Successful extrusion processing requires a dry waste (<2% moisture) within a given particle size range. It is necessary to remove all residual moisture from the waste prior to extrusion processing since the extruder operates above the volatility point of water. Due to the hygroscopic nature of sodium carbonate, the sample was dried in a vacuum drying oven to get a free flowing powder that would sieve easily. The original sample consisted of a range of particle sizes from fine powder to large chunks. The sample was repeatedly passed through a jaw crusher until the resulting powder was able to pass through a 20 mesh sieve but be retained by a 200 mesh sieve. This provided a particle size range of 75 to 1000 microns. From previous experience at BNL, this particle size distribution was within acceptable processing limits for extrusion.

Table II. Radioactive Isotopes in the MSO Waste Salt

Isotope	Radioactivity (pCi/g)
Cobalt-16 (Co)	0.30
Cesium-137 (Cs)	133
Europium-152 (Eu)	0.12
Europium-154 (Eu)	0.23
Uranium-238 (U) and daughters	12.7
Uranium-235 (U) and daughters	0.68
Actinium-228 (Ac)	0.22

POLYETHYLENE ENCAPSULATION WASTE PROCESSING

The waste MSO salt was processed at BNL's Environmental & Waste Technology Center using a bench-scale, non-vented, plastics extruder (Killion, 32mm dia.) with an output capacity of approximately 16 kg/hr. Both waste and binder were fed through AccuRate Model 301 volumetric feeders. The waste feeder was calibrated with the MSO salt by taking 3 replicates at feeder output settings of 20, 50 and 80%. The feeder calibration curve is shown in Figure 1. A regression line was produced with a correlation coefficient of 0.993. A nominal waste loading of 50 wt% was selected based on previous successes at BNL processing other wastes with similar physical compositions. The salt was slowly extruded and TCLP test specimens (required to pass through a 9.5 mm sieve) were made by casting the extrudate (waste MSO salt/polyethylene product) into Teflon molds as pellets. The density of the encapsulated product, determined using a Quantachrome Multipycnometer, was 2.43 g/cm^3.

EVALUATION OF MSO SALT WASTE/POLYETHYLENE WASTE FORM LEACHABILITY

TCLP was conducted, in accordance with 40 CFR 261, on polyethylene encapsulated MSO salt waste and on untreated MSO salt waste in order to provide baseline data. Extraction fluid pre-testing of salt/polyethylene samples resulted in a pH of 10.69 when mixed with distilled deionized water and pH 2.04 after adding 1 N HCl to the solution. The untreated salt had a pH of 12.41 when mixed with distilled deionized water and pH 11.74 after adding 1 N HCl to the solution. Therefore, Extraction Fluid #1 was used for salt/LDPE samples and Extraction Fluid #2 for the untreated MSO salt.

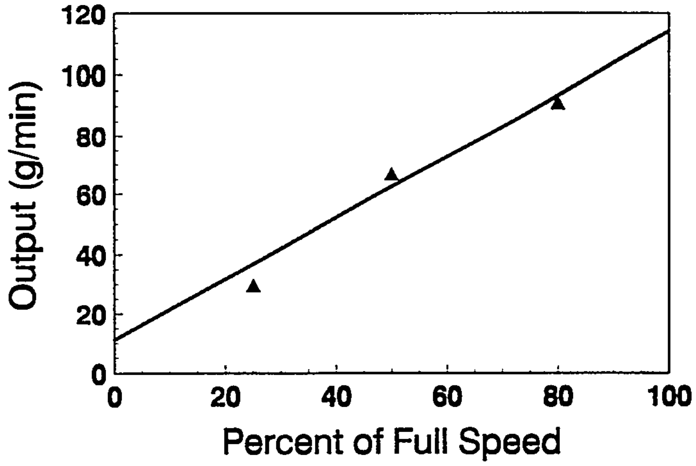

Figure 1. **Calibration Curve of Volumetric Feeder with MSO Waste Salt.**

Following the 18-hour extraction period, leachates were filtered through a 0.7μm glass fiber filter reserving approximately four 50 ml aliquots of each filtrate for analysis. A HACH DR/2000 Spectrophotometer was used to determine total chromium concentrations. It was decided to monitor chromium concentrations in the leachates since chromium was present in the largest quantity and the technique for chromium detection is straightforward. The HACH procedure for total chromium is a calorimetric detection method that first oxidizes trivalent chromium in the sample to the hexavalent form. The technique recommends an acid digestion prior to analysis to help break down the chromium substances into components that can be analyzed. Difficulties were encountered while performing the EPA acid digestions that consumed the majority of the filtrate aliquots. In summary, the digestion required 100 ml of sample be reduced to 15-20 ml by heating (without boiling) after acidifying the sample with nitric acid. After reducing the volume and allowing the sample to cool to room temperature, the samples repetitively gelled and became unusable. The reason for this was not apparent.

A small amount of the MSO waste salt/polyethylene filtrate remained which allowed one analysis without performing an acid digestion. In this case, 10 ml of filtrate was diluted in 100 ml "Q" water which, after performing the HACH procedure, yielded a chromium concentration of 0.16 ppm. Accounting for the dilution factor, the concentration of chromium in the filtrate was 1.6 ppm. This chromium concentration is well below the RCRA chromium concentration limit of 5 ppm. Additional replicates were not possible since all aliquots were consumed and the limited scope of this study prevented the preparation of additional waste form/pellet specimens for TCLP testing. However, the accuracy of the HACH procedure was proven while testing the baseline or untreated MSO waste salt leachate.

Sufficient untreated salt filtrate remained to create a stock solution containing 3 ml filtrate diluted in 100 ml "Q" water. Three dilutions were made from this stock solution: 1ml stock solution in 25 ml "Q" water, 2 ml stock solution in 5 ml "Q" water, and 3 ml stock solution in 25 ml "Q" water. Following the HACH procedure, the diluted solutions resulted in concentrations of 0.14, 0.29 and 0.44 ppm, respectively. Accounting for the dilution factor, the chromium concentrations averaged 120 ± 3 ppm in the filtrate. Considering a 20 to 1 dilution of the original untreated salt to TCLP extraction fluid, 120 ppm chromium in the filtrate would represent 2400 ppm chromium in the salt. This value seems appropriate since the original untreated salt was characterized to contain 3800 ppm chromium and it is likely that not all of the chromium was leached during the 18 hour extraction period. Thus, polyethylene encapsulation reduced the chromium leachability by more than three orders of magnitude, compared with untreated salts. A summary of the TCLP results for untreated (baseline) waste salt compared with encapsulated waste salt is shown in Table III.

Table III. TCLP Chromium Concentrations of Untreated and Encapsulated MSO Salt Waste at a Waste Loading of 50 wt.%.

TCLP Test	Chromium Concentration (ppm)
Untreated MSO Salt Waste	2400
Encapsulated MSO Salt Waste	1.6
RCRA Limit	5

SUMMARY/DISCUSSION

Waste salt from Rockwell's Energy Technology Engineering Center MSO process was successfully encapsulated using BNL's polyethylene encapsulation process. Due to the limited scope of this effort, waste loadings were not optimized and a thorough characterization of the final waste form was not performed. However, a nominal waste loading of 50 wt% salt was easily processed and produced a final product with a density of 2.43 g/cm^3. Difficulties were encountered while trying to perform acid digestions on the TCLP filtrates. This reduced the quantity of filtrate aliquots available for analysis. However, a non-digested salt/LDPE filtrate sample indicted a chromium concentration within EPA limits. Chromium concentrations detected in the untreated MSO salt/base-line filtrate aliquots were as expected. Preliminary data is promising but additional leach testing of the waste salt is recommended. Further work should focus on monitoring the leaching of other metals, optimizing processing parameters and waste loadings, and fully characterizing the final waste form products (e.g. mechanical integrity, durability, long-term leaching).

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