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Abstract

Pu-238 heat sources are used to fuel radioisotope thermoelectric generators (RTG) used in space missions. The demand for this fuel is increasing, yet there are currently no domestic sources of this material. Much of the fuel is material reprocessed from other sources. One rich source of Pu-238 residual material is that from contaminated combustible materials, such as cheesecloth, ion exchange resins and plastics. From both waste minimization and production efficiency standpoints, the best solution is to recover this material.

One way to accomplish separation of the organic component from these residues is a flameless oxidation process using molten salt as the matrix for the breakdown of the organic to carbon dioxide and water. The plutonium is retained in the salt, and can be recovered by dissolution of the carbonate salt in an aqueous solution, leaving the insoluble oxide behind. Further aqueous scrap recovery processing is used to purify the plutonium oxide.

Recovery of the plutonium from contaminated combustibles achieves two important goals. First, it increases the inventory of Pu-238 available for heat source fabrication. Second, it is a significant waste minimization process. Because of its thermal activity (0.567 W per gram), combustibles must be packaged for disposition with much lower amounts of Pu-238 per drum than other waste types. Specifically, cheesecloth residues in the form of pyrolyzed ash (for stabilization) are being stored for eventual recovery of the plutonium.

Introduction

MSO is not a new technology; it was developed extensively in the 70's by Rockwell and later at DOE complex sites (West, 1992) as a method of treating hazardous organic wastes, and radioactive wastes (McKenzie et al., 1975). At the time, the recovery of materials retained in the salt was not pursued. MSO was sidelined when incineration became a more attractive alternative. That option is no longer available, so MSO has been revisited as a disposal technique in recent years (Gay, 1992).

Our application has two challenges that have not been addressed by others developing the process. First, we need to adapt the process unit to work inside a glovebox, with its ergonomic, available space, and safety restrictions. Second, we need to recover the plutonium "contaminant" from the salt.

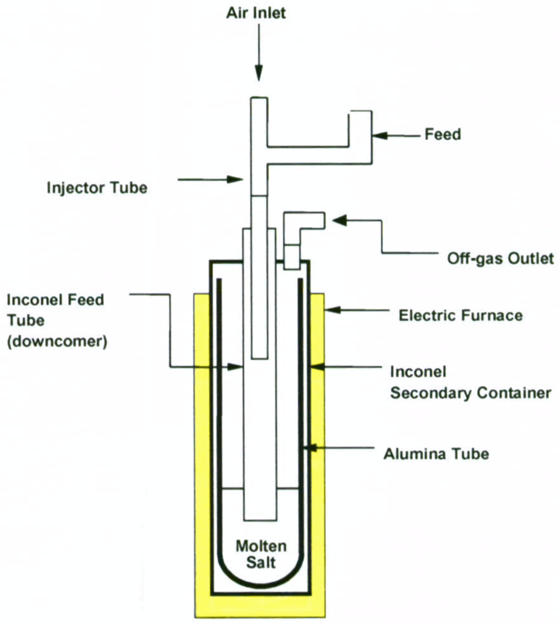
To address these issues, an MSO system was developed and tested extensively in a facility outside of the radiation controlled area. The system was then modified for operation inside a glovebox using an existing furnace. There are two methods used for the addition of ash to the MSO unit, batch mode (addition of ash and salt together in the crucible followed by heating) and continuous mode (automated, controlled addition of ash to the crucible once the salt is molten). The batch mode unit is currently installed in a glovebox and can process up to 100 grams of the plutonium-containing pyrolyzed ash per day. The continuous feed unit can now process 1 g ash/min, up to 240 g per day. Further optimization of parameters will at least double that throughput. Modifications to make a continuous feed unit require more specialized equipment and more extensive testing to assure the safety of the operation in a glovebox. The more efficient unit will be installed in the glovebox line in 2004.

The basics of MSO operation, testing of the current unit in a non-radiological laboratory, installation and modification of the unit for use in a glovebox environment, and results will be discussed.

Method

MSO is a seemingly simple and straightforward application of a well-studied process. The schematic is shown in Figure 1. A secondary unit is placed in a vertically placed tube furnace. Inside there is a crucible which holds the molten salt. When the salt has been heated to the molten phase organic feed is delivered using air to get it into the salt. The feed tube is placed above the salt to reduce corrosion and to prevent the oxidation from occurring before the feed reaches the salt. Another tube, referred to as the downcomer fits over the feed tube and is situated 1 inch from the bottom of the salt bed. The air and feed are forced out the bottom of the downcomer to achieve maximum

Figure 1. Schematic of MSO Unit



residence time in the salt. The downcomer acts as cooling to feed tube and protects it from corrosion.

Chemically the carbonate salts merely provide a matrix for the reaction. The oxidation reaction is most efficient at high temperatures. The temperature chosen is a compromise between reaction efficiency and materials degradation. Sodium sulfate acts to increase the reaction rate, and up to 10% sulfate can be added to achieve a higher reaction rate (up to 10x) (Stelman, et al., 1976) and increased conversion of organics to carbon dioxide and water, the completely oxidized products.

Our particular needs required us to devise an MSO unit that would use the least amount of space in the glovebox, and specifically to fit into a space that contains a 13" high by 6" inner diameter tube furnace situated in a well, so that the top of it was flush with the glovebox "floor". This placement allowed use of the 20" height of the well, in addition to the 45" of space from floor to ceiling. Usable space is further limited by the reach allowed by the gloves. Fortunately, there are two glovebox ports at different heights. The well is situated at the end of the glovebox so can be accessed from 3 sides, but only one pair is close enough to work directly with the unit in the well. The glovebox was not designed for this purpose so placement of the well is not optimal.

Another limitation of the glovebox is the strict requirements for safety. The most critical safety concern is heat. We are working at temperatures well above what a glove can stand without catastrophic failure. Wearing a heat resistant glove over the lead lined imposes only more loss of dexterity and ability to perform any task easily. There is always the hazard of punctures, tears, and weakening in the gloves from any activity.

Finally, our goal is to recover the plutonium oxide from the salt. No one has ever desired to separate a salt "contaminant". The salt retains metal oxides, mainly from corrosion products of the metal pieces of the unit. The salt can contain up to 20 wt% of "contaminants" before it must be replaced. The goal is to maximize plutonium oxide in salt by minimizing the other oxides. The plutonium is easily separated from the salt matrix by dissolving the salt and filtering the solution. The other metal oxides present are also insoluble, impacting the purification down the line.

Another difficulty could be the amount of liquid generated by dissolution of a kilogram or more of salt. The solubility of sodium carbonate is 29 g/100 ml. An awkward amount of solution could be generated in that process. Solution would present another waste issue, that of sheer volume. All of the separation challenges are preceded by the need to access the salt, which requires removal of the salt from the crucible. When the salt cools, it becomes "cemented" to metal. Therefore, use of a metal crucible was problematic.

Since we are recovering the plutonium from the salt, we face technical challenges not encountered by other workers. Those challenges include: 1) minimization of insoluble oxides, 2) minimization of (hazardous) solution waste, and 3) method to access salt for recovering plutonium.

Project Overview

The basic components of an MSO unit are as follows: 1) Feed system, 2) Air supply, 3) Downcomer with feed tube, 4) Crucible, 5) Secondary containment, 6) Off-gas conditioning and exhaust. A schematic of the unit is shown in Figure 1. MSO units do not differ much in basic design and ours was modeled after one (of several) built by Rockwell (Grantham et al., 1975). Significant differences in the type of feed, available space, and our process goal of recovering plutonium oxide from the salt dictated innovative modifications of the feed system, containment materials, dimensions, and salt disposition

Our primary feed is pyrolysis ash, which is the result of heat treatment at 650°C, under argon, of plutonium-contaminated cellulosic cheesecloth, used extensively in the glovebox. It presents a unique test to MSO technology in that it is a feed type never used before. Pyrolysis ash is a light (4 lbs/cubic ft), dusty material that retains some fibrous structure after ashing. This presents problems for feeding. First, the material is easily dispersible. It carries plutonium with it and creates a corrosive coating and ash contamination where it settles. Second, the lightness and small fibers work together to create bridging when the ash is moved by mechanical means. The feed should approach the ideal condition of being dustless, heavier, and not cause bridging.

Feed system development has historically been an engineering challenge to MSO technology. The primary problem is the introduction of a feed into the oxidation environment in such a way as to prevent the premature oxidation of the material in the feed tube or at tube/salt interface. The downcomer is a sheath around the air/feed tube that is used to protect the feed tube and reduce clogging. It is longer than the feed tube and has a larger diameter. It extends almost to the bottom of the salt bed. This prevents the salt from touching the feed tube exit, while providing a wider diameter interface for salt, air and feed to meet. Air fills the downcomer, providing insulation from the heat that would cause premature oxidation inside the feed tube.

Corrosion is one of the thorniest issues facing users of MSO processing. The highly alkaline, oxidizing, and high temperature environment in the salt will quickly destroy most metals and many ceramic materials. The corrosion products like iron, nickel and chromium oxides from typical "corrosion resistant" metal alloys will also remain in the salt, as well as the plutonium oxide. These products shorten the lifetime of the salt and create more difficulties in plutonium purification and liquid waste disposal. The downcomer and crucible are in direct contact with the salt and materials selection for them has been a constant subject of research and testing.

Most users of MSO do not have the same waste issues as we do, nor are they interested in reclaiming any elements in the salt. Most MSO users also employ larger units, which prevent them from using ceramic materials with more promising anti-corrosion characteristics.

The choice of ceramics requires consideration of the thermal shock stability of the material as well as the corrosion resistance. For example, alumina has been shown to be very corrosion resistant to molten salt, but like many ceramics, it can break unpredictably when subjected to thermal gradients or thermal cycling. Thermal gradients exist in the feed tube and downcomer as ambient air is accelerated into the salt. The crucible sees the salt/air interface, as well as the temperature gradient from the salt, at 920°C, to the top of the secondary vessel, at 200°C.

The height of the MSO unit is based on experiments done by Rockwell, which studied the salt splash level as a function of air speed at the salt surface. This results in a unit ideally having a 6:1 ratio of height:diameter (Grantham et al, 1975). Our glovebox height is the limiting factor in the unit design, having a height of 45 in. This would dictate the maximum unit height of no more than 24 in. But, the feed system, and fittings and connections on the lid also require space above the unit. Another factor is that the furnace is only 15 inches tall. Anything longer than that will be outside the heating area. Other units employ a longer furnace that completely ensconces the unit. This change needs to be evaluated. Finally, given the restrictive movement in the glovebox, the smallest, lightest unit possible will increase worker safety.

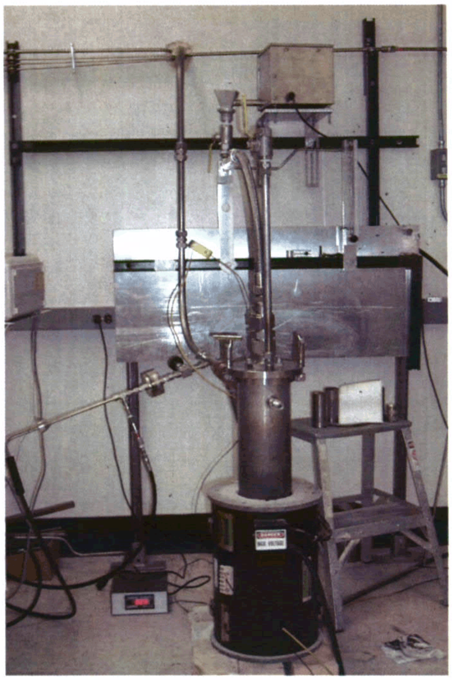
History

Initially, development of the continuous feed unit was the goal. There was a prototype unit used to establish the working parameters of the system. A bank of analytical units was integrated into the exhaust system to observe CO_2, CO, O_2 and total hydrocarbon. They were used to measure the efficiency and completeness of the oxidation reaction in the salt.

A larger unit was designed based on those studies (Figure 2), but developing or procuring a suitable mechanical feed system for delivering the ash remained an obstacle. Therefore we took a two-pronged approach, where we developed a smaller unit where the feed was essentially done in batch mode by mixing the ash with salt and heating them together.

The main difference between the batch and continuous mode system is that the batch mode loads feed by mixing it with the salt prior to heating the unit. The continuous mode supplies a steady stream of feed. The continuous feed operation has greater complexity but simplifies the process and maximizes throughput. The continuous mode system can be run each day without having to remove the salt, so a lot of time (and

Figure 2 Continuous Feed MSO Unit



exposure) is saved with not having to unload and reload the salt and ash. See Table 1 for list of other differences.

It proved to be a good idea to get a simpler unit working in the glovebox in order to determine how the salt would react with the plutonium and what changes would be needed to the proposed unit before deciding on introduction of a more complicated unit. Early on, we found that the larger unit already fabricated would be too large for the available space and reach of gloves.

There is an authorization basis requirement for any process done in a plutonium facility that provides an envelope of allowed activities that have been determined to be safe operations. For activities new to the box, the approval process can be more time-consuming. We were able to introduce a batch-mode operation because it required minimally different activities than a molten salt reduction process done in that area previously. This was an added incentive to beginning with the batch mode unit.

Table 1 Differences between batch and continuous mode MSO processing

Characteristic	Continuous Mode Unit	Batch Mode Unit
Size	5.5" OD x 24" tall	5.5" OD x 17" tall
Feed mode	Mechanically metered by screwfeeder and delivery by suction created by the eductor into the air stream going into the melt.	Mix with salt before heating
Air supply mode	Compressed air accelerated by eductor into unit. Various pressures not exceeding 40 psi.	Compressed air ast 20 psi controlled by flow meter.
Downcomer/Feed Assembly	1.5" OD outer tube (downcomer) almost to bottom. 1" feed air tube inside downcomer and 8" from bottom of the crucible	3/8" Inconel 600 sparge tube almost to bottom of crucible (no downcomer)
Air volume	0.3-3 scfm	4-6 scfh
Throughput	250 g feed / run (4 hr). Reaction rate determined rate at 1 g/min (minimum).	50-90 g feed / run. Volume limited

The batch mode MSO unit began operation on July 1, 2003. There have been valuable lessons learned from initiating a simpler operation. Primarily, our expectations were born out. Activities in the real space of the glovebox have suggested changes in the unit and auxiliary systems, e.g., exhaust system, general plumbing and placement, and especially fittings, such as bolts and compression fittings. Second, optimum parameters in the test lab need to be reoptimized for the changed physical setting and addition of plutonium in the glovebox. The most significant information garnered from processing in the glovebox was about just how important it was to take into account the ergonomic, space, and movement restrictions in the glovebox. There is an enormous corrosion factor with Pu-238, everything must be optimized for ease of maintenance and operability.

Clearly, further work on the continuous feed unit must address this reality. It must be “downsized” and rebuilt with the more “glovebox friendly” changes that improved the safety and ease of operation for the batch unit in the glovebox. To that end we have built a plywood mock-up of the glovebox area where the unit will reside. Lead-lined gloves have been put in, and we have built it so that the unit and furnace will sit exactly the same in that mock-up as in the real space. We continued with a search for a suitable feed system while implementing the batch mode system in the glovebox. We found a suitable screwfeeder, which will be the largest (35 lb.) piece of equipment we need to place relative to the unit.

Currently, the focus has been to finish work on the continuous feed unit. Looking at our early data with more experienced eyes, we have revised estimations of throughput upward, and design changes due to that must be built in and tested. The placement of the equipment, especially the screwfeeder, in the glovebox is a priority because it may generate further design modifications. We are still experimenting with new materials which hold promise for more stable ceramic crucibles.

Results

Materials

A significant technical challenge for any MSO operation stems from the extreme corrosive capacity of the alkaline salt in an oxidizing environment at high temperatures. In the ‘70s, when most studies were done, a nickel metal alloy, Inconel 600, proved to have the best corrosion resistance for an easily obtainable commercial material (. It has been used as a crucible as well as outer vessel on other units.

There are two problems with using that material for our purposes. We need to recover plutonium. This is not easily accomplished if the crucible containing the salt and plutonium is metal. The salt sticks to the metal like cement. Other workers removed salt by via a vacuum system to transfer it from the crucible while still molten. That option presents a significant safety hazard in a glovebox. Furthermore, although Inconel 600 is corrosion resistant, it still corrodes over time, releasing more metal oxide contaminants into the salt. This leads to faster loading of the salt and more contaminants mixed with the plutonium needing removal during the purification.

Suitable ceramic materials are by far more corrosion resistant than any metal. Fortunately, the salt adheres less to the surfaces of most of these materials and allows removal of the salt from the crucible in a single plug (Figure 3). Also, the build up of

Figure 3 “Popsicle Stick”

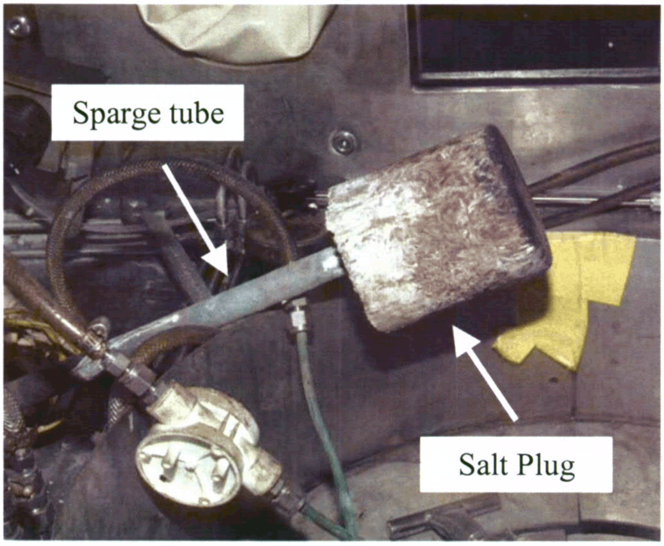


Figure 3:. Sparge tube is used as a handle to remove the salt from the ceramic in a single plug. Shown is first result of batch mode run in a glovebox using Pu-238 contaminated ash. Black material on the bottom is $^{238}PuO_2$.

corrosion products (e.g. alumina, zirconia) in the salt is negligible. The disadvantage is the fragility of most of these materials. More importantly, many are sensitive to thermal cycling and fail unpredictably after several cycles. Finally, this sensitivity requires the use of a longer heating period to melt the salt in order to fall within the thermal shock parameters.

Many ceramics were tested for corrosion resistance along with Inconel 600 and an iron-aluminide material developed at Oak Ridge National Laboratory (Newcomb, 1995). Generally, oxides (MgO, Al_2O_3, ZrO_2) are the most corrosion resistant in this basic, oxidizing environment (Lay, 1983), but that group have thermal shock values (ΔT) of 200°C to 300°C. Alumina is the most robust of these materials, as well as being easily attainable and relatively inexpensive. Silicon containing materials (SiAlon, SiC) dissolved in our tests, with Mullite being the most corrosion resistant of that group. It is also easily attainable and relatively inexpensive. It is more thermally shock resistant than alumina, but the silicon interacts with plutonium, so is highly undesirable as a contaminant (in the quantities shed by the Mullite) of the plutonium. A titania-alumina composite that we tried also dissolved.

Only one ceramic that we tried, aluminum nitride, was chosen for further testing as having both excellent corrosion resistance (Table 2), and ability to withstand thermal cycling. Problems remain with aluminum nitride being difficult to engineer into a suitably sized crucible. Procurement of test crucibles is in progress (expected date 3/15).

Recently (2/15), we contacted a vendor of ternary ceramics (Barsoum, 2001), a class of titanium-containing carbide and nitride compounds that are machinable as well as have phenomenal resistance to thermal shock. Despite the poor behavior of the titania-alumina composite, we plan to test the Ti_3AlC_2 and Ti_4AlN_3 materials.

Table 2 Corrosion rates for some ceramic materials

Corrosion Rates in g/(mm$^{\wedge 2}$ day)

Material	1st week	2nd week	3rd week	4th week	5th week	Avg.
AlN	1.425E-05	9.570E-06	2.530E-05	2.482E-05	3.166E-05	2.112E-05
Mg-ZrO_2 sq	-5.592E-06	-2.400E-06	7.059E-07	3.986E-06	8.521E-06	1.044E-06
Al_2O_3 rod	***	***	***	1.456E-05	1.330E-05	1.393E-05
Al_2O_3 sq	***	***	***	1.128E-05	7.351E-06	9.317E-06

Table 2: Materials were kept at 950°C for a total of five weeks, with weights taken at the end of each week. Alumina coupons begun at Week 4.

Originally, we used ceramic for both the crucible and downcomer/sparge tube. The downcomer needed to be lifted from the salt while it was still molten because it would not survive repeated heating and cooling cycles. Because of the fragility of the ceramic, it was also not easy to connect to the metal fittings for the feed/air tubes to it or to fit and seal it through the lid (Figure 4) We now use Inconel 600 for downcomer material for the following reasons. 1) Our tests in the batch mode show that the ash reaction went to completion faster using the metal sparge tube. We think this has to do with the ash, which tends to rise to the top of the froth. We have found when the ash is not completely consumed that it layers on top of the salt. The metal may not allow the ash to stick to it, so more falls back down to react. 2) The Inconel 600 can remain in the salt when the salt is cooling and heating, requiring no operator working with the unit while it is still hot. 3) When removing the salt from the crucible after a batch mode operation, we found that the metal sparge tube, now stuck in the salt, could be used as a sort of "Popsicle stick" to assist in pulling the plug from the crucible (Figure 3). The salt can be "wiggled" out using a little water to loosen the salt from the ceramic. When ash remains,

Figure 4: Ceramic downcomer fittings to airline and through lid

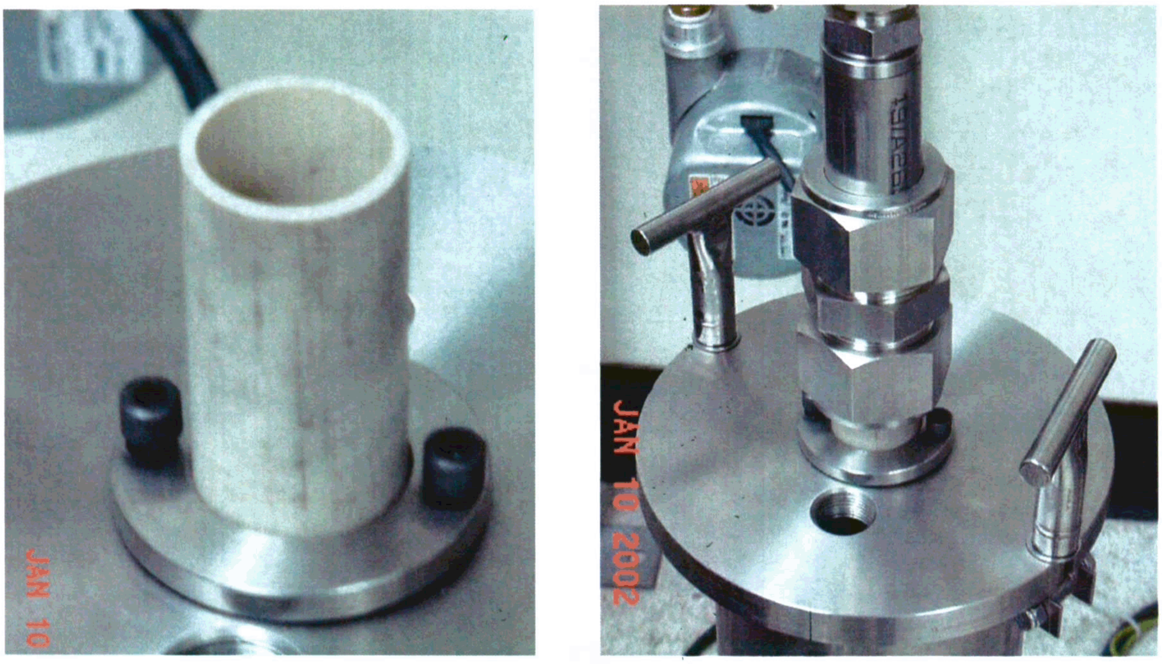


Figure 4: Ceramic is held in place in lid by flange compressing Viton O-ring. The large compression fitting connects the ceramic downcomer and metal feed/air tube. The ferrule on the ceramic side is exchanged for Viton O-rings.

it sticks to the top and sides of the crucible and the salt cannot be retrieved without breaking the crucible. The processing can be repeated, assuring the destruction of the small amount of remaining ash. We have not yet tried this with the downcomer of the continuous feed unit. The continuous feed unit does not need to have the salt removed after each run, so it could become a moot point. 4) Finally, it makes the attachments to the tube and sealing in the lid much easier. We have traded an increase in metal oxides from corrosion ($1.2\text{x}10^{-4}$ g/mm^2/day) for the added simplicity and safety of this design.

Size and Throughput

MSO reactors can be any size. Experimental units have been the size of a test tube up to an industrial-sized unit 17 ft high by 33 in diameter built by Rockwell that was never deployed. The available space in the glovebox is dictating the size of our unit. The height to diameter ratio for a unit is typically 6:1 (minimally 4:1) (Grantham, 1975). This parameter is based on the volume and velocity of air being bubbled through the salt and the amount of splashing and salt entrainment resulting from this activity. The oxidation reaction occurs in the frothing of the molten salt mixed with air, so factors affecting that are important for the success of the reaction.

Our greatest limitations are the height of the glovebox (45") and size of the furnace. Our batch unit uses a crucible that has a 4.0" OD and is 12" high to match the size of unit used in the previously authorized process. The height dimension was also dictated by the older unit. The unit fit the furnace height. The furnace sits in a well with the top of the furnace flush with the glovebox floor. The height dimension could cause a decrease in throughput by reducing the air flow rate in order to avoid salt entrainment in the exhaust. Our tests showed a flow rate of 4-6 scfh is sufficient to oxidize the amount of available ash in the batch mode unit. The available ash is limited by the volume of the ash, since the ash and salt must both be loaded into the crucible before heating. Almost the entire volume of the crucible is loaded with the ash/salt mixture. So the final parameters for the batch mode process were dictated by the amount of ash, rather than air. Salt entrainment has not been an issue.

The ratio of salt to ash is also important to the success of the batch mode reaction. Too much ash affects the viscosity of the molten mixture. That in turn affects the efficiency of the reaction. The salt:ash mix have an acceptable ratio range of 15-25 g salt per gram ash (Remerowski, experimental results) in order to perform efficiently enough to completely oxidize the ash in the 3 hr allotted run time.

Those ash loading constraints are not an issue in the continuous mode unit. The amount of air vs the height of splash then become the issue. Some of the entrainment has been circumvented by the use of a baffle followed by an expansion trap in the exhaust line. A row of 3/16th inch holes has been drilled around the bottom of the 1.5 inch diameter Inconel 600 downcomer. This has served two purposes. First, it produces smaller bubbles which create both a froth of smaller bubbles for greater reaction surface area. Second, the bubbling is not as "violent", so the crucible is subject to less mechanical force. These results were obtained by observation of the behavior of a zinc chloride solution (at room temperature) made to a density of 2g/ml, the density of the molten salt. The solution is put into a clear plastic container of crucible dimensions, and the lid, with air supplying portion of the unit, is placed over it.

Feed System

Two approaches were taken to solve the unfriendliness of our main feedstock to mechanical metering. One was to use an additive to the ash that would change the characteristics of the feed to make it more amenable to mechanical feeding. For example, it is much easier to pump liquid into the system, so ash in a liquid matrix would make a better feedstock. Two organic liquids, ethylene glycol and mineral oil, were mixed with the ash and tested.

The other additive tested was a polystyrene polymer that is liquid at 110°C and solid at room temperature, could be mixed easily with the ash when in the liquid phase, and produced an ash/plastic block when cooled. The block could be broken in 1/8" pieces and fed easily using a small screwfeeder.

The disadvantage to additives is that only a maximum of 10% ash in the matrix is achievable. The organic matrices must also be consumed by the process reaction, thus lessening the ash throughput. A throughput of 1 g/min (or more) pure ash is acceptable given the limited processing time in the glovebox; but an ash throughput of less than that amount is not. LDPE (low density polyethylene), a similar polymer, has been fed successfully at a rate of 5 g/min which would not give the needed throughput. Another more important disadvantage is that the additional operator time preparing the feed also increases exposure.

The other option was to find a mechanical feeder that, perhaps with some modification, could feed the ash. Screwfeeders abound, but tend to be too large to put into a glovebox. A small screwfeeder (AccuRate, 300 Series) was tested with several modifications to help the ash to fall in the path of the helix: 1) stainless steel covers for the inside walls of the hopper to reduce friction, 2) increased steepness of the hopper walls, 3) attached a vibrator to the side of the unit, and finally 4) sent ash to the vendor to have them test different helix sizes, types, and gear ratios. None proved successful.

Further searches identified a steel screwfeeder (K-Tron, model K-CV-KT20 twin screw volumetric feeder) with features that effectively feed the pure ash. It features a stainless steel hopper having a rotating agitator, like that of a flour sifter, which breaks up the bridging and pushes the material into the screw mechanism. A double screw with shallow grooves more effectively "grabs" the ash and pushes it uniformly along the length of the helices. Vendor tests proved that the ash could be effectively moved at a rate of approximately 1 g/min (or faster) with sufficient accuracy for our purpose. The unit is small (22" x 17" x 21" ht, weighing 35 lbs.), but still substantial in terms of glovebox space. The unit must be customized to minimize height and weight, and employ added safety features, such as interlocks and emergency stops.

Salt Composition

Temperature plays a significant role in MSO processing. Both oxidation rate and materials degradation increase with temperature. A compromise must be found to minimize reaction time with material degradation.

Commercial MSO operations use sodium carbonate because it is inexpensive. Sodium carbonate melts at 850°C, and sodium sulfate at 884°C. The disadvantage of using that salt is that the typical (compromise) reaction temperature range of 900°C to 920°C to is not much higher than these melting points. During processing, temperature fluctuations occur due to changes in air flow rate and the exothermic oxidation reaction. In the past, these changes have been great enough to cause partial solidification of the sodium carbonate salt during processing, which halts the run.

We employ a potassium-sodium carbonate eutectic mixture that melts at 706°C (Janz & Lorenz, 1961). In addition to having the lower melting point, the eutectic mixture has a higher solubility due to the contribution of the potassium carbonate, which is 3 times greater than the sodium salt (29 g/100 ml). Our experimental data determined the potassium-sodium mixture has a solubility of about 50 g/100 ml.

Second, a modeling study predicts that the increased neutron production associated with (α, n) reactions from the light elements is highest for sodium and a factor of three lower for a 40% potassium-60% sodium mixture (Shores, 2002). The predictions from these calculations have not yet been tested experimentally.

Sodium sulfate acts to increase the oxidation reaction rate by up to a factor of 10 when used in 1-10 wt% amounts in the primary salts (Stelman et al., 1976). We have shown that the reaction goes to completion more quickly and that CO_2 production is increased (compared to CO) with the addition of as little as 1% sulfate. The amount of sulfate is important in the case of the batch mode operation. If too much is added, the initial reaction, i.e., when all the ash is available, can be vigorous and cause the salt to overflow the crucible. The sulfate when added at 1% is spent after 4 runs and must be replenished. The addition of sulfate guarantees that the reaction goes to completion reproducibly within our run time. Without sulfate the reaction rate "tails off", typically leaving a small amount of unreacted ash, which affects the ease of salt removal. (See Materials section.)

Past work has shown that the sulfate has little effect on the reaction of easily oxidized material like LDPE (low density polyethylene). In the continuous mode, the ash does not "build-up" as in the batch mode. But ash is the least reactive material that we have tested. (Others have used graphite for reaction studies because of its slow reaction rate.) In one experiment, the addition of sodium sulfate during the run did increase the ratio of CO2:CO produced by ash oxidation (Figure 5). Reaction efficiency is improved, but we are still experimenting with the effects of sodium sulfate used with the continuous mode unit to increase ash throughput.

Efficiency and Throughput

Our goal is maximum throughput. Therefore, some efficiency of the reaction (maximum CO_2, minimum HC and CO) can be sacrificed, within the envelope of our air quality emission standard. This is a very, very small operation. The greatest amount of

Figure 5: Efficiency of reaction using Na_2SO_4

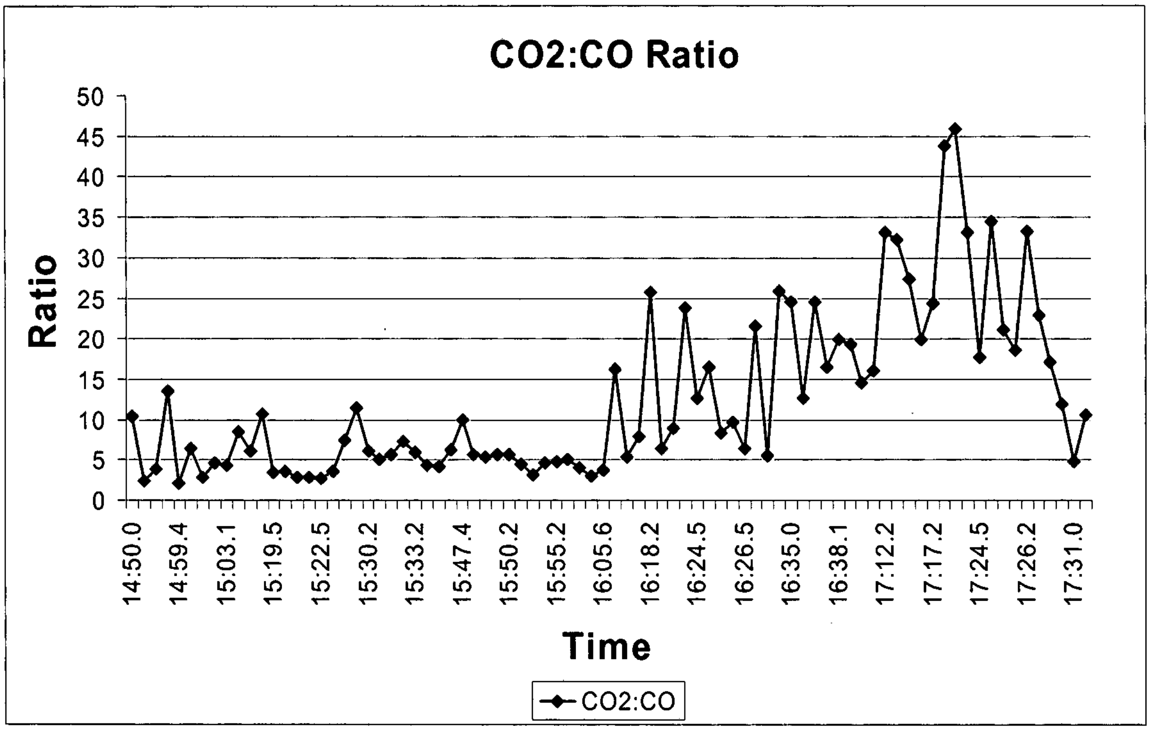


Figure 5: Ash processed at 1 g/min increases efficiency as measured by complete oxidation reactions (CO_2) vs incomplete (CO) when sodium sulfate to 6 wt% is added.

carbon monoxide off-gas produced was in the range of 3000 ppm. Over a four hour processing period per day, this is an acceptable level. Our levels of hydrocarbon for the continuous mode are quite low, at levels of 100-200 ppm. The level increases with increased feed rate and has reached 2000-3000 ppm (with no scrubber) at the highest feed rates for LDPE and Reillex ion exchange resin. In the batch mode, hydrocarbons come off the ash (93% C, 4% H, 3%O) in a concentrated manner because of the slow heating of the salt/ash mixture under argon. (Figure 6) With the addition of a simple 4 M NaOH scrubber, the hydrocarbon content of the final exhaust is significantly lower.

The continuous mode unit reached peak efficiency at the lowest feed rates, about 1 g/min. This was measured by the total hydrocarbon present in the off-gas. It was less

Figure 6 Hydrocarbon off-gas from batch mode processing of ash

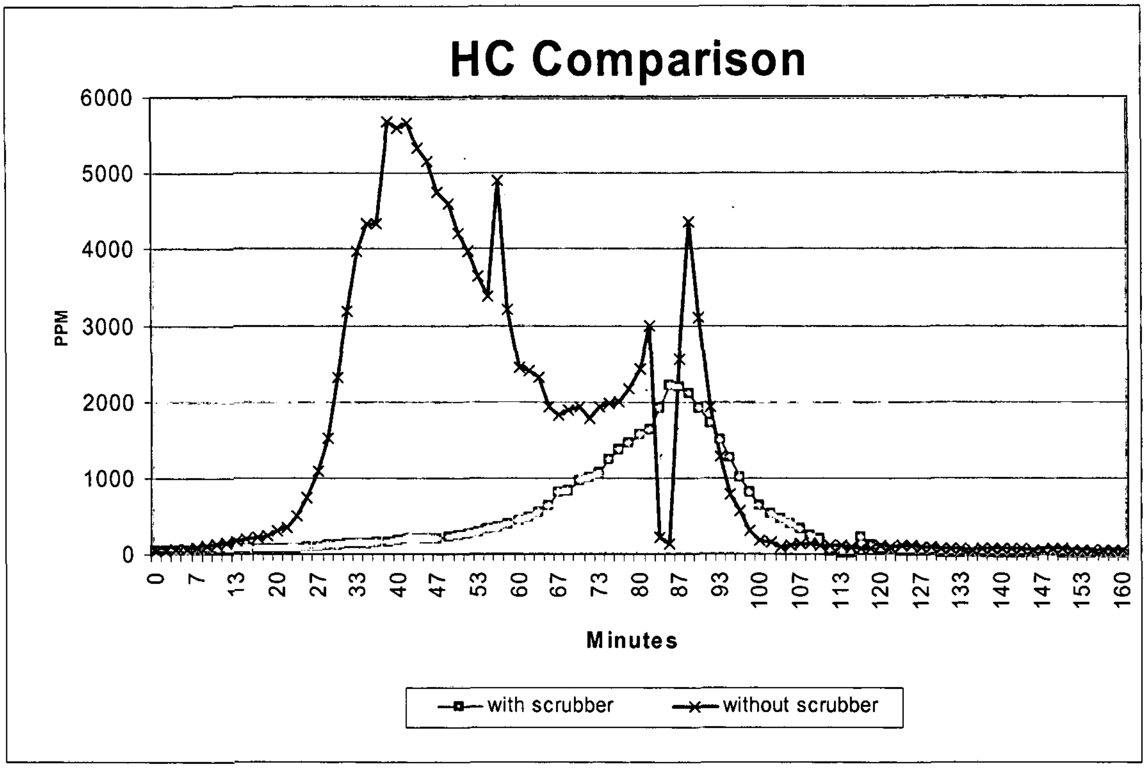


Figure 6: Fifty grams of ash mixed with salt being heated to 850°C under argon. First peak comes off at about 500°C, second between 650°C and 750°C. Salt is molten at 850°C and higher. Off-gas is bubbled through four liters of 4 M NaOH scrubber.

than 50 ppm. Since hydrocarbon production is not a problem downstream, the feed rates are dictated by maximizing the carbon dioxide content of the exhaust. Air delivered at 1 scfm has been sufficient (and may even be lowered) for the reaction rate occurring in the salt for all materials tried. Ash, especially, does not consume a fraction of the oxygen content of the air delivered at that rate.

More work is needed to optimize the reaction in the continuous unit. We plan to consult more experienced workers in this next phase of the project.

Plutonium Recovery and Waste Disposal

Several experiments were performed to develop the method for $^{238}PuO_2$ reclamation from salt. First, we have shown from the batch process (Figure 3) and from the results of other workers (Bird, 1994) that the $^{238}PuO_2$ layers on the bottom of the crucible, therefore, the entire salt plug does not have to be dissolved to claim the $^{238}PuO_2$. Second, the solubility of the Na_2CO_3/K_2CO_3 eutectic mixture is greater 40% higher than Na_2CO_3 alone, which reduces the amount of liquid waste generated by this process. Finally, using a ceria surrogate mixed with spent salt from a metal crucible operation, we have shown that the ceria and almost all of the other metal oxides are completely insoluble and can be easily filtered from the salt solution. This impure form of the plutonium oxide is the base material for further purification.

This is a waste minimization process, so attention to production of further waste has been scrutinized carefully. The status of Pu-238 TRU waste as being no-path-forward adds to the problem. The sources of waste are as follows: 1) broken crucibles, 2) spent salt, 3) salt solutions.

We are addressing each of these streams with the view of minimizing their impact. We continue seeking a ceramic material that will survive multiple thermal cycles, not only to reduce waste but save time and increase worker safety. We have chosen to use a metal downcomer/sparge tube which will contribute to the metal oxide content of the salt. This will shorten the lifetime of the salt, but enhances worker safety and is useful in the act of removing salt from the crucible, so decreasing the possibility or necessity of breaking the crucible. It is the most corrosion resistant choice and is estimated to last for a year or more. The salt must be replaced when the contaminant content reaches 20 wt%.

This mostly arises from the metal oxides. Since the plutonium is the major contributor and is removed as it builds up from the bottom of the plug, the salt life will be extended. Further, the salt can be recrystallized to further extend the life. Finally, the salt solution can be sent to the liquid waste treatment facility here. The solution is minimized because of the concentration of the plutonium on the bottom.

Conclusion

A batch mode MSO unit is operational inside a plutonium-238 glovebox. The operating parameters have been optimized for maximum throughput and minimum waste. The unit can process up to 100 g of Pu-238 contaminated pyrolysis ash per run. Up to 10% of that material is plutonium oxide.

Work continues on the development of a continuous feed unit which can process at least twice the amount of material than the batch unit per run. We have a mechanical feed system now which we are integrating into the unit. It will be necessary to optimize the reaction in that system, since proof of principle was the main goal of our earliest efforts. Further (small) design changes may be needed before the glovebox size and reaction rate constraints are fully met.

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