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Los Alamos
NATIONAL LABORATORY

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ABSTRACT

This report describes tests on a proposed flowsheet designed to stabilize combustible residues that were generated at the Rocky Flats Environmental Technology Site (RFETS) during the machining of plutonium metal. Combustible residues are essentially laboratory trash contaminated with halogenated organic solvents and plutonium metal. The proposed flowsheet, designed by RFETS, follows a glovebox procedure that includes 1) the sorting and shredding of materials, 2) a low temperature thermal desorption of solvents from the combustible materials, 3) an oxidation of plutonium metal with steam, and 4) packaging of the stabilized residues. The role of Los Alamos National Laboratory (LANL) in this study was to determine parameters for the low temperature thermal desorption and steam oxidation steps. Thermal desorption of carbon tetrachloride (CCl_4) was examined using a heated air stream on a Rocky Flats combustible residue surrogate contaminated with CCl_4. Three particle sizes of plutonium metal were oxidized with steam in a LANL glovebox to determine the effectiveness of this procedure for residue stabilization. The LANL results show that these two steps will take significantly longer to perform than originally thought; 12 hours will be needed to process one 500 gram batch of combustible residues.

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LIST OF ACRONYMS

CST	Chemical Science and Technology
DOT	Department of Transportation
DTA	Differential Thermal Analysis
HEPA	High-Efficiency Particulate Air
ISSC	Interim Safe Storage Criteria
LANL	Los Alamos National Laboratory
NMT	Nuclear Materials Technology
RFETS	Rocky Flats Environmental Technology Site
PI	Pressure Indicator
PID	Proportional/Integral/Derivative
PLC	Process Logic Controller
STP	Standard Temperature and Pressure
TE	Temperature Element (thermocouple)
TRU	Transuranic
WIPP	Waste Isolation Pilot Plant
WIPP-WAC	Waste Isolation Pilot Plant Waste Acceptance Criteria

BACKGROUND

During plutonium machining operations, the Rocky Flats Environmental Technology Site (RFETS) generated approximately 2.5 metric tons (145 drums) of combustible residues. Combustible residues (sometimes referred to as organic wet combustibles) are a heterogeneous mix of cellulosic (paper, towels, coveralls, etc.) and rubber materials (booties, gloves, etc.) that are essentially the trash coming from the machining operations. These residues are considered high risk because they contain solvents (predominantly carbon tetrachloride, CCl_4), cutting oils, and pyrophoric plutonium metal. The core unit operations of the proposed combustible residues stabilization process consists of a low temperature thermal desorption step to remove volatile organic contaminants followed by a steam passivation step to convert plutonium metal to the oxide.

Stabilization Criteria: The product of the combustible residues stabilization process is required to meet a strict set of criteria identified by a number of sources such as the Criteria for Interim Safe Storage (ISSC) of Plutonium-Bearing Solid Materials,[1] the Waste Isolation Pilot Plant Waste Acceptance Criteria (WIPP-WAC),[2] and Department of Transportation (DOT) regulations.[3] Listed below is a summary of the criteria that the stabilized combustible residues need to meet.

- No gas generation should occur when the stabilized product is immersed in water.
- The headspace of the 55 gallon drum containing the stabilized product should have less than 7510 ppm CCl_4.
- The free liquid in the 55 gallon drum containing the stabilized product should be less than 2 liters with a pH between 2 and 12.
- The stabilized product can not be pyrophoric.
- The Differential Thermal Analysis (DTA) of the stabilized product can not have an exotherm below 60°C.

RFETS Flowsheet: RFETS personnel proposed a flowsheet for stabilizing the combustible residues.[4] Details of the RFETS stabilization process, illustrated in Figure 1, include opening fifty-five gallon drums of combustible residues in a contamination control area, bagging the drum contents, and transferring them into a glovebox. Within the glovebox, non-combustible material will be separated from the combustible residues; the combustible feed materials will then be mechanically shredded into 0.25 to 1 inch square debris. Small batches of the shredded combustible material (500 grams) will be placed into nylon mesh bags and loaded into 2 gallon Parr® pressure reactors; five reactors will be used in the process. Volatilization of organic solvent contaminants will be achieved by low temperature thermal desorption either under slight vacuum or with an air or nitrogen flow.

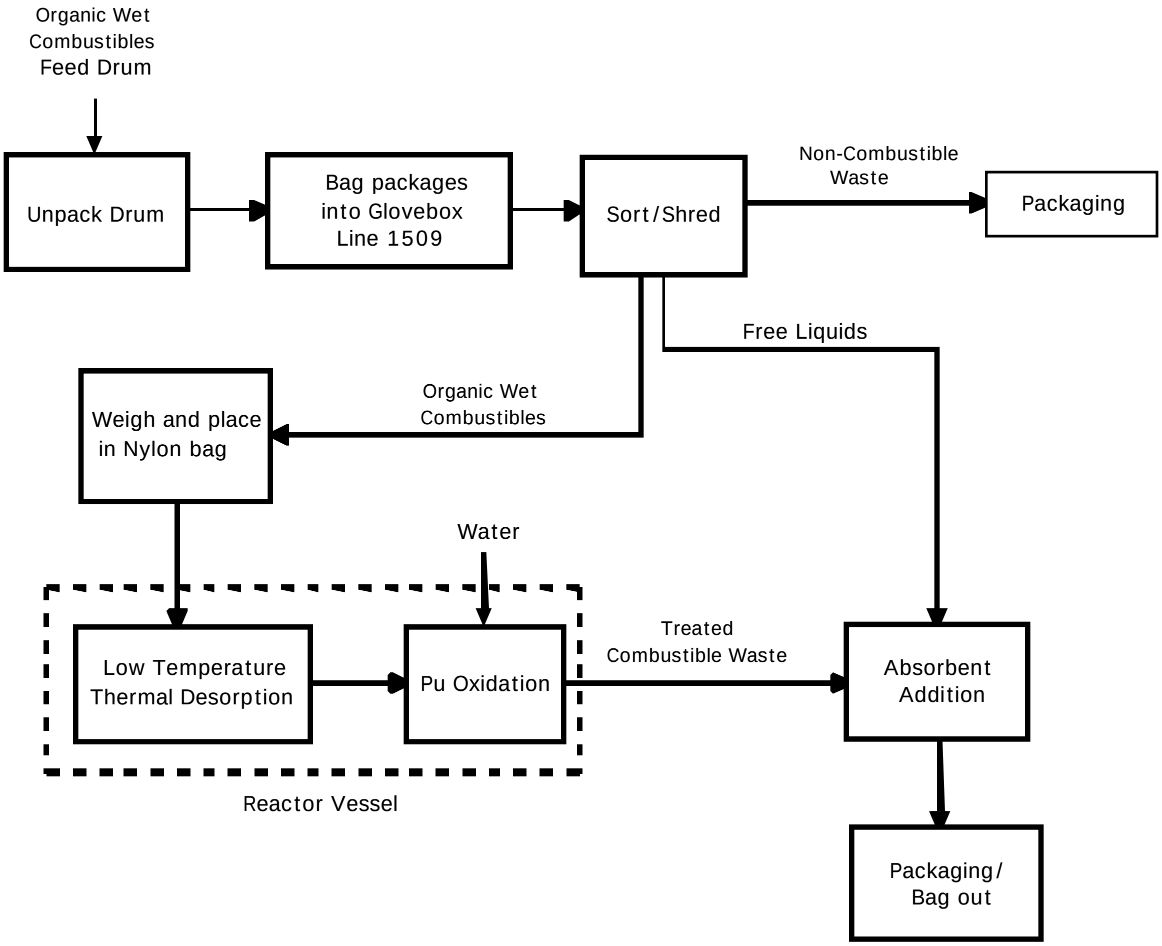


Figure 1. RFETS Flowsheet for Stabilizing Combustibles Residues Contaminated with Plutonium Metal and Organic Solvents.

The reactor will be sealed after thermal desorption and steam or hot water will be introduced into the vessel. Steam will be used to convert the plutonium metal to a non-pyrophoric plutonium oxide. The allotted time for the desorption and metal conversion step is two hours. After passivation, the vessel and contents will be cooled, the vessel vented, and the combustible material removed. Finally, the treated combustibles will be packaged with an inert absorbent material to absorb any free water and drummed for storage and eventual shipment to WIPP.

Parr® Reactor System: The reactor system to be used at RFETS consists of a 2 gallon Parr® pressure reactor made from C276 alloy and a Parr® model 4843 cascade controller. A similar system was used in the LANL low temperature steam oxidation studies. The system is described in Figure 2. The reactor heater system has an aluminum block electric heater with internal cooling water coil. The controller

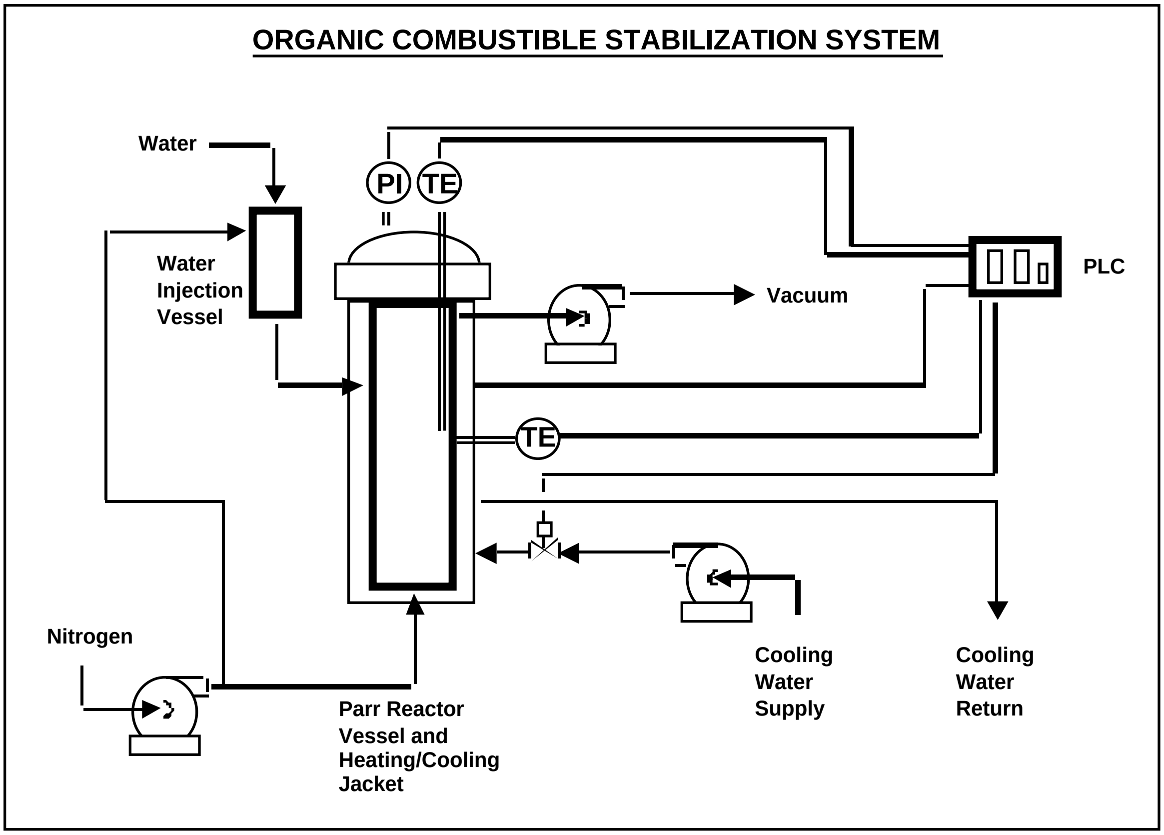


Figure 2. Parr® Reactor System.

system uses internal and external thermocouples to maintain the internal reactor temperature at the desired process temperature. A stainless steel, 1-L, vessel is used to introduce hot water into the reactor. The hot water is directed against the wall of the reactor to generate steam.

LANL Demonstration and Testing: Because many of the operating parameters for the RFETS process were undefined, it was necessary for LANL to determine the operational parameters for the two main steps of this process; the low temperature thermal desorption and the conversion of plutonium metal to oxide with steam. One parameter that was originally set for these two steps was the total time to perform them. In order to meet processing schedules, a total of 2 hours were allotted for these steps. We have performed preliminary work on this project using cerium as a surrogate metal for plutonium.[5,6] That work defined the temperature limits for operating the reactor. The low melting point of some of the plastic materials and the onset of charring by the cellulosic materials maximized the operational temperature at 130°C. Fortunately the oxidation rate of pure plutonium metal by steam has a maximum at 110°C.[7] Oxidation studies on cerium metal confirmed that oil coated cerium is oxidized slowly by boiling water or steam at ambient pressure. At the elevation in Los Alamos (~7500') this occurs at a temperature of ~93°C. With the aid of a Parr® reactor steam was produced at ~110°C and 10-20 psi. This enabled us to oxidize 1 to 2 grams of oil coated cerium in 2 hours. In addition, this work determined that an equal weight of water was required to completely wet the combustible residue surrogate material. This information was useful for setting up the thermal desorption and plutonium metal oxidation experiments described in this report. The work described below is for "wet surrogate" (oil coated cellulosic and plastic materials) containing CCl_4 or plutonium alloy. The report covers experiments on handling and dealing with the removal of CCl_4 from wet surrogate and steam oxidation experiments that attempted to convert three sizes of plutonium metal (turnings, >40 mesh, and <40 mesh) to an oxide within the wet surrogate matrix.

EXPERIMENTAL

Preparation of Surrogate

Preparation of Cutting Oils: The two cutting oils used in machining operations at RFETS were Texaco Transultex-A, a low viscosity cutting oil, and Texaco Transultex-H, a very high viscosity cutting oil. This work obtained the oils from Berridge Distributing company in Santa Fe, NM. A 50/50 weight percentage mix was prepared. This mixture will be referred to as the "cutting oil mix".

Preparation of Dry Surrogate: "Dry surrogate" was obtained from Safe Sites of Colorado located at the RFETS. The composition is given in Table 1. The weight percent of the components that make up the dry surrogate result in a 50/50 weight percent mix of cellulosic and plastic material. This material was shredded into 0.25 to 1 inch square debris before sending to LANL.

Table 1. Dry Surrogate Composition

Material	Weight Percent
Kimwipes/Paper Towels	50
Polyethylene Bags	18
PVC Bags	9
Cotton Cloth/Coveralls	8
Rubber/Surgeon Gloves	5
Rubber Booties/Overshoes	4
Cloth Booties/Overshoes	4
Anti-C Coveralls	1
Tyvek's	1
Total	100

Preparation of Wet Surrogate: A 28.6 weight percent oil-loaded surrogate was prepared by placing 4500 g of dry surrogate in a large polyethylene bag and adding 1800 g of the cutting oil mix, in small increments, while mixing thoroughly by hand. The homogenized oil-loaded surrogate is henceforth called "wet surrogate". The wet surrogate was stored in the sealed bag until needed.

Preparation of Wet Surrogate with Carbon Tetrachloride: An attempt was made to prepare a uniformly mixed surrogate/CCl_4 sample by slowly adding 200 g of CCl_4 to 500 g of wet surrogate in a 2 L beaker and mixing. This was repeated until all the CCl_4 was added to the wet surrogate. The mixture was then transferred to a hop sack (a 10" x 24" coarse mesh nylon sack normally used for brewing beer, L. D. Carlson Kent, OH) and the sack placed into a 5.25" x 13" Rocky Flats stainless steel reactor basket. During this process, 80 of the 200 grams of CCl_4 were lost through evaporation. Because of this, all other additions of CCl_4 were poured directly into the bagged wet surrogate in the reactor (see below). This minimized CCl_4 evaporation during the addition and reduced the worker exposure to CCl_4, but obviously gave an unmixed CCl_4 / wet surrogate sample. The addition of 200 g of CCl_4 to 500 g of wet surrogate gave a 28.6 weight percent CCl_4 loaded wet surrogate. The addition of CCl_4 lowered the weight percent oil loading to 20.4%.

Low Temperature Thermal Desorption Experiments

Experimental Setup: A series of experiments was conducted to determine the parameters for desorbing CCl_4 from wet surrogate. A measured amount of wet surrogate (500 g) was added to a hop sack and placed in a Rocky Flats stainless steel reactor basket. The basket was placed inside a two gallon Parr® reactor that had been preheated to 50°C. The experimental set up is shown in Figure 3. This set up approximates the Rocky Flats system shown in Figure 2. The reactor was controlled with a Parr® 4842 PID controller that sensed the internal reactor temperature through a thermocouple located between the wall of the reactor and the reactor basket. Two hundred grams of CCl_4 were added to the surrogate after the basket was placed in the reactor. When replacing the reactor lid onto the body of the reactor, care was taken to position the surrogate thermocouple into the center of the surrogate; this precaution allowed us to obtain as accurate a reading as possible of the internal surrogate temperature. Desorbed CCl_4 was removed from the reactor by passing 110°C air through the reactor. Thermocouples were mounted on the inlet and outlet of the air purge lines. The reactor, surrogate, inlet air, exit air, and reactor pressure were monitored over time. The surrogate was re-weighed at the end of each experiment to determine CCl_4 weight loss.

Desorption Procedures: Carbon tetrachloride was removed by two experimental procedures.

- *No Induction Procedure:* In this procedure, 110°C air was passed through the reactor at 75 L/min immediately after adding CCl_4 to the wet surrogate and replacing the reactor lid. Although prior experiments had established that CCl_4 desorption was more efficient at faster flow rates, 75 L/min was the maximum achievable with the house air supply. Air was used because it provided an uninterrupted gas flow throughout the experiment. We observed no significant difference in the amount of CCl_4 removed per unit time between nitrogen and air at the same flow rate. Immediately after the CCl_4 was added, the reactor set point was raised to 110°C.

- *Induction Procedure:* The second procedure included a one hour induction period after adding CCl_4 to the wet surrogate. This was achieved by having the inlet and outlet air flow ports closed after sealing the reactor and keeping them closed for 1 hour. The reactor set point was raised to 110°C at the start of the

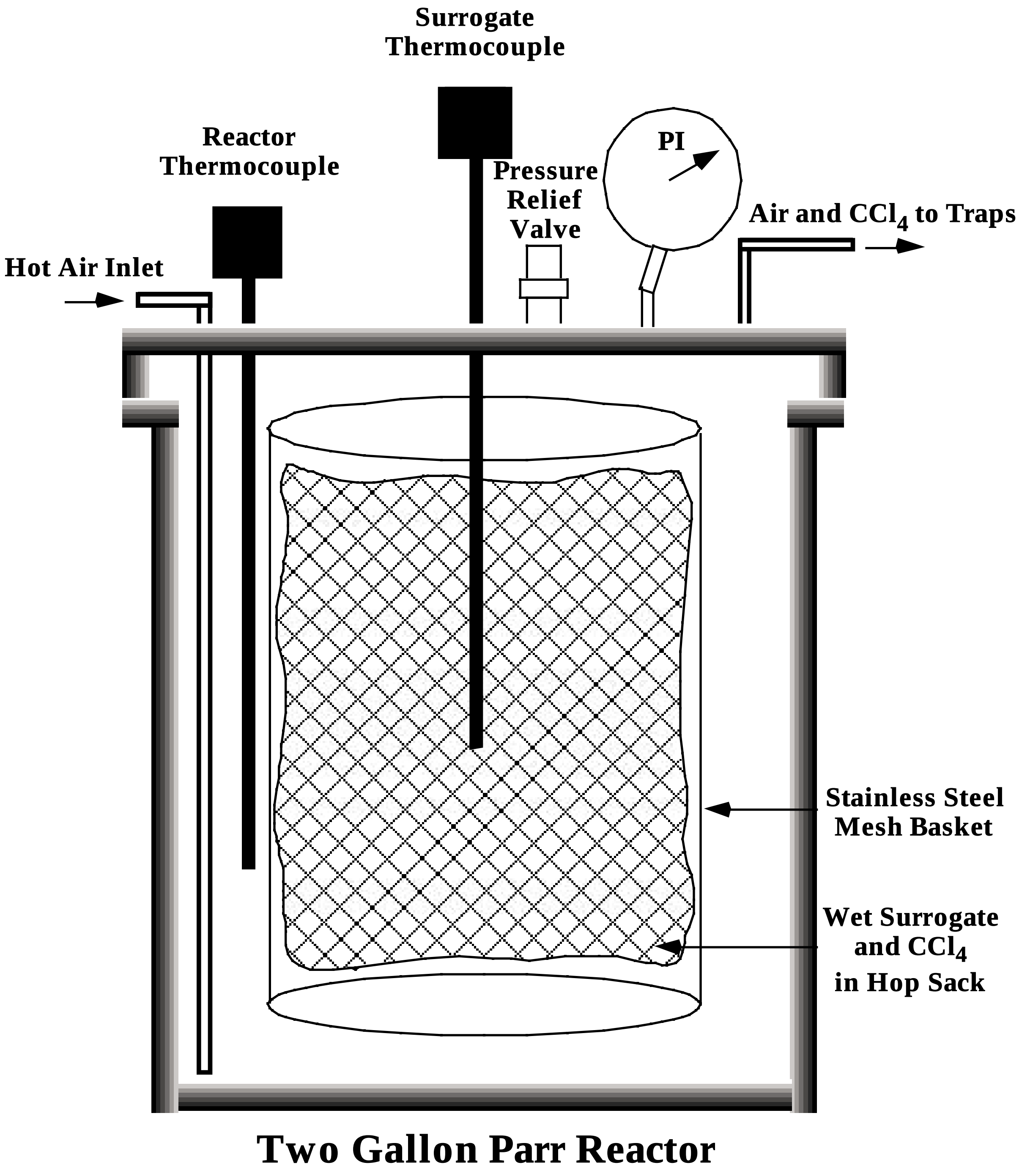


Figure 3. Two Gallon Parr® Reactor Used for Carbon Tetrachloride Desorption Experiments.

induction period. The induction period's purpose was to allow CCl_4 vapors to serve as a heat transfer fluid that would raise the internal surrogate temperature at a faster rates. Temperature/pressure data were collected during the induction period. After one hour, the average temperature of the surrogate was ~80°C. At this point the 75 L/min air flow was started and temperature/pressure data collected over time.

Trapping of Carbon Tetrachloride: Attempts were made to trap desorbed CCl_4 entrained in the off-gas in order to measure the effectiveness of our CCl_4 removal process**.** The trapping system consisted of filters (to trap surrogate lint), copper cooling coils, 500 mL cold traps, Swagelok fittings, stainless steel tubing, flow valves, Tygon tubing and Dewars. A flexible tube was attached with a quick disconnect from the reactor unit to a 140 micron filter, 60 micron filter, and 7 micron HEPA filter series to trap surrogate lint. The filter series was then attached to a T-junction that allowed the air flow to be directed to a specific trapping vessel; the air flow was directed to one trapping vessel at a time. Each junction was attached with Tygon tubing to a copper cooling coil that was then attached to a cold trap. The cold traps were vented into a laboratory hood. Three cooling schemes were examined:

- A copper cooling coil cooled with ice water in series with a cold trap cooled in a dry ice/ethylene glycol (-15°C) slush bath. The cold trap was weighed every 15 minutes.
- A copper cooling coil cooled with a dry ice/ethylene glycol (-15°C) slush bath in series with a cold trap cooled with a dry ice/acetone (-77°C) slush bath. The cold traps were weighed every 15 minutes.
- A copper cooling coil cooled with a dry ice/acetone (-77°C) slush bath in series with a cold trap cooled with liquid nitrogen (-196°C). This set up caused plugging of the cold trap outlet by condensed CCl_4; for safety reasons, we abandoned this method.

Carbon Tetrachloride Analysis: Gas samples were taken from the head space of the Parr® reactor by attaching a 100 mL gas tight syringe, fitted with a threaded syringe connector, that interfaced to the reactor through a quick disconnect fitting. Samples of the head space gas were taken after the post-desorption wet surrogate temperature reached 110°C. At this point the reactor air flow was stopped and the reactor was sealed for 10 minutes. The syringe was attached, the valve to the sample port was opened, and a full syringe of sample was withdrawn, the valved closed, and the syringe expelled into the hood; this was repeated three times before the actual sample for analysis was taken. Three samples were then drawn into three separate 100 mL syringes. These samples were analyzed for CCl_4 by GC/MS. The procedure is a DOE approved method for analyzing drum headspaces for volatile compounds.[8] An average value of 634 ± 160 ppm CCl_4 was obtained for six samples from two induction experiments. The blank averaged 13 ± 2 ppm CCl_4 for an experiment following the induction procedure with no CCl_4 added.

Reheating of Surrogate with Hot Water: After the CCl_4 desorption, various amounts of hot (>90°C) water were added to the hot (~95°C) wet surrogate to determine the amount of water that would be needed to quickly bring plutonium-containing desorbed surrogate to >100°C. After opening the reactor, water was added to the center of the surrogate, the reactor was re-sealed and the surrogate temperature measured as a function of time. After these initial experiments, two hot water (90°C) injections experiments were performed with the glovebox reactor configured similar to Figure 2. These experiments injected 500 and 600 mL of water onto the wall of a hot reactor containing 500 grams of 25°C wet surrogate; this was done to produce as much steam as possible within a short amount of time.

After the temperatures profiles of the water addition experiments were completed, the water was desorbed from the wet surrogate using a 110°C air flow of 75 L/min. The reactor, surrogate, inlet air, exit air, and reactor pressure were monitored over time. The surrogate was re-weighed at the end of each experiment to determine water loss; on average, 3 grams of water were removed per minute.

Plutonium Oxidation Experiments

Glovebox Reactor: A Parr® reactor system was installed in a Vacuum Atmospheres glovebox operating, under argon, at a negative pressure of 0.25-0.5" (water column). The system is similar to the one described in Figure 2. A Parr® Model 4843 cascade controller used the temperature of an internal thermocouple relative to an external thermocouple that touched the outside of the reactor wall to adjust the reactor temperature. These experiments were not preceded by a CCl_4 desorption step because preliminary experiments showed that this led to excessive corrosion of the glovebox reactor; presumably HCl produced by the reaction of CCl_4 and water led to this corrosion. No air or nitrogen flowed through the reactor during the oxidation runs. A port at the top of the reactor was valved through a 7 micron HEPA filter to an external pump. Through appropriate valving, the pump was used to charge the water addition vessel with water and then inject it into the reactor. Heating tape around the vessel allowed the water to be warmed to 90°C prior to injection.

Plutonium Metal Samples: Three sizes of plutonium alloy samples were obtained from LANL's Plutonium Facility. Turnings, ~0.3 mm in diameter, random length and curled, were obtained from machining a block of plutonium alloy. Two mesh sizes of plutonium alloy were prepared by sawing rods of plutonium alloy. The sawdust was sieved through a 40 mesh screen to produce <40 mesh and > 40 mesh fractions. The >40 mesh material was potentially larger in diameter than the turnings, ~0.6 mm. After preparation, all the samples were submerged in the cutting oil mix and stored in the oil until use; this was done to retard oxidation of the metals.

Plutonium Metal Analysis: The metal content of the three types of plutonium was determined by allowing weighed amounts (~0.5 grams) of each metal to react with 1-

1.9 M sulfamic acid (NH_2SO_3H) in a 290 mL Parr® pressure reactor.[9] The H_2 gas pressure generated from the reaction was monitored with time. The glovebox temperature was also taken with time. A normal run required at least 8 hours. The reactor volume was corrected for the volume of reagents in the reactor to give the void volume.

Small Scale Oxidation vs. Time Experiments: Each plutonium experiment was configured as depicted in Figure 4. This consisted of a 100 mL support beaker that held a 50 mL beaker which in turn supported a 40 mL Coors Gooch crucible containing the plutonium / wet surrogate sample. A 9.0 cm Whatman #541 filter paper, folded in quarters, held ~0.5 g of plutonium metal mixed into 2.5 g of wet surrogate. The crucible was used to prevent water from pooling within the plutonium / wet surrogate sample. A Kimwipe in the 50 mL beaker that contacted the bottom of crucible initiated the flow of water by a wicking action. For each oxidation run, three individual samples were prepared using the three plutonium metal types. Before mixing with the surrogate, the metal was washed with hexane, weighed, and then re-oiled with the cutting oil mix. The turnings were chopped before weighing so that they could be more easily mixed with the wet surrogate.

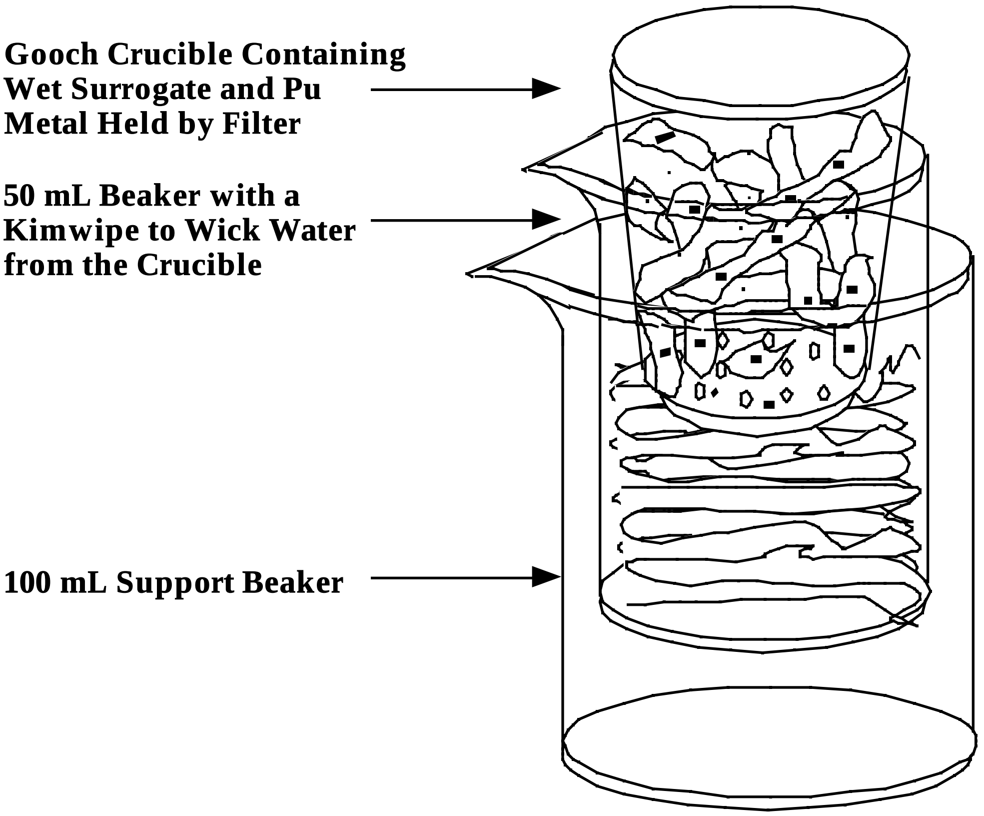


Figure 4. Apparatus for Small Scale Steam Oxidation Experiments.

One sample of each of the plutonium metal types was configured as in Figure 4, then placed into the reactor basket, which was then put inside the 2 gallon Parr® reactor containing 100 mL of water. The reactor was brought from ambient temperature to 110°C, a process that took ~90 minutes. The internal temperature of the reactor above the samples, the temperature of reactor external wall, and the reactor pressure were monitored with time. Time for the oxidation started when the internal temperature reached 110°C and continued for the desired length of time. Reactor pressure at ~110°C ranged between 25 and 40 psi during this time. When the oxidation time was complete, the reactor was cooled and the samples removed after the internal temperature was <40°C. The pH of the water and moist surrogate was taken with pH paper and the characteristics of the plutonium/surrogate sample noted. Black plutonium oxide produced from the oxidation smeared and discolored the wet surrogate material. This made it difficult to see how much metal was left in the sample. This also prevented recovering and weighing remaining unreacted metal fragments from the wet surrogate.

Determination of Metal Content in a Plutonium/Surrogate Sample: The filter containing the plutonium/wet surrogate sample, the Kimwipe, and the condensed water (~20 mL) from the 50 mL beaker were transferred to a 100 mL polypropylene beaker and then placed into a 290 mL Parr® reactor. The plutonium/wet surrogate sample was tamped down to insure that it was submerged in the water. A 20 mL disposable polystyrene beaker containing ~13 mL of either 1.0 or 1.9 M sulfamic acid was carefully placed on top of the surrogate material, and the reactor sealed. In some cases the sample was allowed to sit for 1 hour before mixing to determine if any gas generation occurred by the reaction of plutonium metal with water; in other cases, the sulfamic acid was immediately mixed with the sample. Pressure/temperature vs. time data were taken over the next 24 hours. After gas generation ceased, the sample was removed and examined. An absence of dark metal fragments and the presence of a purple solution indicated a complete reaction.

Differential Thermal Analysis: Samples consisting of wet surrogate, unoxidized plutonium turnings/wet surrogate, steam oxidized plutonium turnings/wet surrogate, steam oxidized >40 mesh plutonium/wet surrogate, and steam oxidized <40 mesh plutonium/wet surrogate were submitted for DTA analysis. Approximately 2.5 grams of wet surrogate and 0.3-0.5 grams of plutonium were used in these samples; the oxidation procedure was as described above. The oxidized samples went through a two hour steam oxidation. Systag Radix Solo model 3 ovens were used for the analyses, controlled by Systag RCI88 controllers. The analyses were performed over a temperature range of 25˚C to 185˚C, at a linear scan rate of 2˚/minute.

RESULTS AND DISCUSSION

Low Temperature Carbon Tetrachloride Desorption Experiments: The surrogate material, when placed into the hop sack, has poor heat and mass transfer properties. These characteristics retard the desorption of volatile species from the surrogate using the reactor setup. We have compared the desorption of CCl_4 from the surrogate using two different methods in effort to increase the efficiency of this process. Representative heating profiles for CCl_4 removal under no induction and induction conditions are shown in Figures 5 and 6. Both methods attempted to desorb 200 grams of CCl_4 from 500 grams of wet surrogate. The no induction method immediately began with a continuous flow of 110°C air at 75 L/minute as

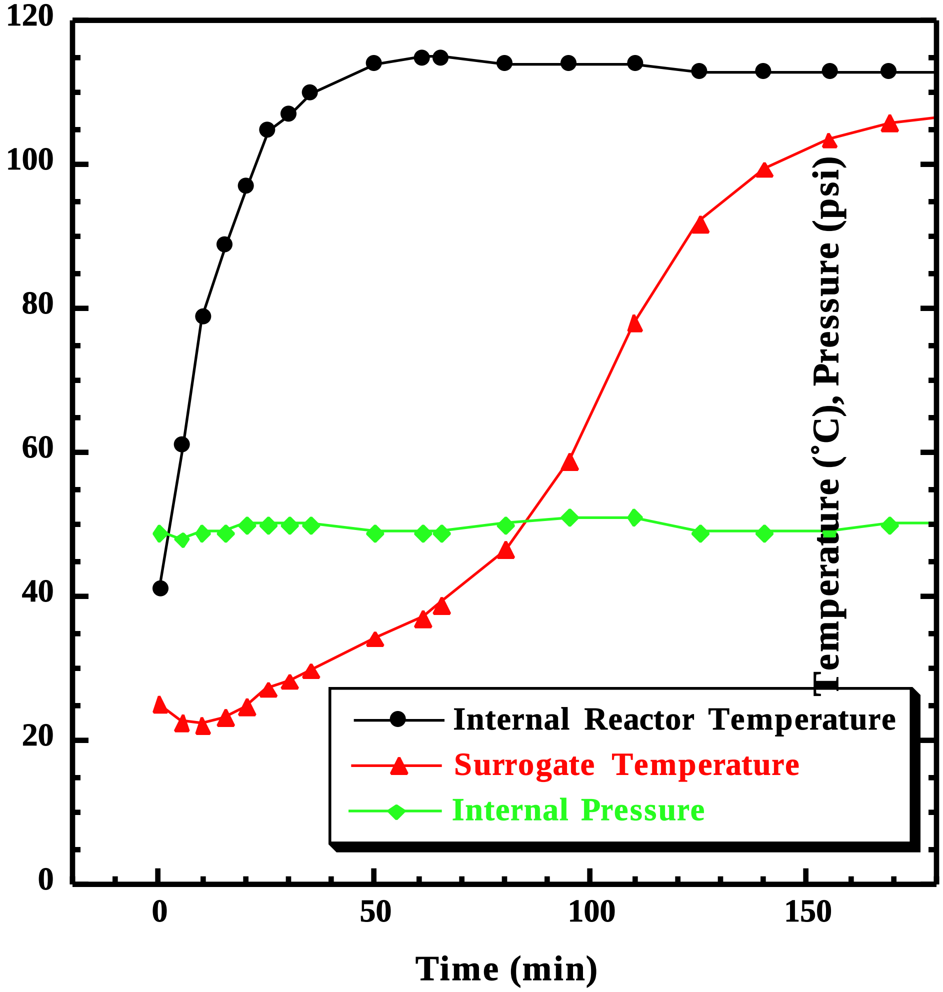


Figure 5. Representative Heating Profile for No Induction Conditions.

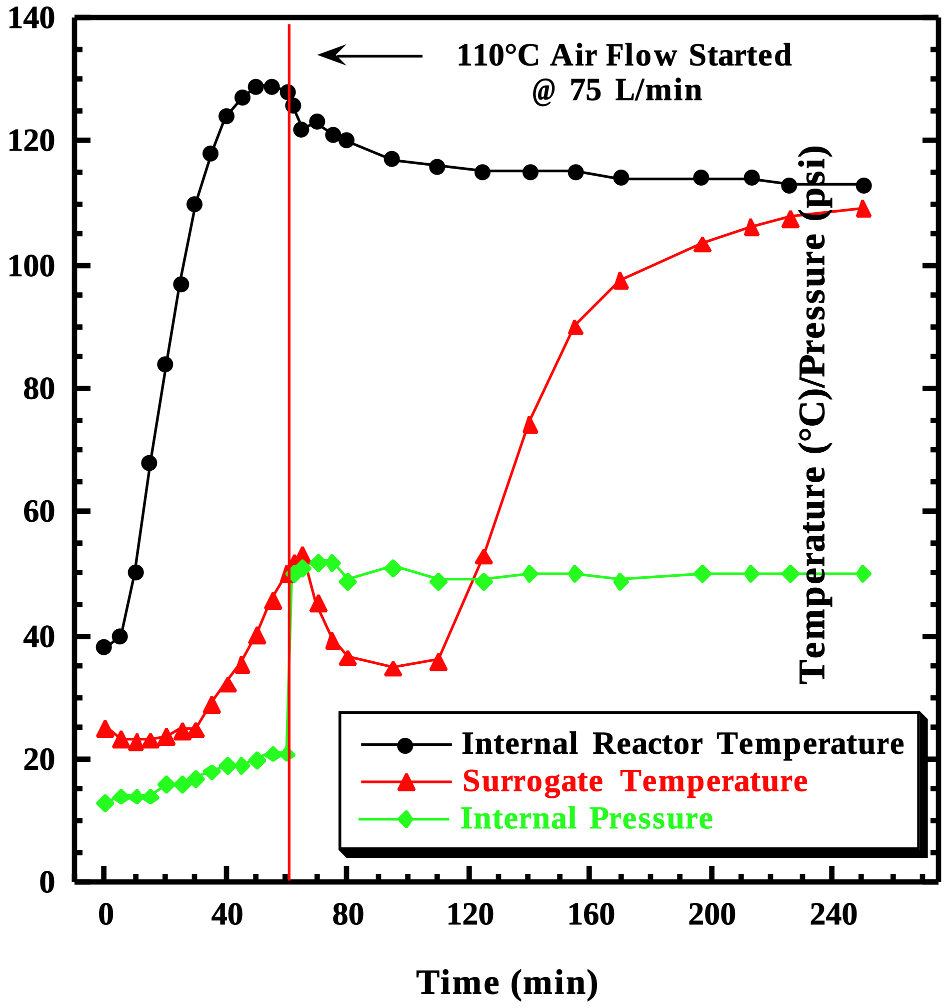


Figure 6. Representative Heating Profile for Induction Conditions.

the reactor was brought from 50°C to 110°C. The induction method delayed the air flow for one hour while the reactor was brought to temperature. Both methods showed an initial cooling of the surrogate during the first 20 minutes due to evaporative cooling as the CCl_4 vaporized. The no induction method showed a slow rise in temperature in the surrogate temperature over the next 50 minutes. After 70 minutes, the rate of temperature rise increased, suggesting that most of the CCl_4 was gone and evaporative cooling effects were no longer slowing the warming of the surrogate. The induction method was an attempt to speed up the desorption process by using volatilized CCl_4 as a heat transfer fluid. Higher surrogate temperatures were obtained during the induction period, but as soon as the air flow was started evaporative cooling effects quickly dropped the surrogate temperature to a level comparable to the no induction method prior to its more rapid temperature rise beyond the 70 minute point.

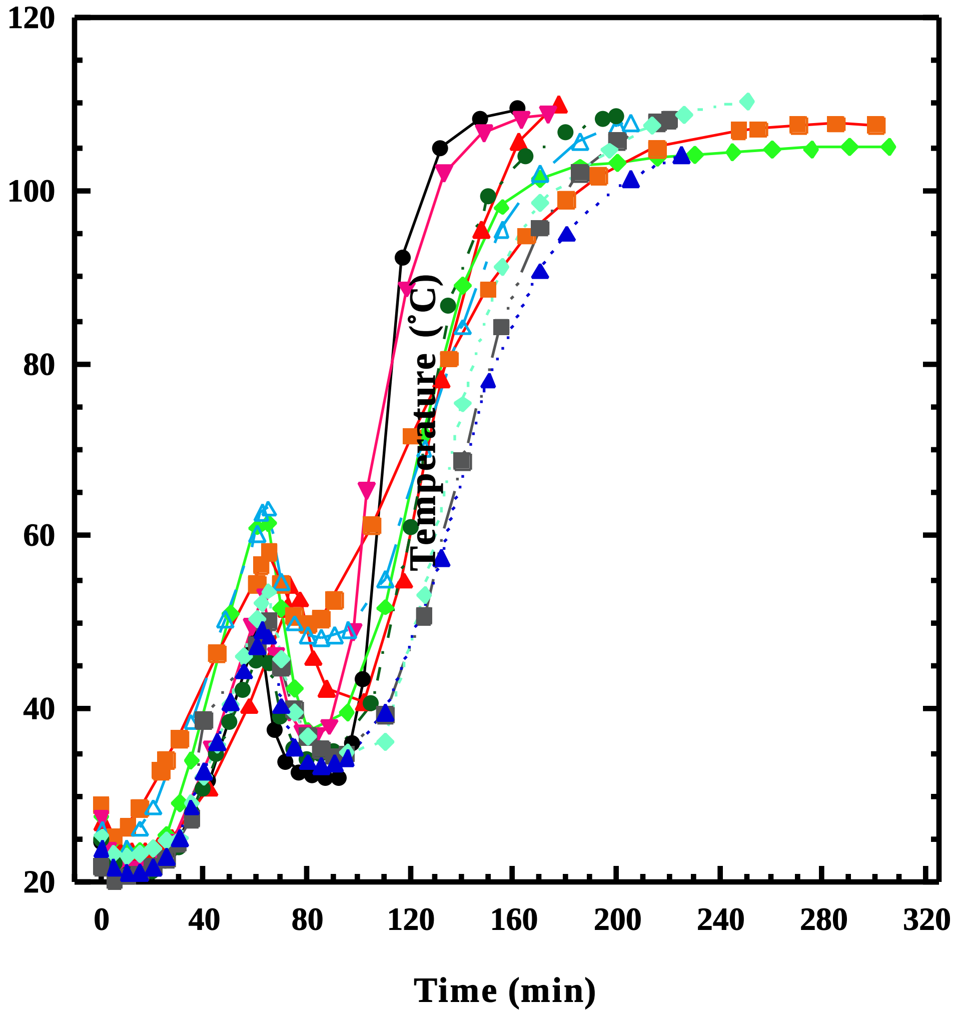


Figure 7. Carbon Tetrachloride Desorption Experiments Using Induction Conditions.

Multiple experiments using both methods were run to determine the average time it took for the surrogate to reach 105°C. The average time for 10 induction runs, including the 60 minutes induction period, was 192 ± 43 minutes. These runs are shown in Figure 7. This compares to 169 ± 68 minutes for 6 runs using the no induction method. The large standard deviations obtained for the desorption methods are attributed to variability in the packing of surrogate, placement of CCl_4 in the surrogate, and placement of thermocouple in surrogate. Surrogate composition and the size of the cut may also effect heat transfer.

Since there are no plans to monitor the CCl_4 desorption it may be necessary to run either desorption process for the average time plus one standard deviation. This is ~235 minutes for both methods. Thus, there is no clear advantage to using either method. This time period may be too conservative since the head space analysis showed an average of 634 ± 160 ppm CCl_4 at the end of an average induction desorption run (~200 min), indicating that >98% of the CCl_4 was removed; the surrogate contained <0.7% weight percent CCl_4. This is well below the criteria of 7510 ppm CCl_4 required for stabilized combustible residues.[2]

The criterion for CCl_4 removal however is not the only important concern. We experienced serious corrosion problems with the glovebox reactor and equipment. Much of this has to do with the moist environment that is produced by the oxidation step (see below). We eliminated desorption experiments in the glovebox because of the extra corrosion caused by HCl produced from the reaction of residual CCl_4 with the water added in the subsequent steam oxidation step. Thus, removing as much CCl_4 as possible may increase the overall throughput of the process by eliminating some of the downtime required to repair or replace corroded equipment.

There was no difference between using air or nitrogen for the CCl_4 desorption. The reactor and surrogate heating profiles were the same and both removed CCl_4 with the same efficiency. The Rocky Flats process plans to use five reactors; these reactors will have their hot (>200°C) outer surfaces exposed. Because the shredded surrogate tends to get dispersed throughout the glovebox, it is advisable to use nitrogen to retard any combustion that may occur when combustible material contacts the hot reactor surfaces.

Other problems that need to be rectified are the trapping of CCl_4. We were unsuccessful in doing this at the flow rates used in this process. We also noted that some oil distilled with both the CCl_4 and water removal portions of our experiments. A thin film of cutting oil was also dispersed throughout the Parr® reactor outlet manifold.

Finally, the inefficiency of the desorption methods begs the question: are there more efficient methods for desorption? In our opinion, desorption of CCl_4 or other volatiles would be more efficient when the shredded material is dispersed. We lost 80 grams of CCl_4 in 10 minutes while trying to prepare a homogenized CCl_4/surrogate sample. Since an off-gas system is required for the shredding operation, it might be a better idea to desorb CCl_4 during this operation while the material is highly dispersed.

Reheating of Surrogate with Hot Water: After desorption of volatile organics from the combustible residues, the plutonium metal in these materials needs to be converted to an oxide by steam oxidation. Haschke, Allen, and Stakebake have shown that plutonium corrosion (oxidization) rates by steam achieve a maximum at 110°C.[7] The rate falls off at higher and lower temperatures. This is fortunate for the stabilization process since the material in the combustible residues either starts to char or melt above 130°C. Obtaining and maintaining a temperature of 110 ± 10°C is thus a crucial requirement for this process.

The maximum plutonium loading expected for actual RFETS combustible residues is expected to be 8 weight percent. Stoichiometrically, only 6 grams of water should be required to oxidize the 40 grams of plutonium present in 500 grams of combustible residues. Because the wet surrogate absorbs an equal weight of water and the fact that we have observed slow heat transfer from the reactor to the surrogate in our experiments, it was necessary to test the ability to achieve and hold the optimum operating temperature after water was added to the reactor.

Figure 8 shows how the temperature of the post-CCl_4 desorption wet surrogate varies with time as a function of the amount of water added. The average maximum temperatures measured for each water weight added are given in Table 2. The figure shows that even though hot (>90°C) water was being added to the hot (~95°C) wet surrogate, there was actually a 15-40°C decrease in the surrogate

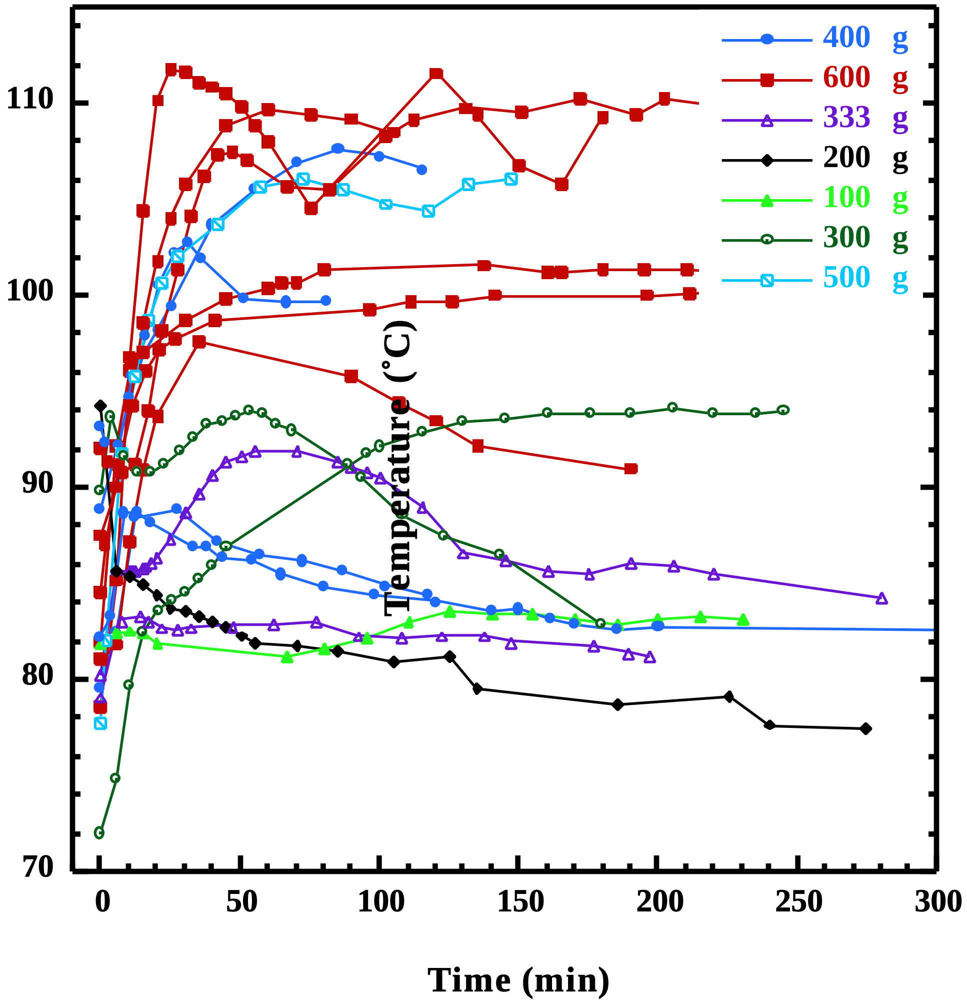


Figure 8. Heating Profiles for the Addition of Water to Surrogate after Carbon Tetrachloride Removal.

Table 2. Average Maximum Surrogate Temperature as a Function Water Added

Water Added (g)	Maximum Temperature (˚C)
100	94
200	84
300	94 ± 1
333	88 ± 6
400	97 ± 10
500	106
600	105 ± 6

temperature; this was most likely due to an evaporative cooling effect. The maximum temperatures were generally reached within 100 minutes after the addition of the boiling water to the reactor. Variability in the observed maximum surrogate temperatures was due to differences in the heating behavior of the Parr® reactor controller from one experiment to the next and the effect of different placement of the thermocouple in the surrogate for each experiment. Within the time limits of these experiments (≤300 minutes), none of the water additions of < 400 grams even reached 100°C and, in addition, tended to actually cool with time. Optimum temperatures (>100°C) are achieved with the addition of >400 grams of water. Because the surrogate can absorb an almost equal weight of water and the fact that the two 400 gram additions showed a decrease in temperature with time suggest that >500 grams of water may be required to achieve and maintain the optimum oxidation temperatures. The 500 gram threshold is consistent with the water sorbing properties of the wet surrogate. An additional 100 grams of water may generate enough free steam to act as heat transfer fluid to maintain the operating temperature within the wet surrogate.

Test were made of these conclusions with the glovebox reactor system since it more realistically simulates the RFETS apparatus Figure 2. Figures 9 and 10, respectively, show the internal and external temperature profiles for the injection of 500 and 600 grams of 90°C water onto the walls of a hot reactor containing 500 grams of 25°C wet surrogate. The initial 70 and 100 minutes of Figures 9 and 10, respectively, merely show the warming of the reactor to 110°C without the surrogate in it. An open container of water (~1 L) in the reactor facilitated this process. Notice how the internal and external temperatures parallel each other. At this point the can of water was replaced with the Rocky Flats basket containing the hop sack of wet surrogate. The 500 gram water addition, initiated at 85 minutes, shows that the surrogate temperature rapidly increased from 25°C to 100°C in less than 10 minutes. However, the surrogate temperature remained at 100°C for 20 minutes even as the reactor controller continued to instruct the reactor to heat in order to drive the surrogate temperature of 110°C. The unresponsive nature of the surrogate temperature to reactor heating is apparently due to little or no free water being

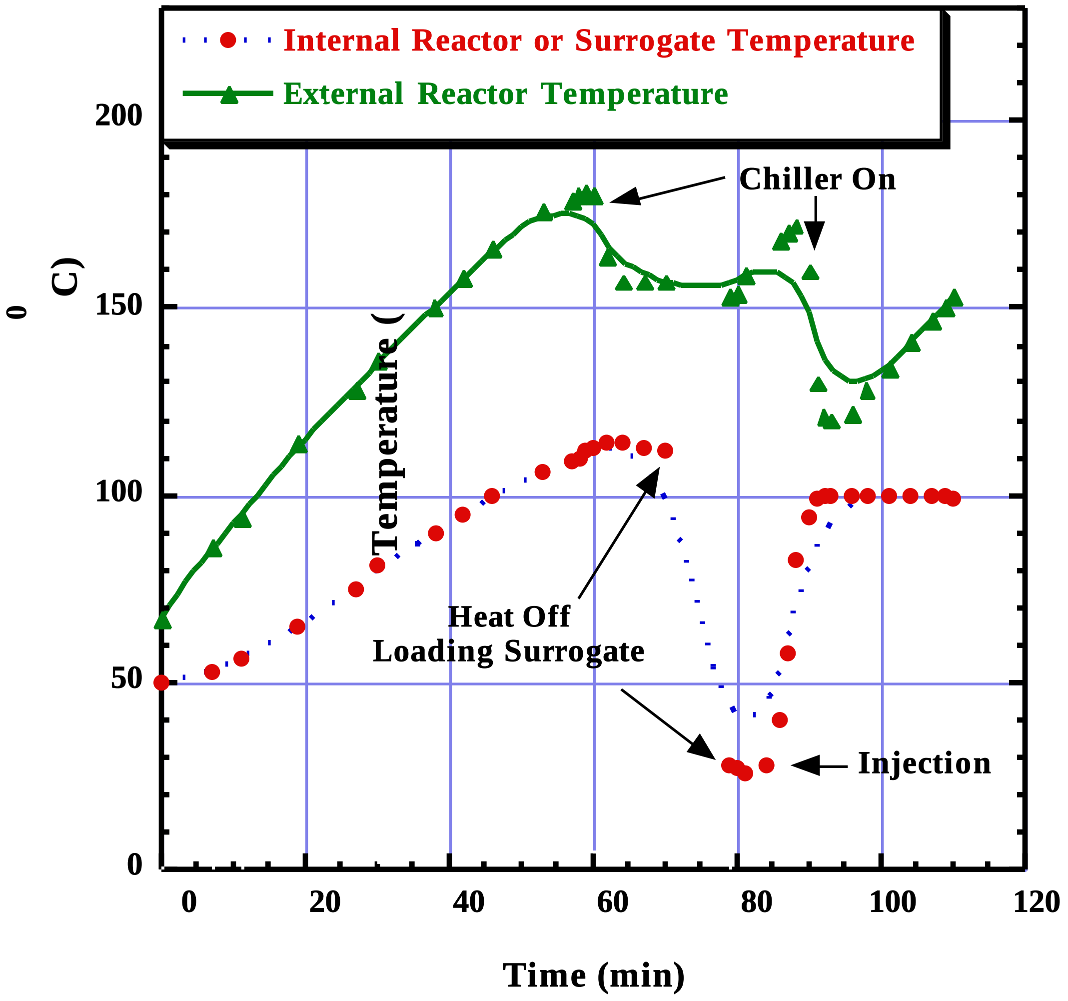


Figure 9. Temperature Profile for the Injection of 500 g of 90°C Water into 25°C Wet Surrogate.

available to transfer heat from the reactor wall to the surrogate. On opening the reactor, no free water was observed in the bottom of the reactor; all of the water was sorbed by the surrogate. In contrast, the 600 gram injection, initiated at 105 minutes, showed that the surrogate did respond to the reactor temperature; from 120 through 170 minutes the surrogate temperature profile roughly mimics the external temperature profile. The extra water presumably allowed sufficient free steam to act as a heat transfer fluid in this system; on opening the reactor, free water was observed in the bottom of the reactor.

Six 500 gram samples of stabilized combustible residues will be shipped in each drum to WIPP. If more than 333 mL of water are required to carry out the oxidation of each sample, then a drying step will be needed to insure that the drum does not exceed the WIPP-WAC limit of two liters of free water per drum[2]. To remedy this

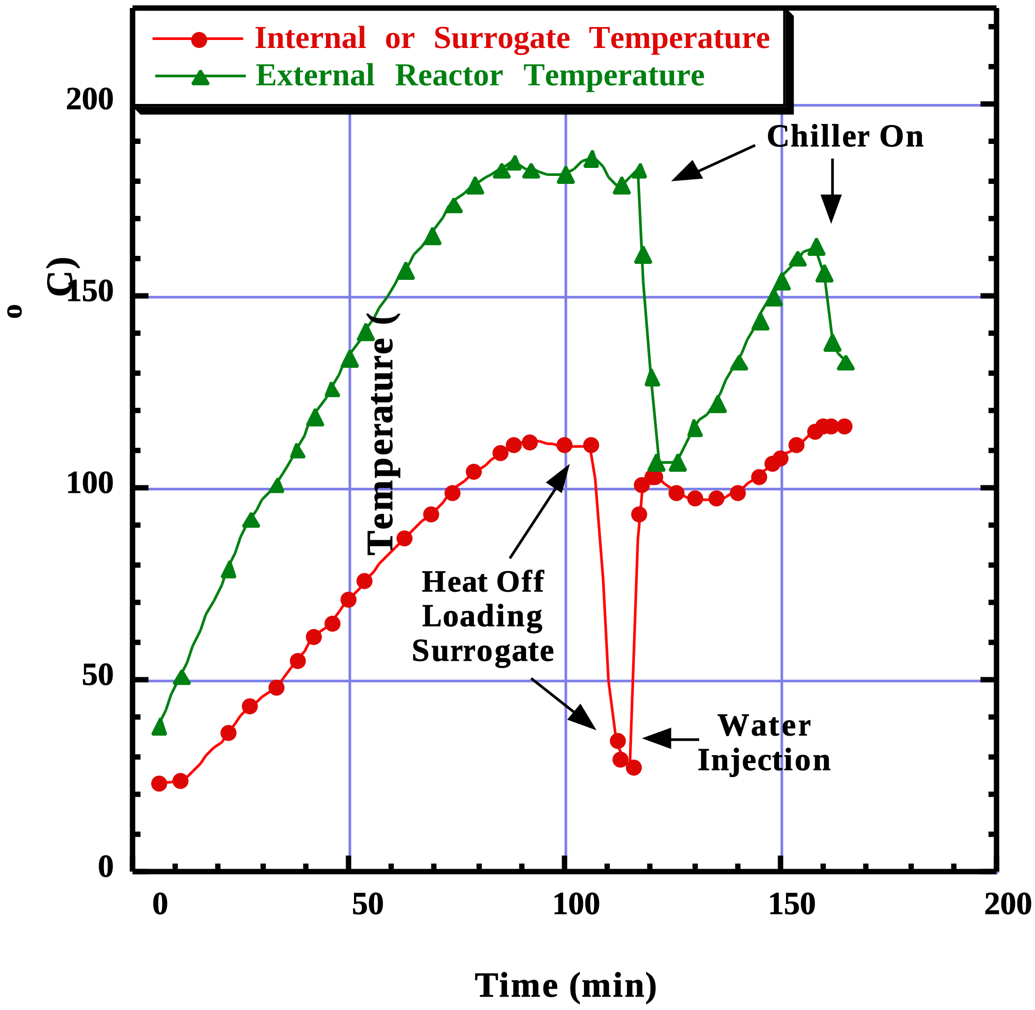


Figure 10. Temperature of Profile for the Injection of 600 g of 90°C Water into 25°C Wet Surrogate.

problem we desorbed excess water from the samples at an average rate of 3 g/min using a 75 L min 110°C air flow. Unfortunately, this will require more processing time than originally purposed by the RFETS flowsheet. This desorbed water will also produce a potential secondary waste water problem. On the positive side, desorbing the water into the off-gas system, followed by reactor cooling, will eliminate much of the condensation within the glovebox. This is helpful in preventing equipment corrosion and enhances the safety of the operation because it reduces glovebox windows fogging that can obstruct worker vision.

Plutonium Oxidation Studies: Oxidation of unstabilized plutonium metal with steam is reported to be rapid at 110°C, with phase-stabilized plutonium reacting 10^{-5} times slower.[7] RFETS combustible residues generated during machining activities are expected to be of the latter type. We therefore studied the oxidation of phase-stabilized plutonium that was of three particle size distributions: turnings which were ~0.3 mm in diameter that were of random length and were curled, > 40 mesh material, and <40 mesh fines. The turnings were cut to shorter lengths so we could make a more homogenous sample. The >40 mesh material actually had a larger diameter than the turnings (0.6 mm), but with a shorter length. The metal content of the three types of plutonium was determined by allowing weighed quantities of the alloys to react with an excess of sulfamic acid. Sulfamic acid reacts with plutonium metal according to the stoichiometry given in equation 1.[9] The pressure

$$\mathrm{Pu} + 3\mathrm{NH_2SO_3H} \longrightarrow \mathrm{Pu^{3+}} + 3\mathrm{NH_2SO_3^-} + 1.5\mathrm{H_2} \qquad (1)$$

from the H_2 gas generated can be measured to determine the amount of metal present. The stoichiometry of this reaction was tested with cerium prior to using it as a tool to determine plutonium metal content. The expected amount of gas generated for the total oxidization of Ce to Ce^{3+} was measured in these preliminary experiments, indicating that this method is directly applicable to Pu oxidizing to Pu^{3+}. Normally, HCl would be allowed to react with the metal, but the corrosive properties of HCl on stainless steel prevented us from performing these experiments in our glovebox and with the small Parr® reactor. Sulfamic acid is known to react quickly with plutonium metal without being corrosive to 316 stainless steel.[9] The theoretical pressure of the gas generated was calculated in torr at STP according to equation 2:

$$P(\mathrm{torr})_{\mathrm{theor}} = \frac{n\ R\ T\ (760)\ (1.5)}{V} \qquad (2)$$

where:
n = moles Pu (assume pure Pu)
R = 0.08205 L atm / mole °K
T = 273K
V = void volume (L) of the vessel (0.290 L - volume of sample)
760 = conversion factor from atm to torr
1.5 = stoichiometric factor for the moles H_2 generated per mole of Pu

The percent metal was calculated from equation 3:

$$\%\ \mathrm{Metal} = \frac{100\ [P(\mathrm{torr})_{\mathrm{exp}}]}{P(\mathrm{torr})_{\mathrm{theor}}} \qquad (3)$$

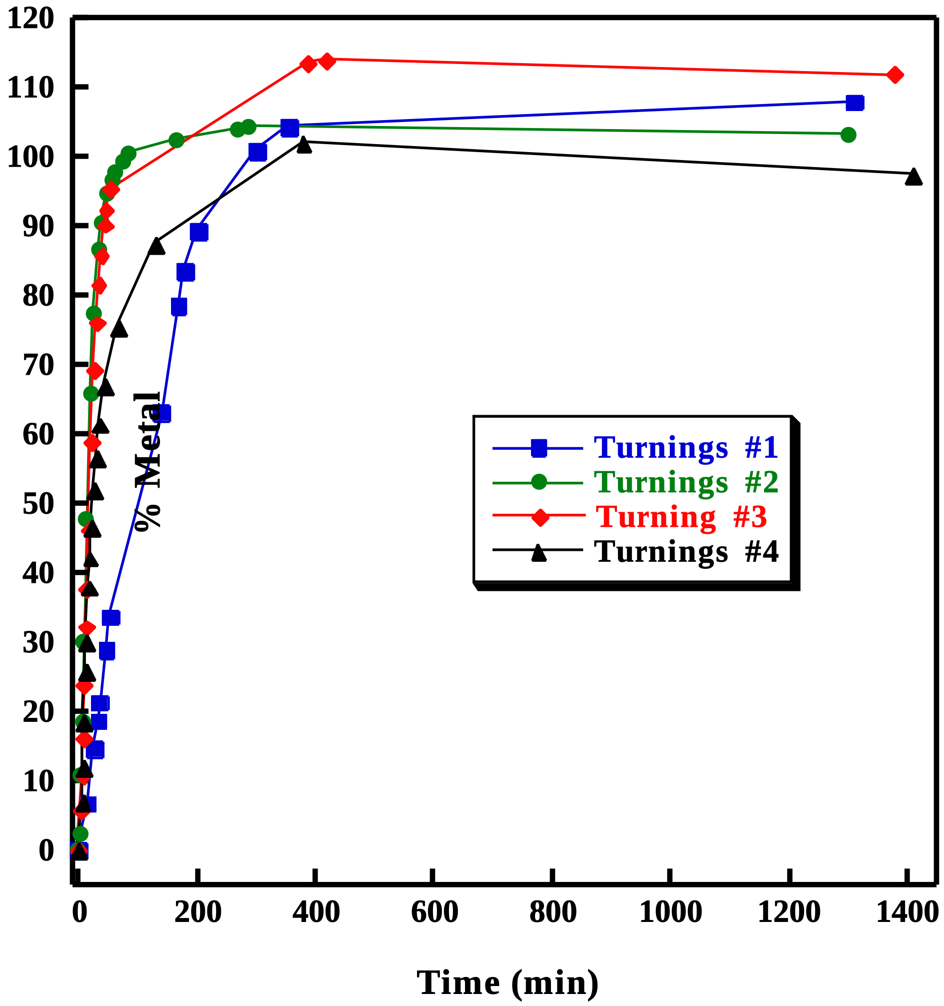


Figure 11. Percent Metal vs. Time for Unoxidized Plutonium Turnings.

The experimental pressure, P(torr)$_{exp}$, was adjusted to 273˚K and corrected to standard pressure for the elevation at Los Alamos (at 7500 feet the normal pressure is ~571 torr). All the sulfamic acid experiments were graphed as percent metal vs. reaction time. Figures 11 shows the results for unoxidized plutonium metal turnings. The unoxidized >40 mesh and <40 mesh materials had similar graphs. The final point was taken as the percent metal in the sample. The results for all three metal types are listed in Table 3 with the average plutonium metal content calculated with ± one sigma error. Within experimental error, the three metals contain about the same percentage of plutonium. We obtained greater than 100% metal for the starting samples. This is probably due to a bias in the weighing of the plutonium metal. The error in the analyses is most likely due to normal experimental error but also to barometric pressure changes. Barometric readings were taken at the start of the experiment and used as a baseline for the entire

Table 3. Percent Metal in Plutonium Metal Types Before Oxidation

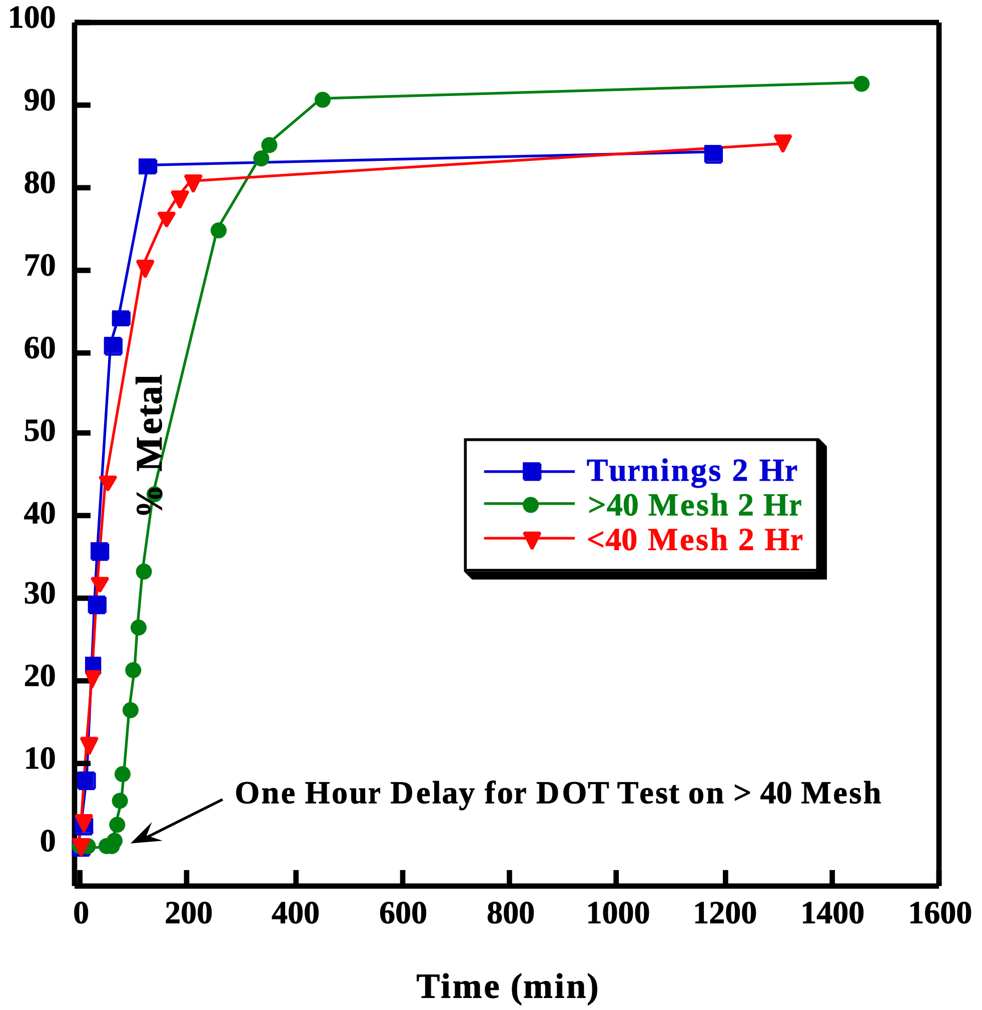
Run	Turnings	>40 Mesh	<40 Mesh
1	107.9	104.7	102.6
2	103.0	111.7	90.5
3	111.8	108.4	
4	97.3	104.6	
Average	105.0	107.4	96.5
± 1 σ Error	6.6	3.6	8.2

dissolution period; the atmospheric pressures during experiments could have increased or decreased.

The sulfamic acid method was particularly useful for analyzing the post-oxidation samples. The plutonium in these samples was unrecoverable, not only because it was dispersed in the wet surrogate matrix, but also because the metal character had changed. The post-oxidation plutonium was covered with a sludge that would easily smear on anything it contacted. It was impossible to recover the fine bits of metal from the sludge/wet surrogate matrix. In addition, the metal pieces that were observable appeared to be smaller and more fragile than the unoxidized metal. In fact, the sulfamic acid method was developed to make the analysis of these samples possible.

Preliminary plutonium oxidation experiments have noted two phenomena that necessitated the use of the apparatus shown in Figure 4. One, we observed that plutonium metal became passivated when submerged in water. Second, the steam reaction with the metal tends to break the metal into smaller fragments. The apparatus shown in Figure 4 allowed condensed water to drain from the plutonium/surrogate sample; the Kimwipe in the 50 mL beaker was positioned to touch the bottom of the Gooch crucible in order to initiate the flow of water from the crucible. The filter held the plutonium/surrogate sample and prevented fine metal from passing through the relatively large crucible pores and becoming submerged in the water that collected in the 50 mL beaker.

Three steam oxidation experiments were performed using the sample set-up shown in Figure 4. Each run included one sample of each metal type. The oxidation times at 110°C were 1, 2, 6, and 18 hours. After removal from the reactor, the contents of each sample were analyzed using the sulfamic acid method. Figures 12 plots percent plutonium metal vs. time for the three metal types after a two hour oxidation. Similar plots were obtained for the other oxidation times. The >40 mesh curve includes a 1 hour delay before the sample was contacted with the sulfamic acid. This was a test to see if the post-oxidation sample would produce any gas when submerged in water. Little or no gas was observed in this test or with other post-



Figures 12. Percent Plutonium Metal in the Oxidized Metals as a Function of Time for a Two Hour Oxidation.

oxidation samples that were subjected to this same treatment. Thus, we can say that the post-oxidation samples met the DOT criterion for no gas generation. Table 4 summarizes the percent metal left after the 1, 2, and 6 hour oxidations of each metal type. There is not a drastic difference in reactivity of the three metal types even though they were different sizes. Since the oxidation is surface area dependent, the <40 mesh plutonium might be expected to oxidize 2-5 times faster than the other two metal types. Longer oxidation times produced more of a sludge coating on the metal particles and resulted in smaller fragments of metal. The pHs of all oxidized samples were between 6.0 and 6.5 and therefore meet ISSC and WIPP-WAC standards for this criterion. Water that would temporarily pool in the crucible holding the sample could give variability to the results because it could passivate any metal that it submerges. Water pooling appeared to cause the failure of the 18

Table 4. Percent Metal in Plutonium Metal Types After Oxidation

Oxidation Time (Hours)	Turnings % Metal	>40 Mesh % Metal	<40 Mesh % Metal
1	94.4	98.4	94.3
2	84.2	92.6	85.3
6	49.2	45.2	56.6

hour oxidation experiments. The 18 hour samples were wetter upon removal from the reactor than the shorter reaction time samples. All three metal types showed ~100% metal remaining after the steam oxidation. If processing large amounts of surrogate (or Rocky Flats shredded residue), caution is advised as a very damp or saturated surrogate may have the same effect as pooled water on the sample. We realize that this statement is contrary to our advisement to use a large amount of water to get the combustible materials up to the optimum operating temperatures for the steam oxidation. What these statements mean is that a more specific water addition envelope may have to be defined for this process to operate correctly.

The percent oxidation was measured relative to an average value for each starting metal type and is calculated using equation 4:

$$\% \text{ oxidation} = \frac{(\% \text{ Metal})_{\text{initial}} - (\% \text{ Metal})_{\text{final}}}{(\% \text{ Metal})_{\text{initial}}} \qquad (4)$$

where:

$(\% \text{ Metal})_{\text{initial}}$ = pre-oxidation % Pu metal

$(\% \text{ Metal})_{\text{final}}$ = post-oxidation % Pu metal

Table 5 summarizes percent oxidation vs. time for the three metal types. Except for the 6 hour value for the >40 mesh sample there appears to be a trend in the extent of oxidation with particle size that is the inverse of what would be expected; the percent oxidation decreases with particle size! Perhaps the expected surface area effect is being negated by surface oxides that coat all the metal types. This data has implications for the plutonium metal in the Rocky Flats combustible residues. Even if those materials contain plutonium much finer than 40 mesh, they may not be any more reactive than the plutonium used in these experiments. Figure 13 plots the percent oxidation vs. time for each type of metal. The average oxidation percentage for the three plutonium metal types increases linearly over 6 hours. Although the plutonium is becoming more finely divided with longer oxidation times, the linear percent oxidation curve suggests that the dispersal of the metal has no effect on the extent of oxidation. If fifty percent oxidation occurred in 6 hours, then an extrapolation of data suggests that complete oxidation might occur in 12 hours.

Table 5. Percent Oxidation vs. Time

Oxidation Time (Hours)	Turnings	>40 Mesh	<40 Mesh	Ave. ± 1s Error
1	10.1	8.3	2.3	6.9 ± 4.1
2	19.9	13.8	11.6	15.1 ± 4.3
6	53.1	57.9	41.3	50.8 ± 8.5

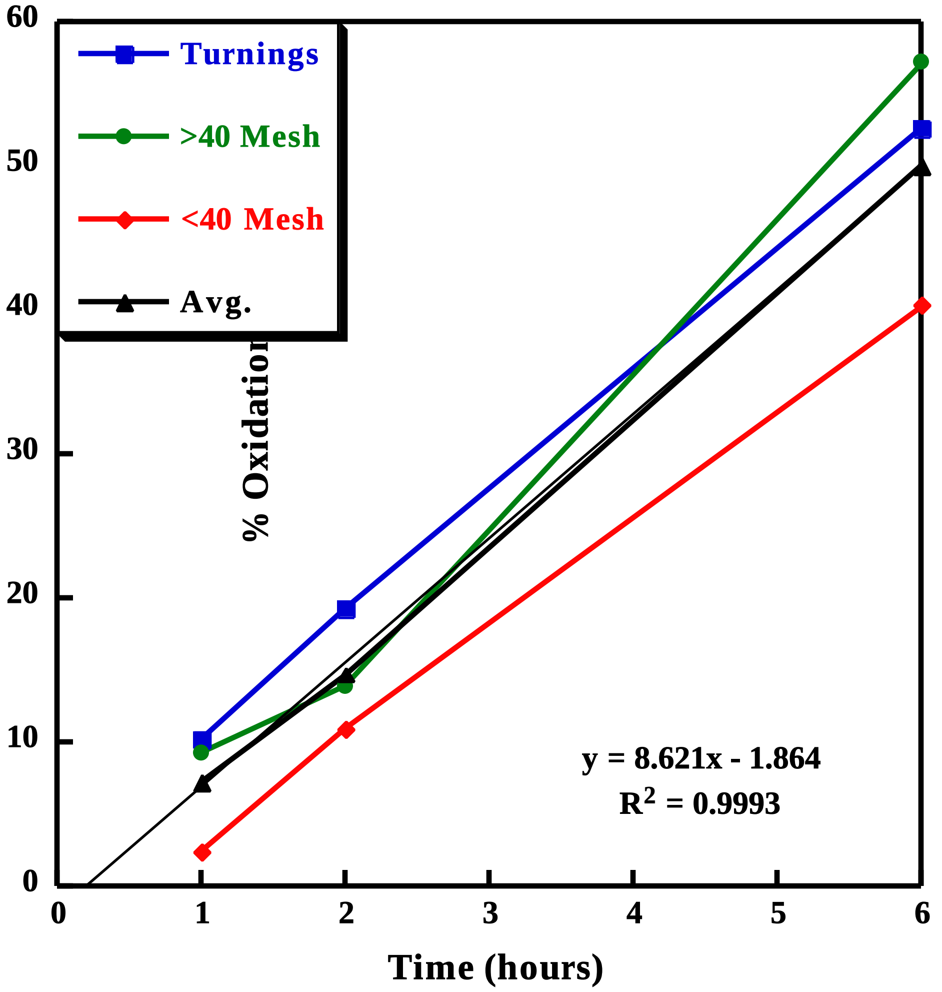


Figure 13. Percent Oxidation vs. Time for Each Type of Metal.

Haschke et. al. predict that a 0.5 gram sample of 40 mesh unstabilized plutonium would oxidize in 35 minutes. Oxidation of stabilized plutonium may be as much as 10^{-5} times slower.[7] The oxidation of the stabilized plutonium metal types in this work is significantly higher than predicted. The fact that all three metal types oxidize at about the same rate, and in linear fashion, suggests the actual surface areas of these metals may be much higher than the calculations based on the metal particle sizes. Perhaps microscopic cracks formed in the metals during machining and the surface areas in these cracks really accounts for a much larger surface area. This may account for the higher oxidation rate. If all the metal types have about the same surface area resulting from these types of cracks, then the nearly uniform oxidation rate can be understood.

Our earlier oxidation experiments have shown that additives such as sulfamic acid, H_2O_2 or CCl_4 can enhance the oxidation.[5,6] The addition of additives is not considered an option for this process. However, residual CCl_4 from the desorption process may react with water to produce HCl, resulting in an enhanced oxidation. However, HCl causes reactor corrosion and could drop the pH of the product out of WIPP-WAC compliance.

We submitted five of our small scale (~0.5 grams plutonium) samples for DTA analysis. The samples were surrogate only, surrogate/plutonium with no oxidation, surrogate/plutonium turnings with a two hour oxidation, surrogate/>40 mesh plutonium with a two hour oxidation, and surrogate/<40 mesh plutonium with a

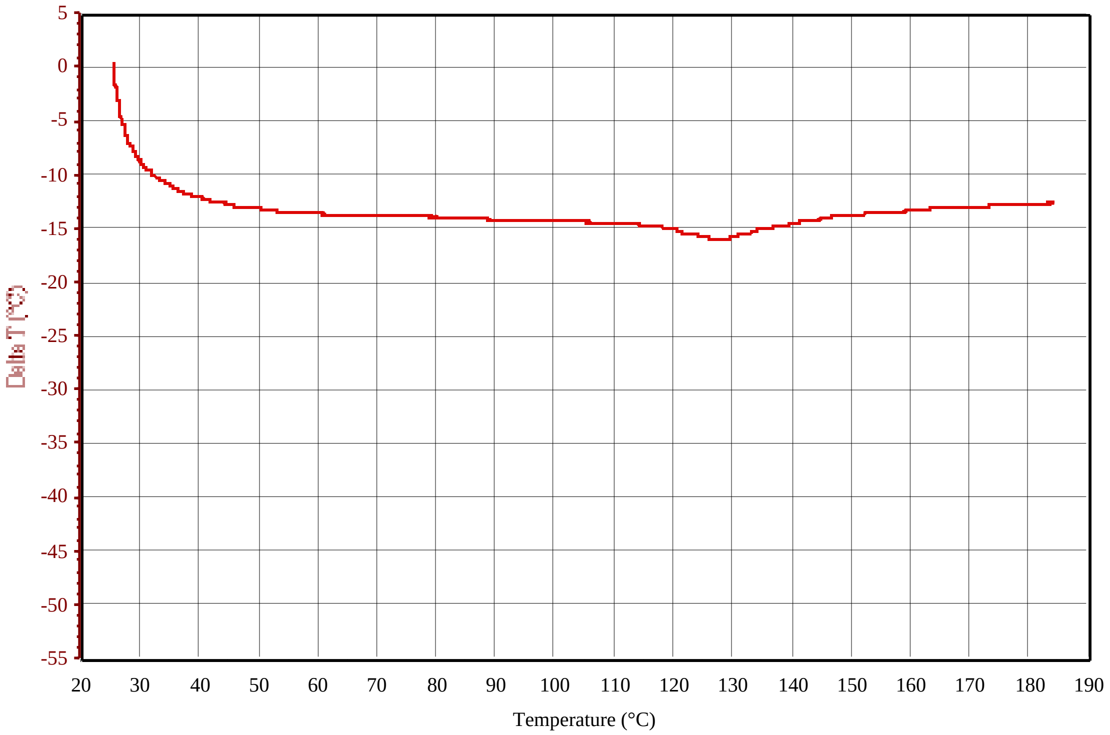


Figure 14. Differential Thermal Analysis Plot for Oxidized Plutonium Turnings and Surrogate.

two hour oxidation. The surrogate/oxidized plutonium turnings plot is shown in Figure 14. Beginning at 25˚C and ending between 100˚C and 110˚C there is a slow sweeping endotherm. This was typical of the five analyses. Thus all the oxidized samples passed the Rocky Flats stabilization criterion of not having an exotherm below 60˚ C. All sample baselines exhibit a slight endotherm of less than an absolute magnitude of 5˚C, that started between 120˚C and 130˚C and ended just before 140˚C. This was likely due to a common substance in the samples that went through a phase change, such as a melt. This is consistent with the earlier observation that the surrogate starts to melt and become sticky at about these temperatures.

SUMMARY AND CONCLUSIONS

The major conclusions that the LANL work has reached for the RFETS proposed process to stabilize combustible residues are listed below.

Carbon Tetrachloride Desorption

- Wet surrogate has poor heat and mass transfer properties. Surrogate composition and cut may affect these properties.
- Desorption of CCl_4 from wet surrogate using either the induction or no induction method gave highly variable results. The induction method may be a slightly more consistent method.
- An average of 634 ± 160 ppm CCl_4 remained in the headspace of the reactor after a 200 minute induction desorption procedure; >98% of the CCl_4 was removed from the wet surrogate; this meets the WIPP-WAC regulations.
- The large standard deviations for the desorption methods are caused by variability in the packing of surrogate, composition and cut of the surrogate, placement of CCl_4 in the surrogate, and placement of thermocouple in the surrogate.
- If no process monitoring is used to measure the CCl_4 concentration coming off the reactor, then a set time of ~240 minutes should be allotted for the desorption step to insure that sufficient removal of CCl_4 has occurred.
- Condensing the desorbed CCl_4 from high velocity gas streams was inefficient.
- Air or nitrogen can be used for the for CCl_4 desorption; safety concerns would warrant the use of N_2.
- Residual CCl_4 left after desorption may react with water during the steam oxidation step to produce HCl; this may lead to unwanted corrosion problems.
- Dispersal of the shredded material may be a more efficient desorption method than the reactor desorption methods; CCl_4 evaporation rates in an open system can be as high as 8 g/min.

Water Additions

- Wet surrogate sorbs an equal weight of water; 500 grams of surrogate sorbs 500 grams of water.
- The weight of 90°C water added to wet surrogate affects the maximum surrogate temperature within a closed 110°C reactor; maximum temperatures are reached within 100 minutes.
- Free water in the closed hot reactor is required to efficiently transfer heat from the reactor to the wet surrogate.
- In general, >500 grams of 90°C water are needed to rapidly bring 500 grams of wet surrogate to the optimum plutonium oxidation temperature range, 100°C - 120°C.

- Within 300 minutes, addition of <400 grams of 90°C water to 500 grams of wet surrogate failed to reach 100°C.
- Variability in the observed maximum surrogate temperatures are due to differences in the heating behavior of the Parr® reactor from one experiment to the next and the effect that different placements of the thermocouple within the surrogate has on the observed temperature and, for cascade controllers, how that surrogate temperature effects the reactor heating.
- If more than 333 mL of water are required to oxidize the plutonium in a Rocky Flats combustible sample, then a drying step will be needed to insure that the six samples per WIPP barrel do not exceed the limit of two liters of free water.
- Desorption of excess water from water saturated wet surrogate with 75 L/min 110°C air averaged 3 g/min. Desorption of excess water has operational and safety benefits.
- Some oil distills during the CCl_4 desorption and water evaporation steps.

Plutonium Oxidation

- Submersing the plutonium used in this study in water inhibits the oxidation. This observation may conflict with the water addition requirements for the oxidation.
- The residual water in the oxidized sample had a pH between 6.0 and 6.5. The oxidized samples generated little or no gas when submerged in water for 1 hour. DTA analyses of the oxidized samples exhibited no exotherms below 60°C. These samples meet the DOT and WIPP-WAC criteria.
- The three sizes of plutonium metal oxidized at approximately the same rate. Based on the calculated surface areas, the < 40 mesh metal should have reacted 2-5 times faster than the >40 mesh metal and metal turnings.
- The plutonium used in these studies oxidized significantly faster than expected for stabilized plutonium but slower than pure plutonium metal.
- The average oxidation rate for the plutonium metals used in this work was nearly linear over 6 hours.
- Fifty percent oxidation occurred in 6 hours; complete oxidation might occur in 12 hours.
- Residual CCl_4 from incomplete desorption could enhanced the water oxidation through the production of HCl. However, HCl causes reactor corrosion and could drop the pH of the product out of WIPP-WAC compliance.

The original RFETS processed allotted two hours to perform the desorption and oxidation steps. In summary, the LANL work has shown that these steps will take significantly longer than this. Assuming that: 1) no process monitoring is used for the CCl_4 desorption, 2) 500 mL of water are used for the oxidation, 3) 6 hours are required for the steam oxidation to produce samples that meet the stabilization criteria, 4) water desorption occurs at 3 g/min, and 5) the reactor needs 60 minutes to cool to 50°C, then 12 hours will be needed to process one 500 gram batch of combustible residues.

Application of LANL Results to RFETS

The purpose of this section is to recommend the Parr® reactor configuration that should be used by RFETS personnel for the stabilization of organic contaminated combustible residues based on the information gathered during experimentation. This recommendation maintains that the desorption process continues to be done within the reactor because not enough data has been obtained for desorbing CCl_4 from dispersed shredded material to justify altering the original process description. Table 6 summarizes the suggested operating parameters.

Table 6. RFETS Operating Parameters for Stabilizing Combustible Residues

Process	Parameter	Value
Batch Preparation	Combustible Residue Batch Size	500 g
Desorption	Air or N_2 Flow Rate	75 L/min
	Air or N_2 Temperature	110°C
Desorption Completion	Internal Thermocouple Temperature	90°C
Plutonium Oxidation	Water Feed Batch Size	500 mL
	Water Preheat Temperature	100°C
	Internal Oxidation Temperature	100°C - 120°C
	Oxidation Processing Time	6 hours
	Cool Reactor Temperature	50°C

System Configuration: Details of the system configuration are illustrated in Figures 1 and 2. The Design of the system varies slightly compared to the original RFETS design. Design modifications are as follows:

- The water injection tube should allow the liquid to contact the side of the reactor when injected. This will flash the water to vapor.
- The process logic controller (PLC) system must be outside of the glove box environment. Frequent failure of the PLC was attributed to corrosion from process steam. In addition, CCl_4 vapor will react with water to give HCl which will lead to further corrosion.
- The basket should not be constructed with the stainless steel mesh as originally designed as corrosion of the welded edges caused the mesh to fray; frayed metal is a potential safety hazard since it may cause glove failure. The basket should be constructed of a stainless steel rod frame that forms a frame for the nylon hop sack.

Batch Size and Batch Preparation: The batch size should be limited to 500 grams of surrogate as additional material would need to be compacted in order to fit into the reactor basket. Compacting the material would decrease the mass and heat transfer rates during desorption and oxidation. The use of the nylon hop sack is advised as the sack increases the ease of material handling and decreases combustible material spread outside the reactor basket. Oxidation water should be prepared by adding 500 mL to the water supply vessel and beginning the preheat process. The water should be preheated to 100°C prior to reactor injection during oxidation.

Desorption of Volatile Organic Material: After the reactor is sealed and all inlet and outlet valves closed, it should be inductively preheated for one hour. The air inlet and off-gas outlet should next be opened and the system sparged with 110°C air at 75 L/minute until the internal thermocouple (the thermocouple in center of the combustible material) reaches 90°C.

Plutonium Oxidation: The oxidation should begin by pulling a vacuum on the reactor then closing all valves. Next, the drain should be opened to the (preheated) water supply and the water transferred into the reactor vessel. When the internal thermocouple (thermocouple in center of combustible material) reaches 100°C, this temperature (between 100°C and 120°C) should be held for 6 hours. Finally, the reactor should be allowed to cool to approximately 50°C and the vessel should be vented before breaking the collar seal.

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