

CHARACTERIZATION AND PROCESSING OF PYROCHEMICAL SALTS

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ABSTRACT

The Rocky Flats Environmental Technology Site currently stores over 100,000 kg of plutonium-containing residue materials which must be prepared for final disposal. This material includes approximately 16,000 kg of pyrochemical salts remaining from the plutonium recovery processes operated during the Site's production era. Based on process knowledge, the pyrochemical salts were originally thought to pose a safety risk due to the possible inclusion of reactive, pyrophoric, or shock sensitive materials. The baseline plans for disposing of the salts included a minimum requirement to pyro-oxidize the salt with a chemical oxidant (sodium carbonate) to stabilize any reactive metals (e.g., calcium, magnesium, sodium, potassium, and plutonium) that may be present in the salt residue. Although the pyro-oxidation has started, a body of characterization data has been collected as well, which shows that the safety hazards associated with the salts are considerably less than anticipated. As a result, future plans include repackaging of salts into a robust stainless steel container, commonly known as the Pipe Component, without pyro-oxidation. Some categories of salts will continue to be pyro-oxidized, but a significant fraction will be repackaged without pyro-oxidation, reducing the processing time and exposure, and providing a significant cost savings. The characterization program and the continued observations during processing have provided information that has improved processing plans.

INTRODUCTION

The Rocky Flats Environmental Technology Site currently stores over 100,000 kg of plutonium-containing solid residue materials which must be prepared for final disposal. This material includes approximately 16,000 kg of pyrochemical salts remaining from the plutonium recovery processes operated during the Site's production era. The salts fall into three broad categories:

- Calcium Chloride based salts, primarily CaCl_2 with calcium oxide and calcium metal. It may also contain other chloride salts, including NaCl , KCl , ZnCl_2 , and CsCl .
- Electrorefining (ER) salts containing equimolar NaCl/KCl with additions of MgCl_2 and other minor constituents, and
- Molten Salt Extraction (MSE) salts containing equimolar NaCl/KCl with additions of MgCl_2 up to 30% and other minor constituents.

Based on process knowledge, the pyrochemical salts were originally thought to pose a safety risk due to the possible inclusion of reactive, pyrophoric, or shock sensitive materials. Evaluation of the potential hazards caused all the pyrochemical salts to be classified as "High Risk." The baseline plans for disposing of the salts included a minimum requirement to pyro-oxidize the salt with a chemical oxidant (sodium carbonate) to stabilize any reactive metals (e.g., calcium, magnesium, sodium, potassium, and plutonium) that may be present in the salt residue.

Characterization of the salts was initiated in parallel with preparation of the pyro-oxidation processing equipment. The initial characterization activities were designed to provide moderate confidence knowledge of each of the individual categories of salt material, with respect to safety

and effectiveness of the planned processes. The first stage of characterization (to moderate confidence) has now been completed for all pyrochemical salt, and several categories of material have been characterized further to provide high confidence data. Pyro-oxidation of one salt category, the calcium-chloride based salts has also commenced.

APPROACH

Within each of the three categories of salt, there are multiple smaller groups referred to as Item Description Codes (IDCs). Each IDC is distinct from the others based on process origin and/or physical or chemical characteristics. Within each IDC, salts may be stored in 55-gallon drums (each drum containing multiple smaller containers), or in a variety of other smaller containers. A statistical sampling scheme was developed for the characterization program that treated each IDC separately, and also separately treated the 55-gallon drums and the other containers. Using a hypergeometric distribution, sample sizes were identified such that *IF no "hits" are observed in the sampled population, THEN there is 80% confidence that not more than 15% of the containers in the total population contain material showing the parameter being tested.*

As a second step in this process, some IDCs were selected to receive further characterization to assure 95% confidence that not more than 5% of the population show the parameter being tested (95/5% confidence). If characterization data shows that there is 95/5% confidence that the possible hazards are not present, then the IDC may be reclassified from High Risk to Low Risk.

The analysis requirements were developed based on the process history of each IDC, and the expected characteristics of the material. All salts were tested for water reactivity and all underwent a Differential Thermal Analysis (DTA) test to identify reactive materials. Particle size distribution was measured to determine what fraction of material was likely to be dispersible, and to better understand the air reactivity.

Shock sensitivity was measured on the ER salt because these salts could possibly contain small amounts of shock sensitive material formed during the electrowinning process.

Moisture content was initially measured only in IDCs that were believed to be moderated^a in order to confirm the moderation status. As the program progressed, it was determined that moisture content could also be important for other applications, such as determining the propensity for hydrogen gas generation (radiation from the plutonium will cause water to decompose, creating hydrogen gas). Additional moisture content data was sought later in the program.

Volatile and semi-volatile organic compounds were not expected in the pyrochemical salts based on the process history, so measurements were not made for these compounds.

RESULTS

The CaCl_2 salts are divided into nine IDCs, for which a total of 69 samples were obtained. Originally, three other IDCs (413, 426 and 415) were considered CaCl_2 salts. Characterization of the chemical constituents in these IDCs caused reclassification of IDC 415 as MSE salt and IDCs 413 and 426 as ER salt. With the change to IDCs 415 and 426, they were considered better candidates for repackaging than for pyro-oxidation. Since CaCl_2 salts had begun undergoing

pyro-oxidation, there was no need to determine if they could be recategorized as Low Risk. (Pyro-oxidation would mitigate any reactive material risk.) Thus no additional samples were obtained to achieve 95/5% confidence with regard to risk parameters.

The ER salts are divided into seven IDCs (including IDC 413 and 426) for which a total of 193 samples were obtained. The MSE salts are divided into nine IDCs (including IDC 415) for which a total of 160 samples were obtained. Additional samples are still being taken to achieve 95/5% confidence for most of the IDCs in these two groups. Figure 1 shows part of the sampling procedure for a typical MSE salt; Figure 2 shows the sampling for a typical ER salt. The sampling requires removal of small containers from the 55-gallon drums into a glove-box, where the entire contents of the small container is examined. Individual samples are removed for laboratory analysis.

All the salts contain plutonium, an alpha-emitter, and are thus handled in a manner which minimizes potential for contamination and exposure. In addition, the MSE salts often contain significant quantities of americium, which also emits gamma radiation, and may require additional precautions. During sampling activities, radiation levels and contamination of containers inside a 55-gallon drum (not the normal situation) are measured and recorded. Since the drums and other containers will eventually be re-opened for repackaging or processing, the radiation and contamination information is valuable to ensure safe and effective future operations.

None of the salt IDCs showed signs of pyrophoricity or flammability. The water reactivity test confirmed the presence of small amounts of reactive metal in all IDCs, but the average reactivity remained below the lowest level that requires placarding or other measures for the Department of Transportation. Exothermic reactions were observed below 150°C for about 40% of the samples. The majority of these reactions did not show the characteristic shape of strong exothermic reaction (sudden steep rise in temperature of the sample), but appeared more likely to be



Figure 1. Sampling of a Typical MSE Salt
Contents of Container is Emptied into Pan for Examination in the Glove Box



Figure 2. Sampling of a Typical ER Salt

an acceleration of the usual slow oxidation process taking place in the salt (Figures 3a and 3b). A combination of exotherms, with a shallow increase in temperature below 150°C, followed by a stronger exotherm above 150°C, was not uncommon. The most likely candidate for the stronger exotherm is rapid oxidation of small particles of plutonium metal. Particles that were encased in salt during initial processing would not have oxidized during the years of storage. The increased temperature would cause release of bound water from the salt encasing the Pu. The water would accelerate the oxidation reaction of the Pu metal. In fact, the majority of clear exothermic reactions initiate at temperatures that correspond to the loss of waters of hydration from the relevant salts.

Three of the IDCs produced samples where an exotherm was observed at a temperature below 60°C. One exothermic event was observed initiating between 50°C and 60°C in IDC 414 (a CaCl₂ salt), two events in IDC 413 (an ER salt) and one event in IDC 654 (an ER salt). All the reactions that initiated below 60°C were shallow and tailed off before leading into higher temperature reactions. However, one other sample of IDC 654 showed a sharply increasing reaction that initiated between 70 and 100°C (Figure 3c). Even this stronger exotherm did not resemble an "ignition" event but is more likely an increase in Pu oxidation initiated by release of water of hydration.

Impact testing was performed on ER salts, and none of the 172 samples analyzed showed any sign of shock sensitivity.

Since pyro-oxidation of CaCl₂ salts had started, observations during processing were also used to enhance understanding of the material. A key observation was the foaming of material during heating. This was attributed to a higher than expected moisture concentration in the salt.

Moisture concentration data was collected for some of the salt IDCs, and showed an average value less than one weight percent for all three groups, with a 95% confidence limit up to about three weight percent. The pyrochemical processes that generated the salt were performed at high enough temperature to expect drying to have occurred. However, years of storage could allow the hygroscopic salts to absorb moisture from the air. The observed levels of moisture are consistently below the theoretical maximum level that could be achieved by hydrating the salts (10% or more, depending on the exact composition).

DISCUSSION

As the 95/5% confidence characterization is completed for individual IDCs, the data is analyzed to determine if a basis exists for reclassifying the IDC as Low Risk. A Low Risk IDC is not required to undergo pyro-oxidation prior to disposal. To date, three of the ER salt IDCs and three of the MSE salt IDCs have been reclassified as Low Risk, and more are expected as new data analysis is completed.

Much of the data analysis for risk classification focuses on the reactive metal content. The water reactivity tests provide a measurement of the total reactive metal. For each IDC, this information is extracted and a conservative analysis performed to determine the effect of instantaneously reacting all the metal in a container. If the heat produced by the reaction could be withstood by the container with no negative effects, the material is considered Low Risk from a reactivity

standpoint. In all cases analyzed to date, there has been a significant margin between the temperature achieved by the postulated reaction and the temperature of concern.

The DTA data has also been scrutinized to determine if unexpected or hazardous reactions may occur. A comparison of water reactivity and DTA data from the same container suggests that the water reactivity data bounds the DTA data (showing reactions of plutonium and other metals that may not be air reactive). Calculations of the potential plutonium reactivity compared to the measured reactions on the DTA also suggest that much of the plutonium in the container is no longer in a reactive metal form. Since the salts have been stored for years, it is reasonable to conclude that most of the plutonium has oxidized over time into an unreactive form. Some pieces of plutonium may now be protected by an oxidation layer or by a protective salt layer, and still contain metal. But they are not directly hazardous unless the unreacted surface is exposed. The repackaging process would examine material and remove obvious pieces of metal to further reduce the hazard.

In the majority of the cases, the safety hazards associated with the salts are considerably less than anticipated. There is no evidence of pyrophoricity or shock sensitivity. There is some reactive material (plutonium metal, and other residual metals) present in all IDCs, but the level is low enough not to be a concern.

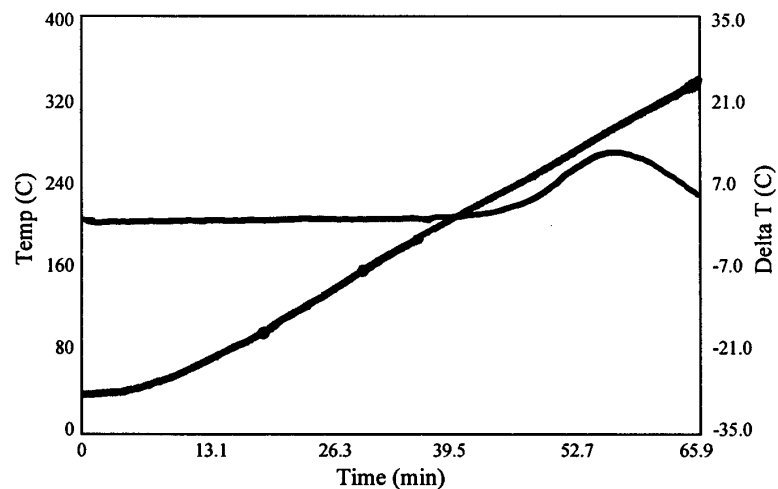


Figure 3a. Typical DTA plot showing a small, shallow exotherm (IDC 414, a CaCl_2 salt). The temperature of the DTA unit is shown on the left axis in degrees C (the smoothly increasing line). Time is shown across the bottom axis. The difference between the DTA unit temperature and the sample temperature is shown on the right axis in degrees C. The slow increase in temperature of the sample as the DTA unit is heated indicates an increased rate of reaction of the sample, probably oxidation of residual plutonium.

Figure 3b. Typical DTA plot showing a small exotherm beginning at about 90°C followed by a stronger, rapid exothermic event beginning above 160°C. This combination of exotherms is not uncommon in the salt samples.

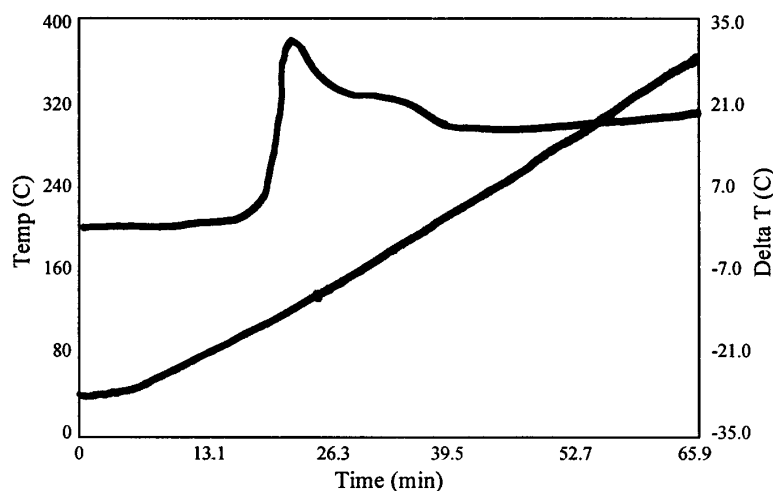
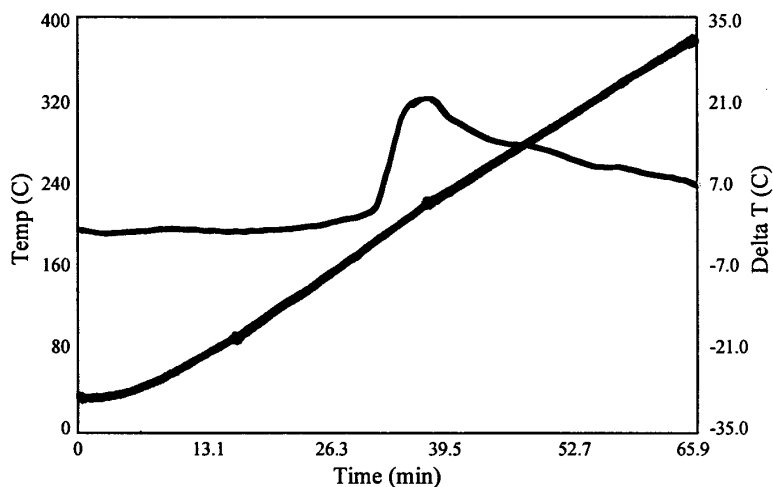


Figure 3c. Stronger exothermic reaction observed in one sample of IDC 654, an ER salt. Note the more rapid increase in temperature of the sample over a short time period. This type of behavior at a temperature below 150°C is less common among the salt samples. The exotherm likely results from increased oxidation of plutonium following release of bound water from the salt matrix.

As a result, future plans include repackaging of salts into a robust stainless steel container, commonly known as the Pipe Component, without pyro-oxidation. The CaCl_2 salts will continue to be pyro-oxidized, but the majority of the ER and MSE salts will be repackaged without pyro-oxidation. Removing the requirement for pyro-oxidation eliminates throughput restrictions associated with the furnace operation. More repackaging stations can be set up in the available facilities, making it possible to complete preparation of all the salt for final disposition sooner than originally expected.

RECOMMENDATIONS

The processing and disposition plan for the pyrochemical salts was formulated based on the possible risks and hazards that could be associated with the material. A number of the perceived risks have been shown to be non-existent or much less serious than originally believed. As a result, there is much more flexibility available in selecting the path to final disposition. Without a technical requirement to perform pyro-oxidation of the salt, the choices for processing or repackaging can be based on other factors including exposure, cost, time, and productivity.

The characterization of the salts has shown the current configuration to be less hazardous than believed, allowing the site to better prioritize resources to ensure that true safety hazards are addressed with highest priority. Characterization has also provided information that increases the flexibility for handling the salts. Adequate characterization greatly increases the probability of success when planning a material-processing program.

FOOTNOTES

- a. Moderation describes the effect on plutonium activity of hydrogen-containing compounds such as water. Previously, materials containing greater than ten weight percent water were considered moderated. The current definition involves a hydrogen-to-plutonium ratio greater than three.