

TECHNICAL INITIATIVES IN RESIDUE DISPOSITION AT THE ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE

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ABSTRACT

Safe Sites of Colorado (SSOC) brought initiative and massive effort in FY98 to enable accelerated stabilization and disposition of Rocky Flats Environmental Technology Site (RFETS) residues. The creativity and persistence paid off. One example of a distinctly SSOC strategic initiative is the "Pipe and Go" plan for site residues. The "Pipe and Go" concept can be defined as "demonstrate that site residues are sufficiently non-reactive to be placed in a stout shipping container for internment at the Waste Isolation Pilot Plant (WIPP)." This simple concept, based on measurements and analysis, has provided an altered perspective on the residue issue. During FY98, a number of perspectives associated with the residue problem were simplified.

One prior concern was that residues contain too much plutonium and are too attractive from a potential diversion perspective for disposition at WIPP. A credible alternative perspective was developed and approved. Proof was provided that controls on residues, while in transit to and underground at WIPP, were comparable to controls imposed by the International Atomic Energy Agency for excess plutonium. SSOC provided a Safeguards Termination Variance Request and plan for implementation, which included a Vulnerability Study of every step of the disposal route. The Safeguards Termination Variance was approved by the Department of Energy (DOE) Office of Safeguards and Security.

Residues were previously thought to lack a disposition path. It was thought to be necessary to process residues into two material types, TRU waste and plutonium, which have established disposition paths. This perspective led to a processing baseline that incorporated significant costly and slow processing. Coming into FY98, the baseline was to distill salts, vitrify ash, and wash combustibles. The selected processes required demonstration testing, and technical difficulties were encountered. The processing would have generated TRU waste. The prospect for achieving site closure by 2010 was not good. "Pipe and Go" in concert with the Safeguards Termination Variance eliminated the processing in favor of straightforward repack of residues and brought closure plans into focus.

A third concern was that residues are unstable and must be processed for safe storage. Early concerns about hydrogen accumulation were resolved and the highest risk materials, ion exchange resins and leaded gloves, were stabilized. Concerns associated with the safety of stored residues were mitigated through an intensive and disciplined, statistically based program to characterize and gain a thorough understanding of residue risk. The data to date have established that the residues are safe as is and do not require processing to mitigate hazards.

A final concern was that the Transuranic Package Transporter II (TRUPACT-II) allowance of 325 grams of plutonium would make the transport of residues to WIPP uneconomical. SSOC conceived, designed, and established the licensing agreement of a stout shipping container that

allows 2800 grams of plutonium per TRUPACT-II which opened the way for effective and economical shipment of residues to WIPP.

The collective effect of these SSOC initiatives, which were clearly “it can’t be done” concepts, was a total shift in the disposition strategy for site residues. The initiatives directly accelerated site closure by some three years and saved at least \$170 million and significant radiation dose to the workforce. The multiple SSOC residue teams have pressed hard to overcome barriers associated with setting product requirements and with multiple facility start-ups. The facilities have successfully started up and are ramping up to full production rates. To date, approximately 13 percent of the residue backlog has been prepared for final assay and disposition.

INTRODUCTION

This paper summarizes the progress toward answering the two questions that drive the Residue Disposition Program at RFETS:

1. Are the residues safe?
2. How and when can they be dispositioned?

The safety of the residues as presently stored is of highest concern. Some of the early concerns regarding safety of the residues were validated; others were not. Elevated levels of hydrogen gas were found in drums of salt and sludges. Drum venting eliminated the concerns about flammable gas accumulation. Other urgent safety concerns associated with resins and leaded gloves were mitigated. The characterization data to date has indicated that the vented drums are safe as they sit. Continued characterization is being performed to gain statistical confidence, and the continuing priority will be the identification and mitigation of emergent safety issues. This paper provides background on the safety issues and summarizes recent characterization data.

WIPP continues to be the primary answer to dispositioning the residues. The disposition plan calls for minimal processing and repackaging to meet safe storage and WIPP criteria. Due to the increasing desire to accelerate closure of RFETS, it is important to keep the residue flowsheet as simple as possible and to utilize existing nuclear facilities to the extent possible to reconfigure the residues. This paper addresses initiatives undertaken by Safe Sites of Colorado to accelerate the residue program at savings in excess of \$170 million. One initiative is the request for variance from the safeguards termination requirements to greatly simplify the flowsheet. Another initiative aimed at accelerating the residue program is known as "Pipe and Go."

BACKGROUND

Residue Origin

Byproduct materials from past RFETS plutonium processing were designated as residues, as opposed to transuranic (TRU) waste, if the plutonium concentration exceeded the economic discard limit (EDL) for the material of interest. The approximately 102 metric tons of residues were set aside for subsequent processing for plutonium recovery. With the end of the Cold War, the EDL has no relevance, and the residues are now regarded as higher plutonium level TRU waste. The residues have been categorized into four “buckets,” or groupings which have common disposition paths, with the following bulk weights:

- Ash--26 metric tons of incinerator ash, graphite fines, and sand, slag, and crucibles from incineration and reduction operations.
- Salts--16 metric tons of electrorefining, molten salt extraction, direct oxide reduction, and miscellaneous other salts from pyrochemical operations.
- Combustibles--20 metric tons of paper, plastics, and coveralls which were the feedstock to incineration.
- Dry/Repack--40 metric tons of miscellaneous inorganics, i.e., metals, glass, etc.

Safety Concerns

In March 1994, W. V. Conner published a report (Reference 1) citing safety concerns associated with the chemistry and packaging configuration of the residues. Conner was concerned about the potential of hydrogen and other flammable gases from radiolytic decomposition of plastic and other hydrogenous materials. He cited the potential of shock sensitive plutonium hydride production and noted the potential for container corrosion due to free acid and carbon tetrachloride. Conner's report cited the lack of definitive characterization information. In the absence of data, he derived the potential chemical reactions and emphasized the need for data to substantiate or dispel his concerns. The Defense Nuclear Facilities Safety Board (DNFSB) published Recommendation 94-1 in May 1994 citing similar concerns about residue safety and requiring the stabilization of "possibly unstable" residues within 3 years with stabilization of all residues within five years.

D. F. Dustin developed a risk categorization scheme (Reference 2) as a basis for specifying "possibly unstable" residues for processing priority. The scheme established eight safety parameters: (1) flammable gas formation, (2) shock sensitivity, (3) flammability, (4) pressurization, (5) container corrosion, (6) incompatible chemicals, (7) radiation exposure, and (8) toxic exposure. Based on process knowledge, Dustin derived the probability and consequence of the existence of each parameter for each material type. He applied a weighted numerical value to each material type and ranked the risk from high (Category I) to low (Category V).

Corrective Actions

Actions were taken to mitigate the risks of the Category I materials. Beginning in December 1995, all residue drums were vented to eliminate the potential for flammable gas accumulation. Washing in weak caustic neutralized organic nitrated ion exchange resins, which have an explosion potential when dry. The resins were then combined with liquid waste (from Building 771 tank draining) and processed by cementing in the Building 774 bottle box operation. Rubber glovebox gloves that had been in contact with nitric acid were also identified as risk Category I due to the visible indication of a white powder in areas where the glove was cracked, exposing the lead shielding to nitric acid. There was concern that the powder could be a shock sensitive leaded compound lead fulminate. This concern was not validated. The gloves were bagged into a glovebox in Building 776 and wiped down with wet Kim-wipes and repackaged. These actions reduced the risk of all Category I items to Category II. The risk Category II through V

items were prioritized for processing. Processing plans and schedules were developed to support commitments to the DNFSB for meeting Recommendation 94-1.

Residue Characterization

A characterization program was developed by K. A. Phillips in December 1995 to gain definitive risk data on the residues. The first priority of the program was to determine if there were any further safety concerns which would indicate the need for immediate action. The plan also supports validation of the priority of processing established by Dustin. The program was also directed at verifying that the residue chemistry was compatible with the selected processes, and, finally, environmental data was to be collected to verify the Resource Conservation Recovery Act (RCRA) status of the materials. The characterization data from approximately 1200 containers sampled to date generally indicate that the residues are safe as they are presently stored. The data also demonstrated that some residues, initially designated as high risk, are in fact low risk. The packaging materials are generally in good shape with no indication of serious corrosion or breach of containment. There has been no indication of shock sensitivity or significant reactivity (Reference 3).

BASELINE PROCESSING PLAN

The processing plans were based on the premise that the residues, when reconfigured to meet the Interim Safe Storage Criteria and WIPP Waste Acceptance Criteria, were subject to safeguards control. This is a key point because WIPP will not be safeguarded, and materials shipped to WIPP must previously be removed from safeguards control. In Reference 4, a Department of Energy memorandum, the status of non-special nuclear material (SNM) plutonium containing materials was clarified. Threshold limits of plutonium concentration were set, based on the attractiveness of the material, above which the material was required to be safeguarded. The Safeguards Termination Limits (STLs) and original average plutonium concentrations for RFETS residues are compared in Table I.

Table I. STL and Plutonium Concentration Comparison for Residues

	Average Plutonium Concentration (%)	STL (%)
Salt	6	0.2
Ash		
SS&C and Oxides	3	0.2
Ash, Soot, and Heels	5	2.0
Combustibles		
Wet/Dry Combustibles	0.5	1.0
HEPAs and Sludges	3	1.0
Fluorides	40	0.2
Dry/Repack		
Misc. Metals and Graphite	0.6	1.0
Crucibles and Firebrick	1	5.0

For materials exceeding the STL, there were two options. The plutonium could be separated from the matrix to bring the matrix within the STL for disposal at WIPP. The plutonium would be dispositioned along with other RFETS special nuclear material. Alternatively, the material could be reduced in attractiveness by making the plutonium "practically irrecoverable" and raising the STL. Task teams were formed by DOE Rocky Flats Field Office and by DOE-Headquarters around each of the major residue categories to establish flowsheets that would most expeditiously bring the residues into STL compliance.

The salt team considered options including blending to the STL and aqueous dissolution and salt distillation to separate the actinides. Salt distillation was selected based on development work underway at Los Alamos National Laboratory. The oxidized salt is brought to molten temperature, around 950°C, and vacuum is applied to selectively volatilize the salt from the actinide heel into a separate cooled chamber. The distilled salt is packaged for disposal at WIPP, and the heel is packaged for disposition with SNM.

Distillation was incorporated into the baseline stabilization plan. The salt had to be oxidized prior to distillation, to eliminate the carryover of volatile plutonium compounds. Eight to ten distillation units were planned for installation in B Module of Building 707. Demonstration and testing (D&T) was initiated to set the distillation parameters, and a design contract for the RFETS units was placed. Significant technical difficulties were encountered during the demonstration phase. One complication was that the oxidant choice for salt oxidation--sodium carbonate--caused foaming in the subsequent distillation step so the D&T effort focused on oxidant choice. Vanadium pentoxide was selected to avoid the foaming. However, performance problems were encountered such that the distilled salt exceeded the STL plutonium concentration of 0.1 weight percent. The resultant actinide heel was consistently below the target of 50% plutonium for the Materials Disposition (MD) program. The recommended resolution of the technical issues was to revert to sodium carbonate as the oxidant but to incorporate a chlorination step after oxidation to eliminate unreacted carbonate and relieve foaming problems in the subsequent distillation step. The safety and logistics issues associated with this more complicated flowsheet made distillation a highly undesirable process for RFETS. The bottom line was that distillation was not a viable process for preparing salt residues for disposition.

The ash team considered options including blending to the STL and cementation or vitrification to reduce material attractiveness. Vitrification was selected. The parameters for frit type, ratio, temperature, and time were established through D&T at Savannah River Site and Pacific Northwest National Laboratory. The D&T effort established that incinerator ash had to be calcined prior to vitrification to prevent a phase separation of the ash from the frit. Calcination tests at a local research laboratory, using rotary and fluid bed calcination were unable to achieve the desired throughput. The two-step thermal process of calcination followed by vitrification would not support the site closure schedules.

The disposition of the combustible and dry/repack materials did not involve the technical complexity of salt and ash. The combustibles and dry/repack teams established that packaging with nominal blending was adequate to meet the STL.

ACCELERATION INITIATIVES

A plan was developed to overcome the technical difficulties associated with residue processing and accelerate the disposition of residues and site closure. The concept is based on the proven integrity of the pipe overpack container (POC) and the characterization data to date that indicate that the residues are relatively benign. The proposal is that the POC be credited with the mitigation of any untoward event resulting from residue storage and shipment such that stabilization processing is not required. The materials that are intended for use with the POC--salts and ash--would be repackaged into the POC for disposal at WIPP. The plan was conceptualized as "Pipe and Go." A key element of the plan was the pipe component, which is contained within a 55-gallon drum. The pipe component is a stout 0.69 cm walled stainless steel pipe, 15.2 or 30.5 cm inner diameter by 63.5 cm long. The pipe component was developed to allow increasing the plutonium limit of TRUPACT-II shipments. The prior limit of 325 grams per TRUPACT-II was based on the TRUPACT-II criticality limit. The pipe component was drop and fire tested at Sandia National Laboratories and was approved by the Nuclear Regulatory Commission for use with TRUPACT-II in February 1997. This certification supports packaging each pipe component to the 200 fissile gram equivalent allowance at WIPP with 14 drums per TRUPACT-II which raises the 325 gram limit to 2800 grams.

A second element of the "Pipe and Go" concept promoted by SSOC was an initiative to request variances from the STLs to allow residue categories below 10 weight percent plutonium, packaged to Interim Safe Storage Criteria and WIPP Waste Acceptance Criteria, to be exempted from safeguards requirements and shipped to WIPP. The basis for the exemption requests is that residue categories with less than 10 percent plutonium, when packaged to the 200 FGE limit, cannot roll up into Category II quantities of SNM. The Level IV equivalent controls are in place for wastes at RFETS, and the materials will be controlled to prevent diversion through physical controls at RFETS until internment at WIPP, 0.5 miles underground. The safeguard termination request was approved by the DOE-Office of Safeguards and Security and implemented by the DOE Rocky Flats Field Office.

The combined savings of the STL variances and the "Pipe and Go" initiative are estimated at approximately \$170 million due to the avoidance of stabilization processing and processing to meet the STL. The cost of processing of the actinide heel resulting from distillation is included in the estimate. In view of the technical difficulties associated with the baseline processing, these changes were imperative to achieve site closure by 2006.

"PIPE AND GO" PLAN

Progress toward the disposition of site residues is significant. The SSOC residue project team has pressed beyond the technical and administrative hurdles associated with setting product requirements and with multiple facility start-ups. The product lines—salt, ash, wet combustibles, dry/repack, and sand, slag, and crucible—are ramping up to production throughput. Approximately 13,000 kg of the total residue backlog of 102,000 kg, or approximately 13 percent, have been prepared for final disposition. The status is summarized below as of the end of January 1999.

Salts

Salt stabilization processing to comply with DNFSB 94-1 was initiated prior to the approval of "Pipe and Go." The plan incorporated oxidation of reactive species such as sodium, plutonium, potassium, and calcium. The salts were to be brought to 900°C in a stationary pyrochemical furnace with addition of sodium carbonate with stirring. The oxidized salt was to be removed in its stainless steel can, placed in a convenience container, bagged out of the line, measured by calorimetry, and placed within the pipe component inside of the 55-gallon drum. The equipment was sized to meet the DNFSB commitments and 10,000 additional kilograms by September 30, 1999, and all 16,000 kg processed by May 2002. Ten new furnaces were constructed in four new gloveboxes in A Module of Building 707. In-line segmented gamma scanners (SGS) were incorporated for batching and six out of line calorimeters were acquired for final assay. Readiness preparations were completed for the salt oxidation process, and the system was started in January 1998. To date, 2200 kg of the total 16,000 kg of salt have been processed. The salt project team is in the process of switching to "Pipe and Go," with elimination of the oxidation step, as adequate supporting characterization data become available. The salt is batched to less than 10 percent plutonium, repackaged in Building 707, and assayed using calorimetry/gamma spectroscopy of each container. The containers are placed in the pipe component within a 55-gallon drum for storage and ultimate disposition. Augmented repack capacity will be added in Building 371 to support the 2006 site closure target.

Ash

The 94-1 stabilization plan for the ash materials--incinerator ash, graphite fines, and sand, slag, and crucibles--incorporated thermal stabilization to oxidize reactive species such as plutonium, calcium, and magnesium. The material was to be batched into flat pans for heating to 500°C for 2 hours in air in muffle furnaces. The oxidized ash was to be placed in a metal can and packaged in the pipe component within a 55-gallon drum for shipment to WIPP. The equipment was sized to meet the DNFSB commitments of 4000 kg of graphite fines and sand, slag, and crucible to be processed by May 1998 and all ash processed by May 2002. Six new muffle furnaces were planned to be placed in existing gloveboxes in E Module of Building 707. Two new segmented gamma scan (SGS) units were planned. The approval of "Pipe and Go" allowed elimination of the stabilization step. The ash is batched to ensure compliance with the 10 weight percent safeguards termination limit, size reduced using a hammermill, and repacked and assayed to meet WIPP requirements. The assayed containers are placed into the pipe overpack container for storage and ultimate disposition. Ash repack was started in December 1998 in Building 707, and 1200 kg of the total 26,000 kg have been repacked to date.

Combustibles

The combustibles are repackaged in filtered plastic bags or metal containers within drums in Room 3701 of Building 371. The combustibles are not placed in the pipe components due to the low plutonium content of the matrices. The combustibles are inherently gas generating due to the radiolytic decomposition of the hydrogen bearing matrix material. Typically the wattage limit of 0.08 watts/drum will be met before the drum volume becomes limiting. A technology has been developed and implemented to measure gas generation from combustible drums to establish the allowable plutonium loading limit. Testing to date indicates that the gas generation is significantly lower than the published wattage tables predict. The allowable plutonium per drum

can be increased from limits below 10 grams per drum to levels between 80 and 120 grams per drum, depending on the matrix. Gas Generation Testing is expected to result in the certification of 350 existing drums without repackaging. As of the end of January 1999, 38 drums (1088 kg) of wet combustibles have passed gas generation testing. This represents a reject rate of 35 percent of the candidate drums. An effort is underway to recover the rejects by verifying the layers of plastic containment to gain a higher wattage limit. Drums that require repackaging will result in a factor of four to five fewer outgoing drums based on gas generation testing. Combustible repackaging was started up in Building 371 in November 1998, and 440 kg of 20,000 kg total have been repacked to date.

Dry/Repack

The Dry/Repack "bucket" contains miscellaneous glass, metal, and other inorganics that contain no safety risk associated with material stability. No processing of the materials was planned. Gas generation testing will decrease the number of drums requiring repackaging. A total of 250 backlogged drums of dry drums is expected to pass gas generation without repackaging. To date, 21 drums (1153 kg) of the candidate drums have been tested and all have passed. The contents of drums that require repackaging will be size reduced with tools and equipment, as required, and repackaged to facilitate safe storage, transportation, and to meet WIPP Waste Acceptance Criteria. The pipe component will be incorporated for the higher plutonium loading, but the leaner materials will be packaged to meet packaging requirements within drums. A repack line was started up in D Module of Building 707 in June 1998. A repack station was also established in Building 776. To date, 4700 kg of dry/repack residues have been repacked. Sand, slag, and crucible residues are being repacked in Building 371 for shipment to Savannah River Site for further processing. To date, 1900 kg of sand, slag, and crucible residues have been repacked with shipment pending finalization of the Safety Analysis Report for Packaging (SARP).

REFERENCES

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