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U.S. Department of Energy Implementation of Chemical Evaluation Requirements for Transuranic Waste Disposal at the Waste Isolation Pilot Plant

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List of Acronyms and Abbreviations

AK	acceptable knowledge
AKA	Acceptable Knowledge Assessment
AKE	acceptable knowledge expert
BoK	Basis of Knowledge
CBFO	Carlsbad Field Office
CCEM	Chemical Compatibility Evaluation Memo
DSA	Documented Safety Analysis
LANL	Los Alamos National Laboratory
NCR	nonconformance report
RTR	real time radiography
TRU	transuranic
WAC	Waste Acceptance Criteria
WHB	waste handling building
WIPP	Waste Isolation Pilot Plant

Executive Summary

This report summarizes new controls designed to ensure that transuranic waste disposed at the Waste Isolation Pilot Plant (WIPP) does not contain incompatible chemicals. These new controls include a Chemical Compatibility Evaluation, an evaluation of oxidizing chemicals, and a waste container assessment to ensure that waste is safe for disposal. These controls are included in the Chapter 18 of the Documented Safety Analysis for WIPP (1).

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1.0 Introduction

The Waste Isolation Pilot Plant (WIPP), located approximately 26 miles outside of Carlsbad, New Mexico was built by the U.S. Department of Energy for the permanent disposal of the nation's transuranic (TRU) waste[1]. WIPP received its first shipment of waste in March of 1999 and operated for 15 years until two accidents occurred February of 2014 resulting in the suspension of waste emplacement operations.

The first accident, an underground fire, occurred in a salt hauler truck as a result of poor or deferred maintenance (2). The second, unrelated accident occurred nine days later. This accident was an uncontrolled exothermic reaction involving a mixture of organic material acting as a sorbent and nitrate salts. The 55-gallon drum containing this mixture pressurized as a result from the reaction, causing failure of the drum locking ring and displacement of the drum lid; this resulted in release of radioactive material followed by the spread of contamination in the mine and ventilation system (3, 4).

This accident caused a reassessment of WIPP's waste acceptance criteria (WAC), especially the use of organic absorbents in conjunction with oxidizing chemicals, such as nitrate salts. WIPP revised its WAC in 2016 to prohibit mixing these types of materials (5). These revised criteria were included in the facility's Documented Safety Analysis (DSA; i.e., the operating license for the facility) as nuclear safety controls. The controls include a Chemical Compatibility Evaluation, an evaluation of oxidizing chemicals, and a waste container assessment. These controls are now required for all waste disposed at WIPP beginning after the reopening of WIPP in January 2017 (5).

By the end of 2016, 25,690 containers of TRU waste had been certified as acceptable for disposal (6) but not yet emplaced in WIPP. Approximately 230 containers were in the waste handling building (WHB) on the surface at WIPP while the rest remained at generating sites awaiting shipment. The containers had been certified to meet the WAC in effect at the time (i.e., during or prior to 2014). All of these containers—referred to as "previously certified"—are subject to the new controls (criteria) established in 2016. The Department is in the process of evaluating all of the previously certified containers to verify that they meet the new WAC and, thus, whether the containers can be disposed at WIPP without additional data or repackaging. Repackaging is time consuming, costly, and hazardous (due to the potential for spread of contamination). Therefore, it is desirable to avoid repackaging if possible.

[1] Transuranic waste is waste which has been contaminated with alpha emitting radionuclides possessing half-lives greater than 20 years, contains concentrations greater than 100 nCi/g and consist of elements whose atomic weight exceeds that of uranium.

2.0 New Requirements

As part of the process for characterizing and certifying TRU waste for disposal, it is necessary to consider the range of possible chemical combinations that could occur in each waste stream.

Potential adverse chemical reactions (e.g., generation of heat, fire, explosion, or toxic fumes) that stem from combining potentially incompatible chemicals must be evaluated to support safe and compliant waste management. To expand upon this evaluation, chemical compatibility has been enhanced to require formal documentation and generation of a chemical compatibility evaluation memo (CCEM) for the waste stream, or sub-population of the waste stream, as needed (5). The CCEMs are written by the Certified Programs[2] using procedural requirements based on the method described in the 1980 EPA method EPA-600/2-80-076, “A Method for Determining the Compatibility of Hazardous Wastes.” The CCEM documents and communicates the evaluation, including the conclusions. CCEMs that identify potential chemical incompatibility will provide the basis for placing an administrative hold on the affected waste via issuance of a nonconformance report (NCR). CCEMs showing potential chemical incompatibility are provided to the Carlsbad Field Office (CBFO) for information only. CCEMs concluding that the waste is acceptable are provided to CBFO for formal review and approval (5).

The evaluation of oxidizing chemicals is used in conjunction with the acceptable knowledge (AK) procedures of the Certified Programs[3]. This evaluation specifies when waste with oxidizing chemicals is acceptable as is, or when treatment will be required—and if so, guidance on the treatment that must be performed (7).

To ensure that the AK documentation relating to the management of potentially reactive, corrosive, ignitable, and incompatible TRU waste materials is adequate, current, and accurately described in existing AK Summary Reports, a onetime AK assessment must be performed for waste streams having a population of previously certified but unshipped containers. New AK Summary Reports and the supporting documentation must address all of the current evaluation parameters or an AK assessment must be performed (5).

3.0 Implementing New Requirements

At the beginning of 2017, there were 25,690 previously certified containers. These containers were certified using previous requirements and must meet the new requirements listed in Chapter 18 of the DSA. Immediately after completion of the operational readiness review for the

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[2] There are two programs that can certify waste for shipment to WIPP. The Central Characterization Program is managed from Carlsbad and the Advanced Mixed Waste Treatment Program is managed from Idaho.
[3] The AK process provides a description of the waste and how it was generated including the chemicals used.

reopening of WIPP in November 2016, two waste streams were cleared for chemical compatibility, oxidizing chemicals, and container assessment. One stream, ID-RF-S3114, contains about 5000 containers and the other, SR-211H-PUOX, has about 300 containers. WIPP has been disposing of these two streams almost exclusively since it reopened (6).

Approximately 20,000 containers of previously certified waste remain that must be evaluated against the new requirements. Because of regulatory issues, the Department has been prioritized verification of several waste streams from Los Alamos National Laboratory (LANL).

Waste stream LA-MHD01.001 is a mixed heterogeneous debris waste stream that comes from the Technical Area 55 (TA-55) Plutonium Facility Building 4 (PF-4) at LANL and will serve as an example of how the new requirements are implemented. Plutonium recovery operations began on July 1, 1979, at TA-55, where plutonium was extracted from residues and scraps to recover as much as possible (4).

4.0 Acceptable Knowledge Summary

The AK Summary report provides basic information regarding the waste stream contents, how they were generated, the physical and chemical processes used, and a list of chemicals used in the facility. In the case of TA-55, there are over 20 unit processes and about 275 different chemicals. Many of these use nitric acid and will, therefore, contain nitrates as oxidizing chemicals.

The summary report serves as a starting point and is used to build a mass balance around each unit process to determine where chemicals leave the process. Some leave as product and the rest leave as waste. The process alters the chemical and its properties. For example, sodium dichromate (Cr VII) is used as an oxidizing agent and is converted to hydroxide (Cr III) in the process. Some starting chemical material may be found in the waste because it is common to use excess material to drive reactions to completion (or near completion). For example, if plutonium oxalate is precipitated from solution, it would be common to use an excess of oxalic acid (or sodium oxalate) to ensure that virtually all of the plutonium forms the oxalate. In this case, the excess oxalate is removed with the waste solution and is treated at the nearby waste water facility. The plutonium oxalate product is heated to recover plutonium oxide and the oxalate is converted to carbon dioxide, which is driven off as a gas.

Each unit process used in TA-55 was evaluated to determine what chemicals were used, as well as their likely end state and form in various waste streams. Additionally, some waste is treated when it is generated to facilitate handling and to render the waste non-reactive. For example, ion exchange resins and some nitrate salts are mixed with cement and allowed to harden prior to disposal. A mass balance was used to evaluate chemical compatibility of various wastes in their final, treated form.

5.0 Chemical Compatibility Evaluation

The CCE determines if the chemicals in the waste stream are compatible. The evaluation begins with list of all the chemicals used in the waste stream, based on the AK Summary Report. A table showing all of the chemicals, materials, and their use or description is developed to aid in the evaluation. If chemicals in the waste are determined to be incompatible (that is, there is the possibility of an adverse reaction or combustion), the waste cannot be accepted for disposal without treatment to remove the incompatibility.

The identified chemicals and materials that were listed for the facility are assigned a maximum quantity for the waste stream as follows:

Trace- less than 1 weight percent

Minor- 1-10 weight percent

Dominant- 10+ weight percent

"Incompatible" refers to the materials/chemicals that, when mixed, can lead to consequences including:

- Generate extreme heat or pressure, fire or explosions, or violent reactions
- Produce uncontrolled toxic mists, fumes, dusts, or gases in sufficient quantities to threaten human or environmental health
- Produce uncontrolled flammable fumes or gases in sufficient quantities to pose a risk of fire or explosions
- Damage the structural integrity of the device or facility, threaten human/environmental health in any other way

To be considered for WIPP disposal, the CCE must demonstrate one or more of the following conclusions:

1. The chemical/material is not present in a quantity or form sufficient to produce adverse reactions. This determination is made based on the documented use of the chemical/material and waste management practices of the generator site, and the judgment of the AK expert (AKE), considering relevant AK source documentation.
2. The chemical/material, including reaction products, was rendered non-reactive or unavailable for adverse reactions with other chemicals/materials of concern in the

waste stream.

3. Other chemicals/materials of concern were rendered non-reactive, unavailable for reaction, or are not present in the waste stream.
4. Anticipated incompatible reactions have already occurred during waste generating processes or subsequent waste management activities (e.g., passivation of sodium metal, neutralization of acidic solutions, reaction of hydrofluoric acid on silica-based absorbents, oxidation of cellulosics by nitric acid) and will therefore not occur in the future.
5. The reaction between chemicals/materials will result only in inconsequential reactions and cannot lead to one of the four reaction consequences previously mentioned.

Some chemicals and materials were determined to be potentially present as a part of the TA-55 process but at an insignificant concentration that would not contribute to an adverse reaction or would not be present in the waste.

6.0 Acceptable Knowledge Assessment

After completing the CCE, but before the oxidizer evaluation, the waste stream undergoes a container-by-container evaluation (10). The Acceptable Knowledge Assessment (AKA) is a container-by-container evaluation to determine whether the waste in the container is consistent with documented contents. It compares documented contents with real time radiography (RTR) and visual examination records to determine whether documented contents are consistent. For example, if the waste is reported to be from high temperature operations from a specific laboratory (room) and radiography shows the presence of crucibles, then there is a fairly high confidence that the contents came from the assigned laboratory, because crucibles are used in high temperature operations.

The AKA report also provides information regarding the processes and procedures being used at the facility when the waste was generated. This information, combined with chemical data, provides insight into the likely waste contents and distribution of chemicals, including oxidizers. In the case of PF-4 waste, there is also information regarding solid waste type, which is included with the container. For example, a waste code of A30 is applied to used equipment. One container in the waste stream carried a waste code of A30. The RTR data showed that the container held a high temperature furnace. Thus, the RTR was used to confirm the waste description (code) and overall confidence in determining that the waste is acceptable for disposal at WIPP is increased (8).

7.0 Evaluation of Oxidizing Chemicals in TRU Waste

Because the radiation release in 2014 was caused by an exothermic reaction of nitrate salts and organic materials, the Basis of Knowledge (BoK) was developed to provide criteria for evaluating oxidizing chemicals in TRU waste to determine acceptability at WIPP. An oxidizing chemical is a chemical that yields oxygen that can enhance the combustion of organic materials (7).

The BoK evaluation involves a series of steps, or individual evaluations, as follows:

- Verify the presence of oxidizing chemicals. This amounts to listing the potential chemicals and, if possible, establishing quantity or concentration expected.
- Evaluate how the chemicals may be distributed in the waste. This involves some estimate of whether the oxidizing chemicals were mixed with diluents and whether the resulting mixture is reasonably homogeneous.
- Assess whether acids or bases have been neutralized. In some cases (e.g., neutralization with magnesium hydroxide) neutralization significantly alters the behavior of oxidizing chemicals.
- Determine whether organic sorbents were used, because the sorbent may provide fuel for a reaction to propagate. This includes sorbent materials such as rags, wipes, sorbent pads and pillows.
- Evaluate the combination of inorganic material with oxidizing chemicals (i.e., the use of inorganic sorbents with oxidizing chemicals).
- Evaluate potential mixtures of organic and inorganic materials mixed with oxidizing chemicals.
- Oxidizing chemicals that may be the sole component of the waste.
- Assess the effectiveness of oxidizing chemicals solidified in a cement or grout matrix
- Assess surfaces that may be contaminated with oxidizing chemicals.

The MHD01 waste stream from LANL may contain the following oxidizing chemicals:

- Nitric acid
- Mercuric nitrate
- Lead nitrate
- Vanadium pentoxide
- Sodium nitrate
- Potassium nitrate

This represents the verification of oxidizers in the waste stream.

The BOK evaluation discussed above was applied to the MHD01 waste stream. In a population of 76 containers of MHD01 waste currently stored at Waste Control Specialist (WCS) in Texas, 58 containers (about 75%) passed all of the evaluations described in this report (9).

8.0 Current Status

There are about 20,000 containers of previous certified waste that must be evaluated to determine whether they can be disposed of at WIPP. Since the disposal site reopened in January 2017, the Department evaluated 225 containers and approved 194 for disposal other than RF-S3114 and SR-PUOX. LANL waste from PF-4 is extremely heterogeneous due to the nature of the work done at PF-4. Each waste container is a unique mix of waste and requires significant effort to perform the required evaluations. This situation is expected to continue until the LANL waste streams at WCS are completed.

References

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