Office of Environment, Health, Safety and Security
Operating Experience Level 3

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Nitrate Waste Evaluations

PURPOSE

This Operating Experience Level 3 (OE-3) document provides information to clarify proper methods for evaluating potential hazards of nitrate wastes. This information stems from expert review of responses to OE-2: 2015-1, *Evaluation of Nitrate-Bearing Transuranic Waste Streams* (June 2015).

BACKGROUND

On February 14, 2014, an airborne radiological release occurred at the Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP) near Carlsbad, NM. On March 4, 2014, an Accident Investigation Board (AIB) was appointed to determine the cause of the release. The Phase 2 investigation report was issued on April 16, 2015.

The AIB determined that the release was caused by an exothermic reaction involving the mixture of organic material and nitrate salts present inside a transuranic (TRU) waste drum. The drum had been remediated and certified to meet the WIPP Waste Acceptance Criteria (WAC) at the Los Alamos National Laboratory (LANL), and was subsequently shipped to WIPP for permanent disposal. While the drum was stored at WIPP, heat from exothermic chemical reactions caused an increase in internal pressure exceeding the drum's venting capacity, leading to drum failure and a rapid release of its contents. The AIB also determined that other drums had been remediated with organic materials, making them susceptible to this failure mode. For this reason, DOE field organizations were requested by OE-2: 2015-1 to review all nitrate-bearing TRU waste streams that used neutralizers and/or absorbents for mitigation.

Except for LANL, which had already declared a Potential Inadequacy in the Safety Analysis, every responding site concluded that their waste streams did not present an ignitability hazard similar to the WIPP scenario because an oxidizer was not present in the waste. In all cases, the LANL – Carlsbad Operations Difficult Waste Team (DWT) agreed with that conclusion, but in some cases found that the conclusion followed from a technical rationale not provided by the site. The discussion below provides methods for testing materials for the presence of an oxidizer, and potential sources of error in making conclusions about ignitability hazards that were identified based on the responses to OE-2: 2015-1.

METHODS FOR TESTING SOLID MATERIALS FOR THE PRESENCE OF AN OXIDIZER

The Environmental Protection Agency's (EPA's) Solid Waste (SW) 846 Method 1040, *Test Method for Oxidizing Solids*, provides a technical basis for "assessing the relative oxidizing hazard of solid substances, including solids, granular materials, and other materials that can be formed into a conical pile" by measuring the burning rate of a substance relative to a reference material. For this test, the waste is mixed with cellulose in both 1:1 and 4:1 ratios by mass. The mixtures are ignited with an electrically-heated wire, and the burning time of each mixture is measured. The burning times are compared to the burning times for a variety of mixtures of potassium bromate and cellulose.

The test divides the waste material into four categories of oxidizers based on a comparison of burning rates between the reference mixture and the two waste mixtures. For a waste form to be considered Category IV substance (lowest ignitability), it should not ignite and burn faster than the 3:7 potassium bromate to cellulose standard at either ratio of cellulose. To provide a strong technical basis that a waste material lacks the oxidizer property, the test must be performed on a representative surrogate mixture and the absorbent used with the waste, or a bounding mixture of the oxidizer and the sorbent used in the waste.

The United Nations (UN) 0.1 *Test of Oxidizing Solids* (see the United Nations *Manual of Tests and Criteria*) is very similar to the SW-846 test. Either of these tests, applied to the appropriate waste mixtures, would be an acceptable technical basis for determining whether a site's waste requires the use of EPA's D001 code due to the oxidizer property.

POTENTIAL SOURCES OF ERROR IN MAKING CONCLUSIONS ABOUT IGNITABILITY HAZARDS

(1) Some responses seemed to assume that neutralization phenomena would mitigate the oxidizer characteristic of certain materials. From a chemical standpoint, this is not the case. Lowering the pH of a substance reduces its corrosivity characteristic but may not substantially affect its oxidizer property.

(2) Some responses seemed to assume that if the waste were solidified from a solution of less than 70% nitric acid, it cannot be an oxidizer, because the acid from which it derived was not an oxidizer. This concept might stem from the Department of Transportation's Hazardous Materials Table in 49 Code of Federal Regulations §172.101, which is referenced in the Resource Conservation and Recovery Act definition of an oxidizer. In this table, aqueous nitric acid at less than 70% concentration is not listed as an oxidizer. However, this assumption is valid only for aqueous solutions of nitric acid, and does not apply after the nitric acid is converted to a salt or a solid by sorption. The resulting nitrate salt is an oxidizer. The Department of Transportation classifies solid nitrate salts as oxidizers but not aqueous nitric acid because, unlike nitric acid, which is volatile and will evaporate as water evaporates, nitrate salts concentrate in the wastes with the loss of water.

(3) Some responses seemed to assume that when a material passes the EPA-SW-846 Method 1030 test, the material cannot be an oxidizer. This is not quite the case. The test establishes whether an ignitable solid is present but does not provide information regarding the oxidizer property of the tested material. Pure nitrate salts will not propagate a flame (i.e., will pass a Method 1030 test) but will readily produce an oxidizer result from the Method 1040 test, which is designed to give information on whether waste will stimulate the combustion of organic material.

(4) Some responses seemed to rely on the argument that long storage of nitrate waste without untoward events means an oxidizer is not present. This is not necessarily true. Oxidizer may be present in a stable form and would cause stored organic materials to burn more vigorously, once ignited by some means. The intent of the OE-2 issuance was to warn TRU waste owners of the potential short and long-term hazards of combining organic absorbents with oxidizers such as nitrate waste in both liquid and solid form.

(5) Some responses seemed to rely on vendor claims without examining the vendor's supporting data. Vendor testing data should be thoroughly evaluated to ensure it supports the vendor's claims.

(6) Some responses seemed to assume that widespread use of a particular reagent or other mitigation method across the TRU

waste complex with no reported events justifies adopting that method. This approach, if used, needs to focus on the specific applicability of the proposed method to the type of waste in question. At Hanford's Plutonium Finishing Plant, for example, the use of glycerin as a fogging agent to reduce airborne radioactive contamination was ill-advised in a room containing nitrate salts because of potential ignitability concerns.

DISPERSAL OF OXIDIZERS

One defensible argument to declare a waste form free of the oxidizer property when an oxidizer is present is the dispersal of the oxidizer into a sufficient quantity of matrix so that combustion cannot be supported. The DWT has performed scoping tests using a modified SW-846 Method 1040 test, in which the burning rates of various mixtures of potassium nitrate and organic sorbents were compared. These tests showed that, once dried to constant weight, mixtures of potassium nitrate and organic absorbents may be categorized as non-oxidizers when the nitrate salt is less than 30% of the mixture by mass. Estimating the mass mixture of such potential oxidizers may be used as an initial screening tool in TRU waste. However, actual waste matrix characteristics must be fully understood to determine the real oxidizing potential of a specific TRU waste before conclusions on acceptability can be determined.

These scoping studies should only be used to evaluate previously packaged waste and not to justify continued use of organic sorbents to treat oxidizers. Although dispersal of an oxidizer into an organic matrix may generate a mixture that is too rich in fuel to assign the oxidizer property, the consequence of error if a worker miscalculates the required ratio is much higher when using an organic matrix as the absorbing agent, compared to using an inorganic matrix. Of particular concern are cellulose and other sorbents that contain alcohol functional groups. These have the potential to react exothermically with oxidizers, particularly nitrates, and self-heat, which could give rise to thermal runaway reactions. Therefore, wastes containing oxidizers that are repackaged or generated in the future should only use compatible inorganic matrices as the mitigating agents. Further studies are ongoing.

CONCLUSIONS

(1) Affected technical personnel should review and understand the information shared in this document.

(2) When the DWT examined the data regarding each waste stream in response to the OE-2: 2015-1, the DWT found that the nitrates present in the final waste forms are at concentrations below 30% and often have additional factors, such as the presence of moisture or inert inorganic matrices, that may provide additional safety margin.

(3) Oxidizers, including, but not limited to nitrate wastes, should not be mixed with organic absorbents in future TRU waste packaging or remediation. Doing so may create an immediate hazard or may render the waste unacceptable for disposal in the future.

(4) Engineered absorbents may exhibit the characteristics of organic absorbents, and users should fully understand the properties of the absorbents in combination with the specific waste form before using them in TRU waste.

(5) Since DOE assumes that all TRU waste will eventually be disposed at WIPP, the WIPP WAC applies beginning at the point in which the waste form is created and continues to apply throughout the life-cycle of the waste. The WAC prohibits TRU waste exhibiting characteristics of ignitability, reactivity or corrosivity.

(6) Any proposed use of organic absorbents or engineered absorbents in combination with potentially oxidizing TRU waste, wet or dry, should be evaluated and approved by the National TRU Program, Carlsbad Field Office.

This OE-3 document requires no follow-up report or written response.

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