Summary of WIPP Hypotheses – 06/06/2014

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Background

The following hypotheses are the combined effort of two independent teams who met separately to evaluate data and develop independent hypotheses for the radioactive material release at the WIPP site. Both teams recognized that inhomogeneity within the drums due to the drum mixing and packaging operations creates a level of complexity and uncertainty that likely will never be fully understood.

The teams evaluated scenarios and applied judgment to subjectively grade hypotheses as:

- Anticipated: expected
- Possible: plausible
- Unlikely: not expected, but cannot be ruled out
- Extremely Unlikely: not expected
- Beyond Extremely Unlikely: inconceivable

This analysis has provided the basis for further work (paper and experimental studies) to support or to refute these hypotheses.

Chemical Reactivity Hypotheses

1) **Possibility that process changes introduced incompatible chemicals.** We found evidence for multiple process changes in the dealing with nitrate salts over several years. The addition of organic materials, as potential fuels, with nitrate salts (strong oxidizer) could be incompatible. These include the following:
   a. **Waste Lock**
      i. The use of Waste Lock to remove liquids introduced organic material. Following its discovery, a new procedure was introduced to remove liquids (remediate wastes) employing zeolite. Kitty litter was a common commercial source of zeolite. Given that drum 68660 did not contain Waste Lock, we have not focused on this potential at this time and no experiments are currently planned on Waste Lock. (Extremely Unlikely)
   b. **Swheat kitty litter**
      i. The use of Swheat kitty litter introduced organic material in contact with $NaNO_3$. It is possible that the conditions could have lead to hydrolysis reactions leading to the creation of materials with the potential for flammability, greater than the starting materials (e.g., generation of fufurals). Completed experiments (Table 1) suggest this is now unlikely. (Unlikely)

ii. There remain questions about interaction of Swheat with nitric acid, or other metal nitrate salts. There are a number of experiments underway to evaluate the sensitivity and thermal stability of Swheat kitty litter in contact with nitric acid and other metal nitrate salts (see **Table 1**). (Possible)

c. **Citric acid**

i. Citric acid was employed to neutralize alkaline liquids prior to mixing with kitty litter, and it is possible that it was used to compensate for basic conditions if the operator overshot neutralization using acid neutralizer. The majority of waste drums were acidic, so citric acid use was employed infrequently relative to triethanolamine. Citric acid was not documented as having been used with drum 68660.

ii. There are no current tests being conducted with citric acid, but we suggest that tests with citric acid and nitrate salts should be conducted in the future. (Unlikely)

d. **Triethanolamine (TEA)**

i. Prior to September 2013, a dry formula acid neutralizer containing sodium carbonate and an organic polymer was employed to neutralize acidic liquids prior to mixing with kitty litter. After September 2013, acidic liquids found in parent drums were neutralized with an aqueous formulation TEA,[1] then absorbed on Swheat kitty litter and packaged in daughter drums.[2] Triethanolamine reacts with nitric acid to produce triethanolammonium nitrate, $(TEA)NO_3$, an energetic material.[3]

ii. An experimental test matrix has been developed to evaluate the chemical reactivity of TEA and Swheat kitty litter with nitrate salts and nitric acid and to evaluate their sensitivity and thermal stability (see **Table 2**). (Possible)

e. **Other potential reactive chemicals**. Our review suggests the potential for other reactive chemicals, such as the presence of NH_3 in nitrate salts from evaporator bottoms, or the presence of furfurals from the hydrolysis of the Swheat cellulose materials, or the presence of ketones produced by trace quantities of transition metals (e.g., Fe, Ti, Cr). In addition, we cannot rule out the presence of other organics that may have been in the waste stream in vials, pipettes etc. These chemicals could react with residual nitric acid in the drums to create reactive species.

i. An analytical characterization plan has been developed to analyze emptied parent waste drums for the presence of these or other chemicals as a potential source for reactive species (see **Attachment A**). (Possible)

2) **Trigger Mechanisms.** A variety of triggers may be available to initiate exothermic reactions.

a. We found records indicating that drum 68660 contained a glove box glove.[4] In current practice, these gloves would most likely be tungsten-lined (gloves that contain a bismuth/tungsten/lanthanum mixture) as opposed to older lead-lined gloves. We note that lead-lined gloves in a nitric acid environment have led to energetic events at Rocky Flats,[5] Mound,[6] and Los Alamos.[7] This leads to the hypothesis that the glove box glove or lead flakes introduced from lead liners in some drums, including 68660, may provide a trigger mechanism. Two series of tests have been designed to evaluate these hypotheses. (Possible)

    i. Experiments have been developed to test the influence of lead with HNO_3, Swheat, and TEA (See **Table 2**).
    ii. Experiments have been developed to test a tungsten-lined glove (containing W, Bi, La) in the presence of HNO_3 and Swheat (see **Table 2**)

b. We discussed the potential for internal (a clogged filter) or external flammable gas buildup and ignition from an electrostatic discharge. There are no further plans to test this hypothesis at this time. (Possible)
c. We discussed the potential for self-heating or external heating of a drum to raise the temperature high enough to initiate a chemical reaction. Many of the chemical experiments being performed could add insight into the viability of this hypothesis. (Possible)

3) **Radiation Chemistry**. Radiolysis of organic materials in drums can produce hydrogen, in addition to other gases with potential to increase pressure, heat, or both inside drum 68660.
    a. Experience from LANL and Rocky Flats,[8] and simple calculations suggest that gas generation and heating from radiolysis should be minor based on radionuclide inventory of drum 68660, especially over the several month time-frame between packaging and radiological release from drum 68660.
    b. For completeness, more sophisticated radiolysis calculations have been initiated to better quantify radiation chemistry effects in drum 68660. (Unlikely)

4) **Trace Metal Impurities**. We considered the potential for trace metal impurities (ie, Fe, Mn, Al, etc.) to facilitate decomposition or nitration of organics in the drum.
    a. We are developing a literature review and assessment of the potential catalytic or stoichiometric processes from trace metal impurities over a bounding range of pH. (Possible)

Broad View Hypotheses

5) **Green Burst hypothesis**. A "Green Burst" and "arcing noises" in the power substation adjacent to the WIPP site in Carlsbad was reported at 22:50 just 23 minutes prior to the CAM-151 radiation alarm trigger.[9] The proximity of these two events is remarkable.
    a. Our hypothesis is that the "green burst" was a modulation of the normal corona discharge glow (not a burst) at the high-voltage input to the substation due to ionized gases caused by ionizing radiation escaping from WIPP prior to the CAM alarm trigger.

b. CAMS are located *c.a.* 6ft above the floor,[9] likely for maintenance. Hot gases associated with the radiological release may have carried radioactive particulates near the ceiling, well above the height of CAMS during the initial event. This would have allowed radionuclide particulate emissions from WIPP prior to the CAM alarm because the air was not HEPA filtered prior to the CAM trigger.
c. It is recommended that additional radiological survey swipes be taken near the substation for evidence of contamination. (Possible)

6) **Potential Relationship to Truck Fire**. Elevated temperature in Panel 7 due to ventilation changes and hot gases from the underground truck fire[10] may have raised temperature in Panel 7, resulting in an exothermic reaction.
    a. Preliminary modeling efforts demonstrate the capability to model drums and rooms, and estimate that temperatures in Panel 7 will likely asymptotically approach 30 °C after several hundred days in an unventilated condition.
    b. Preliminary models indicate that a more detailed understanding of the air-flow through rooms and panels is necessary to fully explore this hypothesis. Further modeling efforts should be conducted. (Unlikely)
    c. Consideration was also made of the possibility for an ember from the truck fire to have propagated to Room 7. (Extremely Unlikely)
    d. Similarly, the truck fire led to confusion which could have allowed a worker to inadvertently leave something behind that initiated the fire (e.g., filter cartridge) (Unlikely)

7) **Potential for a Criticality Event**. Due to extremely low quantities of fissionable materials available and allowed in waste drums, we have no criticality concerns.[11]
    a. Criticality expertise has examined criticality safety at every stage. At no time was there ever enough material present to generate a criticality concern. (Beyond Extremely Unlikely)

8) **Potential issues with other waste containers in Panel 7.** We note that there are a variety of waste containers in Panel 7, and there is a need to understand the waste characteristics and processing parameters for all containers in the room.
    a. Drums in Panel 7 contain wastes from SRS, INL, and LANL. Further analysis of the material in drums from SRS and INL must be complete and are in process. (Possible)
    b. Drums containing cemented wastes from LANL are not of concern – historical process documentation shows no organic material went into these drums. (Extremely Unlikely)
9) **Other materials or mechanisms could have led to the incident**, and include:
    a. MgO bags
    b. Debris/trash
    c. Forklift insult
    d. Other mechanical insult (Unlikely)

10) **Arson/Sabotage.** This is a possibility we considered, but we do not have the expertise to assess this hypothesis. (Unlikely)

Recommendations

1) Both teams recommend active cooling of waste drums whose parents had significant volumes of liquid (> 5 gallons) of unknown pH and neutralization status, or had low pH's (pH ≤ 1) and were neutralized with liquid TEA after September 2013.
    a. Use of evaporative cooling
    b. Use of a refrigerated truck or a low temperature freezer
2) An additional compensatory measure would be to add water or weakly basic water to remediate drums, followed by cementation of the resulting waste stream. This recommendation will be discussed with NMED and any authorizations obtained from NMED.

References

1) May 19, 2014 Energy Solutions memo from Miles Smith to Dan Cox entitled "Correction to Transmittal of Neutralizers Used in Nitrate Salt Processing."
2) WCRRF procedure EP-WCRR-WO-DOP-1198, section 10.3.
3) U.S. Patent, 3,401,067, Sept. 10, 1968, "Aqueous Slurry Type Explosive Compositions Sensitized with at Least One Alkanolamine Nitrate".
4) May 20, 2014 Energy Solutions memo from Miles Smith to Dan Cox entitled "Revision 1, Nitrate Salt Waste Containers at WCS, WIPP Panel 7, and LANL Data Summary."
5) J. L Long, C. J Smith, "Unstable Material Formed by reacting leaded Glove Box Gloves with Nitric Acid," RFP-2648, Rocky Flats Plant, The Dow Chemical Company, Golden, Colorado, 1977; T. C. Johnson and J. W. Lindsay, "Flammability of Lead Dry Box Gloves," RFP- 1354, Rocky Flats Plant, The Dow Chemical Company, Golden, Colorado, 1969.
6) Mound accident in "Serious Accidents USAEC Issue No. 293, August 26, 1968."
7) D. Christensen, D. Bowersox, B. McKerley, R. Nance, LA-11069, "Wastes from Plutonium Conversion, and Scrap Recovery Operations."
8) W. V. Conner, "Evaluation of Residue Drum Storage Safety Risks" June 17, 1994, RFP-4826.
9) "Phase 1 Radiological Release Event at the Waste Isolation Pilot Plant on February 14, 2014," US DOE, Office of Environmental Management Accident Investigation Report, April 2014.
10) "Underground Salt Haul Truck Fire at the Waste Isolation Pilot Plant February 5, 2014," US DOE, Office of Environmental Management Accident Investigation Report, March 2014.
11) ANSI/ANS-8.1, Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors, 1998.

Attachments
Table 1. Test Matrix for SWheat Kitty Litter reactivity I
Table 2. Test Matrix for SWheat Kitty Litter reactivity II
Appendix A. Analytical Plan for Emptied Parent Waste Drums

Attachments

Table 1. Test Matrix for SWheat Kitty Litter reactivity I

Test Series 0 (completed)	Nitrate Source	Acid Conc.	Neutralizing Agent	Product Sensitivity and Thermal Testing WX-7 Analytical Report #51924
Swheat Kitty Litter mixed wet	KNO_3	None	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter ground and mixed dry	KNO_3		None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter wet and allowed to dry	KNO_3 dissolved in water		None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter nitrated under forcing conditions	None	Concentrated nitric and sulfuric	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter ground and mixed dry	$NaNO_3$	None	None	Impact, ESD, friction, DSC **Results in WX-7 Analytical Report #51927**
Swheat Kitty Litter ground and mixed dry	$NaNO_3$/ KNO_3 (1:1)	None	None	Impact, ESD, friction, DSC **Results in WX-7 Analytical Report #51927**
Test Series I (completed)	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Product Sensitivity and Thermal Testing WX-7 Analytical Report #51934**
Swheat Kitty Litter*	$NaNO_3$	0.001M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	$NaNO_3$	1M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	$NaNO_3$	5M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter* Aging Studies	$NaNO_3$	0.001, 1M and 5M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability will be completed on samples weekly for 2 months
Test Series II (planned)	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Reactivity, thermal stability studies, and degradation product isolation and identification**
Swheat Kitty Litter*	$NaNO_3$	0.001M HNO_3	None	Head space analysis at ambient temperature & 80C; nuclear magnetic resonance spectroscopy to characterize products
Swheat Kitty Litter*	$NaNO_3$	1M HNO_3	None	Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Swheat Kitty Litter*	$NaNO_3$	5M HNO_3	None	Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Test Series III (partially completed)	**Nitrate Source**	**Acid Conc.**	**Neutralizing Agent**	**Product Sensitivity (WX-7 Analytical Report #51933), Thermal Testing, and degradation product isolation and identification**
Swheat *	$NaNO_3$	1M and 5M HNO_3	Kolorsafe Neutralizer Triethanol-amine (TEA)	Impact, ESD, friction, DSC, vacuum stability; Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Triethanolamine nitrate salt (TEAN)	None	None	None	Impact, ESD, friction, DSC, vacuum stability; Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Swheat**	$NaNO_3$	1M HNO_3	TEA	Impact, ESD, friction, DSC, vacuum stability; Head space analysis at ambient and 80C; nuclear magnetic resonance spectroscopy to characterize products

*1:3 ratio $NaNO_3$ solutions to SWheat by volume, superstaturated solutions of $NaNO_3$ in the indicated HNO_3
**1M HNO3 saturated with NaNO3 titrated neutralized with TEA, addition of 0.3 wt% $NaNO_2$ then 3 volumes of SWheat kitty litter

Attachments

Table 2. Test Matrix for SWheat Kitty Litter reactivity II. Reactivity Studies of SWheat Kitty litter mixtures with Lead and Tungsten and Triethanolamine.

Test Series I	**Nitrate Source**	**Acid Concentration**	**Neutralizing Agent**	**Product Sensitivity and Thermal Testing, characterization**
Triethanolamine	HNO_3	1M HNO_3	None	Look for formation of nitrate esters
Triethanolamine	HNO_3	7M HNO_3	None	Look for formation of nitrate esters
Triethanolamine	HNO_3	16M HNO_3	None	Look for formation of nitrate esters
Test Series II	**Metal source**	**Acid Concentration**	**Neutralizing Agent**	**Reactivity and, thermal stability studies, and breakdown product isolation and identification**
Swheat Kitty Litter*	Pb flake	1M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	Pb flake	7M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	Pb flake	16M HNO_3	None	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	W **	1M HNO_3	none	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	W **	7M HNO_3	none	Impact, ESD, friction, DSC, vacuum stability
Swheat Kitty Litter*	W **	16M HNO_3	none	Impact, ESD, friction, DSC, vacuum stability
Test Series III	**Nitrate Source**	**Acid Concentration**	**Metal source**	**Product Sensitivity, Thermal Testing, and breakdown product isolation and identification**
Triethanolamine nitrate/Swheat	$NaNO_3$	1M, 7M, 16M	Pb	Impact, ESD, friction, DSC, vacuum stability. Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products
Triethanolamine nitrate salt/Swheat	$NaNO_3$	1M, 7M, 16M	W**	Impact, ESD, friction, DSC, vacuum stability. Head space analysis at ambient temperature and 80C; nuclear magnetic resonance spectroscopy to characterize products

*1:3 ratio $NaNO_3$ solutions to SWheat by volume, superstaturated solutions of $NaNO_3$ in the indicated HNO_3

W** - tungsten lined glove is the source

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memorandum

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SUBJECT: Analytical Plan for Emptied Parent Waste Drums

Four emptied parent waste drums from TA-54, Area G, have been identified for sampling and subsequent analyses. Two of the drums were selected based upon their similarity to the parent of the breached drum, S855793 (daughter is 68660), which contained free liquid and recorded as having low pH (0). The other two drums were also chosen for having free liquid, one where no note was made as to the pH, which was typically indicative of a drum with liquid in the 3-5 pH range, and the other with a noted pH of 3. These two will provide a basis for comparison with the low pH drums. All would have been treated with Kolorsafe Spilfyter liquid neutralizer. The drum IDs are as follows:

S864694 (69139 is 85-gallon overpack ID) 4 gallons of free liquid, pH 0, processed 12/15/2013
S851436 (69173 is 85-gallon overpack ID) 4 gallons of free liquid, pH 0, processed 1/14/2014
S822952 (68492 is 85-gallon overpack ID) 7 gallons of free liquid, processed 11/5/2013
S818449 (68645 is 85-gallon overpack ID) 6 gallons of free liquid, pH 3, processed 11/11/2013

Various sample types including smears, headspace gases, residual liquids, and residual solids will be collected from each waste drum.

Radionuclide Inventory

The smears will be digested with concentrated mineral acids to yield a homogeneous stock solution. If the smears do not contain sufficient actinide activity, then the liquids and/or solids may be digested or dissolved for analyses. Aliquots of dissolved sub-samples will be analyzed for the following isotopes using the analytical methods specified below. Reported measurements will include propagated analytical uncertainty, which is dominated by statistical measurement uncertainty and absolute isotope-dilution spike calibrations. If any of these analytes are not detected, then a limit of detection will be reported.

1. Uranium concentration and isotopic composition by isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS). The reported analytes will include ^{234}U, ^{235}U, ^{236}U, and ^{238}U.
2. Neptunium-237 concentration by ID-ICP-MS.
3. Plutonium concentration and isotopic composition by ID-ICP-MS and alpha spectrometry. Reported analytes will include: ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu.

4. Americium concentration and isotopic composition using alpha spectrometry and untraced ICP-MS. Analytes will include ^{241}Am and ^{243}Am.
5. Curium concentration and isotopic composition by alpha spectrometry. The method will survey for ^{242}Cm, ^{243}Cm, and ^{244}Cm.

Organic Inventory

C-CDE will support analyses for permanent gases and organic compounds in headspace gas samples. Gas (headspace) samples collected using a gas tight sampling syringe or an evacuated sampling bottle are analyzed for Volatile Organic Compounds (VOCs) using Gas Chromatography/Mass Spectrometry (GC-MS) and for selected permanent gases using GC with a Thermal Conductivity Detector (GC-TCD). Permanent gas concentrations are reported to ~ 25 ppmv. Detection Limits for VOCs in gas headspace sample is <1 ppmv.

VOCs can also be concentrated using solid phase microextraction (SPME) for detection of trace levels of organic vapors (<1ppm) detection. Gas sampling of TRU waste containers is generally performed through the sampling port incorporated in the NucFil-019DS Drum Vent. The sampling port septum mitigates potential for release of radioactive materials and gas sampling can be performed before the drum lid is removed. Gas and SPME sampling can be performed without perturbation of drum content.

GC and GC/MS analysis can be extended to the characterization of dry or wet solids, and free liquids using sampling methods appropriate for the sample matrix and organic compounds of interest.

Solid and liquid samples can be heated to evolve volatile compounds (heated headspace) or extracted with a variety of solvents prior to sample analysis for volatile, semi-volatile compounds using GC/MS or low volatility organics using LC/MS. Extraction solvents can be filtered to remove radioactive particulates which facilitate sample handing. SPME can also be used to mitigate carryover of radioactive particulates.

Volatile organic compound analysis is performed with GC/MS using quadrupole and high resolution, accurate mass - mass spectrometry. This provides for the quantitative analysis of target compounds as well as nearly unambiguous compound identification.

Inorganic Inventory

Residual free liquids and/or solids (salts) will be phase separated. If free liquids and salt residues are not identified in the drums, absorbed liquids and/or additional swipe samples will be acquired and the analytical plan will be re-evaluated. Applicable C-AAC procedures are referenced below.

Solids will be analyzed as follows, in order of priority depending on quantity retrieved:

1. Gamma spectrometry on bulk sample for comparison to C-NR swipe sample (WI-42; non-destructive).
2. Ion chromatography for nitrate and other anions (ANC212). Sample must be digested in DI water for this analysis.
3. Free acid determination (titrimetric; ANC123). Sample must be digested in DI water for this analysis.

4. Direct solid screening by x-ray diffraction (ANC500) and micro-xray fluorescence (ANC1325) for bulk elemental composition. Any insoluble solids from IC and free acid determinations will also be characterized.
5. Trace element composition by plasma spectroscopy (ANC102 and 221). Sample is digested in nitric acid for this analysis.
6. Moisture content determination by Loss-On-Ignition (ANC124).

Free liquids will be analyzed as follows, in order of priority depending on quantity retrieved:

1. Gamma spectrometry on bulk sample, for comparison to C-NR swipe sample (WI-42; non-destructive).
2. Ion chromatography for nitrate content, and other anions (ANC212).
3. pH and/or titrimetric acid determination (ANC123).
4. Organic constituents using either Liquid Chromatography/ Mass Spectrometry (LC-MS) and/or GC-MS.
5. Total carbon content, measured by combustion analysis (ANC228) of a dried aliquot, and/or Chemical Oxygen Demand (non-routine).
6. Trace element composition by plasma spectroscopy and/or xray fluorescence (ANC102, 221, and 1325).

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