
From: Vigil-Holterman, Luciana R
Sent: Monday, April 20, 2015 11:10 AM
To: Brandt, Michael Thomas; Haagenstad, Mark P; Clark, David Lewis; Funk, David John; Selvage, Ronald Derek; Gordon, Derek J; Robinson, Bruce Alan; Bacigalupa, Gian A; Diaz, Tammy; Juarez, Catherine L; kathryn.roberts@state.nm.us; timothy.hall@state.nm.us; john.kieling@state.nm.us; coleman.smith@state.nm.us; Nickless, David J; Turner, Gene E
Cc: Erickson, Randy; Cabbil, Cheryl Denise; 'Nickless, David'; 'Maggiore, Peter'
Subject: HSG Data Report and Presentation Slides for NMED-LANL Meeting held on Thursday, April 16, 2015
Attachments: LA-UR-15-22763.pdf; LA-UR-15-22764.pdf; LA-UR-15-22661.pdf

As requested, attached are documents promised by LANL personnel during the technical discussion meeting at the NMED-HWB offices on Thursday, April 16, 2015.

Attached are LA-UR-15-22763, LA-UR-15-22764, and LA-UR-15-22661.

Thank you.

Luciana Vigil-Holterman for Mark Haagenstad

Mark Haagenstad
Environmental Protection Division
Compliance and Permitting Group
Los Alamos National Laboratory
Office: (505) 665-2014
Mobile: (505) 699-1733

Review of LANL Approach to Safe Storage of Suspect Containers and Safety Basis for Future Remediation

David J. Funk, David L. Clark, and
Julie Minton-Hughes

April 16, 2015

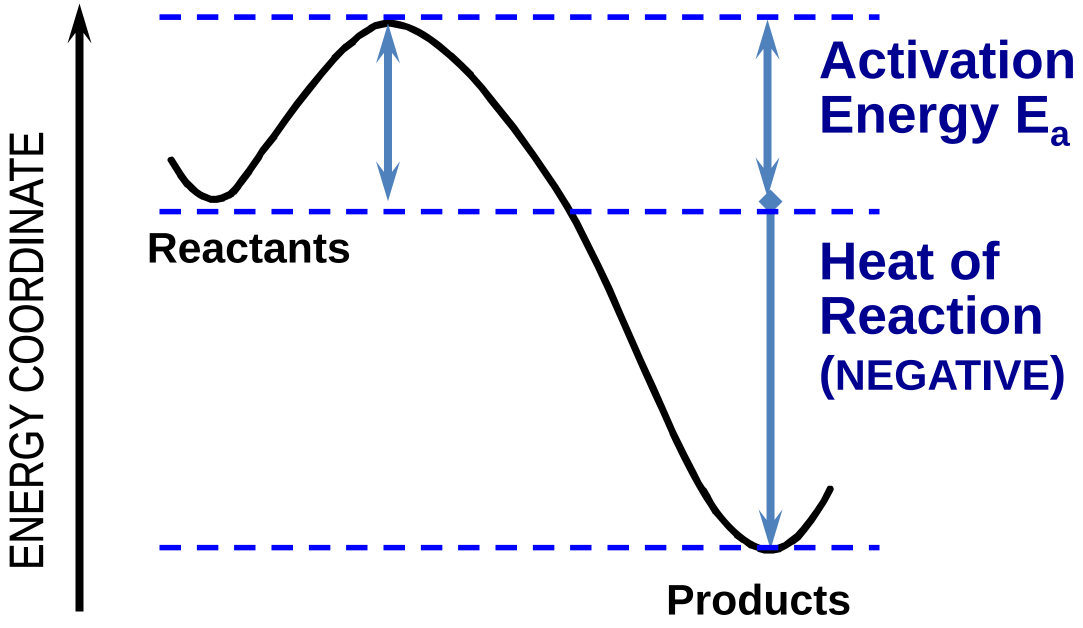
Temperature Control of RNS Waste Provides Defense-in-Depth for Storage, and Margin for Worker Safety, when Processing

- The data available indicate that the RNS drums are exhibiting very little biotic or abiotic activity
- Were the same processes active in the set of drums onsite, at WIPP, or WCS, as in 68660, the drums would likely have already "cooked off"
- The current posture at all three sites is safe: any steps to introduce cooling will increase margin and is prudent as a defense-in-depth measure
- Processing will require cooling, but the final parameters have yet to be quantitatively determined

Temperature Control Strategy: Scientific Basis

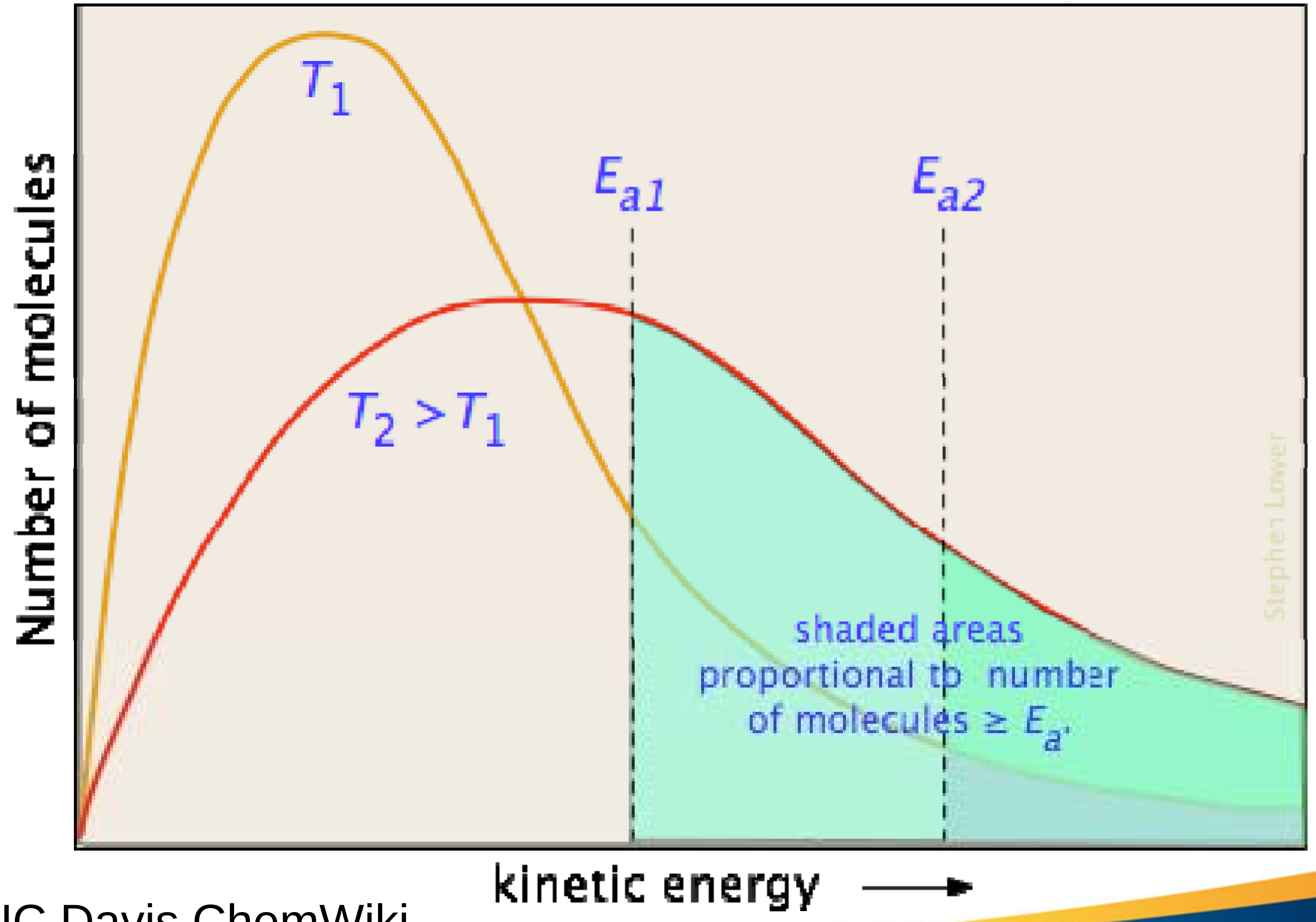
Arrhenius equation – first order kinetics:

$$k(T) = A\, e^{(-Ea/RT)}$$



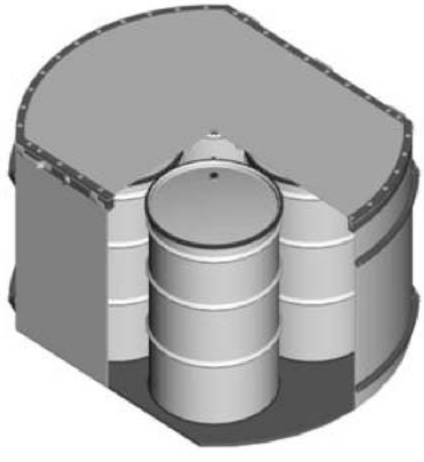
Energy diagram for exothermic reaction

Plot showing the effect of temperature on the number of molecules that have enough energy to react



UC Davis ChemWiki

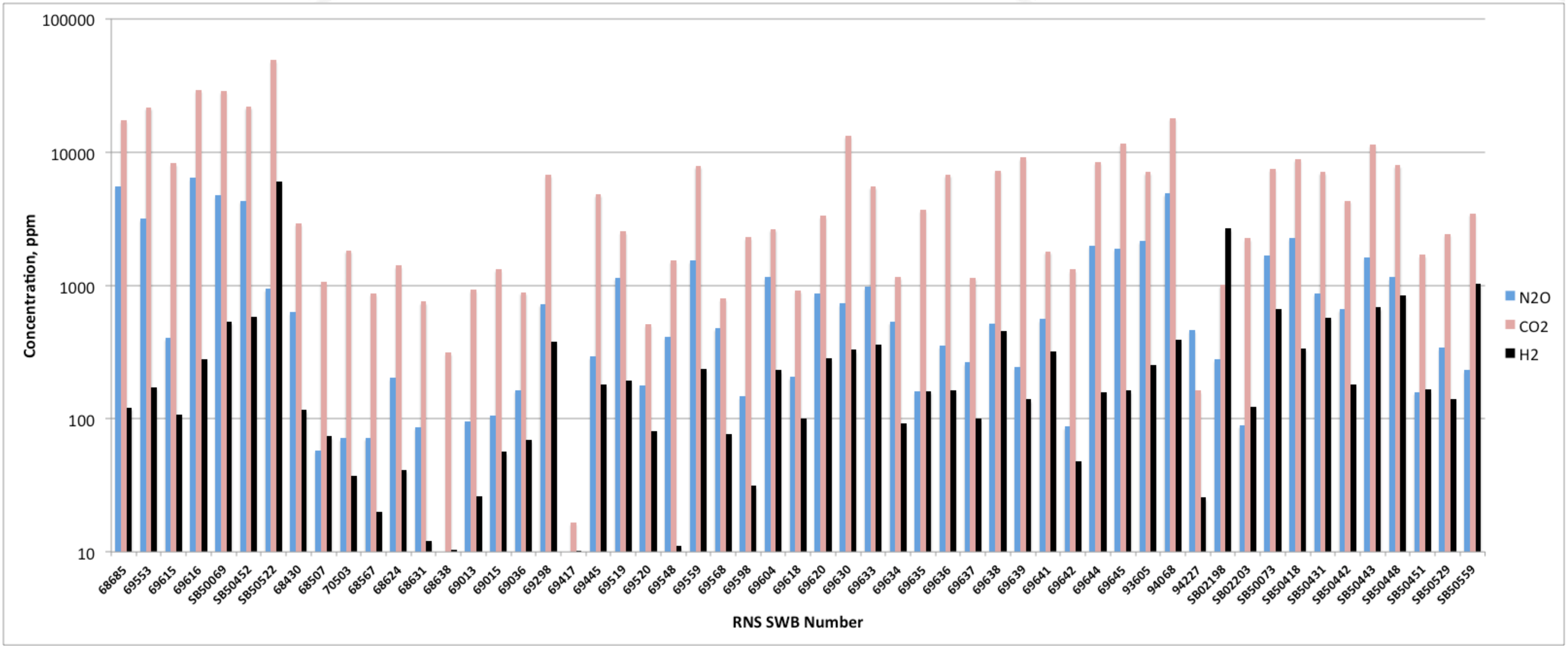
What do the headspace gases of the RNS waste tell us about what's going on inside the drums?



Standard Waste Box

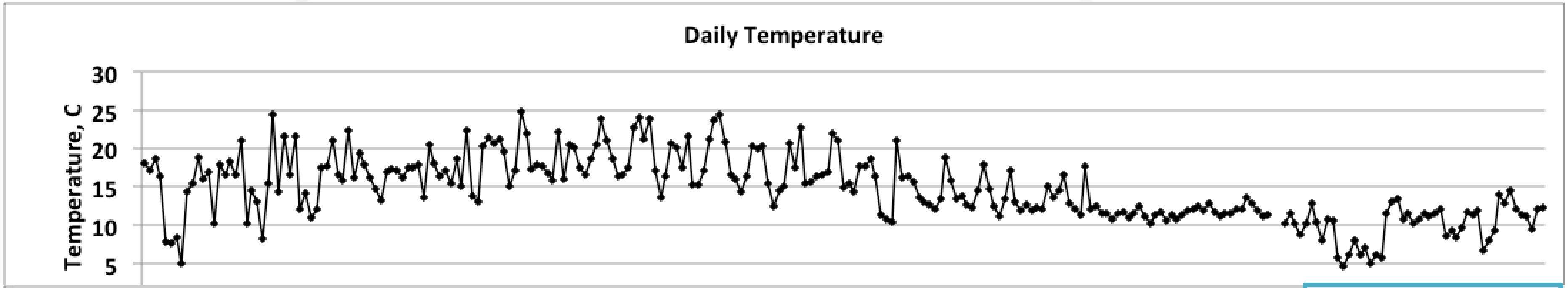
Headspace Gas Monitoring in 55 SWBs

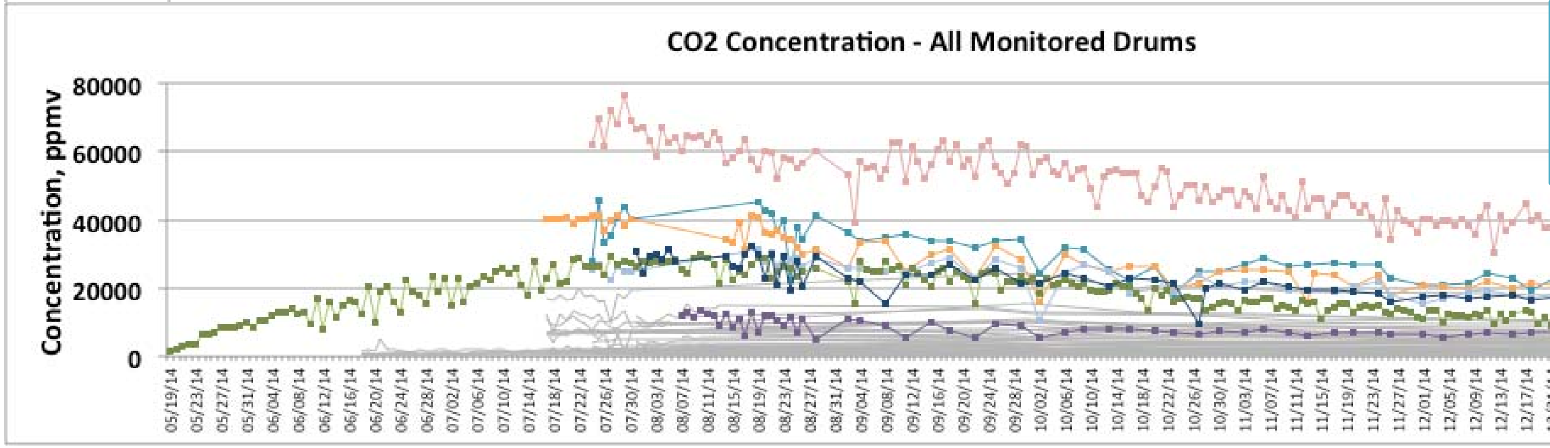
Average concentrations span a large range



- Hydrogen levels do not pose an immediate safety concern
- Drums with highest concentrations exhibit similar (but not identical) gas concentration signatures

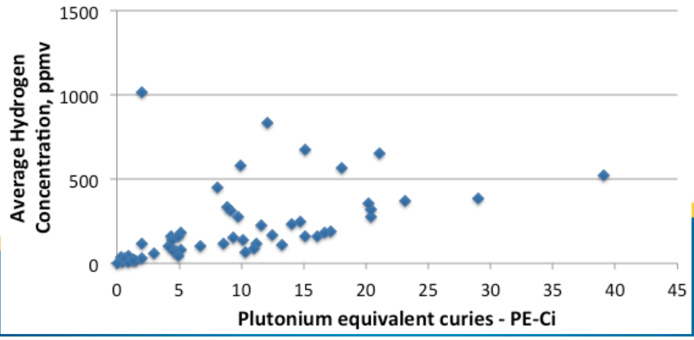
Temperature-dependent reactions control CO_2, N_2O; Radiolysis controls H_2



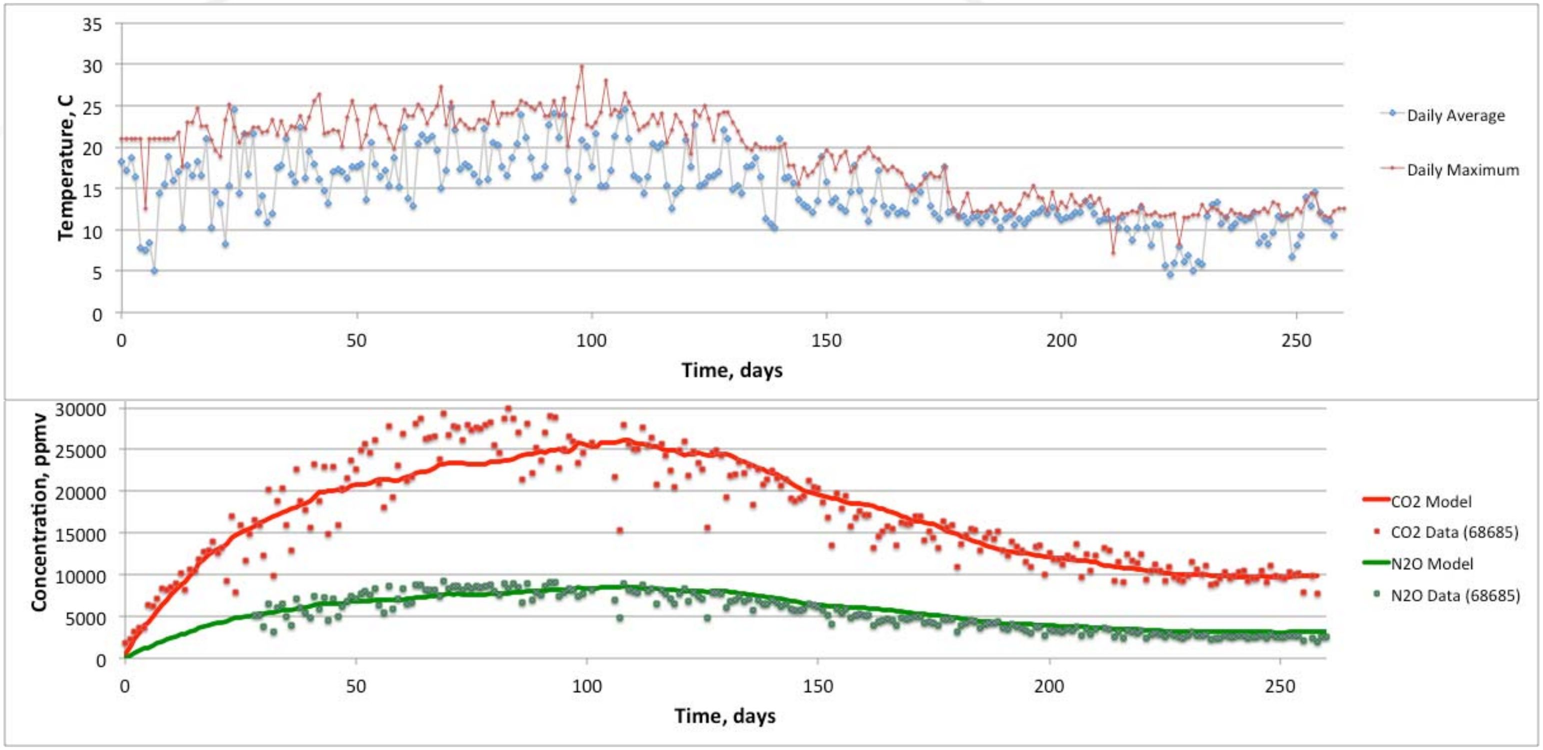


Many drums have low gas concentrations, a few are “elevated” and are being monitored more frequently

Hydrogen is relatively constant with time (no T dependence) and is correlated with PE-Ci of the waste



Model of Headspace Gases Balances Reaction Against Venting and Air Exchange



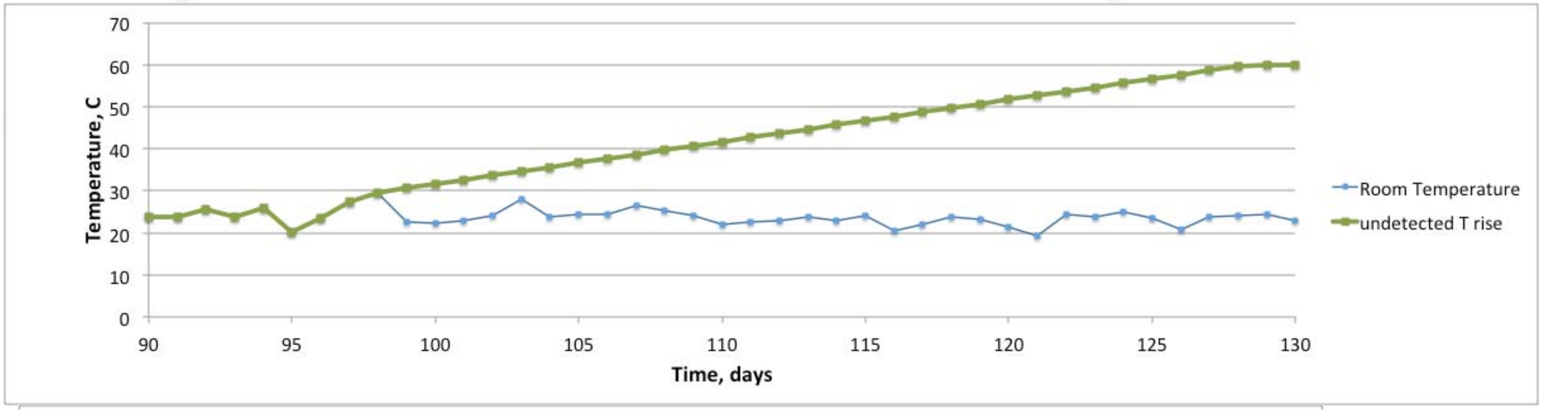
Model Reaction: $C_6H_{10}O_5 + 6NaNO_3 \rightarrow 3Na_2CO_3 + 3CO_2 + 5\ H_2O + 2\ N_2 + N_2O + O_2$

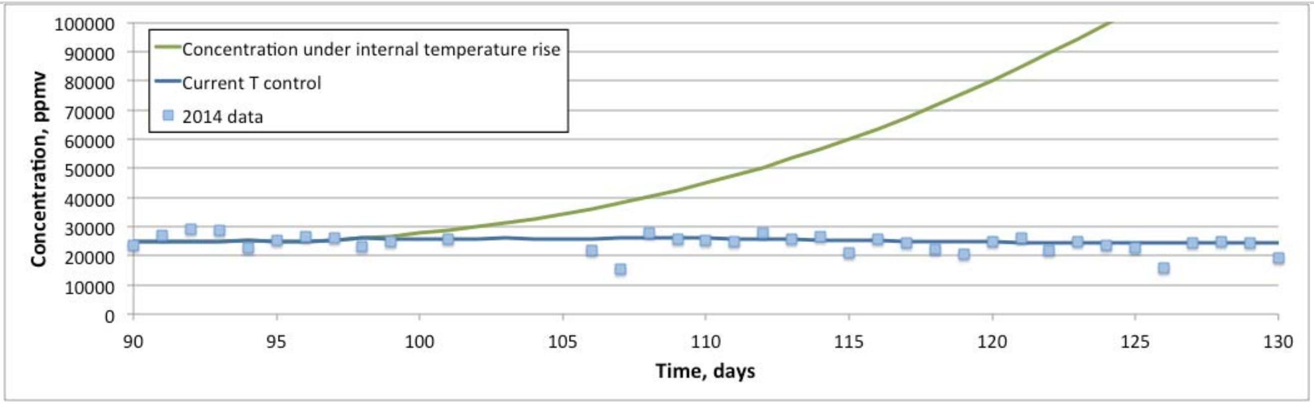
Results

- Very low gas generation rates (4-5 cc/min)
- Of order 1 W heat generation rate or less in a drum
- Uncertainty analysis shows this is a robust result

What if conditions change abruptly?

The model suggests that we will quickly detect changes of this magnitude in the headspace gas monitoring data





Other Observations

- Ventilation-induced drying is very slow
- Filter clogging would result in relatively rapid pressure rise

The Process of Thermal Runaway or “Cook off”

- “Cook off” results when exothermic chemical heating cannot be offset by cooling from thermal transport out of the drum (conduction/convection/ radiation), leading to thermal runaway.
- Exothermic condensed phase chemistry is generally described by a rate equation that is exponential in temperature (Arrhenius) and first order or greater in reactant concentration, and if such reactions satisfy the energy balance criterion for cook off, the maximum time to runaway is bounded because a slow, linear, temperature rise is not possible.
- As no other drums have exhibited a release, a significant amount of time has passed, and current levels of reactivity are very low, we have an expectation that the risk of another event is significantly reduced and would be considered unlikely, if a “chemistry only” scenario is active.

Cook off may be activated through either biotic or abiotic processes

Current configuration poses minimal risk to worker and public – biotic scenario

- Hydrogen and methane are expected products of anaerobic bioactivity
  - To date, we have not observed any detectable methane, and hydrogen levels correlate with the level of radioactivity in the drum and do not exhibit temperature dependence (as CO_2 does), facts that are consistent with radiolysis activity alone for hydrogen generation.
- Aerobic biotic activity would imply ~1 Watt of thermal activity (assumes digestion yields equivalent chemical heat as oxidation)
  - Derived from the analysis of CO_2 production

1 Watt would heat up 2 gallons of water 0.11 °C in one hour, assuming no heat losses

Current configuration poses minimal risk to worker and public – chemistry only scenario

- If all of the drums were uniform, specifically, that they were all well mixed and of identical composition, they would have cooked off by now
- To validate this hypothesis with modeling, we will use the bounding values for thermal conductivity derived from drum cooling studies, and the construction of an allowable and credible set of Arrhenius kinetic parameters (both the pre-exponential factor and activation energy), to bound the allowable chemical rates that meet the following conditions:
  - Enable cook-off of 68660 after 72 days
  - Consistent with the CO_2 and N_2O from oxidative chemistry generation
- Intuitively, we expect that this modeling will demonstrate that under a “chemistry only” scenario, all of the remaining drums are safe from cook-off, provided that the drums are not exposed to external temperature conditions greater than any that have been observed to date in TA-54-0375.

In both biotic and abiotic scenarios, heat generation is much less than conduction/convection/radiative losses, eliminating the possibility of thermal runaway

Our analysis supports a defense-in-depth strategy that could include the cooling of the drums while in storage

- The drums are unlikely to have the chemical or bioactivity required to initiate thermal runaway under our current storage configuration.
- Such an event would likely have been catalyzed by the temperatures observed last summer: the fact that such an event did not occur lends credence to the fact that the likelihood of a repeat event is significantly diminished.
- We will be conducting further experiments (bio) and modeling (thermal) to reinforce the hypotheses described, in the near future.
- We note that the WIPP drums are in a steady-state environment that is comparable to the worst-case environment experienced by LANL drums (25 °C) and with the exception of 68660, there are no other known examples of a cook-off event.
- WCS drums have experienced harsh temperatures (60 °C) that should have led to cook-off if the contents were similar to our surrogate and those likely in 68660.

A defense-in-depth strategy provides increased margin against a WIPP like event

We have examined a set of Temperature Controlled Storage Alternatives

- 6 Options considered
  - Existing Temperature Control
  - Improve PermaCon® Efficiency
  - Upgrade the Existing System
  - Supplemental Cooling
  - Cooling Blankets
  - Temporary Refrigerated Structure(s)

Requirements for the Study included:

- HEPA filtration required
- Fire Suppression System required
- Spacing is 2 feet between containers and 3 foot aisle spacing
- 1 feet required for heat dissipation; therefore, no stacking
- Keep temperature above 0°C (32°F)

Limitations and Assumptions

- Area G is the only storage location considered
- Additional electrical must be provided through temporary power (generators) or an upgrade
- Safety Basis and RCRA permit modifications can be worked in parallel

Option 1
Existing Temperature Control

- 375 PermaCon® Systems
  - At least 6 air changes per hour
  - 15,000 CFM
  - HEPA-filtered exhaust
  - -0.1 w.g between Permacon and Dome
  - -0.05 w.g between Cells 1 & 3 and Cell 2
  - 15°F below the design temperature of 89°F (personnel comfort)
  - Pre-action FSS

Pros

- No change to existing configuration
- Has fire suppression
- Has HEPA filtration
- No additional cost for implementation

Cons

- Temperature is not as low as other options
- PermaCon® not available for other activities

Cost: *None*

Schedule: *Already implemented*

Temperature: *26°C (78°F)*

HEPA Filtration: *Yes*

Fire Suppression: *Yes*

Option 2
Improve PermaCon® Efficiency

- Includes
  - Sealing of cracks and rollup doors to reduce infiltration.
  - Reducing the number of air changes
  - Adding insulation or lowering the ceiling
- Not expected to provide a large temperature decrease
  - 3° to 5° C cooler than Option 1
- Pros and Cons vary based on the choices made

Pros

- Improved electrical efficiency
- Minimal change to existing configuration

Cons

- System response to releases maybe be impacted
- Temperature reduction is minimal
- Rollup doors use will be limited
- Installation performed in respiratory protection and on ladders
- Structural and seismic evaluation because of additional weight

Cost: *Depends on sub-option selected*

Schedule: *Depends on sub-option selected*

Temperature Reduction: *3°C to 5°C < existing temperature control*

HEPA Filtration: *Yes*

Fire Suppression: *Yes*

Option 3
Upgrade Existing System

- Adds additional air movers, dampers, and duct work to re-circulate the air
- Permanently improves heating and cooling capabilities

Pros

- Temperature as low as 18.3°C (65°F)
- Increased electrical efficiency
- Improves overall heating and cooling capability

Cons

- Substantial changes system
- Increased ventilation system complexity
- Increase in power demand
- Longer design time compared
- Weight added to structure will require evaluation

Cost: *$10K - $100K*
Schedule: *6 to 12 months*
Temperature Reduction: *5.5°C < existing temperature control*
HEPA Filtration: *Yes*
Fire Suppression: *Yes*

Option 4
Supplemental Cooling

- Uses a vendor to supply a chiller unit
- Pumps cold air into existing system
- Could be powered with generators or permanent power

Pros

- Can cool to a low as 5°C
- No need to move containers
- No need to change existing PermaCon® configuration
- Could be removed seasonally

Cons

- Subcontract process
- May need NEPA permitting for generator
- Additional fuel loading from the generator
- Requires modification to the electrical system

Cost: *$10 - $100K (generators)/$100K - $500K (permanent electrical)*

Schedule: *3 to 6 months*

Temperature Reduction: *20°C < existing temperature control*

HEPA Filtration: *Yes*

Fire Suppression: *Yes*

Option 5
Cooling Blankets

- Thermally insulating blankets with integrated liquid cooling hoses
- Provide cooling through conduction.
- Each waste container would require
  - Cooling blanket
  - Hose
  - Chiller unit
- No off-the-shelf cooling blanket is available

Pros

- Can reach 10°C

Cons

- Temperature monitoring method needs to be re-evaluated
- Introduces additional liquids into facility
- Maintenance frequency is weekly
- Custom unit is necessary
- Each container will need separate chiller unit
- PermaCon® penetration(s) (2 per SWB)

Cost: *$100K to $500K*

Schedule: *18 to 24 months*

Temperature Reduction: *15.5°C < existing temperature control*

HEPA Filtration: *Yes*

Fire Suppression: *Yes*

Option 6
Temporary Refrigerated Structure

- Uses a vendor specializing in modular, temporary structures for hazardous chemical response
- Can maintain the temperatures down to 5°C
- Includes fire suppression and ventilation
- May not include HEPA-filtration
- Can be fire- and blast-rated

Pros

- Refrigerated structure will reach 5°C
- Can be powered with temporary generator
- Could be fire-/blast-rated
- Can be located within Dome 375

Cons

- HEPA and exhaust options limited
- Relocation of containers
- Subcontracting process
- Structural/seismic evaluation needed
- Requires relocation of all waste containers
- Additional fuel loading and permitting requirements for generator

Cost: *$100K - $500K*

Schedule: *9 to 12 months*

Temperature Reduction: *20°C < existing temperature control*

HEPA Filtration: *Yes*

Fire Suppression: *Yes*

Comparison of Options

Options	Container spacing	HEPA filtration	FSS	Worker Impact	Temp	Time to Imple-ment	Cost	Long-term impact	Over-all Score
Existing temperature control	1	1	1	1	-1	1	1	-1	4
Improve PermaCon® efficiency	1	1	1	-1	-1	1	0	0	2
Upgrade the existing system	1	1	1	-1	-1	-1	-1	1	0
Supplemental cooling	1	1	1	0	1	0	0	-1	3
Cooling blankets	1	1	1	-1	0	-1	-1	-1	-1
Temporary refrigerated structure	1	0	1	0	1	-1	-1	-1	0

Each option is given a 1, 0, or -1 based on its ability to meet each of the criteria

Alternatives Study Conclusions

Based on scoring in Comparison Table, preferred options are:

1. Existing Temperature Control
2. Supplemental Cooling
3. Improve PermaCon® Efficiency
4. Temporary Refrigerated Structure
5. Upgrade the Existing System
6. Cooling Blankets

Path Forward: Recommended safing and processing of RNS drums

Render drums safe from further reaction

- *Temperature* has a powerful effect on both chemical and biological reactions
  - Cooling RNS drums to below freezing (-10 °C) will inhibit both chemical and biological activity
  - Process at 10 °C (50 °C below lowest T exotherm

Center for Chemical Process Safety, AIChe, 1995

Processing of 'safed' drums

- ***Cementation*** – one of the most commonly used methods for conditioning radioactive wastes
  - Caveat on water addition initiating biological activity (drums can't sit)
- ***Natural mineral absorbants*** – bentonite, zeolite, attapulgite, etc, absorb water and remove oxidizing characteristic of waste
  - Caveat on gas phase nitration catalysis by zeolites/metal oxides

Processing requires a means to establish process variables

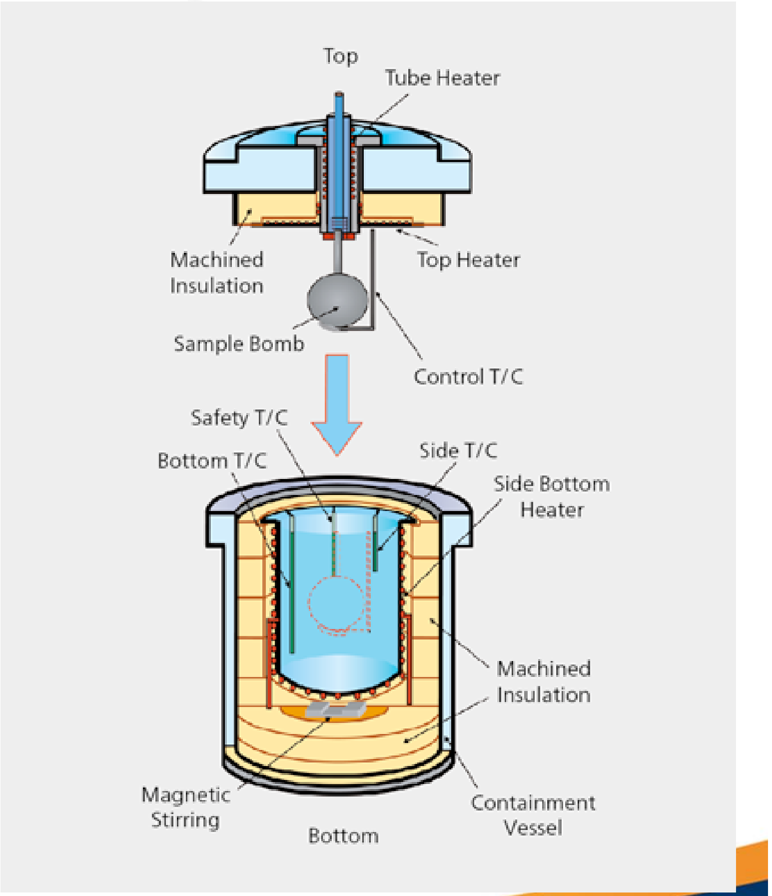
- The 50 °C chemical processing guideline is useful, but experiments and analysis are required to establish nuclear process variables
- The current surrogate is expected to be a “worst case” and tests were “scoping” in nature
  - The salt/Swheat mixtures were “tuned” to be highly reactive and ground with mortar and pestle to establish uniformity for small scale testing
  - While potentially sufficient for establishing kinetic parameters, the results will provide a “worst case” estimate of reactivity
  - Waste morphology (particle size of Swheat, salt, etc.) must be examined to establish effect on kinetics
- We are developing NQA-1 test plan to establish Arrhenius kinetics that will support the development of process parameters, and we will require additional process studies to factor in the effects of morphology

Need to establish scientific basis for process variables which will feed controls within our safety basis

“Worst case” scoping surrogates exhibit thermal sensitivity and runaway at 55-60 °C (APTAC)

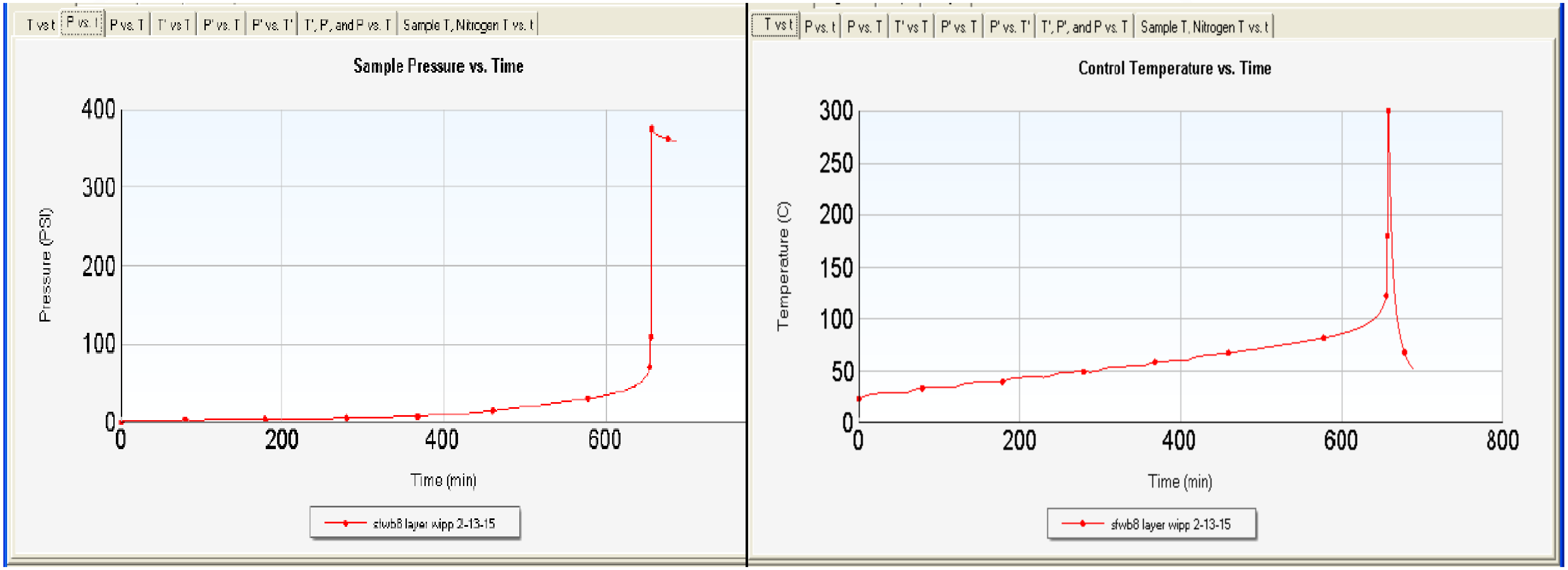
- Adiabatic Pressure Tracking Accelerated Calorimetry – measure amount and rate of heat release
  - In order to simulate the worst-case scenario with no heat exchange with the surroundings, we use the APTAC quantitatively measure changes in temperatures, enthalpy, and pressure. The use of adiabatic systems has the advantage that no heat loss is allowed from the sample; affording the ability to simulate the behavior in a real larger-scale system.
- An NQA-1 test plan is in development that will refine our initial scoping measurements; the results will support processing and Safety Basis decisions

Accelerating Rate Calorimeter



"Worst case surrogates" exhibit thermal sensitivity and runaway at 55-60 °C (APTAC)

- SFWB8 – Swheat Formulated with WeisBrod salt mixture 8
  - Data below is from SFWB8 layered with absorbed Swheat



Worst case might indicate that all RNS drums "should" have cooked off

Safing followed by reprocessing will lead to inert TRU waste, protecting workers and the public

- Safing minimizes the potential for additional events
  - The chemical and biological processes occurring within the drums are “reset”
- “Cold” waste is in a state that minimizes hazards to workers that will be processing the waste
- Processed waste eliminates the potential for an environmental release that could affect the public
  - Testing will be conducted with UNS/Swheat surrogates to demonstrate the effectiveness of the processing

Temperature Control of RNS Waste Provides Defense-in-Depth for Storage, and Margin for Worker Safety, when Processing

- The data available indicate that the RNS drums are exhibiting very little biotic or abiotic activity
- Were the same processes active in the set of drums onsite, at WIPP, or WCS, as in 68660, the drums would likely have already “cooked off”
- The current posture at all three sites is safe: any steps to introduce cooling will increase margin and is prudent as a defense-in-depth measure
- Processing will require cooling, but the final parameters have yet to be quantitatively determined

Chemistry Investigations into WIPP: Key Findings and Comparison with the Technical Assessment Team (TAT) Report

Led by

David L. Clark and David J. Funk

April 16, 2015

LA-UR-15-22764

What Caused the Radiation Release at WIPP?

Specific Chemical Reaction? or Broader Issue?

Chemical Reactivity

- Process Changes
- Trigger Mechanisms
- Radiation Chemistry
- Trace Metal impurities

Broader Issues

- Relationship to Truck Fire
- Green Burst
- Criticality Event
- Issues with other waste containers
- Other Materials
- Arson/ Sabotage

What Caused the Radiation Release at WIPP?

A Hypothesis driven investigation – focus on chemical reactivity

- **1. Process changes**
  - Triethanolamine Possible
  - Swheat /HNO_3/other metal salts Possible
  - Swheat /$NaNO_3$ Possible
  - Other reactive chemicals Possible
  - Citric Acid Unlikely
  - Waste Lock Beyond extremely unlikely
- **2. Trigger Mechanisms**
  - Glove box glove Possible
  - Lead contaminant Possible
  - Pressure build up/electrostatic discharge Possible
  - Internal or external heating Possible
- **3. Radiation Chemistry**
  - Pressure build up of radiolysis gases Unlikely
  - Radiolytic heating Unlikely
- **4. Trace Metal Impurities**
  - Decomposition or nitration of organics Possible

Process changes introduced unstable chemical mixtures *and* potential triggers to initiate an exothermic event

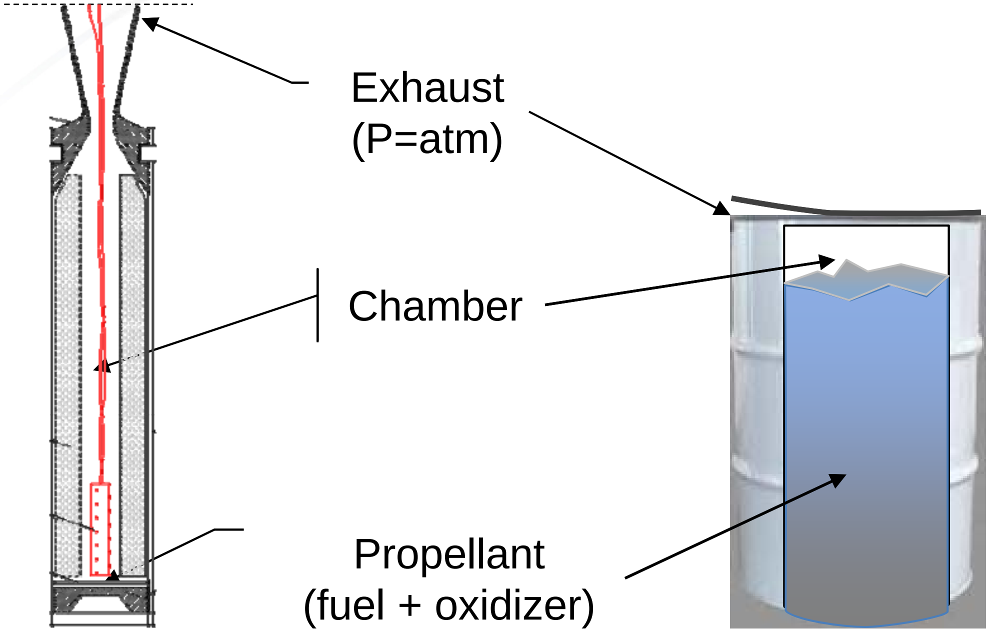
Chemical reagents for processing nitrate salt wastes have changed several times

1. Process changes

- **Triethanolamine** Possible
- **Swheat /HNO_3/other metal salts** Possible
- **Swheat /$NaNO_3$** Possible
- **Other reactive chemicals** Possible
- **Citric Acid** Unlikely
- **Waste Lock** Beyond extremely unlikely

- Process changes introduced organic kitty litter (fuel) with metal nitrate salts (oxidizer)
- Process changes introduced other organic materials as neutralizers
  - Triethanolamine (TEA), Citric acid
  - TEA reacts with nitric acid to produce an energetic material, triethanolammonium nitrate (TEAN)
  - 68660: 2 gal pH=0 liquid prior to neutralization
- Experiments (DSC, TAM, etc.) show exothermic behavior for $NaNO_3$/Swheat near 330 °C, and $NaNO_3$/TEAN/Swheat near 220 °C
- There needs to be a trigger mechanism to raise temperatures in a drum

Thermochemical modeling (Cheetah[2]) of cellulosic fuel + $NaNO_3$ indicates significant reaction energy available



Exhaust
(P=atm)

Chamber

Propellant
(fuel + oxidizer)

- Combustibility likely curtailed above 20% water.[1]

Reaction rate is controlled by chamber pressure and reactant temperature

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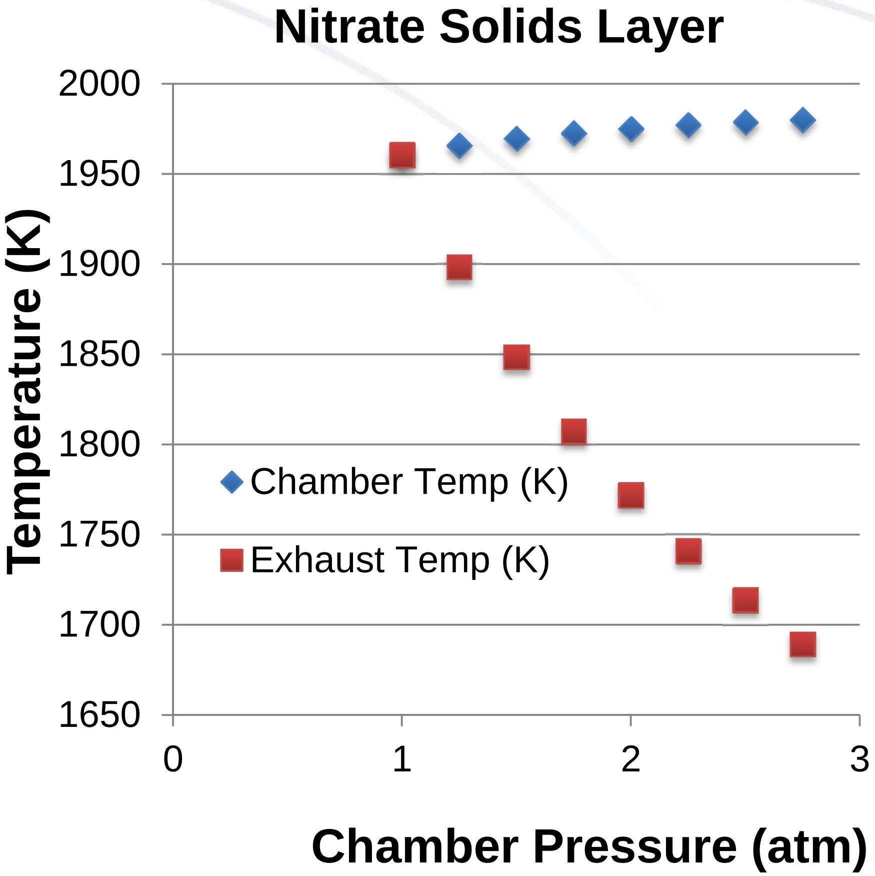
[1] Beitel, G.A., ARH-LD-123.April, 1976 Hanford Waste Engineering Plant

[2] L. Fried and P. Souers, “CHEETAH: A next generation thermochemical code”, UCRL-ID-117240, 1994

Cheetah modeling results predict hot exhaust products

- Combustion products include H_2, CO, and CH_4 which potentially enriches room with fuel
- Gases can be as hot as 1960 K (1687 °C)
- This temperature is well above the flash point of most the gases
- **Still need a trigger to start the reaction**



We expect that product gases would ignite upon mixing with the air increasing the dispersion of exhaust products

Evaluation of possible trigger mechanisms

2. Trigger Mechanisms

- **Glove box glove** Possible
- **Lead contaminant** Possible
- **Pressure build up/electrostatic discharge** Possible
- **Internal or external heating** Possible

- Drum 68660 had bismuth-lined (Bi, W, La) glovebox glove (218.6 g Bi; 29.4g W; 29.4g La)
- Lead liners in some drums introduced lead contaminants (corrosion), or the liner itself to drum
    - Lead-lined glovebox gloves in nitric acid led to energetic incidents at Mound, Rocky Flats[1] and LANL[2]
- Literature review indicates metal nitrates can be catalysts for nitration of organics
- Self-heating is well-known in agriculture
- Complexity of mixtures often leads to the onset of exotherms at lower temperatures[3]
    - We have observed NO_2 formation leading to Swheat nitration

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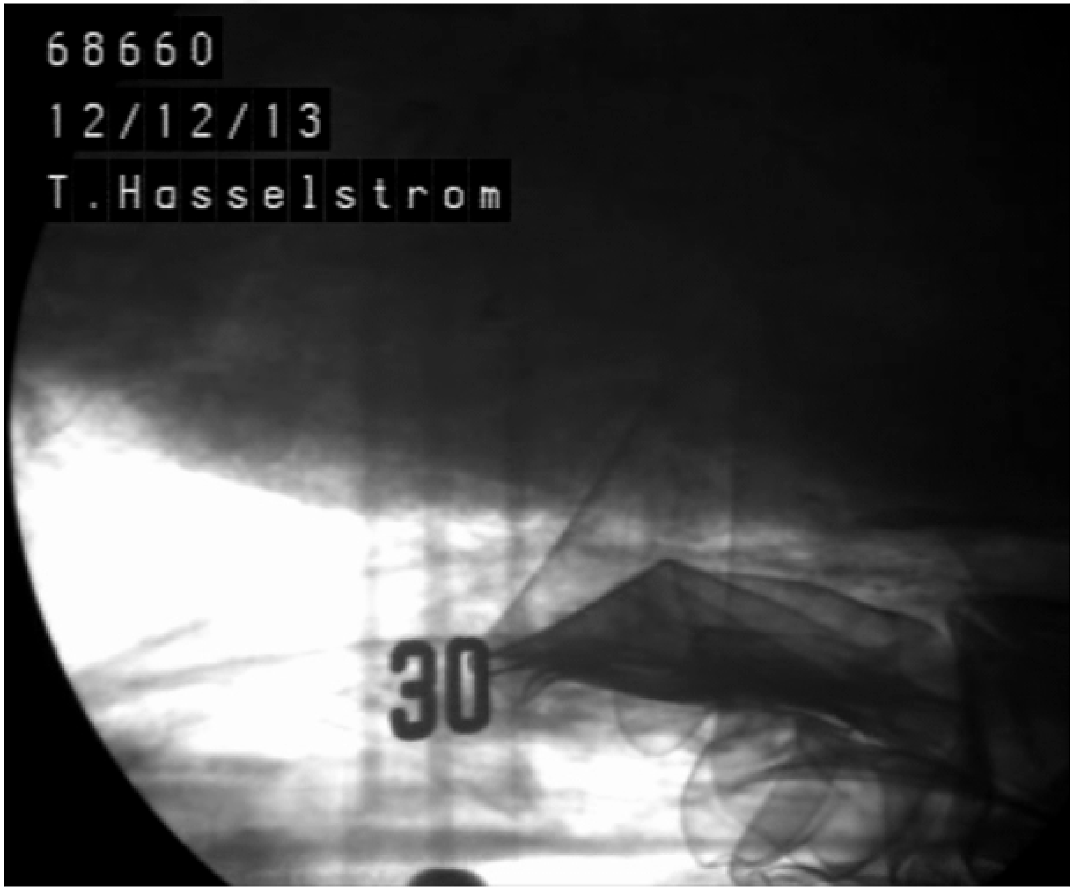
[1] J.L Long, C.j Smith, “Unstable Material Formed by reacting leaded Glove Box Gloves with Nitric Acid” RFP-2648 (1977)

[2] LA-11069 D. Christensen, D. Bowersox, B. McKerley, R. Nance, “Wastes from Plutonium Conversion, and Scrap Recovery Operations. http://osti.gov/scitech/servlets/purl/5587648

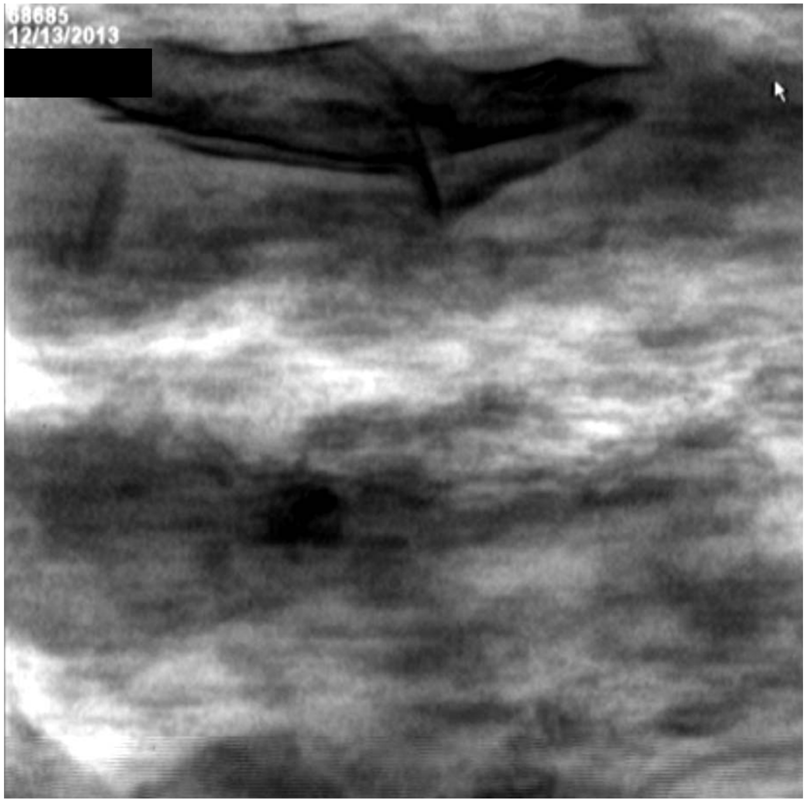
[3] R.D. Scheele, R. L. Sell, J. L. Sobolik and L. L. Burger, “Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste, PNL-10213

Real Time Radiography reveals glovebox gloves and lead liner

Glovebox gloves: 68660

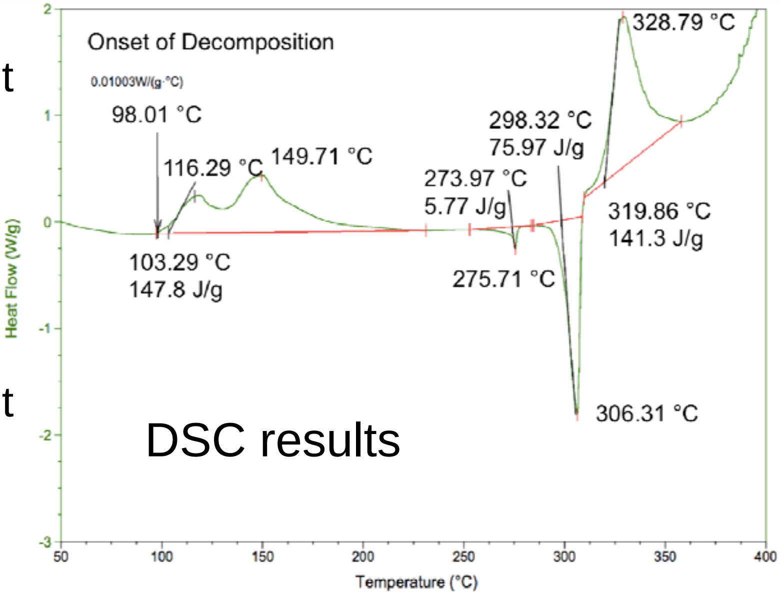


Lead liner: 68685



Matrix Reactivity Studies show a range of exotherm onset temperatures

- Na(NO_3)/Swheat – 330 °C
- HTEA(NO_3)/Swheat – 220 °C
- Na(NO_3)/Mg(NO_3)$_2$/Swheat – 165 °C
- Fe(NO_3)$_3$/Swheat – 154 °C
- Pb/TEAN/Swheat – 110 °C
  - 1M HNO_3 – no change in decomposition onset
  - 8M and 16 HNO_3 – new exotherm
- Bi-lined glove/Nitrate/Swheat – 110 °C
- Bi-lined glove/TEAN/Sweat
  - 1M HNO_3 – no change in decomposition onset
  - 8M and 16M HNO_3 – new exotherm
- Surrogate mixture of nitrate salts - 60 °C



DSC results

Thermochemical modeling of processes provides surrogate salt composition for drum-scale testing

- Stream Analyzer (OLI) software is used to model the processes
- The derived mixtures of metal nitrate salts with Swheat show:
  - Lower exotherm temperatures - 60 °C
  - Evidence of incompatibilities leading to decomposition and NO_2 evolution, followed by Swheat nitration (as high as 6-7%)
  - Material remains insensitive to spark, friction, and mechanical stimuli
- Mg, Fe, and Pb appear to be the main contributors to these processes

A goal of the full-scale drum tests is to reproduce the event with surrogates

Table 1. Important metal ion concentrations (median values) in evaporator bottoms from Veazey, et al.[2] (in g/l)

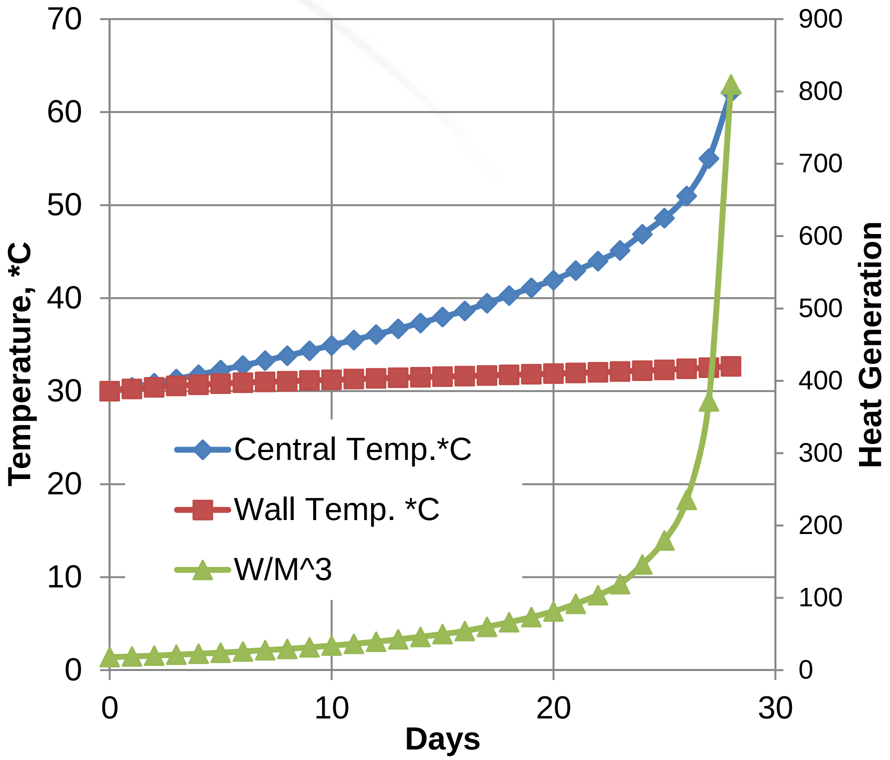
	Ion Exchange	Oxalate Filtrate
Ca	61	10.5
Mg	58.7	13.3
K	17.6	4.8
Fe	17.0	7.9
Na	7.4	23.9
Al	4.6	2.3
Cr	3.0	1.94
Ni	1.8	1.205
Pb	0.19	0.056


Salt mixture with 5% 4M HNO_3, 50% Swheat before (left) and after heating @ 100 C for 30 min

Veazey, G. W.; Castaneda, A. *Characerization of TA-55 Evaporator Bottoms Waste Stream*; NMT-2:FY 96-13; Los Alamos National Laboratory: Los Alamos, NM, 1996

Chemical Self-heating: Models for $Pb(NO_3)_2$ Reaction in Drum

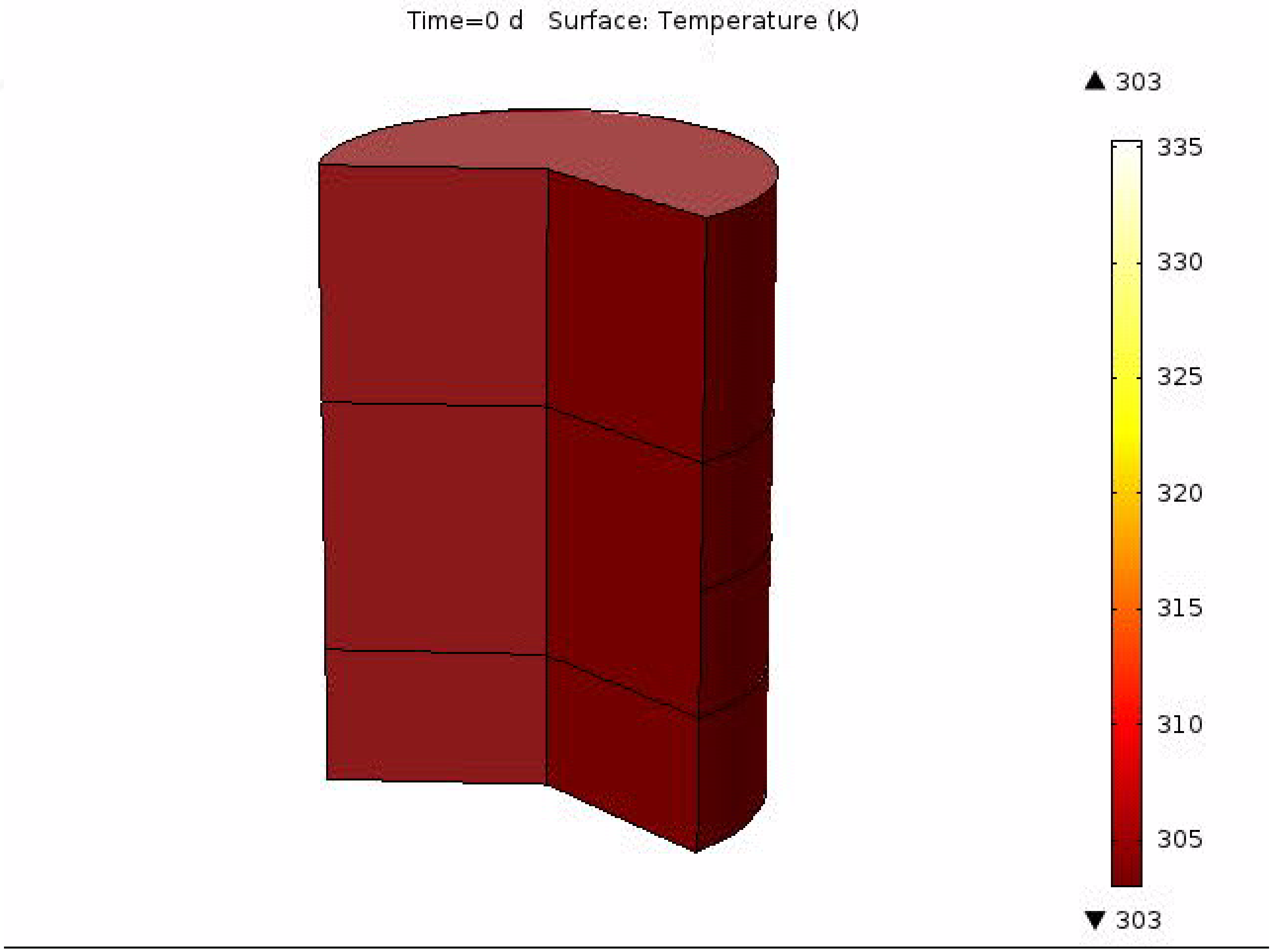
- Activation parameters derived from literature
- At 0.55 g/cm^3 (neat Swheat density)
    - Initial reaction: 13 W/m^3
    - Run away reaction in 168 days
- At 0.79 g/cm^3 (3:1 Swheat to liquid)
    - Initial reaction: 18 W/m^3
    - Run away reaction in 28 days
- ***Run away time highly dependent upon variables***



Mishra, B. ; Raraz, A.G. ; Olson, D.L. ; Averill, W.A, Journal of Hazardous Materials, 1998, Vol.57(1), pp.13-28

B. Mishra, A. G. Raraz, D. L. Olson, W. A. Averill,, Journal of Hazardous Materials, 1997; 56(1):107-116.

Example – Temperature Output from $Pb(NO_3)_2$ model



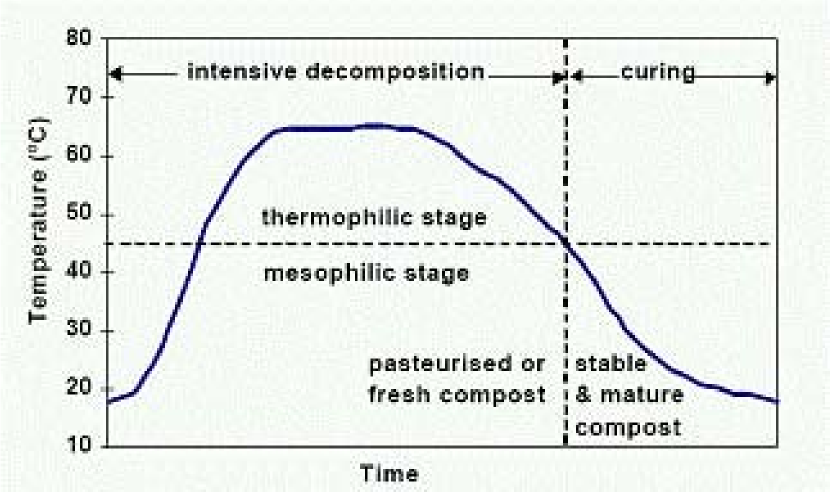
Biological Self-heating

- ***Common Examples:*** Hay Bales, grain silos, and compost piles.
- ***Bacteriological activity***: Organic materials can undergo self-heating due to bacteriological activity.
- The most important factor in promoting bacteriological activity is <u>moisture content</u>.
- Water addition to Swheat/nitrate salt simulants initiates biological activity

ALFALFA & FORAGE NEWS

How to Prevent Hay Fires? Don't Add Water! April 25, 2013

http://newhampshirefarms.net



Path Forward: Recommended safing and processing of RNS drums

Render drums safe from further reaction

- The rates of most chemical and biological reactions are sensitive exponential functions of temperature

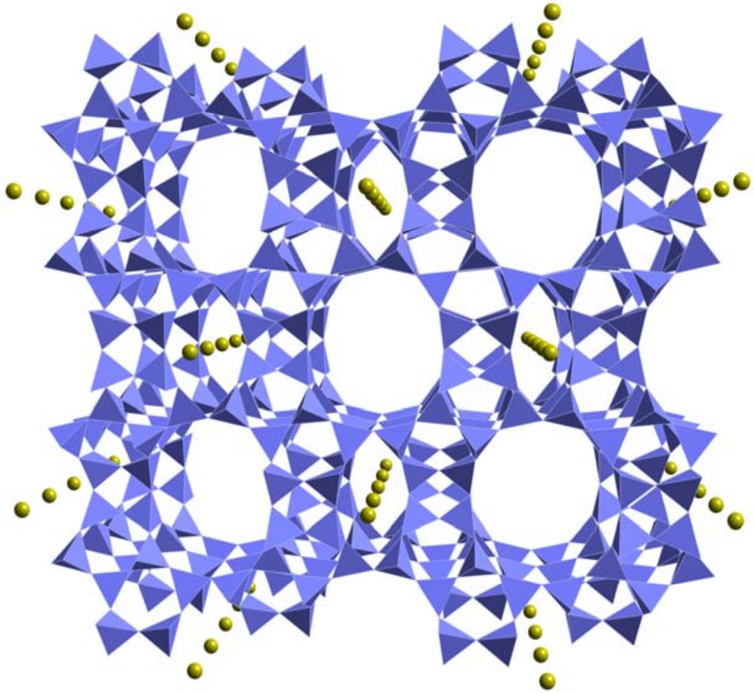
$$k = Ae^{-Ea/RT}$$

- Typical E_a ~ 10-30 kcal/mol corresponds to a rate increase of 2-3 fold increase for every 10°C rise in temperature
- *Temperature* therefore has a powerful effect on both chemical and biological reactions
  - Cooling RNS drums to below freezing (-10 °C) will inhibit both chemical and biological activity – a reset of the "clock"

Path Forward: Recommended safing and processing of RNS drums

Processing of ‘safed’ drums

- ***Cementation*** – one of the most commonly used methods for conditioning radioactive wastes
  - Caveat on water addition initiating biological activity (drums can’t sit)
- ***Natural mineral absorbants*** – bentonite, zeolite, attapulgite, etc, absorb water and remove oxidizing characteristic of waste
  - Caveat on gas phase nitration catalysis by zeolites/metal oxides



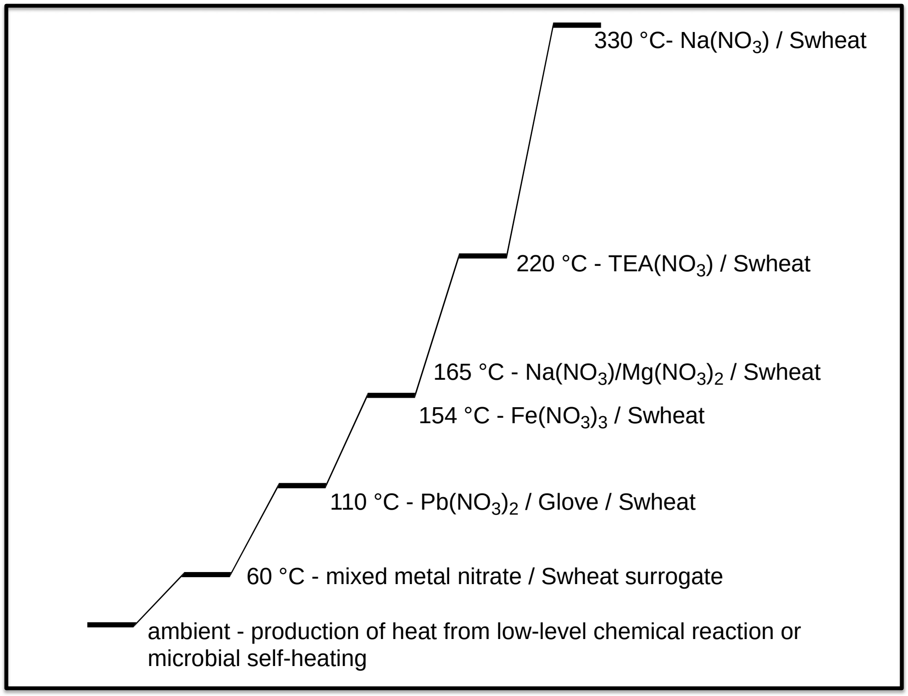
An illustration of the natural zeolite mineral mordenite ($NaAlSi_5O_{12}\bullet 3H_2O$), showing a polyhedral representation of a ringed aluminosilicate framework, looking down the c axis and highlighting channels for uptake of water or other ions. The green atoms are sodium ions of the structure.

Safing followed by reprocessing will lead to inert TRU waste, protecting workers and the public

- Safing minimizes the potential for additional events
  - The chemical and biological processes occurring within the drums are “reset”
- “Cold” waste is in a state that minimizes hazards to workers that will be processing the waste
- Processed waste eliminates the potential for an environmental release that could affect the public
  - Testing will be conducted with “worst case” surrogates to demonstrate the effectiveness of the processing

Summary

- The nitrate salt/Swheat organic kitty litter mixture creates the potential for an exothermic reaction and breach in Drum 68660
- An additional trigger mechanism is likely required to initiate chemical reactions needed to breach a drum



330 °C- $Na(NO_3)$ / Swheat

220 °C - $TEA(NO_3)$ / Swheat

165 °C - $Na(NO_3)/Mg(NO_3)_2$ / Swheat

154 °C - $Fe(NO_3)_3$ / Swheat

110 °C - $Pb(NO_3)_2$ / Glove / Swheat

60 °C - mixed metal nitrate / Swheat surrogate

ambient - production of heat from low-level chemical reaction or microbial self-heating

Notional ladder of stepwise biological or chemical reactions that may increase the temperature inside a drum.

- Currently, the most likely scenario: production of heat, either from low-level chemical reactions or the growth of natural microbes, in concert with mixed metal nitrate salts, bismuth lined glovebox gloves and/or lead nitrates when combined with the Swheat organic kitty litter, generated a stepwise series of exothermic reactions that heated and pressurized the drum resulting in the venting of high-temperature gases and radioactive material into the room.

Application of the Scientific Method from Independent Laboratories Yields Truths

- Scientific Method is founded upon the notion that independent thinking about natural phenomena yields common solutions: those supported by the laws of nature
- Not surprisingly, while the details may vary slightly, the overarching truths will be similar, when properly accounting for natural laws
- KEY in upcoming slides: Agreement; Difference

The independent analysis of the WIPP event by Los Alamos and the TAT share more similarities than differences

Key Findings: identified through extensive literature review, experimental and modeling efforts

The nitrate salt/Swheat organic kitty litter mixture creates the potential for an exothermic reaction and breach in Drum 68660 ***TAT Key Judgment 1***

- Simple mixtures of metal nitrate salts (oxidizer) with Swheat organic kitty litter (fuel) create the potential for exothermic chemical reactions. ***TAT Report Pages 53-54, 200***
- Relatively high temperatures are required (160 - 330 °C), similar to studies of Hanford Tank wastes (150 - 350 °C).* ***TAT Report Pages 54, 200***
- Simple (freshly prepared) nitrate salt/Swheat organic kitty litter mixtures were unreactive to electrostatic discharge (ESD) friction, or impact test procedures typically used to test the safety of energetic materials. ***TAT did not comment***
- Due to insulating nature of the nitrate salt/Swheat mixture, time-dependent chemical changes cannot be fully ruled out. ***TAT Report – aging, Page 200***

*Scheele, Sell, Sobolik, Burger, Pacific Northwest National Laboratory, 1995, PNL-10213

Key Findings (continued)

An additional trigger mechanism is likely required to initiate chemical reactions needed to breach a drum. *TAT does not specifically discuss triggers.* ***TAT requires a series of reactions that ultimately led to runaway.***

- Temperatures needed to initiate chemical reactivity may be substantially lowered when a combination of conditions exist including:
  - Initial high acid concentration of free liquids (pH ~ 0). ***TAT Report Page 27***
  - Significant quantities (> 1 gal) of neutralized (with triethanolamine), absorbed free liquids. ***TAT Report Page 225***
  - Presence of reactive or catalytic metals like Mg, Fe, Bi, or Pb. ***TAT Report Page 226 (Pb leads to more "violence")***
  - Presence of Bi containing glovebox gloves *TAT concludes glovebox glove did not participate in the reaction, Page 61*
  - The potential for biological self-heating that could lead to chemical reactivity at substantially lower temperatures. *TAT agrees with bioactivity, but argues that self-heating predominately chemically induced, Page 190*

Key Findings (cont.)

An additional trigger mechanism is likely required to initiate chemical reactions needed to breach a drum

- Complex mixtures of metal ions, particularly Fe and Mg, can generate NO_2 that facilitates the nitration of Swheat. ***TAT Report, Page 200***
- Complex salt mixtures produce exothermic behavior as low as 60 °C. ***TAT Report Pages 219, 225-6;*** *(dried 3.5 M Nitric/Swheat, Pages 30, 225-6).*
- Bi associated with the glovebox glove, generates a vigorous exothermic reaction (60 °C) with nitrate salt/Swheat organic kitty litter. *TAT concludes glovebox glove did not participate in the reaction, Page 61*
- Still important to understand how drum temperature can reach 60 °C (140 °F), well above ambient temperature conditions ***TAT Report discusses the fact that the chemistry cannot be quantitatively determined, Page 27***
- Neutralization of free liquids, and sorption onto Swheat establishes conditions (moisture with near-neutral pH) that will support the growth of natural biological activity. ***TAT Report Page 194***
- Spontaneous self-heating from biological activity may be sufficient to raise the temperature to 60 °C *TAT agrees with bioactivity, but argues that self-heating predominately chemically induced, Page 190*

Key Findings (cont.)

Isotopic analysis indicated that a single drum was involved, and Computational Fluid Dynamics indicated that the damage could be described by output from 68660. Key Judgment 3

- Analysis of the isotopics was consistent with the distributions available from the waste stream. CCS-6:14-050, "Analysis for Comparing Historical Measurements of Parent Drums to Air Sample Measurements from WIPP", E.Kelly, B. Weaver, and S.V. Wiel shows that the most likely number of bags resulting in the measured isotopic ratios from the WIPP air samples is 4 or 5. ***TAT Report indicates dominant source was 68660, Page 162, Key Judgment 3***
- Modeling of the drum event yields runaway in ~70 days. ***TAT Report Pages 28, 31, 76. Results very sensitive to input parameters (e.g., 0.29 W radiolytic heating changes runaway to 75 days).***
- Fluid Dynamic simulations have indicated that the damage could have been caused by hot gases from combustion products of 68660. ***Consistent with TAT report pages 37, 141***. *However, LANL mechanism requires a short release of hot gas to cause the damage observed.*

The most likely scenario

Production of heat, either from low-level chemical reactions or the growth of natural microbes, in concert with mixed metal nitrate salts, bismuth lined glovebox gloves and/or lead nitrates when combined with Swheat organic kitty litter, generated a stepwise series of exothermic reactions that heated and pressurized the drum resulting in the venting of high-temperature gases and radioactive material into the room.

- The commingling of Swheat (fuel) and nitrate salts (oxidizer) created a temperature-sensitive mixture with the potential for exothermic reaction leading to drum failure. ***Key Judgment 1***
- Exhaust gases (modeled *ca* 1600 °C) hot enough to ignite when they contact air.
- Drum contents are sufficient to generate increased temperature and pressure that eventually led to failure of the drum: *it is not necessary to invoke an external heat source to explain the event*. ***Key Judgment 2, 4***
- The use of Swheat absorbent in the processing of nitrate salt TRU wastes can be pinpointed as the critical processing decision that led to the failure of drum 68660, regardless of the details of the thermal processes that enabled the drum to achieve temperatures sufficient for thermal runaway. ***Key Judgment 1***

The TAT Scenario

A combination of exothermic chemical reactions and radioactive decay heat heated the drum contents in localized regions of the drum which evaporated free liquid and waters of hydration in the nitrate salts. Chemical reactions continued until a runaway reaction occurred or heated up the liquid fraction containing TEAN so that the TEAN decomposition reaction began leading to a thermal runaway condition. During heating the partial pressure of nitric acid in the vapor phase was increased, which lead to increased oxidation of the organic compounds in the Swheat Scoop®. Heat from the exothermic chemical reactions continued to increase the temperature of the drum contents, which in turn increased the reaction kinetics, the production of gaseous products, and also initiated chemical reactions with higher activation energies. At this stage, a self-sustaining condition was achieved such that the dissipation of heat to surrounding regions of the drum could not keep up with that produced by the exothermic chemical reactions. Heat and gas production ultimately proceeded at such a rate to pressurize the drum and overcome the venting and drum ring enclosure.

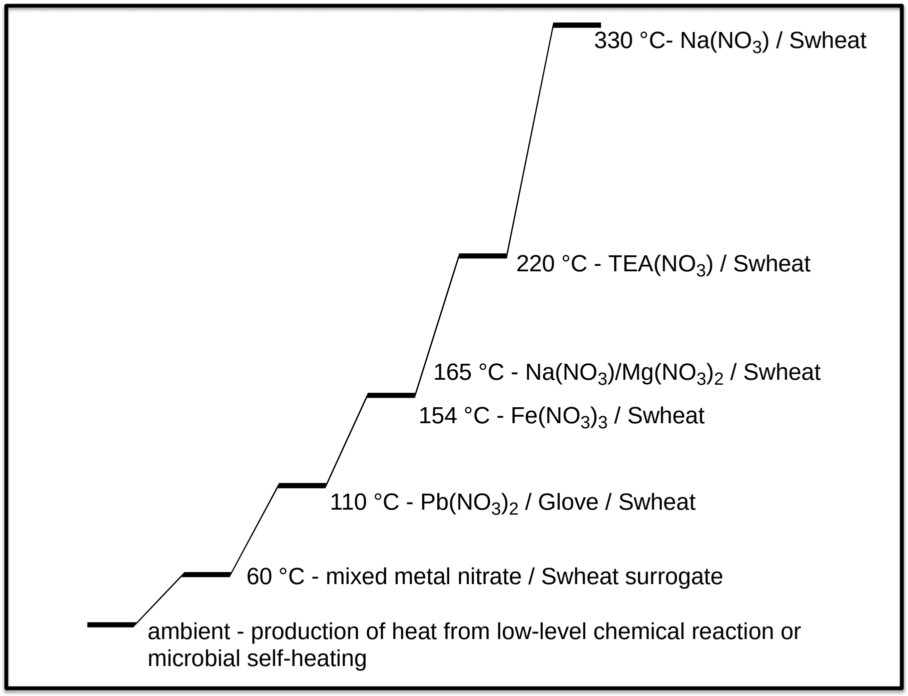
Key Differences

- TAT agrees with the possibility of bioactivity, but argues that self-heating predominately chemically induced.
- TAT concludes that glove box glove did not play a role due to its proximity relative to the salt, and a lack of Bi/La/W measured in debris testing.
- TAT discusses aspects of drying of the salt/Swheat mixtures – LANL would argue that this is not likely during the short time between processing and the event
- CFD simulations require different timescales – LANL requires short durations, TAT requires long duration.
- Nitration of Swheat implicated in LANL experiments as key to lowering runaway – TAT acknowledges but does not require

Summary

- The nitrate salt/Swheat organic kitty litter mixture creates the potential for an exothermic reaction and breach in Drum 68660

- An additional trigger mechanism is likely required to initiate chemical reactions needed to breach a drum



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LA-UR-15-22661

Title: Interpretation of Headspace Gas Observations In Remediated Nitrate Salt Waste Containers Stored at Los Alamos National Laboratory

Author(s):
Robinson, Bruce Alan
Leibman, Christopher Patrick

Intended for: Report

Issued: 2015-04-14 (Draft)

Interpretation of Headspace Gas Observations in Remediated Nitrate Salt Waste Containers Stored at Los Alamos National Laboratory

Bruce A. Robinson

Christopher P. Leibman

April 10, 2015

Executive Summary

This study supports the case for the use of gas concentration measurements of the Standard Waste Box (SWB) headspace as an interpretive tool for discerning the type and rate of gas-generating reactions within the Remediated Nitrate Salt (RNS) waste drums in storage at Los Alamos National Laboratory (LANL). Model results imply that the measurements could provide an early warning for the occurrence of heat-generating chemical and biological reactions in the drums, enabling actions to be taken before self-heating at low temperatures triggers a runaway exothermic reaction at higher temperatures. The study conclusions are summarized below.

1. The headspace gas concentrations are consistent with a description consisting of the combination of a radiolysis mechanism for hydrogen gas generation and low-level, temperature-dependent chemical reactions such as oxidation for the generation of other gases such as carbon dioxide and nitrous oxide. Many of the SWBs have low levels of reaction product gases, whereas a subset exhibit higher concentrations indicative of somewhat higher levels of reactivity. The ratios of gases within the drum for the SWBs with the highest gas concentrations exhibited a similar characteristic signature, but with variability from drum to drum.

2. A simple mathematical and numerical model of the headspace gas behavior provides a plausible description of the long-term variations of concentrations of gases such as carbon dioxide and nitrous oxide in the SWB headspace. The model balances a gas generation source term from reactions in the RNS drum with mixing from the outside atmospheric air due to ventilation of the SWB. Excellent fits to the concentration data for Drum 68685 (a sibling to the drum that breached in WIPP) were obtained throughout the entire time period since the RNS drum was placed within the SWB in May of 2014. Figure ES-1 below shows this result.

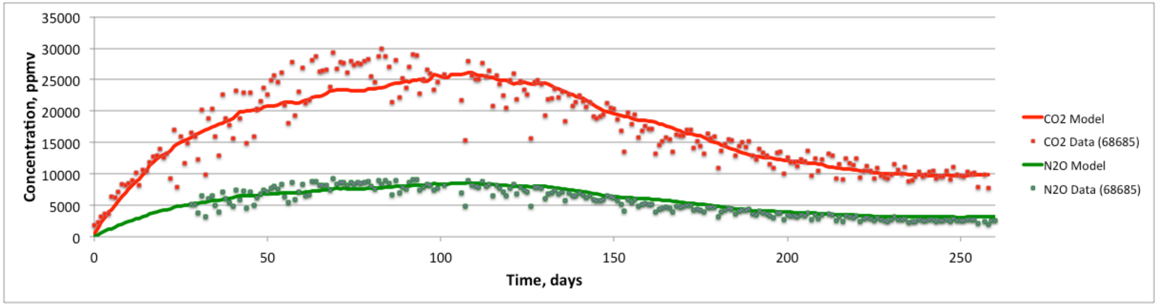

Figure ES-1 Simulation results compared to data for carbon dioxide and nitrous oxide concentrations for Drum 68685.

3. The model results for Drum 68685 suggest a low level of chemical reaction within the RNS waste drum. Gas generation rates due to reaction are predicted

to be a minute fraction of the ventilation rates into and out of the SWB, and calculated heat generation rates for a reasonable postulated reaction (oxidation of Swheat, which appears to have the correct stoichiometry based on the simultaneous fit to the carbon dioxide and nitrous oxide data) are also very low, nominally 1 W or less for the drum. If other reactions are occurring, these could also generate heat, but if they also generate carbon dioxide, this should have been reflected in the form of higher concentrations. Therefore, the level of carbon dioxide in the drums appears to provide a bound on the level of reactivity and heat generation; this bound is very low from a thermal perspective. Investigations should focus on the potential for reactions not involving the generation of carbon dioxide to attempt to identify other important reactions not reflected in the headspace gas data.

4. The reaction rates exhibit a significant temperature dependence, which explains the higher concentrations of carbon dioxide and other gases in the SWB headspace in the summertime compared to the winter. A model reaction exhibiting an Arrhenius temperature dependence was employed in the model. Calibrations to the data led to values of 15-20 kcal/mol for the activation energy. This range is well within the 10-30 kcal/mol range suggested by Clark and Funk (2015) for such reactions. The low level of reactivity also implies that at these rates, reactants will not be depleted for many years, and that the pattern of higher concentrations under the summertime temperature conditions will repeat itself this summer in a predictable manner. This prediction constitutes a blind test of the validity of the model.

5. Uncertainties in the model have been evaluated to estimate how tightly the model bounds parameters like heat generation rates, given the lack of perfect information on temperatures, available gas volumes inside the SWB and internal drums, and ventilation rates. Reaction and heat generation rates are unlikely to be more than about a factor of two higher than the rates cited above that were derived from the data fit. Other parameter combinations that would lead to higher rates produce simulations that begin to deviate significantly from the observed data.

6. The model could be applied to the data from other SWBs containing the LANL RNS wastes, but this study focused principally on Drum 68685. It is likely that different reaction rates and ventilation rates would be required to simulate other drums, which points to the uniqueness of each drum as a separate system. Notably, all seven of the drums being subjected to daily headspace gas sampling appear to have characteristic behavior similar to that of 68685: higher concentrations of carbon dioxide and other headspace gases than the other drums, and temperature dependence of the concentrations.

7. The drums are currently under temperature control within the Permacon, but there have also been efforts to study the possibility of enhancing the ability to keep the drums cooler throughout the year, including in the summer months.

Simulations were performed to examine the effect of these actions on reaction rates. As expected, the model predicts reaction rates and gas concentrations in the SWB headspace to be lower for lower temperatures. As a defense-in-depth measure, temperature control seems prudent. However, recalling that even under the current level of temperature control, gas generation rates are low, it is unlikely that this additional curtailing of the concentrations represents a meaningful additional factor of safety over an already safe storage condition. Moreover, if cooling is achieved by placing the drums in a refrigerator, ventilation conditions will also be affected, which would likely result in added uncertainty in the interpretation of concentration values, and thus added complexity to the technical arguments supporting the efficacy of the cooling measures taken.

8. Scenarios developed to examine the response of SWB headspace gases to abrupt changes in reactivity suggest that concentrations are a very sensitive means for observing such changes. In a simulation postulating a rise in temperature within an RNS waste drum of 1 ^{o}C per day (presumed to be undetected by measurements on the outside of the SWB), the model suggests that within about five days, the headspace gases would deviate enough from their current state to provide a high likelihood that this off-normal condition would be detected. This is illustrated in Figure ES-2 below. Even if one assumes conservatively that this time is 10 days, the RNS waste temperature would still be well below the temperature specified by Clark and Funk (2015) and SRNL (2015) as the onset temperature for runaway exothermic reactions for this waste. Further work should be performed to solidify this conclusion by considering issues of detectability of deviations, given that the data are not perfectly smooth, and to make sure that additional drums beyond the seven receiving daily sampling are monitored more frequently for purposes of detecting incipient chemical reactions that might be the precursor of thermal runaway conditions.

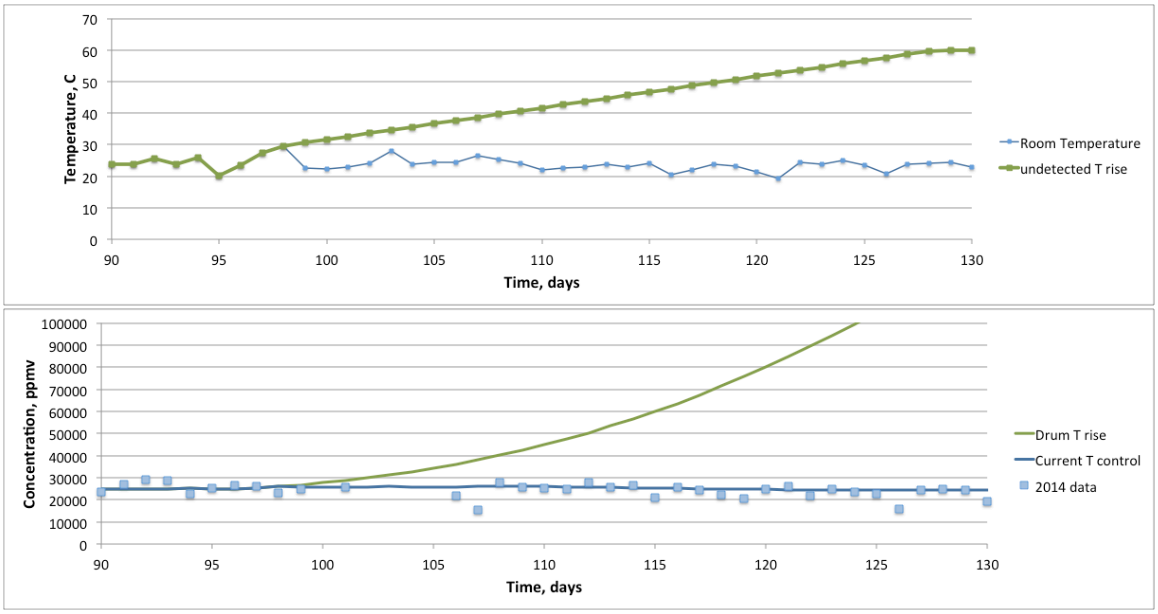

Figure ES-2 Simulation of hypothetical scenario in which the RNS waste drum experiences an undetected temperature rise due to low-level chemical or biological reaction. Top figure: Postulated RNS waste drum temperature profile. Self-heating begins at day 98, when it deviates from the temperature in the room. Bottom: Simulated carbon dioxide concentrations. The green curve is the simulated response to self-heating within the RNS drum. The simulation tracks the baseline scenario until the postulated change, after which concentrations climb rapidly. The 2014 concentration data and the model under a scenario of the current temperature control ("Current T control") is superimposed to show the level of data scatter expected when using these data to detect off-normal conditions.

1 Introduction

On February 14, 2014, a release of radioactivity occurred at the Waste Isolation Pilot Plant (WIPP), resulting in distribution via airborne transport of radioactivity within the repository and to the surrounding environment in the vicinity of the facility. When definitive photographic evidence became available (May 15, 2014) that the breached drum was indeed an RNS waste drum processed at LANL (Drum 68660), LANL implemented additional precautions and controls, including overpacking of the 55-gallon RNS waste drums into Standard Waste Boxes (SWBs)[1] and storage in a Permacon at TA-54, Area G, in Dome 375, as well as moving all unremediated nitrate salt (UNS) containers[2] to a Permacon at TA-54, Area G, in Dome 231. RNS waste drums similar to those at LANL had previously been shipped to WIPP (422 drums, emplaced in the WIPP underground), and to the low level radioactive waste facility in Andrews, Texas managed by Waste Control Specialists, LLC (WCS) (109 drums, subsequently placed in shallow underground storage). Both WIPP and WCS subsequently have also taken precautions to protect workers, the public, and the environment.

Drums at LANL continue to be managed and monitoring results are reported to the New Mexico Environment Department (NMED) under the LANL Nitrate Salt Bearing Waste Container Isolation Plan (Isolation Plan: LANL, 2014). Drums are currently stored under HEPA filtration and the temperature controls provided by the buildings, with active fire suppression systems. Monitoring of the drums consists of hourly visual inspections, daily temperature measurements of the SWBs containing the RNS waste drums, and periodic sampling and analysis of the headspace gases within these SWBs.

The LANL Chemical Diagnostics and Engineering Group (C-CDE) began characterizing headspace gases in LANL SWBs containing RNS waste on May 8, 2014. Results of this monitoring campaign are described in detail in Leibman et al. (2015). Gas samples of TRU drum headspace were analyzed for Volatile Organic Compounds (VOCs) by Gas Chromatography/Mass Spectrometry (GC-MS) and for permanent gases using GC with a Thermal Conductivity Detector (GC-TCD). Permanent gases are those that remain gaseous at standard temperature and pressure and include helium, hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, and nitrous oxide. This initial characterization was conducted to determine if causal factors which could lead to drum failure could be quickly identified to prevent recurrence. Of immediate concern was the potential to produce explosive or flammable concentrations of gas from unanticipated chemical

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[1] *Upon completion of this process on May 18, 2014, there were 57 RNS waste containers at LANL, overpacked into a total of 55 SWBs.*

[2] *At the time that LANL suspended further processing of UNS waste on May 2, 2014, there were a total of 27 UNS waste drums that had not yet been processed. The move of these drums to Dome 375 was completed on June 3, 2014.*

reaction of the nitrate salt waste with organic absorbent. These initial analyses and other monitoring did not suggest that runaway chemical reactions were occurring in any of the remediated or un-remediated nitrate salt waste drums. Since these initial characterization activities, headspace gas analysis has continued to see what trends in individual gas concentrations or relative concentrations were observed, and to gain further insight into potential mechanisms that could have contributed to the breach of drum 68660 in the WIPP repository.

With the collection of a significant quantity of headspace gas and temperature data for the RNS waste drums, it is reasonable to suspect that additional insights into the nature of chemical reactivity within the drums can be derived from a modeling and analysis activity. These insights could play a key role in LANL's ongoing efforts to confirm the safety of the RNS waste in its current storage configuration. Such studies, as well as the recently published studies of the WIPP radiation release event (Clark and Funk, 2015; SRNL, 2015), could also inform future directions for management and ultimate treatment of the waste. Finally, it is anticipated that the Accident Investigation Board (AIB) report will issue findings related to the reactive chemistry occurring within the RNS waste drums that will need to be answered. The models and interpretations developed herein also satisfy this need.

The remainder of this report is organized as follows. First, a description of the configuration of the waste is presented along with a presentation and qualitative interpretation of the headspace gas data. These descriptions emphasize those aspects that influence the development of a mathematical model of headspace gas behavior. Then, a conceptual and numerical model of the system is developed, including assumptions and simplifications required to result in a tractable mathematical model. Then, headspace gas modeling results are presented for the SWB containing Drum 68685, a LANL RNS waste container (a sibling of Drum 68660 that breached in the WIPP underground) for which daily headspace gas measurements are available. Finally, the implications of the results to the management of RNS waste at LANL are discussed by using the model to examine the various scenarios for cooling the waste, as well as various scenarios for detecting off-normal conditions should the RNS waste drums exhibit increased reactivity in the future.

2 Headspace Gas Monitoring for RNS Waste

The RNS waste at Los Alamos has undergone monitoring of the headspace gases on a regular basis since the time it was determined that a Los Alamos waste drum had breached at WIPP. This section summarizes the configuration of the waste drums and presents a high-level overview of the data collected.

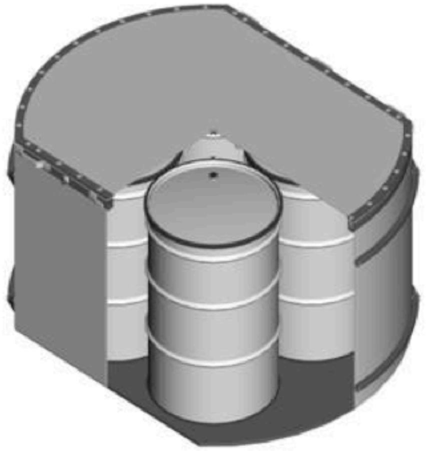
2.1 Configuration of RNS Waste Stored at Los Alamos

There are currently 57 RNS waste containers at LANL, overpacked into a total of 55 SWBs. Figure 2-1 provides a diagram and physical dimensions of a SWB for a configuration containing four 55-gallon drums. For most of the RNS waste containers at Los Alamos, including Drum 68685, the SWB overpack contains one 55-gallon drum containing RNS waste, and three additional drums that are either empty dunnage drums or which contain non-nitrate salt TRU waste. The SWBs are fitted with filtered vents to allow gases generated within the container to vent to the atmosphere. This is a standard precaution built into such a system to prevent the buildup of flammable gases within the container.

The headspace gases monitored in the LANL RNS waste drums are obtained from the headspace of the SWB overpack containing the 55-gallon RNS waste drum. Thus, SWB headspace gas concentrations are measurements of the gases contained within the space outside of the 55-gallon drums but within the SWB. Gas concentrations are impacted by gas generation within the 55-gallon RNS waste drum and by communication with the outside air through the SWB and drum filter vents. Venting of the SWB provides a mechanism for mixing of the headspace gases with outside air, as well as the escape of gases from the SWB. As the pressure conditions within the room change due to barometric or room ventilation changes, the gas flow may be either into or out of the SWB. When the SWB is "exhaling," gases are released at the concentrations present within the SWB headspace. When the SWB is "inhaling," the SWB is supplied with atmospheric air.

The volume available for gas mixing is uncertain due to the lack of perfect knowledge on the volume of waste within the internal drums. However, gas transfer between the SWB headspace and the 55-gallon dunnage drums should be relatively rapid in most cases because either the lid of dunnage drum is removed or the lid is on but the bung is removed.

These factors are important to the mathematical model of the system developed in the next section.



Standard Waste Box

Table 1 – SWB Weights

Component	Weight (pounds)		
	Maximum Gross	Nominal Tare	Net Content
SWB	4,000	640	3360

Table 2 – SWB Dimensions

Dimension	Approximate Measurement (Inches)	
	Inside	Outside
Height	36 9/16	36 7/8
Length	68 ¾	71
Width	52	54 ½

Source: http://www.wipp.energy.gov/library/cpp/cpp/standard%20waste%20box%20%28swb%29.htm

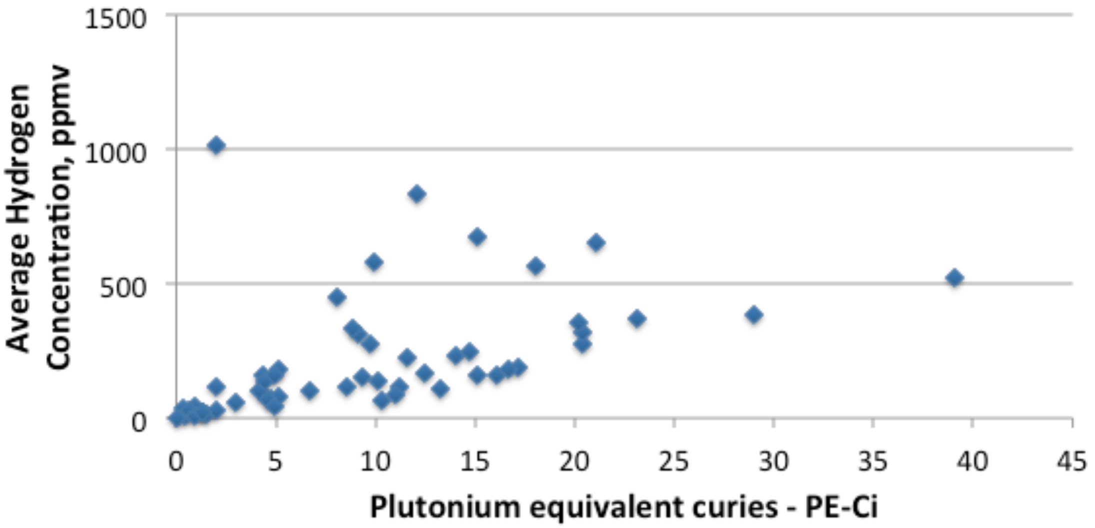
Figure 2-1 Diagram and physical dimensions of a Standard Waste Box (SWB)

2.2 Summary of Headspace Gas Data

Leibman et al. (2015) report on the sample collection and gas concentration analysis methods for the headspace gases in the RNS waste drums at Los Alamos. This section describes some of the key results from this monitoring campaign, setting the stage for the modeling effort that follows in the remainder of this report. Data up to February 3, 2015 are used in all plots and analyses; results will be updated as needed to reflect the most recent measurements.

Measurements of permanent gases, including helium, hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, and nitrous oxide, have been conducted at least monthly, and for several drums, as frequently as daily, for the 55 SWBs containing the 57 RNS waste drums. The principle purpose of these measurements is to monitor for flammable gases such as hydrogen and to detect any chemical reactivity such as oxidation reactions that may be occurring in the drums.

The data support the conclusion that the predominant source of hydrogen is radiolysis of the drum contents as a result of decay of the radioactive transuranic elements in the waste. Figure 2-2 is a correlation of the average hydrogen concentration versus the activity in the drum for the 55 SWBs. Such a correlation is not expected to be perfect because of variability between drums such as venting characteristics of individual drums, inaccuracies in the activity measurement and the heterogeneity of drum contents. Nonetheless, a correlation does exist, suggesting a radiolysis mechanism. Also, as illustrated in Figure 2-3 for Drum 68685, the hydrogen concentration is generally constant with time, in contrast to trends for other gases such as carbon dioxide that suggest a temperature-dependent behavior (see below). Both of these observations support radiolysis as the controlling the mechanism for hydrogen generation.



Note: Two drums, SB50522 and SB02198, are not included because their average hydrogen concentration levels exceed the maximum on the plot (5953 ppmv and 2640 ppmv, respectively). Each of these drums has exhibited a steady decline in hydrogen concentration since monitoring since began, and future monitoring will track the concentration to detect future trends.

Figure 2-2 Correlation of hydrogen concentration in headspace gas versus the drum activity for the 55 SWBs containing RNS waste.

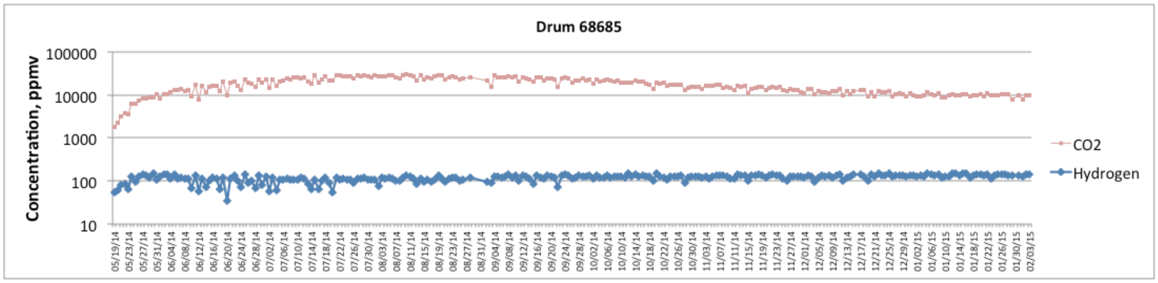


Figure 2-3 Trends of concentration for carbon dioxide and hydrogen gases in Drum 68685.

Leibman et al. (2015) found that the ratios of gases within the drum for the SWBs with the highest gas concentrations exhibited a similar characteristic signature, but with variability from drum to drum. This statement is supported by the average ratios of gases for the seven containers with the most extensive monitoring history (Figure 2-4). In addition to these averages, the ratios exhibit varying degrees of time dependence (Figure 2-5), which may be due to temperature dependence of multiple chemical reactions. For example, for Drum 68685, the carbon dioxide/nitrous oxide ratio ranges from about 3:1 at the beginning of monitoring to about 4:1 after 260 days; at the other extreme, these ratios for SWB 50522 are about 65:1 initially, and drop to about 35:1 after 260 days. Multiple chemical reactions that perhaps exhibit different temperature dependence would be required to quantitatively explain this behavior. The carbon dioxide/nitrous oxide ratio of approximately 3:1 in Drum 68685 is used to postulate a simplified description of the chemical reactivity in that drum later in this report. However, it is important to recognize that different chemical reactions contribute to gas generation and some variability should be expected across the drum population.

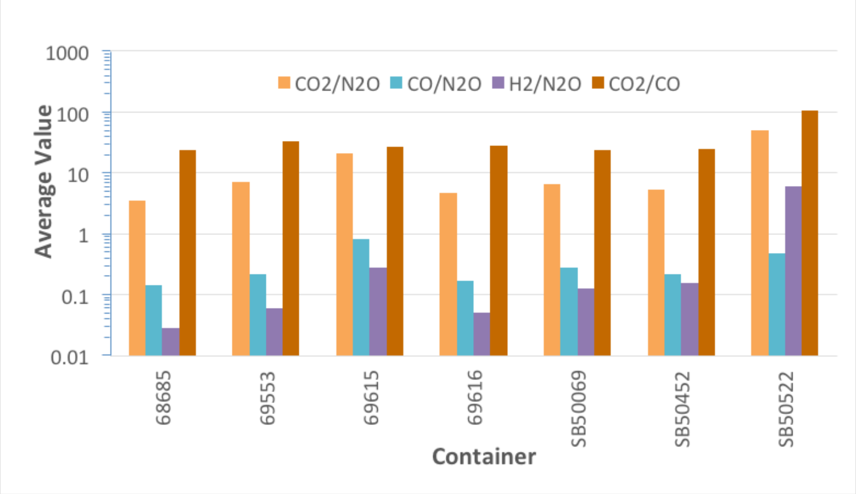


Figure 2-4 Average gas concentration ratios in the headspace of SWBs containing RNS waste. Reproduced from Leibman et al. (2015). These seven drums exhibit the highest concentrations of the 55 SWBs in storage.

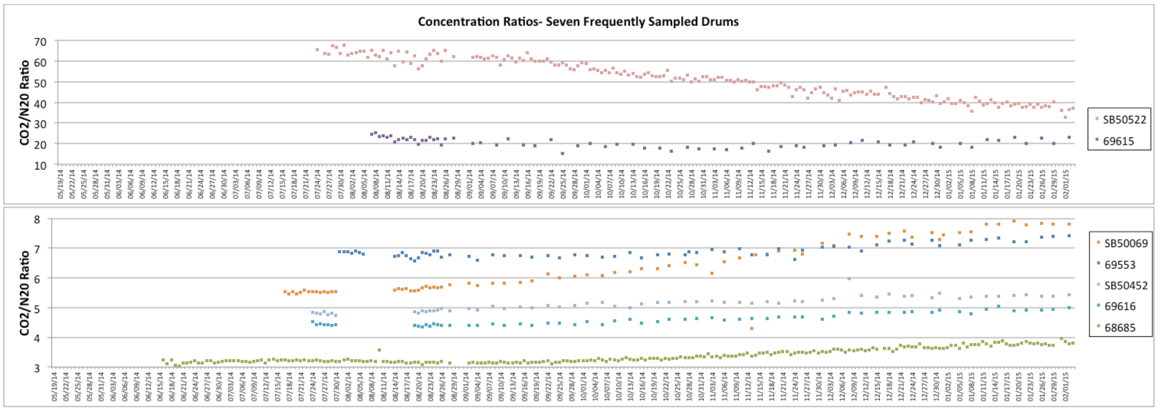


Figure 2-5 Time-varying ratio of carbon dioxide/nitrous oxide concentration for the most frequently monitored SWBs containing RNS waste. Top panel: two drums with the highest ratios; Bottom panel: five drums with the lower ratios.

Figure 2-6 shows the carbon dioxide concentration-time histories of the seven most frequently sampled drums. All drums with high concentrations exhibit the same characteristic decline in concentration, explained in the model developed later as temperature-dependent reaction kinetics in the RNS waste drum, modulated by mixing with atmospheric air due to ventilation of the SWB.

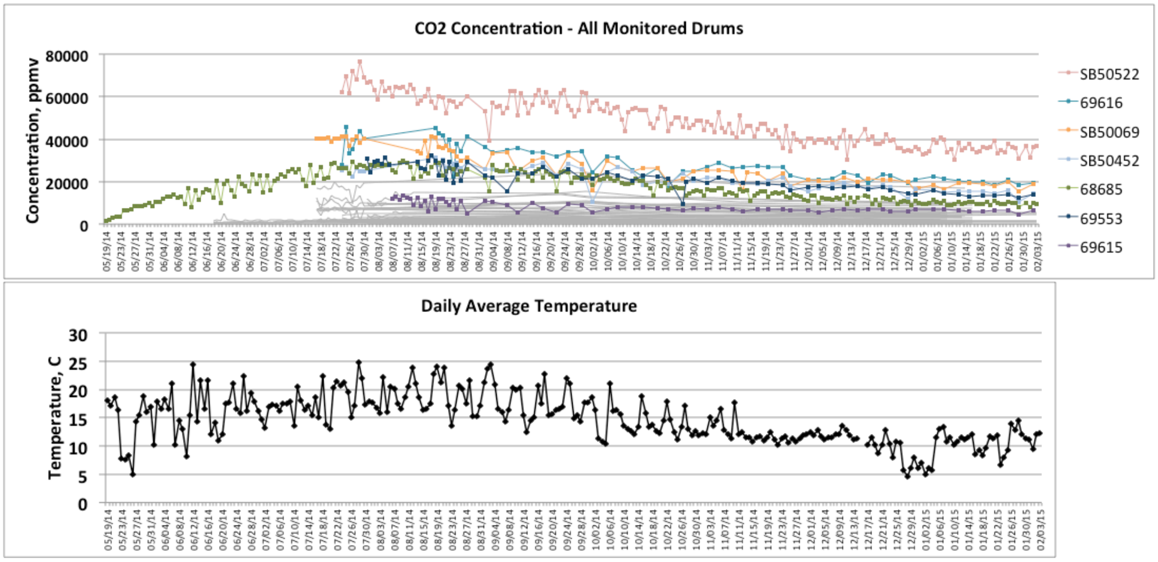


Figure 2-6 Carbon dioxide concentration-time and temperature-time histories of the seven most frequently sampled drums. Gray lines are curves plotted for the remaining 48 SWBs. Top panel: concentrations; Bottom panel: daily average temperatures for the cell containing Drum 68685.

In contrast to the seven drums with highest carbon dioxide concentrations, many drums have much lower concentrations, for example with maximum carbon dioxide concentrations less than 10,000 ppmv. These are depicted in Figure 2-6 as thin gray curves at lower concentrations. Many of these drums exhibit either flat concentration profiles with time, or steadily increasing values, but at much lower levels than the frequently sampled drums highlighted in Figure 2-6. The average concentrations of carbon dioxide, nitrous oxide, and hydrogen for all drums are represented in Figure 2-7, and Table 2-1 indicates the groupings of containers into separate bins of similar carbon dioxide concentrations. The selection of the bin for a given SWB was performed manually, choosing the bin based on the overall concentration of the majority of the measurements for that drum, rather than using a maximum or average value. The overall statistics are presented at the bottom of the table. Based on a qualitative criterion that carbon dioxide concentrations >10000 ppmv in the SWB headspace meet the definition of a "reactive" waste drum, 11 drums fit into this category, including all seven of the most frequently sampled drums, as well as four others: Drums 69183, 69630, 69645, and 94068. However, note that there is some reactivity in most of the drums, and that the term "reactive" must be placed into context through an assessment of the level of gas generation. The model developed in the remainder of this report provides that context.

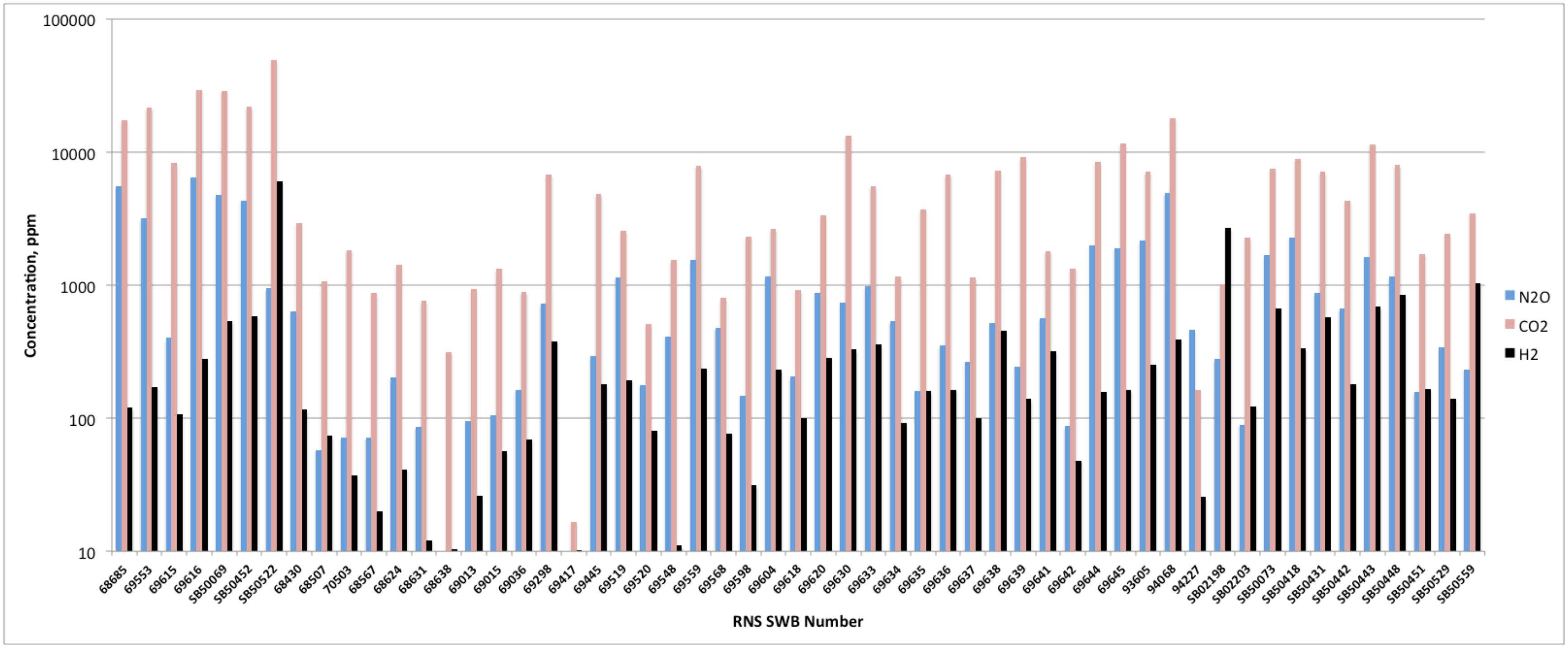


Figure 2-7 Average concentrations of gases in each of the 55 SWBs containing RNS waste

Table 2-1 Carbon dioxide concentrations within the 55 SWBs containing RNS waste drums

			Carbon Dioxide Concentration (ppmv)					
RNS Drum ID	Parent Drum ID	SWB ID*	<1000	1000-2000	2000-5000	5000-7500	7500-10000	>10000
68408	S842463	SB02198		✔				
68430	S833846				✔			
68507	S853279			✔				
68540	S842181	70503		✔				
68553	S842181	70503						
68567	S816837		✔					
68624	S824184			✔				
68631	S825810		✔					
68638	S825810		✔					
68648	S855139	SB50442			✔			
68665	S853492	SB50529			✔			
68685	S855793							✔
69013	S870213			✔				
69015	S851418			✔				
69036	S873554		✔					
69076	S852530	SB50452						✔
69079	S901114	SB50073					✔	
69183	S870478	SB50443						✔
69208	S851772	SB50069						✔
69280	S841251	SB50431					✔	

			Carbon Dioxide Concentration (ppmv)					
RNS Drum ID	Parent Drum ID	SWB ID*	<1000	1000-2000	2000-5000	5000-7500	7500-10000	>10000
69298	S841251						✔	
69361	S892963	SB50451		✔				
69417	S822876		✔					
69445	S823229					✔		
69490	S892963	SB50522						✔
69491	S891387	SB50448					✔	
69519	S816768				✔			
69520	S813471			✔				
69548	S851416			✔				
69553	S841627							✔
69559	S832148						✔	
69568	S825664		✔					
69595	S852588	SB50418					✔	
69598	S793450				✔			
69604	S816768				✔			
69615	S843673							✔
69616	S841627							✔
69618	S818412			✔				
69620	S816768				✔			
69630	S843672							✔
69633	S851418					✔		
69634	S851416			✔				

			Carbon Dioxide Concentration (ppmv)					
RNS Drum ID	**Parent Drum ID**	**SWB ID***	**<1000**	**1000-2000**	**2000-5000**	**5000-7500**	**7500-10000**	**>10000**
69635	S851418				✔			
69636	S843672					✔		
69637	S813471				✔			
69638	S822679						✔	
69639	S843673						✔	
69641	S813471					✔		
69642	S818412				✔			
69644	S793450						✔	
69645	S822679							✔
92459	S910171	SB50559			✔			
92472	S910171	SB50559						
92669	S823187	SB02203			✔			
93605	S824541						✔	
94068	S851852							✔
94227	S813475		✔					
Color Legend		**Total**	**7**	**11**	**12**	**4**	**10**	**11**
Frequently sampled drums	Two RNS drums in an SWB							

* If SWB ID is blank, the SWB is referred to by its RNS drum ID

3 Model Development

This section presents a conceptual and numerical model of the transient behavior of gases within the SWB headspace for containers hosting the 55-gallon RNS waste drums. The subsections below include the conceptual model with accompanying assumptions and simplifications, followed by the mathematical model developed to simulate the headspace gas concentrations.

3.1 Conceptual Model

In principle, a fully realistic depiction of the concentrations of headspace gases within the SWB would consider the transient processes of ventilation flows into and out of the SWB, temperature and spatially dependent reaction and gas generation within the 55-gallon drum, expulsion of those gases into the SWB headspace, and gas flow and mixing above and between the drums inside the SWB. Given the complexity of those processes and the lack of input data to inform such a model, an idealized model approximating the key processes is a more practical approach. The following simplifications and assumptions are made for the conceptual model developed herein.

Gases within the headspace of the SWB are perfectly mixed. The ventilation of the drum should result in gas circulation and mixing, and molecular diffusion of gases within the open space should be rapid, leading to homogenization of gas concentrations. Mole fractions of generated gases such as CO_2 do not exceed a few percent, so gravitational accumulation of gases heavier than air at the bottom of the SWB should be minimal. An implication of this assumption is that there is a single, time-varying value of concentration within the headspace, and that the sampling campaign provides a measurement of that concentration-time history.

Average gas flow rates are in balance at any point in time. In other words, the inflows equal the outflows. Here we make a distinction between the short-term transients of induced inflow and outflow via ventilation, versus the long-term average flows that we desire to represent in the model. From the perspective of a representation of the long-term behavior of the system, the inflow is the time-averaged flow rate into the SWB during periods when it is inhaling. The rate of gas generation from reactions occurring within the RNS waste drum is another “inflow” into the SWB headspace. Likewise, outflows are the time-averaged flow rates while the SWB is exhaling. Because the gas pressure in the SWB is approximately atmospheric (at the local conditions where the drums are stored), there is no net accumulation of gas within the headspace in the long term. This assumption stipulates that an averaged representation of the inflow and outflow (controlled by cyclic changes in barometric pressure, temperature variability, and transients in room airflow) that ignores the short-term “on/off” nature of ventilation flows is sufficient for a model of the long-term mass balance of gases within the SWB.

Chemical reactions within the RNS waste drum generate gases that feed the SWB headspace; these reactions follow an Arrhenius temperature dependence. While there may be multiple reactions, as implied by the analysis of headspace gas data presented earlier, this model assumes that a single reaction with Arrhenius temperature dependence is the sole source of permanent gases such as CO_2 and N_2O that are observed. This is a simplification made out of necessity, given the inherent complexity of the RNS mixtures and lack of detailed information on the reactions. However, it is acknowledged that if multiple reactions occur, there may be shifts in the dominant stoichiometry as a function of temperature.

Temperatures measured in the room where the SWB is stored are an appropriate input for calculating the reaction rates within the RNS waste drum. Temperature is controlled within the Permacon in which the RNS waste is stored, but the system is not kept at a uniform temperature: generally, temperatures are somewhat higher in the summer and cooler in the winter. Figure 3-1 shows the daily temperatures measured in the cell in which the SWB containing Drum 68685 is stored. Two forms of the data are presented: the daily average temperature averages the diurnal temperature swings from day to night, whereas the daily maximum temperature simply records the maximum temperature of that day. In addition to the seasonal variability, there are higher-frequency diurnal variations in temperature. From separate experiments conducted at Los Alamos to understand the rates of heat transfer within the drum, we know that the characteristic response time of a drum in this configuration is of the order of a few days. Therefore, diurnal fluctuations should be damped, such that the drum experiences a bulk temperature that can be well represented by the daily average or daily maximum temperature. Conversely, the drum response time is short compared to the long storage periods that the model is designed to simulate. Therefore, the assumption that room temperatures track the measured temperatures in the vicinity of the drums is an appropriate approximation. Finally, this assumption also requires that heat generation rates due to reaction within the RNS drum are too small to impact the bulk average temperature within the drum. In the model analysis, this assumption is tested *ex post facto* by estimating the heat generation rates that would accompany the reactions in the drum to determine if they would be sufficient to provide significant warming of the contents.

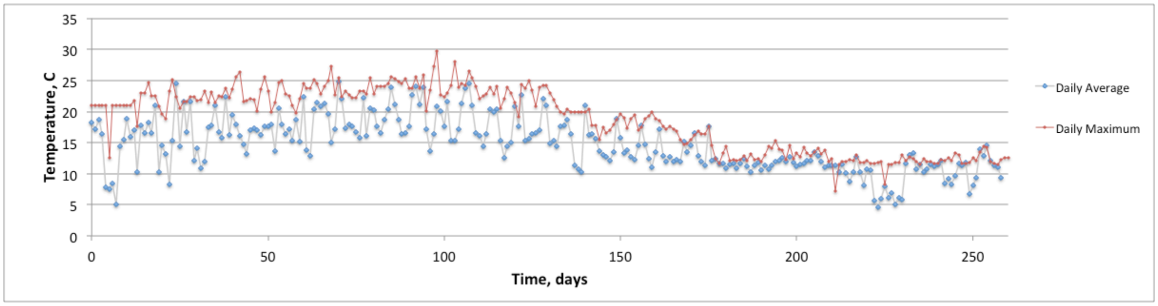


Figure 3-1 Measured temperatures within the cell containing the SWB of Drum 68685.

3.2 Mathematical Model

Given the assumptions outlined above, a mass balance in the SWB headspace for a gas constituent such as CO_2 or N_2O generated from the RNS waste can be described as follows:

$$V_{HSG}\frac{dC}{dt} = -Q_{out}C + Q_{in}C_{in} + \chi(T) \tag{1}$$

where

$$\chi(T) = Ae^{-E_a/RT} \tag{2}$$

In these equations, C is the concentration of a particular gas in the headspace (mol/L); t is time (s); T is temperature (K); C_{in} is the atmospheric concentration of the gas (mol/L); V_{HSG} is the volume of the headspace gas within the SWB (L); $\chi(T)$ is the rate of generation of the component (e.g. carbon dioxide or nitrous oxide) being simulated (mol/s); E_a is the activation energy of the reaction within the RNS waste drum (kcal/mol); R is the universal gas constant (1.987e-3 kcal/mol-K); A is a lumped term with units of mol/s containing the pre-exponential factor and a scaling factor that establishes the actual molar generation rate of the gas within the RNS waste drum; Q_{in} is the long-term average gas flow rate into the system due to SWB inhalation (L/s); and Q_{out} is the long-term average gas flow rate out of the system due to SWB exhalation (L/s). Due to gas generation within the RNS drum, Q_{in} and Q_{out} are not equal to one another, but are related through the following expression:

$$Q_{out} = Q_{in} + Q_{gen} \tag{3}$$

where Q_{gen} is the volumetric generation rate of all gases due to reactions within the RNS drum, and is calculated from the following expression:

$$Q_{gen} = \frac{\chi(T)RT}{P_{HSG}X_g} \tag{4}$$

In this equation, the universal gas constant is 0.08206 L-atm/mol-K, P_{HSG} is the pressure in the headspace, assumed to be 0.7849 atm, the mean atmospheric pressure that the elevation of Los Alamos, New Mexico, where the drums are stored, and X_g is the fraction of the total gas generated from reaction that is the constituent being modeled. In other words, if, for example, carbon dioxide is being simulated in the model, other gases will be generated along with it, and are accounted for by this fraction, which is obtained from the stoichiometry of the reaction presumed to be occurring within the RNS waste drum that is giving rise to the gas generation.

This mass balance equation is closely related to the continuous stirred tank reactor (CSTR) model that is commonly employed in the field of chemical engineering to describe well-mixed reactors, except that in this case, the inlet and outlet flow rates are not necessarily equal due to the generation of gas due to RNS waste reactions. Equation (1) is solved numerically using a simple Picard integration scheme in the spreadsheet titled *HSG model calculations.xlsx* that accompanies this report. Details of the numerical calculations are presented in that spreadsheet, along with the numerical verification tests performed to ensure that the solutions obtained are accurate. A summary of the verification tests is presented in Appendix 1.

In the presentation of the results in the remainder of this report, the units of the parameters of time and concentration are converted to days and ppmv, respectively, to enable comparison to the available data.

4 Model Results

This section presents model results describing the long-term transient behavior of carbon dioxide and nitrous oxide in the headspace gases. The most complete data set is for Drum 68685, a sibling drum of 68660, which also exhibits some of the highest concentrations of carbon dioxide of any of the RNS drums in storage at LANL.[3] The first subsection presents a detailed set of modeling results for this drum. Then, a more general set of modeling results are presented in the next subsection, to illustrate the characteristic types of headspace gas behavior that are occurring in other drums. Following that, the behavior of headspace gases under different possible cooling scenarios is presented in Section 4.3, and the potential use of these measurements to detect anomalous reactions that would be indicative of initial heating within the RNS waste drum is discussed in Section 4.4.

4.1 Model of Drum 68685

It is necessary to define a chemical reaction involving the evolution of carbon dioxide and nitrous oxide in order to simultaneously simulate the behavior of both gases in the same model. For Drum 68685, we adopt the cellulose oxidation reaction suggested by Leibman et al. (2015):

$$C_6H_{10}O_5 + 6NaNO_3 \rightarrow 3Na_2CO_3 + 3CO_2 + 5\ H_2O + 2\ N_2 + N_2O + O_2$$

This reaction was first postulated when cellulose was considered as a denitrifying reagent for Hanford tank waste prior to waste vitrification (Scheele et al., 2007). While the Swheat kitty litter cannot be simply characterized as $C_6H_{10}O_5$, it serves to illustrate the potential products from oxidation of the Swheat by nitrate salt oxidizer present as a bulk material in the waste stream. In this reaction, the first reactant is an idealized representation of the repeating portion of a cellulose molecule. Although this model reaction is idealized, it allows for a specification of the stoichiometry and the heat of reaction on a per-mole basis. Thus, in this model, one mole of cellulosic material generates seven total moles of permanent gas, of which three moles are carbon dioxide (CO_2) and one mole is nitrous oxide (N_2O). Leibman et al. (2015) describe this model reaction to be exothermic with a heat of reaction of -577.013 kcal/mol. This stoichiometric ratio and heat of reaction are used in the overall simulation of results below.

Other inputs are set as follows:

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[3] *While Drum 68685 is a sibling of the drum that breached in WIPP, there are significant differences between the two that preclude the expectation that they will behave identically. For example, Drum 68660 contains a layer of waste from the absorption of free liquid with Swheat, whereas the Swheat used in 68685 was only in the form of Swheat/Salt mixtures.*

The atmospheric concentrations of carbon dioxide and nirous oxide, used as the input concentrations when the SWB is inhaling, are 400 ppm and 0.325 ppm, respectively.[4]

Headspace gas volume V_{HSG}: the total inner volume of the SWB is approximately 1900 L, some of which may or may not be taken up by the presence of the four 55 gallon drums. The drums, each of which are 208 L, are either empty or partially filled with RNS or other waste. Each dunnage drum in the SWB containing Drum 68685 has a lid, but the bung is removed, implying that the headspace gas volume may include the empty volume within the dunnage drums as well as the remainder of the gas volume in the SWB. The other extreme is that gas exchange from the headspace to the dunnage drums is limited, to the point that only the volume within the SWB but outside the 55 gallon drums is available for headspace gases to mix. In the study, we treat this as an uncertainty that is examined with a sensitivity analysis: the main model result is performed with the maximum volume ($V_{HSG} = 1900\ L$); the other extreme is modeled assuming the minimum volume ($V_{HSG} = 1900 - 4 \cdot 208 = 1068\ L$).

The parameters Q_{in}, A, and E_a are adjustable in the model in order to fit the available data. Fitting was performed manually.

The simulated headspace gas concentration results using the daily maximum temperature data and the minimum headspace gas volume are shown in Figure 4-1. The fit to the data is excellent. For this model, the flow rate and reaction parameters have distinctly different influence on the transient behavior. The flow rate (or more precisely, the characteristic turnover time of the headspace gas, V_{HSG}/Q_{in}), controls the initial rate of rise of the concentration values; the turnover time is 22 days for this simulation. The reaction parameters control the ultimate level of the concentration values as well as the difference in the highest concentrations at around 100 days (at the highest temperatures in the summer) versus the lower values at low winter temperatures (from day 230 to the end of the simulation). The stoichiometry of the model reaction controls the relative levels of carbon dioxide and nitrous oxide: the 3:1 stoichiometric ratio of the generated gases is reflected in the data, as observed by Leibman et al. (2015). This numerical model supports that observation, in that the transient behavior of both gases are well represented by the model.

One of the outputs of the model is the gas generation rate due to reaction, which, when combined with the heat of reaction, gives a prediction of the heat generation rate in the RNS waste drum. Predicted gas generation rates are very small, ranging from 4 to 5 cm^3/min during the initial and summer months, declining to about 2 cm^3/min in the winter. This compares to the fitted value for Q_{in} of 60 cm^3/min. An implication of this model is that the rate of gas generation

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[4] *From information on atmospheric concentrations of trace gases found at the following Website*: http://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-1.

is a small fraction of the ventilation rates into and out of the drum (i.e., $Q_{in} \approx Q_{out}$). Thus, measuring gas generation rates via direct flow rate measurements is likely to be masked by the much greater inlet and outlet ventilation flows. If more vigorous reactions were to occur associated with thermal runaway, the rates of gas generation would be much larger and probably could be measured.

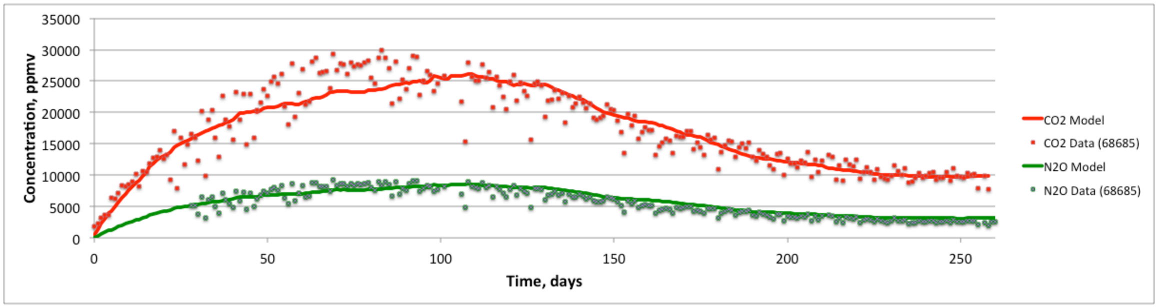

Figure 4-1 Simulation results for carbon dioxide and nitrous oxide concentrations for Drum 68685. Daily maximum temperature record and minimum SWB headspace volume used.

Heat generation rates from this reaction are shown in Figure 4-2. The predicted heat generation rate in the drum is very small, averaging about 0.8 to 1 W during the summer, declining to about 0.3 to 0.4 W under the colder winter storage conditions. This level of heat generation is likely to be easily dissipated through the SWB and into the room. This result supports the conclusion that internal heating in these drums due to this reaction is inconsequential, and confirms the model assumption that the drum temperature is controlled by the temperature of the storage unit, with no substantial heat contribution from internal heating. This also suggests that the assumption of negligible internal heating yields a self-consistent model: the amount of reaction predicted by the model from fitting of the headspace gas concentration data under that assumption is too small to result in internal heating. The caveat to these results is that there could be other reactions occurring that generate heat without gas generation. There should be additional investigation into the possibility of such reactions, and later the possibility of these reactions being detected in the headspace gas measurements is examined.

The prediction of the total amount of carbon dioxide generated over the 260 day simulation period is about 18.6 moles, which would come from the reaction of 18.6/3 = 6.2 moles or 1 kg of Swheat. This is a very small fraction of the total amount of Swheat available for reaction, implying that there are ample quantities of reactants available to supply continued gas generation at these low rates for as long as these drums stay in storage. From this result it follows that the reaction and gas generation rates are likely to track the storage temperature as it rises again in the summer of 2015, as the reactions are unlikely to be limited by the quantity of available reactants for the foreseeable future. This prediction constitutes a blind test of the validity of the model. Concentrations should track the seasonally dependent temperatures of the storage unit in a predictable way, as long as the drum configuration in storage remains as it is today. Any significant deviations from predictions would be evidence of a change in the reaction characteristics of the drum. Increased gas generation above that predicted in the future would be evidence of other reactions. Deviation from the prevailing trends in gas concentrations may provide a useful indicator to confirm whether incipient reactions, either the ones modeled or additional reactions unlike those observed to date, are occurring. Use of these results to interpret future headspace gas concentrations, including the potential for diagnosing incipient heat-generating reactions, is described in Section 4.4 below.

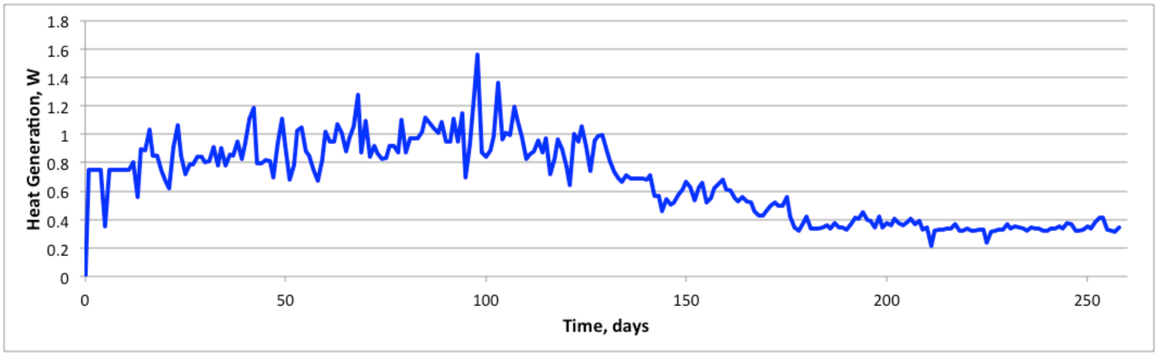

Figure 4-2 Simulation of heat generation assuming the postulated Swheat reaction for Drum 68685.

Some of the parameters in the model are uncertain; for this reason, it is important to establish the uncertainty around the key results just presented. To do this, three additional models were developed. The first model assumes that the minimum gas volume (1068 L) is available in the headspace. For this model, an equally good fit the concentration data is obtained (not shown), with the changes to the other parameters yielding somewhat lower gas generation (14.3 moles of carbon dioxide over the 260 day period, compared to 18.6 moles when the smaller volume is assumed), and lower heat generation (maximum heat output of about 0.6 to 0.8 W compared to the 0.8 to 1 W range for the previous case). The general conclusions that the level of reactivity, attributable to the aforementioned denitrifying reaction, is low and generates minimal heat still hold.

A second sensitivity study used the daily average temperature as the temperature input to the model, and resulted in a similarly good fit to the data. The predicted gas and heat generation rates were marginally larger than the case presented in detail above.

A third model was developed to attempt to establish an upper bound on the gas generation rate (and heat generation rates) and still obtain a reasonable fit to the data. Increasing the pre-exponential factor alone to increase the rate results in proportionally higher concentrations in the headspace gas. In principle, these concentrations can be made lower again in the model by increasing the inlet flow rate to achieve the proper rate of dilution within the SWB. However, this results in shorter turnover times within the SWB, resulting in an inability to simulate the early-time concentrations: the predicted rate of increase is too fast compared to the data. Figure 4-3 illustrates this effect for an increase in reaction rate by a factor of three, and offsetting this by an increase in ventilation rate (the turnover time is 7.3 days for this simulation). The plateaus are still adequately fit, but the initial rise is too fast. This analysis roughly establishes a cap on how high the reaction rates could be compared to the model developed earlier: the reaction and heat generation rates cannot be more than about a factor of two and still explain the observed concentrations. As with the other sensitivity analyses, this uncertainty does not place into question the fundamental conclusion from the previous result that gas and heat generation rates are very low within the RNS drums in storage at LANL.

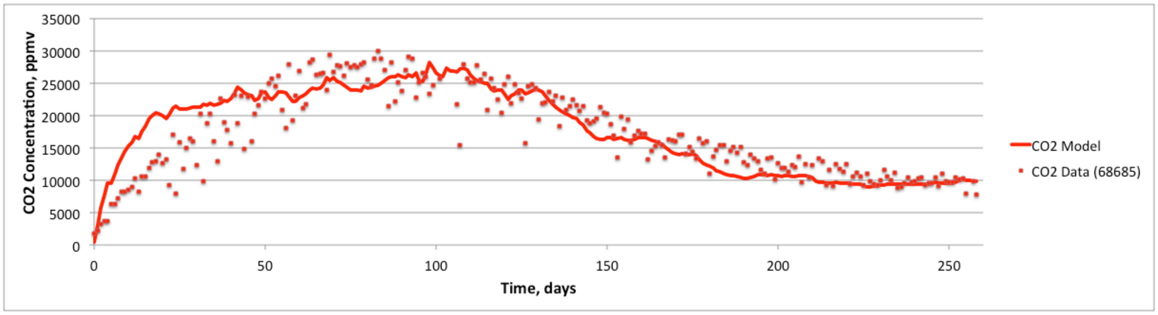

Figure 4-3 Simulation attempting to fit the carbon dioxide concentrations for Drum 68685 with higher reaction rates combined with higher ventilation rates.

As a final consistency check, the activation energy required to fit the data was about 15 kcal/mol for the case presented in detail above, whereas the case in which the daily average temperature was used as input required adjustment of this value to 20 kcal/mol (and compensating for this change by adjusting the pre-exponential term to achieve the fit). The range of 15-20 kcal/mol obtained from this model is within the range proposed by Clark and Funk (2015) of 10-30 kcal/mol as typical of activation energies for reactions of this nature.

An ancillary use of the model is to evaluate the moisture conditions within the drum, including the possibility of drying of the RNS waste contents over time. The RNS waste drums were packaged with significant quantities of water, either as free liquid absorbed with Swheat, or wet nitrate salts mixed with Swheat. Since the Swheat/Salt mixtures have been shown experimentally to be reactive at lower temperatures when they are dried (SRNL, 2015), it is important to understand if significant drying could occur after packaging. For the model result of a time-averaged flow rate due to venting of 60 cm^3/min, and assuming the inlet air is dry and the exit air is 100% humid,[5] only about 1.6 g/day or 580 g/year (0.58 L/year) would be removed from the drum via evaporation. Therefore, one would not expect the RNS waste to dry significantly in its current storage configuration, either to date or many years into the future.

4.2 Application of the model to other drums

The model results in the previous section provide a self-consistent description of the processes controlling the concentrations of gases in the headspace in SWBs containing RNS waste drums. Although the general conclusion of low gas generation and heat generation rates apply to all drums, Section 2.2 demonstrated that each drum has its own set of unique conditions that will change the details of the transient concentration behavior within SWB headspace. The model developed herein would explain this behavior through a combination of slower kinetics and slower venting rates. A few example calculations with different parameter values are presented in Figure 4-4 to illustrate this point. When only the kinetics are slower (Model 1), the curve retains its same shape but the carbon dioxide concentrations are lower (peaking at about 5000 ppmv compared to close to 30,000 ppmv for Drum 68685). To explain concentrations in SWBs that rise throughout the entire period (which includes both summer and winter temperature conditions) or reach a plateau (Model 3), slower ventilation rates are also required, such that turnover times in the SWB headspace are greater. Model 2 is an intermediate case that shows a plateau and a slight decline towards the end of the simulation. Thus, drum-to-drum variability in reaction rates and ventilation rates explains the different behaviors of the headspace gases observed in the 55 SWBs.

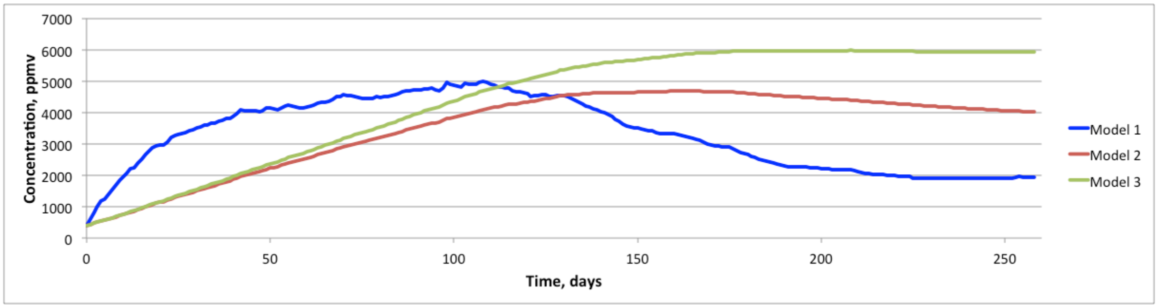

Figure 4-4 Example model results showing different characteristic carbon dioxide concentration behavior depending on the selection of kinetics and flow parameters.

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[5] *These are clearly bounding assumptions applied for analysis purposes: 1) the atmospheric air at Los Alamos, New Mexico is relatively dry, but obviously contains some water vapor, and 2) the water vapor content in the SWB headspace may be limited by the fact that the water in the RNS waste is physically separated from the headspace, and is absorbed or present within small pores in the material, and therefore is less accessible for vaporization than if there were free liquid in the SWB itself.*

4.3 Predicted behavior under alternative storage scenarios

Various scenarios are under consideration by LANL to further reduce the rates of reactions occurring within the drums. To examine the impact of different cooling scenarios a modeling analysis was performed in which it is assumed different levels of cooling are achieved. These were compared to the current temperature control capability, which works to provide a limit to the maximum temperature in the Permacon and to provide for worker comfort.

To enable a simple modeling comparison, it is assumed that if additional cooling capability is installed, that it comes on line on May 19, 2015, exactly one year after the first gas sample was collected.[6] For the current temperature control case, it is assumed that the daily maximum temperatures in the Permacon repeat themselves exactly in 2015. Different cooling capabilities would perform differently, but in general, if the cooling is performed in the Permacon, the highest temperatures would be "clipped" at a particular value, whereas temperatures below this set point would be achieved if the environmental conditions at that time of the year allowed this to occur. For modeling purposes, this is represented by the set of temperature profiles in Figure 4-5, with temperatures above the control point clipped at that temperature. Control temperatures of 20, 15, and 10^{o}C were chosen for this analysis.

Projected carbon dioxide concentrations in the headspace of the SWB under these scenarios are shown in Figure 4-6. All scenarios assume that, in contrast to the low initial concentration at the onset of the Isolation Plan, the initial concentration is 20,000 ppmv, a value likely to be experienced in this SWB in May, after a year of storage. As expected, greater degrees of temperature control result in a lowering of the gas generation rate and concentrations in the headspace. As a defense-in-depth measure, temperature control seems prudent. However, recalling that even under the current level of temperature control, gas generation rates are low, it is unlikely that this additional curtailing of the concentrations represents a meaningful additional factor of safety over an already safe storage condition.

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[6] *Different assumptions could be implemented, but this one simplifies the development of these cases, while still being sufficient for this analysis.*

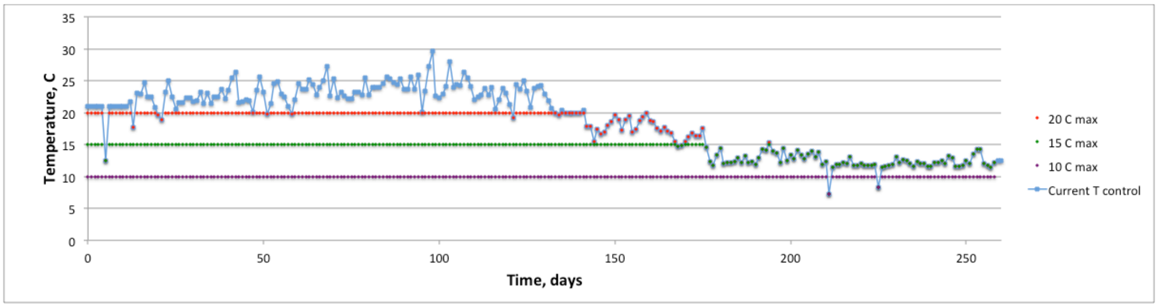

Figure 4-5 Temperature profiles used to examine the impact of different temperature control options on the headspace gas behavior.

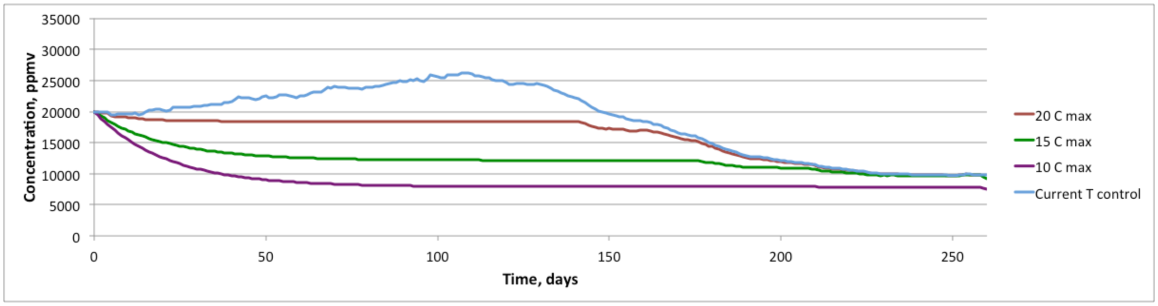

Figure 4-6 Projected carbon dioxide concentrations for the alternative cooling scenarios, compared to the option assuming the current temperature control is applied.

This last statement pre-supposes that there are no additional reactions occurring for which temperature control would be beneficial. For this not to be the case, we would need to postulate an exothermic reaction that does not generate gases, yet is nonetheless occurring now or is triggered at some point in the future. The logic is that if those reactions were occurring and generating significant gases, then they would be detectable in the headspace gas results. The possibility of such reactions should be investigated; in the next subsection, this possibility is explored using the model.

As a final note on temperature control, the lowest temperature set points are likely to require a significant change to the storage configuration of the SWBs, such as placing them in a large refrigerator. This change would not only lower the temperature, but also change the ventilation conditions and thus the inlet and outlet flow rates of the SWB. If the flows during inhalation and exhalation changed significantly, the model presented above would no longer be valid, and the year's worth of information that went into the calibration of the model would need to be regenerated for this revised storage configuration. Lower inhalation and exhalation flow rates would cause the SWB headspace gas concentrations, which presumably will drop in response to the lower temperature, to respond more slowly than before the change. This will likely result in added uncertainty in the interpretation of concentration values, and thus added complexity to the technical arguments supporting the efficacy of the cooling measures taken.

4.4 Detection of precursors to thermal runaway

An important issue for safe management of the RNS waste is to identify key indicators in data such as SWB headspace gases that would provide early warning of the precursors to thermal runaway reactions. At present, a model of gas-phase mass transport (this study) has not been coupled to a thermal transport model to simulate these processes directly. In lieu of a more sophisticated model, plausible scenarios of low-level heat-generating reactions are constructed to examine the degree to which headspace gases respond to changes in the reactivity conditions. If headspace gas concentrations respond relatively rapidly to abrupt changes inside the RNS waste drum, then the sampling campaign can be used proactively to detect these changes, or in the case of absence of deviations from expected behavior, to confirm a safe storage condition. Two types of perturbations are studied in this section: increased reaction rates from undetected temperature rise in the RNS drum, or clogged filters on the RNS drum leading to pressure rise.

A safety issue of great concern for initiating thermal runaway for this waste is the presence of undetected reactivity and low-level heat generation that gradually accelerate to a point at which heat loss from the drum is outpaced by the heat generation rate due to reaction. At that point, temperatures rise, reaction rates increase exponentially, and eventually thermal runaway occurs. Reactivity studies (Clark and Funk, 2015) have established a temperature of 60 ^{o}C for complex nitrate salt mixtures, certain trace metals, and Swheat to exhibit thermal runaway. Today the drums at Los Alamos show no evidence of this behavior, but such an episode cannot be fully ruled out in the future. The reactions that we continue to investigate are those that would provide the initial heating from ambient temperatures to 60 ^{o}C. Current working hypotheses include either microbial reactions or low-level chemical reactions, of which the Swheat oxidation reaction described earlier is an example.

The two scenarios described and simulated below postulate that, for unknown reasons, reactivity conditions undergo a change to a more reactive state at a given point in time. In the first case, we assume that the Swheat reaction exhibits a step change in reaction rate by a factor of 10 at day 101 of the simulation. The resulting effect on the carbon dioxide concentration in the SWB headspace is shown by the red curve Figure 4-7, which is a close-up of the concentration in the time window during which the change occurs. The concentration predicted by the model deviates immediately and substantially from the previous trend (the blue curve), suggesting that such a change could be detected within a matter of a few days.

The second scenario postulates that a reaction independent of the Swheat oxidation reaction, such as microbial activity, provides an internal heat source sufficient to warm the RNS waste. For this scenario, it is assumed that at day 98, the temperature within the waste begins to deviate from the ambient temperature (29.7 °C, the maximum daily temperature on that day in the previous record) without detection in the temperature measurements, ramping at a rate of 1 °C per day.[7] At this rate, the RNS drum contents would reach 60 °C in 30 days, a time frame that is consistent with the breach of Drum 68660 in WIPP: the time between emplacement in WIPP and the breach was about two weeks. Figure 4-8 shows the postulated undetected ramping of waste temperature as it deviates from the temperature in the room. In this case, the reaction that gave rise to the previous headspace gas concentrations becomes a tool for monitoring the conditions within the drum, under the assumption that the reaction will exhibit the same temperature dependence as it has previously as temperatures in the RNS waste drum rise.

The simulation labeled "Drum T rise" in Figure 4-7 shows that the carbon dioxide concentration rises accordingly, reaching values 50% greater than before the excursion after 8 days (with a RNS drum temperature rise to about 38 °C); a doubling of the CO_2 concentration is predicted after 13 days (RNS Drum temperature of 43 °C). It is possible that more aggressive heating could take place with more rapid temperature rise; however, in that case, the time required to detect the changes would be reduced accordingly.

The concentration levels simulated are examples of the degree of change expected. Detectability presumes that one can discriminate a sustained rise from the "normal" scatter in the measurements. To shed light on this issue, concentration data from the record for this drum in 2014 are superimposed on the simulations in the figure. The data are relatively stable on the scale of the concentration deviations we are trying to detect, which is favorable from the standpoint of detectability and avoidance of false positives or failing to detect an actual excursion. Qualitatively, it seems likely that after about 5 days of concentration measurements, or in this case 5 °C of temperature rise within the RNS drum, an excursion from the baseline behavior would be detectable with high confidence. A rigorous statistical analysis of the data should be performed to solidify this conclusion.

Five days probably represents an upper bound on the time required to detect changes in internal reactivity conditions, for the following reason. The analysis just performed assumes that the only means for detecting changes is through temperature and headspace gas concentration changes indicated by the increased rate of reactions occurring at low levels within the drum. However, if

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[7] *It is plausible that such a temperature excursion would go undetected in the temperature record because temperatures are measured on the outside of the SWB, which is thermally shielded from the temperature within the RNS waste drum.*

additional heat-generating microbial reactions or oxidation reactions are the cause of this heating, the character of the gas composition data would likely change dramatically as well. Additional sources of carbon dioxide, the presence of other gaseous by-products, or changes in the relative quantities of other gases would almost certainly accompany a significant change in the reactions occurring in the drum. It is also possible that low-level self-heating might begin to be visible from the SWB temperature measurements. Options should be explored to increase the likelihood of detecting directly such temperature anomalies, perhaps through the use of continuous, real-time infrared monitoring of the SWB in the vicinity of the drum vent. All of these indicators, and any new ones developed to enhance the monitoring program, would be available to diagnose potential incipient reactions causing deviations from the baseline observations.

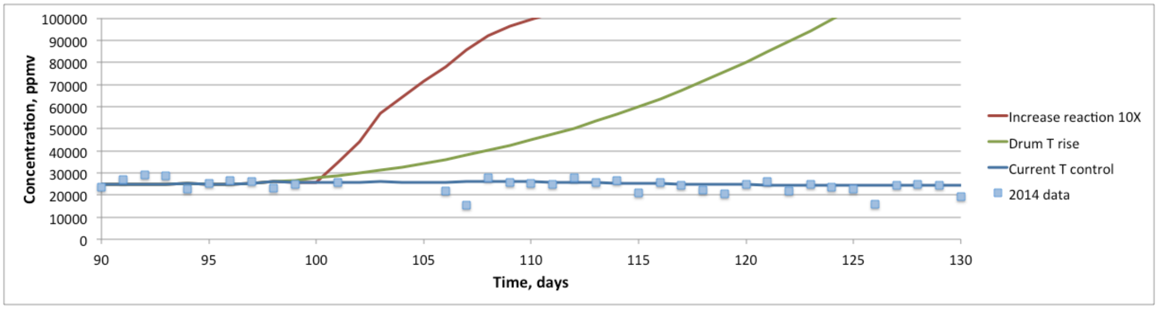

Figure 4-7 Simulated carbon dioxide concentrations for hypothetical scenarios in which reaction conditions change abruptly inside the RNS waste drum. Simulated scenarios track the baseline scenario until the postulated change, after which concentrations climb rapidly.

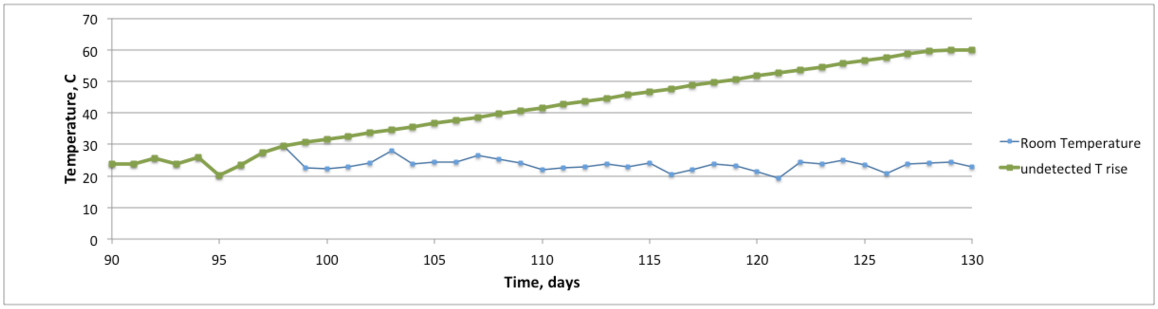

Figure 4-8 RNS waste drum temperature profile postulated for the scenario of undetected temperature rise due to low-level chemical or biological reaction. Self-heating begins at day 98, when it deviates from the temperature in the room.

Finally, note that the conclusions presuppose the continuation of daily analysis of headspace gas concentrations, and the continued storage of these drums in a manner similar to the past. Changes to the storage configuration, such as moving them to storage in a closed refrigerator, would complicate the interpretation and make such diagnostic approaches less useful. This factor must be balanced against the benefits of cooling in reducing reaction rates. Also, daily measurements are currently being made only for seven of the SWBs containing RNS waste drums. Obviously, if incipient reactions begin to occur in drums other than these seven, they could escape timely detection if, for example, they are only being sampled monthly. The seven frequently sampled drums were chosen because their headspace gases are suggestive of a more reactive condition within the RNS waste. In addition, four other drums exhibit carbon dioxide concentrations exceeding 10000 ppmv (Table 2-1). Consideration should be given to adopting a more frequent sampling regimen for those four drums.

An additional safety consideration pertains to the rate of pressure rise in the RNS waste drum under an abnormal situation in which the filters are either blocked or plugged. Although there is no evidence that this condition applies to Drum 68685 or other drums in storage at Los Alamos, a pressure rise calculation can provide perspective on the conditions that would be experienced in other drums, including the breached drum at WIPP, if this were to occur. Taking the reaction rates determined from the model for Drum 68685, the ideal gas law can be applied to calculate the rate of pressure rise under this level of gas generation. Averaging the gas generation rate over the 260 day simulation period, and assuming that 100 L of the total 208 L is occupied by gas (the remainder being solid waste material), the model suggests that generation of gas at the rates estimated for Drum 68685 would lead to a rate of pressure rise under a filter blockage scenario of about 0.6 psi/day.

The SRNL (2015) study estimates drum failure at pressures between 35 and 75 psi, or roughly 20 to 60 psi above atmospheric pressure. These pressures would be reached after 33 to 100 days under a filter blockage scenario at the gas generation rates inferred from Drum 68685. This calculation illustrates the type of pressure rise that would be expected, and suggests a “time-to-failure” not unlike that experienced for the drum that breached in WIPP. Of course, the WIPP drum also experienced temperature rise and increased reaction rates, which would accelerate the process. However, if filter blockage was involved, it is possible that pressure rise at lower temperatures could have provided the initial impetus for increasing the reaction rates, heat generation rates, and ultimately the thermal runaway that resulted. Additional full-scale drum tests being planned by LANL should shed light on this subject.

As for the behavior of the headspace gases in the event of a filter clog in an RNS waste drum within an SWB, the model can be used to simulate this event by forcing the reaction rate in the RNS waste drum to 0 at a particular time. The premise is that the reaction continues to take place within the RNS waste drum, but the reaction gases are no longer expelled into the SWB. Figure 4-9 shows the resulting carbon dioxide concentration for such an event starting at day 98. The headspace gases continue to experience mixing with atmospheric air, but without a source term from the RNS waste drum, the concentration curve starts to deviate towards lower values than would be expected had the clog not occurred. As with the case of a temperature excursion, this deviation from expected values should be detectable in the headspace gas concentration trends.

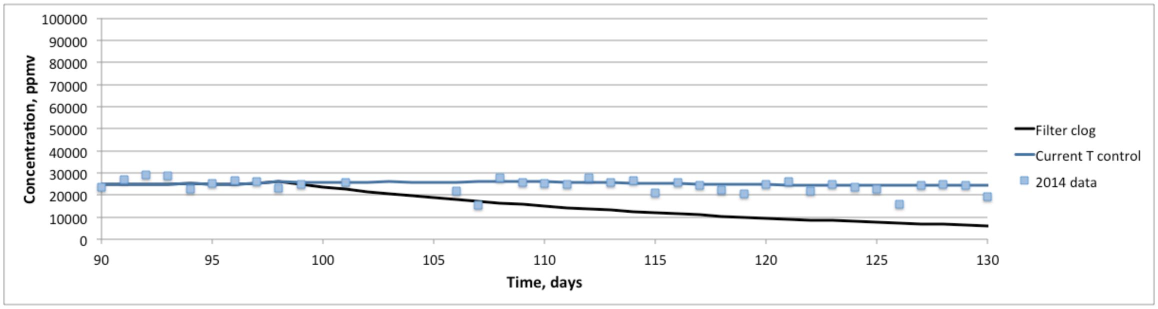

Figure 4-9 Simulated carbon dioxide concentrations for a hypothetical scenarios involving a clogging of the filter on the RNS waste drum.

5 Conclusions

This study supports the case for the use of gas concentration measurements of the SWB headspace as an interpretive tool for discerning the type and rate of gas-generating reactions within the RNS waste drums in storage at LANL. Model results imply that the measurements could provide an early warning for the occurrence of heat-generating chemical and biological reactions in the drums, enabling actions to be taken before self-heating at low temperatures triggers a runaway exothermic reaction at higher temperatures. The study conclusions are summarized below.

1. The headspace gas concentrations are consistent with a description consisting of the combination of a radiolysis mechanism for hydrogen gas generation and low-level, temperature-dependent chemical reactions such as oxidation for the generation of other gases such as carbon dioxide and nitrous oxide. Many of the SWBs have low levels of reaction product gases, whereas a subset exhibit higher concentrations indicative of somewhat higher levels of reactivity. The ratios of gases within the drum for the SWBs with the highest gas concentrations exhibited a similar characteristic signature, but with variability from drum to drum.

2. A simple mathematical and numerical model of the headspace gas behavior provides a plausible description of the long-term variations of concentrations of gases such as carbon dioxide and nitrous oxide in the SWB headspace. The model balances a gas generation source term from reactions in the RNS drum with mixing from the outside atmospheric air due to ventilation of the SWB. Excellent fits to the concentration data for Drum 68685 (a sibling to the drum that breached in WIPP) were obtained throughout the entire time period since the RNS drum was placed within the SWB in May of 2014.

3. The model results for Drum 68685 suggest a low level of chemical reaction within the RNS waste drum. Gas generation rates due to reaction are predicted to be a minute fraction of the ventilation rates into and out of the SWB, and calculated heat generation rates for a reasonable postulated reaction (oxidation of Swheat, which appears to have the correct stoichiometry based on the simultaneous fit to the carbon dioxide and nitrous oxide data) are also very low, nominally 1 W or less for the drum. If other reactions are occurring, these could also generate heat, but if they also generate carbon dioxide, this should have been reflected in the form of higher concentrations. Therefore, the level of carbon dioxide in the drums appears to provide a bound on the level of reactivity and heat generation; this bound is very low from a thermal perspective. Investigations should focus on the potential for reactions not involving the generation of carbon dioxide to attempt to identify other important reactions not reflected in the headspace gas data.

4. The reaction rates exhibit a significant temperature dependence, which explains the higher concentrations of carbon dioxide and other gases in the SWB headspace in the summertime compared to the winter. A model reaction exhibiting an Arrhenius temperature dependence was employed in the model. Calibrations to the data led to values of 15-20 kcal/mol for the activation energy. This range is well within the 10-30 kcal/mol range suggested by Clark and Funk (2015) for such reactions. The low level of reactivity also implies that at these rates, reactants will not be depleted for many years, and that the pattern of higher concentrations under the summertime temperature conditions will repeat itself this summer in a predictable manner. This prediction constitutes a blind test of the validity of the model.

5. Uncertainties in the model have been evaluated to estimate how tightly the model bounds parameters like heat generation rates, given the lack of perfect information on temperatures, available gas volumes inside the SWB and internal drums, and ventilation rates. Reaction and heat generation rates are unlikely to be more than about a factor of two higher than the rates cited above that were derived from the data fit. Other parameter combinations that would lead to higher rates produce simulations that begin to deviate significantly from the observed data.

6. The model could be applied to the data from other SWBs containing the LANL RNS wastes, but this study focused principally on Drum 68685. It is likely that different reaction rates and ventilation rates would be required to simulate other drums, which points to the uniqueness of each drum as a separate system. Notably, all seven of the drums being subjected to daily headspace gas sampling appear to have characteristic behavior similar to that of 68685: higher concentrations of carbon dioxide and other headspace gases than the other drums, and temperature dependence of the concentrations.

7. The drums are currently under temperature control within the Permacon, but there have also been efforts to study the possibility of enhancing the ability to keep the drums cooler throughout the year, including in the summer months. Simulations were performed to examine the effect of these actions on reaction rates. As expected, the model predicts reaction rates and gas concentrations in the SWB headspace to be lower for lower temperatures. As a defense-in-depth measure, temperature control seems prudent. However, recalling that even under the current level of temperature control, gas generation rates are low, it is unlikely that this additional curtailing of the concentrations represents a meaningful additional factor of safety over an already safe storage condition. Moreover, if cooling is achieved by placing the drums in a refrigerator, ventilation conditions will also be affected, which would likely result in added uncertainty in the interpretation

of concentration values, and thus added complexity to the technical arguments supporting the efficacy of the cooling measures taken.

8. Scenarios developed to examine the response of SWB headspace gases to abrupt changes in reactivity suggest that concentrations are a very sensitive means for observing such changes. In a simulation postulating a rise in temperature within an RNS waste drum of 1 ^{o}C per day (presumed to be undetected by measurements on the outside of the SWB), the model suggests that within about five days, the headspace gases would deviate enough from their current state to provide a high likelihood that this off-normal condition would be detected. Even if one assumes conservatively that this time is 10 days, the RNS waste temperature would still be well below the temperature specified by Clark and Funk (2015) and SRNL (2015) as the onset temperature for runaway exothermic reactions for this waste. Further work should be performed to solidify this conclusion by considering issues of detectability of deviations, given that the data are not perfectly smooth, and to make sure that additional drums beyond the seven receiving daily sampling are monitored more frequently for purposes of detecting incipient chemical reactions that might be the precursor of thermal runaway conditions.

Acknowledgements

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References

Clark, D. L. and D. J. Funk, 2015. Waste Isolation Pilot Plant (WIPP): Chemical Reactivity and Recommended Remediation Strategy for Los Alamos Remediated Nitrate Salt (RNS) Wastes. LANL Report LA-CP-15-20082.

Los Alamos National Laboratory (LANL), 2014. Revised LANL Nitrate Salt-Bearing Waste Container Isolation Plan, LANL Document LA-UR-14-23820, May 29, 2014.

Leibman, C., D. Martinez, and J.-M. Sansinena, 2015. Transuranic Remediated Nitrate Salt Waste Headspace Gas Sampling and Characterization. LANL internal report, February 17, 2015.

Savannah River National Laboratory (SRNL, 2015). Waste Isolation Pilot Plant Technical Assessment Team Report, SRNL-RP-2014-01198, Rev 0, March 17, 2015.

Scheele, R., et al. (2007). Evaluation of Exothermic Reactions from Bulk-Vitrification Melter Feeds Containing Cellulose, Pacific Northwest National Laboratory report PNNL-16677.

Appendix 1. Analytical Solution and Test Cases for Numerical Model

With a temperature-dependent reaction, as well as inlet and outlet flow rates that are not necessarily equal, a numerical solution procedure was required to solve the model equations. To verify the correct numerical implementation, an analytical solution was developed under the more restrictive assumptions of constant temperature and $Q_{out} = Q_{in}$, that is, negligible contribution to the gas flow rates from the generation of additional gases due to reaction.

Under those additional assumptions, Equation 1 reduces to:

$$\tau \frac{dC}{dt} = -C + C_{in} + \frac{\chi}{Q} \qquad \text{(A1)}$$

where $\tau = V_{HSG}/Q$, Qis the gas flow rate in or out, and χ is no longer temperature or time dependent. The analytical solution to this equation is

$$C = C_{in} + \frac{\chi}{Q} + (C_0 - C_{in} - \frac{\chi}{Q})e^{-t/\tau} \qquad \text{(A2)}$$

Different combinations of the initial concentration, reaction rate, and τ lead to different transient concentration curves. Figure A-1 shows that the numerical model closely matches the analytical solution for different combinations of these parameters, thereby verifying the correct implementation of the model. Details of the parameters used for these comparisons are provided in the spreadsheet "*HSG model.xlsx*" that accompanies this report.

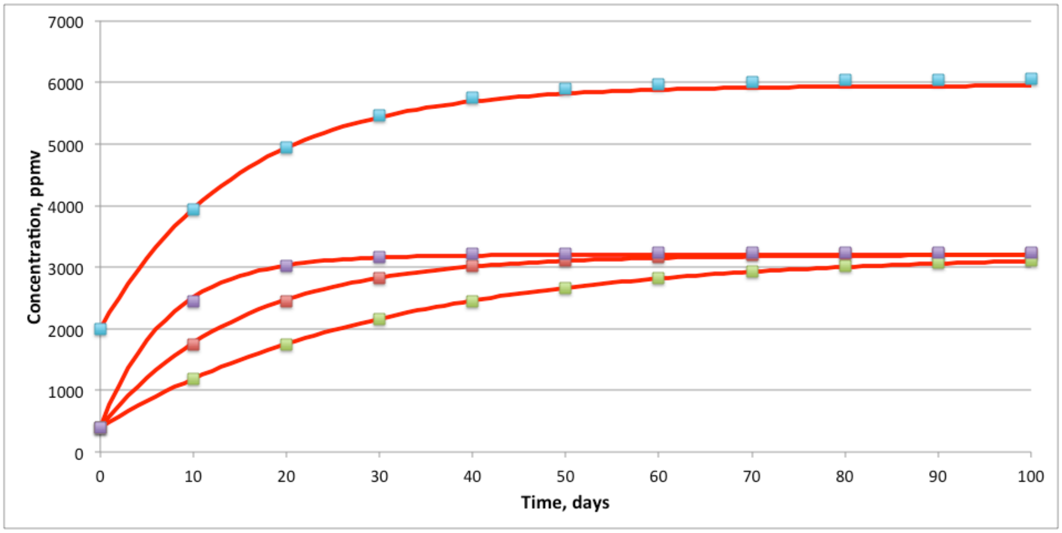

Figure A-1 Comparison of numerical model (curves) and analytical solution (points) for four different combinations of parameters.