SAND2022-16747C

Thermal Analysis of Aged Nitric Acid-soaked Kitty Litter in TRU Waste Drums

X-rays of drum 68660

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February 26-March 2, 2023 Phoenix, Arizona, USA

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Background

- 1970 s & 1980s waste from plutonium recovery
  - Nitric acid-washed metal nitrate salts
  - Transuranic elements
- Liquids removed (remediated) with absorbent*
- Waste called remediated nitrate salt (RNS)
- RNS Drum 68660 thermally ignited in repository
- Root cause of ignition unknown for 8 years
- Repository shut down for 3 years (2014-2017)
- 113 RNS drums currently stored in Texas

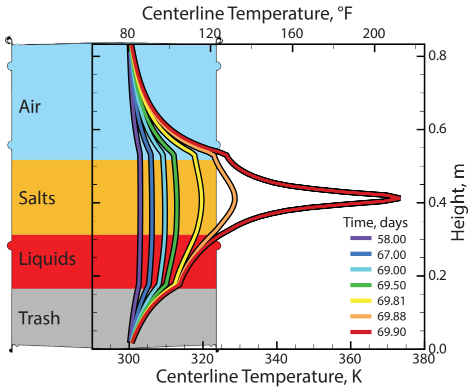
*Most of the waste was mixed with an inorganic absorbent, but a fraction was mixed with an organic absorbent (kitty litter).

X-rays of drum 68660

Before accident

After accident

Surrogate

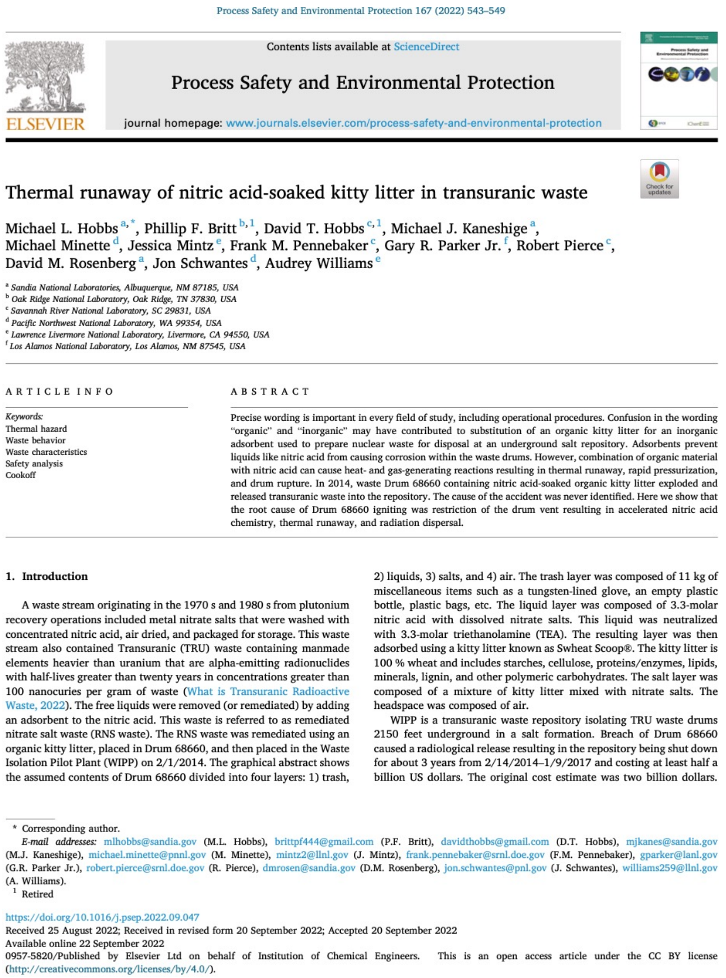


Model

Could similar RNS drums thermally ignite after more than 8 years?

Modeling decomposing waste*

Details in *Process Safety and Environmental Protection* **167** (2022) 543-549



Process Safety and Environmental Protection 167 (2022) 543–549

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.journals.elsevier.com/process-safety-and-environmental-protection

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Thermal runaway of nitric acid-soaked kitty litter in transuranic waste

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ARTICLE INFO

Keywords:
Thermal hazard
Waste behavior
Waste characteristics
Safety analysis
Cookoff

ABSTRACT

Precise wording is important in every field of study, including operational procedures. Confusion in the wording "organic" and "inorganic" may have contributed to substitution of an organic kitty litter for an inorganic adsorbent used to prepare nuclear waste for disposal at an underground salt repository. Adsorbents prevent liquids like nitric acid from causing corrosion within the waste drums. However, combination of organic material with nitric acid can cause heat- and gas-generating reactions resulting in thermal runaway, rapid pressurization, and drum rupture. In 2014, waste Drum 68660 containing nitric acid-soaked organic kitty litter exploded and released transuranic waste into the repository. The cause of the accident was never identified. Here we show that the root cause of Drum 68660 igniting was restriction of the drum vent resulting in accelerated nitric acid chemistry, thermal runaway, and radiation dispersal.

1. Introduction

A waste stream originating in the 1970 s and 1980 s from plutonium recovery operations included metal nitrate salts that were washed with concentrated nitric acid, air dried, and packaged for storage. This waste stream also contained Transuranic (TRU) waste containing manmade elements heavier than uranium that are alpha-emitting radionuclides with half-lives greater than twenty years in concentrations greater than 100 nanocuries per gram of waste (What is Transuranic Radioactive Waste, 2022). The free liquids were removed (or remediated) by adding an adsorbent to the nitric acid. This waste is referred to as remediated nitrate salt waste (RNS waste). The RNS waste was remediated using an organic kitty litter, placed in Drum 68660, and then placed in the Waste Isolation Pilot Plant (WIPP) on 2/1/2014. The graphical abstract shows the assumed contents of Drum 68660 divided into four layers: 1) trash, 2) liquids, 3) salts, and 4) air. The trash layer was composed of 11 kg of miscellaneous items such as a tungsten-lined glove, an empty plastic bottle, plastic bags, etc. The liquid layer was composed of 3.3-molar nitric acid with dissolved nitrate salts. This liquid was neutralized with 3.3-molar triethanolamine (TEA). The resulting layer was then adsorbed using a kitty litter known as Swheat Scoop®. The kitty litter is 100 % wheat and includes starches, cellulose, proteins/enzymes, lipids, minerals, lignin, and other polymeric carbohydrates. The salt layer was composed of a mixture of kitty litter mixed with nitrate salts. The headspace was composed of air.

WIPP is a transuranic waste repository isolating TRU waste drums 2150 feet underground in a salt formation. Breach of Drum 68660 caused a radiological release resulting in the repository being shut down for about 3 years from 2/14/2014–1/9/2017 and costing at least half a billion US dollars. The original cost estimate was two billion dollars.

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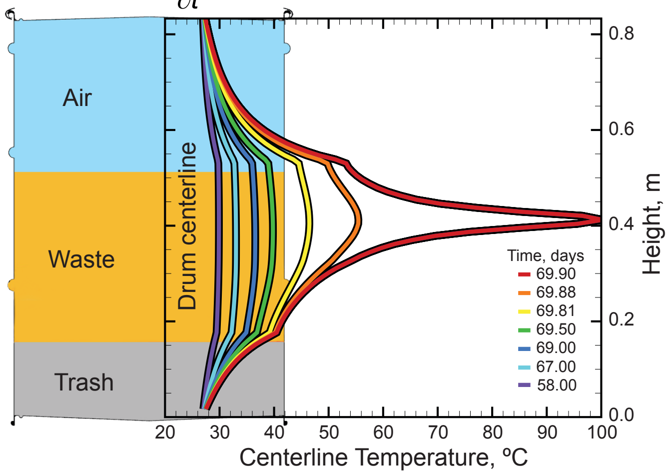
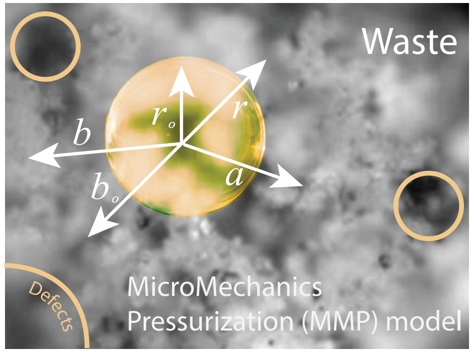
https://doi.org/10.1016/j.psep.2022.09.047
Received 25 August 2022; Received in revised form 20 September 2022; Accepted 20 September 2022
Available online 22 September 2022

Thermal/chemical

$$\rho_b C_b \frac{\partial T}{\partial t} = \nabla \bullet \left(k \nabla T \right) + rhMw_{waste} + q_v$$



Spherically elastic mechanics



**Waste* is kitty litter (wheat), $Ca(NO_3)_2{*}4H_2O$, $Mg(NO_3)_2{*}6H_2O_2$, $NaNO_3$, $Fe(NO_3)_3{*}9H_2O$ + *minors*

$C_{2.16}H_{8.64}N_{1.2}O_{7.3}Mg_{0.34}Na_{0.22}Ca_{0.06}Fe_{0.03} \longrightarrow 3.38\ H_2O + 0.45\ CH_4 + 1.2\ CO_2 + 0.6\ N_2 + 0.04\ H_2 + 0.01\ Fe_3O_4 + 0.28\ MgCO_3 + 0.11\ Na_2CO_3 + 0.06\ CaMg(CO_3)_2$ + heat

Waste is either permeable, impermeable, or both.

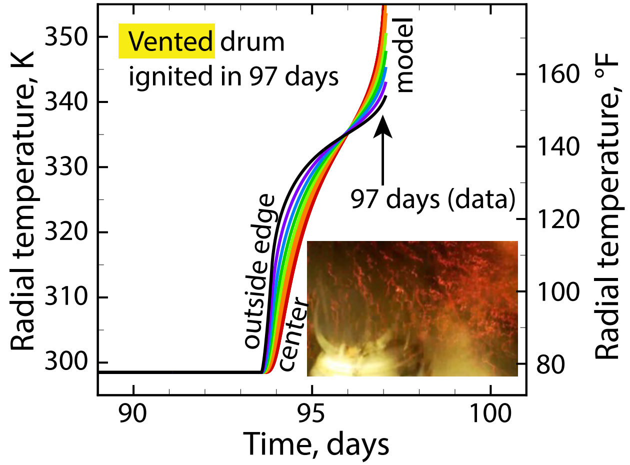
What caused runaway in Drum 68660?

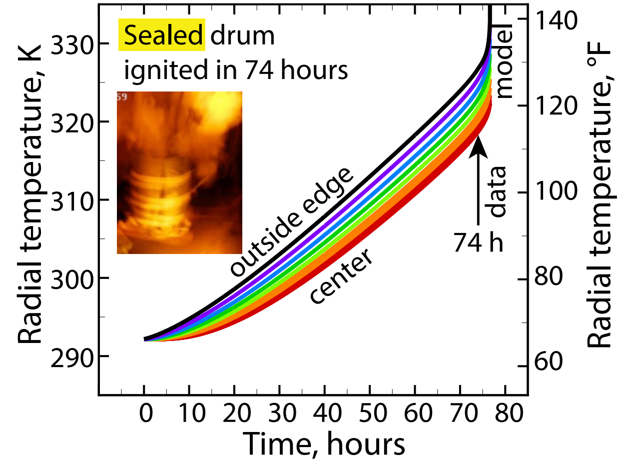
- Contents were not unique or unknown
- Only 1 drum known to have ignited
- Culprit: nitric acid-soaked organic kitty litter (yes)
- Culprit: incompatible acid neutralizers (no)
- Hypothesis: runaway caused by restricted vent
- Observation: reaction rates decelerate when vented
- Observation: reaction rates accelerate when sealed

Acceleratory **Acceleratory** **Deceleratory**

$$rate = 1.6\times10^{15}\left(\frac{P}{P_o}\right)^{5.4}\exp\left(\frac{-17360}{T}\right)\left[\text{Waste}, \frac{kmol}{m^3}\right]$$

LANL drum tests





Pressure dependent rate expression matches observations.

Predicting runaway in Drum 68660

Drum 68660 timeline

Lifespan is 73 days

Ignition time of 42 days

Radiography 12/12/2013

Birth 12/3/2013

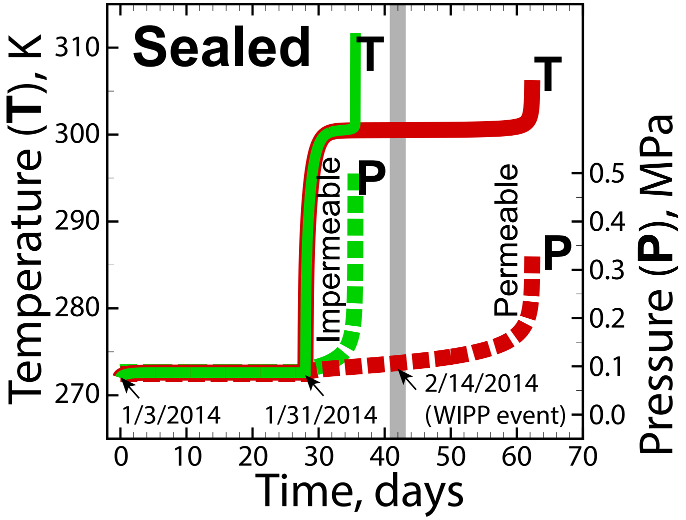
Flamability 1/3/2014 restricted?

Shipped 1/29/2014

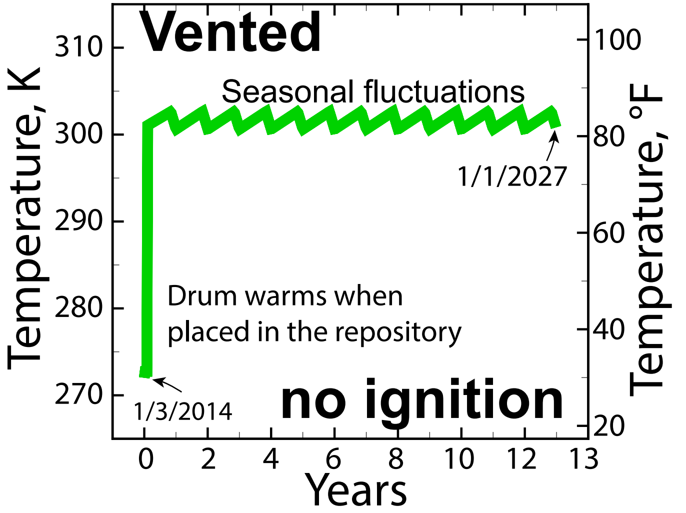
Repository 1/31/2014

Runaway 2/14/2014

A

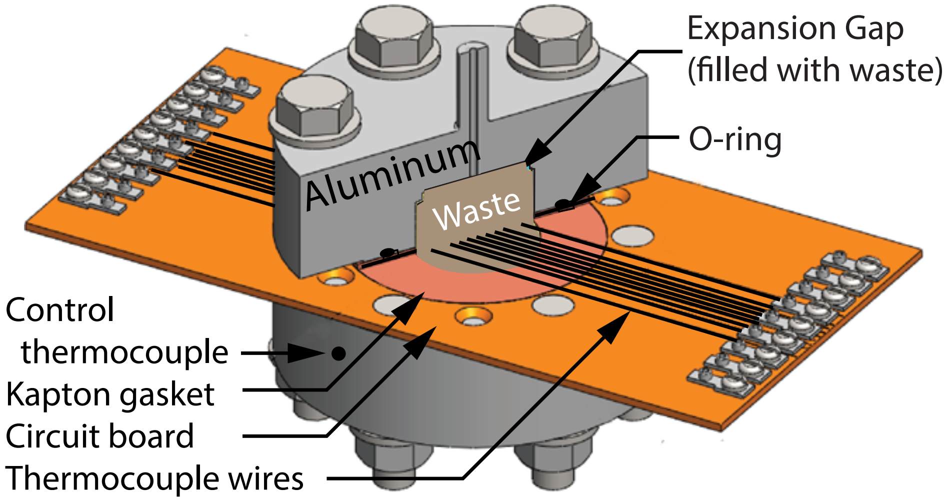


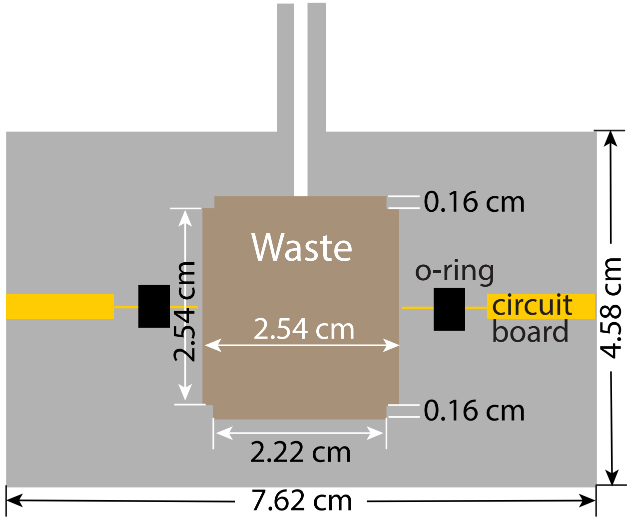
B



Drum 68660 would not have runaway with ample venting.

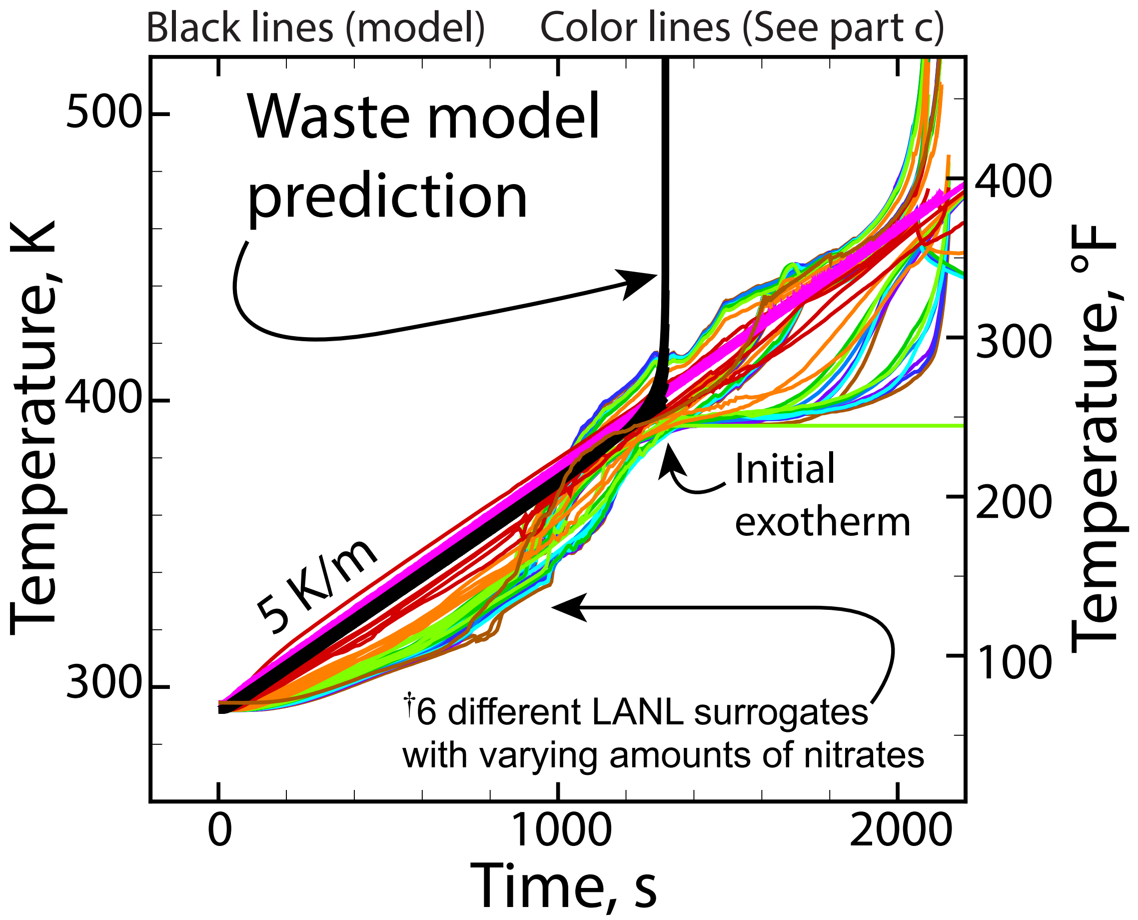
Sandia Instrumented Thermal Ignition (SITI) experiment





Legend

TC#	Radius, mm
1	0.00
2	1.70
3	2.55
4	3.40
5	4.25
6	5.11
7	5.96
8	8.81
9	11.7
Aluminum	

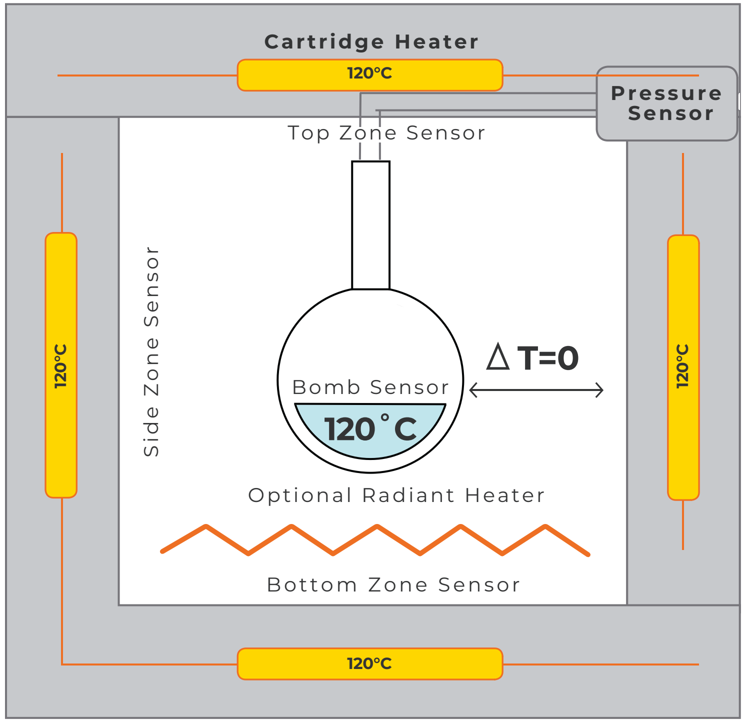


†$Ca(NO_3)_2*4H_2O$, $Cr(NO_3)_3*9H_2O$, $Fe(NO_3)_3*9H_2O$, $Mg(NO_3)_2*6H_2O$, $NaNO_3$, $Pb(NO_3)_2$, oxalic acid $(COOH)_2$, H_2O, and kitty litter

Similarity of reactive contents outweighs waste diversity.

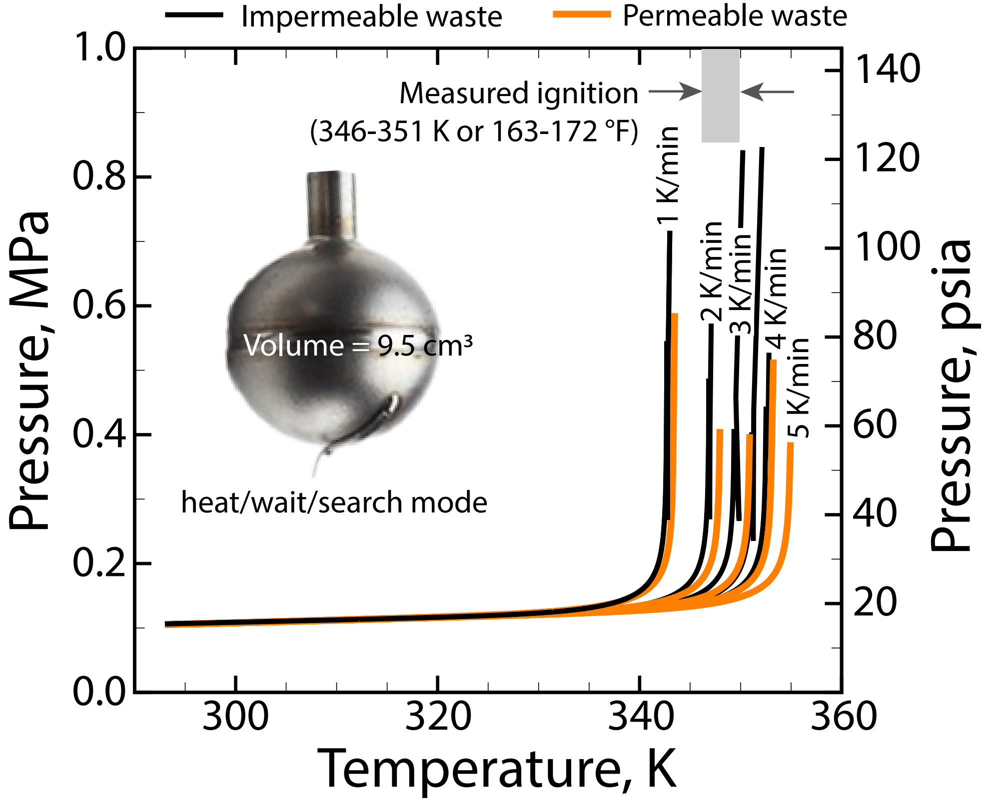
Accelerating Rate Calorimeter (ARC) at PNNL

Thermal hazard technology



Heat/wait/search mode

Model validation



Vessel damage*

*Scheele (2016, 2017)

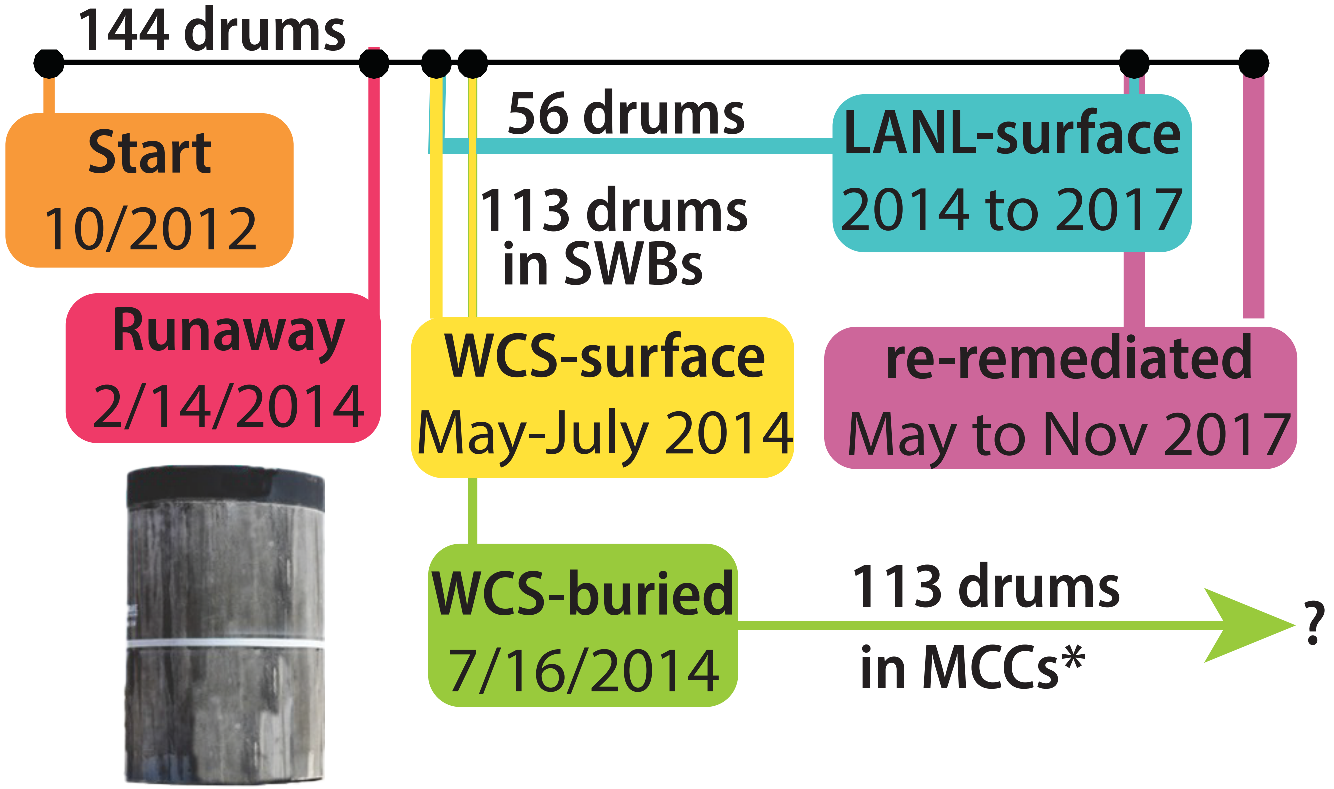
Validated with data from LANL, WIPP, SNL, and PNNL.

What about 113 RNS drums in Texas?

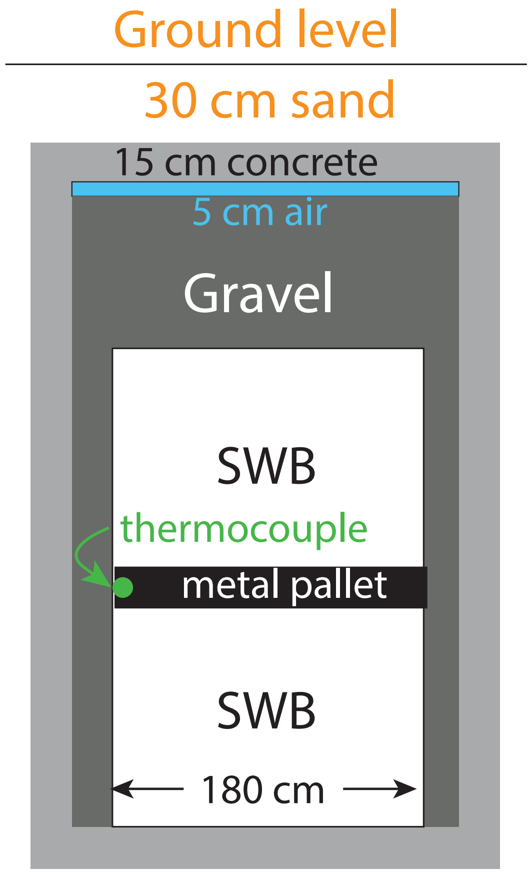
Modeling RNS drums at Waste Control Specialists (WCS)

Fate of 313 RNS drums

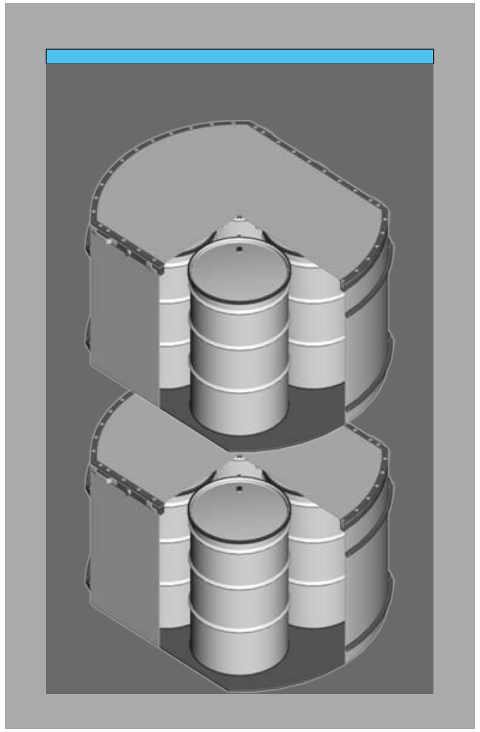
(144 WIPP, 56 LANL, 113 WCS)



*Modular concrete container

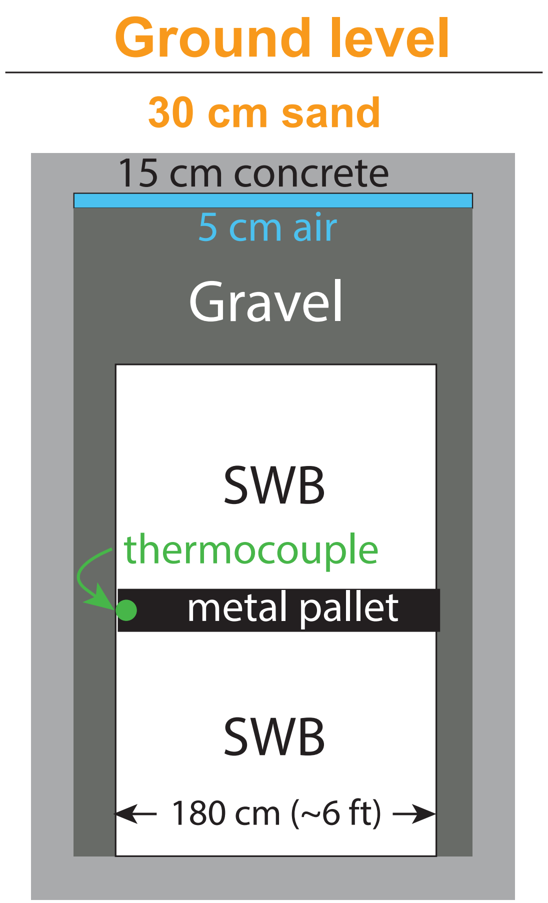


2 Standard Waste Boxes (SWBs) in MCC

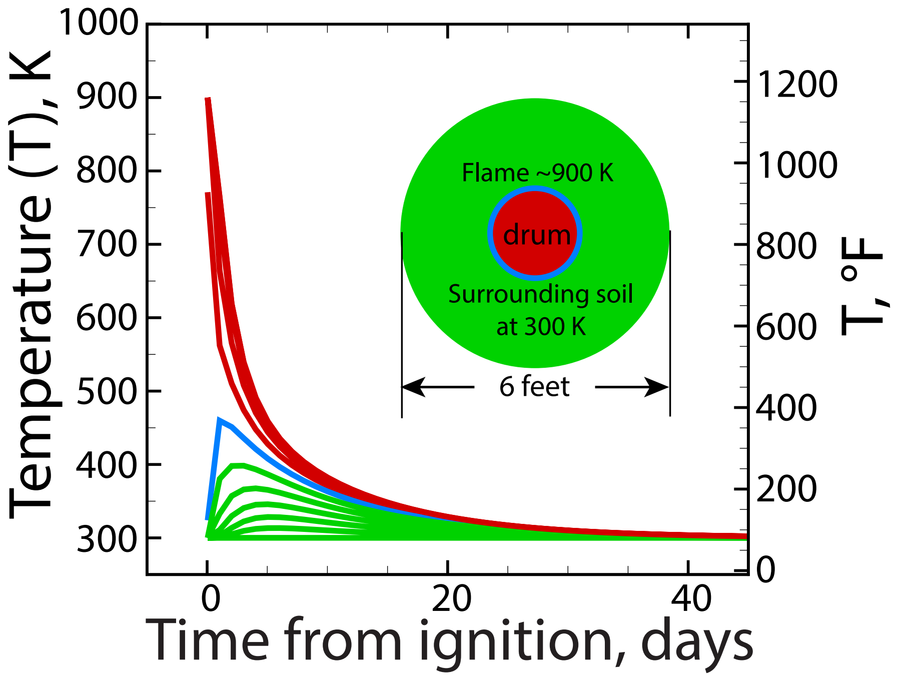


Model application to aging RNS drums buried at WCS

Have buried RNS drums ignited?



T decay following runaway



Radial dist., in: 3.6, 7.2, 10.8, 14.4, 18, 21.6, 25.2, 28.8, 32.4

Inside Edge Surroundings

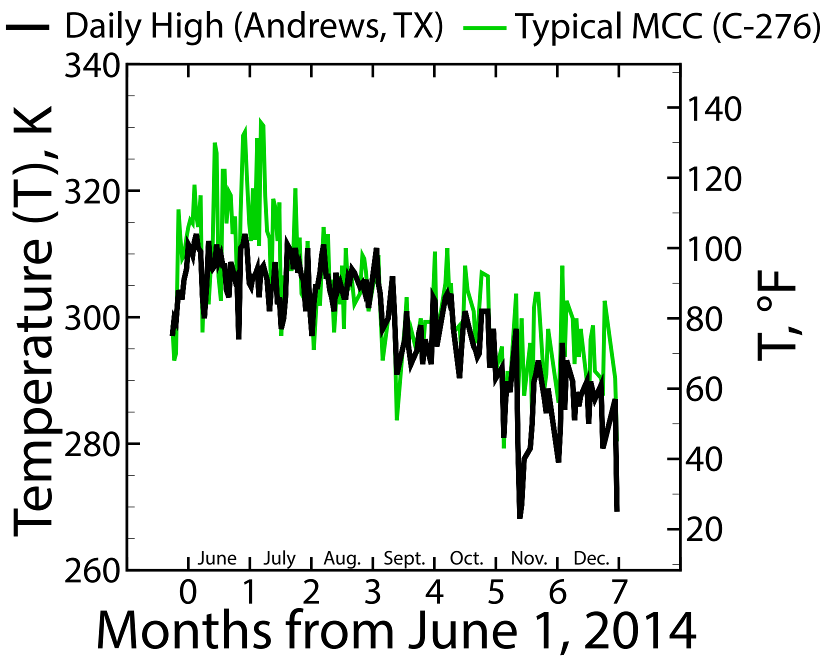
Observations

- Ignites and burns
- Adiabatic flame temp., 900 K
- Conductive energy dissipation
- Runaway drum cools in 40 days
- Thermocouple should see 100 K change within 10 days
- No such excursions measured
- Are the buried RNS drums safe?

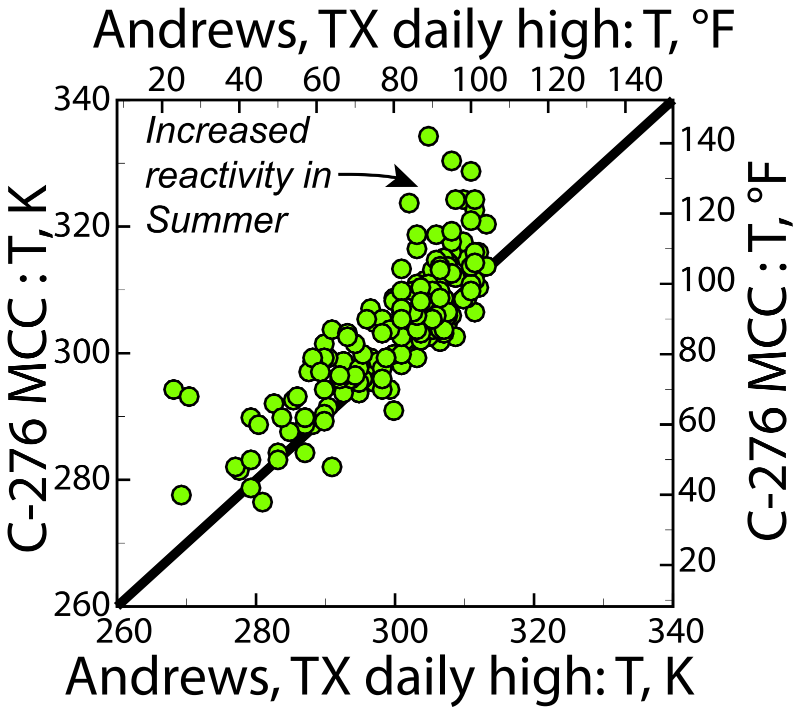
Thermocouples capable of detecting thermal runaway

Temperature data shows reactivity

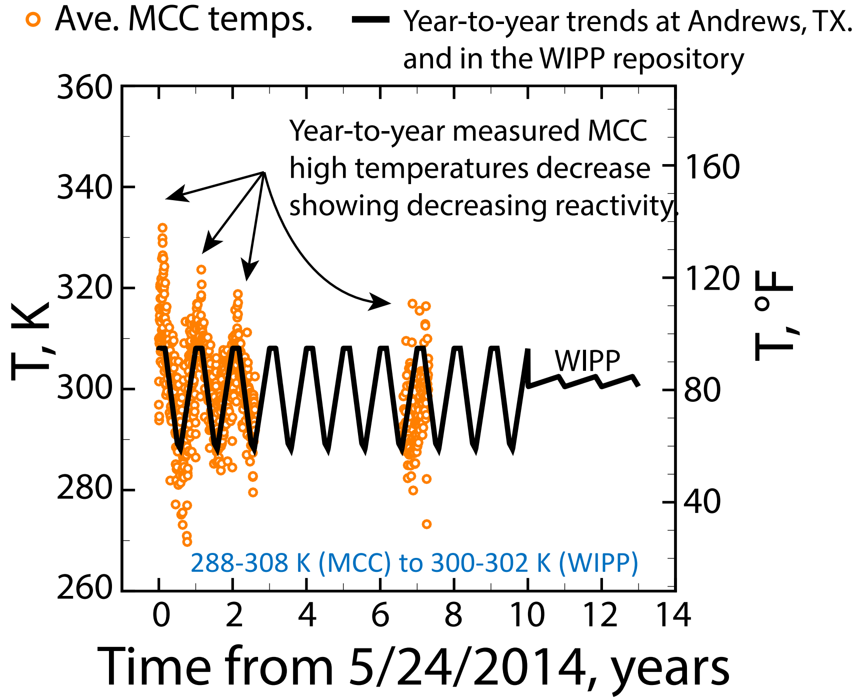
Initial data in 2014



Initial data in 2014



Estimates for 13 years

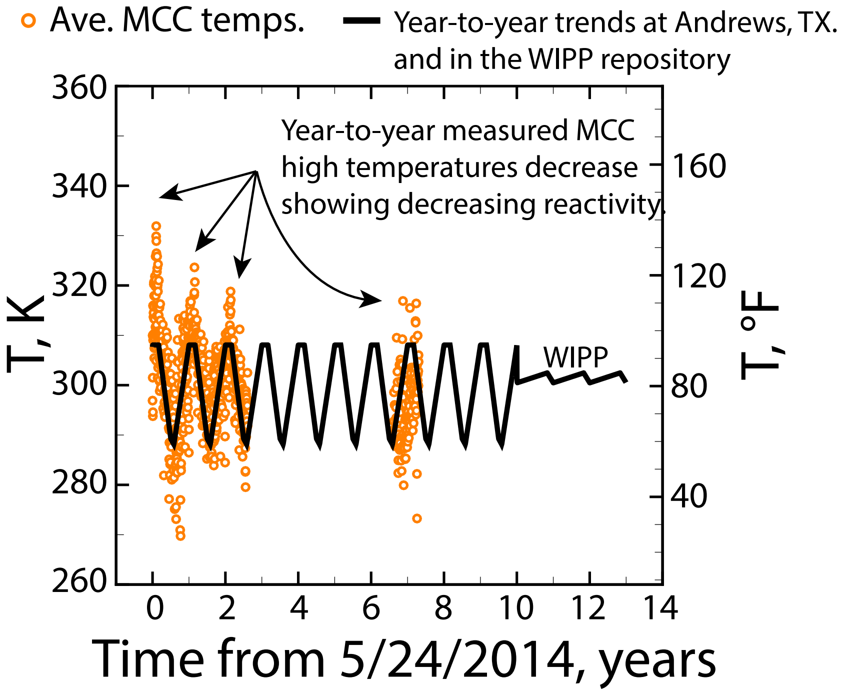


Seasonal temperature changes with no unusual excursions

Seasonal reactivity fluctuations supported by CO_2 and N_2O measurements

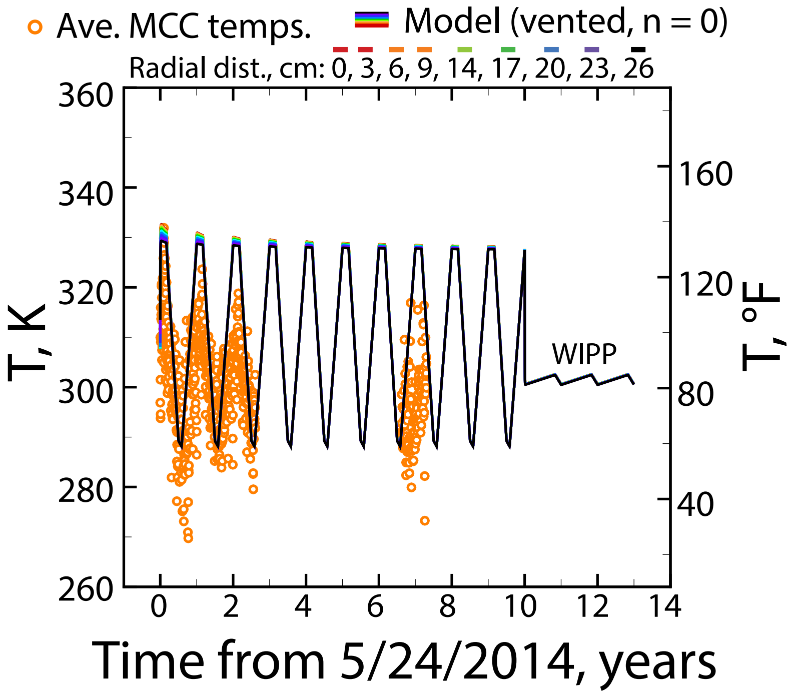
High temperatures accelerate rates

High of 308 K (95 °F)



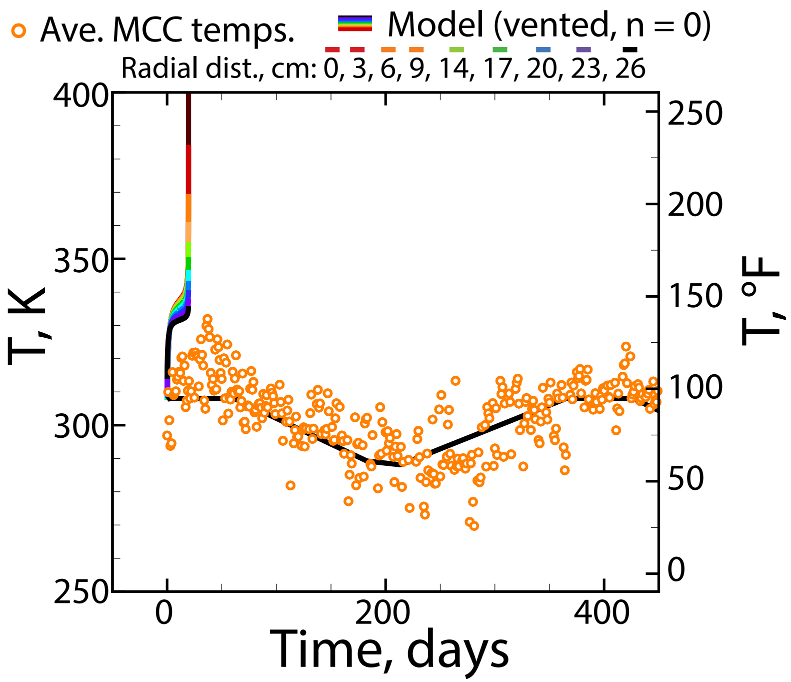
Vented: no ignition

High of 327 K (129 °F)



Vented: no ignition

High of 328 K (131 °F)



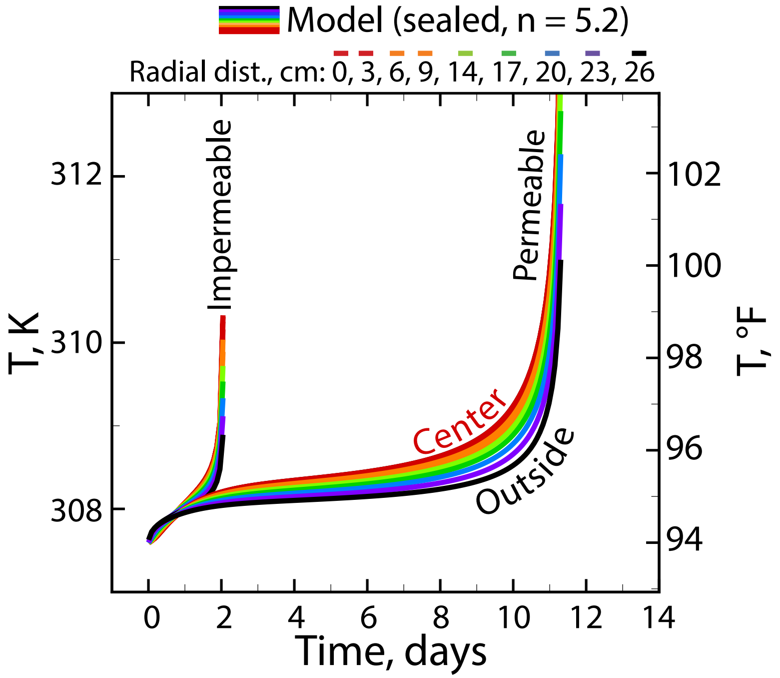
Vented: ignition

Thermal runaway is unlikely in vented drum

Pressure accelerates rates

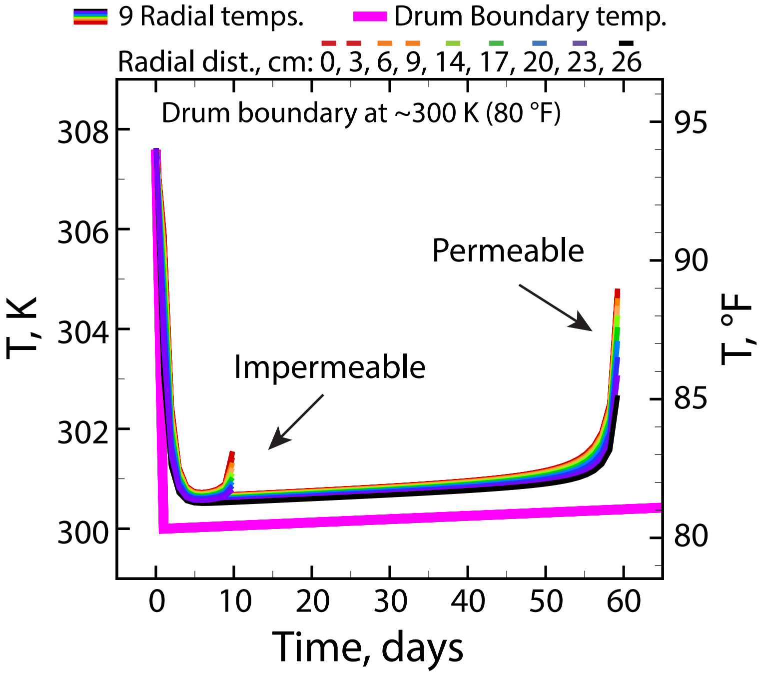
8 psi change results in order of magnitude increase in reaction rate (*e.g.*, $[(14.7+8)/14.7]^{5.4} = 10.4$)

Boundary at 307.8 K (94 °F)



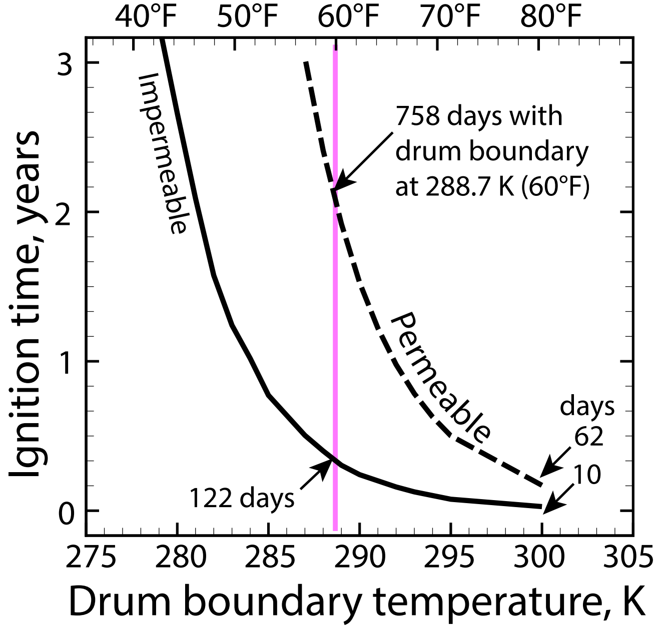
Sealed: ignition

Boundary at 300 K (80 °F)*



Sealed: ignition

Cooling mitigates

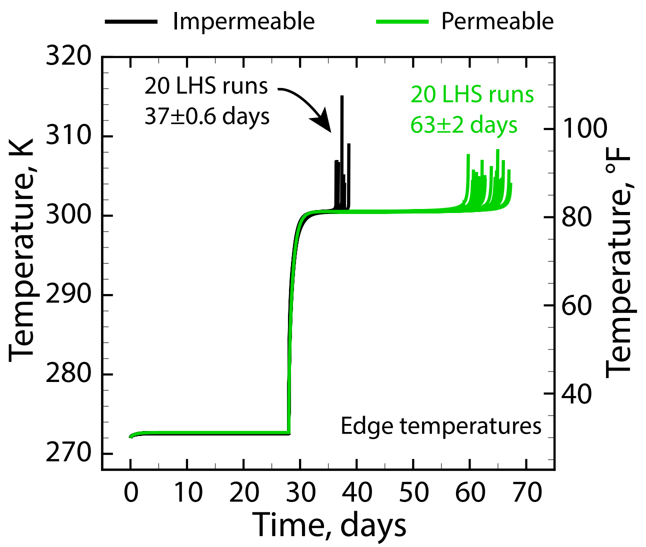


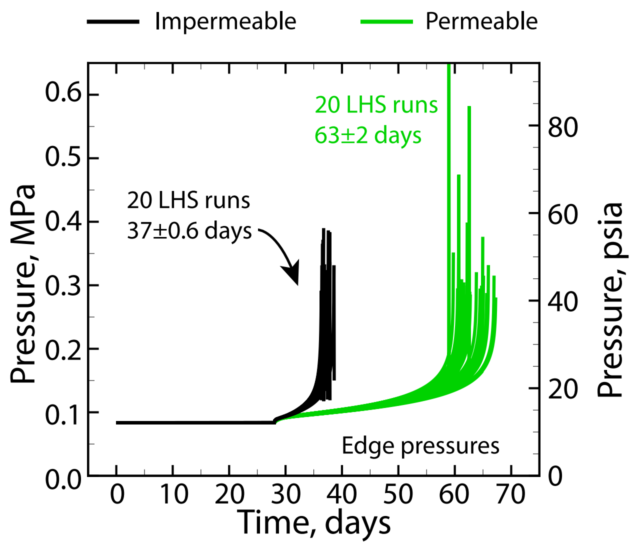
Sealed: delayed ignition

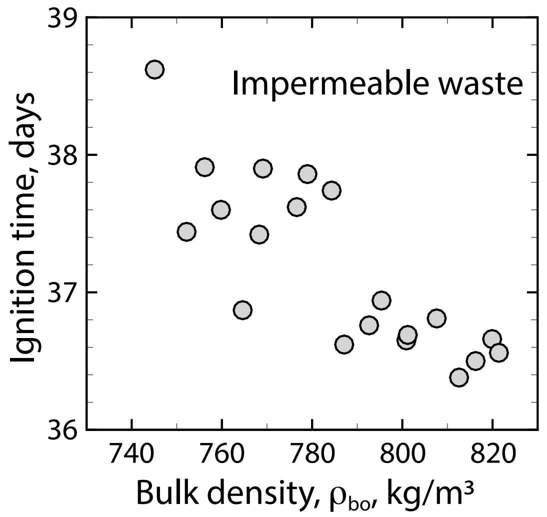
*Vented drum ($n = 0$) placed at WIPP after 10 years, then becomes sealed ($n = 5.4$)

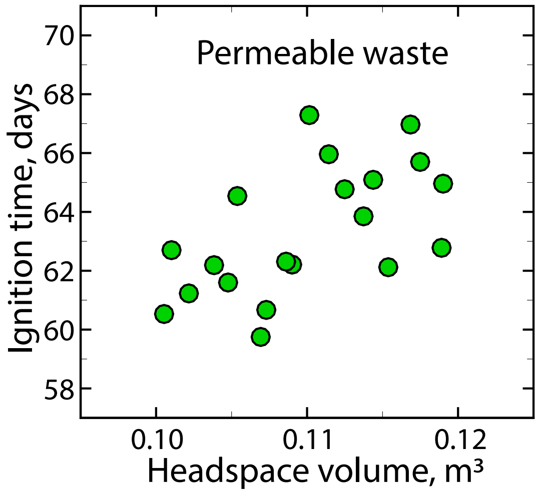
Plugged drum can runaway even after aging for 10 years

Uncertainty in Drum 68660 predictions









Uncertainty parameters

#	Symbol	Description	Range	mean	r for 68660 impermeable	r for 68660 permeable
1	$C_{p,273}$	Specific heat at 273 K, J/kgK	1090-1210	1150	0.09	0.06
2	$C_{p,343}$	Specific heat at 343 K, J/kgK	1490-1650	1570	0.02	0.01
3	k	Thermal conductivity, W/mK	0.2-0.6	0.4	-0.24	-0.05
4*	ρ_{bo}	Bulk density, kg/m^3	745-825	785	-0.82*	-0.67*
5	$\dot{q}_{decay}$	Radiation source, W	0.12-0.18	0.15	-0.12	-0.09
6*	V_{ex}	Excess vol. (i.e, headspace), m^3	0.10-0.12	0.11	0.06	0.58*
7	U_{hrxn}	Heat of reaction multiplier	0.95-1.05	1	-0.14	0.03
8*	ω_{h2o}	Moisture mass fraction	0-0.066	0.033	-0.39*	-0.24
9*	X	Rate multiplier	0.95-1.05	1	-0.33*	-0.37*
10	ε	Emissivity	0.45-0.55	0.5	-0.27	-0.13

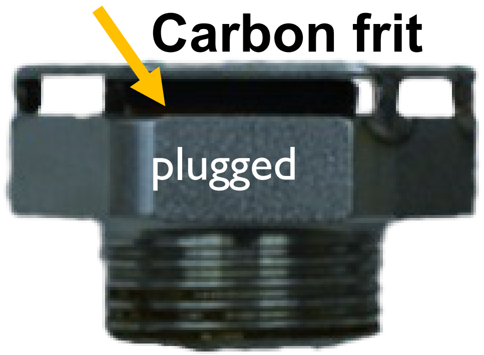
*$|r| \geq 0.3$ is significant

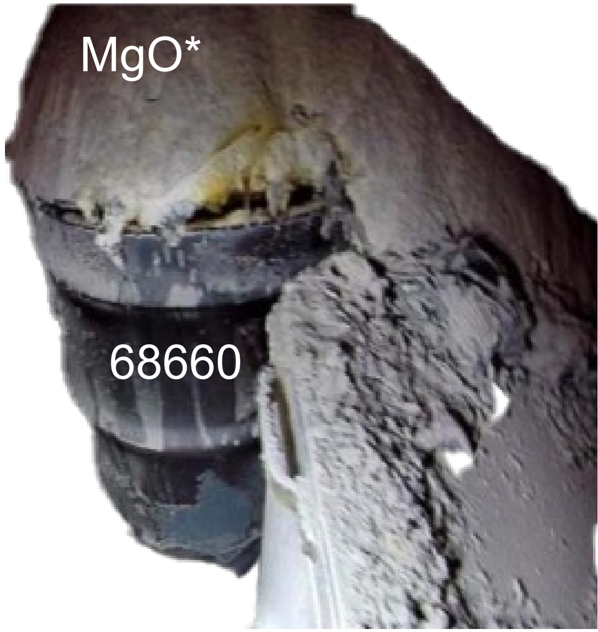
- Latin Hypercube Sample analysis
- Important parameters
  - Initial bulk density
  - Moisture mass fraction
  - Headspace volume
  - Rate multiplier

Most significant assumption is bed permeability

Summary and conclusions

- Modeling LANL drum tests shows pressure dependency
- Model verified experimentally at multiple laboratories
  - Drum tests at LANL
  - Small-scale SITI tests at SNL
  - Small-scale ARC tests at PNNL
  - Accident at WIPP
- Pressurization (not *unique* composition) caused runway
- Contents of RNS drums are not fundamentally different
- Model applied to RNS drums stored at WCS
  - Vented drums are relatively safe
  - Sealed drums are dangerous





*Limits TRU dissolved in brine and adsorbs CO_2

Pressurization caused runaway in Drum 68660