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1	1	Design Authority R.R. Ames	<i>R.R. Ames</i>	8/7/97	74-03	1	1	MATTHEW MEYER	<i>MATTHEW MEYER</i>	8/7/97	T3-28
		Design Agent									
1	1	Cog.Eng. R.Clinton	<i>R. Clinton</i>	8/7/97	74-03						
1	1	Cog. Mgr. R.M Irwin	<i>R.M Irwin</i>	8/7/97	74-03						
		QA									
1	1	Safety Bobby Baker	<i>Bobby Baker</i>	8/7/97	7306						
1	1	Env. K. McDonald	<i>K.M. McDonald</i>	8/7/97	74-03						

18. Signature of EDT Originator <i>RLC</i> 8/7/97	19. Authorized Representative for Receiving Organization <i>M. Irwin</i> 8/7/97	20. Design Authority/ Cognizant Manager <i>M. Irwin</i> 8/7/97	21. DOE APPROVAL (if required) Ctrl. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments
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TECHNICAL INFORMATION FOR THE RELOCATION AND TREATMENT OF ARGONNE NATIONAL LABORATORY DRUMS

R. Clinton

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Abstract: The technical information in this document is to evaluate waste drums stored in Solid Waste Project Management facilities that contain organic and potentially flammable gases. The document provides an evaluation of the planned venting of potentially flammable gases and the potential risks associated with the task.

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Technical Information for the
Relocation and Treatment of Argonne National
Laboratory Drums

08/06/97

Executive Summary

In the Central Waste Complex (CWC), there are 352 drums from the Argonne National Laboratories (ANL) that have been determined to potentially contain flammable gases. This was discovered after performing an investigation on 8 of these drums. The investigation was performed because some of the drums exhibited characteristics of bulging. Also, drums that exhibited no characteristics of bulging were investigated to determine their condition. In the investigation, verification using Real Time Radiography was performed on the drums. The verification revealed that there was headspace of approximately 6 inches in all of the drums observed. Solid Waste Project Management (SWPM) decided that it was necessary to puncture and vent the drums. The gases released were monitored, and it was determined that the drums vented some organic gases. The readings from the drums vented were not conclusive as to what kind of organic gases were released. However, it has been assumed that the gases released may have contained methane gas. It has been determined that the waste streams of these Argonne drums need to be vented and overpacked to minimize the potential hazards associated with the storage of these containers.

Background

A few drums exhibiting bulging characteristics were discovered in one of the storage buildings in the CWC. The generator of the waste drums was contacted by SWPM. It was learned from the generator that some of the Argonne drums contained crushed corn cobs (used as absorbents) and other miscellaneous organic material. SWPM performed a search of the SWITS database to determine the number of drums that were a part of the waste stream and to obtain a location for them. Using the database, it was learned that there are 352 ANL drums stored in the CWC. With further information from the generator, SWPM learned that the Argonne waste drums consisted of primarily two streams. One stream consists of 26 drums which contain stabilized sludge from a passivation sump. These 26 drums are packaged with absorbents. Some of the 26 drums are presently bulged. The other stream consists of 326 drums which contain soil/sludge from a "shoot and burn" pit. The 326 drums are packaged with crushed corn cobs used as the absorbent. The 326 drums do not presently show any signs of bulging.

Both streams of drums contain organic gas, which potentially consists of flammable gases, as demonstrated by the verification and venting at T-Plant. It has been determined that the gases may have come from anaerobic decay of the organic constituents within the drums. The ANL drums were stored at CWC in 1994, so the waste has been undergoing the decay process for 3 years. The decaying of organic material produces methane gas and miscellaneous gases. There is no definitive way of determining the actual methane content based on initial readings. Also, there is no way of knowing whether the gases that have been generated are the sole result of anaerobic decay. However, SWPM can demonstrate bounding concentrations based upon the void space available

and the potential pressure found within a sealed drum can be used to evaluate the potential risk.

The radiological contents within the Argonne drums are small. The drums do contain some alpha constituents, but the curie amount for each drum in the two waste streams is low. In addition, the dose rate is less than 1 mrem per hour for each drum at contact, so there is not a significant radiological dose concern.

Evaluation

There were 8 drums verified by x-ray at the T-Plant. It was discovered during the verification that there was on average 6 inches of headspace at the top in the 55 gallon (208 liter) drums. In that 6 inches of void space, it is conservatively assumed that all of the gas is methane. It is assumed that the internal pressure exerted by the gas is from 1 atm to 2 atm above normal atmospheric pressure. This assumption is based on document UCRL-CR-115037, Fire Testing of 55 Gallon Metal Waste Drums for Dry Waste Storage, prepared by Lawrence Livermore National Laboratory. The study found that the gaskets blew at roughly 13.5 psi - 14 psi. Personnel in Transportation and Packaging and Solid Waste Project Engineering have estimated approximately 16 psi. It must be noted that assuming 2 atm above atmospheric pressure is very conservative because as testing has demonstrated that an open-head drum can not sustain that level of internal pressure without thermally fusing the lid gasket to the lid and drum.

The calculations were performed to evaluate the effect of venting pure methane gas into the environment within the 221-T Headend greenhouse and the 221-T Tunnel greenhouse. As previously stated, the assumption that the drums are venting pure methane gas is very conservative because there is no definitive evidence to verify the assumption. The calculations evaluate conditions at 1 atm and 2 atm of internal drum pressure, with and without ventilation in the greenhouses. Also, the calculations evaluate venting one drum at a time and the bounding case of venting 4 drums simultaneously.

Calculations of Potential Methane Release

PV = nRT	P	=	760 mL torr = 1 atm
	V	=	44.5 L = 6 inch void in 55-gallon drum
	n	=	Derived through calculation
	R	=	0.08205 L atm/mol K
	T	=	80 °F = 27 °C = 300 K

1 atmosphere = 760 torr = 14.70 lbs/in.²

- Therefore 6 inches of void space in a 55-gallon drum will contain 44.5 L of gas at ambient (atmospheric) pressure.
- For this calculation, all of the gas in the void space will be considered methane.

- For this calculation, the volumes of gas contained will be determined using total pressure exerted on the gas (internal + external/ambient).
- At 2 total atm of pressure (~ 30 psi), the quantity of methane released is:

$$(2 \text{ atm}) (44.5 \text{ L}) = n (0.08205) (300 \text{ K})$$

$$n = (2 \text{ atm}) (44.5 \text{ L}) / (0.08205) (300 \text{ K})$$

$$n = 89.0 / 24.61 = 3.61 \text{ mole of methane}$$

Assuming all methane is released, at STP 1 mole of gas occupies 22.4 L.

When released to the atmosphere (STP) 3.61 moles of methane will expand to give:

$$3.61 \times 22.4 \text{ L/mol} = 81 \text{ L of methane.}$$

- At 3 total atm of pressure (~ 44 psi, ~30 psi above atmospheric), the volume of gas released is 2 atmosphere of pressure

$$n = (3 \text{ atm}) (44.5 \text{ L}) / (0.08205) (300 \text{ K})$$

$$n = 133.5/24.61 = 5.42 \text{ moles of methane}$$

$$\text{When released, } 5.42 \text{ moles of methane} = 5.42 \times 22.4 = 121.5 \text{ L.}$$

Calculations for LEL:

Given: LEL for methane = 5.3% in air [Sax, 1984]

Tunnel

- Tunnel greenhouse has dimensions of 17 ft by 32 ft by 12.5 ft = 6,890 ft³ (195,103 L)
- The following is based on passive ventilation of the punctured drums into the greenhouse (i.e., greenhouse is NOT ventilated - drums are punctured and allowed to ventilate without greenhouse being exhausted).
- With 1 atm of inner pressure (2 atm total), a calculated total of 81 L of methane will be released. 81 L released into 195,103 L of greenhouse volume gives:

$$\% \text{ methane in air} = 81 / 195,103 \times 100 = 0.04\%$$

$$\% \text{ of LEL} = 0.04\% / 5.3\% \times 100 = 0.75\% \text{ of the LEL}$$

for 4 drums punctured simultaneously, the value is

$$\% \text{ methane in air} = (4 \times 81) / 195,103 \times 100 = 0.16\%$$

$$\% \text{ of LEL} = 0.16\% / 5.3\% \times 100 = 3.1\% \text{ of the LEL}$$

With 2 atm inner pressure (3 atm total), 121.5 L of methane will be released

$$121.5 / 195,103 \times 100 = 0.06\%$$

$$\% \text{ of LEL} = 0.06\% / 5.3\% = 1.13\% \text{ of LEL}$$

4 drums punctured simultaneous

$$\% \text{ methane in air} = (4 \times 121.5) / 195,103 \times 100 = 0.25\%$$

$$\% \text{ of LEL} = 0.25\% / 5.3\% = 4.7\% \text{ of LEL}$$

Headend

- The headend greenhouse has volume of 12 ft by 8.5 ft by 10 ft = 1,020 ft³ (28,883 liters) for the section of greenhouse where operations will be conducted.
- Once again, the following are based on a non-ventilated greenhouse (same as above)
- With 1 atm of inner pressure (2 atm total), 81 L will be released.
$$\% \text{ methane in air} = 81 / 28,883 \times 100 = 0.28\%$$
$$\% \text{ of LEL} = 0.28\% / 5.3\% \times 100 = 5.28\% \text{ of LEL}$$

4 drums punctured simultaneously

$$\% \text{ methane in air} = (4 \times 81) / 28,883 \times 100 = 1.12\%$$
$$\% \text{ of LEL} = 1.12\% / 5.3\% \times 100 = 21.1\% \text{ of LEL}$$
- With 2 atm inner pressure (3 atm total), 121.5 L will be released.
$$\% \text{ methane in air} = 121.5 / 28,883 \times 100 = 0.42\%$$
$$\% \text{ of LEL} = 0.42\% / 5.3\% \times 100 = 7.92\% \text{ of LEL}$$

4 drums punctured simultaneously

$$\% \text{ methane in air} = (4 \times 121.5) / 28,883 \times 100 = 1.68\%$$
$$\% \text{ of LEL} = 1.68\% / 5.3\% \times 100 = 31.7\% \text{ of LEL}$$

Ventilation in Greenhouses

The following are based on ventilation presently in the greenhouses at the tunnel and headend. Ventilation will assist in dissipation of gas from the drums.

Note: For maximum dissipation, containers should be placed at opposite end of greenhouse exhaust inlet (for either greenhouse).

Tunnel

Greenhouse has a volume of 6,890 ft³ with a 1,000 cfm exhauster (7 minutes for one air change). Based on previous ANL drums punctured, audible ventilation (which would be all of the gas exhausted until the drum reached ambient pressure) took 10 to 15 seconds. However, Industrial Hygiene monitors detected continued off-gassing for 10 to 15 minutes (which was the gas remaining at ambient pressure and gas entrained in waste).

Therefore, the pressurized gas vents off in 10 to 15 seconds, leaving the remainder at ambient pressure (or one atmosphere).

- At one atmosphere (14.7 psi)
 - = (1 atm) (44.5 L) = n (0.08205) (300 K)
 - = (1 atm) (44.5 L) / (0.08205) (300 K)
 - = 44.5 / 24.61 = n = 1.81 mole of methane

At STP 1 mole of gas occupies 22.4 L.

when released to the atmosphere (STP) 1.81 moles of methane

$$= 1.81 \text{ mol} \times 22.4 \text{ L/mol} = 40.5 \text{ L of methane, approximately 41.0 L.}$$

At one atmosphere, the drum holds approximately 41.0 L of methane (in the void space). This 41.0 L is what remains at ambient pressure after the pressurized volume is released. So the gas venting in the first 10 to 15 seconds is the total amount minus 41.0 L. This gives:

- At 1 atm internal (2 atm total) = 81 L of gas
 - 81 L - 41 L = 40 L coming off in the first 10 to 15 seconds
 - 4 drums punctured simultaneously = 40 L x 4 = 160 L

- At 2 atm internal (3 atm total) = 121.5 L of gas
 $121.5 \text{ L} - 41 \text{ L} = 80.5 \text{ L}$ coming off in the first 10 - 15 seconds.
4 drums punctured simultaneously = 320 L

If the volume of gas vented in the first 10 to 15 seconds is ventilated from the greenhouse in 30 seconds, this gas gives

$$1,000 \text{ cfm} \times 0.5 \text{ minutes} = 500 \text{ ft}^3 (14,158 \text{ L})$$

Therefore, the gas coming from the drums in the first 10 to 15 seconds will be diluted to approximately 14,158 L. This gives

- At 1 atm internal (2 atm total)
 $1 \text{ drum} = 40 \text{ L} / 14,158 \text{ L} \times 100 = 0.28\% (5.28\% \text{ of LEL})$
 $4 \text{ drums} = (40 \text{ L} \times 4) / 14,158 \times 100 = 1.13\% (21.32\% \text{ of LEL})$
- At 2 atm internal (3 atm total)
 $1 \text{ drum} = 80.5 \text{ L} / 14,158 \text{ L} \times 100 = 0.57\% (10.75\% \text{ of LEL})$
 $4 \text{ drums} = (80.5 \text{ L} \times 4) / 14,158 \text{ L} \times 100 = 2.26\% (42.64\% \text{ of LEL})$

Headend

Volume of the greenhouse is 1,020 ft³ with a 500 cfm exhauster (2 minutes for one air change). The following is based on the assumptions used for previous calculations.

If volume of gas vented in the first 10 to 15 seconds is ventilated from greenhouse in 30 seconds

- $500 \text{ cfm} \times 0.5 \text{ minutes} = 250 \text{ ft}^3 = 7,079 \text{ L}$
- At 1 atm internal (2 atm total)
 $1 \text{ drum} = 40 \text{ L} / 7,079 \text{ L} \times 100 = 0.57\% (10.75\% \text{ of LEL})$
 $4 \text{ drums} = (40 \text{ L} \times 4) / 7,079 \text{ L} \times 100 = 2.26\% (42.64\% \text{ of LEL})$
- At 2 atm internal (3 atm total)
 $1 \text{ drum} = 80.5 \text{ L} / 7,079 \text{ L} \times 100 = 1.13\% (21.32\% \text{ of LEL})$
 $4 \text{ drums} = (80.5 \text{ L} \times 4) / 7,079 \text{ L} \times 100 = 4.52\% (85.28\% \text{ of LEL})$

Ventilation in Greenhouse (1 minute)

Tunnel: $1,000 \text{ cfm} \times 1.0 \text{ minutes} = 1,000 \text{ ft}^3 = 28,320 \text{ L}$

- At 1 atm internal (2 atm total)

1 drum = $40 \text{ L} / 28,320 \text{ L} \times 100 = 0.14\%$ (2.64% of LEL)

4 drums = $(40 \text{ L} \times 4) / 28,320 \text{ L} \times 100 = 0.56\%$ (10.57% of LEL)

- At 2 atm internal (3 atm total)

1 drum = $80.5 \text{ L} / 28,320 \text{ L} \times 100 = 0.28\%$ (5.28% of LEL)

4 drums = $(80.5 \text{ L} \times 4) / 28,320 \text{ L} \times 100 = 1.13\%$ (21.32% of LEL)

Headend: $500 \text{ cfm} \times 1.0 \text{ minutes} = 500 \text{ ft}^3 = 14,160 \text{ L}$

- At 1 atm internal (2 atm total)

1 drum = $40 \text{ L} / 14,160 \text{ L} \times 100 = 0.28\%$ (5.28% of LEL)

4 drums = $(40 \text{ L} \times 4) / 14,160 \text{ L} \times 100 = 1.13\%$ (21.32% of LEL)

- At 2 atm internal (3 atm total)

1 drum = $80.5 \text{ L} / 14,160 \text{ L} \times 100 = 0.56\%$ (10.57% of LEL)

4 drums = $(80.5 \text{ L} \times 4) / 14,160 \text{ L} \times 100 = 2.26\%$ (42.64% of LEL)

Ventilation in Greenhouse (1.5 minutes)

Tunnel: $1,000 \text{ cfm} \times 1.5 \text{ minutes} = 1,500 \text{ ft}^3 = 42,480 \text{ L}$

- At 1 atm internal (2 atm total)

1 drum = $40 \text{ L} / 42,480 \text{ L} \times 100 = 0.09\%$ (1.7% of LEL)

4 drums = $(40 \text{ L} \times 4) / 42,480 \text{ L} \times 100 = 0.38\%$ (7.17% of LEL)

- At 2 atm internal (3 atm total)

1 drum = $80.5 \text{ L} / 42,480 \text{ L} \times 100 = 0.19\%$ (3.58% of LEL)

4 drums = $(80.5 \text{ L} \times 4) / 42,480 \text{ L} \times 100 = 0.75\%$ (14.15% of LEL)

Headend: $500 \text{ cfm} \times 1.5 \text{ minutes} = 750 \text{ ft}^3 = 21,240 \text{ L}$

- At 1 atm internal (2 atm total)

1 drum = $40 \text{ L} / 21,240 \text{ L} \times 100 = 0.19\%$ (3.58% of LEL)

4 drums = $(40 \text{ L} \times 4) / 21,240 \text{ L} \times 100 = 0.75\%$ (14.15% of LEL)

- At 2 atm internal (3 atm total)

1 drum = $80.5 \text{ L} / 21,240 \text{ L} \times 100 = 0.38\%$ (7.17% of LEL)

4 drums = $(80.5 \text{ L} \times 4) / 21,240 \text{ L} \times 100 = 1.51\%$ (28.49% of LEL)

Conclusion

According to the calculations, venting the drums should not present an excessive risk. The assumptions used to perform the calculations were very conservative. The calculations demonstrate that venting 4 drums simultaneously would not exceed the LEL for methane. It must be mentioned that only 2 drums can be vented simultaneously at T-Plant at this time. Since this is the case, only half of the amount calculated for 4 drums can be considered. Venting two drums is well below the LEL, so the ventilation system within either greenhouse should be sufficient to dissipate the gases safely. When venting one or more drums, the intent is to maintain levels at 10% of the LEL or less. The concentration of methane in either greenhouse should not reach a flammable concentration at the exhaust point. The only concern should be the concentrations near the drum vent as the waste is being vented.

Recommendation

The Argonne drums should be vented and overpacked. Precautions will need to be taken in order to ensure safety. Precautions should include the use of non-sparking tools (puncturing apparatus included). The drums should be handled carefully to avoid creating an ignition source that may ignite potential flammable gases. Monitoring should be done in order to avoid exceeding the LEL. The drums should be overpacked in 85 gallon (321 liter) drums with NucFil filters. The NucFil filters will allow light organics gas, such as methane, to vent naturally after the drums have been punctured.

References

Sax, Irving, Dangerous Properties of Industrial Materials, 6th Edition, Van Nostrand-Reinhold Co., 1984.

Lawrence Livermore National Laboratory, Fire Testing of 55 Gallon Metal Waste Drums for Dry Waste Storage, UCRL-CR-115037, July 1993