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Sub-scale Drum Test Memo

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Introduction

A series of sub-scale (10-gallon) drum experiments were conducted to characterize the reactivity, heat generation, and gas generation of mixtures of chemicals believed to be present in the drum (68660) known to have breached in association with the radiation release event at the Waste Isolation Pilot Plant (WIPP) on February 14, 2014, at a scale expected to be large enough to replicate the environment in that drum but small enough to be practical, safe, and cost effective.

These tests were not intended to replicate all the properties of drum 68660 or the event that led to its breach, or to validate a particular hypothesis of the release event. They were intended to observe, in a controlled environment and with suitable diagnostics, the behavior of simple mixtures of chemicals in order to determine if they could support reactivity that could result in ignition or if some other ingredient or event would be necessary. There is a significant amount of uncertainty into the exact composition of the barrel; a limited sub-set of known components was identified, reviewed with Technical Assessment Team (TAT) members, and used in these tests. This set of experiments was intended to provide a framework to postulate realistic, data-supported hypotheses for processes that occur in a "68660-like" configuration, not definitively prove what actually occurred in 68660.

Basis for Drum Contents

From fragmentary information collected as part of its creation, 68660 appears to have been assembled as follows: Nitrate salt residues from plutonium processing facilities at the Los Alamos National Laboratory (LANL) were removed from drum S855793 and repackaged for disposal in the Waste Isolation Pilot Plant (WIPP) near Carlsbad, NM. The nitric acid solutions produced from the plutonium recovery and purification process (known as the MINO2 process) contained a number of metal ions and were concentrated through evaporation until the nonvolatile salts in the evaporator were close to saturation. The concentrated solution was poured into a water-cooled tray and flash-crystallized to produce solid nitrate salts. After filtration to remove the bulk of the acidic supernatant liquid, the nitrate salts were briefly washed with 3.3 M nitric acid and vacuum dried. The nitrate salts contained residual supernatant liquid as well as water from the waters of hydration in the crystallized salts. A variant of the plutonium recovery process produced oxalate salts. Residues of the oxalate processwere not washed with 3.3 M nitric acid because it would accelerate decomposition of any oxalic acid present in the salts and could result in pressurization of the sealed 55-gallon drums containing the salts with oxalate.

Drum S855793 was generated in October 1985 and was reported to contain 14 bags of nitrate salts, four of which resulted from an oxalate precipitation process. Documentation of the original, detailed chemical composition of the nitrate salt waste transferred from S855793 to Drum 68660 does not exist. Drum S855793 was placed in a glove box and free liquids containing water, nitric acid and dissolved metal nitrates were drained and neutralized to a pH of approximately 7 with a mixture of triethanolamine (TEA) and water, commercially known as Kolorsafe® liquid acid neutralizer. The neutralized liquids were then sorbed onto an organic wheat-based sorbent (Swheat Scoop©) and placed in a new drum lined with a PVC bag. The remaining moist, still acidic, nitrate salts from the parent drum were mixed with additional Swheat and a portion of this mixture was placed in the same drum as the neutralized nitric acid/Swheat mixture. After filling the drum to about 60% of capacity, the PVC bag was taped closed, the drum lid installed, and the drum (68660) removed from the glovebox.

Given that the contents of S855793, particularly the liquid contents, are largely uncharacterized (other than very general pH statements) some simplifying assumptions have been made:

Observables: The volume of liquid recovered from S855793 was approximated at 2 gallons. The pH was approximated at 0.

There are a number of pieces of information missing that may affect the behavior of 68660; salt mixture composition, concentration of acid, mixture heterogeneity, amount and position of ion-exchange resin, presence and position of lined glove (including what species it was in contact with). For the purposes of this experiment, most of these were ignored and assumptions were made concerning only two of them: 1st) the rough composition of the salt mixture in the parent waste and 2nd) the concentration of acid in the liquid layer. These experiments are designed to probe the environment defined by these two characteristics. The rationale for the values chosen for these characteristics is detailed below.

Salt mixture composition

The 68660 parent comes from MIN02 evaporator process. There are two barrels that are the product of the same process: S802701 and S813389 were opened and their contents analyzed, the results presented at the July 21, 2014 TAT meeting held at LANL. These barrels presented widely varying salt compositions: S802701 contained predominantly sodium nitrate, a highly acidic liquid, and minimal levels of magnesium, calcium, and lead. S813389 contained an almost 2:1 mixture of sodium and magnesium, much less acidic liquid, and almost no calcium or lead. LANL modeling of salt composition in the MINO2 waste stream predicts a salt composition much closer to S813389 than S802701 but may be based on a different process; the sodium:magnesium ratio is almost reversed, and large amounts of calcium are predicted, unlike conditions found in either barrel opened. Preliminary plans were to use a salt composition closer to S802701 than S813389, with a sodium content about 24.5% and a magnesium content around 1.5% (S802701 had a sodium content of about 24% and a magnesium content around .017% with lead at 170 ppm). Following a phone conference with Pacific Northwest National Labs (PNNL), Savanah River National Labs (SRNL), and Sandia, a salt ratio of sodium to magnesium nitrate that resulted in a final metal ratio of 1:1 (Na:Mg) was agreed upon. In addition, no other metal cations were identified at this time as being significant enough to the chemistry or composition to suggest inclusion in the 10 gallon barrel experiments. At this meeting, ratios of Swheat to liquid and Swheat to mixed salt were also agreed upon (2:1 and 1.2:1 respectively). Upon preparation of the test drums, however, it was found that while Swheat and water combine in a 2:1 ratio without a free liquid residue, the salt-saturated neutralized acid used in the drum experiments required a higher ratio of Swheat to liquid to prevent formation of a free liquid residue. Given the express instruction to remediation personnel to avoid this condition, it was decided to use a ~3:1 Swheat to liquid ratio, which resulted in a very “wet” appearing mixture, but no free liquid.

Nitric acid concentration

The concentration of nitric acid in the 68660 parent drum is an important value to know due to the changes in possible chemistry that may be observed at different acid concentrations. At or below 5M concentration, predominantly acid/base chemistry would be predicted (formation of nitrate salts). Formation of nitrate esters, C and N nitro functionalities, are known in the literature down to roughly 10M nitric acid, though 10M is typically accepted as the lower limit for efficient nitration. Some low yield, inefficient nitration may occur at lower nitric acid concentration, but this area is not well studied (due to its low efficiency).

The liquid in the 68660 parent was listed as having a pH of 0. The minimum nitric acid concentration that would yield a pH of 0 is 1M (1mole/Liter). A maximum concentration number is more difficult to bound, but the following process was used to provide at least a rough framework.

An empty one gallon container of Kolorsafe® neutralizing agent was placed in the drum, ostensibly because whatever liquid was in it was consumed in the neutralization of drum contents. Since we have no data concerning the starting volume of the neutralization agent, or if a partial volume of a second container was used to complete neutralization, the most conservative estimate for an upper bound to nitric acid concentration appears to be what would have required two gallons of Kolorsafe® to neutralize. From the Spilfyter catalogue the neutralization capacity of the Kolorsafe® acid neutralizer is given as 1.8 L required to neutralize a 1 gallon spill of 10% by weight nitric acid solution. One molecule of TEA will neutralize one molecule of nitric acid. Thus, the concentration of the neutralizer may be found from the number of moles of nitric acid in 1 gallon of 10% by weight nitric acid solution and dividing by the volume used (1.8 L of neutralizer). In 1000 g of such a solution, 100 g would be nitric acid. 100 g/63.01 g/mol nitric acid = 1.587 mols nitric acid. Density of a 10% solution is 1.0523 g/ml which means that 1000 g = 950.3 ml. This comes to 1.587 mol/0.9503 L = 1.67 mol/L. 3.8 L per gallon = 6.346 mols nitric acid in 1 gallon of 10% by weight solution. 6.346 mols/1.8L (the amount of Kolorsafe® required to neutralize it) = 3.5 mol/L of TEA in Kolorsafe®.

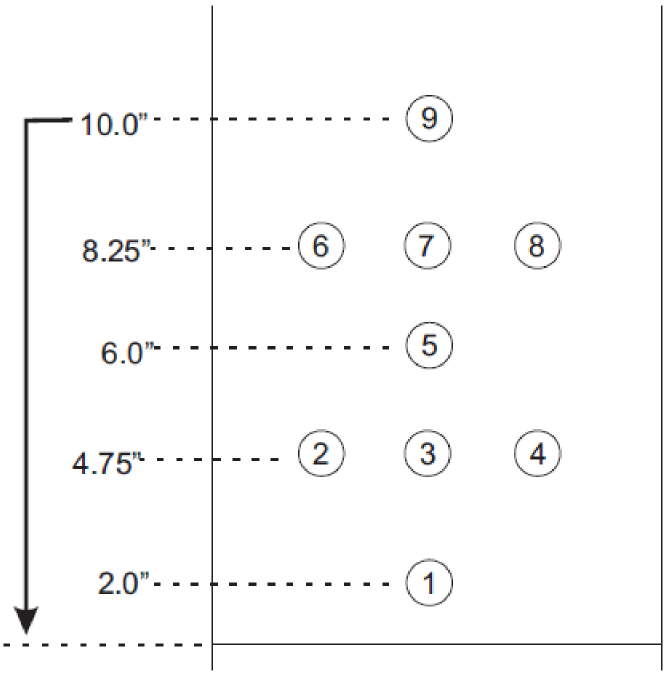
If 1 gallon of Kolorsafe® was sufficient to neutralize the liquid contents of the 68660 parent drum (2 gallon volume), then the concentration of acid in the liquid (and thus any un-neutralized interstitial liquid) would be close to half the neutralization capacity of the Kolorsafe® (1.75 mol/L). If two gallons of Kolorsafe® were required to neutralize the liquid contents of the 68660 parent drum, then the concentration of acid in the liquid would be equal to the concentration of the neutralizing agent (3.5 mol/L).

Titration of Kolorsafe® using commercially obtained 68% nitric acid resulted in a value of 3.3 M for TEA content (neutralization capacity). This agrees well with the neutralization capacity cited in the Spilfyter product catalogue. In addition, it was noted that the parent drum nitrate salts were washed with 3.3 M nitric acid prior to original packaging. For these reasons, an upper limit of 3.3 M was established for concentration of acid in liquid recovered from the parent drum.

Experimental Procedure

The objective of this set of experiments was to produce a simplified, scaled-down surrogate for the 55-gallon barrel (68660). Upon consideration of facilities, monitoring equipment, and scale-effects, an instrumented 22 gauge steel, 10 gallon barrel was down-selected as the preferred test vehicle. Part number P/N N110FRC-U 10 gallon barrels were obtained from General Container Corp for this purpose. Holes for Swagelok thermocouple pass-throughs were drilled and sealed at SNL. The barrels are unlined steel but a polyethylene (PE) liner was used to prevent gross contact between the barrel walls and interior contents. The PE liner was pierced to allow passage of the thermocouples into the barrel contents. Physical dimensions of the drum are: Inside diameter 14”, inside height 15.5”. A total of six barrels were prepared. Two were planned as relative control examples: barrel A uses a combination of only water and Swheat in a 1:2 ratio (volume to volume) in a single uniform layer. This control is to exhibit the behavior of wet Swheat with no acid or nitrate salts present. Barrel B consists of neutralized nitric acid and Swheat Scoop© in a 1:2 ratio (volume to volume) in a single uniform layer. This control is to exhibit the behavior of wet Swheat in the presence of triethanolammonium nitrate (TEAN), the product of nitric acid and Kolorsafe® liquid acid neutralizer with no free acid or nitrate salts present. Four additional experiments were prepared, envisioned as pairs to elucidate the effects of non-functioning vents and the presence of small amounts of lead respectively. Barrels C and D consist of a bottom layer containing neutralized acid adsorbed on Swheat in a 1:3 (liquid:Swheat) volume ratio, and a top layer of acid-wet mixed sodium and magnesium nitrate salts combined with Swheat in a 1:1.2 (salt:Swheat) volume ratio. Barrel D contained a small amount of Lead nitrate, which was not added to Barrel C. Barrels A, B, C, and D were equipped with vents open to the atmosphere for the duration of the

Watlow Thermocouple,Type 'K', 1/8 Inch Sheath 27.60 552.00
Dia. x 8 Inches Long, Grounded, Round Tip,
36-#24 Fiberglass Leads, Mini Male Plug part number 20CKFGR036F



TC 1,4,5,8,9, extended in 6.75” from inner wall
TC 3,7 extended in 3.5” from inner wall
TC 2,6 extended in 1.5” from inner wall

TC 2,3,4,6,7,8 were at interfaces

Figure 1 Physical layout of thermocouples in each simulant barrel.

experiment. Barrels E and F, identical in constituents to barrels C and D, respectively, were equipped with pressure transducers and the open vent was eliminated; a gas sampling valve was used to collect headspace gas. While a gasket was used to improve the seal of the lids used on all barrels, no particular effort was made to ensure that the seal on E and F was gas-tight to a specific pressure. Thermocouples were placed according to figure 1.

General procedure: A metal nitrate salt mixture was prepared then slurried up in 2 L of a previously salt-saturated nitric acid solution. The resulting mixture was allowed to sit for 24 hours, then the liquid decanted. Less than 2 L of liquid was typically recovered from each mixture in this method; the total volume of the recovered liquid was brought to 2 L with the salt-saturated nitric acid solution used to prepare the initial slurry. The recovered liquid was then brought to a neutral pH (~5-7) via the addition of Kolorsafe® liquid acid neutralizer. The resulting neutralized liquid (a solution of water, metal nitrate salts, and triethanolammonium nitrate) was then mixed with Swheat in a 3 to 1 Swheat to liquid ratio (by volume) and placed in the bottom of the barrel. Thermocouple 1 was positioned to be roughly in the center of this layer and thermocouples 2, 3, and 4 were adjusted so that they were positioned just at the top of this layer (so that they would be in the interface between this bottom layer and the next). The solid residue, nitric acid wetted mixed metal nitrate salts, was then broken up with a metal scoop (the layer tended to significantly consolidate upon standing) and mixed with Swheat in a 1.2 to 1 Swheat to nitrate salt ratio (by volume). This mixture was then added on top of the first layer. Thermocouple 5 was positioned to be roughly in the center of this layer and thermocouples 6, 7, and 8 were adjusted so that they were positioned just at the top of this layer (so that they would be at the interface between this top layer, and the empty head-space at the top of the barrel). Thermocouple 9 was positioned in the void head-space in the top portion of the barrel. The barrel liners contained a significant amount of excess material past the top of both the barrel contents, and the top lip of the barrel. This excess was trimmed off with scissors providing less than 6 inches of excess materials above the barrel lip. The excess material was folded down but not twisted or secured. The barrel tops were then attached using a clamping band. The barrels were then wrapped in thermal insulation and placed in a firing pad, thermocouple and pressure sensor leads connected, and data acquisition started.

Temperature was recorded for each thermocouple in one minute increments and recorded via a datalogger. Data was recovered from the data-logger daily. Pressure measurements were captured using digital pressure transducers. A gas sample from the headspace of each barrel was collected daily.

Preparation of salt saturated nitric acid solution

General procedure: A 3.3 M nitric acid solution was prepared by diluting 836 mL concentrated nitric acid (70% by weight) to 4 L. Salt-saturated nitric acid solution was prepared by diluting 627 mL of concentrated (70% by weight) nitric acid up to 3 L with water then adding approximately 1 kg $Mg(NO_3)_2*6H_2O$ and 800-1000 g $NaNO_3$ (until the solution is saturated). The resulting slurry was brought to a total of 4 L via the addition of 3.3 M nitric acid (as previously prepared).

Preparation of metal nitrate salt mixtures

General procedure: For each experiment containing Na and Mg nitrate salts, 1.9 kg (±0.1 kg) of sodium nitrate and 5.4 kg (±0.1 kg) of magnesium nitrate hexahydrate were combined in a plastic bucket. A metal rod was used to break up any significant agglomerations of the powder. For experiments containing lead nitrate, ~3.1 g of lead (II) nitrate was also added dry and mixed in with a metal rod.

Preparation of simulant mixtures

General procedure: 2 L of the salt-saturated nitric acid solution was added to the metal nitrate salt mixture in a plastic bucket. The resulting slurry was stirred with a plastic rod at hourly intervals for approximately 6 hours, then allowed to sit undisturbed at least overnight (in some cases over the course of a weekend). Supernatant liquid was then decanted and the recovered liquid and solid treated as noted above.

Barrels were loaded on 11/14/2014 and 11/17/2014. The observation period ran until 1/13/2015 for a total of 57 days. SNL had a holiday break from 12/24/2014- 1/5/2015.

Results

Six test barrels were prepared:

A. **Swheat + water/single layer**: 8 L water + 16 L Swheat (8 kg water + 10.3 (±0.1) kg Swheat)

B. **Neutralized acid and Swheat/single layer:** (4 (±0.1) L 3.3 M nitric acid+ 4 (±0.1) L Kolorsafe® liquid acid neutralizer + 10.3 (±0.1) kg Swheat)

C. **Two layers, vented:**

   - Neutralized acid bottom layer: 2 L decanted liquid + 974 ml Kolorsafe® liquid acid neutralizer + 8 L (5 kg) Swheat.
   - metal nitrate salt upper layer: 5.4 (±0.1) kg magnesium nitrate hexahydrate + 1.9 (±0.1) kg of sodium nitrate + interstitial liquid + 3.2 (±0.1) kg Swheat.

D. **Two layers with lead, vented:**

   - Neutralized acid bottom layer: 2 L decanted liquid + 913 ml Kolorsafe® liquid acid neutralizer + 8 L (5 kg) Swheat
   - metal nitrate salt upper layer with lead: 5.4 (±0.1) kg magnesium nitrate hexahydrate + 1.9 (±0.1) kg of sodium nitrate + interstitial liquid + 3.2 (±0.1) kg Swheat + 0.0032 kg lead (II) nitrate.

E. **Two layers, un-vented:**

   - Neutralized acid bottom layer: 2 L decanted liquid + 962 ml Kolorsafe® liquid acid neutralizer + 8 L (5 kg) Swheat.
   - metal nitrate salt upper layer: 5.4 (±0.1) kg magnesium nitrate hexahydrate + 1.9 (±0.1) kg of sodium nitrate + interstitial liquid + 3.2 (±0.1) kg Swheat.

F. **Two layers with lead, un-vented:**

- Neutralized acid bottom layer: 2 L decanted liquid + 923 ml Kolorsafe® liquid acid neutralizer + 8 L (5 kg) Swheat.
- metal nitrate salt upper layer with lead: 5.4 (±0.1) kg magnesium nitrate hexahydrate + 1.9 (±0.1) kg of sodium nitrate + interstitial liquid + 3.2 (±0.1) kg Swheat + 0.0032 kg lead (II) nitrate.

Decanted solution characterization

Barrel	Recovered (±50 mL)	Make-up (mL)	Neutralization (mL Kolorsafe)	Acid Conc (mol/L)	Na Conc (ppm)	Mg Conc (ppm)	Density (g/mL)
C	1950	20	974	1.6	N/A	N/A	1.36
D	1350	650	913	1.5	24364	57275	1.39
E	1300	700	962	1.6	22193	51188	1.38
F	1300	700	923	1.5	24316	56253	1.39

Barrel construction observations:

Barrels A and B contain 1:2 liquid to Swheat ratios (all ratios are volume to volume with ± 200 mL accuracy) as this was the ratio referenced in both process documents and interviews with personnel preparing drum 68660. However, the intent of this process was to absolutely prevent the occurrence of any free liquid that would cause rejection of the drum from WIPP and require reprocessing. During the construction of A and B it was noted that water combined with Swheat in the desired ratio to yield a moist (but not excessively wet) material, in the combination of neutralized acid (barrel B) in the concentrations listed above, resulted in a material that left behind an oily residue. This residue is conjectured to be the product of neutralization: TEAN in solution with water. When salt-saturated nitric acid was neutralized and sorbed onto Swheat, it was found that a 1:2 liquid to Swheat ratio was insufficient to eliminate all free liquid. Additional Swheat was added in portions until no free liquid was visible. The final ratio used was close to 1:3 liquid to Swheat. This same ratio was used in barrels C, D, E, and F for immobilization of the neutralized salt saturated acid solutions. For all liquid/Swheat mixtures, the final mixture was a very moist, almost doughy mass with a faint wheat (bread) odor. The combination of acid-wet mixed metal nitrate salts with 1:1.2 (salt:Swheat, the salt/Swheat mixture used in the top layer of the barrels) produced a moist, but not free flowing material more akin to damp sand.

The acid concentration in 68660 was hypothesized as between 1 and 3.3 M as discussed above. The concentration of acid in the liquid decanted from the simulant mixtures was only ~1.5 M. Due to severe time constraints, very few preliminary experiments were performed; one of the impacts of this was lack of optimization in the simulant preparation process. The amount, in both mass and volume, of sodium and magnesium salts that would be required to saturate 3.3 M nitric acid solution was significantly underestimated. Saturation of 3 L of 3.3 M nitric acid solution yielded almost 4 L of salt saturated solution that contained only 2.48 M nitric acid. This became further diluted when introduced to the mixed metal salts as part of simulant preparation. The large amount of water associated with the magnesium nitrate contributed significantly to this effect.

The discrepancy between the amount of liquid decanted from simulant mixture C and that recovered from simulant mixtures D, E, and F may be attributed to increased efficiency of recovery in C due to issues in material settling and/or change in personnel. The experimental data does not suggest that the presumably higher liquid content in the mixed metal salt portions of D, E, and F resulted in a difference in behavior between C and the remainder of the mixed salt simulants.

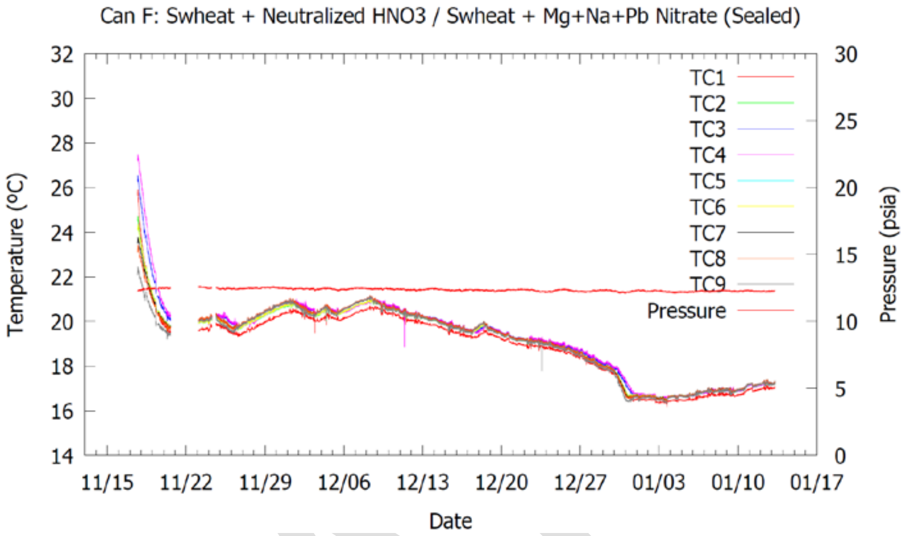


Figure 2 Temperature data collected for Barrel F over the course of the experiment. Thermocouples correspond to the arragnement shown in figure 1.

Figures 2 and 3 show recorded temperatures for the duration of the experiment. Figure 2 shows all thermocouples (and the pressure reading) for barrel F. Figure 3 shows readings from thermocouple 3 (see figure 1 for thermocouple placement) for each barrel and a temperature reading for the firing pad (Drum A Pad, equivalent to the environmental condition surrounding each barrel). Only these two examples are shown due to the nature of the data collected: there was no deviation of barrel internal temperature away from ambient (as measured by the pad thermocouples) greater than the limits of discrimination for any of the thermocouples measured. In addition, both sealed barrels (E and F) did not register a deviation from atmospheric pressure of more than 1 psi.

Thermocouples recorded for barrel E (Can E) contained significant amounts of noise and were consistently lower than ambient temperature for a significant portion of the observation period. This appears to be due to a systematic equipment bias associated with the datalogger channel they were recorded on. The issue was repaired 12/22 and from that point on it is clear that barrel E was tracking with the ambient temperature in agreement with the remaining five barrels.

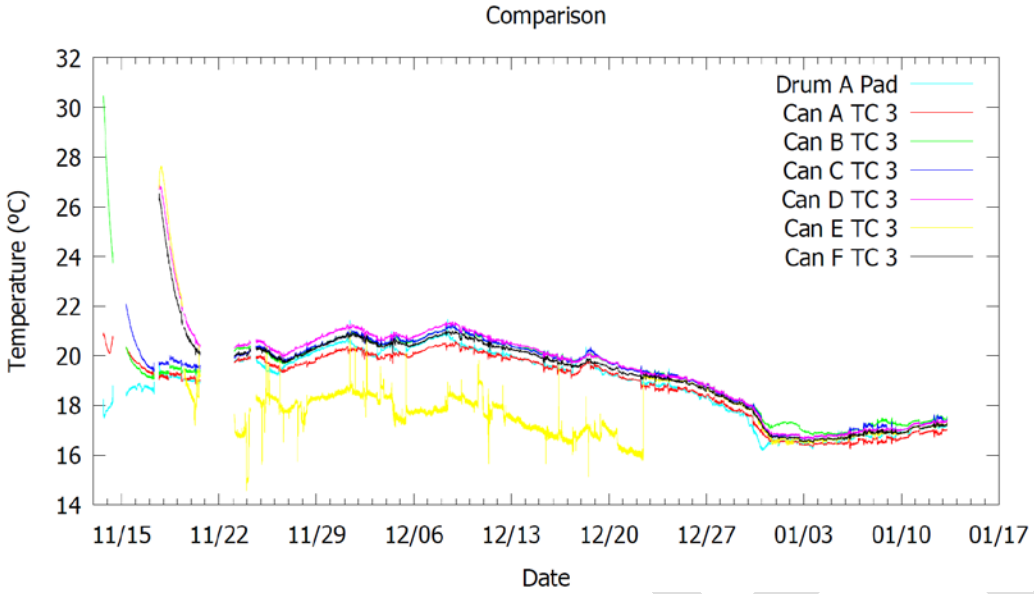
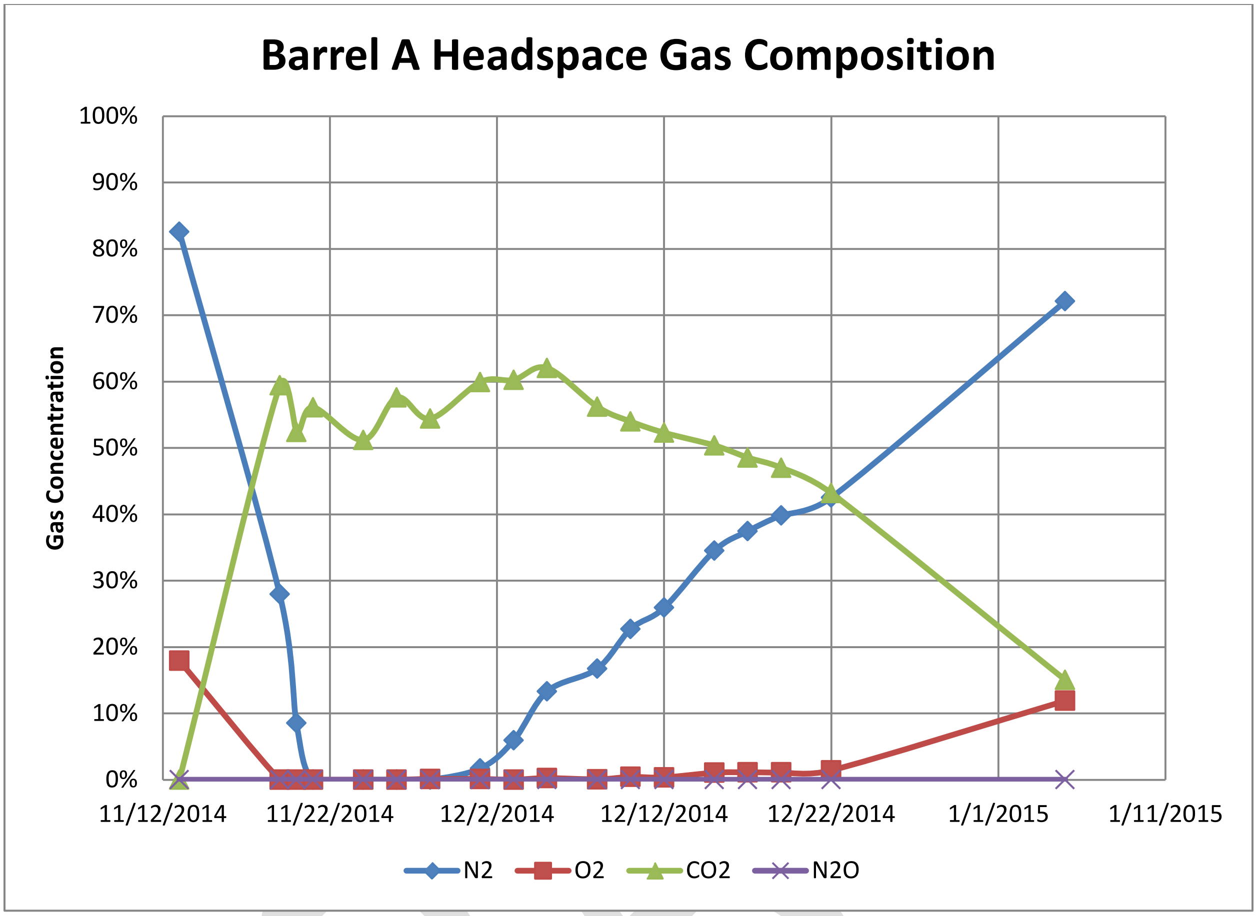


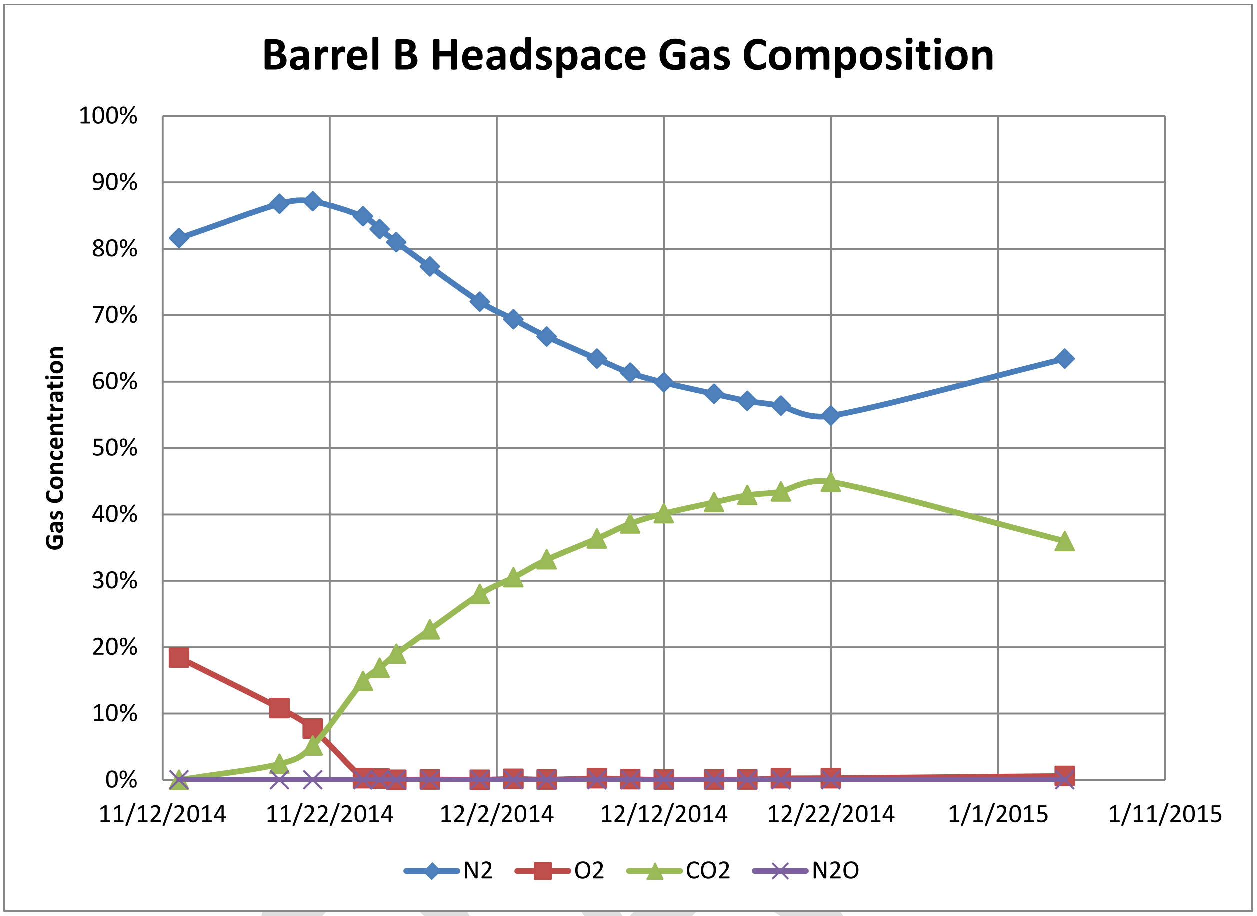
Figure 3 Comparison of thermocouple 3 for each barrel over the course of the experiment. "Drum A Pad" was the name given to the thermocouple measuring the ambient temperature immediately outside Barrel A.

Headspace gas was collected intermittently: early in the experiment samples were taken daily during the week. Over the holiday break, at the end of the overall observation period, only two samples were taken: one on 12/22/2014 and a final one on 1/5/15. No headspace gas samples were taken following the final sample collected 1/5/15. Headspace gas was collected into evacuated cylinders attached to the barrel vent. For sealed barrels (E and F) the vent was sealed with a quarter-turn manually operated valve. Headspace gas samples were analyzed on a GCMS for N_2, O_2, CO_2, NO, and N_2O, typically within two days of being collected. While gas samples were collected every day, only every other sample collected was analyzed. If unexpected results were found between consecutive samples analyzed, the intervening sample would then be subjected to analysis. All headspace gas samples and "air control" samples were injected at the same pressure: 25±2 torr. Headspace gas samples were analyzed on an Agilent 7890A GC coupled with an Agilent 5975C triple axis mass spectrometer using an Agilent PoraBondQ capillary column and helium carrier gas. Samples were analyzed and compared with a 12-component gas calibration standard for detector response of specific analytes. Air control samples (from ambient atmosphere) were injected at the same pressure as the analytes (25 ±2 torr) and provide a measure of day-to-day same-operator/same-instrument scatter and a comparison for overall headspace gas content, since only the species of interest were analyzed (N_2, O_2, CO_2, NO, and N_2O). The amount of sample passing through the detector (total counts) for air was used as a total content standard for the pressure injected; the same volume and pressure of sample injected at the same temperature should contain the same number of molecules. The % composition of the analytes of interest (as mol fraction) for each barrel and their total content compared to the air control sample are shown in the tables below.



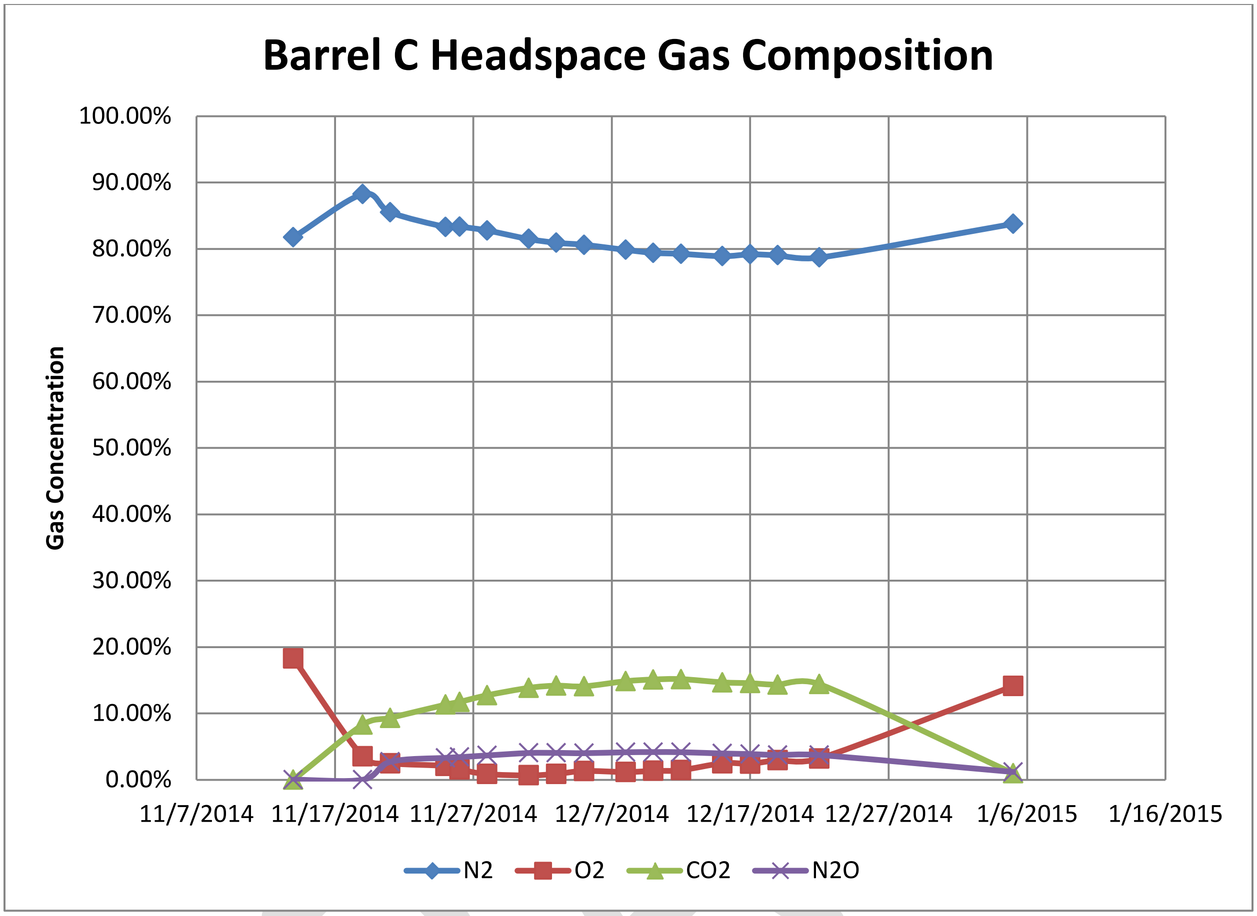
Barrel A headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/13	82%	18%	0%	0%	100%
11/19	32%	0%	68%	0%	87%
11/20	14%	0%	86%	0%	61%
11/21	0%	0%	100%	0%	56%
11/24	0%	0%	100%	0%	51%
11/26	0%	0%	100%	0%	58%
11/28	0%	0%	100%	0%	54%
12/1	3%	0%	97%	0%	62%
12/3	9%	0%	91%	0%	66%
12/5	18%	0%	82%	0%	76%
12/8	23%	0%	77%	0%	73%
12/10	29%	1%	70%	0%	77%
12/12	33%	0%	67%	0%	79%
12/15	40%	1%	59%	0%	86%
12/17	43%	1%	56%	0%	87%
12/19	45%	1%	53%	0%	88%
12/22	49%	2%	50%	0%	87%
1/5	73%	12%	15%	0%	99%



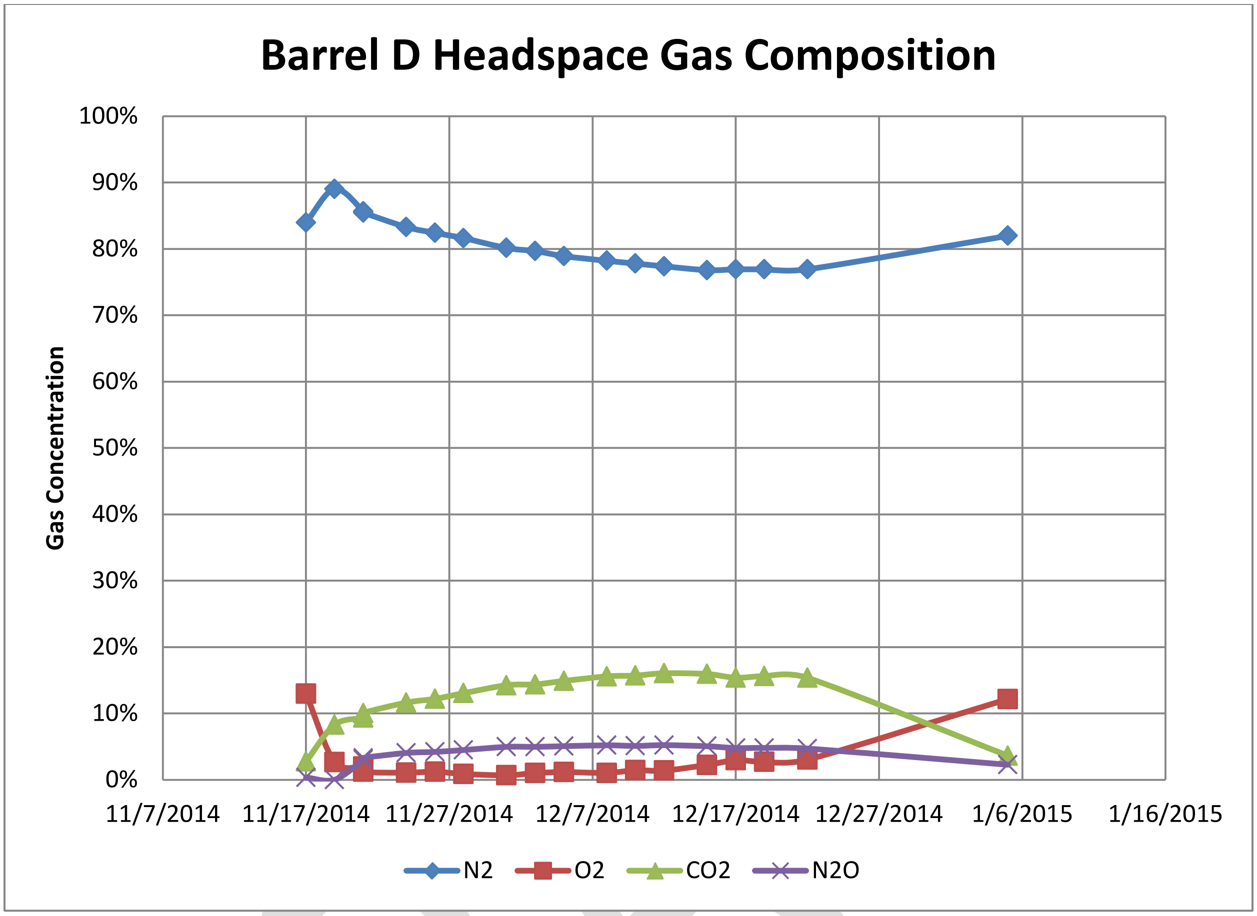
Barrel B headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/13	82%	18%	0%	0%	103%
11/19	87%	11%	2%	0%	90%
11/21	87%	8%	5%	0%	98%
11/24	85%	0%	15%	0%	105%
11/25	83%	0%	17%	0%	92%
11/26	81%	0%	19%	0%	101%
11/28	77%	0%	23%	0%	92%
12/1	72%	0%	28%	0%	103%
12/3	69%	0%	30%	0%	99%
12/5	67%	0%	33%	0%	110%
12/8	63%	0%	36%	0%	99%
12/10	61%	0%	39%	0%	96%
12/12	60%	0%	40%	0%	98%
12/15	58%	0%	42%	0%	100%
12/17	57%	0%	43%	0%	96%
12/19	56%	0%	43%	0%	100%
12/22	55%	0%	45%	0%	101%
1/5	63%	1%	36%	0%	96%



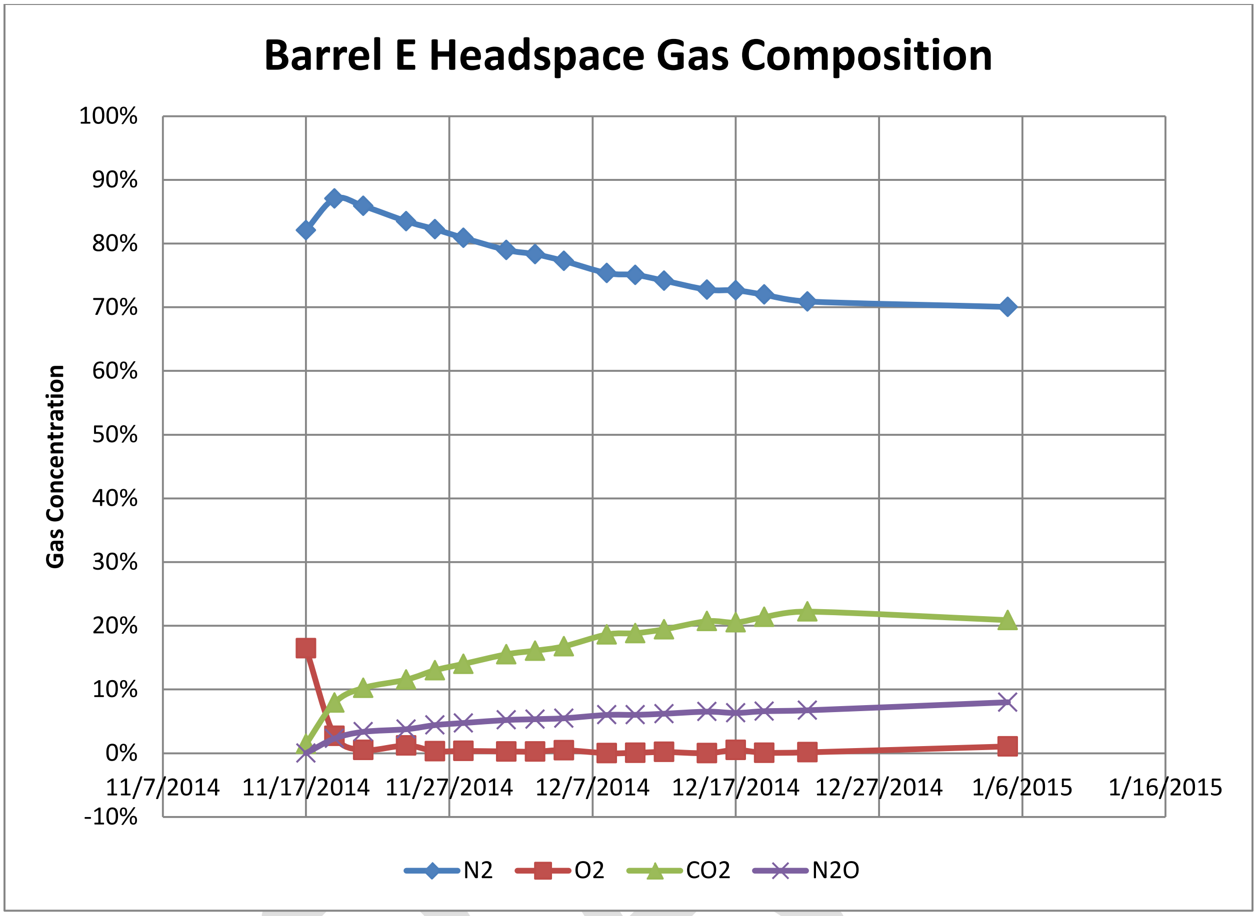
Barrel C headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/14	82%	18%	0%	0%	99%
11/19	88%	3%	8%	0%	88%
11/21	86%	2%	9%	3%	107%
11/25	83%	2%	11%	3%	100%
11/26	83%	2%	12%	3%	99%
11/28	83%	1%	13%	4%	94%
12/1	81%	1%	14%	4%	99%
12/3	81%	1%	14%	4%	98%
12/5	81%	1%	14%	4%	110%
12/8	80%	1%	15%	4%	100%
12/10	79%	1%	15%	4%	97%
12/12	79%	1%	15%	4%	99%
12/15	79%	2%	15%	4%	105%
12/17	79%	2%	15%	4%	98%
12/19	79%	3%	14%	4%	94%
12/22	79%	3%	14%	4%	97%
1/5	84%	14%	1%	1%	93%



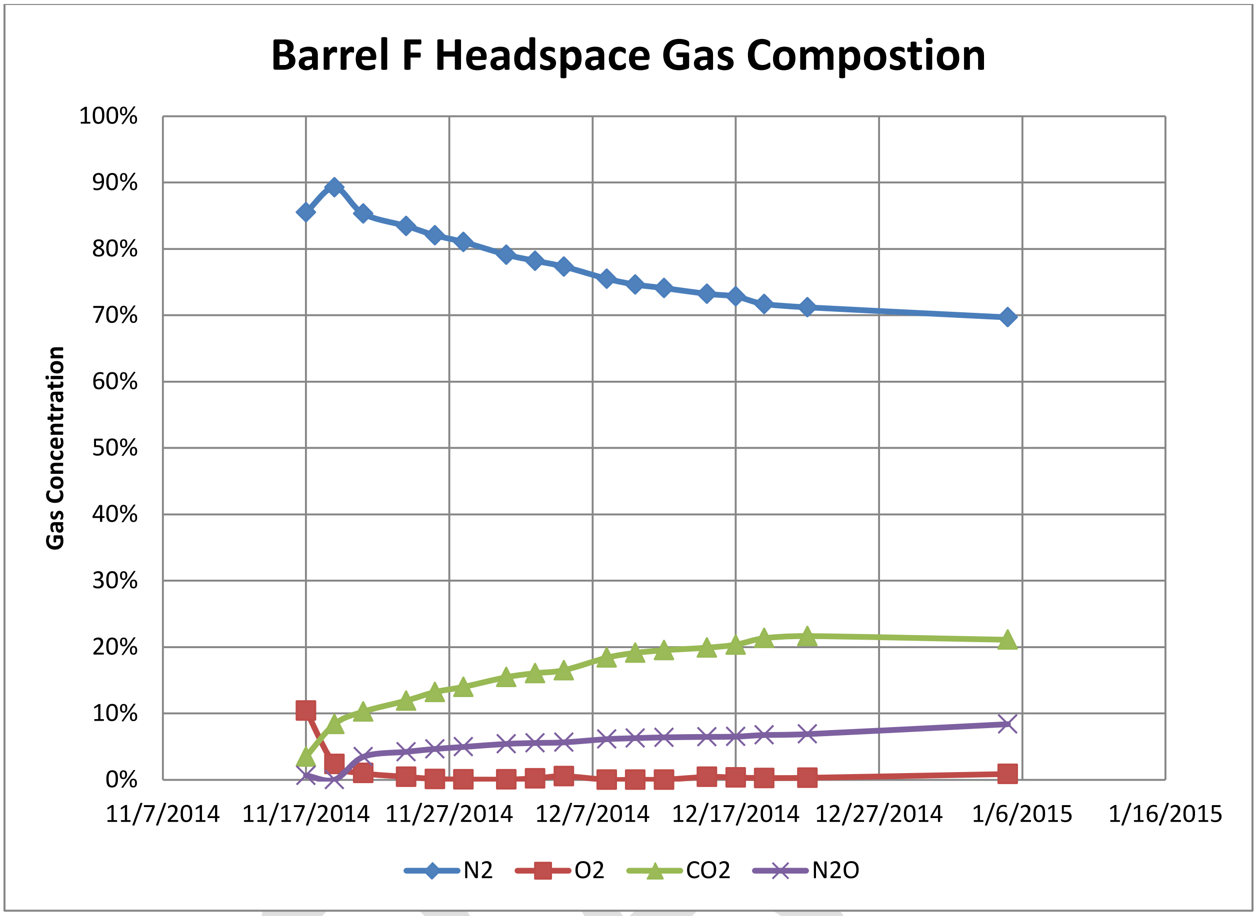
Barrel D headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/17	84%	13%	3%	0%	102%
11/19	89%	3%	8%	0%	95%
11/21	86%	2%	9%	3%	99%
11/24	83%	1%	12%	4%	104%
11/26	82%	1%	12%	4%	100%
11/28	82%	1%	13%	4%	93%
12/1	80%	1%	14%	5%	98%
12/3	80%	1%	14%	5%	100%
12/5	79%	1%	15%	5%	105%
12/8	78%	1%	16%	5%	95%
12/10	78%	1%	16%	5%	97%
12/12	77%	1%	16%	5%	94%
12/15	77%	2%	16%	5%	98%
12/17	77%	3%	15%	5%	95%
12/19	77%	3%	16%	5%	97%
12/22	77%	3%	15%	5%	94%
1/5	82%	12%	4%	2%	90%



Barrel E headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/17	82%	16%	1%	0%	95%
11/19	87%	3%	8%	2%	103%
11/21	86%	1%	10%	3%	107%
11/24	83%	1%	12%	4%	86%
11/26	82%	0%	13%	4%	101%
11/28	81%	0%	14%	5%	102%
12/1	79%	0%	16%	5%	98%
12/3	78%	0%	16%	5%	102%
12/5	77%	0%	17%	5%	104%
12/8	75%	0%	19%	6%	95%
12/10	75%	0%	19%	6%	96%
12/12	74%	0%	19%	6%	101%
12/15	73%	0%	21%	7%	98%
12/17	73%	1%	21%	6%	92%
12/19	72%	0%	21%	7%	94%
12/22	71%	0%	22%	7%	88%
1/5	70%	1%	21%	8%	92%



Barrel F headspace gas composition data

Date	N_2	O_2	CO_2	N_2O	Total compared to air
11/17	85%	10%	3%	1%	109%
11/19	89%	2%	8%	0%	95%
11/21	85%	1%	10%	3%	101%
11/24	83%	0%	12%	4%	101%
11/26	82%	0%	13%	5%	95%
11/28	81%	0%	14%	5%	97%
12/1	79%	0%	15%	5%	105%
12/3	78%	0%	16%	6%	98%
12/5	77%	1%	17%	6%	104%
12/8	75%	0%	18%	6%	94%
12/10	75%	0%	19%	6%	93%
12/12	74%	0%	20%	6%	95%
12/15	73%	0%	20%	6%	101%
12/17	73%	0%	20%	6%	99%
12/19	72%	0%	21%	7%	93%
12/22	71%	0%	22%	7%	93%
1/5	70%	1%	21%	8%	93%

Disassembly observations:

At the end of the observation period the barrels were opened and small samples of the contents removed and sent to SRNL for evaluation of biological activity. During the course of sampling the barrels it was noted that visual (and olfactory) changes had occurred over the course of the experiment.

Figure 4 Barrel A 11/13/14

Figure 5 Barrel A 1/17/15

Figure 6 Barrel B 11/13/14

Figure 7 Barrel B 1/13/15

Figure 8 Barrel C 11/17/14

Figure 9 Barrel C 1/13/15

Barrels A, B, and C are shown as representative samples: barrels A and B for their appearance as controls and barrel C as representative of the group of barrels C, D, E, and F, the four of which had similar appearance and odor.

Observations of note:
Barrel A had an overpowering odor that we attributed to significant bacterial or fungal activity. The wet Swheat mixture had darkened slightly in visual appearance and settled about 3 inches over the observation period. A sample of this material was supplied to SRNL for biological activity analysis.

Barrel B had an odor described as “rotted apple cider”, again attributed to bacterial or fungal activity. In addition, there were a number of either bacterial or fungal colonies visible as white fibrous masses on the top of the Swheat/neutralized acid mixture. The wet Swheat mixture had darkened slightly in visual appearance and settled about 2 inches (slightly less than in barrel A). A sample of this material was supplied to SRNL for biological activity analysis.

Barrels C, D, E, and F all had similar appearance and odor. No significant notable odor. The Swheat/mixed metal salt top layer appeared to have lightened in color compared with the as-prepared sample. The bottom Swheat/neutralized acid layer appeared to have significantly darkened, consolidated, and solidified compared with the as-prepared sample. Samples of both the top and bottom layer were supplied to SRNL for biological activity analysis.

All barrels exhibited significant corrosion (rust) on both the interior walls of the barrel and the interior of the barrel lid. In some cases it appeared that corrosion products may have flaked off of the lid interior and fallen down onto the surface of the top layer.

Discussion

There was a lack of measurable heat evolution in any configuration examined. Whether this was as a result of a lack of significant exothermic reactions occurring in the matrix or of efficient heat dissipation from the system to its surroundings is unknown. Steps were taken to reduce thermal communication between the pad and the barrel contents (barrels wrapped in insulation, placed on foam insulation pads, top-covered with foil lined foam) but the close tracking of interior barrel content temperature with ambient pad temps indicates that, even at the center of the barrel (thermocouple # 3), thermal communication was good at the time-scale of ambient pad temperature change. For this reason the only definitive statement that can be made is that if an exothermic reaction was active, it did not produce enough heat to overcome dissipation to the environment.

In contrast, headspace gas analysis provides an interesting insight into the chemical and biological processes active in the different configurations and material sets investigated. Barrel A contained only water and Swheat . This combination of materials provided the most robust headspace gas activity of all the materials studied. It has been noted that Swheat contains active biological organisms that will colonize both Swheat constituents and adsorbed favorable nutrients, such as TEAN. The rapid evolution of CO_2 in barrel A is consistent with an active biological digestion process. One matter of note in barrel A is that while it appears that CO_2 completely displaces other headspace gas constituents in a matter of days, total detector count for these samples falls to almost 50% of the control sample, indicating presence of significant (almost 50%) species in the headspace gas that were not captured in the analysis. Since both analyte and air control samples were injected at the same pressure, if all species are accounted for, total detector count should be the same.

While this presents a significant question regarding the actual, active processes in barrel A, its impact to the investigation as a whole is reflected in comparison of overall barrel A activity to the rest of the experimental group. In short, barrel A presents a headspace gas profile unique to water/Swheat and is not seen in the other material sets. As a control this provides negative information that is nonetheless cogent: the biological processes active in barrel A are not seen in any of the other experimental configurations or material sets.

Barrel B containes neutralized nitric acid (4 L of 3.3 M nitric acid neutralized with 4 L of Kolorsafe liquid acid neutralizer) adsorbed on Swheat. The mixture in barrel B exhibited CO_2 development that, superficially, appears to be similar to that seen in barrel A. The difference between these two systems is that the gross constituents of barrel B headspace gas remain the same species: N_2, O_2, CO_2. The headspace gas in barrel B produced detector counts similar to the air control for the entire length of the experiment (average 99 ± 5%). It may be important to note that the absolute amount of CO_2 developed in barrel B appears to be similar to that produced in barrel A (about 50% of the total free volume in the headspace was occupied by CO_2 in both barrel A and barrel B). This suggests that whatever biological or chemical pathway that was active in CO_2 evolution in barrel A may have also been active in barrel B. This also suggests that whatever process in barrel A that led to the anomalous headspace behavior (almost 50% of the headspace gas was not detected or identified with the GC/MS analysis used) was *not* active in barrel B. In addition, trace analysis of both barrel A and barrel B headspace gas indicated the presence (< 0.1%) of typical, expected fermentation products such as ethanol and isopropanol. Neither barrel A nor barrel B show any traces of NO, N_2O, or possible nitration products such as methyl nitrate or methyl nitrite.

Barrels C and D exhibit similar enough behavior that they can be addressed as a repetition of a single experiment. There is no detectable difference in either their temperature or headspace gas data. This suggests that the lead nitrate present in barrel D had no appreciable impact on the observed behavior. It is important to note that only ambient temperature behavior was observed in these experiments; if a constituent would have a significant, perhaps even dominant, effect at raised temperature, this experiment would not bear that out. The behavior of barrel C and barrel D is in marked contrast to that seen in barrel A and barrel B. In barrel C and barrel D, what appears to be initial consumption of O_2 is balanced with CO_2 production, with CO_2 never comprising more than 20% of the total headspace gas volume. Then, three days into the experiment, N_2O, interpreted as a marker for either nitrate salt oxidation of organics, or nitrate salt decomposition, appeared. This species was not detected over the period of observation for either barrel A or barrel B. While barrel C and barrel D were equipped with vents and thus had gas phase communication with the surrounding environment, it is unclear how much equilibration occurred over the course of the experiment, or what the rate of exchange between interior and ambient atmosphere was. The reduction in CO_2 and N_2O content and rise in both O_2 and N_2 at the end of the experiment is interpreted as these species equilibrating to their ambient atmospheric concentrations. This suggests that the processes resulting in CO_2 and N_2O evolution had, at this point, either halted or slowed such that the barrel internal headspace was once again dominated by the characteristics of the external atmosphere rather than the result of internal reactions. Trace (< 0.1%) amounts of methyl nitrite and methyl nitrate along with various low molecular weight ketones and esters (anticipated hydrolysis products) were detected in both barrel C and barrel D. These species were not detected in barrel A or barrel B. It is unclear if the methyl nitrite and methyl nitrate are products (or byproducts) of nitrate salt nitration of Swheat constituents or if they were simply released as fragments of existing species, or over what time frame they were produced (the trace analysis was a snapshot taken at roughly the mid-point of the observation period).

Barrels E and F exhibit similar enough behavior that they will be addressed as repetition of a single experiment, similar to barrels C and D. Barrel E and barrel F were distinct from the other barrels in that they were sealed without an open vent. Access to the headspace was through a manually operated quarter-turn valve that was opened only during headspace gas sampling. While barrel E and barrel F were not purposefully vented, no particular effort was made to ensure that they were gas tight. The lids on all the barrels were sealed with a rubber gasket and clamped with a locking band. No effort was made to evaluate the seal formed by this arrangement. The temperature data recorded for barrel E is both very noisy and anomalously low compared both to barrel F and to all of the other barrels, until 12/22/2014. At this time, in preparation for the holiday shut-down, the thermocouple leads for barrel E were removed and reattached, at which point the discrepancy was eliminated. From this point on the temperature in barrel E tracks well with both the other barrels and the internal temperature of the firing pad that the experiment was performed in. Much like barrel C and barrel D, barrel E and barrel F differed from each other only in that barrel F contained a very small amount of lead nitrate while barrel E did not. The close agreement between barrel E and barrel F in headspace gas activity suggests that they are virtually identical to each other and their similarity to barrel C and barrel D suggests that venting has little effect on the overall chemistry that occurred in all four barrels. The only significant difference between barrels C/D and barrels E/F is that barrel E and barrel F do not trend back to atmospheric content levels in O_2 and N_2 as barrels C/D do toward the end of the experiment. Given that barrel E and barrel F are effectively isolated from the surrounding atmosphere, this isn't surprising. This also lends further credence to the proposition that significant gas forming reactions had either slowed or halted by the end of the observation period (@ 6 weeks).

Conclusions:

The mixture of neutralized acid, sodium nitrate, magnesium nitrate, and Swheat used in the experiments was insufficient to generate any measurable temperature rise in the configuration and scale used. The close tracking of internal barrel temperature with the temperature of the firing pad the barrels were located in indicates that barrel contents were not sufficiently thermally isolated from the surrounding environment. The thermal data developed in these experiments should not be taken as supporting the supposition that the material sets used do not produce exothermic reactions at ambient temperature. Heat loss to the environment was too poorly controlled to allow for any conclusive statements about heat generation or thermal run-away.

Mixtures of water/Swheat (barrel A) and TEAN/water/Swheat (barrel B) exhibit similar amounts and rates of CO_2 evolution. However, the anomalous behavior observed in the water/Swheat system headspace gas composition precludes a strong statement that identical reactions are occurring in the TEAN/water/Swheat system. All of the full, layered mixtures that contain neutralized acid adsorbed on Swheat in the bottom layer and mixed metal salts and Swheat in the top layer exhibit similar headspace gas behavior. This behavior is not consistent with what was observed in either water/Swheat or neutralized acid/Swheat mixtures. We attribute the significant evolution of CO_2 in the water/Swheat and neutralized acid/Swheat mixtures to predominantly biological processes. We believe that the headspace gas data developed supports the assertion that these same processes are not as active in the mixtures containing the metal nitrate salts.