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Shipment and Disposal of Solidified Organic Waste (Waste Type IV) to the Waste Isolation Pilot Plant (WIPP)

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ABSTRACT

In April of 2005, the last shipment of transuranic (TRU) waste from the Rocky Flats Environmental Technology Site to the WIPP was completed. With the completion of this shipment, all transuranic waste generated and stored at Rocky Flats was successfully removed from the site and shipped to and disposed of at the WIPP. Some of the last waste to be shipped and disposed of at the WIPP was waste consisting of solidified organic liquids that is identified as Waste Type IV in the Contact-Handled Transuranic Waste Authorized Methods for Payload Control (CH-TRAMPAC) document. Waste Type IV waste typically has a composition, and associated characteristics, that make it significantly more difficult to ship and dispose of than other Waste Types, especially with respect to gas generation. This paper provides an overview of the experience gained at Rocky Flats for management, transportation and disposal of Type IV waste at WIPP, particularly with respect to gas generation testing.

OVERVIEW

Gas generation requirements for Waste Type IV (Type-IV) waste involve quantifying two specific gas generation rates: 1) total gas generation rate and 2) hydrogen/methane gas generation rate. In January 2003, Rocky Flats initiated a gas generation testing program with the intent to test roughly 700 drums of Type-IV waste. These tests were being performed under the original Rocky Flats gas-generation test protocols established in 1998. Nearly half of the drums of Type-IV waste tested under the original test protocol exceeded the gas generation rate limits established in the TRUPACT-II, Safety Analysis Report (SAR), Revision 19.[1] At this time, noncompliance with both total gas generation rate limits and hydrogen/methane gas generation rate limits were observed.

In response, Rocky Flats initiated extended duration testing to get a better understanding of the behavior of the Type-IV waste under prolonged elevated temperature conditions both for total gas generation and hydrogen/methane generation. It was suspected that the exceedences for total gas generation rates were the result of volatilization of volatile organic compounds (VOCs) like carbon tetrachloride and 1,1,1-trichloroethane instead of an actual gas generation mechanism. Specifically, it was thought that samples or measurements were being collected too early in the drum heat up cycle, thus not allowing the system (waste, drum, and test canister) to come to a steady state condition with respect to the volatilization of VOCs. As such the volatilization of VOCs was inappropriately contributing to and elevating the quantification of the total gas generation rate. It was also suspected that exceedences to hydrogen/methane gas generation rate limits may have been due to some sort of entrapment of hydrogen gas that was slowly generated during waste storage in the waste matrix and that upon heating of the drum a large quantity of trapped hydrogen gas was rapidly released thereby biasing high the actual hydrogen/methane gas generation rate measurement. The extended testing was initiated to determine when, if ever, the system would reach a steady state condition. It was assumed that a steady state condition would be indicated when the hydrogen/methane and total generation rates would level off. The biggest question was how long it would take for this to occur.

Approximately 90 drums were tested for periods from 20 to 38 days. Two general observations were observed, one expected and the other not. The expected observation was that the tests generally showed that the systems reached a pseudo steady state with respect to total gas generation rate after about five days of heating. This was indicated after the systems appeared to reach relatively constant pressure and temperature. This was nearly three days longer than the original testing program requirement of 66 hours. However, even at a steady state condition, some drums were still exceeding the allowable Revision 19 total gas generation rate limit.

The second, more perplexing and problematic observation was that the observed hydrogen/methane generation rates in a significant number of cases never came to a steady state condition even though the system and the total gas generation rates had. The results have varied widely and even the longest duration tests did not definitively show that the rate leveled off. In general, roughly 50% of the drums tested under this extended test program exceeded either the hydrogen/methane or the total gas generation rate, or both.

NEW REVISION 20 TRUPACT-II SAR REQUIREMENTS

In Revision 20 of the TRUPACT-II SAR [2], a higher total gas generation rate limit (based on 60 days versus the original 1-year period) was established and new higher hydrogen/methane generation rate limits based on two shipping period changes were adopted. The shipping period changes consisted of a 20-day shipping period (as opposed to the original 60-day limit) for sites within 1000 miles of WIPP, and a special 10-day “controlled” shipment shipping period subject to special administrative controls. Additionally, the gas generation testing requirements were also modified to specify as follows:

"… The test will be terminated after sufficient data are obtained to calculate the hydrogen gas generation rate.

The term "sufficient data" is defined as data on the parameters needed to quantify a bounding and applicable gas generation rate for the container under the test conditions prescribed in the UFGTP. In the case of containers that are tested at room temperature (Waste Types I, II, and III), sufficient data is measurement of the flammable gas concentration, temperature, and pressure. For these containers there is no thermal equilibration of the contents with respect to the testing temperature and the gas generation rates are constant or decreasing (see Appendices 3.2 and 3.3 of the CH-TRU Payload Appendices). For containers that are tested at an elevated temperature (Waste Type IV), a thermal equilibration period exists. Measurements are taken after the equilibration period to quantify the maximum flammable gas and total gas generation rates. ***In this case, sufficient data is measurement of flammable gas and total gas generation rates, temperature, and pressure during a testing period that is extended until the rates are shown to remain constant or decrease, or until the testing period (time from container isolation and commencement of heating to the collection of the final gas sample) equals or exceeds the time of the allowed shipping period.*** *In all cases, the collection of data as described herein ensures that the measured rates determined through testing are representative of the gas generation properties of the container over the allowed shipping period. The measured rates are then compared to the respective limits to demonstrate compliance with the allowable gas generation rates. …' [emphasis added]*

In order to reduce the amount of gas-generation testing required for large waste streams, WIPP received approval from the Nuclear Regulatory Commission (NRC) to implement a statistical based testing approach for test category wastes.

5.2.5.5 Implementation of Unified Flammable Gas Test Procedure Long-Term Objective
The long-term objective of the UFGTP is applied to a population of containers with consistent gas generation properties. The long-term objective of the UFGTP may be implemented once the required data have been collected through measurement and/or testing for a subpopulation of these containers. If a bounding FGGR value for compliance determination can be established and shown to be below the maximum allowable FGGR for the population, no further need exists to test every container in the population. If the bounding FGGR value exceeds the maximum allowable FGGR, the population will continue to be processed under the measurement and testing methodology of the UFGTP. This methodology is consistent with that used in the determination of dose-dependent G values in Appendix 3.3 of the CH-TRU Payload Appendices. Site implementation of the UFGTP long-term objective must be documented in site-specific programs approved by DOE-CBFO.

The new, higher Rev. 20 total gas-generation rate limits for drums was high enough to pass even the worst known case failures found at Rocky Flats. However, even with the Rev. 20 changes, Rocky Flats still found it had a challenge when it came to meeting the hydrogen generation rate limits for a small subpopulation of drums.

Testing and certifying the Type-IV waste drums became one of the biggest challenges to successfully disposing of all transuranic waste from the Rocky Flats site.

In mid-2003, Rocky Flats felt that the only way it would be able to meet the new requirement of the Rev. 20 CH-TRAMPAC was to test each drum to the full duration of the chosen transportation period. To maximize success, it was decided that the new special condition 10-day shipping period would be used and as such, the testing protocols were modified to test for a full 10 days. All data previously generated under the original testing regime was discarded and Rocky Flats re-started testing all its Type-IV waste drums for a minimum of 10 days.

Even under 10 day shipping period conditions, some small number of the Type-IV waste drums continued to exceed the applicable hydrogen/methane gas generation limit as configured. Therefore, Rocky Flats could not apply the Long-term objective and had to test every drum. In some cases, Rocky Flats tested a drum several times, and in a number of cases, had to repackage the drum and re-test in order to get the waste to pass.

BACKGROUND

Rocky Flats Type-IV wastes were generated primarily from the Organic and Sludge Immobilization System (OASIS).

- There were over 700 208 liter/55-gallon drums (drum(s)) of Solidified Organic (referred to as Type-IV) waste identified at Rocky Flats (over 9, 000 drums at INEEL).
- Approximately 500 drums of the Type-IV inventory were produced primarily from the solidification of TRU waste oils and solvents using the OASIS process.
- Concentrations of flammable organic solvent gases in drum headspace exceeded the original TRUPACT-II limit of 500 parts per million (ppm) for about 50% of the inventory tested, but typically ranged between 1,000 to 2,000 ppm.
- Non-flammable organic compounds, primarily carbon tetrachloride and 1,1,1-trichloroethane, typically exceeded 10,000 ppm.
- Small-scale tests performed in FY 02 on "hot" samples at Argonne National Laboratory-West (ANL-W) showed higher than excepted levels of hydrogen generation.
- Initial elevated-temperature gas-generation tests at INEEL and Rocky Flats confirmed the ANL-W findings that excessive amounts of hydrogen and Volatile Organic Compounds (VOCs) were generated – exceeding the allowable limits established by SAR in many cases.
- Due to the excessive amounts of gases generated during the elevated temperature test, increased pressures (>10 psi) were experienced within the test canisters, potentially exceeding the allowable pressure limit for payload containers transported in the TRUPACT-II.
- ~ 10% of the OASIS drums had free liquid exceeding the 1% by volume WIPP Waste Acceptance Criteria limit - these containers required mitigation.

- Roughly 70 drums had been overpacked into 321 liter/85-gallon overpacks (overpack(s)) due to drum integrity.
- After two years of being overpacked approximately 30 overpacks showed some signs of corrosion.
- All overpacks were eventually repackaged into new drums and gas-generation tested or re-tested.
- The waste is Resource Conservation and Recovery Act (RCRA) Regulated, thus requiring permitted storage and treatment areas.
- No demonstrated methodology to treat waste and no treatment facilities existed at Rocky Flats

Issues

The NRC requires that shippers must ensure that at no point in time during the assumed 60, 20, or 10-day transport period that the concentrations of hydrogen within any layer of confinement within the TRUPACT-II payload exceed five volume percent (5%). To verify compliance with this requirement, a computer model was developed, using conservative assumptions, to predict hydrogen concentrations and diffusion between layers of confinement to establish limits on how much hydrogen a waste can produce within a waste package and not exceed 5% hydrogen in the innermost layer of confinement. The determination of a G-value[1] associated with each waste form and the hydrogen diffusion coefficients of the different packaging materials is key to the ability to establish hydrogen generation and total gas-generation limits. If the G-value is unknown, then the generator must test payload containers of the waste to determine compliance with underlying conditions of the TRUPACT-II limits.

The TRUPACT-II SAR also establishes an internal pressure limit of 50 psig, originally assuming a one-year transport period, which changed to a 60-day period with the approval of Rev. 20. To control these conditions, the computer model uses a reverse calculation to determine maximum allowable pressure for each individual package within the TRUPACT-II assuming that the centerline temperature rises to 57^{o}C and that each of the 14 drums will generate gas at the same rate.

Due to the complexity and variability of the Type-IV wastes, a realistic G-value for these wastes has not been established. In this case, the SAR requires that all Type-IV be subjected to an elevated temperature (57^{o}C) gas-generation testing to determine potential amounts of flammable gases (H2, methane, etc) and the total amounts of all gases produced under simulated worst-case shipping scenarios.

In FY 2000, small-scale, heated, gas-generation testing performed by Dave Barber, ANL-W, found higher than expected rates of hydrogen generation.[3] Barber also found that the rate diminished over time.

[1] The CH-TRAMPAC of the SAR describes the G Value as the gas generation potential of a waste material type (quantified by the "G value" for hydrogen, which is the number of molecules of hydrogen generated per 100 electron volts (eV) of energy absorbed).

In late 2001, Rocky Flats tested 8 drums of the OASIS waste at room temperature and found that the hydrogen generation was extremely low. It was hoped that this trend would also be seen during the elevated temperature tests. In late 2001 and 2002, limited full-drum elevated-temperature testing performed at INEEL and Rocky Flats shattered this hope by showing that nearly 50% of Type-IV drums may exceed the current TRUPACT-II limits:

- roughly 15% failed for hydrogen generation only
- roughly 30% failed for total gas generation only
- roughly 5% failed for both.

Even though Barber’s small-scale gas-generation tests showed that higher rates of hydrogen generation were an issue, the limited full-scale (drum) testing resulted in the highest rate of failures due to the total gas-generation rather than hydrogen generation.

In May of 2001, Rocky Flats hosted a meeting of several TRUPACT-II and gas-generation experts to discuss the findings from the limited testing performed at Rocky Flats and INEEL and to develop a theory as to why the waste was behaving the way it was and recommend management options.

The experts speculated that the drums might have been failing for total gas generation rate because the samples were being taken too soon in the heat-up cycle and that the waste and the test canisters had not yet reached a steady state condition. The group felt confident that longer-term testing (i.e. extended testing) would demonstrate that both the internal drum pressure and the hydrogen generation rates would not continue to build-up to unacceptable levels.

The original testing period for the heated test was approximately five days, in which the first sample was taken after 66 hours and the second 42 or more hours later. The original purpose of the extended test was twofold, first to demonstrate that the total gas generation rate would decrease over time once the waste matrix reached thermal equilibrium, and second to help Rocky Flats determine how to adjust the testing protocols for production. It was also believed that data gathered from the extended tests would result in enough positive data to allow Rocky Flats to certify the entire population of drums based on the testing of a statistically representative sampling of the population (Long-Term Objective). Originally, the extended duration testing was to occur at Argonne National Laboratory-West (ANL-W) using Rocky Flats generated drums that were stored at the INEEL site. However, due to funding and schedule constraints, the ANL-W testing did not occur. Instead, Rocky Flats initiated limited scope extended duration tests.

Rocky Flats, and others, were convinced that the extended duration testing would demonstrate that the waste, if tested under the right conditions, would meet existing total gas and hydrogen/methane gas generation limits. This turned out not to be the case.

Extended Testing

The gas-generation testing systems consist of a simple heated stainless steel bell-jar/canister that can isolate and heat a drum. The canister is fitted with sampling ports that allow for the sampling of the gases and measurement of the pressure built up within the canisters. The Rocky Flats Program used a gas chromatograph and a calibrated pressure transducer to measure hydrogen and the pressure within the canister. The hydrogen generation rate is calculated from the difference in the hydrogen concentration in the canister between the first and second gas sample. The total gas generation rate is calculated from the change in pressure between the first and second measurements according to the equation $n_2 - n_1 = V^*(P_2 - P_1)/RT$. Where the gas is assumed to behave as an Ideal Gas, n is the number of moles of gas, V is the void volume of the canister, R is the Gas Constant, T is the temperature, and P is the measured pressure in the canister. The Program utilizes a WIPP approved computer model to calculate both the hydrogen and total gas-generation rates and determine if the measured rates meet or exceed the allowable TRUPACT-II limits.

Nearly 90 drums of Type-IV waste were tested for extended periods of time under the Heated Gas-Generation Testing procedure. The initial batches were tested for 20 days with subsequent batches tested for even longer durations. Multiple gas samples were taken and internal pressure was monitored during the test period to determine the hydrogen and total gas-generation rates over time.

Observations from Extended Testing

Two general observations were made. First, the waste generally appeared to reach thermal equilibrium after 5 days rather than the 66 hours as established in the original testing protocols, and second, in many cases, the hydrogen generation rate did not reach a steady state condition until well after the waste reached a thermal steady-state. In several cases, the hydrogen generation rate was still increasing after 30 days.

As predicted, the total gas generation rate reached a relatively constant value near zero typically by the fifth day. This was indicated as the pressure within the canisters leveled off after a relatively sharp increase for the first two to three days of heating.

The second and more surprising observation was associated with hydrogen generation rates. In the small-scale testing of real waste performed at ANL-W, Dave Barber observed that the hydrogen generation rate would initially increase as the sample was being heated then level off as the waste reached thermal steady-state condition, and then decrease and approach zero over a short period time (5 to 7 seven days). The observed peak rate was much higher than anticipated. Barber postulated that the unexpectedly high initial rates of hydrogen generation were being driven by a series of complex oxygen and heat-dependent chemical reactions rather than radiolytic reactions. It was anticipated that full-drum testing would behave in the same manner as Barber's small-scale tests.

However, the initial drum-scale tests performed for approximately 20 days showed that in many cases the hydrogen generation rate actually increased over long periods of time. Under the 20-day tests, several drums continued to show an increase in the hydrogen generation rate; roughly 15 days after the waste reached a thermal steady-state condition. In fact, in some cases, the rate appeared to increase exponentially rather than linearly. In other cases, the drums showed a decrease in the rate over time as anticipated.

The inconsistent results led the Rocky Flats team to initiate another series of even longer-term tests. In general, the longer-term tests did provide additional support to the theory that the rates would level off, and possibly even decrease over time. However, there were still two drums in which the hydrogen rates were still increasing slightly after 36 days of testing. It should be noted that these two drums were considered low-generators, meaning the rates of hydrogen generation were roughly an order of magnitude lower than the allowable 60-day rate.

Drum corrosion was another important observation that was noted during these extended tests. A number of drums that had increasing or fluctuating hydrogen generation rates also showed signs of corrosion at the completion of the tests. In some cases the drums had to be overpacked because of container integrity concerns.

Free liquids were found inside the canisters as the canisters were being unloaded in a number of tests. In some cases, the liquid was clear and evaporated after several minutes of ventilation. In other cases, the liquid was rusty looking and in one case the liquid was black. Typically, the rusty looking liquid had a low pH, while the clear and the black liquid did not register a pH, thus presumed to be a volatile organic compound.

Another interesting observation was that the hydrogen generation rates quickly decrease after the canister had been purged with nitrogen. The Rocky Flats Fire Protection Engineering organization initially established a 1% hydrogen by volume (1% hydrogen) operational control limit for the gas-generation-testing program. When the hydrogen concentration within the canister approached the 1% limit, the canister was vented and purged (V&P) with nitrogen to reduce the hydrogen concentration and the testing was continued. It was quickly noted that in almost every case where the V&P occurred, the hydrogen generation rate quickly decreased and continued to decrease until the test was terminated.

10-Day Production Testing

Based on the information derived from the extended testing and an understanding of the new conditions in Rev. 20, Rocky Flats decided that the only way that it could meet the TRUPACT-II transportation requirements was to plan on using the special condition 10-day transport period and to test each drum to the full 10-days.

Rocky Flats had 36 drum sized canisters and 4 overpack sized canisters (85-gallon drum) and established a two week testing regime, which entailed the unloading/loading of drums into the canisters, the heating and sampling of the canisters, and the termination and cooling of the canister prior to unloading. Typically, two sets of samples would be taken during the two-week period.

The typical testing sequence went as follows:

Unloading and loading of the canister	1st Monday and Tuesday.
Isolation of canisters and initiation of test	1st Tuesday afternoon.
Leak test and monitor	1st Wednesday
Monitoring of temperature and pressure	daily
First Sampling	2nd Tuesday (after 7 days of heating)
Second/Final Sampling/termination	2nd Friday

Based on previous observations, Rocky Flats made a conscious decision not to test overpacks even though the program had been audited and approved by CBFO. Instead, Rocky Flats developed and implemented a project to repackage all overpacked drums into new drums. In addition to the overpacks, Rocky Flats also decided to repackage any drum with liquids and any drum that required the elimination or reduction of confinement layers in order to meet the 10-day gas-generation rate limits. Nearly a third of the inventory ended up being repackaged.

[NOTE: Liquid mitigation was accomplished by using a custom blend of super-adsorbent (N962) produced by Nochar, Inc and distributed by UltraTech International. The blend was formulated to adsorb and solidify both organic and aqueous based liquids. Most commercial adsorbent products are made specifically for aqueous or organic, but not both.]

Based on the extended testing, it was suspected that there would be some drums that would challenge even the 10-day rate limit. So, the repackaging process was designed to result in a drum configuration that would allow for the highest allowable gas-generation limit for a drum. To accomplish this, the rigid liner containing the waste was removed from the original drum and placed into a new drum with no additional liner bags. If the original waste was contained in liner bags, the bags were slit to eliminate them as a confinement layer. Additionally, the original rigid liner lid was not replaced. Therefore, the resulting drum was considered to have zero layers of confinement.

The overall hydrogen build-up within the canisters during the 10-day test challenged the Project's ability to complete a full test run. The original program had an administrative control limit of 1% hydrogen within the canister. After the first sampling, if the hydrogen concentration within the canister exceeded 1% hydrogen, the test had to be terminated and the canister vented and purged. If the test run could not be completed a gas-generation rate could not be established and the drum could not be certified. This limitation definitely became an issue during extended test, but was also a constraint for the 10-day production test. Ultimately, the program was able to get an Operations Order (Ops Order) approved, which allowed for continued testing as long as the hydrogen concentration was less than 2.5% and that the calculated generation rate did not exceed 1.97E-07 mole/second. There were a few cases where the test had to be terminated due to exceeding the Ops Order conditions. In these cases, the drums were re-tested using the overpack sized bell-jars, which had a larger void volume between the drum and the bell-jar.

General Results 10-day Testing
Ultimately, all Type-IV waste drums were certified under the 10-day shipping period. Hydrogen gas generation rates ranged from essentially non-generators (0 m/s) to a few that exceeded the 10-day rate, even with zero-layers (1.2E-07 m/s).

Table I, Results of a Typical Test Batch, provides a good example of the results of a typical test batch. This test batch had several drums with a negative hydrogen rate (listed as zero “0”) and several with hydrogen generation rates that exceeded the 10 day limit, as originally configured and tested. It also shows that many drums also had negative total gas generation rates as well.

Table I. Results of a Typical Test Batch

Tested Drum	H2_Rate	Total_Rate	Pass/Fail	10-Day Ship Cat	10-Day 0 layers	H2 Initial PPM	H2 Final PPM	Initial Press/torr	Final Press/torr
D58529	4.55E-08	1.67E-07	Fail(H)	Pass	Pass	1218	4898.6	711	715
D66285	2.86E-08	-2.62E-08	Pass	Pass	Pass	1105.2	3224.7	778	777
D67661	3.44E-08	-4.64E-07	Pass	Pass	Pass	1597.5	4330.3	728	709
D68988	6.22E-09	-5.41E-07	Pass	Pass	Pass	522	1024.3	694	675
D68993	5.77E-09	-6.03E-07	Pass	Pass	Pass	729.4	1182.4	726	705
D70196	5.22E-08	4.94E-07	Fail(H)	Pass	Pass	4832.5	8346.1	859	881
D70202	6.59E-08	1.06E-06	Fail(H)	fail	Pass	1540.5	4282.1	760	788
D70433	4.75E-08	3.65E-07	Fail(H)	Pass	Pass	8034.1	12027.5	754	765
D71326	1.02E-07	-5.65E-07	Fail(H)	fail	Pass	11657.5	17960.6	942	921
D72289	3.78E-08	-1.39E-07	Fail(H)	Pass	Pass	2025.6	4548.7	867	862
D72796	2.6E-08	-7.91E-08	Pass	Pass	Pass	1656.8	3471.6	827	824
D93683	3.76E-08	-2.95E-07	Fail(H)	Pass	Pass	1128.5	2740.9	668	658
D99553	1.68E-09	-8.71E-08	Pass	Pass	Pass	0	121.1	803	800
DA2206	1.86E-09	-1.3E-07	Pass	Pass	Pass	0	139.1	764	760
DC1206	2.4E-09	1.74E-07	Pass	Pass	Pass	0	165.4	839	842
DC2428	1.17E-09	5.91E-08	Pass	Pass	Pass	0	88.9	756	758
DC4906	7.81E-10	-1.06E-07	Pass	Pass	Pass	152.9	210	789	788
DC7161	1.4E-09	8.13E-08	Pass	Pass	Pass	270.5	366.1	827	830
D76200	3.02E-09	-4.03E-07	Pass	Pass	Pass	356.1	568.1	826	809
DD6550	1.26E-09	-8.05E-08	Pass	Pass	Pass	140	253.3	648	645
DD6551	7.69E-10	7.08E-08	Pass	Pass	Pass	176	233.5	773	771
DD6029	0	2.19E-07	Pass	Pass	Pass	232.3	127.6	808	818
DD6030	4.15E-10	3.98E-07	Pass	Pass	Pass	334.8	362.5	855	872
D76784	0	2.01E-07	Pass	Pass	Pass	739.2	638	797	802
D72591	1.17E-08	4.96E-07	Pass	Pass	Pass	1684.6	2449.4	886	904
D67430	1.25E-08	-5.22E-08	Pass	Pass	Pass	1087.3	2038.6	757	755
D72981	7.68E-08	4.7E-07	Fail(H)	fail	Pass	7607.6	12934.7	833	850
D71932	6.45E-09	-2.79E-07	Pass	Pass	Pass	308.7	781.8	767	761
D72982	6.63E-08	5.09E-07	Fail(H)	fail	Pass	6431.2	10845.6	873	889
D93688	7.48E-09	2.88E-08	Pass	Pass	Pass	409.9	932.6	824	825
D93681	7.43E-09	7.08E-07	Fail(T)	Pass	Pass	239.7	535.5	718	739
D67706	1.09E-08	-7.83E-07	Pass	Pass	Pass	683.7	1563.4	713	693
D71144	1.74E-08	-9.46E-08	Pass	Pass	Pass	1231.8	2428.7	837	834
D76867	6.09E-08	3.32E-07	Fail(H)	fail	Pass	5884.7	10074.3	838	853
D69831	3.94E-08	-2.52E-07	Fail(H)	Pass	Pass	2868.4	5636.4	826	817
D68264	4.39E-09	1.17E-07	Pass	Pass	Pass	167.1	348.2	697	696
DC4239	9.53E-10	-4.03E-08	Pass	Pass	Pass	170.5	240.7	763	764
DC2430	7.57E-10	-2.25E-07	Pass	Pass	Pass	456.8	511.8	795	787

D93683	3.9E-08	-4.39E-07	Fail(H)	Pass	Pass	1128.5	1978.7	668	660
D70202	7.2E-08	0.0000016	Fail(H)	fail	Pass	1540.5	3055.2	760	779
D93681	8.3E-09	7.6E-07	Fail(T)	Pass	Pass	239.7	407.8	718	726
D68264	0	7.92E-08	Pass	Pass	Pass	167.1	139.9	697	696

Drums highlighted in yellow exceeded the 10-day limit as configured. These had to be repackaged with zero layers of confinement in order to meet the limit. "f(T) = failed for total gas, "f(H)" = failed for Hydrogen/methane.

Table II, General Results of the Type-IV Waste Gas Generation Testing Program, provides the general results of the gas generation program– note the numbers may not be exact

Table II. General Results of the Type-IV Waste Gas Generation Testing Program

Number of Type-IV	Passed 60 day	Failed 60 day H2/Total	Failed 1-yr Total limit	Pass 10 day/2 layers	Pass 10 day/1 layer	Pass 10 day/0 layers	Pass 60 day
700	553	126	21	69	36	21	21

All the drums that exceeded the 10-day hydrogen limit were eventually repackaged into new drums with zero layers of confinement.

The numbers presented are some what misleading. Rocky Flats was eventually able to certify all drums, but in many cases it required a drum to be repackaged and re-tested in order to get the drum to pass. Rocky Flats performed nearly 900 10-day tests in order to qualify the 700 drums. In a few cases, besides repackaging with zero layers of confinement the drum had to be fitted with a high diffusion (5X) drum filter in order to meet the 10-day drum limit.

Another interesting observation was that in some cases, drums tested multiple times actually had increases in hydrogen generation rates. This was primarily observed in non-repacked drums, however it was also observed in a small number of repacked drums. In other cases, non-repacked drums tested multiple times showed a decrease in the hydrogen-generation rates

Drums tested before and re-tested after repack always showed a decrease in the hydrogen generation rate —at least with the 10 drums that actually had before and after test data.

THOUGHTS

Due to the fact that the Rocky Flats Gas-Generation Testing Program was designed as a production process and not a research project, the information gathered from extended testing performed by Rocky Flats is not rigorous enough to be used to develop and defend any scientific conclusion. Thus, this paper concludes by presenting some general thoughts.

First and foremost, with the wide range of results seen in the testing of the Type IV waste, WIPP was correct in its decision not to attempt to establish a "G-Value" for the Type-IV waste streams.

Second, Dave Barber's suspicion that the unexpected hydrogen generation rates produced from these wastes were the result of oxygen-dependent chemical reactions may have merit. However, his thoughts on how fast the oxygen would be consumed may have been off only because he did not factor in other potentially contributing reactions, such as drum corrosion, into his postulation. Barber's tests were solely focused on the behavior of the waste and not the waste and drum as a whole system.

Rocky Flats now believes that corrosion of the drums does contribute to the overall hydrogen generation. This would explain why the hydrogen generation rate would increase over time or when a drum was tested multiple times and why the rate would decrease when repackaged into a new drum.

It has been well accepted throughout the DOE Complex that radiolytic and/or chemical decay of chlorinated hydrocarbons, such as carbon tetrachloride, will produce free radicals of hydrogen and chlorine, which can recombine and produce hydrochloric acid (HCl) vapors in the head-space of the drum. Additionally, with cemented waste, such as the OASIS waste, moisture will also be produced. The HCl and moisture could combine and condense out and produce HCl liquid that will attack the mild-steel drum. The addition of heat during the testing cycle simply accelerates the oxidation/corrosion process, which also generates hydrogen. Rocky Flats also suspected that somewhere in the system, oxygen was being produced at a rate slightly less than the rate of consumption required. This could involve the water, which could disassociate and produce hydrogen and oxygen.

Rocky Flats had been told by several experienced chemists that we could be seeing the result of a series of complex catalytic and electrolytic interactions occurring between the waste, the headspace gases, and the mild-steel drum, which are again accelerated by heating.

Rocky Flats believed that they may inadvertently demonstrated Barber's postulation that an oxygen dependent chemical reaction contributed to the hydrogen generation rate when we vented and purged the systems to reduce the hydrogen concentration in the canisters. As mentioned above, after venting the canister, we purged with nitrogen and restarted the run. In most cases, the hydrogen generation rate dropped off quickly. Rocky Flats now suspects that they artificially depleted the oxygen, as well as the hydrogen, by venting and purging the canisters with nitrogen. Unfortunately, the analytical system was not set-up to analyze for oxygen, therefore no direct data was collected to support this thought.

The observed liquids are probably the easiest to explain. At the test temperature, the volatile organic compounds and moisture contained in the waste are driven off the waste and into the headspace of the drum and canister until it reaches equilibrium. Once the test is terminated and the canister cools, the gases condense out at the coolest area of the canister, the base plate. The rusty looking, low pH liquid is quite possibly HCl (as explained above). The clear liquids, which simply evaporated after a few minutes of ventilation, could have been VOCs like carbon tetrachloride or trichloroethane. The black liquid was most likely an organic liquid attacking and deteriorating the black o-ring material.

All drums of type-IV waste were shipped to WIPP once they were certified as meeting all the applicable TRAMPAC WIPP Waste Acceptance Criteria requirements.

REFERENCES

1. TRUPACT-II Safety Analysis Report, Revision 19
2. TRUPACT-II Safety Analysis Report, Revision 20
3. Observations of Excessive Hydrogen from Transuranic Waste Type IV Solidified Organics, D. Barber, K. Carney, and J. Demirgian, 2002.