*Application of Cryogenic Grinding
to Achieve Homogenization
of Transuranic Wastes*

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CONTENTS

	Page
LIST OF FIGURES	vii
LIST OF TABLES	xi
GLOSSARY OF TERMS	xiii
EXECUTIVE SUMMARY	xv
ABSTRACT	1
1. PARTICLE SAMPLE SIZE	3
1.1. Objective	3
1.2. Equipment Design and Materials Selection	3
1.3. Analysis Methods	4
1.4. Sampling Methods	6
1.5. Materials Test Results	7
1.6. Conclusions	15
2. VOLATILITY OF ORGANIC COMPONENTS OF SELECTED MATERIALS	17
2.1. Objective	17
2.2. Equipment Design and Selection	17
2.3. Materials Studies	21
2.4. Experimental Test Plan	23
2.5. Conclusions	44
3. GLOVEBOX OPERATIONS	45
3.1. Objective	45
3.2. Glovebox Pressure Tests	45
3.3. Glovebox Filter-Shredding Tests	54
3.4. Thermal Stress on Glovebox and Components	64
3.5. Conclusions	66
APPENDICES	
A. Paper submitted to American Glovebox Society: Cryogenic Liquid Introduction System for Gloveboxes	A-1
B. Paper submitted to American Glovebox Society: Demonstration of a Cryogenic Grinding System in a Glovebox	B-1

FIGURES

	Page
1-1. Schematic of laboratory-scale mixer for testing particles of various sizes.....	4
1-2. Mixer and 0.125-in. material.....	6
1-3. Separation of materials in beaker of water.....	7
1-4. Confidence interval for 0.125-in. particles	14
1-5. Confidence interval for 0.25-in. particles	14
1-6. Confidence interval for 0.375-in. particles	15
2-1. Shredder and mixer assembly	18
2-2. Instrumentation system	19
2-3. Inficon Model 200 Residual Gas Analyzer (RGA).....	19
2-4. Volatile Organic Sampling Train (VOST).....	20
2-5. Schematic of the VOST	21
2-6. Vapor pressure vs temperature for solvents of interest in Rocky Flats Environmental Technology Site (RFETS) contaminated wastes.....	22
2-7. System setup for testing of volatility of solvent-contaminated materials at RFETS.....	24
2-8. Spectral signal for methylene chloride (CH_2Cl_2).....	24
2-9. Spectral signal for CH_2Cl_2 with the predominant peak at mass 49 expanded	25
2-10. Spectral signal for trichlorofluoroethane ($\text{CCl}_2\text{F}-\text{CClF}_2$ [R113]).....	25
2-11. Spectral signal for $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113) with predominant peak at mass 101 expanded	26
2-12. Spectral signal for carbon tetrachloride (CCl_4).....	26
2-13. Spectral signal for CCl_4 with the predominant peak at mass 117 expanded.....	27
2-14. Comparison of signal levels of materials tested.....	28
2-15. Vapor pressure data for CH_2Cl_2	29
2-16. Vapor pressure data for $\text{CCl}_2\text{F}-\text{CClF}_2$	29

FIGURES (continued)

	Page
2-17. Vapor pressure data for CCl_4	30
2-18. Correlation data for ppm levels of CH_2Cl_2	31
2-19. Performance data for CH_2Cl_2	33
2-20. Performance data for $\text{CCl}_2\text{F}-\text{CClF}_2$	34
2-21. Performance data for CCl_4	34
2-22. Evaporation rate of CH_2Cl_2 in oily cloth matrix	35
2-23. Sample LabVIEW [®] template during data collection	36
2-24. Locations for sampling volatile organic compounds (VOCs) during cryogenic grinding	37
2-25. Strip-chart data for cloth material	39
2-26. Strip-chart data for Tyvek [™] material	39
2-27. Shredder temperatures during test operations with Tyvek material	40
2-28. Shredder temperatures during second three test operations with Tyvek material	41
2-29. Shredder metal and gas temperatures during Tyvek material test operations	41
3-1. Los Alamos-developed system for introducing high-flow-rate gaseous nitrogen (GN_2) into a glovebox	46
3-2. Plot of ventilation capacity of glovebox with the system installed for introducing GN_2	47
3-3. Nitrogen boiloff from a 20-cm × 20-cm pan	48
3-4. Nitrogen boiloff from a 20-cm × 30-cm pan	48
3-5. The model-predicted rate of nitrogen gas generation from a liquid nitrogen (LN_2) spill	49
3-6. Model-predicted values for nitrogen boiloff rate vs spill area	50
3-7. Model-predicted values for nitrogen vapor generation rate as a function of spill area	50

FIGURES (continued)

	Page
3-8. Locations of sensors for acquiring pressure and temperature measurements during the spill tests	51
3-9. Differential pressure vs time for LN ₂ spill 1 (test) in the glovebox	52
3-10. Temperature vs time for LN ₂ spill 1 (readings 1 through 4). Measurements were made at selected glovebox locations.	52
3-11. Temperature vs time for LN ₂ spill 1 (readings 5 through 8). Measurements were made at selected glovebox locations	53
3-12. Results of cooldown of water-saturated filter element by submersion in LN ₂	54
3-13. The LN ₂ feed system for cryogenic grinding in a glovebox	55
3-14. Schematic of dewar connection	56
3-15. Schematic of glovebox connection	56
3-16. Schematic of manifold	57
3-17. The LN ₂ glovebox dewar and spill containment pan	57
3-18. Modified ice shaver that served as a shredder to demonstrate cryogenic grinding in a glovebox	58
3-19. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 3	59
3-20. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 3 (readings 1 through 4)	59
3-21. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 3 (readings 5 through 8)	60
3-22. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 4	60
3-23. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 4 (readings 1 through 4)	61
3-24. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 4 (readings 5 through 8)	61
3-25. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 5	62

FIGURES (continued)

	Page
3-26. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 5 (readings 1 through 4).....	63
3-27. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 5 (readings 5 through 8).....	64
3-28. Plot of von Mises stress vs time for a LN ₂ spill in a glovebox	65
3-29. Graphic representation of glovebox temperature distribution during an LN ₂ spill.....	65
3-30. Graphic representation of glovebox stress distribution during an LN ₂ spill	66

TABLES

		Page
1-1.	Statistical Symbols and Terms.....	5
1-2.	Results of Paper Mixing Test 1.....	8
1-3.	Results of Paper Mixing Test 2.....	9
1-4.	Results of Bean Mixing Test 1.....	10
1-5.	Results of Bean Mixing Test 2.....	10
1-6.	Results of Mixing Test for 0.125-in. Particles.....	11
1-7.	Results of Mixing Test for 0.25-in. Particles.....	12
1-8.	Results of Mixing Test for 0.375-in. Particles.....	13
2-1.	Material Mixes for Volatility Tests.....	32
2-2.	Mixed-Matrix Materials in Shredder and Mixer and RGA Signals.....	38
2-3.	Results of Gas Chromatography Analysis of Shredded Cloth Samples	42
2-4.	Results of Gas Chromatography Analysis of Shredded Tyvek™ Samples	43
2-5.	Results of Gas Chromatography Analysis of Solid Samples.....	43

GLOSSARY OF TERMS

AO	always open
$\text{CCl}_2\text{F}-\text{CClF}_2$ (R113)	trichlorotrifluoroethane (R113)
CCl_4	carbon tetrachloride
cfm	cubic feet per minute
CHCl_3	chloroform
$\text{CH}_2:\text{CHCl}$	vinyl chloride
CH_2Cl_2	methylene chloride (dichloromethane)
CH_3Cl	methyl chloride (chloromethane)
CST	Chemical Science and Technology (Division)
CRC	<i>CRC Handbook of Chemistry and Physics</i>
DESO	double-end shutoff
DOE/RFFO	Department of Energy Rocky Flats Field Office
DP	differential pressure
ESA	Engineering Sciences and Applications (Division)
GN_2	gaseous nitrogen
HEPA	high-efficiency particulate air
ksi	1000 pounds per square inch
LANL	Los Alamos National Laboratory
LN_2	liquid nitrogen
NC	normally closed
NIST	National Institute of Standards and Technology
NMT	Nuclear Materials Technology (Division)
NO	normally open
PID	proportional integral derivative
ppm	parts per million

GLOSSARY OF TERMS (continued)

PRV	pressure relief valve
RFETS	Rocky Flats Environmental Technology Site
RGA	residual gas analyzer
scfm	standard cubic feet per minute
TA-55	Technical Area-55, often used as shorthand for the Los Alamos Plutonium Facility
TCLP	total concentrate leachate procedure
VOC	volatile organic compound(s)
VOST	Volatile Organic Sampling Train
WC	water column

EXECUTIVE SUMMARY

Staff from the Nuclear Materials Technology (NMT) and the Engineering Sciences and Applications (ESA) divisions at Los Alamos National Laboratory (LANL) collaborated with staff from the Department of Energy Rocky Flats Field Office (DOE/RFFO) and the National Institute of Standards and Technology (NIST) at Boulder, Colorado, to develop and refine the technology needed for safe and effective processing of actinide-containing solid waste at the Rocky Flats Environmental Technology Site (RFETS).

LANL contributions were fourfold. Task 1 was to demonstrate the effectiveness of a one-sixth-scale mixer (relative to a mixer outlined in a related NIST report¹) and to determine the optimal particle size for achieving a homogeneous mix of particles. Task 2 was to determine whether operation of the shredder/mixer at below the industry standard temperature of -40°C would be required to prevent volatile materials from escaping the five predetermined oily matrix materials. Tasks 1 and 2 followed the code of federal regulations (40 CFR 7.1.3) and solid waste regulations (SW-846) for sampling wastes. Task 3 was to demonstrate, by both modeling and experimentation, safe cryogenic grinding in a glovebox. Task 4 was to prepare a report on our findings.

Five mixed-matrix materials representing the types of contaminated waste common at RFETS were selected as test materials for the development of the processes. These materials were Kimwipes[®], rubber gloves, cloth coveralls, Tyvek[™] coveralls, and plastic drum liners.

Task 1—Homogeneity of particle mix. The objectives of Task 1 were threefold:

- To determine the optimal size of particles for a 10-g sample that will be used to determine the contents of a 55-gal. drum;
- To evaluate the effectiveness of different mixing and sampling schemes in producing a homogenous mixture in a representative 10-g sample; and
- To perform laboratory-scale tests with results that can be extrapolated to expected operations-scale conditions.

Samples of the five matrix materials were shredded to nonuniform pieces approximately 0.125 in., 0.25 in., and 0.375 in. in diameter and mixed in the one-sixth-scale mixer constructed along the designs of the NIST mixer. For comparison purposes, single-matrix materials, specifically, paper and beans, were subjected to the same tests as the selected mixed-matrix materials. For each test, the theoretical (statistical) result for an 80% confidence interval was compared with the experimental result. Test results for the

¹ J. D. Siegwarth and J.A. Scott, "Cryogrinding Process Update," National Institute of Standards and Technology report (February, 1995).

0.375-in. particles were closest to the theoretical results, although test results for the 0.125-in. particles were comparable. Test results for the 0.25-in. particles were farthest from the theoretical results. The design of the paddle-wheel mixer apparently favored mixing the larger 0.375-in. particles and the smaller 0.125-in. particles. It is speculated that the clearances between the paddles and the housing must be set specifically to establish the optimum mixing for the particle sizes being mixed. The amount of material in the mixer and the paddle orientation also influence the mixing effectiveness. In our experimentation, it just happened that the conditions were such that the mixing effectiveness favored the larger and smaller sizes.

Because the paddle-wheel mixer did make a homogeneous mixture of both the single- and mixed-matrix materials, it will suffice to produce the needed homogeneous samples of waste. The sample size that a shredder will need to provide to the mixer will be dependent on the design of the mixer, as was demonstrated; but the design can favor a larger particle size, thereby reducing the amount of shredding necessary.

Task 2—Optimal temperature for operation of shredder/mixer. Because the mixed-matrix materials often contain volatile elements in the form of organic-species solvents, an optimal operating temperature for the shredder/mixer—a crucial design criterion—was required. Specifically, we needed to determine whether the shredder/mixer should be operated below the industry standard of -40°C to keep the volatile contents from escaping the mixed-matrix materials. The -40°C temperature is crucial because standard industrial equipment is operable at this temperature, but operation below this temperature requires using cryogenic components in place of bearings and similar parts.

The use of a residual gas analyzer (RGA) greatly enhanced the work on Task 2. The RGA facilitated the performance of a much larger variety of tests (including the temperature dependencies) requested by the DOE/RFFO staff as the project progressed and made possible the acquisition of a much greater amount of data than had been planned. This instrument is a mass spectrometer that can be used to observe gaseous species in the lower-mass ranges. The RGA provided data over a range of temperatures in the different oily matrices. We also measured the vapor pressures as a function of time. Gas and solid samples taken during the shredding and mixing process were analyzed by Chemical Science and Technology (CST) Division staff at Los Alamos. RGA samples taken during these tests were calibrated to parts-per-million (ppm) levels to estimate the amount of volatile organic material present. Because the concern about operating temperature is based on the volatility of the solvents in the mixed-matrix materials, we compared their vapor pressures at sea level with those at the higher altitudes of Los Alamos and Rocky Flats. This comparison was made to determine the effect of the oily matrices on the volatility of the solvent.

A comparison of vapor pressure measurements obtained by the RGA to vapor pressure measurements values in the literature indicated significant differences. Such differences were expected because the shredder/mixer is a dynamic system that disturbs the equilibrium, whereas the literature values are acquired at established equilibrium.

However, test results enabled us to establish the sensitivity of the RGA as in the range of the tens or hundreds of ppm, depending on the specific solvent species.

Experiments to determine the vapor pressures of the solvents in the various oily matrix materials indicated that the vapor pressures vary depending on the solvent species. However, vapor pressures are still significant at the low temperatures at which the experiments were conducted. For example, at -40°C the RGA signal intensity for methylene chloride (CH_2Cl_2) alone is about 9×10^{-10} , whereas for the oily Kimwipes[®] matrix it is about 1.5×10^{-10} , but the vapor concentration is still on the order of 8,000 ppm above the oily matrix.

Our next set of tests for CH_2Cl_2 in the oily cloth matrix was to determine the vapor pressure as a function of time for room temperature and at -50°C . The boiling point of CH_2Cl_2 is above room temperature. After 5 min at room temperature, the vapor pressure is reduced by an order of magnitude. As a comparison, it takes approximately 30 min to obtain a similar result for -50°C . Since the solvent concentration can be related directly to the vapor pressure, the lowering of the vapor pressure equates to a loss in concentration in the matrix. This argument also follows from the higher vapor pressure at -50°C at later times compared to the room temperature plot.

Additionally, we checked the vapor pressure of CH_2Cl_2 in the five matrices and Freon R113 for oily Kimwipes[®] that had been standing in unsealed plastic bags for 20–48 h. After these time periods, no mass spectra could be obtained. (For CH_2Cl_2 , the sensitivity is on the order of 20 ppm; and for Freon [$\text{CCl}_2\text{F}-\text{CClF}_2$] R113, the sensitivity is about 200 ppm.)

The cryoshredder that we built to do the volatility studies was combined with the paddle-wheel mixer used in Task 1. Temperatures were measured with thermocouples placed in numerous positions, and data were collected using LabVIEW[®] software. A template of the LabVIEW screen displays on the computer screen temperature measurements with thermocouple placement during the experiments. Strip chart-type data output is captured during the test and then plotted. Sampling for the volatile solvent and the solvent in the solid followed a procedural process for sampling that was dictated by CST personnel. We ran two spiked samples through this procedure. ("Spiked" refers to adding a known amount of a volatile organic compound to solid materials and mixing these together. After processing, the solid materials are analyzed to determine the effects of the organic compound.) The CST analysis for these results showed that the organic compounds were present in the solid matrix after the cryoshredding, but that the quantities were less than the original spiked materials. The analysis of the gas sample taken during the processing also showed large quantities of organic compounds. This confirmed the indication from the RGA during processing, which showed a significant solvent vapor pressure. So, there is a significant loss of solvent during the process.

In conclusion, it became obvious that there were separate regimes for the operation of the complete system that need to be considered in connection with this volatility concern. The RGA results show that in a very short period of time (5 min) at room temperature a significant amount of gas will be released from the oily matrix materials. This release of

gas occurs even when the solvents have boiling points above room temperature. Therefore, even though the cryogenic shredder may be operated at -40°C , there will be a significant amount of solvent material volatilized while opening the drums and bags and while performing the warmup of the matrix material for repackaging. This suggests that one needs to freeze constituents immediately, or at least as soon as possible. In any event, one will see a significant amount of vapor pressure for a large number of species at and below -40°C . Therefore, monitoring for solvents on-line, as part of the glovebox system, may be a way of capitalizing on the volatility of the organic solvents. One may be able to "screen" materials as they are processed in order to determine whether they should be analyzed for organics by the use of an RGA system.

It should be noted that the lower-boiling species that are less than room temperature (for example, methyl chloride CH_3Cl , which boils at -24.2°C) have such high vapor pressures that it was determined that they could not be effectively loaded into a matrix for testing. The CST personnel who performed the gas and solid testing, as well as other people throughout the Laboratory, were consulted in order to come up with an appropriate method to load these high-vapor-pressure species into the predetermined matrices. No such method was found. If we are to give further consideration to these low-boiling-point species, the exact matrix needs to be identified. It is probable that some of the species are generated by radiolytic decay of plastics. Another possibility is that the solvent may be a component in the production of the plastic. There may be other possibilities as well.

Task 3—Cryogenic demonstration in a glovebox. The objective of Task 3 was to do a cryogenic grinding demonstration in a glovebox in the Los Alamos Plutonium Facility (Building PF-4, Technical Area [TA]-55). As part of this demonstration, we split the tasks into two categories, experimental and modeling. The result of this effort will enhance future designing at RFETS of a system that includes many safety considerations. Experimental work at Los Alamos included the design and implementation of a pressure feedback liquid nitrogen (LN_2) introduction system into the glovebox, controlled gas pressurization tests inside the box, LN_2 spill tests in the glovebox, and actual cryogenic grinding of in-line flow-through HytrexTM filters in the glovebox. Modeling characterized the effect of the use of cryogenic LN_2 on glovebox negativity and on thermal-induced stresses. Analysis also predicted the thermal performance of the equipment for the expected operating conditions. All of the experimental work was used to confirm model predictions. A significant number of nonradioactive environment tests also were done before the cryogrinder was installed in the glovebox.

Calculations for the glovebox LN_2 introduction system are presented in Section 3 of this report. Basically, the LN_2 introduction system is controlled by the operator using cryogenic solenoid valves. The system senses a loss of pressure negativity in the glovebox and automatically closes these valves. As part of the LN_2 control in the glovebox, we constructed a dewar and a containment pan. The pan was designed, based on the modeling, to have a surface area of 2000 cm^2 . The limited surface area is discussed in the modeling part of this report.

The glovebox ventilation tests were done to determine the flow capacity of our glovebox; i.e., with our model, we could determine how much LN_2 could be spilled in the glovebox. Flow rate of gaseous nitrogen (GN_2) into the glovebox was as high as 35 standard cubic feet per minute (scfm).

LN_2 spill tests in the glovebox for our dewar size of 2 L (test volumes up to 1.5 L) resulted in negativity losses of about 0.1 in. of water in the 2000- cm^2 pan. These results are mainly used to confirm the model. For comparison, the glovebox total negativity is about 0.6 in. of water.

We did cryogenic grinding of 12 Hytrex filters. Three of these ground radioactive filters were sent for study to researchers in the field of combustibles. The other nine filters were disposed of as radioactive. The Hytrex filters come from processing and are moist. The freezing of a filter uses about 1 L of LN_2 . The filter is best ground at a temperature that is between 77 K and room temperature (293 K). The cryogenic grinding apparatus that was used in the glovebox was a modified snow cone machine. As with Task 2, we used LabVIEW® software and continuously obtained temperature and pressure readings for inside the glovebox. Some of this data is presented and interpreted in this report.

In conclusion, the glovebox tests confirmed the model calculations, and we demonstrated successfully and safely the use of such a system in a glovebox. Much of our data, experience, and the modeling will help the design and implementation of the RFETS cryogenic grinding system. Another result of our work is the discovery that the operating temperature for the cryogrinder was best between 77 K and 273 K. Therefore, one may base the operating temperature of the grinder on these results instead of basing it on volatility. When grinding the filters, we also observed a pressure gain caused by a significant release of GN_2 into the box. After grinding, the filter temperature was typically less than -50°C .

Other considerations that we were asked to investigate were the effect of the process on volume reduction and the use of the process as sample feed for alternatives to incineration. Some items, such as 2-L bottles, will show volume reduction; but the size of the particle produced will dictate the amount of reduction (i.e., a 0.375-in. particle is better for volume reduction than a 0.125-in. particle). In general, many matrices actually increase in volume for the various particle sizes. Alternatively, the particles generated from this process are much better, perhaps ideal, for combustible processes. A 0.125-in. size is probably better than a 0.375-in. size for these processes. Finally, it should be noted that this process can be modified for various purposes. For example, the process could provide small particles for hydrothermal or oxidation reduction processes.

In general, we accomplished our tasks. We demonstrated homogeneity; we studied the volatility of the volatile organic compounds (VOCs) at different temperatures for different matrices; and we performed a safe cryogenic operation in a radioactively contaminated glovebox. Moreover, we collected considerably more data/results than we initially expected.

APPLICATION OF CRYOGENIC GRINDING TO ACHIEVE HOMOGENIZATION OF TRANSURANIC MIXED WASTES

by

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ABSTRACT

This paper describes work done at Los Alamos National Laboratory (LANL) in collaboration with the Department of Energy Rocky Flats Field Office (DOE/RFFO) and with the National Institute of Standards and Technology (NIST), Boulder, Colorado. Researchers on this project have developed a method for cryogenic grinding of mixed wastes to homogenize and, thereby, to acquire a representative sample of the materials. There are approximately 220,000 waste drums owned by the Rocky Flats Environmental Technology Site (RFETS)—50,000 at RFETS and 170,000 at the Idaho National Engineering Laboratory. The cost of sampling the heterogeneous distribution of waste in each drum is prohibitive. In an attempt to produce a homogeneous mixture of waste that would reduce greatly the cost of sampling, researchers at NIST and RFETS are developing a cryogenic grinder. The Los Alamos work herein described addresses the implementation issues of the task. The first issue was to ascertain whether samples of the "small particle" mixtures of materials present in the waste drums at RFETS were representative of actual drum contents. Second, it was necessary to determine at what temperature the grinding operation must be performed in order to minimize or to eliminate the release of volatile organic compounds present in the waste. Last, it was essential to evaluate any effect the liquid cryogen might have on the structural integrity and ventilation capacity of the glovebox system. Results of this study showed that representative samples could be and had been obtained, that some release of organics occurred below freezing because of sublimation, and that operation of the cryogenic grinding equipment inside the glovebox was feasible.

1. PARTICLE SAMPLE SIZE

1.1. Objective

The objectives of Task 1: Particle Sample Size were as follows:

- To determine how the size of particles in a 10-g sample affects its usefulness in representing the contents of a 55-gal. drum;
- To evaluate the effectiveness of different mixing and sampling schemes in producing a homogeneous mixture and a representative 10-g sample; and
- To conduct laboratory-scale tests whose results could be extrapolated to operations-scale conditions.

We constructed a one-sixth-scale version of the National Institute of Standards and Technology (NIST) conceptual designed mixer and used it to mix various materials of the type and size expected to be encountered in actual use at Rocky Flats Environmental Technology Site (RFETS). By varying the mixing and sampling configurations, we gained insight into the optimal construction and operating parameters for a full-scale mixer.

After establishing a protocol for conducting the sampling and mixing processes, we conducted tests to quantify the accuracy and precision with which a sampling scheme could produce a representative sample. Although the total concentrate leachate procedure (TCLP) requires a sample of at least 100 g and may require two or three samples, we used a 10-g sample diluted in a 100-mL solution. Federal regulations (40 CFR 7.1.3) require particles smaller than 1 cm in their smallest dimension, and commercial shredders are unlikely to produce particles smaller than 0.0625-in. in diameter. A 10-g sample would probably contain no more than 450 particles of the required size¹. We conducted warm testing only for the first task and did not cryogenically cool the samples. Later sections of this report detail cryogenic grinding experiments and their results.

1.2. Equipment Design and Materials Selection

To obtain equipment to do the particle generation, mixing, and analysis, we first attempted to procure from a commercial vendor a shredder or granulator that could produce samples from the soft materials needed for the experiments. Contacts with a number of companies indicated that their equipment was high in cost (\$15,000 to \$22,000 for a small shredding unit) and limited in availability (delivery times ranged from eight weeks to many months). For these reasons, we asked Nelmor Company (whose cost and time estimates met our schedule and budget needs) to shred the materials we would supply. To evaluate the mixing characteristics of a paddle-wheel mixer being designed for the project, we used two office paper shredders to produce 0.0625-in. and 0.125-in. particles of paper, cloth, and Tyvek™ samples for the first mixer tests.

Using the design by Siegwarth¹, we constructed a laboratory-scale mixer from a cylindrical air compressor tank approximately 1 ft in diameter and 20 in. in length (see Fig. 1-1). We mounted four pairs of paddles along a shaft attached on the axis of the tank and installed a variable-speed motor to drive the shaft at various speeds. The paddles (4-in. by 4-in. square) were rotated to an angle of plus and minus 20 to 25 degrees with respect to their direction of motion. This rotation ensured that the sample materials would be pushed toward the center of the mixer as they were lifted and tossed.

Fig. 1-1. Schematic of laboratory-scale mixer for testing particles of various sizes.

Materials selected for testing were those that most commonly require disposal by the method under consideration. They were plastic drum liners, cloth coveralls, Kimwipes®, latex gloves (rubber), and Tyvek coveralls contaminated with a variety of solvents.

1.3. Analysis Methods

After each mixer run, we took several samples. We characterized each sample by determining the specified percentage of each of the materials in the sample. We evaluated the accuracy of sample measurements by comparing the mean measurement to the known value. If, as hoped, the sample estimates fell in a normal distribution, the sample mean would equal the population mean. Table 1-1 defines the relevant statistical symbols used in this analysis.

The precision with which sample measurements represent the known value is characterized by the confidence interval, which is represented by the error bars associated with the sample mean. Given a desired confidence of 80%, we calculated the interval around the sample mean that, 80% of the time, will contain the population mean. Chapter 9 of the relevant solid waste

¹ J. D. Siegwarth and J.A. Scott, "Cryogrinding Process Update," National Institute of Standards and Technology report (February, 1995).

regulation SW-846² calls for an 80% confidence interval for the purposes of evaluating solid wastes against regulatory thresholds.

As an example, the 80% confidence interval for plastic in a mixture with an average weight of 21.75% of total, using 6 samples, and with a sampling deviation of 1.118% is

$$\bar{x} \pm t_{n-1; \alpha/2} * s_{\bar{x}} = 21.75 \pm t_{5; .1} * \frac{1.12}{\sqrt{5}} = 21.75 \pm 1.476 * .5$$

(The variable t must be looked up in a t-distribution table.) Thus, there is 80% confidence that the percentage of plastic in the mixture is between 21.01% and 22.49%.

Table 1-1. Statistical Symbols and Terms

Symbol	Definition
x	Variable, such as the percentage of plastic in drum
x_i	Individual measurement of x (one sample)
μ	Population mean (true value of x)
n	Number of samples
$\bar{x}$	Mean of sample measurements
$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}$	Variance of sample
$s = \sqrt{s^2}$	Standard deviation of sample
$s_{\bar{x}} = \frac{s}{\sqrt{n}}$	Standard deviation of mean of sample
$\bar{x} \pm t_{n-1; \alpha/2} s_{\bar{x}}$	Confidence interval for μ , where t is from the t-distribution list

² "Sampling Plan," in *Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods*, 3rd edition, EPA Publication SW-846, 955-001-00000-1 (Washington, D.C.: Government Printing Office).

1.4. Sampling Methods

Samples consisting of particles in each of the three sizes produced by initial shredding were mixed. Approximately equal parts by weight of each type of material were randomly introduced into the mixer; thus the total sample in a given run was approximately 20% plastic drum liner particles, 20% cloth coverall particles, 20% Kimwipes particles, 20% latex glove particles, and 20% Tyvek coverall particles. The total amount of material in the mixer was typically just less than half the volume of the mixer. Visual inspection indicated that this amount of material provided the best agitation and mixing, for samples consisting of the larger-sized particles. However, adequate mixing of the 0.125-in. particles required larger quantities of the materials.

For each test, the mixer was run for 10 min at approximately 90 rpm. At the end of each mixing period, six 10-g samples were taken from the center of the mixer for each test. Figure 1-2 shows the mixer after mixing the 0.125-in. material.

The samples proved difficult for separating into the constituent materials. The materials were too fine to separate by hand, and the cloth particles were typically a fine lint that adhered to all other materials. After experimenting with different methods, we found that, because of differences in density (see Fig. 1-3), simply stirring the sample in a beaker of water caused the cloth and Kimwipes particles to sink to the bottom, while the Tyvek, latex, and plastic particles floated at the top. After removing the particles from the water and allowing them to dry, we could remove the latex by hand. Thus, we could separate the 0.25-in. and 0.375-in. samples into three components: cloth/paper, Tyvek/plastic, and latex. We were unable to separate the latex particles from the 0.125-in. samples, so these samples were separated into only two components: cloth/paper and Tyvek/plastic/rubber.

Fig. 1-2. Mixer and 0.125-in. material.

Fig. 1-3. Separation of materials in beaker of water.

1.5. Materials Test Results

The degree to which a sample represents the entire mixer contents can be determined by establishing its accuracy and precision. The accuracy of the sample is related to the difference between the sample characteristics acquired after mixing and the sample characteristics known before mixing. Precision is indicated by the standard deviation and confidence interval of assigned values of the pre- and post-mixing samples. Because the paper samples and the 0.125-in. samples had only two components after mixing, we performed calculations for one of the components and took the other to be symmetrical.

We chose the 80% confidence interval because it is specified by regulation (SW-846) for the purpose of evaluating solid wastes for chemical contamination, and we performed the calculation as required by the regulation. If the value is 2.08, as it is for the latex component of the 0.375-in. sample, there is an 80% probability that the true percentage of latex in the mixer is the sample mean (23.07%) plus or minus 2.08.

1.5.1. Paper Tests

Before receiving shredded materials from Nelmor, we used shredded paper particles, approximately 0.125 in. by 0.25 in., as mixing samples. After mixing known quantities of white and blue paper, we extracted 10-g samples from the mixer's center and manually separated them into white and blue constituents. We conducted several mixing tests with paper samples in order to set gross mixing parameters. By visually observing the mixing in progress, we were able to

vary mixer speed, paddle orientation, mixing time, and total amount of material in the mixer. After setting these mixer parameters, we conducted additional tests, extracted mixed samples, and manually separated the constituents. Results of paper mixing, shown in Tables 1-2 and 1-3, indicate good accuracy and precision—less than 2% variation from the true value. Mixing the paper for 5 min gave the best absolute accuracy.

Table 1-2. Results of Paper Mixing Test 1

<u>Mixer Contents</u>		
	(g)	(%)
White	807.3	85.60
Blue	135.8	14.40
Total	943.1	100.00

Sample	Weight of Sample		Percentage of Sample	
	White	Blue	White	Blue
1	8.696	1.346	86.60	13.40
2	8.737	1.268	87.33	12.67
3	8.617	1.325	86.67	13.33

$t(n = 3, 80\% \text{ confidence}) -1.886$

Precision

	White
Mean	86.87
Standard Deviation	0.40
80% Confidence Interval ($\pm$)	0.44

Accuracy

True %	85.60
Sample %	86.87
Difference	-1.26

Table 1-3. Results of Paper Mixing Test 2*

<u>Mixer Contents</u>		
	(g)	(%)
White	882.5	87.94
Blue	121.0	12.06
Total	1003.5	100.00

Sample	Weight of Sample		Percentage of Sample	
	White	Blue	White	Blue
1	9.088	1.373	86.88	13.12
2	8.956	1.408	86.41	13.59
3	9.002	1.109	89.03	10.97

t(n=3, 80% confidence)-1.886

Precision

	White
Mean	87.44
Standard Deviation	1.40
80% Confidence Interval (±)	1.52

Accuracy

True %	87.94
Sample %	87.44
Difference	0.50

*Shredded pieces of white and blue paper were mixed for 1 min at 90 rpm, after which mixing three samples were taken. The different-colored pieces were separated manually.

1.5.2. Bean Tests

Samples consisting of beans and peas offered a higher-density alternative to paper samples. Such samples are also easy to count. Because beans and peas weigh more than paper by volume, we did not fill the mixer to the same level we had used with paper. When sampling revealed that a 10-g sample would amount to only about 70 beans and peas, we conducted the test with 100-g samples. Results of bean and pea mixing, shown in Tables 1-4 and 1-5, indicate a definite lower limit on the number of particles needed to make up the sample. Table 1-4 shows the results for 10-g samples, and Table 1-5 shows the results for 100-g samples.

1.5.3. Nelmor Materials Tests

The Nelmor Company shredded the Tyvek coveralls, cloth coveralls, Kimwipes, latex gloves, and plastic drum liners we provided and, for each material type, returned 500 g–1000 g of particles in each of three sizes: 0.125-in., 0.25-in., and 0.375-in. The size was established as the particle passing through a square mesh of that size. We had dyed the Kimwipes material red or black so that we could readily distinguish it from the white Tyvek material.

Table 1-4. Results of Bean Mixing Test 1*

Mixer Contents	(g)	(%)
Black Turtle Beans	4865.7	68.10
White Navy Beans	1353.2	18.94
Green Split Peas	926.2	12.96
Total	1080.0	100.00

Sample	Weight of Sample			Percentage of Sample		
	Black	White	Green	Black	White	Green
1	8.253	0.616	1.508	79.53	5.94	14.53
2	8.035	1.716	1.464	71.65	15.30	13.05
3	7.172	2.387	0.58	70.74	23.54	5.72

t(n=3, 80% confidence)-1.886

Precision			White
	Mean		14.93
	Standard Deviation		8.81
	80% Confidence Interval (±)		9.59
Accuracy	True %		18.94
	Sample %		14.93
	Difference		4.01

*Three types of small beans and peas were mixed for 5 min at 90 rpm, after which 10-g samples were taken. Only white beans were counted from the sample.

Table 1-5. Results of Bean Mixing Test 2*

Mixer Contents	(g)	(%)
Black Turtle Beans	4865.7	68.10
White Navy Beans	1353.2	18.94
Green Split Peas	926.2	12.96
Total	7145.1	100.00

Sample	Weight of Sample			Percentage of Sample		
	Black	White	Green	Black	White	Green
1	66.946	22.078	10.185	67.48	22.25	10.27
2	67.44	17.872	8.963	71.54	18.96	9.51
3	60.738	19.64	7.79	68.89	22.28	8.84

t(n = 3, 80% confidence) -1.886

Precision			White
	Mean		21.16
	Standard Deviation		1.91
	80% Confidence Interval (±)		2.08
Accuracy	True %		18.94
	Sample %		21.16
	Difference		-2.22

*Same as Bean Mixing Test 1, but with three additional 100-g samples taken.

The results of mixing and sampling the materials shredded by Nelmor were less accurate than the results of mixing and sampling paper or beans. The materials shredded by Nelmor occasionally formed clumps and were separated less easily into components. For example, latex particles in one of the bags received from Nelmor were clumped, apparently as a result of the heating that occurred during shredding. We treated clumped particles by freezing them with liquid nitrogen (LN₂) and grinding them by hand. We separated the frozen and ground components by stirring them in water, as described previously; but a small amount of cross-contamination of all components between matrices remained in these samples.

Tables 1-6, 1-7, and 1-8 show the mixing results for the materials shredded by Nelmor for the 0.125-in., 0.25-in., and 0.375-in. particles, respectively. Reasonable values were obtained for all tests. However, the accuracy for the 0.25-in. particles was poorer than the accuracy for both the 0.125-in. particles and the 0.375-in. particles. Such a finding indicates that we cannot assume a universal trend toward better mixing as particle size decreases. Instead, optimal results are likely to be obtained by tailoring the mixing parameters.

Table 1-6. Results of Mixing Test for 0.125-in. Particles*

<u>Mixer Contents</u>		
	(g)	(%)
Cloth	580.5	30.62
Kimwipes	407.0	21.47
Tyvek	292.7	15.44
Plastic	280.1	14.78
Rubber	335.4	17.69
Total	1895.7	100.00

Sample	Weight of Sample		Percentage of Sample	
	Cloth/ Kimwipes	Tyvek/plastic/ latex	Cloth/ Kimwipes	Tyvek/plastic/ latex
1	5.066	5.377	48.51	51.49
2	5.021	5.464	47.89	52.11
3	4.759	5.220	47.69	52.31
4	5.242	5.477	48.90	51.10
5	4.510	4.581	49.61	50.39
6	5.607	6.121	47.81	52.19

t(n = 6, 80% confidence) -1.476

Precision		Cloth/Kimwipes	Tyvek/plastic/rubber
	Mean	48.40	51.60
Accuracy	Standard Deviation	0.75	0.75
	80% Confidence Interval (±)	0.45	0.45
	True %	52.09	47.91
	Sample %	48.40	51.60
	Difference	3.69	-3.69

*The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into two components: cloth/Kimwipes and Tyvek/plastic/rubber.

Table 1-7. Results of Mixing Test for 0.25-in. Particles*

<u>Mixer Contents</u>		
	(g)	(%)
Cloth	201.0	20.40
Kimwipes	164.2	16.66
Tyvek	219.4	22.27
Plastic	194.7	19.76
Latex	206.0	20.91
Total	985.3	100.00

Sample	Weight of Sample			Percentage of Sample		
	Cloth/ Kimwipes	Tyvek/ plastic	Rubber	Cloth/ Kimwipes	Tyvek/ plastic	Latex
1	3.827	4.647	1.392	38.79	47.10	14.11
2	2.376	4.452	2.417	25.70	48.16	26.14
3	2.503	4.834	1.333	28.87	55.76	15.37
4	3.539	4.465	1.219	38.37	48.41	13.22
5	2.365	3.965	3.384	24.35	40.82	34.84
6	2.464	4.325	1.890	28.39	49.83	21.78

t(n = 6, 80% confidence) -1.476

Precision

	Cloth/ Kimwipes	Tyvek/ plastic	Latex
Mean	30.74	48.35	20.91
Standard Deviation	6.30	4.80	8.46
80% Confidence Interval (±)	3.80	2.89	5.10

Accuracy

True %	37.06	42.03	20.91
Sample %	30.74	48.35	20.91
Difference	6.32	-6.32	0.00

*The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into three components: cloth/Kimwipes, Tyvek/plastic, and latex.

Table 1-8. Results of Mixing Test for 0.375-in. Particles*

<u>Mixer Contents</u>		
	(g)	(%)
Cloth	212.7	19.69
Kimwipes	213.8	19.80
Tyvek	216.0	20.00
Plastic	210.7	19.51
Latex	226.8	21.00
Total	1080.0	100.00

Sample	Weight of Sample			Percentage of Sample		
	Cloth/ Kimwipes	Tyvek/ plastic	Latex	Cloth/ Kimwipes	Tyvek/ plastic	Latex
1	3.606	4.117	2.276	36.06	41.17	22.76
2	3.796	3.839	1.839	40.07	40.52	19.41
3	3.997	4.963	2.096	36.15	44.89	18.96
4	3.424	3.873	2.201	36.05	40.78	23.17
5	3.386	3.792	2.638	34.49	38.63	26.87
6	3.443	3.989	2.786	33.70	39.04	27.27

$t(n = 6, 80\% \text{ confidence}) = -1.476$

Precision		Cloth/ Kimwipes	Tyvek/ plastic	Latex
	Mean	36.09	40.84	23.07
	Standard Deviation	2.20	2.22	3.53
	80% Confidence Interval ($\pm$)	1.32	1.34	2.13

Accuracy	True %	39.49	39.51	21.00
	Sample %	36.09	40.84	23.07
	Difference	3.40	-1.33	-2.07

*The ingredients were mixed for 10 min at 90 rpm, after which mixing six samples were taken. Each sample was separated into three components: cloth/Kimwipes, Tyvek/plastic, and latex.

Findings further indicate that the precision of the sample measurements was better than their accuracy. Good precision, of course, indicates consistency. However, accuracy is more desirable than precision because consistently inaccurate measurements may still be precise. Extracting samples from random locations probably would increase the accuracy of the findings. For these tests, we routinely extracted samples from the center of the mixer because material at other locations was visibly less well mixed. This biased sampling apparently resulted in reduced accuracy. Figures 1-4 through 1-6 show that precision increases with the number of samples, a finding that should be universally true. The greatest gain in precision occurs when three samples are used.

Fig. 1-4. Confidence interval for 0.125-in. particles.

Fig. 1-5. Confidence interval for 0.25-in. particles.

Fig. 1-6. Confidence interval for 0.375-in. particles.

1.6. Conclusions

Equipment characteristics (such as paddle design, speed, and volume) and duration of the mixing were more significant contributors than particle size to sample accuracy. A paddle-type mixer seems to be adequate, but the paddle orientation along the axis of rotation and the orientation of the mounting spokes should be variable. Also, the paddles should be variable in speed. Tests similar to those reported here should be performed to determine the optimal settings for variables. The mixer volume should be twice the size of the expected contents and should be filled to the level that produces the desired homogeneous mix.

All the particle sizes tested appeared suitable for producing a 10-g sample representative of a larger mixture. Special attention should be given to mixers in which particles accumulating in certain positions receive insufficient mixing. In the mixer design used for this study, poorly mixed accumulations were observed close to the end caps and at the opposite end from the end caps. Insufficient quantities of particles and particles too small to be picked up by the paddle because of the clearance between the mixer wall and paddle also caused poorly mixed particles. In addition to the overall ease of running cryogen-embrittled materials through the shredder, cryogenic techniques also may improve the mixing operation by ensuring that the particles remain discrete. Samples extracted either randomly or systematically from distributed positions in the mixer will provide better accuracy, even if such samples are analyzed as a single sample.

2. VOLATILITY OF ORGANIC COMPONENTS OF SELECTED MATERIALS

2.1. Objective

During the years when nuclear weapons compounds were manufactured at Rocky Flats Environmental Technology Site (RFETS), carbon tetrachloride (CCl_4) was used as a lubricant for machining; and chloromethane (CH_3Cl), or methylene chloride (CH_2Cl_2 , also called dichloromethane), and Freon-113 ($\text{CCl}_2\text{F}-\text{CClF}_2$) were used as degreasing fluids. Waste materials contaminated with these chemicals, as well as with methyl chloride (CH_3Cl) and vinyl chloride ($\text{CH}_2=\text{CHCl}$), were placed in drums and sent to storage. The present need is to use cryogenic grinding to homogenize contaminated wastes, while minimizing the release of organic species.

In order to determine whether volatile organic components (VOCs) of five selected materials were released during the shredding and mixing processes when these processes are performed at a temperature of -40°C , we sprayed both materials and equipment with liquid nitrogen (LN_2) before shredding and mixing. Gas and metal thermocouples installed throughout the system ensured that constant low temperatures were maintained as needed. The temperature of -40°C is the temperature guaranteed by industrial warranty on the equipment for cryogenic operations: below this temperature, standard bearings and other components must be replaced with cryogenic components. Thus, these tests would determine one of the design criteria (the desired operating temperature) for the shredder/mixer system.

Because we knew the characteristics of the VOCs being tested, effects of the grinding process could be determined by comparing pre- and post-grinding samples. However, we also explored characteristics of VOCs that were present in the mixed-matrix materials of concern. The mixed matrix represented actual expected composition of material in storage.

2.2. Equipment Design and Selection

When the procurement of a commercial shredder capable of meeting experimental schedule and budget needs proved impossible, we procured an off-the-shelf garden shredder—the Snapper—and modified it to meet experimental requirements. We replaced the 8-hp gasoline motor with a 10-hp electric motor that featured a motor-speed controller. We converted the original drive to a belt-and-sprocket drive and geared it to operate at maximum shredder speed at full controller power. The manufacturer's recommended operating speeds were in the 1100–1800 rpm range. We removed the chipper part of the shredder and moved the bearings away from the cooled areas of the shredder. We sharpened the leading edges of the "hammers" and modified the upper and lower funnels. We sealed the unit and strengthened its ability to accommodate thermal loads. We assembled and shock-mounted the motor and shredder on a movable stand. We instrumented the shredder with thermocouples and gas sampling ports and then insulated it.

The mixer used in the mixing tests described in Section 1 was instrumented, insulated, and incorporated in the output end of the shredder. Figure 2-1 shows the final shredder/mixer assembly.

A Hewlett-Packard HP 3852 scanner, a Macintosh computer, and LabVIEW® software (Fig. 2-2) monitored temperatures during the testing. We used an Inficon model 200 Residual Gas Analyzer (RGA) with supporting vacuum system (Fig. 2-3) to do on-line sampling for the volatile organic compounds. A Volatile Organic Sampling Train (VOST) collected the gas samples on thermal desorption tubes (Figs. 2-4 and 2-5), which were sent to the analytical chemistry group for gas analysis.

Fig. 2-1. Shredder and mixer assembly.

Fig. 2-2. Instrumentation system.

THE QUADREX 200 RGA

INFICON
LEYBOLD-HERAEUS

Fig. 2-3. Inficon Model 200 Residual Gas Analyzer (RGA).

Fig. 2-4. Volatile Organic Sampling Train (VOST).

Fig. 2-5. Schematic of the VOST

2.3. Materials Studies

The volatility of the various compounds being examined made it difficult for us to simulate their storage conditions at RFETS. However, by designing a test plan around organic solvents known to exist in the wastes, we hoped to gather significant information for designing a cryogenic grinding system that would facilitate the characterization of solvent-containing wastes in the RFETS drums.

Both CCl_4 and CH_2Cl_2 are members of the series of chlorinated methane molecules that include CH_2Cl_2 or CH_3Cl , and trichloromethane, or chloroform (CHCl_3). In general, the vapor pressure of the species increases with the number of hydrogen atoms that are present in the molecule. For example, the vapor pressure of CH_2Cl_2 is 12 torr at -40°C , and the vapor pressure of CCl_4 is 2 torr at -40°C . Because of the significant difference in the vapor pressure between the two species, the effect of cryogenic grinding on the volatility of the organic species will be more pronounced if CH_2Cl_2 is the contaminant.

CH_2Cl_2 is a liquid at room temperature, boils at 40°C , and freezes at -95°C . The vapor pressure ranges from 12 torr at -40°C to 422 torr at 25°C . Actual CH_2Cl_2 vapor pressure observed in these studies is dependent on both the system temperature and the CH_2Cl_2 thermodynamic activity. CH_2Cl_2 is an excellent degreasing agent. Therefore, as it becomes contaminated with grease, its vapor pressure decreases because of the chemical interaction between the CH_2Cl_2 ; and the grease lowers the thermodynamic activity of the CH_2Cl_2 .

The plot in Fig. 2-6 covers a wide range of melting and boiling points for the four solvents of interest here (CH_3Cl , CH_2Cl_2 , CCl_4 , and $\text{CCl}_2\text{F}-\text{CClF}_2$ [R113]) and illustrates the vapor pressure vs temperature characteristics for these materials as presented in the literature. The concern for operating temperature in the cryogenic grinder is based on the volatility of the solvents; volatility is reflected in the vapor pressure of the various solvent species.

Fig. 2-6. Vapor pressure vs temperature for solvents of interest in Rocky Flats Environmental Technology Site (RFETS) contaminated wastes.

The vapor pressure of these four solvents is extremely high at room temperature, 25°C. Atmospheric pressure is 760 torr at sea level, but the atmospheric pressure at both Los Alamos National Laboratory (LANL) and RFETS is significantly lower. Furthermore, even at -40°C vapor pressures of these solvents is significant. Therefore, even though the boiling points of the different solvents vary significantly—for example, CH_3Cl has a much lower boiling point (-24.2°C) than CH_2Cl_2 (+40°C)—the concern about the escape from the matrix materials of components that have boiling points above room temperature remains significant. In addition, a solvent such as CH_3Cl , which has a low boiling point, also has a significant vapor pressure of 10 torr below -90°C; thus, one does not contain such solvents at -40°C. Interestingly, trichlorofluoroethane R113 ($\text{CCl}_2\text{F}-\text{CClF}_2$ [R113]) is very much like CH_2Cl_2 in its vapor pressure characteristics; however, at its melting point of -34°C, R113 has a significant vapor pressure of 16 torr. This report provides data about the effect

of the oily matrices on the volatility of the solvent they contain.

CH_3Cl was removed from consideration because of the difficulty of attempting to spike the material with this solvent and then evaluate that material. CH_3Cl is a high-pressure gas at room temperature and would be difficult to contain within any matrix.

2.4. Experimental Test Plan

To develop a database reflective of the performance and capability of the equipment and materials, we conducted the experimental test in three steps: material evaluation, mixed-matrix testing, and shredder testing.

2.4.1. Materials Evaluation

After choosing CH_2Cl_2 , CCl_4 , and $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113), as test materials, we used the experimental test setup shown in Fig. 2-7 to evaluate the response and sensitivity of the equipment. The RGA recorded the signal for the partial pressure of the volatile gas that was mixed with air at atmospheric conditions (pressure of 590 torr and temperature of 22°C). The volatile gas was placed in the 4.3-L control-volume sample container, which was not sealed hermetically but could be evacuated to clean the system of all gases. For all tests, we obtained samples as follows. We heated the metal line between the control volume and the sampling valve to at least 60°C . We adjusted the sampling valve to regulate the total pressure in the RGA sensor to 3.5×10^{-4} torr. We used the vacuum pump to evacuate the sample line at valve VV with the sampling valve VS closed. We closed valve VV, opened atmospheric valve VA, opened sampling valve VS, then closed VA. This process enabled us to extract a gas sample from the control-volume sample container at atmospheric pressure, while maintaining "dynamic" equilibrium between the air and the organic materials. We repeated this process three times, and on the third time the signal on the RGA was read and recorded. We then repeated the process a fourth time and read the signal intensity again in order to verify that there was no significant change. We arrived at the same numbers the third and fourth times.

We used the setup illustrated in Fig. 2-7 to determine the response of the RGA to the three materials. We placed small quantities of liquid in the control-volume sample container at room temperature and obtained spectral responses for the three materials. Figure 2-8 is the spectral response of the RGA for CH_2Cl_2 , and Fig. 2-9 is an expanded view of the organic molecule that fragments into various species detected on the RGA at smaller mass numbers. Figure 2-10 is the spectral response of the RGA for $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113), and Fig. 2-11 is an expanded view of the predominant peak at mass 101. Figure 2-12 is the spectral response of the RGA for CCl_4 , and Fig. 2-13 is an expanded view of the predominant peak at mass 117.

The naturally occurring isotopic ratio for chlorine is about 75% ^{35}Cl and 25% ^{37}Cl . Because of this phenomenon, when observing mass spectra of chlorine molecules, there will be a 3:1 ratio in spectral peaks shifted by two mass units. For example, in Figs. 2-8 and 2-9 the mass of 49 represents $\text{CH}_2^{35}\text{Cl}$ and C^{37}Cl . Because of this ratio phenomenon, the signal amplitude at mass 49 is dominated by $\text{CH}_2^{35}\text{Cl}$ and not C^{37}Cl . This finding also considers the fact that ion fragmentation is dominated more by $\text{CH}_2^{35}\text{Cl}$ than by C^{35}Cl . Moreover, there is an isotopic shift for $\text{CH}_2^{35}\text{Cl}$ and $\text{CH}_2^{37}\text{Cl}$ at masses at 49 and 51 respectively, the shift being dominated in the ratio of mass 25 to 37.

Fig. 2-7. System setup for testing volatility of solvent-contaminated materials at RFETS.

Fig. 2-8. Spectral signal for methylene chloride (CH₂Cl₂). See text for explanation of mass spectrum.

Fig. 2-9. Spectral signal for CH_2Cl_2 with the predominant peak at mass 49 expanded.

Fig. 2-10. Spectral signal for trichlorofluoroethane ($\text{CCl}_2\text{F}-\text{CClF}_2$ [R113]). Total signal at mass 101 is not shown.

Fig. 2-11. Spectral signal for CCl₂F-CClF₂ with predominant peak at mass 101 expanded.

Fig. 2-12. Spectral signal for carbon tetrachloride (CCl₄).

Fig. 2-13. Spectral signal for CCl_4 with the predominant peak at mass 117 expanded.

Using the setup shown in Fig. 2-7, we conducted a set of tests on the organic solvent gases (mixed only with air) and evaluated the RGA response with these gases at reduced temperatures. We placed a small quantity of pure liquid at the bottom of the control-volume sample container and reduced the temperature by chilling the bottom of the container to less than -100°C . We regulated the temperature of the sample by first chilling an LN_2 dewar and then placing the instrumented sample container in the dewar. For the three materials studied, we reduced the temperature to at least -100°C . We allowed air to enter the central volume in order to maintain atmospheric pressure when reducing the temperature. The temperature of the control-volume sample container was slowly increased by injecting small quantities of room-temperature air at the bottom of the dewar. To sample for each data point, we followed the procedure described in Section 2.4.1. We allowed the temperature of the materials to reach thermal equilibrium, and we monitored temperature by placing thermocouples on the bottom and side of the control-volume sample container.

The results of those tests are shown in two formats. Figure 2-14 shows the signal amplitude as a function of temperature for the predeominant mass peaks of the compounds; and Figs. 2-15, 2-16, and 2-17 compare the experimental data we acquired with data in the literature. We compared the vapor pressure data of the volatile organic materials in the form of $1/T$ vs $\log P$ with $1/T$ vs the log of the RGA response multiplied by the sample temperature. In these figures, the slope of the line indicates whether the tests were conducted in equilibrium conditions. As shown in the plots, the slopes are not the same, although the procedures used were being developed for sampling during the shredding process. As expected, our data differ from data in the literature. We tried to emulate the method of measurements as would be done in the actual shredding test. Data in the literature were obtained at established equilibrium, whereas extraction of samples disturbs equilibrium. We are conducting tests under dynamic, rather than equilibrium, conditions; and, therefore, expect different results. Because of the dynamics, the data in the center

portion of the graphs are typically closer to equilibrium conditions than are the data on either end.

Fig. 2-14. Comparison of signal levels of materials tested.

Fig. 2-15. Vapor pressure data for CH_2Cl_2 .

Fig. 2-16. Vapor pressure data for $\text{CCl}_2\text{F}-\text{CClF}_2$.

Fig. 2-17. Vapor pressure data for CCl_4 .

Known quantities of saturated vapor were carefully injected into the evacuated control-volume sample container, which was then backfilled with air and allowed to stand as a closed system for a predetermined amount of time. A sample was then run through the RGA. A calibration curve using the predominant peaks for each of the three gases (CH_2Cl_2 , $\text{CCl}_2\text{F}-\text{CClF}_2$, and CCl_4) related the response of the RGA to ppm levels of the gas. Figure 2-18 shows the results of the correlation. Calibration of the RGA to ppm levels gives an idea of the amount of volatile organic material present. From these tests, we were able to establish the sensitivity of the RGA in the range of 10s to 100s of ppm, the range depending on the solvent. For example, the RGA is more sensitive to CH_2Cl_2 than to $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113). This sensitivity is dependent on the ion fragmentation of the molecules, the isotopic distribution of the fragments, and the dynamic equilibria of the testing.

Fig. 2-18. Correlation data for ppm levels of CH₂Cl₂.

2.4.2. Mixed-Materials Tests

The purpose of the next set of experiments was to determine the vapor pressure of the three selected solvents (CH₂Cl₂, CCl₄, and CCl₂F-CClF₂) in the various oily mixed-matrix materials that constitute waste at RF. The system setup illustrated in Fig. 2-7 was used to do the evaluation. The three organic compounds were tested with some of the oily mixed-matrix materials, and only the CH₂Cl₂ was tested with all five materials.

We prepared the sample by mixing CH₂Cl₂ into the oil, mixing the oil/CH₂Cl₂ mix into the solid materials (cloth, latex, plastic, Kimwipes®, and Tyvek™). We spread the materials on the base of the control-volume sample container and sealed the system. We did this quickly in order to minimize the release of the organic solvent materials. We included enough oil to be absorbed by or to cover the solid material. Table 2-1 shows the constituent ratios of material, oil, and VOC in the samples. Various tests were performed later on these samples. Additional information in Table 2-1 will be discussed in subsequent text.

Table 2-1. Material Mixes for Volatility Tests

Material/Oil/VOC (quantities in g)	RGA Signal at Beginning	Test Duration (h)	RGA Signal at End
Cloth/oil/CH ₂ Cl ₂ (20/20/5.9)	$1.10 \times E-09$	36	Background
Rubber/oil/CH ₂ Cl ₂ (40/15/5.3)	$7.8 \times E-10$	36	Background
Plastic/oil/CH ₂ Cl ₂ (30/15.4/5.5)	$1.38 \times E-09$	48	Background
Kimwipes/oil/CH ₂ Cl ₂ (10.5/20.2/4.7)	$5.8 \times E-10$	36	Background
Tyvek/oil/CH ₂ Cl ₂ (10.1/20.8/ 5.6)	$1.05 \times E-09$	36	Background
Kimwipes/oil/CCl ₄ (10/20.2/5)	$1.2 \times E-10$	—	—
Kimwipes/oil/R113 (10/21/5.6)	$1.05 \times E-09$	20	Indication above background

After the materials were placed at the bottom of the control volume and sealed, the temperature was reduced by chilling the bottom of the control-volume sample container to less than -100°C . To maintain atmospheric pressure in the system, air was allowed into the control volume as the system was cooled. The temperature of the sample was regulated in the control-volume sample container by first chilling an LN₂ dewar and then placing the instrumented control volume inside the dewar. The temperature of the control volume was increased slowly by injection of small quantities of room-temperature air at the bottom of the dewar. The results of those tests are shown in Fig. 2-19, where the signal amplitude for the five mixed-matrix materials is plotted as a function of temperature for the selected mass peaks of the compounds. The sampling for each data point was performed as described in Section 2.4.1. The upper line on Fig. 2-19 is the RGA response for the CH₂Cl₂ by itself and was previously shown in Fig. 2-14. As expected, the signal intensity is lower for mixed-matrix materials with solvents than for the solvents alone.

Fig. 2-19. Performance data for CH₂Cl₂.

The two other solvents, CCl₄ and CCl₂F-CClF₂ (R113), were tested with only one solid material, Kimwipes. The ratio of oil, Kimwipes material, and VOC is shown in Table 2-1. The results for the two materials are shown in Figs. 2-20 and 2-21. Note that the temperature for these tests is as low as -100°C, and it appears that we observed significant sublimation for the CCl₂F-CClF₂ (R113) and the CCl₄. Unlike the results obtained with CH₂Cl₂ as the VOC, the vapor pressures of the CCl₂F-CClF₂ (R113) and CCl₄ are not changed significantly when these VOCs are in the oily matrix. In general, the vapor pressures of these solvents are still significant at low temperatures in the oily matrices. We conducted an additional test on the CCl₂F-CClF₂ (R113) to evaluate repeatability and determine whether the matrix was saturated or whether the sampling process was depleting the material concentration. Figure 2-20 shows that a second test two hours later gave the same results as the initial test.

Fig. 2-20. Performance data for $\text{CCl}_2\text{F-CClF}_2$.

Fig. 2-21. Performance data for CCl_4 .

The purpose of the next set of tests for CH_2Cl_2 in the oily cloth matrix was to determine vapor pressure as a function of time at room temperature and at -50°C . In Fig. 2-22, note that the boiling point of CH_2Cl_2 is above room temperature. After 5 min at room temperature, the vapor pressure is reduced by an order of magnitude; but it takes approximately 30 min to achieve a similar result at -50°C . Because the solvent concentration can be related directly to the vapor pressure, the lowering of the vapor pressure equates to a loss in concentration in the matrix. This argument also follows from the higher vapor pressure at -50°C at later times compared with the vapor pressure at room temperature.

Fig. 2-22. Evaporation rate of CH_2Cl_2 in oily cloth matrix.

Additionally, we checked the vapor pressure of CH_2Cl_2 in the five matrix materials and that of $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113) in oily Kimwipes. These checks were made after the materials had been placed in unsealed plastic bags for 20–48 hours. After these time periods, no mass spectrum could be obtained (see Table 2.1). As indicated in Fig. 2-18, for CH_2Cl_2 the sensitivity is about 20 ppm, and for $\text{CCl}_2\text{F}-\text{CClF}_2$ (R113) it is about 200 ppm.

2.4.3. Shredder Tests

We combined the cryoshredder that we built to do the volatility studies (see Fig. 2-1) with the paddle-wheel mixer we used in Task 1. We used thermocouples in numerous locations to measure temperatures and used LabVIEW software to collect data. Figure 2-23 shows the LabVIEW template used to display temperature measurements with thermocouple placement during the experiments.

Fig. 2-23. Sample LabVIEW® template during data collection.

The system was set up to do gas sampling during the cryogenic grinding, as well as sampling with the RGA, which had been previously used to estimate the quantities of constituents in the various mixed-matrix materials. Staff of LANL's Chemical Science and Technology (CST) Division established the procedure for sampling for the volatile solvent and the solvent in the solid. They also followed the procedural guidelines described in the original test plan for Task 2 agreed upon between DOE, National Institute of Standards and Technology (NIST) at Boulder, and LANL. Figure 2-24 shows the system setup and the sampling locations.

Fig. 2-24. Locations for sampling VOC during cryogenic grinding.

Table 2-2 shows the types and quantities of constituents forming the two mixed-matrix materials for which CH_2Cl_2 was evaluated in accordance with the following procedure:

1. Liquid CH_2Cl_2 combined with vacuum pump oil was mixed with the solid material in the ratios shown in the first column of Table 2-2. The resulting mixture was quickly placed in the bottom of the same control-volume sample container used in conjunction with the RGA. The sample container was then cooled to less than -40°C ; and the temperature was monitored, as previously described.
2. After steady-state temperatures had been reached, gas samples (denoted as Sample A) were extracted through the VOST into sorption tubes.
3. The shredder and mixer were turned on. The shredder operated at about 1100 rpm and the mixer at 90 rpm. The temperature of the system was established at less than -40°C by LN_2 , which was poured into the inlet of the shredder. The metal and gas temperatures were recorded throughout the process.
4. Half the volume of the noncontaminated material (cloth or Tyvek) was chilled, using LN_2 , and then run through the shredder.
5. After half of the noncontaminated material was shredded, the contaminated sample was quickly poured out of the chilled control-volume sample container and into the shredder. When the RGA indicated the presence of the CH_2Cl_2 , a gas sample (denoted as Sample B) from the top end of the shredder was extracted through the VOST. This step in the process normally takes about 5 minutes.
6. The remaining half of the chilled noncontaminated material was passed through the shredder, and the mixer was allowed to run until most of the material appeared to have passed from the shredder into the mixer.

7. Five minutes after the shredding process stopped, with the mixer still running and both mixer and material chilled to less than -40°C , another gas sample (denoted as Sample C) was extracted through the VOST.

8. Finally, the system was turned off; and a solid sample (denoted as Sample BB) was extracted from the mixer and placed in a 1-L sealed container fitted with two gas valves.

We used this process first with the cloth material and later with the Tyvek material. To make it easier for the materials to pass through the 0.375-in. screen in the shredder, we preshredded them into somewhat smaller pieces using a material slicer. The shredder used in the test produced cotton-like particles from both the cloth and the Tyvek materials during the cryogrinding process. However, one would not expect to preshred items with the system being developed by DOE, RFETS, and NIST.

Table 2-2. Mixed-Matrix Materials in Shredder and Mixer and RGA Signals

VOC/Material/Oil Mix (ratio in g)	Quantity in Shredder (g)	Quantity in Spike (ppm) Calculated	Quantity in Mixer (ppm) Calculated	RGA Signal
$\text{CH}_2\text{Cl}_2/\text{cloth/oil}$ (2.7/40/20)	740	45,000	3650	1.8×10^{-11}
$\text{CH}_2\text{Cl}_2/\text{Tyvek/oil}$ 1.3/40/20	490	21,700	2650	1.3×10^{-11}

Figures 2-25 and 2-26 show strip-chart data as a plot of temperature vs time for the cloth and Tyvek materials, respectively. The chart begins when Sample A was taken, and the chart ends before the material was dumped into the shredder.

Fig. 2-25. Strip-chart data for cloth material.

Fig. 2-26. Strip-chart data for Tyvek material.

Figures 2-27 through 2-29 show the time-and-temperature profiles for the shredder metal and gas temperatures during the test operations with Tyvek material. Note that the system is operating at temperatures less than -40°C . Operation at such low temperatures was a primary objective in the test plan for Task 2.

Fig. 2-27. Shredder temperatures during test operations with Tyvek material.

Fig. 2-28. Shredder temperatures during second three test operations with Tyvek material.

Fig. 2-29. Shredder metal and gas temperatures during Tyvek material test operations.

2.4.4. Sampling Methods

This section presents the results of gas sampling and gas chromatography. The following tables show the results of the gas analysis performed by staff in LANL's Organic Analysis Group (CST-12). Table 2-3 shows the results of the cloth shredding test. Two gas samples for each location were taken from the desorption tubes. One would indicate high levels of organic compounds; the other, low levels of these compounds. The low-level sample tube was saturated because of the large quantity of organic materials spiked into the sample. Table 2-2 shows the calculated quantity of the organic material in both the spike material and the bulk in the mixer after shredding.

Table 2-3. Results of Gas Chromatography Analysis of Shredded Cloth Samples					
Sample ID	Sample Location	Temperature (°C)	Material Tested	Analysis Gas	Results (µg/L)
AAC4373	A	-50	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (high levels)	61,000 (19,000 ppm)
AAC4374	A	-50	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (low levels)	Saturated
AAC4375	B	-40	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (high levels)	27,000 (8,400 ppm)
AAC4376	B	-40	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (low levels)	Saturated
AAC4377	C	-40	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (high levels)	15,000 (4,800 ppm)
AAC4378	C	-40	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ (low levels)	Saturated

Table 2-4 shows the results of shredding Tyvek material. Only one sample was taken at each location. The quantity of Tyvek material detected is lower than the quantity of cloth material detected, because less CH₂Cl₂ was added to the Tyvek material.

Table 2-4. Results of Gas Chromatography Analysis of Shredded Tyvek™ Samples

Sample ID	Sample Location	Temperature (°C)	VOC Tested	Analysis Gas	Results (µg/L)
AAC4379	A	-50	CH ₂ Cl ₂ in Tyvek/oil	CH ₂ Cl ₂ (low levels)	26,000 (8,300 ppm)
AAC4380	B	-50	CH ₂ Cl ₂ in Tyvek/oil	CH ₂ Cl ₂ (low levels)	21,000 (6,700 ppm)
AAC4381	C	-50	CH ₂ Cl ₂ in Tyvek/oil	CH ₂ Cl ₂ (low levels)	5,700 (1,800 ppm)

A sample of solid material taken during each test operation was tested for CH₂Cl₂, as described in step B, and a sample was extracted when the mixed-matrix materials were being prepared (see Fig. 2-19). Because the first two samples were sealed in a closed container, the gas contained within the matrix material was released into the container when the samples were warmed to room temperature. The gas in the container (head space) was analyzed to determine the amount of gas left in the sample after the shredding operation. Concentrations of CH₂Cl₂ were detected in the cloth sample, but the Tyvek sample was lost during the chemical analysis process. Table 2-5 presents the results of gas chromatography analysis of the solid materials. The first two were from the shredding operation and the last from a solid sample that had been partially exposed to the atmosphere for 14 days.

Table 2-5. Results of Gas Chromatography Analysis of Solid Samples

Sample ID	Sample Location	Temperature (°C)	VOC Tested	Analysis Gas	Sample Size (g)	Results (µg/L)
AAC4382	BB	20	CH ₂ Cl ₂ in cloth/oil	CH ₂ Cl ₂ in head-space cloth	16	49
AAC4383	BB	20	CH ₂ Cl ₂ in Tyvek/oil	CH ₂ Cl ₂ in head-space Tyvek	15	lost in shredder 2.9
AAC4384	—	20	CH ₂ Cl ₂ in cloth/oil after 14 days	CH ₂ Cl ₂ in cloth	40	2.8

The original quantity of 740 g of cloth was spiked with 3,650 ppm of CH₂Cl₂. In analyzing the first sample of Table 2-5, we found the 16 g of cloth to contain 49 ppm of CH₂Cl₂. It appears that only about 2,300 of the original ppm was accountable (740 g divided by the 16-g sample times the 49 ppm detected at the end equals 2,266 ppm). The quantity of

2,300 is about two-thirds of the original. In the Tyvek sample, the original quantity of CH_2Cl_2 was 2,650 ppm loaded in a material of 490 g of Tyvek. The comparison was done as above for the second sample of Table 2-5. It appears that only about 98 ppm of the original material was recovered after the shredding operation. A number of factors may contribute to the reduced quantities of VOCs after shredding.

2.5. Conclusions

Separate regimes for the operation of the complete system should be considered as an option for addressing volatility concerns. The RGA results show that the oily-matrix materials will in a very short period of time (5 min) at room temperature release a significant quantity of solvent as gas (see Fig. 2.21), even when that solvent has a relatively high boiling point—one above room temperature. Therefore, even when the cryogenic shredder is operated at -40°C , a significant amount of solvent material volatilizes during the opening of the drums and bags containing the materials and during the warmup process when the materials are being repackaged. Thus, the release of VOCs during shredding may, in fact, be a moot issue because such compounds readily are released at room temperature during other parts of the operation. In any event, because a significant amount of vapor pressure occurs for a large number of VOCs at and below -40°C , on-line monitoring for solvents, as part of the glovebox system, may be a way to capitalize on their volatility. Screening materials during processing will enable us to determine whether an RGA system should be used to determine their VOC contents.

The boiling points of some VOCs are so low (less than room temperature for CH_3Cl) that these VOCs cannot be loaded effectively into a matrix material for testing. Those who performed the gas and solid testing, as well as other specialists throughout LANL, were challenged to devise an appropriate method to load these high-vapor-pressure species into the predetermined matrix materials; but no such method has been presented yet. Further consideration of low-boiling-point species requires identification of the exact matrix in which they can be found. Some of the species may be generated by radiolytic decay of plastics or may exist as a component in the production of the plastic.

Additionally, those solvents with relatively high boiling points are likely to benefit most from cryogenic shredding and mixing because these operations last a long time in comparison to the time required for unpacking and packaging operations.

Material balances in an open system have become a difficult task, as can be seen from the scatter of the data. The results of these tests are trends that can aid understanding material-handling requirements in a cryoshredding operation. For example, the VOC cannot be tested during shredding.

3. GLOVEBOX OPERATIONS

3.1. Objective

The objective of Task 3 was to demonstrate cryogenic grinding in a glovebox at the Los Alamos Plutonium Facility (TA-55) Building PF-4. This demonstration included using experimental data to verify analytical models. The results of this effort, which takes into account many safety considerations, will enhance the design of a cryogenic grinding system for use at the Rocky Flats Environmental Technology Site (RFETS). The demonstration included the following elements:

- Glovebox pressure tests to predict the glovebox negativity in the presence of liquid nitrogen and heat sources;
- Modeling of thermally induced stresses in the glovebox and comparison with allowable yield stress of the stainless steel in the glovebox;
- Use of a containment pan to reduce the thermal stresses on the glovebox in the event of a liquid nitrogen (LN_2) spill;
- Shredding of contaminated filters in the glovebox at cryogenic temperatures;
- Use of temperature and pressure data, taken during shredding tests, to predict the thermal performance of the equipment under the expected operating conditions; and
- Use of glovebox pressure tests and thermal stress modeling to address operational safety issues and to support the development of procedures and associated safety reviews for glovebox demonstrations.

All tasks included both experiments and analytical modeling.

3.2. Glovebox Pressure Tests

The typical pressure inside the glovebox is maintained at less than the ambient pressure of 0.5 in. of water. To achieve this condition, each glovebox is separately vented through a high-efficiency particulate air (HEPA) filter and, additionally, the boxes are interconnected to a centrally vented trolley tunnel. Because of the interconnectivity of the system, the unique ventilation characteristics of each glovebox must be determined empirically. Specifically, we needed measurements of glovebox pressure differential as a function of nitrogen gas generation from LN_2 boiloff so that we could specify the maximum gas generation rate.

We designed and built the system shown schematically in Fig. 3-1 to introduce room-temperature gaseous nitrogen (GN_2) into a glovebox under controlled conditions. The system features a high-capacity regulator connected to a pressurized nitrogen source. The regulator discharges GN_2 directly into the glovebox through a throttle valve, an in-line filter, and a check valve. Results of a test using the operating procedure we developed are shown in Fig. 3-2.

Fig. 3-1. Los Alamos-developed system for introducing high-flow-rate gaseous nitrogen (GN₂) into a glovebox.

Fig. 3-2. Plot of ventilation capacity of glovebox with the system installed for introducing GN₂.

After testing the system and procedure, we conducted separate spill tests outside the glovebox to acquire information about the thermal behavior of LN₂. Specifically, we wanted to determine the rate at which nitrogen vapor is generated in relation to the quantity spilled and the geometrical boundaries of the spill. We simulated the spill by pouring LN₂ into various-sized containment pans. Figures 3-3 and 3-4 show data for two spill areas, defined by the dimensions of a 20-cm × 30-cm uninsulated pan and a 20-cm × 30-cm insulated pan, respectively. In the initial stage of boiloff, when film boiling was present, the vapor generation rate was a function only of the boiling surface area. The vapor generation rate is greatest at time 0, during film boiling, and decreases as the pan temperature decreases. Eventually, as the pan cools, the temperature difference decreases and transition to nucleate boiling occurs. The heat fluxes and boiloff rates are reduced greatly under these conditions. The boiloff rate becomes steady at approximately 0.5 g/s in the nucleate boiling regime.

Fig. 3-3. Nitrogen boiloff from a 20-cm $\times$ 20-cm pan.

Fig. 3-4. Nitrogen boiloff from a 20-cm $\times$ 30-cm pan.

The figures include predictions from the thermal model for comparison purposes, and data from the spill tests verify the accuracy of the analytical model. Fig. 3-5 shows the rate of nitrogen gas generation predicted by the model during a spill in the 2000-cm² pan planned for use in the glovebox. Initially, the boiloff rates are the same for both the insulated and the uninsulated pans; but, after transition to nucleate boiling, the insulated pan has a lower boiloff rate. The volumetric gas generation rate assumes a gas mixing temperature of 300 K, which is a conservative assumption. The mixed-gas temperature included in the detailed thermal model will yield a more accurate determination of the volumetric vapor generation rate.

Fig. 3-5. The model-predicted rate of nitrogen gas generation from a liquid nitrogen (LN₂) spill.

Figure 3-6 shows the model-predicted maximum rate for nitrogen boiloff as a function of spill area for film boiling and nucleate boiling in both the insulated and uninsulated containment pans. As Fig. 3-6 indicates, both the model and the test data show that the maximum vapor generation rate occurs during film boiling. Figure 3-7 shows the resulting vapor generation rate as a volumetric flow rate. The volumetric flow rate is temperature-dependent; and Fig. 3-7, to represent the two extreme cases, shows the volumetric flow rates at both ambient and saturation temperatures. At 300 K, the gas is warmed fully and the volumetric flow rate is highest; at 75 K, the gas is adiabatic and the volumetric flow rate is lowest. The actual value for the volumetric flow rate will be between these two extremes

Fig. 3-6. Model-predicted values for nitrogen boiloff rate vs spill area.

Fig. 3-7. Model-predicted values for nitrogen vapor generation rate as a function of spill area.

After installing instrumentation for acquiring temperature and pressure measurements at the locations cited in Fig. 3-8, we tested the effects of an LN₂ spill (LN₂ spill 1) in a 2000-cm² containment pan located inside the glovebox. Figure 3-9 shows glovebox pressure measurements, and Figs. 3-10 and 3-11 show temperature measurements. Because of the isolated location of the pressure transducer, we observed no significant pressure excursions. The pressure transducer was attached to a small diameter tube (about 2 ft long) that could have dampened quick pressure changes in the glovebox. Another test is planned, using a shorter tube.

Fig. 3-8. Locations of sensors for acquiring pressure and temperature measurements during the spill tests.

Fig. 3-9. Differential pressure vs time for LN₂ spill 1 (test) in the glovebox.

Fig. 3-10. Temperature vs time for LN₂ spill 1 (readings 1 through 4). Measurements were made at selected glovebox locations.

Fig. 3-11. Temperature vs time for LN₂ spill 1 (readings 5 through 8). Measurements were made at selected glovebox locations.

In order to determine nitrogen gas generation rates, we conducted cooldown tests on individual filter elements. Figure 3-12 shows the transient temperature response and the corresponding vapor generation rate for complete submersion of one-third of a water-saturated filter element. These data are needed to verify that the glovebox pressure negativity is not violated during filter-shredding tests.

Fig. 3-12. Results of cooldown of water-saturated filter element by submersion in LN_2 .

Results of the LN_2 spill tests and the filter cooldown tests and comparison of the analytical modeling with glovebox ventilation measurements provide a complete understanding of the behavior of LN_2 in a glovebox. We can use this information to set operational limits for the amount of LN_2 to be used in cryogenic grinding in a glovebox and to predict accurately the consequences of an LN_2 spill in a glovebox.

3.3. Glovebox Filter-Shredding Tests

Before conducting the required shredder performance tests in the instrumented glovebox, we designed a new, safer LN_2 feed system.

In the glovebox LN_2 feed system, shown in Figs. 3-13 through 3-16, the operator controls the LN_2 supply to the glovebox dewar through cryogenic solenoid valves. (For details, see Appendix A: Cryogenic Liquid Introduction System for Gloveboxes.) The operator uses a remote switch at the glovebox to open and close the cryogenic solenoid valve at the LN_2 supply dewar and is, therefore, able to control the supply while monitoring the fill level in the glovebox dewar. The feed system includes a redundant safety feature, a glovebox pressure monitor that automatically closes the valves in the event glovebox negativity drops below a predetermined point. To ensure appropriate control of the LN_2 in the glovebox, we constructed a dewar and containment pan as shown in Fig. 3-17. Legs attached to the dewar prevent it from accidentally tipping over. The modeling indicated that a containment pan with a surface area of 2000 cm^2 would be optimal (see Section 3.2).

For the filter-shredding tests, we used 12 moist, contaminated Hytrex filters that had been used in processing activities. (For more details, see Appendix B: Demonstration of a Cryogenic Grinding System in a Glovebox.) Before shredding these filters, we placed insulated gloves over the rubber glovebox gloves to protect the rubber from the cryogenic operating temperatures and keep it flexible. A room-temperature filter was inserted into a special filter holder. An extended handle on the filter holder enabled the operator to slowly immerse the holder in the LN_2 dewar, thereby reducing the possibility of LN_2 splashing.

Fig. 3-13. The LN_2 feed system for cryogenic grinding in a glovebox.

Fig. 3-14. Schematic of dewar connection.

Fig. 3-15. Schematic of glovebox connection.

Fig. 3-16. Schematic of manifold.

Fig. 3-17. The LN₂ glovebox dewar and spill containment pan.

Once the filter and holder were enclosed fully by the dewar, the operator fed more LN_2 into the dewar until the filter and holder were immersed completely. Each filter required about 1 L of LN_2 to cool down. After cooldown, the holder and the frozen filter it contained were removed from the dewar; the frozen filter was then placed in the funnel of the shredder. The shredder is an ice-shaving machine—high-speed ice-shaver Model 103, 115-vac, 12-amp, manufactured by S. T. Echols, Inc., Bismarck, Missouri—with modifications, as shown in Figure 3-18. The filter was pushed slowly into the spinning blades and shredded. The shredded filter material was collected in the hopper underneath the machine and packed for later removal.

Fig. 3-18. Modified ice shaver that served as a shredder to demonstrate cryogenic grinding in a glovebox.

We used LabVIEW® software to collect pressure and temperature data continuously during the shredding. Figures 3-19 through 3-27 show data from three of the tests (runs 3, 4, and 5). In runs 3 and 4, glovebox pressure differential fluctuations remained within 0.10 in. of water of the nominal pressure differential of -0.5 in. of water; but in run 5, a pressure excursion of 0.3 in. of water was measured at filter insertion. Such a reading corresponds more nearly to the steady-state prediction of pressure rise. Additional experiments and modeling are planned to investigate more fully the transient effects of pressure rise when a filter is quickly inserted in the LN_2 bath.

Fig. 3-19. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 3.

Fig. 3-20. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 3 (readings 1 through 4).

Fig. 3-21. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 3 (readings 5 through 8).

Fig. 3-22. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 4.

Fig. 3-23. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 4 (readings 1 through 4).

Fig. 3-24. Temperature vs time of glovebox cryogenic grinding demonstration, run 4 (readings 5 through 8).

Fig. 3-25. Pressure vs time plot of glovebox cryogenic grinding demonstration, run 5.

Fig. 3-26. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 5 (readings 1 through 4).

Fig. 3-27. Temperature vs time plot of glovebox cryogenic grinding demonstration, run 5 (readings 5 through 8).

3.4. Thermal Stress on Glovebox and Components

Finite-element analyses were performed on the glovebox structure to calculate thermal stresses resulting from LN_2 spills coming into direct contact with the glovebox floor. The thermal boundary condition for the spill was defined as a heat flux that is a function of the temperature difference between the fluid and the wall. The temperature difference varies with time. Initially, a vapor layer isolates the bulk liquid from the glovebox floor; it insulates and impedes the cooldown of the metal floor.

The von Mises stress, which is a measure of the maximum distortional strain energy of the structure, is used as the failure criterion. Figure 3-28 shows that the maximum von Mises stress occurs 6 s after the spill. Initially, the heat capacity of the wall slows development of the temperature gradient in the wall; and, later, the diffusion of heat away from the spill zone reduces the temperature gradient. The superposition of these two effects results in the stress distribution shown in Fig. 3-28.

Because the maximum von Mises stress in the glovebox floor occurs 6 s after the spill, the temperature and stress distributions at that time have been calculated (see Figs. 3-29 and 3-30). Maximum von Mises stress was calculated to be 38.9 thousand pounds per square inch (ksi) or 26.8 megapascals (MPa), but yield stress of the glovebox wall is 42 ksi (241 MPa). This analysis is a worst-case scenario because it assumes that the LN_2 is in direct contact with the glovebox floor. Use of a spill containment pan with a standoff from the glovebox floor would significantly reduce thermal stress in the event of an LN_2 spill.

Fig. 3-28. Plot of von Mises stress vs time for a LN_2 spill in a glovebox.

Fig. 3-29. Graphic representation of glovebox temperature distribution during an LN_2 spill.

Fig. 3-30. Graphic representation of glovebox stress distribution during an LN_2 spill. Glovebox stress measurements are in psi, rather than ksi.

3.5. Conclusions

Tests confirmed predictions and calculations based on modeling. We successfully demonstrated that cryogenic grinding can be safely done in a glovebox. Test results can be used to design and implement a cryogenic grinding system at RFETS.

The nitrogen vapor generation rate predicted by the model was in agreement with data measured in the LN_2 spill tests. Warm-gas pressurization tests of the glovebox were used to determine ventilation capacity. These data helped to define limits on nitrogen vapor generation rates during equipment operation.

Finite-element modeling of thermal stresses in the glovebox floor, resulting from a direct LN_2 spill, showed that allowable yield stress was not exceeded. A test spill, in which LN_2 directly contacted the glovebox floor, represented a worst-case condition. The design called for using spill containment pans with thermal standoffs to prevent LN_2 overflowing the dewar and directly contacting the glovebox floor. Studies of effects of LN_2 spills indicated no glovebox structural problems that would preclude use of a cryogenic grinding system.

Pressure changes resulting from LN_2 evaporation were less than 0.3 in. of water during cryogenic operation of the shredder. These findings were less than the predicted steady-state pressure excursions. Additional experiments are planned to further analyze the transient effects of LN_2 boiloff and glovebox negativity.

**APPENDIX A. CRYOGENIC LIQUID INTRODUCTION
SYSTEM FOR GLOVEBOXES**

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CRYOGENIC LIQUID INTRODUCTION SYSTEM FOR GLOVEBOXES

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ABSTRACT

A new system for safely introducing cryogenic liquid into gloveboxes is an important part of the Los Alamos-developed cryogenic grinder for use inside a glovebox (see Appendix B. "Demonstration of a Cryogenic Grinding System in a Glovebox"). Because the temperature of liquid nitrogen (LN_2) is 77 K at atmospheric pressure and the volume expansion ratio from liquid to gas is about 1000 to 1, the use of LN_2 in a glovebox raises serious concerns. If too much LN_2 evaporates inside the glovebox, it could cause the glovebox to lose negativity and suffer a loss of containment capability, which may expose personnel to hazardous or radioactive materials. If LN_2 overflows the dewar, it could contact the glovebox gloves, making them brittle and possibly resulting in their cracking. Such cracking also would result in the loss of glovebox containment.

The cryogenic liquid introduction system features a pushbutton pendant switch that enables the operator to open and close a cryogenic solenoid valve that controls the flow of LN_2 to the glovebox dewar. By using the switch, the operator can feed LN_2 into the glovebox dewar without leaving the glovebox to turn on and off the feed from the supply dewar. By remaining at the glovebox, the operator is able to monitor more closely the glovebox pressure and the dewar configuration. To mitigate the possibility of operator error, the system incorporates, as a backup safety feature, a solid-state pressure gauge with set-point relays that will automatically close another solenoid valve that is in series with the one controlled by the operator. This system is becoming the standard for introducing cryogens into gloveboxes at Los Alamos National Laboratory (LANL).

INTRODUCTION

Chemical processing of radioactive materials, an important alternative and/or adjunct to their incineration, requires that they be ground into small, uniformly sized particles for more efficient removal of their radioactive components (see "Demonstration of a Cryogenic Grinding System in a Glovebox"). Such processes must take place inside a glovebox, and conditions inside the glovebox must be carefully controlled to reduce environment, safety, and health concerns. Liquid nitrogen (LN_2) is commonly introduced in the glovebox to cool the special materials before they are ground. However, because the temperature of LN_2 is 77 K at atmospheric pressure and the volume expansion ratio from liquid to gas is about 1000, its use inside a glovebox poses special concerns. If too much LN_2 evaporates inside the glovebox, it could cause the glovebox to lose negativity and suffer a loss of containment capability. If LN_2 overflows the dewar, it could contact the glovebox gloves, causing them to crack and expose the operator. The system developed at Los Alamos ensures delivery of the desired amount of LN_2 from the supply dewar to the glovebox dewar and reduces the possibility of overfilling the glovebox dewar and causing a spill. This system for introducing cryogenic liquids into a glovebox provides redundant safety

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features for both operator and automatic process controls.

CRYOGENIC LIQUID INTRODUCTION SYSTEM

The cryogenic liquid introduction system, shown schematically in Fig. 1, enables the operator to feed LN_2 into a dewar inside the glovebox while at the same time monitoring glovebox pressure and dewar fill level. The operator controls the LN_2 transfer at the glovebox by activating a pushbutton pendant switch. Such a system obviates the need for the operator to leave the glovebox location to start and stop the LN_2 flow at the supply dewar. Thus, the operator can easily monitor glovebox pressure and the dewar configuration during filling.

Fig. 1. Schematic of the cryogenic liquid introduction system developed at Los Alamos.

The system also has a solid-state pressure gauge with set-point relays that will automatically close another solenoid valve that is in series with the one controlled by the operator. If the operator activates the switch to feed LN_2 into the glovebox after the pressure has exceeded

the set point, the solenoid valve activated by the pressure gauge relays will close, thereby preventing the flow of LN_2 into the glovebox. An overpressure warning light and an audible alarm will alert the operator that the set point has been exceeded. When an alarm occurs, a latch relay is set to force the operator to review the system before continuing to feed LN_2 into the glovebox. A level sensor in the LN_2 dewar causes the solenoid valve to shut off automatically when the dewar is full.

The apparatus connecting the 160-L LN_2 supply dewar to a supply hose leading to the glovebox dewar is shown schematically in Fig. 2. In this apparatus, a pipe union is attached to the supply dewar, and a double-end shutoff (DESO) quick disconnect serves as a simple and quick means of separating the supply dewar from the external transfer line. A cryogenic pressure release valve (PRV) has been placed between the female DESO quick disconnect and the manual shutoff valve on the dewar next to the pipe union. This valve releases the pressure created by warming LN_2 when both the manual valve and the DESO quick disconnect are closed. The PRV is attached to the manifold by a stainless steel standoff, which serves to thermally isolate the valve, making it warmer and less susceptible to freezing as ice builds up during condensation. The male DESO quick disconnect is connected to a 6-ft flex hose and facilitates easy attachment of the hose to the supply dewar.

Fig. 2. Schematic of supply dewar connection, showing the pressure relief valve (PRV) between the pipe union and the DESO quick disconnect.

The schematic rendering of the LN_2 feed manifold (Fig. 3) shows the two cryogenic solenoid valves in series. One valve is controlled by the operator through the pendant switch, and the other is controlled by both the level sensor in the glovebox dewar and the pressure gauge on the glovebox. Once again, a cryogenic PRV is placed on a standoff located between points at which the transfer line could become closed off.

The connection of the manifold to the glovebox is illustrated schematically in Fig. 4. A check valve prevents backflow of the glovebox air when the LN_2 transfer is not in process, and a manual cryogenic valve is located between the check valve and the glovebox penetration point. Because the transfer line is subject to the temperature of the LN_2 flowing through it and significant thermal stresses would result if the transfer line directly contacted the glovebox wall, penetration of the transfer line into the glovebox occurs through a thermal isolating standoff. Another cryogenic PRV is located between the manual valve and the transfer line inlet to the glovebox. Pipe insulation

placed on the external transfer line reduces condensation and the possibility of contact with the operator's skin.

Fig. 3. Schematic of LN₂ feed manifold showing the two cryogenic solenoid valves between three PRVs.

Fig. 4. Schematic of valve system at the glovebox connection point.

To prevent it from tipping over, the LN₂ dewar inside the glovebox, shown schematically in Fig. 5, may have legs or be attached to the glovebox wall. A short, flexible line installed between the glovebox penetration point and the connection to the dewar introduction tube allows thermal contractions of the transfer line to occur without stressing the line and attachment points. A gas phase separator terminates the introduction tube at the bottom of the dewar and prevents excessive splashing during the LN₂ filling process. When the LN₂ reaches the preset limit on the level sensor in the glovebox dewar, one of the cryogenic solenoid valves will close to prevent an overflow. Because the air inside the LANL gloveboxes is very dry, little condensation occurs on the transfer line inside it.

As Fig. 5 illustrates, the dewar is placed inside a containment pan, which limits the glovebox surface area that would be affected by a cryogen spill. Use of a containment pan reduces the boiloff rate of the cryogenic liquid, thereby preserving glovebox negativity, and decreases the likelihood that LN₂ will make contact with glovebox gloves and cause them to crack.

Fig. 5. Schematic of the LN₂ dewar inside the glovebox.

CONCLUSIONS

The cryogenic liquid introduction system facilitates the safe introduction of LN₂ into the glovebox. Additionally, this system greatly reduces the potential for temperature effects leading to the possibility that glovebox gloves will crack as a result of contact with the LN₂. The traditional method of putting a transfer line through the pencil drop hole is unacceptable for long term use at the Los Alamos Plutonium Facility, whereas the introduction system discussed in this paper is now in place and is quickly becoming the standard. Our system enables operator and instrument feedback about the amount of cryogenic liquid feeding into a glovebox, in order to limit vapor generation that could lead to overpressurization of the glovebox.

**APPENDIX B. DEMONSTRATION
OF A CRYOGENIC GRINDING SYSTEM
IN A GLOVEBOX**

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DEMONSTRATION OF A CRYOGENIC GRINDING SYSTEM IN A GLOVEBOX

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ABSTRACT

The preparation of actinide-containing materials for removal of radioactive components is a key element in waste disposal efforts throughout the Department of Energy Complex. Central to the process are cooling and subsequent grinding of such materials into uniform, small-size particles. Because working with actinide compounds and other chemical species is hazardous, such work must be performed inside a glovebox. Los Alamos scientists have developed a safe, reliable cryogenic grinding system and have demonstrated it inside a glovebox. Glovebox pressure tests were performed to predict the glovebox negativity in the presence of the cryogenic liquid nitrogen (LN₂) and heat sources, and thermally induced stresses in the stainless steel glovebox were modeled for comparison with allowable yield stress. Finally, in order to obtain the temperature and pressure data needed to predict the thermal performance of the equipment under the expected operating conditions, contaminated filters were shredded in the glovebox at cryogenic temperatures. Results show the system to be effective as designed but indicate need for a containment pan to reduce thermal stresses on the glovebox and to reduce LN₂ boiloff rates in case of an LN₂ spill (see also Appendix A. "Cryogenic Liquid Introduction System for Gloveboxes").

INTRODUCTION

The glovebox demonstration of a cryogenic grinder verified the feasibility of cryogenically processing materials in a glovebox environment and addressed important safety issues in the use of cryogens in a glovebox. Cryogenic grinding was developed as a method to prepare actinide-containing materials for chemical processing as well as for further treatment, such as alternatives to incineration. Previous methods of preparing such materials posed a significant risk to glovebox operators, who routinely cut contaminated filters with hacksaws. In the new process, glovebox operators use LN₂ to freeze the filters before shredding or grinding them to a uniform size. However, because the temperature of LN₂ at atmospheric pressure is 77 K and the LN₂ volume expansion ratio from liquid to gas is about 1000 to 1, its use in a glovebox raises serious safety concerns. To develop a safer cryogenic grinding system in a glovebox, we measured LN₂ boiloff rates during liquid spills, modeled thermal stresses resulting from LN₂ spills in the glovebox, and measured and modeled the ventilation rate of the glovebox (see Appendix A. "Cryogenic Liquid Introduction System for Gloveboxes"). The information acquired led to development of operating procedures and safety reviews for glovebox demonstrations of the cryogenic grinding system.

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GLOVEBOX NEGATIVITY

To ensure the safety of operators performing work inside a glovebox, the pressure inside the glovebox must be maintained below the ambient pressure at the desired differential of 0.5 in. of water. To maintain this pressure, each glovebox is separately vented through a high-efficiency particulate air (HEPA) filter and all the gloveboxes are interconnected to a centrally vented trolley tunnel. Because of the interconnectivity of the system, each glovebox has unique ventilation characteristics that must be empirically determined. Measurements of the glovebox pressure differential as a function of the rate of nitrogen gas generation from liquid boiloff were used to specify the maximum gas generation rate. A room-temperature ventilation test of the glovebox provided the information needed to determine the ventilation characteristics of the glovebox, and LN_2 spill tests were conducted and modeled to determine the generation rate of cold gas.

A system to introduce room-temperature gaseous nitrogen (GN) under controlled conditions features a high-capacity regulator connected to a pressurized nitrogen source. This regulator discharges GN through a throttle valve, an in-line filter, and a check valve through a duct directly into the glovebox. Figure 1 shows the results of a test of the operating procedure. A curve fit was used to extrapolate the data and determine the gas flow rate at zero negativity (Fig. 1). We used a conservative safety margin of 30% to define the maximum safe flow rate allowable for this particular glovebox as 52 cubic feet per minute (cfm).

Fig. 1. The ventilation capacity of the demonstration glovebox. DP is the differential pressure in water.

We used the results of LN_2 spill tests to determine the rate of nitrogen vapor generation as a function of spill quantity and geometry. In the initial stage of boiloff, when film boiling is present, the vapor generation rate is a function of surface area. The vapor generation rate is highest at time zero and decreases as the pan temperature decreases. In Fig. 2, which shows the vapor generation rate as a volumetric flow rate, the highest and lowest volumetric flow rates can be seen. The volumetric flow rate is temperature dependent. At 300 K the gas is fully warmed and the volumetric flow rate is greatest. At 75 K the gas generation is assumed to be adiabatic, resulting in the lowest volumetric flow rate. The actual value will be between these two extremes. Using the data shown in Figs. 1 and 2 and assuming complete warming of the vapor to 300 K, a worst-case analysis, we fixed the maximum allowable size of the containment pan at 2000 cm^2 .

Fig. 2. Nitrogen vapor generation rate (boiloff) vs spill area inside the glovebox.

GLOVEBOX STRUCTURAL MODELING

We used 1500 shell elements to model the glovebox structure in the COSMOS finite-element analysis program and used the results to calculate the thermal stresses created when LN_2 directly contacts the glovebox floor. The thermal boundary condition for an LN_2 spill onto the glovebox floor was defined as the boiling heat flux that is a function of the area covered by the spill and the temperature difference between the spilled LN_2 and the wall. We postulated an LN_2 spill that would cover a circular area with a diameter two-thirds the width of the glovebox floor. The thermal boundary conditions on other glovebox surfaces were defined as convection to the glovebox external air temperature using temperature-dependent, turbulent, natural-convection heat transfer coefficients.

Because this is a transient heat transfer problem, the thermal stresses are also time dependent. Calculations of the stresses at each time step indicate that the maximum stress occurred six seconds after the spill. This stress distribution at six seconds is shown in Fig. 3 as the von Mises stress, which is a measure of the maximum distortional strain energy of the structure and, therefore, serves as the failure criterion. The maximum von Mises stress was 38.9 kips per square inch (ksi) or 268 megapascals (MPa), whereas the yield stress of the glovebox wall was 42 ksi. (The ultimate strength of the stainless steel is 84 ksi; i.e. the sheet will not fracture below 84 ksi.) The maximum stress occurs at the perimeter of the LN_2 spill, the location of the maximum

temperature gradients. This analysis reflects a worst-case scenario because it assumes LN₂ was in direct contact with the glovebox floor. Because of the low thermal conductivity of the stainless steel floor of the glovebox, contact with only a small quantity of LN₂ will produce the large temperature gradients that create the high initial stresses shown in Fig. 3. These stresses are representative of a spill in any location in the glovebox. In addition, because the highest stress was developed within six seconds of the spill, even a small quantity of the liquid nitrogen will produce this stress distribution. The use of a containment pan with a standoff from the glovebox floor would result in a significant reduction in the thermal stress in the event of an LN₂ spill.

Fig. 3. Stress distribution during an LN₂ spill onto the glovebox floor.

GLOVEBOX TESTS

We conducted an LN₂ spill test and a series of shredder performance tests in the instrumented glovebox. Part of the LN₂ control in the glovebox consisted of a dewar with legs attached to prevent it from tipping over and a containment pan to mitigate the effects of spills. Based on the worst-case analysis, in which the LN₂ reaches a temperature of 300K and generates the largest possible amount of vapor, we decided to use a 2000-cm² containment pan.

For the LN₂ spill test, 1 L of LN₂ was quickly poured into a 2000-cm² containment pan. Results indicated about a 0.1 in. of water decrease in glovebox negativity. Modeling results predicted such a pressure change when the cold gas is assumed to be generated at 75 K (the adiabatic case).

To further test the glovebox system, we shredded moist, contaminated Hytrec filters from processing lines. Before shredding began, we placed insulated gloves over the rubber glovebox gloves to insulate the rubber and keep it flexible. Then we inserted a room-temperature filter into a special filter holder with an extended handle to minimize the effects of LN₂ splashing. We then slowly immersed the filter and holder in the LN₂ dewar for cooldown. The slow immersion reduced the possibility of LN₂ splashing and excessive LN₂ boiloff, which would reduce glovebox

negativity. As soon as the filter appeared to be completely submerged, we transferred more LN_2 into the dewar to ensure full immersion of the filter in LN_2 . Each filter required about 1 L of LN_2 to achieve cooldown. We then removed the filter from the dewar and slowly pushed it through the funnel and into the spinning blades of the grinder, a high-speed ice shaver (model 103, 115 VAC, 12 amp, manufactured by S. T. Echols, Inc., Bismarck, Missouri). Finally, the shredded filter material was packaged for later processing.

We used LabVIEW[®] software to collect pressure and temperature data continuously during the shredding of a filter. Figure 4 shows the location of instrumentation used to acquire data. Nine thermocouples measured temperatures in the glovebox. Temperatures of the glovebox floor, wall, air, and passthrough air were measured for comparison with the analytical model used to predict pressure rise during an LN_2 spill.

Fig. 4. Locations of instrumentation to acquire data inside the glovebox.

The pressure in the glovebox was monitored to see how it would change during high LN_2 boiloff rates. Figure 5 shows a pressure variation of only 0.06 in. of water during this filter shredding test. The LN_2 boiloff rate was so low that the pressure variations in the figure are actually due to the gloves being moved in and out of the glovebox. The maximum pressure change observed during all of the filter shredding tests was 0.3 in. of water.

Instruments in the ice chipper measured temperature changes during shredding of the cold filters. The filters were fed into the ice chipper at 8 minutes and shredded continuously for up to 23 minutes. A thermocouple located on a glovebox glove finger between the insulated glove and the glovebox glove measured the effect of handling the cold LN_2 dewar. Figure 6 shows the response of the glove finger thermocouple to insertion of a hand into the glove at 6 minutes. At 8 minutes, when a cold filter was picked up with the glove, the finger temperature began to cool down.

The pass-through air temperature in the glovebox remained nearly constant during shredding, but the temperature of the motor frame increased 10°C due to the motor warming up when shredding filters. The temperature of the glovebox floor remained nearly constant at 10°C during filter shredding.

Fig. 5. Pressure vs time during filter shredding inside the glovebox. Fluctuations in glovebox pressure negativity are mainly due to movement of glovebox gloves by operators.

Fig 6. Temperature vs time during filter shredding inside the glovebox.

Figure 7 shows that the temperature of the glovebox wall and air remained fairly constant. The temperature of the chopper funnel dropped about 7°C during shredding. The temperature under the chopper dropped 50°C as cold filter material fell from the funnel around that thermocouple. This small temperature change was attributed to low LN₂ boiloff rates and good ventilation in the glovebox. Additional experiments and analyses are planned to more fully investigate the transient effects.

Fig. 7. Temperature vs time during filter shredding inside the glovebox.

CONCLUSIONS

The glovebox tests of the cryogenic grinder confirmed the analytical model predictions and successfully demonstrated safe operation in a glovebox.

Results of the LN₂ spill test verified the analytical model and the predicted nitrogen vapor generation rate. Warm-gas pressurization tests of the glovebox were used to determine glovebox ventilation capacity. These data helped define the limits of nitrogen vapor generation rates required to maintain glovebox negativity. Finite-element modeling of the thermal stresses in the glovebox floor resulting from direct contact with LN₂ during a spill showed that the allowable yield stress was not exceeded. This test case represents the worst-case condition because containment pans with thermal standoffs will be used to protect the glovebox if LN₂ spills out of the dewar. The LN₂ spill test revealed no glovebox structural problems. The filter shredding tests demonstrated successful operation of the shredder in the glovebox. Pressure changes of <0.3 in. of water were less than the predicted steady-state pressure excursions and are the result of transient effects, which we plan to analyze in future experiments.