

Characterization of Cover Gas Emissions from U.S. Magnesium Die Casting

Office of Air and Radiation
EPA 430-R-04-004
www.epa.gov/highgwp/magnesium-sf6
May 2004

Table of Contents

	Page
Acknowledgements	ES-1
Executive Summary	ES-2
1.0 Introduction.....	1-1
2.0 FTIR Data and Hardware Quality Analysis/Quality Control Procedures.....	2-1
2.1 Data Analysis Procedures.....	2-1
2.1.1 The Spectrum Analysis Method.....	2-1
2.1.2 Creating the Spectrum Analysis Method	2-2
2.1.3 Reference Generation.....	2-5
2.2 Hardware Procedures	2-6
3.0 Extractive FTIR Sampling Systems	3-1
3.1 Hydrogen/Oxygen Analyzer	3-6
4.0 Test Results.....	4-1
4.1 HFC-134a Cover Gas with Nitrogen and Carbon Dioxide Diluents	4-1
4.2 Novec™ 612 Cover Gas with 85% CO ₂ and 15% Air Diluents	4-4
4.3 SF ₆ Cover Gas with Air Diluent.....	4-8
5.0 Conclusions.....	5-1
5.1 Cover Gas Test Observations.....	5-1
5.1.1 HFC-134a Cover Gas Testing with N ₂ and CO ₂ Diluents	5-1
5.1.2 Novec™ 612 Cover Gas Testing with CO ₂ and Air Diluents.....	5-1
5.1.3 SF ₆ Cover Gas Testing with Air Diluent	5-2
5.2 Cover Gas Degradation.....	5-2
5.3 Occupational Health and Safety.....	5-5
5.4 Global Warming Impact Discussion.....	5-6
5.5 Uncertainty Discussion.....	5-10

List of Tables

1-1	Test Schedule at Palmyra and Hannibal Internet Facilities	1-2
1-2	Magnesium Die Casting Machine Parameters	1-3
2-1	Analysis Method Parameters	2-3
4-1	Data Summary for Machine #32 Running HFC-134a with N ₂ Diluent.....	4-2
4-2	Data Summary for Machine #32 Running HFC-134a with CO ₂ Diluent	4-3
4-3	Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #1 Casting Condition	4-6
4-4	Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #1 Static Condition	4-6
4-5	Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #2 Casting Condition	4-7
4-6	Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #2 Static Condition	4-7
4-7	Data Summary for the SF ₆ Cover Gas on Machine #32	4-9
4-8	Data Summary for the SF ₆ Cover Gas on Machine #4, Sample Point #1.....	4-9
4-9	Data Summary for the SF ₆ Cover Gas on Machine #4, Sample Point #2.....	4-10
5-1	Machine #32 Percent Degradation for Cover Gas Testing	5-4
5-2	Machine #32 Percent Degradation for Cover Gas Testing	5-4
5-3	Comparison of 100-Year GWP Estimates from the Intergovernmental Panel on Climate Change’s Second (1996) and Third (2001) Assessment Reports.....	5-6
5-4	GHG Emission Comparison for Machine #32 Using HFC-134a and SF ₆	5-8
5-5	GHG Emission Comparison for Machine #4 Using Novec™ 612 and SF ₆	5-8
5-6	GHG (Weighted By Gas Flow Rate) Emission Comparison for Machine #32 Using HFC-134a and SF ₆	5-9
5-7	GHG (Weighted By Gas Flow Rate) Emission Comparison for Machine #4 Using Novec™ 612 and SF ₆	5-9

List of Figures

1-1	Cold Chamber #32 at the Internet, Palmyra Facility	1-4
1-2	Cold Chamber #4 at the Internet, Hannibal Facility	1-5
2-1	Reference Generation Hardware Configuration	2-6
3-1	Sampling System Schematic.....	3-2
3-2	Sample Locations for Cold Chamber #32 at Palmyra	3-3
3-3	Sample Locations for Cold Chamber #4 at Hannibal	3-5
3-4	Nova 340WP Oxygen and Hydrogen Analyzer.....	3-6

Acknowledgements

This cooperative study is a product of the Australia/U.S. Climate Action Partnership, initiated in June 2002. The analytical measurements and report preparation was funded by the U.S. Environmental Protection Agency under contract GS-10F-0124J to ICF Consulting. Measurements and analysis were conducted by URS Corporation. The authors wish to express their appreciation and thanks to Intermet and their staff, specifically Al Dimmitt, for contributing not only their facilities, but their valuable assistance and advice, to this measurement study. The support of Australian Magnesium Corporation (AMC), the Cooperative Research Centre for Cast Metals Manufacturing (CAST) and 3M™ for providing the cover gases, expertise and trial staff for this study is also gratefully acknowledged.

Executive Summary

A study was conducted to evaluate alternative cover gases used in cold chamber die-casting. Currently sulfur hexafluoride (SF₆) is widely used for the protection of molten magnesium but with an interest in reducing SF₆ emissions and global climate change impact, the magnesium industry and EPA are evaluating alternative gases. This study examines the use of SF₆, AM-cover™ (supplied by Australian Magnesium Corporation (AMC)) and Novec™ 612 Magnesium Protection Fluid (supplied by 3M™) cover gases under casting and static operating conditions at two Internet magnesium die casting facilities located in Palmyra and Hannibal, Missouri. The AM-cover™ technology utilizes HFC-134a to provide melt protection. Novec™ 612 is a fluorinated ketone. Gas was extracted directly from the crucible headspace above the molten magnesium to characterize degradation product formation resulting from the interaction of the cover gases with the heated melt surface. The results reported are from measurements taken inside the crucible headspace and should not to be mistaken for ambient air emissions data. Tables ES-1 and ES-2 summarize details and results from the study. Measurements were conducted for various sampling scenarios including different cover gases, cover gas mixtures, cover gas flow rates, and die casting processes. The cover gas degradation estimates listed in Tables ES-1 and ES-2 have been corrected for crucible dilution effects.

Table ES-1. Machine #32 Cover Gas Measurements and Observed Degradation

Table	Cover Gas Mixture Components	Sample Location	Cover Gas Mixture Flow ^a (lpm)	Cover Gas Delivery Conc. (ppm)	Cover Gas Measured Conc. ^a (ppm)	Cover Gas Degradation
4-1	HFC-134a/N ₂	#3	21	4,000	83.9	97%
4-1	HFC-134a/N ₂	#4	21	4,000	68.2	98%
4-2	HFC-134a/CO ₂	#4	20	4,000	337.5	89%
4-2	HFC-134a/CO ₂	#6	20	4,000	206.2	93%
4-2s	HFC-134a/CO ₂	#6	20	4,000	268.6	92%
4-7	SF ₆ /Air	#3	65	19,000	12,078	8%
4-7	SF ₆ /Air	#6	65	19,000	12,277	6%
4-7	SF ₆ /Air	#4	65	19,000	11,930	9%

^aAs provided by Internet and AMC

Table ES-2. Machine #4 Cover Gas Measurements and Observed Degradation

Table	Cover Gas Mixture Components	Sample Location	Cover Gas Mixture Flow ^a (lpm)	Cover Gas Delivery Conc. ^a (ppm)	Cover Gas Measured Conc. (ppm)	Cover Gas Degradation
4-3	Novec 612/CO ₂ /Air	#1	612/CO ₂ =48.6, Air=7.3	126	6.9	93%
4-4s	Novec 612/CO ₂ /Air	#1	612/CO ₂ =48.6, Air=7.3	126	8.1	92%
4-5	Novec 612/CO ₂ /Air	#2	612/CO ₂ =45.6, Air=6.8	126	10.0	89%
4-6s	Novec 612/CO ₂ /Air	#2	612/CO ₂ =45.6, Air=6.8	126	12.2	87%
4-8	SF ₆ /Air	#1	37.5	5,000	2,037	47%
4-9	SF ₆ /Air	#2	37.5	5,000	3,347	13%

^aAs provided by Internet and 3M™

HFC-134a Cover Gas Testing with N₂ and CO₂ Diluents

The primary degradation products measured while running HFC-134a with a nitrogen or CO₂ diluent are: CO₂, CO, HF, C₂F₆, and COF₂. Please see Table 2-1 for a listing of chemical formulas and compound names. For machine #32 furnace measurements, HF and C₂F₆ concentrations were on the order of 100 to 200 parts per million (ppm) and 2 ppm, respectively. COF₂ concentrations were below the detectable limit of the FTIR instrument when using an N₂ diluent, but increased to levels greater than 10 ppm with a CO₂ diluent. There was no marked difference in the results obtained during part casting and static (i.e., during periods when no part casting occurred) operating periods. The time series plots for these and other compounds are illustrated in Appendix A. The plots illustrate that additional degradation products, such as H₂CO, CH₄, C₂H₂, and C₂H₄ are formed with the addition of ambient air during the ingot loads. Some compounds such as H₂CO, NO, N₂O and NO₂ also had background levels inside the headspace that sharply increased during ingot loading. Detection of C₂H₂ and C₂H₄ was sporadic, with a few spikes occurring during ingot loading. Other than these spikes, concentrations were close to or below detectable limits.

Novec™ 612 Cover Gas Testing with CO₂ and Air Diluents

The primary degradation compounds measured while using Novec™ 612 as a cover gas are: CO, COF₂, C₃F₈, C₂F₆ and HF. Measurements were conducted during both active casting and static conditions on die casting machine #4. HF was present at relatively constant levels during both operating conditions; however, the concentrations were higher at sample point #2, which is closer to the pump that loads molten magnesium into the die. For example, near the ingot feed door (sample point #1), HF concentrations were on the order of 50 ppm, while on the pump side, concentrations were on the order of 110 to 125 ppm. C₂F₆, C₃F₆ and COF₂ concentrations were on the order of 1 to 2 ppm, 5 to 10 ppm and 5 ppm, respectively during both casting and static conditions. Additional degradation products detected included CH₄, SiF₄, and

H₂CO. SiF₄ was only detected during casting conditions, but at concentrations less than 1 ppm. Similarly, low levels of NO (< 1 ppm) and NO₂ (1 to 4 ppm) were only detected during casting. These levels tended to increase during ingot loading periods.

SF₆ Cover Gas Testing with Air Diluent

The primary degradation compounds measured while using SF₆ as a cover gas are: HF and SO₂. HF concentrations were on the order of 10 to 30 ppm, while NO, N₂O and NO₂ levels were on the order of 2 ppm; however, these levels increased during ingot loading. H₂CO levels remained close to the FTIR detection limit for all cold chamber measurements.

Measured Percent Degradation for Cover Gases

Tables ES-1 and ES-2 list the degradation estimates for all cover gases measured. The degradation estimates, which are corrected for dilution effects (i.e., the effects of air ingress into the crucible headspace), are calculated as the percent difference between the delivery concentration and the measured concentration in the crucible headspace. For all of the tests, average degradation estimates for HFC-134a with N₂ and CO₂ diluents, and Novec™ 612 were 98 percent, 91 percent and 90 percent, respectively. The level of degradation did not vary significantly between casting and static operating conditions. In comparison, degradation estimates for SF₆ were on the order of 10 percent for four tests; however, for one test (on cold chamber machine #4 – sampling location #1) a percent degradation of close to 50 percent was observed. The reason for this high level of cover gas degradation observation is unknown.

Potential Climate Impact

A key factor in evaluating substitute cover gas compounds is their composite global warming potential (GWP) compared to SF₆. For each cover gas compound and its associated degradation products, a composite global warming impact estimate was developed using IPCC third assessment report GWP factors¹. The overall GWP-weighted gas emissions rate for each test scenario (i.e., HFC-134a/CO₂ or N₂, Novec™ 612/CO₂/Air on both machines) was estimated using the measured average concentrations of each gas, their molecular weights and the delivery cover gas flow rates.

Based on this approach, results indicate that HFC-134a and Novec™ 612 have a greenhouse gas (GHG) emissions impact that is more than 95 percent lower than SF₆. Although cover gas degradation product gases such as CF₄ and C₂F₆ contribute to the total GWP of the gas,

¹ IPCC, Climate Change 2001: The Scientific Basis. Intergovernmental Panel on Climate Change, 2001, Cambridge University Press. Cambridge, U.K.

their contribution is negligible when considering their relatively low concentrations, cover gas degradation levels on the order of 90 percent, as well as the large GWP reduction that occurs when switching from SF₆ (GWP = 22,200) to HFC-134a (GWP = 1,300) or Novec™ 612 (a specific GWP was not available; however, fluorinated ketones, of which Novec™ 612 is one, are known to have GWP's close to 1^{2, 3, 4}).

² Milbrath, D. *3M™ Novec™ 612 Magnesium Protection Fluid: It's Development and Use in Full Scale Molten Magnesium Processes*, Proceedings of the 60th Annual International Magnesium Association Conference, May 2003, Stuttgart, Germany.

³ Taniguchi, N., et al. *Atmospheric Chemistry of C₂F₅C(O)CF(CF₃)₂: Photolysis and Reaction with Cl atoms, OH radicals, and Ozone*. *J. Phys Chem. A.*, 107(15); 2674-2679.

⁴ ICF, *Re-evaluation of a C-6 Oxyfluorocarbon (trade name Novec 1230) and References*, Memo prepared by ICF Consulting, Inc. for the Environmental Protection Agency, Global Programs Division, under EPA Contract Number 68-D-00-266. September 10, 2003.

1.0 Introduction

This report presents and interprets the results of a series of cover gas measurements on two cold chamber molten magnesium die casting machines. Measurements were conducted by URS Corporation (URS) at two Internet production facilities located in Palmyra and Hannibal, Missouri between September 29th and October 7th, 2003. Measurements were made in a continuous and real-time fashion with an extractive-type Fourier Transform Infrared (FTIR) spectroscopic system and an extractive-type oxygen (O₂) continuous emission monitor (CEM).

The focus of the study was to assess degradation products and emissions for three different cover gases in cold chamber applications. The cover gases are used to prevent surface burning of the molten metal during processing. The three cover gases evaluated during the study were: 1) SF₆; 2) AM-cover™ (supplied by Australian Magnesium Corporation (AMC)), which uses HFC-134a; and 3) Novec™ 612 Magnesium Protection Fluid (supplied by 3M™). The main objectives of this study were as follows:

- To determine the level degradation of the cover gas within the confines of process crucibles containing molten magnesium.
- To determine the nature of the reaction products expected as the cover gas is degraded during melt protection. Direct measurement by FTIR, and subsequent spectral analyses, was employed to identify the gaseous fluorides, acids and perfluorocarbons that may result from cover gas decomposition.
- To determine the greenhouse gas (GHG) emissions from the new cover gas technologies and overall reduction in GHG emissions attributable to the use of HFC-134a and Novec™ 612 instead of SF₆.

The measurement schedule, sampling locations, and test conditions are summarized in Table 1-1. Typical die casting process parameters are summarized in Table 1-2. The measurements were conducted under these conditions during casting activity, as well as static conditions (i.e., the machine was not casting). Figures 1-1 and 1-2 illustrate the cold-chamber machines that were tested at the Palmyra and Hannibal facilities.

Testing was carried out using existing cover gas distribution and flow controls that were not optimized for either of the alternate cover gases. Due to the high degree of reactivity of HFC-134a and Novec™ 612 some modification of the gas delivery system would be required to achieve the most effective and efficient application scenario possible.

Table 1-1. Test Schedule at Palmyra and Hannibal Internet Facilities

Date	Time	Die Casting Machine	Cover Gas Mixture Components	Sample Location	Cover Gas Mixture Flow ^a (lpm)	Cover Gas Delivery Conc. ^a (ppm)	Test Condition	Ingot Type	FTIR Path Length
1-Oct	0932-1036	Cold #32	HFC-134a/N ₂	#3	21	4,000	Casting	AZ91D	5.1
1-Oct	1036-1236	Cold #32	HFC-134a/N ₂	#4	21	4,000	Casting	AZ91D	5.1
1-Oct	1618-1845	Cold #32	HFC-134a/CO ₂	#4	20	4,000	Casting	AZ91D	5.1
1-Oct	1845-1916	Cold #32	HFC-134a/CO ₂	#6	20	4,000	Casting	AZ91D	5.1
1-Oct	1916-2000	Cold #32	HFC-134a/CO ₂	#4, #6	20	4,000	Static	AZ91D	5.1
3-Oct	0959-1037	Cold #32	SF ₆ /Air	#3	65	19,000	Casting	AZ91D	20.1
3-Oct	1114-1154	Cold #32	SF ₆ /Air	#6	65	19,000	Casting	AZ91D	20.1
3-Oct	1200-1222	Cold #32	SF ₆ /Air	#4	65	19,000	Casting	AZ91D	20.1
6-Oct	1137-1652	Cold #4	Novac TM 612/CO ₂ /Air	#1	612/CO ₂ =48.6, Air=7.3	126	Casting	AZ91D	5.1
6-Oct	1318-1358	Cold #4	Novac TM 612/CO ₂ /Air	#1	612/CO ₂ =48.6, Air=7.3	126	Static	AZ91D	5.1
6-Oct	1450-1654	Cold #4	Novac TM 612/CO ₂ /Air	#2	612/CO ₂ =45.6, Air=6.8	126	Casting	AZ91D	5.1
7-Oct	1530-1655	Cold #4	Novac TM 612/CO ₂ /Air	#2	612/CO ₂ =45.6, Air=6.8	126	Static	AZ91D	5.1
7-Oct	0830-1025	Cold #4	SF ₆ /Air	#2	37.5	5,000	Casting	AZ91D	5.1
7-Oct	1036-1227	Cold #4	SF ₆ /Air	#1	37.5	5,000	Casting	AZ91D	5.1

^aAs provided by Internet, AMC and 3MTM

Table 1-2. Magnesium Die Casting Machine Parameters

Parameter	Cold Chamber #32	Cold Chamber #4
Facility	Palmyra	Hannibal
Furnace Temperature (°F)	1,260-1285	1,275
Ingot Weight (lbs)	25	25
Furnace Capacity (lbs)	3,000	3,000
Ingot Type	AZ91D	AZ91D
Mg Casting Rate (seconds/part)	43	48
Mg Pump Type	Centrifugal	Electromagnetic Pump
Mg Shot Weight (lbs)	4.4	5.4
Metal Throughput (lbs/hr)	368	405
Product	Valve covers	Valve covers
Molten surface area (sq ft)	10.4	10.4
Ingot Loading	Automatic Feed	Automatic Feed



Figure 1-1. Cold Chamber #32 at the Internet, Palmyra Facility



Figure 1-2. Cold Chamber #4 at the Internet, Hannibal Facility

2.0 FTIR Data and Hardware Quality Analysis/Quality Control Procedures

Almost every chemical compound absorbs infrared (IR) light to some degree in a particular region of the mid-infrared spectrum. These absorption properties can be used to identify and quantify chemical compounds in a complex mixture of gases. As stated by Beer's Law, the magnitude of a compound's IR absorbance is directly proportional to the product of its concentration in the mixture and the sample cell optical path length. This is otherwise known as the compound's *optical depth*. The extractive FTIR instruments used by URS are able to achieve parts-per-billion (ppb) detection levels because the optical path length within the measurement cell is magnified many times by reflecting the IR beam between a series of mirrors before it reaches the detector. The mirrors provide a fixed optical path length best suited to the gas mixture being sampled. In this case, optical path lengths of 20.1 meters and 5.1 meters were utilized.

The use of FTIR as an analytical tool requires extensive quality analysis/quality control (QA/QC) procedures on both data analysis and hardware to ensure valid data results. FTIR is often perceived as having poor results due to improper implementation of the proper procedures and protocols. In accordance with ISO requirements, URS utilizes an extensive protocol (Radian DCN#96-133-403-01) to maintain consistency in hardware setup and data analysis. The following sections describe QA/QC procedures used for data analysis and hardware.

2.1 Data Analysis Procedures

2.1.1 The Spectrum Analysis Method

An infrared spectrum analysis is performed by matching the features of an observed spectrum to those of reference gases of known concentration. If more than one feature is present in the same region, then a linear combination of references is used to match the compound feature. The standards are scaled to match the observed band intensities in the sample. This scaling also matches the unknown concentrations. An infrared spectrum can be collected and analyzed in approximately one second, but spectra are normally averaged over a one- or two-minute integration period to produce adequate signal-to-noise limits and ppb detection levels.

The scaled references are added together to produce a composite that represents the best match with the sample. A classical least squares mathematical function is used to match the standards' absorption profiles with those of the observed spectrum in specified spectral analysis

regions. The compounds of interest together with compounds expected to cause spectral interference are included in the analysis region.

2.1.2 Creating the Spectrum Analysis Method

The spectrum analysis method used for the tests at the Internet facilities was developed by URS by selecting the spectral regions and sub-regions that are least affected by primary IR absorbers (H₂O and CO₂, in this case) while also producing the best detection limit possible for the target compounds. Target compounds are initially determined prior to sampling based on cover gas composition. However, many degradation product gases were found during data analysis requiring many iterations of data processing and interpretation. Typically, an analysis method is iteratively refined by using it to analyze a representative set of infrared spectra while varying the method. The optimum method is indicated when both the 95 percent confidence levels and the bias on the individual compounds are minimized. Table 2-1 lists the range of references included in the analysis method used by the FTIR systems for the tests. Each reference is described in terms of its optical depth (i.e., concentration times cell path length (ppm-meters) range. For the Internet testing, new gas references were required for HFC-134a, Novec™ 612 and CO₂ which is discussed in a Section 2.3.

Table 2-1. Analysis Method Parameters for Major Contaminants and Spectroscopic Interferants

Chemical Formula	Compound	SF ₆ (ppm-meters)	HFC-134a (ppm-meters)	Novec™ 612 (ppm-meters)
H ₂ O	water	30,600-2,748,900	30,600-2,748,900	30,600-2,748,900
CO ₂ ^a	carbon dioxide	1,360,368-5,107,369	1,360,368-5,107,369 (CO ₂) 70-2,110 (N ₂)	70-2,110
SF ₆	sulfur hexafluoride	56-280	n/a	n/a
CH ₂ FCF ₃	HFC-134a	n/a	9,700-27,575	n/a
Novec™ 612 ^{a,b}	Novec™ 612	n/a	n/a	21-991
SO ₂	sulfur dioxide	518-10,415	n/a	n/a
CO	carbon monoxide	1,032-101,790	1,032-101,790	1,032-101,790
HF	hydrofluoric acid	1-2,000	1-2,000	1-2,000
COF ₂	carbonyl fluoride	50-1,250	50-1,250	50-1,250
C ₂ H ₂	acetylene	111-5,550	111-5,550	111-5,550
C ₂ H ₄	ethylene	86-2,576	86-2,576	86-2,576
C ₂ F ₆	hexafluoroethane	112-280	112-280	112-280
CF ₄	carbon tetrafluoride	28-112	28-112	28-112
CH ₂ F ₂	dimethyl fluoride	28-560	28-560	28-560
CHF ₃	methyl fluoride	177-5,908	177-5,908	177-5,908
CH ₄	methane	87-30,019	87-30,019	87-30,019
OF ₂	oxygen difluoride	1,750-14,000	1,750-14,000	1,750-14,000
H ₂ CO	formaldehyde	92-1,838	92-1,838	92-1,838
C ₃ F ₈	perfluoropropane	213-1,058	213-1,058	213-1,058
C ₄ F ₈	octafluorocyclobutane	28-560	28-560	28-560
NO	nitric oxide	114-12,961	114-12,961	114-12,961
N ₂ O	nitrous oxide	102-4,076	102-4,076	102-4,076
NO ₂	nitrogen dioxide	34-2,097	66-2,097	66-2,097

^aReferences generated at URS laboratory facilities in Austin, Texas. Note that two different optical depth ranges are required to quantify CO₂ during the HFC-134a tests. High optical depth was required when CO₂ was used as the diluent gas, and a low optical depth was required when N₂ was used as the diluent gas.

^bChemical formula was not provided by 3M™; however, the gas is known to be a fluorinated ketone (C₃F₇C(O)C₂F₅).

After setting up the FTIR instruments on-site, signal-to-noise ratio (SNR) assessments were performed. This was determined by measuring the noise equivalent absorbance (NEA) of each FTIR system while sampling nitrogen. The NEA is derived by ratioing two consecutive single beam spectra to produce a “zero” spectrum, then measuring the peak-to-peak absorbance at a frequency region of interest. This represents the noise level of the instruments under field conditions. By determining the concentration level for each contaminant that scales down its analyzed spectral features to the NEA (representing a SNR of 1 or better), the compound’s SNR-limited minimum detection limit (MDL) can be estimated.

Due to the complexity of the sample matrix, detection limits are calculated using two different methods. The first method is a noise-based detection limit which involves data collection during a “non-process” condition, or when the analyte of interest is not present in the sample stream for a minimum of approximately 20 data points. The standard deviation over this period is calculated and the noise-based MDL is determined. The second method is conducted when the analyte of interest is present in the sample stream. A theoretical noise-based detection limit is determined by comparing the ratio of absorbance intensities and optical depth for the peak-to-peak noise to the ratio of the absorbance intensities and optical depth for the lowest concentration reference used in the analytical method. The equation below shows the calculation for theoretical noise-based detection limits represented as MDL or minimum detection limit.

$$\frac{\text{Peak – to – Peak Noise}}{2 \times \text{MDL} \times \text{Path Length}} = \frac{\text{Reference Absorbance}}{\text{Reference Concentration} \times \text{Reference Path Length}}$$

Note that the MDL is multiplied by two as a conservative estimate. For all MDL calculations, a peak-to-peak noise of 1×10^{-3} absorbance units is used. In some instances compounds absorb infrared light in regions that are interfered with by higher concentration compounds. An example would be CF₄. CF₄ is difficult to detect in a sample stream containing high HFC-134a concentrations since its strongest absorbance peak is in a region that HFC-134a absorbs infrared in. Therefore detection limits are affected and reported as such.

When spectroscopic interferences *are* taken into account for those contaminants that have overlapping absorption features, an increase in their MDLs is expected; consequently, the second method is used. To determine this MDL, a set of spectra was collected during “non-process” periods on the FTIR system and the detection limits during these sets of data were calculated. During this time, it is assumed that there are no process gases present and that any reported is a mathematical anomaly created by interferences. Three times the standard deviation of the set of data is a typical approximation of the method limited MDL. Since emissions are present in the crucible head space even when the tool is idle, this calculation is computed over periods where ambient air is running through the sampling cell. This method is used as an alternative to the theoretical “noise based” detection limit to factor in the effects of interferences. The calculation is a more conservative and practical calculation and therefore is used wherever possible.

2.1.3 Reference Generation

Since the use of HFC-134a and Novec™ 612 within the magnesium industry is relatively new, references were required to be generated for both gases. Additionally, high concentration references for CO₂ were required since it was used as a diluent gas with Novec™ 612 and HFC-134a at concentrations of 85 percent and greater. HFC-134a references were obtained and formatted for utilization with MKS software (MKS was formerly, On-Line Technologies). For the Novec™ 612 cover gas, a sample was obtained from 3M. A series of gas references for Novec™ 612 had to be generated to accurately quantify sample data. A reference set was generated such that it bracketed the expected concentration range from the field sample. References were generated from certified gas standards made gravimetrically on NIST certified scales with a solution of Novec™ 612. The standard was certified at ± 2 percent at 201 ppm Novec™ 612 by HP Gas Products located in Baytown, Texas. The standard was diluted at 5 different levels with nitrogen and gas reference samples were measured in a static condition using the following procedure.

1. Evacuate and fill the FTIR sample cell with nitrogen 5 times
2. Evacuate the cell using a roughing vacuum pump
3. Add ultra high purity (UHP) nitrogen to a cell pressure of 400-650 torr
4. Add Novec™ 612 gas standard while recording pressure differential
5. Fill cell to 750 torr with N₂
6. Measure gas reference

With this approach the pressure was monitored at each reference step with a calibrated Baratron pressure sensor made by MKS. By knowing the amount of standard added with respect to pressure, the concentration can be calculated by the following equation.

$$\text{Reference Concentration} = \frac{\text{Pressure of the Standard Added}}{\text{Total Pressure}} \times \text{Bottle Concentration}$$

Each gas reference sample was saved and used to generate a 5-point calibration curve that was then applied to the Novec™ 612 data. Additionally, a gas standard of 62.92 percent CO₂ was obtained for the high concentration requirements and the procedure was repeated for CO₂. A total of 12 references were collected to generate a twelve-point calibration at high concentrations of CO₂. Figure 2-1 is a schematic of the configuration used for generating the references.

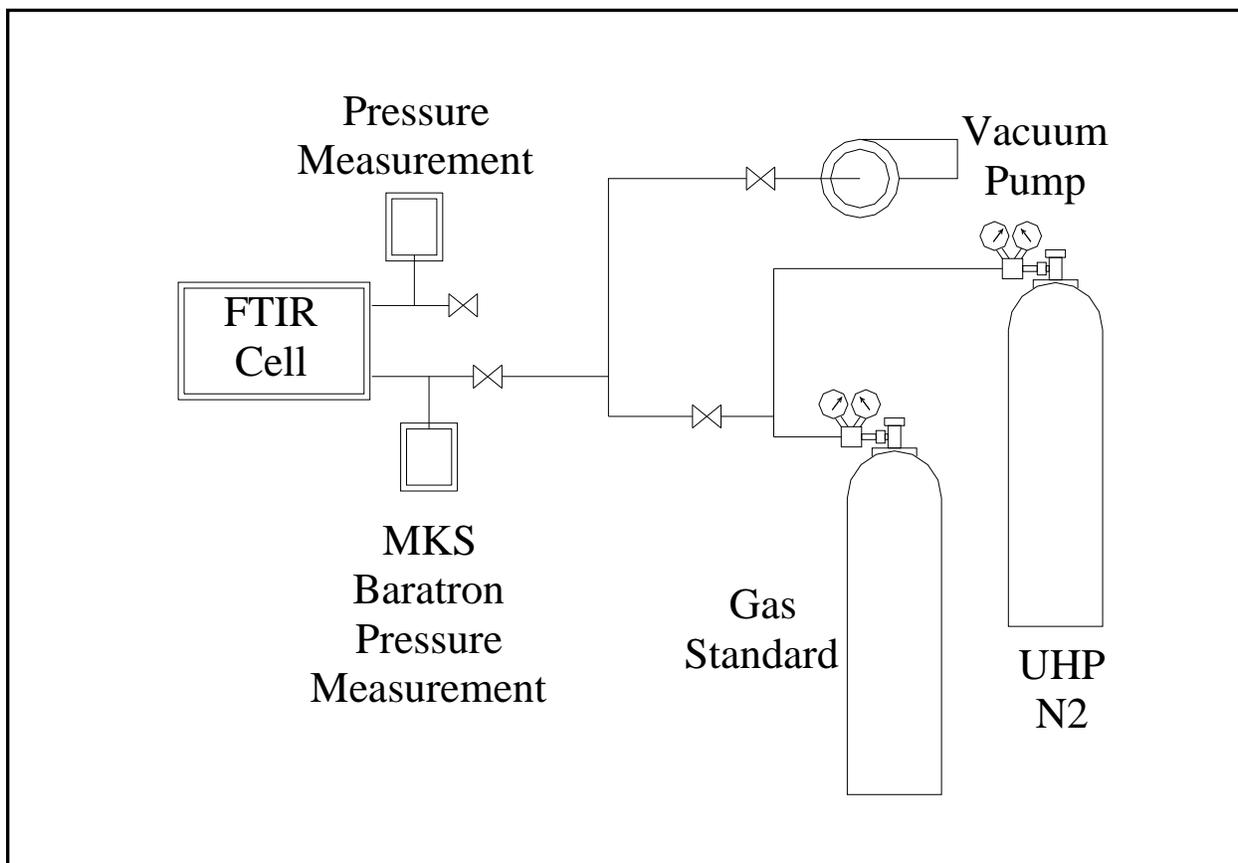


Figure 2-1. Reference Generation Hardware Configuration

2.2 Hardware Procedures

A series of on-site calibration and system checks was performed on each FTIR and sampling system prior to testing to ensure data of known quality. These checks consisted of the following:

- **Cell Leak Checks**

This test checks the integrity of each cell by pulling a vacuum on it and then monitoring the leak rate. The acceptance criteria for this test is a leak rate < 2 torr/minute. The FTIR sample cells on-site were verified to have a leak rate well under 1 torr/minute prior to testing.

- **Infrared Detector Linearity Checks**

For best results, it must be assured that the infrared detector yields a linear response throughout a reasonable absorbance range and all the frequencies in a set of test

spectra. A software linearizer is used to continuously adjust the MCT detector preamp signal in order to achieve the desired response. To optimize the linearizer, background spectra are acquired with and without a polyethylene film card in the IR beam.

Comparison of the strongly absorbing polyethylene bands in the low, mid and high frequency regions against a clean background enables the processor to appropriately set the linearizer terms (offset, linear, quad, cubic and delay). This procedure was run prior to the start of testing, and subsequent spectra were visually checked on a periodic basis to confirm that linearity was maintained.

- **Noise Equivalent Absorbance (NEA) or Signal-to-Noise Ratio (SNR) Tests**

This provides a measure of the system noise, that is the sensitivity of the instrument for the specified spectral resolution (0.5 cm^{-1} , in this case) and number of scans (256, or 2 minute of signal averaging, in most cases). An NEA/SNR test was run upon set-up, then re-checked before the second die-casting machine was sampled. The results for both systems, which were used to assess the field detection limits, were as follows:

20.1m Path Length System 2010

Range = $1000\text{-}1100\text{cm}^{-1}$, RMS Noise= 0.1783 milliAU, SNR= 2435

Range = $2450\text{-}2550\text{cm}^{-1}$, RMS Noise= 0.1836 milliAU, SNR= 2366

Range = $4200\text{-}4300\text{cm}^{-1}$, RMS Noise= 0.4385 milliAU, SNR= 990

5.11m Path Length System 2030

Range = $900\text{-}1000\text{cm}^{-1}$, RMS Noise= 0.1 milliAU, SNR= 4200

Range = $2450\text{-}2550\text{cm}^{-1}$, RMS Noise= 0.1 milliAU, SNR= 3644

Range = $4100\text{-}4200\text{cm}^{-1}$, RMS Noise= 0.37 milliAU, SNR= 1167

- **Path Length**

The sample cell used for these tests was geometrically fixed at 20.1 meters for one FTIR system, and 5.1 meters for the other.

- **Spectrometer Frequency and Resolution Checks**

A real-time check of frequency position and resolution was performed prior to and directly after each round of testing by monitoring a specific water absorption line (present in ambient air). The position of this line must not deviate more than $\pm 0.005 \text{ cm}^{-1}$ from the reference value over the course of each test. Likewise, the linewidth (directly related to instrument resolution) of this line must not deviate more than $\pm 0.05 \text{ cm}^{-1}$ from the reference value over the course of each test.

- **Spectral Background**

A spectral background is essentially a “blank spectrum” in that it does not contain any of the target compounds present in the sample. It was created by purging the cell with ultra-high-purity (UHP) nitrogen while collecting a spectrum. This spectrum was then used by the analytical software to ratio against each sample spectrum to produce an absorbance spectrum for quantitative analysis. A new spectral background was generated prior to each sampling run.

- **Sample Cell Exchange Rate**

Given sampling flow rates on the order of 2 liters/min through either cell during the majority of monitoring tests, a complete sample exchange takes place every 6 seconds for the 5.1 meter cell, and 15 seconds for the 20.1 meter cell. Since spectral signal averaging was conducted over 30 second and 1 minute intervals, each collected spectrum represented an integrated average over multiple sample cell exchanges.

- **FTIR Measurement Error**

As with all analytical devices, extractive FTIR measurements are known to have a given error associated with them. Steps were taken throughout the measurement process to minimize sampling error. Sampling error is dependant on many factors including interferences contained in the sample stream, and optical depth of references that are applied. Errors were minimized by applying a series of references at various optical depths to account for any nonlinearities or dynamic concentrations in the sample matrix. Spectra were also manually inspected for qualitative and quantitative validation. As a result of these efforts, it is believed that the measurements taken in this study have a level of uncertainty that is on the order of 10 percent.

3.0 Extractive FTIR Sampling Systems

Two extractive-type FTIR systems were used for the testing conducted at Internet. MKS FTIR spectrometers and sample cells were used to speciate and quantify the gaseous compounds at each die-casting crucible. In general, the system components include a inconel sample probe (3/8" OD), a heated PFA-grade Teflon extraction line, the on-line FTIR spectrometer interfaced to a heated, nickel-coated sample cell, a sample pump, and rotameter. Given this configuration, real-time monitoring consisted of pulling a gas stream continuously from the sample probe through the sampling system into the heated FTIR sample cell. Sample flow was maintained at approximately 6.5 ft³/hr by a diaphragm pump connected to the outlet of the FTIR cell. The rotameter at the sample cell exhaust was used to monitor the system sample flow. A schematic is shown in Figure 3-1.

Inside each FTIR cell, a set of optically matched gold-plated mirrors reflects an infrared beam through the sample gas multiple times. As the beam passes through the sample, the molecules in the sample absorb some of its energy. After exiting the cell, the infrared beam is directed to a liquid-nitrogen cooled mercury/cadmium/telluride (MCT) detector, a photoconductive device that produces an electrical voltage proportional to the amount of infrared light that strikes it. The strength of the absorption at particular frequencies is a measure of the compound's concentration. The total distance traveled by the infrared beam inside the cell is the cell path length, and is an important variable used in determining sample concentrations. For this project, cell path lengths were fixed at 20.1 and 5.1 meters.

The FTIR sample cell and extraction lines were maintained at a temperature of 150°C (to prevent any condensation losses and preclude the formation of HF mists). Cell pressures were continuously recorded during measurement periods using a pressure sensor calibrated over the 0-900 torr range. Instrumental resolutions were set to 0.5 cm⁻¹ and signal averaging was performed over 30 second and one-minute periods.

As shown in Table 1-2, a total of two cold chamber die-casting machines were tested at the Palmyra and Hannibal facilities. Figure 3-2 illustrates the sample locations on the crucible lid for cold chamber #32 at the Palmyra facility. While 6 sample points were available for extracting gas, only points #3, 4 and 6 were used. Points 3 and 4 are normally used as cover gas injection points; when sampling from these points, the cover gas was equilibrated at the same flow rate over the remaining four injection points. Sampling from point 6 had no impact on cover gas distribution because it is the location of a thermocouple port.

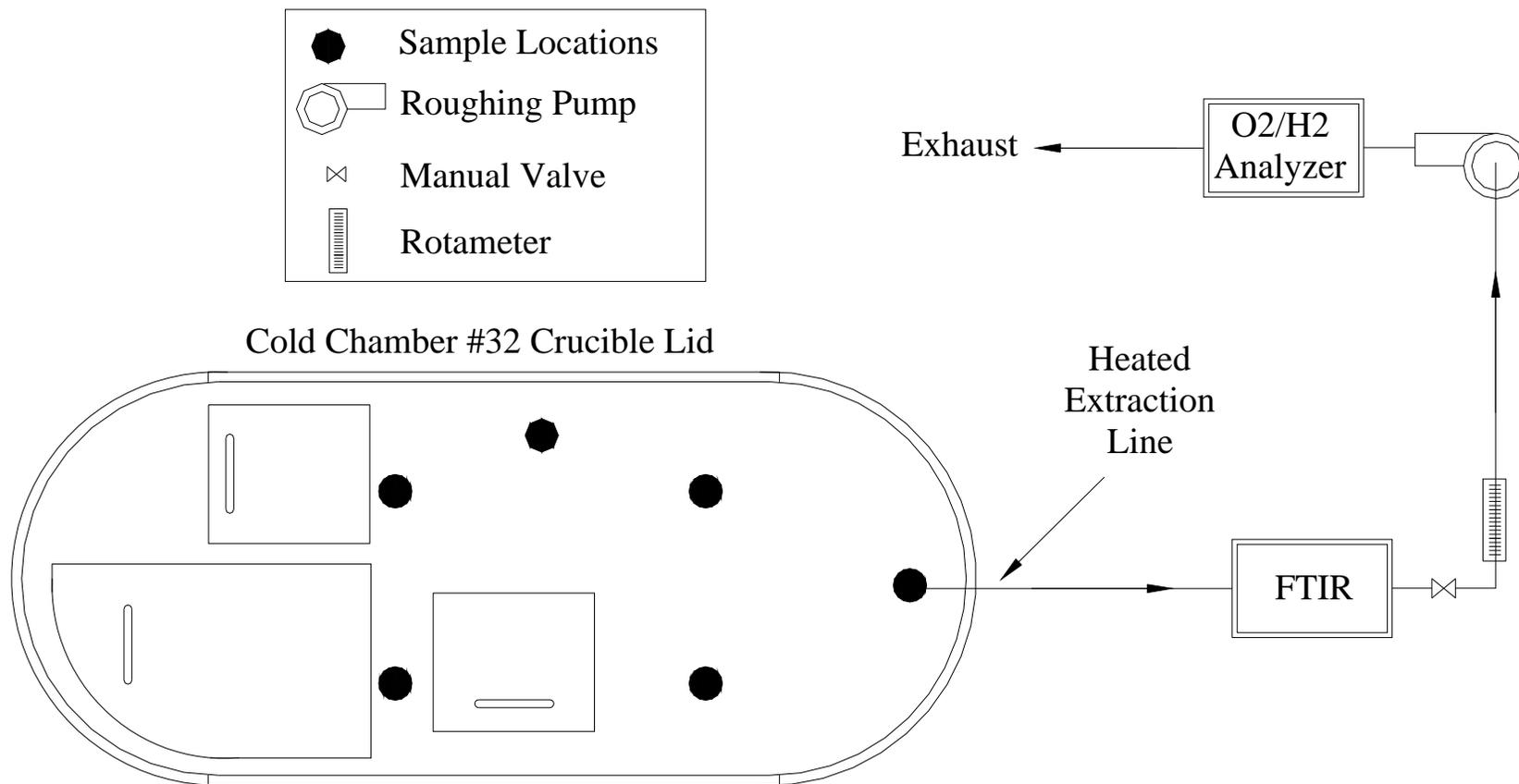


Figure 3-1. Sampling System Schematic

Cold Chamber #32 Crucible Lid

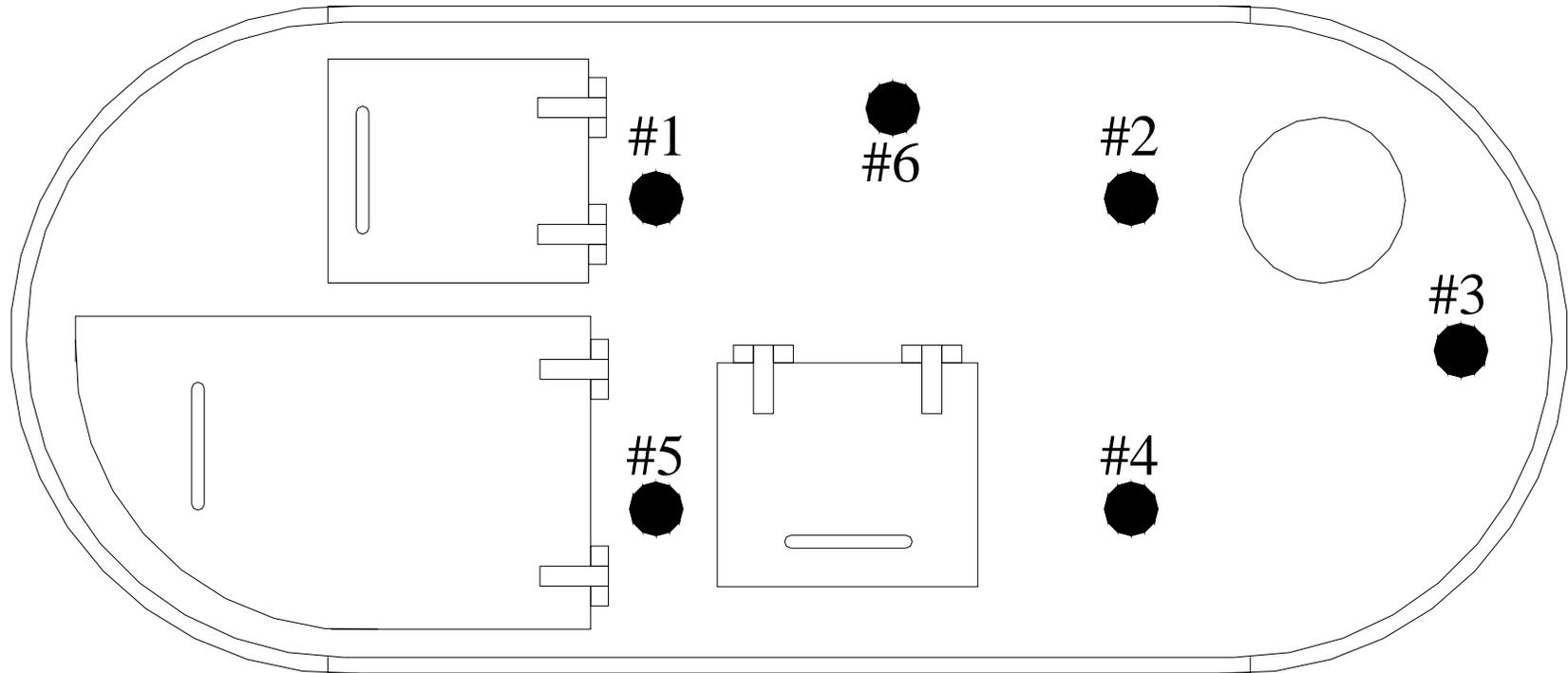


Figure 3-2. Sample Locations for Cold Chamber #32 at Palmyra

Figure 3-3 shows the sample locations for cold chamber #4 at Hannibal. Two sampling points were used, with one near the ingot feed door (sampling point #1) and the other near the pump feed to the die (sampling point #2). Samples at both points were obtained through a stainless steel tube inserted into the headspace along the side of the thermocouples. Consequently, unlike machine #32, the cover gas distribution regime remained constant. For both machine #4 and #32, magnesium ingots were fed to the crucible automatically approximately every 3 to 5 minutes. Please note that the sampling regime (in terms of sampling points and elevation above the melt surface) differed between the two cold chambered machines. As a result, comparison between machines should not be considered to be under strictly identical conditions.

Cold Chamber #4 Crucible Lid

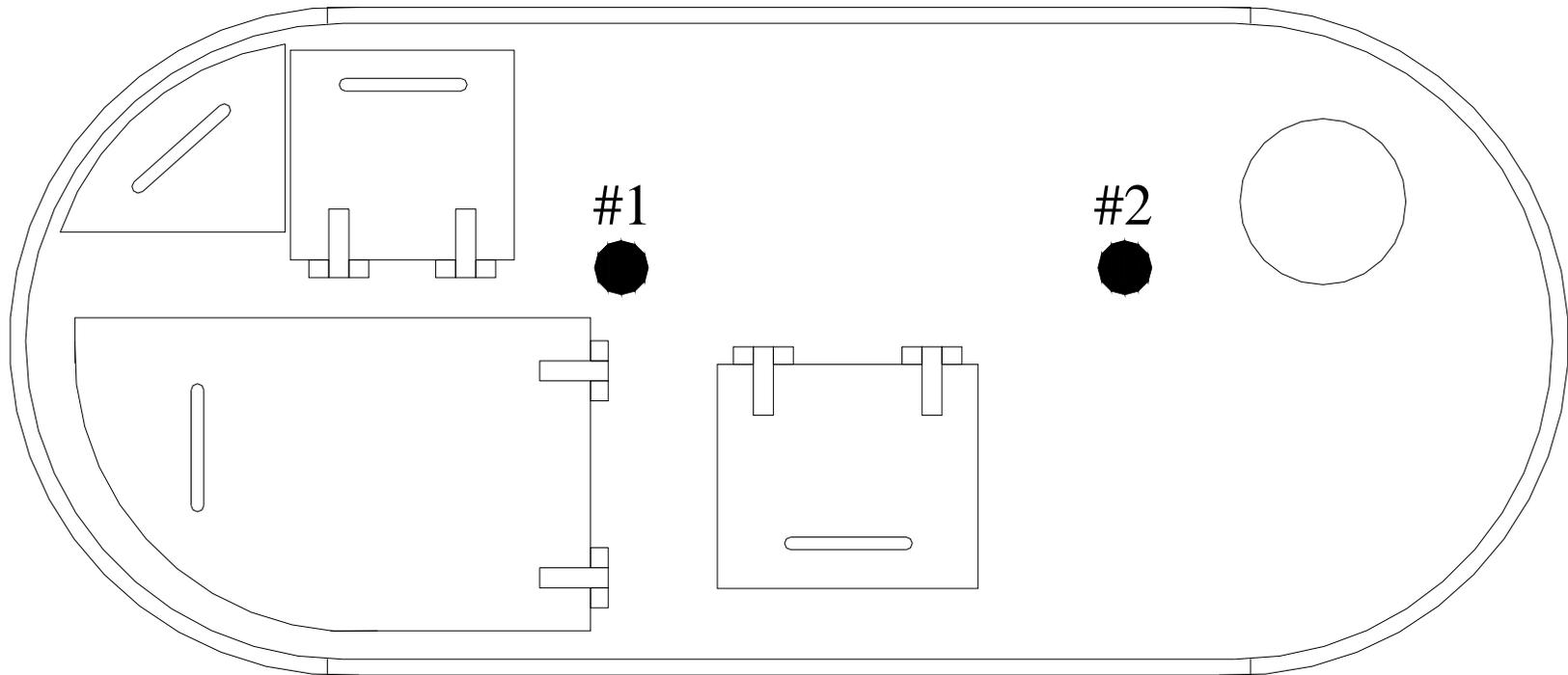


Figure 3-3. Sample Locations for Cold Chamber #4 at Hannibal

3.1 Hydrogen/Oxygen Analyzer

During the testing period, a Nova Model 340WP portable analyzer was used on the HFC-134a and Novec™ 612 cover gas tests for the continuous measurement of oxygen concentrations. The instrument is shown in Figure 3-4. This instrument uses an electrochemical sensor to measure oxygen. A



Figure 3-4. Nova 340WP Oxygen and Hydrogen Analyzer

chemical reaction occurs when the sensor is exposed to oxygen, resulting in a millivolt output proportional to the oxygen concentration in the sample gas. This small voltage is used to display the measured oxygen concentration on the instrument's front panel meter. The analyzer was placed inline with the exhaust of an FTIR sample pump and readings were recorded into field logbooks. The sample system was closed up to that point, eliminating the introduction of ambient air to the sample.

4.0 Test Results

This section presents all the test data and is broken into three main sections divided by cover gas type: SF₆, HFC-134a and Novec™ 612. Table 1-1 shows the test schedule, flow rates and concentrations used during testing. Data collected during sampling downtime (i.e., probe taken out while switching sample points) is excluded from the calculations. Additionally, there are some instances where data values were below detection limits; consequently, “BDL” is reported as the value. In order to calculate average values over a period where data points are below detection limits, a value of “MDL”, the method detection limit, divided by two is used in the average calculation. Normally a range for average values is reported using zero for the low range and the detection limit for the high range. However, the data tables are simplified by using an “average value” of the detection limit divided by two to calculate averages. This only occurs during instances where data values are both below and above calculated detection limits. Detection limits are calculated as 3 times the standard deviation when the analyte is not present in the sample streams. When the analyte is present, a method based detection limit is determined by using the noise-based equation defined in Section 2.2.

The data in this section are presented in summary Tables 4-1 through 4-9. Appendix A presents charts detailing data trends and process activities, such as ingot loading, for all the compounds that were above detection limits.

4.1 HFC-134a Cover Gas with Nitrogen and Carbon Dioxide Diluents

Table 4-1 presents results for data collected at sample locations 3 and 4 on cold chamber #32 (see Figure 3-2) using a nitrogen diluent. The data from the two sample locations were relatively similar, with HFC-134a and C₂F₆ concentrations on the order of 80 ppm and 1.5 ppm, respectively. HF concentrations were considerably lower at location #4 (<1 ppm) compared to location #3 (60 ppm), which may be an indication of increased ambient air infiltration occurring at the crucible lid near location #3. Degradation product gases at detectable parts per million levels include: CO₂, CO, HF, COF₂, C₂F₆, NO, N₂O, NO₂ and CH₄. NO, N₂O, NO₂ levels sharply increased during the drossing, which may indicate that their formation is a function of ambient air dilution. This is possibly confirmed by slight concentration increases during ingot loading. Gases that were below detectable limits include: OF₂, H₂CO, C₃F₈, C₄F₈, C₂H₂, CF₄, CH₂F₂, and CHF₃.

The next test conducted on cold chamber #32 was with HFC-134a cover gas but with CO₂ instead of nitrogen diluent. Table 4-2 summarizes the data.

Table 4-1. Data Summary for Machine #32 Running HFC-134a with Nitrogen Diluent

	H ₂ O (%)	O ₂ (%)	CO ₂ (ppm)	HFC 134a (ppm)	HF (ppm)	COF ₂ (ppm)	CO (ppm)	C ₂ H ₄ (ppm)	C ₂ F ₆ (ppm)	CH ₄ (ppm)	NO (ppm)	NO ₂ (ppm)	N ₂ O (ppm)
Point #3													
Min	0.35	na	1,526.79	22.73	BDL	BDL	179.12	BDL	0.71	BDL	6.99	BDL	4.73
Max	2.19	na	11,317.12	148.41	274.65	3.65	846.21	BDL	1.59	25.13	22.55	1.16	12.81
Avg	0.65	na	4,591.43	83.85	64.44	0.60	424.71	BDL	1.10	6.98	14.85	0.27	7.94
Std Dev	0.40	na	2,646.50	29.24	72.70	0.66	129.67	na	0.18	4.16	2.13	0.21	1.84
Point #4													
Min	0.33	6.80	424.83	8.34	BDL	BDL	2.66	BDL	BDL	BDL	BDL	BDL	BDL
Max	0.90	7.60	22,448.88	429.71	2.05	1.03	1,086.21	36.05	10.05	102.96	55.86	8.56	41.06
Avg	0.41	7.20	4,645.96	68.16	0.56	0.38	383.49	0.61	2.26	7.77	9.62	0.68	10.30
Std Dev	0.06	na	4,025.25	61.31	0.39	0.11	173.52	2.44	1.54	11.59	6.96	1.11	5.69
MDL	0.04	0.10	89.38	1.40	0.73	0.70	0.88	0.63	0.10	0.76	2.59	0.29	0.32

BDL = below detectable limit
MDL = method detection limit
na = not applicable
nc = not calculated

Table 4-2. Data Summary for Machine #32 Running HFC-134a with CO₂ Diluent

	H ₂ O (%)	O ₂ (%)	CO ₂ (%)	HFC 134a (ppm)	HF (ppm)	COF ₂ (ppm)	CO (ppm)	CH ₄ (ppm)	C ₂ F ₆ (ppm)	NO (ppm)	NO ₂ (ppm)	N ₂ O (ppm)
Point #4												
Min	0.28	6.00	48.15	166.32	0.10	BDL	2,187.62	BDL	1.44	7.33	7.07	13.63
Max	3.50	7.60	91.62	602.16	262.45	71.71	11,476.85	4.85	4.35	27.36	23.98	34.11
Average	0.45	6.78	79.94	337.47	197.50	37.73	5,643.24	1.89	2.80	17.13	15.23	23.49
Std Dev	0.52	0.69	7.05	86.93	61.24	12.74	1,703.74	0.70	0.62	3.77	3.88	2.89
Point #6												
Min	0.25	na	72.36	147.58	214.40	4.47	1,724.29	1.38	1.47	26.79	2.86	18.04
Max	0.30	na	78.66	270.23	420.31	13.09	3,071.40	2.90	2.35	37.99	5.60	25.98
Average	0.29	na	75.01	206.22	283.95	8.05	2,267.02	2.26	1.83	32.07	3.89	21.85
Std Dev	0.01	na	1.39	31.93	58.65	2.01	300.93	0.33	0.22	2.93	0.65	1.60
Point #6 Static												
Min	0.26	na	76.15	212.63	190.96	3.16	1,640.54	1.96	1.36	26.23	2.47	18.78
Max	0.29	na	82.42	356.55	239.84	9.91	2,273.98	3.92	1.91	33.50	3.78	27.40
Average	0.27	na	79.64	268.55	211.36	6.11	1,975.95	2.91	1.64	29.21	3.12	23.80
Std Dev	0.01	na	1.62	30.88	11.34	1.41	149.36	0.35	0.17	1.69	0.28	1.76
MDL	0.04	0.10	0.01	1.40	0.22	0.70	0.88	0.35	0.10	0.58	0.30	0.03

BDL = below detectable limit
 MDL = method detection limit
 na = not applicable
 nc = not calculated

Table 4-2 includes data for sample locations #4 and #6 in addition to a sampling period where the die casting machine was in a static condition (not casting). Results from the HFC-134a/CO₂ cover gas mixture were similar to those observed during use of the HFC-134a/N₂ cover gas mixture. The primary difference was the absence of C₂H₂ formation during the HFC-134a/CO₂ test. HFC-134a presence in the crucible headspace was at higher concentrations during the CO₂ diluent test (200 to 300 ppm) compared to N₂ (60 to 80 ppm). Additionally, another variation was that the NO, N₂O and NO₂ levels were more significant during the HFC-134a/CO₂ test (on the order of 15 to 30 ppm, as opposed to less than 10 ppm). The data obtained from sample location #4 and location #6 did not vary significantly, which may result from them being spaced close together. However, location #4 had much higher concentrations for COF₂ and CO. The additional source for CO may be from burning natural gas at the pump feed line into the die, or as a byproduct of CO₂ reacting with Mg.

4.2 Novec™ 612 Cover Gas with 85% CO₂ and 15% Air Diluents

A series of tests were run with Novec™ 612 used as a cover gas. Tests were run at two locations, sample point #1 near the ingot load door and sample point #2 near the magnesium pump. Tables 4-3 and 4-4 present data from sample location #1. Table 4-3 shows results during casting conditions, while results presented in Table 4-4 were taken while the machine was in a static condition. Results indicate that most of the Novec™ 612 cover gas (supplied at 126 ppm) is consumed, with headspace concentrations on the order of 7 to 8 ppm. The level of Novec™ 612 decomposition does not change significantly when comparing active casting (average 7 ppm) versus static conditions (average 8 ppm). The compounds detected include: CO, NO, NO₂, HF, COF₂, CH₄, C₂F₆ and C₃F₈. NO and NO₂ were not detectable during the static testing.

As illustrated in Table 4-3, additional compounds, SiF₄ and H₂CO, were detected at sample location #1. While H₂CO formation maybe expected as a symptom of the presence of hydrocarbons under intense heat, SiF₄ formation was not expected since the source for silicon is unknown. One possibility is that source of silicon may be from the insulation that coats the oven that is used to warm ingots before loading into the crucible.

Tables 4-5 and 4-6 present data from the Novec™ 612 at sampling location #2. As at sample location #1, data were collected with the machine in both a casting and static condition. Novec™ 612 measurements were relatively consistent with those observed on the ingot side. Sampling at location #2 also yielded similar compounds: CO, NO₂, HF, COF₂, CH₄, C₂F₆ and C₃F₈. As at sample location #1, SiF₄ and H₂CO were detected during casting conditions. NO was not detected at sample location #2, and is only detected on the ingot door side, which may be indicative of degradation product formation caused by increased ambient air dilution during ingot loading. This is possibly confirmed by the observation that no NO₂ was detected during the static periods.

By comparing all four tables for the Novec™ 612 cover gas a few observations can be made. Both casting and static conditions produced C₂F₆ and C₃F₈, at concentrations on the order of 1 to 2 ppm and 5 to 10 ppm, respectively. It was also noted that the formation of C₂F₆ and C₃F₈ were not affected by the machine being in a static (non-casting) condition. However, the static condition on the pump side location (sample point #2) seemed to produce higher average levels of COF₂ (25 ppm as opposed to <10 ppm). It was also observed that HF levels were higher on the pump side (sample location #2) compared to the ingot loading side (sample location #1) for both casting and static conditions (i.e., 110 to 126 ppm compared to 50 ppm) even though O₂ levels remained relatively constant throughout the test conditions. Higher HF

concentrations may be due to the fact that the pump side cover gas protective layer is not penetrated during the addition of ingots. Consequently, the protective layer on the pump side remains intact relative to the ingot loading side, and consequently, any excess Novec™ 612 present undergoes thermal degradation instead of reaction with the melt surface. As an additional point of interest, in prior Novec™ 612 measurement trials⁵, the presence of perfluoroisobutylene (PFIB) as a possible by-product of cover gas degradation was noted; however, in these measurements, no PFIB was detected.

⁵ Mibrath, D., "Development of 3M™ Novec™ 612 Magnesium Protection Fluid as a Substitute for SF₆ Over Molten Magnesium," International Conference on SF₆ and the Environment: Emission Reduction Technologies, November 21-22, 2002, San Diego, CA.

Table 4-3. Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #1, Casting Condition

	H ₂ O (%)	O ₂ (%)	CO ₂ (%)	Novec (ppm)	HF (ppm)	COF ₂ (ppm)	CO (ppm)	CH ₄ (ppm)	C ₂ F ₆ (ppm)	NO (ppm)	NO ₂ (ppm)	H ₂ CO (ppm)	C ₃ F ₈ (ppm)	SiF ₄ (ppm)
Minimum	BDL	7.50	55.43	3.68	36.51	1.18	939.94	1.11	0.61	BDL	1.20	0.35	3.19	0.05
Maximum	0.54	7.60	98.20	10.99	78.67	8.55	24,340.95	39.94	1.64	3.62	10.74	9.68	11.00	0.06
Average	0.15	7.55	87.02	6.85	54.39	4.92	10,847.66	7.04	1.04	1.47	4.05	1.30	6.46	0.05
Std Dev	0.12	0.07	9.56	1.47	8.50	1.50	6,695.05	6.17	0.33	0.69	2.19	1.79	1.76	0.02
MDL	0.05	0.10	0.11	0.02	1.37	0.13	0.45	0.76	0.02	0.55	0.66	0.35	0.46	0.05

BDL = below detectable limit

MDL = method detection limit

nc = not calculated

Table 4-4. Data Summary for the Novec™ 612 Cover Gas on machine #4, Sample Point #1, Static Condition

	H ₂ O (%)	O ₂ (%)	CO ₂ (%)	Novec (ppm)	HF (ppm)	COF ₂ (ppm)	CO (ppm)	CH ₄ (ppm)	C ₂ F ₆ (ppm)	C ₃ F ₈ (ppm)
Minimum	BDL	7.70	94.61	6.04	46.63	5.13	2,822.24	0.67	1.34	4.82
Maximum	BDL	7.70	98.59	10.68	57.90	9.13	5,995.77	1.30	1.61	6.16
Average	BDL	7.70	96.85	8.12	52.30	7.39	3,932.86	0.92	1.47	5.47
Std Dev	nc	0.00	0.90	0.93	2.90	0.82	765.93	0.15	0.08	0.33

Table 4-5. Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #2, Processing Condition

	H ₂ O (%)	Novec (ppm)	CO ₂ (%)	CH ₄ (ppm)	CO (ppm)	COF ₂ (ppm)	NO ₂ (ppm)	HF (ppm)	C ₂ F ₆ (ppm)	SiF ₄ (ppm)	C ₃ F ₈ (ppm)	H ₂ CO (ppm)
Minimum	0.09	7.86	73.94	0.79	413.07	5.53	BDL	BDL	0.39	BDL	5.43	BDL
Maximum	0.28	15.63	94.18	38.80	5,682.59	14.36	2.81	151.56	1.18	1.81	14.42	5.01
Average	0.18	12.23	86.10	5.02	2,791.35	9.47	0.82	112.93	0.80	BDL	9.97	BDL
Std Dev	0.04	1.66	3.79	4.18	1,593.56	1.74	0.50	34.37	0.16	0.28	1.99	0.37
MDL	0.05	0.02	0.11	0.76	0.45	0.13	0.66	1.37	0.06	0.61	0.46	1.29

BDL = below detectable limit
 MDL = method detection limit
 nc = not calculated

Table 4-6. Data Summary for the Novec™ 612 Cover Gas on Machine #4, Sample Point #2, Static Condition

	H ₂ O (%)	O ₂ (%)	CO ₂ (%)	HF (ppm)	CH ₄ (ppm)	Novec (ppm)	C ₃ F ₈ (ppm)	COF ₂ (ppm)	CO (ppm)	C ₂ F ₆ (ppm)
Minimum	0.03	7.80	89.41	80.50	0.92	5.17	6.79	15.59	4,520.21	1.41
Maximum	0.22	7.90	95.61	177.54	11.77	12.79	10.67	30.35	11,817.11	1.95
Average	0.04	7.83	92.32	126.21	8.45	10.54	9.75	26.51	8,108.58	1.78
Std Dev	0.03	0.06	1.25	12.38	1.85	1.36	0.57	2.77	1,768.96	0.08

4.3 SF₆ Cover Gas with Air Diluent

In order to evaluate the replacement cover gases (HFC-134a and Novec™ 612), baseline testing using SF₆ was conducted on both machines at the Palmyra and Hannibal facilities. Table 4-7 thru 4-9 shows the data for cold chamber machines #32 and #4.

Average SF₆ concentrations in the cold chamber #32 were 1.2 percent. Compounds measured within the crucible headspace included: CO₂, CO, NO, N₂O, NO₂, CH₄, HF, SO₂ and H₂CO, and details are shown in Table 4-7. An anomaly in the data was observed while sampling at the location #3 on cold chamber #32. Immediately after connecting the sample probe to location #3, hydrochloric acid (HCl) was detected. A maximum concentration of 7 ppm was measured shortly after connecting the probe; however, after this spike, HCl levels decayed below the detection limit for the remainder of the test. This behavior is independent of the process activity and therefore may be attributed to chlorine being stripped from the Teflon core in the extraction line.

SF₆ cover gas testing continued on cold chamber #4 at the Hannibal facility. SF₆ measurements within the crucible headspace were between 0.2 and 0.33 percent. Data tables for the SF₆ testing on both the ingot loading side (sample location #1) and pump side (sample location #2) are shown in Tables 4-8 and Tables 4-9. The tables indicate some uneven cover gas distribution within the same crucible headspace. For example, SF₆ readings averaged at 2,036 ppm (ingot loading side) versus 3,347 ppm (pump side). The detected compounds, CO₂, CO, CH₄, NO, N₂O, NO₂, HF, SO₂ and H₂CO were all slightly higher at the sample location #1. This may be associated with the intrusion of ambient air into the headspace during ingot loading.

Table 4-7. Data Summary for the SF₆ Cover Gas on Machine #32

	H ₂ O (%)	CO ₂ (ppm)	CO (ppm)	CH ₄ (ppm)	N ₂ O (ppm)	NO (ppm)	NO ₂ (ppm)	SF ₆ (ppm)	HF (ppm)	SO ₂ (ppm)	H ₂ CO (ppm)	HCL (ppm)
Point #3												
Minimum	BDL	975.05	2.70	BDL	3.09	1.65	BDL	6,669.69	BDL	125.30	0.63	BDL
Maximum	0.38	2,211.27	15.53	1.34	7.81	11.64	BDL	12,706.61	161.93	356.30	1.20	7.05
Average	0.08	1,290.12	5.47	0.41	6.95	9.52	BDL	12,077.99	109.08	288.95	1.05	1.34
Std Dev	0.05	239.86	3.02	0.19	0.83	1.84	na	1,063.66	40.77	48.04	0.12	1.11
Point #6												
Minimum	BDL	BDL	2.17	0.67	1.15	BDL	BDL	10,587.04	BDL	93.80	0.77	BDL
Maximum	0.11	1,067.19	24.88	3.92	4.06	7.64	15.93	12,831.12	0.30	321.69	1.12	BDL
Average	0.04	411.69	4.35	1.12	2.32	1.76	4.36	12,276.78	0.12	153.84	0.96	BDL
Std Dev	0.01	172.46	3.65	0.39	0.93	1.65	4.20	393.41	0.04	41.00	0.07	na
Point #4												
Minimum	BDL	BDL	2.83	0.64	2.46	1.70	BDL	11,474.55	0.07	177.07	BDL	BDL
Maximum	0.08	708.19	17.37	2.45	3.53	4.65	BDL	12,154.06	0.19	222.24	1.02	BDL
Average	0.05	331.54	5.13	0.95	2.75	3.12	BDL	11,929.89	0.13	199.50	0.91	BDL
Std Dev	0.01	150.56	3.18	0.31	0.23	0.53	na	154.89	0.03	9.19	0.05	na
MDL	0.08	342.48	1.53	0.36	0.12	0.82	3.35	863.88	0.05	10.31	0.57	0.24

BDL = below detectable limit
 MDL = method detection limit
 na = not applicable
 nc = not calculated

Table 4-8. Data Summary for SF₆ Cover Gas with Air Diluent on Machine #4, Sample Point #1

	H ₂ O (%)	O ₂ (%)	CH ₄ (ppm)	CO ₂ (ppm)	CO (ppm)	NO (ppm)	N ₂ O (ppm)	NO ₂ (ppm)	HF (ppm)	SF ₆ (ppm)	SO ₂ (ppm)	H ₂ CO (ppm)
Minimum	0.35	19.90	BDL	206.74	0.73	BDL	2.22	4.11	12.98	1,072.94	45.81	BDL
Maximum	1.04	20.00	32.73	1,848.61	269.97	8.37	14.30	34.87	56.00	3,051.00	335.11	5.93
Average	0.68	19.95	2.16	448.76	30.17	1.97	5.09	14.13	31.68	2,036.70	138.12	0.40
Std Dev	0.15	0.06	3.36	252.26	38.74	1.27	1.91	5.52	6.27	447.53	61.83	0.53
MDL	0.05	0.1	0.76	49.56	0.45	3.19	0.5	0.66	1.37	58.16	7.0	1.29

Table 4-9. Data Summary for SF₆ Cover Gas with Air Diluent on Machine #4, Sample Point #2

	H ₂ O (%)	O ₂ (%)	CH ₄ (ppm)	CO ₂ (ppm)	CO (ppm)	NO (ppm)	N ₂ O (ppm)	NO ₂ (ppm)	HF (ppm)	SF ₆ (ppm)	SO ₂ (ppm)
Minimum	0.16	20.50	BDL	158.86	1.42	BDL	1.56	1.59	BDL	2,059.83	62.62
Maximum	0.53	20.70	2.56	662.98	71.67	3.70	3.92	10.58	25.41	3,899.50	187.21
Average	0.26	20.55	0.56	247.48	6.83	BDL	2.33	3.67	14.07	3,347.14	99.83
Std Dev	0.08	0.10	0.24	81.15	10.13	0.51	0.41	1.08	6.39	386.22	23.99
MDL	0.05	0.1	0.76	49.56	0.45	3.19	0.5	0.66	1.37	58.16	7.0

BDL = below detectable limit

MDL = method detection limit

nc = not calculated

5.0 Conclusions

5.1 Cover Gas Test Observations

5.1.1 HFC-134a Cover Gas Testing with N₂ and CO₂ Diluents

The primary compounds detected when running HFC-134a and a N₂ or CO₂ diluent are: CO₂, CO, HF, C₂F₆, and COF₂. The time series plots in Appendix A show that concentrations of these compounds decreased during ingot loading, which indicates that the gases are originating from inside the crucible. For machine #32, HF and C₂F₆ concentrations were on the order of 100 to 200 parts per million (ppm) and 2 ppm, respectively. COF₂ concentrations were below the detectable limit of the FTIR instrument when using an N₂ diluent, but increased to levels greater than 10 ppm with a CO₂ diluent. There was no marked difference in the results obtained during cold-chamber casting and static (i.e., during periods when no melt casting occurred) periods. The plots in Appendix A also illustrate that additional degradation products, such as H₂CO, CH₄, C₂H₂, and C₂H₄ are formed with the addition of ambient air during the ingot loads. Compounds including H₂CO, NO, N₂O and NO₂ also had background levels inside the headspace that sharply increased during ingot loading. Detection of C₂H₂ and C₂H₄ was sporadic with a few spikes that occur during ingot loading. Other than these spikes, concentrations were close to or below detectable limits. Another trend was that the CO, HF, NO, N₂O and NO₂ and COF₂ concentrations were higher for the HFC-134a/CO₂ testing than HFC-134a/N₂.

5.1.2 Novec™ 612 Cover Gas Testing with CO₂ and Air Diluents

The primary compounds detected when using Novec™ 612 as a cover gas are: CO, COF₂, C₃F₈, C₂F₆ and HF. Measurements were conducted during both casting and static conditions on a cold-chamber die-casting machine. HF was present at relatively constant levels during both conditions; however, the concentrations increase to higher levels during ingot loading. CH₄, SiF₄, and H₂CO were observed to increase during ingot loading. SiF₄ and CH₄ were not detected during the static tests, which may indicate that silicon is entering with the ingot. H₂CO was present without the addition of ingots. Low levels of NO (ingot side only) and NO₂ were detected during casting but were not present during the static conditions. These levels also increased during ingot loading. Since the Novec™ 612 feed concentration was low compared to HFC-134a and SF₆, the average concentrations detected within the crucible headspace was accordingly much lower as well. The highest average concentration of Novec™ 612 was 12 ppm versus average concentrations for HFC-134a (ranging from 70 to 2,760 ppm) or SF₆ (ranging 2,040 to 12,280 ppm).

5.1.3 SF₆ Cover Gas Testing with Air Diluent

The primary compounds detected when using SF₆ are: HF and SO₂. For both cold-chamber measurements, HF concentrations were on the order of 10-30 ppm. Low levels of NO, N₂O and NO₂ (i.e., on the order of 2 ppm) were detected. Additional compounds detected included H₂CO. H₂CO levels remained close to the FTIR detection limit.

5.2 Cover Gas Degradation

One of the main objectives with this cover gas study is to determine the level of degradation. Degradation estimates are calculated as:

$$\text{Percent Degradation} = \frac{\text{Delivery Concentration} - \text{Measured Concentration}}{\text{Delivery Concentration}}$$

Tables 5-1 and 5-2 provide a summary of all the tests and calculated level of degradation. The above equation assumes that the crucible headspace is a well-sealed environment preventing infiltration of dilution air. However, it is not due to ingot loading and seal leaks in the crucible lids. Consequently, in order to correct for ambient air dilution, a dilution factor is calculated by measuring the concentration of specific compounds inside the crucible headspace.⁶

For the HFC-134a testing, dilution factors were estimated using delivery and measured CO₂ data. CO₂ data is used wherever possible since the data is taken by FTIR on a continuous basis. Using CO₂ data is not valid when CO₂ is formed as a by-product of the cover gas process, such as occurs when using an N₂ diluent. It is assumed that dilution levels experienced during the CO₂ test condition will be consistent with dilution levels present during the N₂ diluent tests since measurements were conducted on the same die casting machine and at similar cover gas flow rates; consequently, dilution factors derived from the CO₂ data are applied to the HFC-134a/N₂ data.

For the Novec™ 612 cover gas tests, O₂ values were used to determine dilution inside the crucible. Steady state values for O₂ concentrations during the Novec™ 612 testing were averaged to determine the dilution factor. O₂ readings were used for the dilution calculations because O₂ was the most suitable of the gases in the sample matrix. The level of oxygen in ambient air was measured at a constant 20 percent by volume. It has the lowest chance of

⁶ Please refer to Section 5.5 for a discussion regarding the uncertainty associated with this methodology.

interaction with other gases, therefore minimizing any bias from reaction products. A sample calculation for a 7 percent O₂ reading is shown below.

$$\text{Dilution Factor} = \frac{20\% - 7\%}{20\%} = 0.65$$

The above calculation uses 20 percent by volume O₂ for ambient air. For the Novec™ 612 testing, 7.3 liters per minute (lpm) of air was delivered with 41.3 lpm of CO₂ for a diluent gas. In this case, the O₂ reading must be corrected to account for the incoming O₂ which is determined as:

$$\text{Corrected O}_2 \text{ Value} = 7\% - \left(\frac{7.3}{41.3 + 7.3} \right) \times 20\% = 4.0\%$$

The equation above assumes the O₂ concentration in the air of the delivery gas is 20 percent. Therefore the dilution factor for Novec™ 612 testing is calculated as:

$$\text{Novec}^{\text{TM}} \text{ 612 Dilution Factor} = \frac{20\% - 4.0\%}{20\%} = 0.8$$

Table 5-1. Machine #32 Percent Degradation for Cover Gas Testing

Table	Date	Time	Die Casting Machine	Cover Gas Mixture Components	Sample Location	Cover Gas Mixture Flow ^a (lpm)	Cover Gas Delivery Conc. ^a (ppm)	Cover Gas Measured Conc. (ppm)	Dilution Factor ^b	Cover Gas Degradation	Test Condition
4-1	1-Oct	0932-1036	Cold #32	HFC-134a/N ₂	#3	21	4,000	84	0.79 (± 0.06)	97%	Casting
4-1	1-Oct	1036-1236	Cold #32	HFC-134a/N ₂	#4	21	4,000	68	0.79 (± 0.06)	98%	Casting
4-2	1-Oct	1618-1845	Cold #32	HFC-134a/CO ₂	#4	20	4,000	338	0.80 (± 0.07)	89%	Casting
4-2	1-Oct	1845-1916	Cold #32	HFC-134a/CO ₂	#6	20	4,000	206	0.75 (± 0.01)	93%	Casting
4-2s	1-Oct	1916-2000	Cold #32	HFC-134a/CO ₂	#6	20	4,000	269	0.80 (± 0.02)	92%	Static
4-7	3-Oct	0959-1037	Cold #32	SF ₆ /Air	#3	65	19,000	12,078	0.69 (± 0.17)	8%	Casting
4-7	3-Oct	1114-1154	Cold #32	SF ₆ /Air	#6	65	19,000	12,277	0.69 (± 0.17)	6%	Casting
4-7	3-Oct	1200-1222	Cold #32	SF ₆ /Air	#4	65	19,000	11,930	0.69 (± 0.17)	9%	Casting

^aAs provided by Intermet and AMC

^bRange represents the standard deviation for measured concentrations of indicator compounds.

Table 5-2. Machine #4 Percent Degradation for Cover Gas Testing

Table	Date	Time	Die Casting Machine	Cover Gas Mixture Components	Sample Location	Cover Gas Mixture Flow ^a (lpm)	Cover Gas Delivery Conc. ^a (ppm)	Cover Gas Measured Conc. (ppm)	Dilution Factor ^b	Cover Gas Degradation	Test Condition
4-3	6-Oct	1359-1525	Cold #4	Novec 612/CO ₂ /Air	#1	Novec/CO ₂ =48.6, Air=7.3	126	7	0.77 (± 0.07)	93%	Casting
4-4s	6-Oct	1530-1600	Cold #4	Novec 612/CO ₂ /Air	#1	Novec/CO ₂ =48.6, Air=7.3	126	8	0.77 (± 0.07)	92%	Static
4-5	6-Oct	1451-1655	Cold #4	Novec 612/CO ₂ /Air	#2	Novec/CO ₂ =45.6, Air=6.8	126	10	0.76 (± 0.06)	89%	Casting
4-6s	7-Oct	1600-1654	Cold #4	Novec 612/CO ₂ /Air	#2	Novec/CO ₂ =45.6, Air=6.8	126	12	0.76 (± 0.06)	87%	Static
4-8	7-Oct	1036-1227	Cold #4	SF ₆ /Air	#1	37.5	5,000	2,037	0.77 (± 0.07)	47%	Casting
4-9	7-Oct	0830-1025	Cold #4	SF ₆ /Air	#2	37.5	5,000	3,347	0.77 (± 0.07)	13%	Casting

^aAs provided by Intermet and 3M™

^bRange represents the standard deviation for measured concentrations of indicator compounds.

For the SF₆ cover gas tests, air was used as a diluent gas and therefore O₂ readings were 20 percent inside and outside of the crucible. As a result, CH₄ was chosen as an alternative to O₂ to calculate the dilution factor since its presence is constant in ambient air. Results illustrate that CH₄ values were stable within the crucible headspace and the impact of ingot loading is clearly shown in time series plots. Dilution factors were determined by comparing CH₄ values measured in ambient air to readings taken inside the crucible headspace. As with O₂, steady state values for CH₄ are used to determine dilution so that values are not biased higher during ingot loading. During testing at the Hannibal facility, ambient air concentrations for the SF₆ testing never reached steady state and the readings were deemed unreliable. Therefore, it was assumed that the dilution for the Novec 612™ testing on the same machine is approximately the same as the dilution for the SF₆ testing.

Average percent degradation for HFC-134a with N₂ and CO₂ diluents, and Novec 612™ cover gases were 98, 91, and 90 percent, respectively. SF₆ degradation estimates on the cold chamber tests were on the order of 10 percent; however, during one test an unexpectedly high value of 47 percent was observed. The reason for this occurrence is unknown.

5.3 Occupational Health and Safety

Each of the cover gases evaluated in this study can produce by-products that may be of concern from an occupational exposure standpoint. For example, formaldehyde (H₂CO), carbonyl fluoride (COF₂), hydrofluoric acid (HF), and carbon monoxide (CO), have very low 8-hour time-weighted average exposure limits of 0.75, 2, 3, and 25 ppm, respectively⁷. While gas concentrations presented in this report are in some cases significantly higher than these OSHA levels, it is important to note that these concentrations are not reflective of actual occupational exposure conditions, in that they have been measured within the enclosed crucible headspace, and not ambient air within operator “breathing” zones. To confirm this observation, during some measurement activities at the Palmyra facility, FTIR samples were taken at distances appropriate to operator “breathing” zones. Even though maximum crucible headspace concentrations for H₂CO and COF₂ were above occupational standards, ambient measurements taken outside the crucible were below the FTIR detectable limits of 300 ppb. While this test is by no means a true industrial hygiene analysis, the results illustrate that given the high level of ventilation present at these facilities, the crucible head space gases are contained to such an extent that significant concentrations were not found in ambient air close to the crucible lid. However, further occupational exposure monitoring would be required to confirm these observations.

⁷ OSHA Permissible Exposure Limits (PELs). <<http://www.osha.gov>>

5.4 Global Climate Change Impact Discussion

One of the benefits of using HFC-134a and Novec™ 612 as cover gases within magnesium production and processing is that their contribution to global climate change is significantly lower when compared to SF₆. This is evident when comparing their estimated global warming potentials (GWP). Table 5-3 presents GWP's of several compounds detected during this study.

Table 5-3. Comparison of 100-Year GWP Estimates from the Intergovernmental Panel on Climate Change's (IPCC's) Second (1996) and Third (2001) Assessment Reports

Gas	1996 IPCC GWP	2001 IPCC GWP
Methane	21	23
Nitrous Oxide	310	296
HFC-134a	1,300	1,300
Perfluoromethane (CF ₄)	6,500	5,700
Perfluoroethane (C ₂ F ₆)	9,200	11,900
Perfluoropropane (C ₃ F ₈)	7,000	8,600
Sulfur Hexafluoride (SF ₆)	23,900	22,200

Sources:

IPCC (1996), Climate Change 1995: The Scientific of Climate Change. Intergovernmental Panel on Climate Change, Cambridge University Press. Cambridge, U.K.

IPCC (2001), Climate Change 2001: The Scientific Basis. Intergovernmental Panel on Climate Change, Cambridge University Press. Cambridge, U.K.

The crucible headspace contains a large variety of compounds, but only those with GWP values were used to estimate the overall GWP impact of switching to alternate cover gases (i.e., HFC-134a and Novec™ 612) from SF₆. This calculation was achieved by multiplying the average concentrations (parts per million by volume) for each of the component cover gases and applicable degradation products with their respective GWP factors (obtained from the Third Assessment Report of the Intergovernmental Panel on Climate Change) to obtain a normalized CO₂ GWP value. The total CO₂ GWP equivalent of the gases measured in the crucible headspace for HFC-134a and Novec™ 612 testing scenarios were summed and compared to the corresponding SF₆ condition (or baseline). Tables 5-4 and 5-5 show that when comparing the composite, or overall GHG emissions, the alternate cover gases have a much lower impact. An obvious source for this reduction can be found in a direct comparison of cover gas GWPs. SF₆ has a GWP of 22,200, while HFC-134a's GWP is 1,300. Novec™ 612's GWP has not been supplied by 3M, but is likely to be extremely low (i.e., Novec™ 612 is a fluorinated ketone,

which is assumed to have a GWP on the order of 1⁸). In addition to having lower GWPs, the alternate cover gas compounds have much higher decomposition (on the order of 90 percent) within the crucible headspace compared to SF₆ (on the order of 10 percent). While the decomposition of HFC-134a and Novec™ 612 does produce degradation products with GWPs, their impact is minimal due to the very low concentrations generated. Compared against the SF₆ test, switching to HFC-134a and Novec™ 612 produces a reduction in overall global warming impact of gases inside the crucible headspace on the order of 99 percent.⁹

The above comparison does not include the specific flow rates for each cover gas. In order to provide a more comprehensive analysis of composite GWP, an additional comparison was conducted. Using the ideal gas law, the molecular weights of each gas and the delivery flow rate of the cover gas was used to estimate the composite emission rate in grams per hour (g/hr). This equation can be described as follows:

$$\text{Emission Rate} \left(\frac{\text{grams}}{\text{hour}} \right) = \text{ppm} \times \text{MW} \times \text{lpm} \times \frac{60 \text{ min}}{\text{hour}} \div (38.6 \text{ liters/mole} \times 10^6)$$

ppm = measured average concentration in parts per million

MW = molecular weight in grams per mole

lpm = gas flow in liters per minute

These values were summed to provide a composite GWP value that was weighted by the cover gas flow rate. The overall GWP values were then compared against the corresponding values for SF₆. Based on this approach, both HFC-134a and Novec™ 612 were observed to have a global warming impact greater than 99 percent lower than SF₆.¹⁰ Details of the flow-weighted GWP impacts are presented in Tables 5-6 and 5-7.

⁸ Milbrath, D. *3M™ Novec™ 612 Magnesium Protection Fluid: It's Development and Use in Full Scale Molten Magnesium Processes*, Proceedings of the 60th Annual International Magnesium Association Conference, May 2003, Stuttgart, Germany.

⁹ Please refer to Section 5.5 for a discussion regarding the uncertainty associated with this methodology.

¹⁰ Ibid.

Table 5-4. GHG Emission Comparison for Machine #32 Using HFC-134a and SF₆

Table	Die Casting Machine	Cover Gas Mixture Components	Sample Location	GWP Weighted CO ₂	GWP Weighted HFC-134a	GWP Weighted SF ₆	GWP Weighted CH ₄	GWP Weighted N ₂ O	GWP Weighted C ₂ F ₆	GWP Weighted C ₃ F ₈	Normalized CO ₂ Equivalent	Average by cover gas	Chg from SF ₆
4-1	Cold #32	HFC-134a/N ₂	#3	4,591	109,000	0	161	2,349	13,138	0	129,239	126,310 ^b	>99%
4-1	Cold #32	HFC-134a/N ₂	#4	4,646	88,603	0	179	3,050	26,904	0	123,382		
4-2	Cold #32	HFC-134a/CO ₂	#4	799,398	438,713	0	43	6,953	33,266	0	1,278,373	1,165,677 ^c	>99%
4-2	Cold #32	HFC-134a/CO ₂	#6	750,129	268,088	0	52	6,468	21,796	0	1,046,533		
4-2 ^a	Cold #32	HFC-134a/CO ₂	#6	796,386	349,120	0	67	7,044	19,509	0	1,172,126		
4-7	Cold #32	SF ₆ /Air	#3	1,290	0	268,131,458	9	2,059	0	0	268,134,816	268,508,383 ^d	-
4-7	Cold #32	SF ₆ /Air	#6	412	0	272,544,500	26	686	0	0	272,545,623		
4-7	Cold #32	SF ₆ /Air	#4	332	0	264,843,543	22	813	0	0	264,844,710		

^aIndicates static test (i.e., die casting machine not casting)

^bAverage composite GWP for HFC-134a/N₂ cold-chamber tests (Table 4-1)

^cAverage composite GWP for HFC-134a/CO₂ cold-chamber tests (Table 4-2)

^dSF₆ composite GWP baseline estimate for comparison with HFC-134a/CO₂ and N₂ cold-chamber tests (Table 4-7)

Table 5-5. GHG Emission Comparison for Machine #4 Using Novec™ 612 and SF₆

Table	Die Casting Machine	Cover Gas Mixture Components	Sample Location	GWP Weighted CO ₂	GWP Weighted HFC-134a	GWP Weighted SF ₆	GWP Weighted CH ₄	GWP Weighted N ₂ O	GWP Weighted C ₂ F ₆	GWP Weighted C ₃ F ₈	Normalized CO ₂ Equivalent	Average by cover gas	Chg from SF ₆
4-3	Cold #4	Novec 612/CO ₂ /Air	#1	870,240	0	0	162	0	12,410	55,582	938,394	989,068 ^b	98%
4-4 ^a	Cold #4	Novec 612/CO ₂ /Air	#1	968,471	0	0	21	0	12,667	47,043	1,033,063		
4-5	Cold #4	Novec 612/CO ₂ /Air	#2	860,991	0	0	115	0	9,548	85,722	956,376		
4-6 ^a	Cold #4	Novec 612/CO ₂ /Air	#2	933,429	0	0	159	0	21,641	83,838	1,028,438		
4-8	Cold #4	SF ₆ /Air	#1	449	0	45,214,808	50	1,506	0	0	45,216,813	59,762,118 ^c	-
4-9	Cold #4	SF ₆ /Air	#2	247	0	74,306,474	13	689	0	0	74,307,423		

^aIndicates static test (i.e., die casting machine not casting)

^bAverage composite GWP for Novec™ 612/CO₂/Air cold-chamber tests (Tables 4-3, 4-4, 4-5 and 4-6)

^cSF₆ composite GWP baseline estimate for comparison with Novec™ 612/CO₂/Air cold-chamber tests (Tables 4-8 and 4-9)

Table 5-6. GHG (Weighted By Gas Flow Rate) Emission Comparison for Machine #32 Using HFC-134a and SF₆

Table	Die Casting Machine	Cover Gas Mixture Components	Sample Location	GWP Weighted CO ₂ (g/hr)	GWP Weighted HFC-134a (g/hr)	GWP Weighted SF ₆ (g/hr)	GWP Weighted CH ₄ (g/hr)	GWP Weighted N ₂ O (g/hr)	GWP Weighted C ₂ F ₆ (g/hr)	GWP Weighted C ₃ F ₈ (g/hr)	Normalized CO ₂ Equivalent (g/hr)	Average by cover gas	Chg from SF ₆
4-1	Cold #32	HFC-134a/N ₂	#3	7	363	0	0	3	59	0	432	430 ^b	>99%
4-1	Cold #32	HFC-134a/N ₂	#4	7	295	0	0	4	121	0	427		
4-2	Cold #32	HFC-134a/CO ₂	#4	1,094	1,392	0	0	10	143	0	2,638	2,302 ^c	>99%
4-2	Cold #32	HFC-134a/CO ₂	#6	1,026	850	0	0	9	94	0	1,979		
4-2 ^a	Cold #32	HFC-134a/CO ₂	#6	1,090	1,107	0	0	10	84	0	2,290		
4-7	Cold #32	SF ₆ /Air	#3	6	0	3,956,311	0	9	0	0	3,956,326	3,961,853 ^d	-
4-7	Cold #32	SF ₆ /Air	#6	2	0	4,021,426	0	3	0	0	4,021,431		
4-7	Cold #32	SF ₆ /Air	#4	1	0	3,907,798	0	4	0	0	3,907,803		

^aIndicates static test (i.e., die casting machine not casting)

^bAverage composite GWP for HFC-134a/N₂ cold-chamber tests (Table 4-1)

^cAverage composite GWP for HFC-134a/CO₂ cold-chamber tests (Table 4-2)

^dSF₆ composite GWP baseline estimate for comparison with HFC-134a/CO₂ and N₂ cold-chamber tests (Table 4-7)

Table 5-7. GHG (Weighted By Gas Flow Rate) Emission Comparison for Machine #32 Using Novec™ 612 and SF₆

Table	Die Casting Machine	Cover Gas Mixture Components	Sample Location	GWP Weighted CO ₂ (g/hr)	GWP Weighted HFC-134a (g/hr)	GWP Weighted SF ₆ (g/hr)	GWP Weighted CH ₄ (g/hr)	GWP Weighted N ₂ O (g/hr)	GWP Weighted C ₂ F ₆ (g/hr)	GWP Weighted C ₃ F ₈ (g/hr)	Normalized CO ₂ Equivalent (g/hr)	Average by cover gas	Chg from SF ₆
4-3	Cold #4	Novec 612/CO ₂ /Air	#1	2,893	0	0	0	0	129	790	3,813	4,003 ^b	99%
4-4 ^a	Cold #4	Novec 612/CO ₂ /Air	#1	3,220	0	0	0	0	183	668	4,071		
4-5	Cold #4	Novec 612/CO ₂ /Air	#2	2,686	0	0	0	0	93	1,143	3,922		
4-6 ^a	Cold #4	Novec 612/CO ₂ /Air	#2	2,880	0	0	0	0	207	1,117	4,205		
4-8	Cold #4	SF ₆ /Air	#1	1	0	384,894	0	4	0	0	384,899	508,720 ^c	-
4-9	Cold #4	SF ₆ /Air	#2	1	0	632,539	0	2	0	0	632,541		

^aIndicates static test (i.e., die casting machine not casting)

^bAverage composite GWP for Novec™ 612/CO₂/Air cold-chamber tests (Tables 4-3, 4-4, 4-5 and 4-6)

^cSF₆ composite GWP baseline estimate for comparison with Novec™ 612/CO₂/Air cold-chamber tests (Tables 4-8 and 4-9)

5.5 Uncertainty Discussion

The results of this measurement study should not be interpreted to represent an absolute analysis of HFC-134a, Novec™ 612, and SF₆ cover gas degradation. While this study does present a relatively accurate measurement analysis and approximate comparison of GHG emissions, there are several areas of uncertainty inherent with this methodology. These areas of uncertainty include FTIR error, dilution correction methods, and analytical and operational variation across the two machines evaluated.

Measurements taken by the FTIR are subject to variability inherent with any highly complex analytical device. While all prudent steps were taken to minimize this contributor to uncertainty (see Section 3.2 (page 3-8)), some small degree of error is unavoidable.

The different cover gas feed matrices utilized throughout the study created difficulties in defining a good indicator to estimate cover gas dilution within the crucible headspace. Three indicator compounds were utilized to estimate dilution, CO₂, CH₄, and O₂. Although all these gases may be produced from several sources and consumed in reactions with other components in the headspace, they provided the best available approach under the circumstances (e.g., a foreign indicator compound could not be added to the cover gas, since it could disrupt the cover gas feed mix, and make its application to the melt surface unrepresentative of ideal “test” conditions). However, considering the potential sources for indicator interference, and the subsequent uncertainty associated with the development of dilution factors, the values (i.e., cover gas destruction levels and GHG emissions) presented in this report should be considered as a “best estimate” only, and not an absolute value.

Even though an effort was made to conduct the measurement study on machines as identical as possible; there are some variations to consider when interpreting these results. For example, cold chamber machine #32 uses much higher SF₆ concentrations (19,000 vs. 5000 ppmv SF₆) and flow rates (65 vs. 38 lpm) than machine #4; consequently, it requires more than 4 times the cover gas for adequate melt protection. Additionally, the sampling ports used on both machines were slightly different, which may impact cover gas distribution regimes. Since the crucible headspace is a dynamic reaction space, it is not known how the sampling differences between cold chamber machine #32 and #4 are reflected in the data. Consequently, due to the differences in the analytical sampling and the actual furnaces used, when reviewing the results of this analysis it is important that comparisons only be made between SF₆ and the replacement cover gas compounds for each respective machine, and not between HFC-134a and Novec™ 612.



Office of Air and Radiation (6202J)
Washington, DC 20460

EPA 430-R-04-004
May 2004