Measured SF_6 Emissions From Magnesium Die Casting Operations

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Outline

- Background
- Past Studies
- Experimental Setup
- Results
- Summary

Background

- EPA's Voluntary Partnership
  - 17 Partners: 100% Primary Production; 80% Casting
  - Partners Track and Report Annual SF_6 Usage
- Industry Emission Estimates based on IPCC Methodology
  - 100% SF_6 Consumption = 100% SF_6 Emissions
- Extent of SF_6 Destruction May Vary
  - Industry Opinion Speculates Between 10 to 50%
- Implement Measurement Study to Quantify Degree of SF_6 Destruction

Past Studies

- Hanawalt, J.D. (1972)
  - At approx. 2” above the melt surface, potential SF_6 byproducts, including SO_2 and MgF_2, were identified
- Couling S., et al. (1977)
  - Reported potential SF_6 destruction
- Couling, S., Leontis, T. (1980)
  - Identified CO and HF decomposition products at melt surface
- Tranell et al. (2001)
  - Proposed mechanism for SF_6 melt protection: SF6 dissociates to highly reactive fluorine species. These species form a dense protective film containing MgF_2

Experimental Setup

- Measurements were Conducted on 2 Hot Chambered Die Casting Machines
  - Furnace temp. 650^{o}C; Furnace volumes the same
- Cover Gas Mixture
  - 0.3-0.4% SF_6; 17% CO_2; 83% Dry Air
- Cover Gas Supply
  - Approx. 5 l/min
- Magnesium Alloy Ingot Feeding
  - Every 7-9 minutes

Die Casting Machine

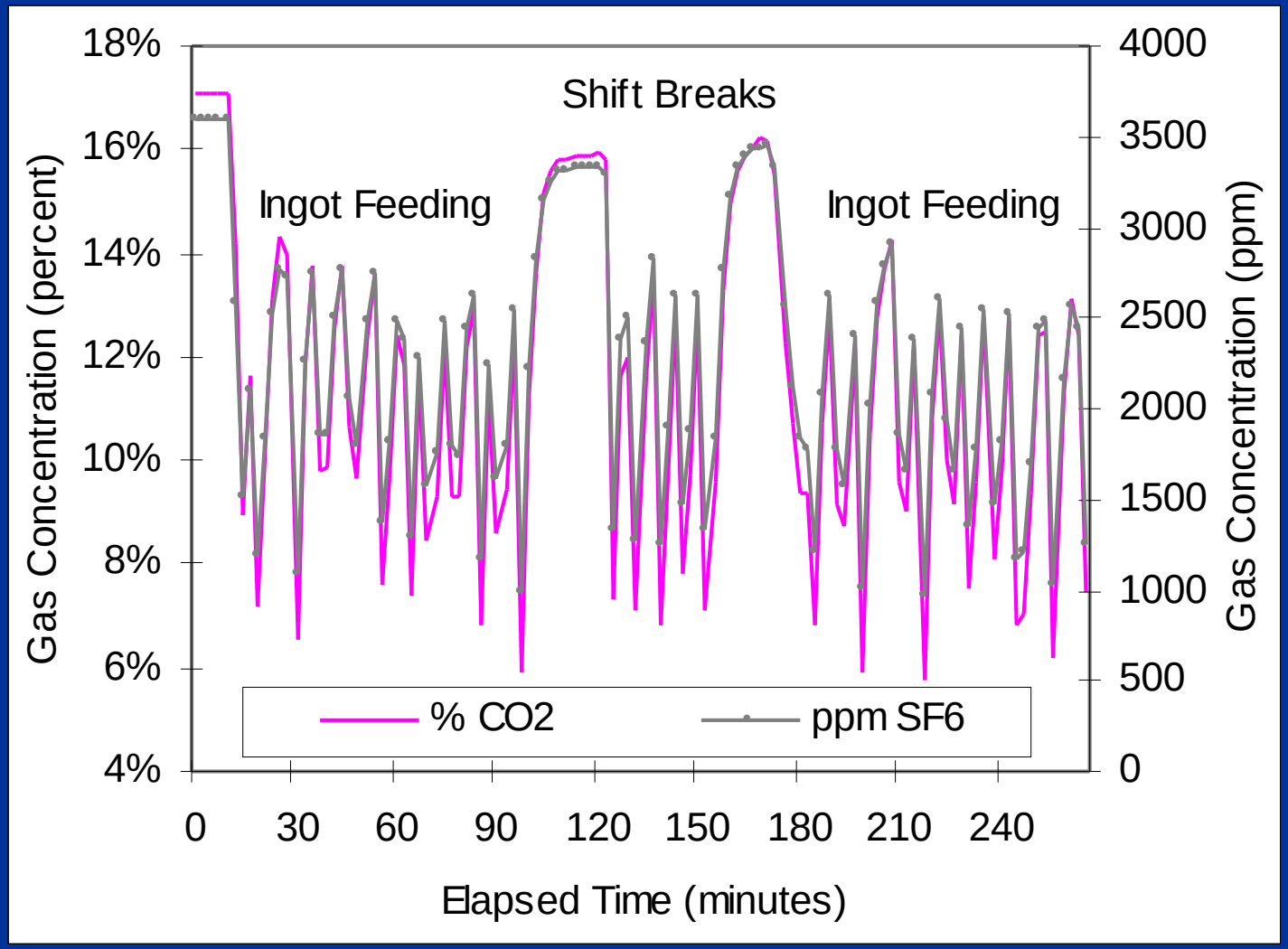
Experimental Design

- Real-Time SF_6 Monitoring using FTIR Systems
- Monel Sample Probe Placed in Furnace Enclosure at Approx. 1-2” above Melt Surface
- FTIR Sample Flow Maintained at 2-3 l/min
- Signal Averaging over Approx. 2 Minute Periods
- Sample Cell/PFA-Grade Teflon Extraction Lines Maintained at 150^{o}C to Preclude Formation of HF and Prevent Condensation Losses

Experimental Design…..contd.

- Test for Homogeneity of Cover Gas in Furnace Head Space
  - Used 2 FTIR systems of 20.1 and 5.1 meter fixed cell path lengths
  - Confirmed uniform distribution of compound concentrations throughout the furnace enclosure
- Gas grab samples taken for GC analysis
  - For CO_2, GC/FTIR samples agree within $\pm$ 9 percent
  - For SF_6, GC/FTIR samples agree within $\pm$ 30 percent

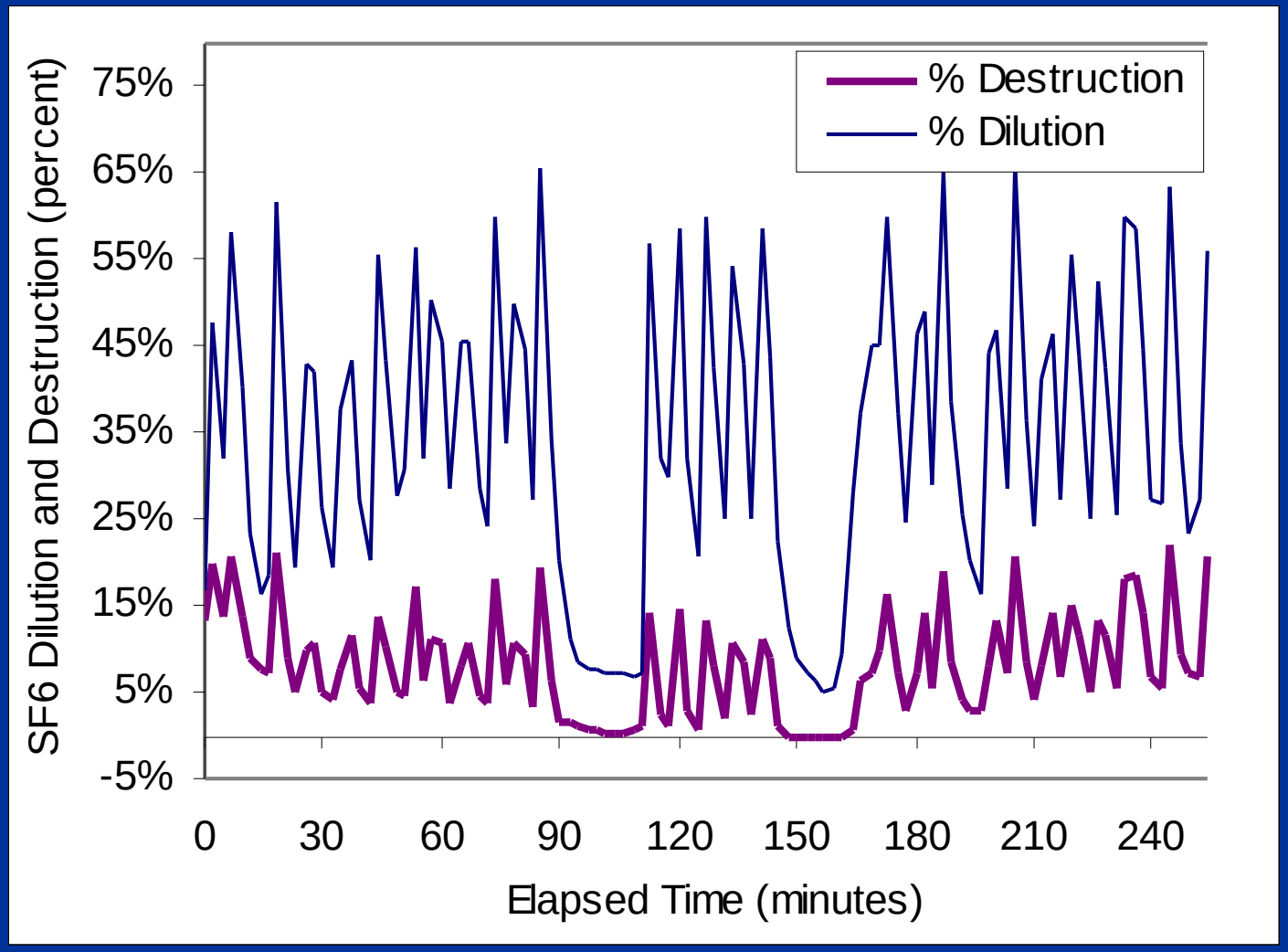
Time Series Plots of SF_6/CO_2 – Machine 1



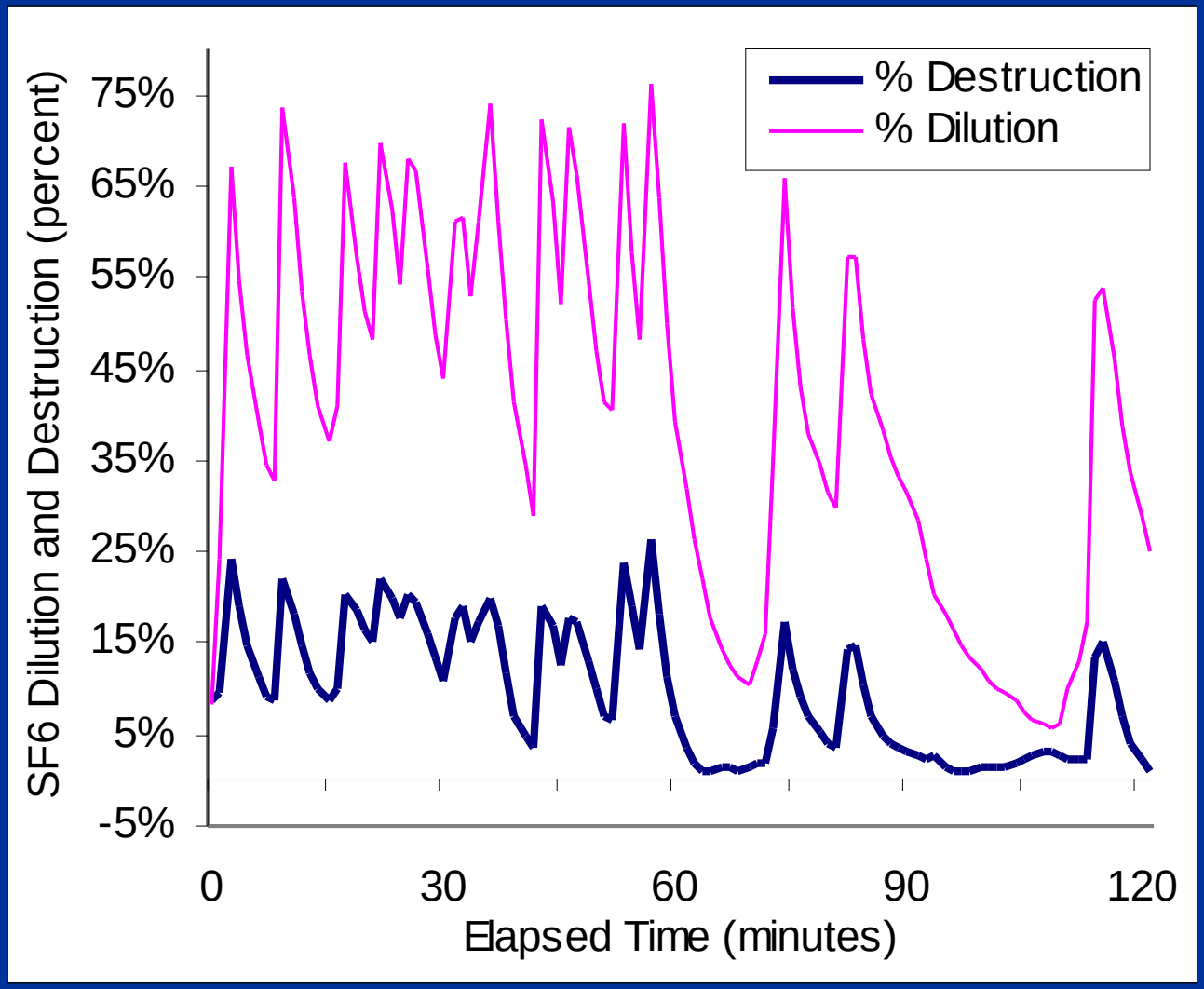
Assumptions

- Reactivity of CO_2 was estimated to be < 0.3% conversion to CO
- Consequently, it was assumed that the observed reduction in measured CO_2, compared to its feed cover gas concentration, is almost solely attributable to ambient air dilution and leakage
- Used CO_2 measurements to estimate dilution/leakage effects, i.e., ratio of headspace concentration to average cover gas content
- Quantity of SF_6 destroyed is defined as the difference between the concentration of SF_6 that was expected to be in the furnace headspace, after factoring in dilution/leakage effects, and the SF_6 that was present in the cover gas feed

SF_6 Dilution and Destruction – Machine 1



SF_6 Dilution and Destruction – Machine 2



Observations

- There appears to be a correlation between SF_6 decomposition and dilution spikes, with an increase in destruction occurring during ingot feeding.
- During ingot feeding, magnesium alloy ingots are added to the furnace via the access lid, which disrupts the SF_6 protective film by creating surface turbulence.
- Also, since SF_6 destruction drops to near zero during work stoppages, it can be concluded that the percent destruction is increased during die casting operations

Results

Operation	Average SF_6 Destruction
Ingot Feeding Periods	15.7 – 20.1 %
Non-Feeding Periods	6.5 – 12.5 %
Staff Breaks/Shift Changes	0.6 – 1.4 %

Measured Byproducts

- FTIR spectral analysis identified HF and SO_2 as the primary reaction byproducts
- No other byproducts were detected above the noise level of the FTIR
- HF and SO_2 concentrations remained low, on the order of 20 ppmv total
- Since there is little release of gaseous byproducts, most of the SF_6 decomposition may occur at the melt surface

Summary

- Maximum SF_6 destruction was observed to occur during ingot feeding operations, and ranged from 16 to 20 percent
- During non-feeding periods the level of destruction decreased to approximately half that observed during feeding periods
- Low levels of byproducts detected – possibility that most of the SF_6 decomposition occurs at the molten metal surface

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