

MEASURED SF₆ EMISSIONS FROM MAGNESIUM DIE CASTING OPERATIONS

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Abstract

Industrial molten magnesium processes primarily utilize sulfur hexafluoride (SF₆) as a cover gas to inhibit surface oxidation, which can result in fires if not controlled. Recent concerns with global warming and subsequent research has determined SF₆ to be a potent and long lived greenhouse gas. Current Intergovernmental Panel on Climate Change (IPCC) Good Practice Guidance for estimating the emissions of SF₆ from industrial magnesium processes assumes that 100 percent of the gas utilized for a given process is emitted directly to the atmosphere. This study examined the SF₆ utilization for a magnesium die-casting process and determined that, for the specific operating conditions, the level of SF₆ destruction was process dependent. Maximum SF₆ 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. While this paper is limited to one facility using a hot-chambered die-casting unit, it does provide a useful step towards defining the true nature of SF₆ emissions from the magnesium industry as a whole.

Introduction

The U.S. magnesium industry is comprised of four major segments including primary magnesium production, die casting, sand casting, and recycling of magnesium products and scrap. The industry has been steadily growing over the past decade at a rate of 5.5 percent per year with most of this growth due to the increased die casting operations (1). Die casting is a process where molten magnesium is injected under high pressure into a steel die or mold to form a wide range of products. The weight and strength characteristics of magnesium materials make them important to the development of more fuel-efficient vehicles, lightweight personal computers, and other applications where high-strength lightweight materials are needed. These characteristics combined with its high resistance to corrosion allow magnesium to be an attractive alternative to aluminum and steel.

Molten magnesium has violent oxidative properties that must be managed for effective processing. The magnesium industry primarily uses sulfur hexafluoride (SF₆) to prevent oxidation and surface burning of the molten metal during the production of primary magnesium, die casting, and recycling operations. SF₆ is used as a source for fluorine species, which are a component in the formation of a dense protective film on the molten magnesium surface (2). SF₆, when used for the protection of molten magnesium surfaces, is a colorless, odorless and nontoxic gas with a concentration between 0.2 to 0.5 percent by volume. Melt losses are lower for SF₆ when compared to other molten magnesium protection compounds, such as SO₂ (3). The use of SF₆ mixtures has been the predominant method for protecting molten magnesium surfaces for several decades.

SF₆ is an extremely stable greenhouse gas, with an atmospheric lifetime estimated at 3,200 years. Its atmospheric concentration is estimated to be approximately 4 parts per trillion (ppt) (4). Although this concentration is small compared to other greenhouse gases, its strong infrared absorption properties and extreme atmospheric inertness make it a highly potent greenhouse gas. Currently, SF₆ emissions from the magnesium industry are estimated based on the assumption that 100 percent of the SF₆ utilized during melt protection operations is emitted to atmosphere (5). However, expert opinion speculates that during melt protection some form of SF₆ destruction, via chemical reaction, may occur. Consequently, this destruction implies that the IPCC methodology overestimates SF₆ emissions inventories. The measurement study described herein provides an initial step towards quantifying the destruction rates of SF₆ during magnesium production and processing operations.

Background

To reduce SF₆ emissions, the U.S. Environmental Protection Agency (EPA) and the magnesium industry jointly developed and launched the voluntary SF₆ Emissions Reduction Partnership for the Magnesium Industry in the late 1990's. Currently, the 16 partners represent 100 percent of primary production and 80 percent of casting operations in the U.S (6). The efforts of the partnership to identify and implement cost effective and technically feasible mitigation options has resulted in a greater than 30 percent reduction in US SF₆ emissions between 1999 and 2001 (7).

One element of EPA's voluntary partnership with the magnesium industry is that partner's track and report annual SF₆ usage. EPA, using IPCC guidelines, employs this information to develop national inventory emissions estimates. Since industry opinion on the extent of SF₆ destruction during magnesium production and processing differs significantly, measurements of SF₆ emissions during these operations are required to establish more accurate emission factors. These factors will be beneficial in accounting for reductions achieved by partners in the SF₆ Emissions Reduction Partnership for the Magnesium Industry and for developing more accurate national greenhouse gas inventories.

Currently, no work has been reported that specifically addresses quantifying the degree of destruction of SF₆. Past measurement studies have been conducted to review the protection mechanism provided by SF₆. In 1972, measurements were conducted to examine the protective atmospheres created by various materials. At SF₆ concentrations greater than 0.2 percent, X-ray diffraction identified several potential SF₆ by-products, including sulfur dioxide (SO₂), and magnesium fluoride (MgF₂) (8). At lower SF₆ concentrations these by-products were not detectable. In 1977, work performed at the Magnesium Research Center at Battelle's Columbus Laboratories compared the metered concentration of SF₆ to that at the molten metal surface (9). The study reported that the SF₆ concentration at the metal surface was about half that

delivered by the metering system, which could indicate a chemical decomposition of SF₆. Additional work using cover gas mixtures containing SF₆, carbon dioxide (CO₂) and air, identified the presence of both carbon monoxide (CO) and hydrogen fluoride (HF), decomposition products of CO₂ and SF₆, at the molten magnesium surface (10). Furthermore, the study suggested that at temperatures in excess of 705 °C, the rate of SF₆ decomposition might accelerate.

A recent study, co-funded by the International Magnesium Association and EPA, has looked at the use of SF₆ and potential alternatives to melt protection (11). It is assumed that the general mechanism for SF₆ melt protection stems from the dissociation of SF₆ to highly reactive fluorine species, such as F or F₂. These species diffuse through the porous magnesium oxide (MgO) layer to form a dense protective film containing MgF₂. Energy Dispersive Spectroscopy indicates that with prolonged exposure to SF₆, the fluorine content of the film grows thicker and results in a stable MgF₂-phase.

Experimental

The measurement study was performed on two hot-chambered die casting machines (Machine A and B) located at the Product Technologies Inc. facility in Minnesota. The machines consisted of a holding furnace assembly for the molten magnesium, pneumatic injection piston, and die press apparatus. The furnaces containing the molten magnesium were electronically heated and controlled using feedback from thermocouples inserted into the pots. The furnaces were approximately 40 inches x 20 inches with a single access door to the sealed container. Cover gas mixtures of 0.3–0.4 volume percent SF₆, 11–15 volume percent CO₂, and 84–89 volume percent dry air were fed to the furnaces at a rate of approximately 5 liters per minute. The measured average cover gas concentration of SF₆ injected into the holding furnaces was 3170 parts per million (ppm) and 3590 ppm for Machines A and B, respectively. The times when the furnace access door was opened to insert additional magnesium alloy ingots was recorded, and typically occurred every 7 to 9 minutes when the die casting units were in operation. Table 1 provides a summary of the die casting process parameters.

Table 1. Die Casting Process Parameters

Parameter	Machine A	Machine B
Casting Alloy	AZ 91D Recycle	AZ 91 D Virgin
Ingot Weight (kg)	6.8	8.2
Ingot Consumption (kg/min)	0.86	0.95
Casting Rate (seconds/part)	31	22
Furnace Temperature (°C)	653	658
Molten Metal Surface Area (m ²)	0.49	0.49
Furnace Capacity (kg)	410 – 450	410 – 450
Cover Gas Composition (volume %)	85% air, 15% CO ₂ , 0.4 % SF ₆	

To speciate and quantify all gaseous compounds produced during the destruction of SF₆ during magnesium die casting operations, continuous and real-time measurements were made using

extractive Fourier Transform Infrared (FTIR) spectroscopic systems from MKS Instruments. Real-time monitoring consisted of pulling a gas stream from a Monel sample probe (3/8 inches outside diameter), placed in the furnace and positioned approximately 1-2 inches above the melt surface, through a heated perfluoroalkoxy (PFA)-grade Teflon extraction line into the heated FTIR sample cell. The sampling probe was installed through the thermocouple manifold and positioned to ensure that regular system operations (alloy feeding, surface skimming) were not disrupted. Sample flow was maintained at approximately 2–3 liters per minute by a diaphragm pump connected to the outlet of the FTIR cell. A rotameter at the sample cell exhaust was used to monitor the system sample flow.

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 resolution was set to 0.5 cm⁻¹ and signal averaging was performed over one or two-minute periods. FTIR calibration and system checks were conducted prior to testing to ensure data quality.

Initially two FTIR sampling systems were setup to simultaneously monitor opposite ends of the furnace enclosure. The objective was to verify that the SF₆ cover gas is homogeneously distributed throughout the enclosure (i.e., any ambient air dilution into the furnace occurs uniformly). FTIR systems with fixed cell path lengths of 20.1 and 5.1 meters were used. While measurements from both systems tracked each other consistently, thus, confirming the uniform distribution of compound concentrations throughout the furnace enclosure, this approach was not utilized during actual thermal degradation studies, since the sum of the sample flow rates for both FTIR systems would be greater than the cover gas injection rate. All tests were conducted using only one FTIR with a fixed cell path length of 5.1 meters.

Gas grab samples were taken from the exhaust stream of the FTIR via one-milliliter syringe pulls, and manually injected into a HP 5890A gas chromatograph (GC), using a thermal conductivity detector (TCD) and a HayeSep Q 80/100 column. Helium, at a flow rate of 40 ml/min, was used as the carrier gas to transport the sample through the column to the detector. The injection port, column, and detector were heated to 225°C, 100°C, and 150°C, respectively. The gas chromatograph was calibrated with a multi-point calibration curve prior to use each day. The gas standards, balanced in nitrogen, used for this calibration were 5 percent SF₆ and 39.98 percent carbon dioxide (CO₂). Calibration slopes for both CO₂ and SF₆ showed less than 10 percent drift from one day to next.

GC samples were run on a periodic basis to confirm the SF₆ (and CO₂) results generated by the FTIR system. The GC values for CO₂ agree favorably with the integrated averages reported by FTIR over the same sampling times, with overall uncertainty within ± 9 percent. The SF₆ values generally agree with FTIR (to within typical EPA Method 301 allowances, ±30 percent), but a consistent negative bias appears to be present. Since it was calculated, based on gas delivery flows, that the cover gas mixture from the plant was expected to contain 0.32 percent SF₆, the FTIR values are deemed to be accurate. Some uncertainty in the comparisons of the two methods was expected because the GC analysis involves single syringe samples and the FTIR monitors

continuously while integrating samples on a one, or two, minute basis. This uncertainty cannot be quantified.

Results

Figure 1 illustrates time series plots of the cover gas constituents (SF_6 and CO_2) from the furnace headspace of Machine A. The measurements on Machine A took place from 4:00pm to 8:15pm on September 17th, 2002. Measurements on Machine B were run on September 18th, 2002. Due to an upset condition in Machine B caused by excessive dilution of the furnace headspace, the first two hours of measurement were not used. This condition resulted from a longer than expected disconnection period for the cover gas source to the furnace headspace, to enable direct measurement of the cover gas by FTIR. Consequently, only measurements obtained during the period 3:30pm to 5:45pm are considered normal. From 4:30pm through 5:45pm, Machine B was stopped a couple of times to undergo maintenance. Consequently, during this period the observed SF_6 and CO_2 concentrations rose to levels close to the cover gas feed composition.

Obvious from the profiles are dilution spikes, represented by sharp reductions in concentration, at approximately 89 minute intervals. These intervals coincide with the opening of the furnace access lid for insertion of the magnesium ingots. Additionally, the profiles illustrate quiet periods when the headspace concentration for both SF_6 and CO_2 rises to a plateau. During these periods (represented in Figure 1 between 100-120 and 160-170 minutes, respectively) die casting production was interrupted, due to staff breaks/shift changes. From Figure 1, the average cover gas composition of SF_6 and CO_2 is 0.36 percent and 17.11 percent, respectively. During normal process operations, the measured SF_6 and CO_2 concentrations ranged from 0.097 percent to 0.34 percent and 5.78 to 16.21 percent, respectively. The difference between the CO_2 and SF_6 measured during normal process operations and their cover gas compositions is assumed to be attributable to both dilution and destruction effects.

Figure 2 illustrates time series plots of the percent CO_2 and percent SF_6 reduced through ambient air dilution effects during direct measurement of the furnace headspace on Machine A. The percent reduction of CO_2 and SF_6 is estimated from the ratio of their headspace concentration to their average cover gas content. It can be seen that the percent reduction of SF_6 was consistently greater than CO_2 . To identify the potential destruction of CO_2 , CO measurements were recorded. The reactivity of CO_2 in the headspace was very low with less than 0.3 percent conversion to CO . Consequently, since the observed reduction in measured CO_2 , compared to the cover gas feed composition, is almost solely attributable to ambient air dilution, the additional percentage reduction of SF_6 must be due to decomposition. Consequently, the quantity of SF_6 destroyed is defined as the difference between the measured SF_6 concentration and that expected to be in the furnace headspace after factoring in dilution effects.

Figure 1. Cover Gas CO_2 , H_2O and SF_6 Concentrations: Machine A

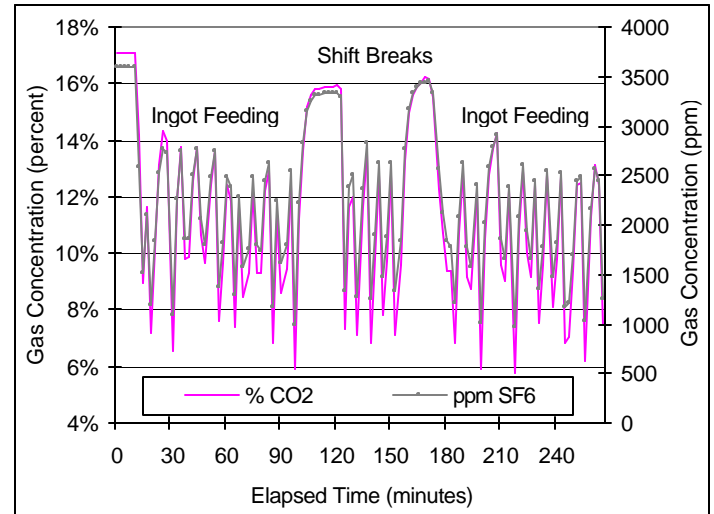
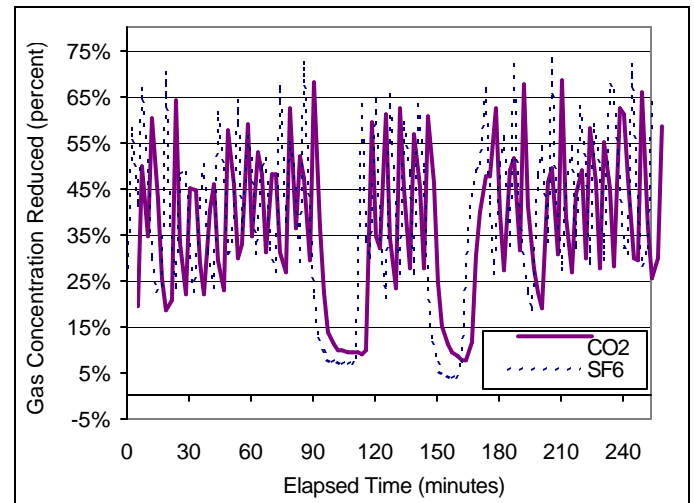


Figure 2. Percent Cover Gas CO_2 and SF_6 Reduction: Machine A



Figures 3 and 4 illustrate the percent dilution and destruction of SF_6 during normal operating periods (i.e., ingot feeding, non-feeding and staff breaks/shift changes) for Machines A and B. The decomposition of SF_6 appears to correlate with dilution spikes, indicating an increase in destruction during ingot feeding. During this feeding operation, magnesium alloy ingots are added to the furnace via the access lid, and as such, the SF_6 protective film is broken, creating surface turbulence and increased destruction. It can also be concluded that the percent destruction is increased during casting operations, as evidenced by its drop to near zero during shift breaks.

Figure 3. SF₆ Dilution and Destruction: Machine A

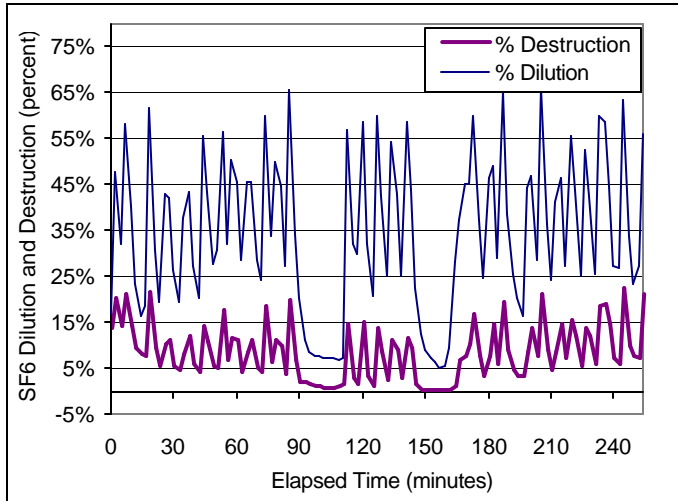
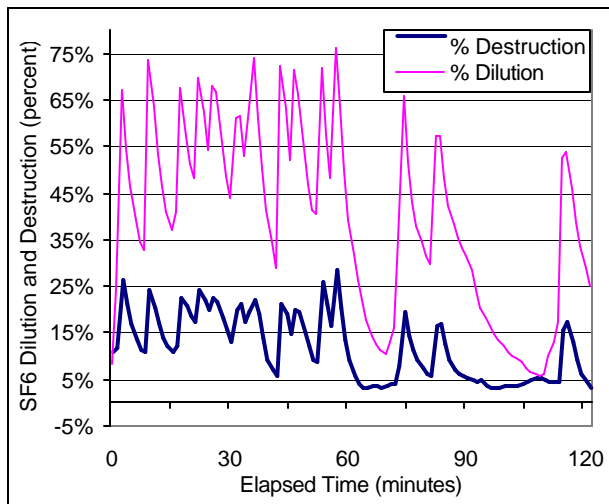


Figure 4. SF₆ Dilution and Destruction: Machine B



Tables 2 and 3 provide a summary of the percent SF₆ dilution and destruction occurring during normal process operations for Machines A and B. Maximum SF₆ destruction was observed to occur during the moments following ingot feeding. During this period the destruction of SF₆, for both machines, was observed to be approximately 16-20 percent, while overall dilution in the furnace ranged from 55 to 68 percent. During non-feeding periods (i.e., the period between the destruction peaks in Figures 3 and 4), SF₆ destruction was on average 6.5 and 12.5 percent for Machines A and B, respectively. Additionally, the average dilutions observed in the furnaces were 31 and 48 percent, respectively. Since furnace dilutions during staff breaks (when the machines were not in operation) were also higher for Machine B compared to Machine A, this may indicate incomplete sealing around the furnace covers and access lid. Both machines utilize different furnace access lid and cover designs. Neglecting the process operations (ingot feeding/non-feeding) to which SF₆ destruction is correlated, the average destruction of SF₆ observed, for the specific operating conditions, was approximately 10 percent. During staff breaks/shift changes, when the machines were not operating, the overall destruction of SF₆ decreased to minimal levels, approximately 0.6 to 1.4 percent.

Table 2. Average SF₆ Dilution and Destruction: Machine A

Operation	Dilution (%)	Destruction (%)
Ingot Feeding	55.2 ± 6.8	15.7 ± 3.7
Non-Feeding Periods	30.7 ± 8.4	6.5 ± 3.2
Staff Breaks	7.5 ± 0.6	0.6 ± 0.4

Table 3. Average SF₆ Dilution and Destruction: Machine B

Operation	Dilution (%)	Destruction (%)
Ingot Feeding	67.9 ± 6.5	20.1 ± 3.3
Non-Feeding Periods	48.4 ± 10.5	12.5 ± 4.8
Staff Breaks	14.5 ± 4.6	1.4 ± 0.4

Given that the percent destruction of SF₆ was measurable throughout, the presence of some reaction by-products in the gas phase was expected. It would stand to reason that the additional H₂O and O₂ introduced during dilution would add to the formation of hydrogenated and oxygenated by-products in the vapor phase. FTIR spectral analysis identified hydrogen fluoride (HF) and sulfur dioxide (SO₂) as the primary reaction byproducts. No other reaction byproducts, above the noise level of the FTIR, were identified. Assuming SF₆ destruction on the order of 10 percent, then the SF₆ decomposition byproducts produced in the vapor phase would be on the order of 150-300 ppm for each machine. However, it was noticed that despite the presence of elevated SF₆ destruction levels, HF and SO₂ concentrations remained low, on the order of 20 ppm total. Consequently, it seems that most of the decomposition of SF₆ may occur at the molten metal surface, with little release of gaseous byproducts.

Conclusions

FTIR measurements were conducted to identify the extent of SF₆ destruction occurring at molten magnesium holding furnaces on two hot-chambered die casting machines at a facility owned by Product Technologies. The overall average SF₆ destruction, based on the specific operating conditions and neglecting observed process variations, was determined to be on the order of 10 percent. For Machine A, SF₆ destruction ranged from 6.5 to 16 percent, while Machine B ranged from 12.5 to 20 percent. The level of destruction was strongly correlated to die casting process operations. During ingot feeding operations, 6 to 8 kg ingots are added to the melt furnace and, consequently, break the in-situ SF₆ protective film. During this heightened melt surface turbulence, SF₆ destruction reached a maximum. Since the level of SF₆ destruction dropped to approximately 1 percent when the casting machine was not operating (i.e., during staff breaks or shift changes), it can be concluded that a minimum level of SF₆ destruction occurs during casting operations. This average minimum level was observed to be 6.5 and 12.5 percent for Machines A and B, respectively. It is possible that this is attributable to the process by which magnesium is injected from the furnace into the die press apparatus (i.e., a piston, operating

every 20 to 30 seconds, injects magnesium via a gooseneck passage into the die cavity). While this operation may create some turbulence within the furnace, the exact nature of its impact could not be defined.

FTIR sampling identified two gaseous reaction byproducts, HF and SO₂. No other decomposition byproducts were identified within the minimum detection limits of the instrument. Due to the low levels of measured byproducts it is assumed that all SF₆ decomposition occurs at the melt surface, without the release of gaseous byproducts.

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