CAPTURE AND RECYCLE FOR EMISSION REDUCTION OF SULFUR HEXAFLUORIDE IN MAGNESIUM CASTING

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ABSTRACT

A partnership between MagCorp and Air Liquide was made to develop and test the potential of reducing sulfur hexafluoride emissions from magnesium casting operations. Air Liquide has developed the Floxal SF_6 Recycle Process, which is capable of capturing dilute SF_6 in the parts per million (ppm) range from casting system exhaust and recycling it as a concentrated feed gas in percentage levels. This process utilizes proprietary membrane technology to separate the SF_6 from air in four stages: pretreatment, compression, separation, and recycling.

In order to benchmark the process, the test program was conducted in three phases. Phase 1 was a pre-test visit, Phase 2 was an on-site analytical campaign to characterize the emissions of the casting process and provide a mass balance on the SF_6, and Phase 3 was a second analytical campaign to measure the performance of the Floxal SF_6 Recovery Unit while it operated. Phase 2 had the largest impact for the recovery system, because the levels of corrosive byproducts and particulate affected the design of the pretreatment. Also, the amount of vacuum pulled from the casting system had to be optimized with the makeup rate so it would not deplete the SF_6 atmosphere.

Preliminary results show that the Floxal Recovery Unit, after one month of service, had a 90% recovery or better of SF_6 supplied to the unit. The Floxal unit produced concentrations of SF_6 in the permeate at approximately 34 ppm, while the product was approximately 0.4%. The machine, on average, increased the concentration of the diluted SF_6 from the casting system 10 times.

INTRODUCTION

MagCorp and Air Liquide Partnership

MagCorp’s facilities have produced magnesium from the waters of Utah’s Great Salt Lake for over 30 years. With a production capacity of 48,000 tons per year, MagCorp employs nearly 500 people. The Great Salt Lake’s magnesium concentration is at least four times greater than that of the world’s oceans: about 0.5%. MagCorp, the largest commercial user of solar energy in the world, uses extensive evaporative ponds to remove water and concentrate the brine to over 8.0% magnesium. After being delivered to the production facility, the magnesium chloride-laden brine is purified, spray dried, and prepared as a molten salt for electrolytic decomposition. In the electrolytics area, magnesium and chlorine are separated via electrolysis. Molten magnesium is transferred from the electrolytic cells and brought to the cast house, where it is refined and cast into a variety of alloyed and pure magnesium products.

The casting process of molten magnesium requires a protective gas to keep the magnesium from burning. Atmospheres of air/SF_6/CO_2 gas mixtures were found to be advantageous compared to SO_2 gas because of their non-obnoxious odor and the non-corrosive nature. MagCorp uses SF_6 for these reasons. Because of the chemical’s strong global warming potential and high cost, MagCorp has been searching for viable alternatives. Air Liquide has developed the technology to reduce SF_6 consumption by using a molecular filtration system to recover and concentrate SF_6 gas. Air Liquide has tested the general concept for this recovery system at several major semiconductor manufacturing sites with promising results. MagCorp has used the system at its plant site, the first of its kind for magnesium, to see if the process was feasible with the plant’s current configuration.

MAGCORP CASTING SYSTEM

MagCorp’s casting facility consists of three conventional covered gravity cast machines (sometimes referred to as horizontal belt casters) and one direct chill caster. For the purpose of the test, the Floxal recycle unit was installed on one conventional cast machine where primary magnesium was cast. Figure 1 shows the general arrangement of the casting machine.

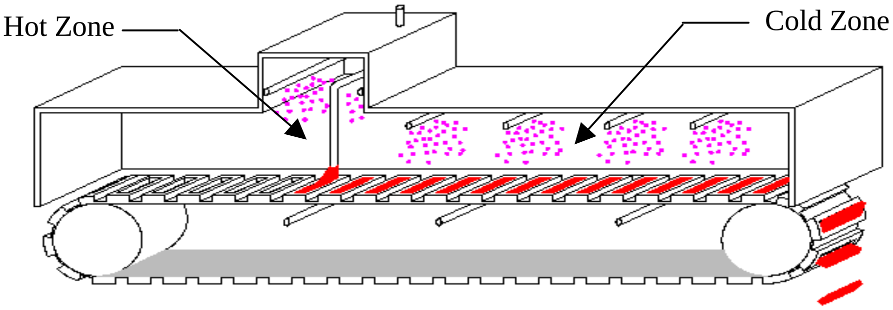

Figure 1. Schematic of cast machine and SF_6 distribution.

The second phase of the project involved data collection defining the composition and quantity of the cover gas stream that was available for recycling. Air Liquide's technical staff measured exhaust gas flow rate, composition, temperature, pressure, and total particulate load. Air Liquide took measurements from various locations on the casting machine. Particular attention was given to collecting data from the port at the top of the casting hood in the "hot zone" where molten magnesium is introduced into the mold. This location was selected first to utilize the chimney effect, whereby hot gases rise and can be collected for recycling, instead of escaping to the atmosphere.

MagCorp was concerned that a high suction rate in the hood from the recycling system could create a disruption of the SF_6 protective layer on the magnesium ingot, burning the metal. Air Liquide addressed this problem by correctly sizing a compressor for the system, using a simulated compressor apparatus with the capability of pulling a wide range of flow rates. The optimal rate was found by adjusting the exhaust "pull" to the highest level at which no burning would occur.

Analysis of the exhaust gas composition was important so the correct pretreatment could be designed to protect the membrane module from degradation. Air Liquide was concerned about Cl_2, F_2, SO_2, HCl, HF, CO_2, CO, and SF_6 in the exhaust gas. These compounds are potential byproducts of the reaction of SF_6 with air and moisture in the casting hood and from other casting facility chemicals. Three different analyzers were used for the detection of these gases: a Fourier-transform infrared spectroscope (FT-IR), an ultraviolet-visible spectrophotometer (UV-Vis), and a non-dispersive infrared photometer (ND-IR). The FT-IR was used to detect all target compounds aside from chlorine, fluorine, and SF_6. UV-Vis was dedicated to the detection of chlorine and fluorine. The ND-IR was used exclusively to quantify the high concentration of SF_6. Attention was given to HF, Cl_2, and HCl to avoid losses due to adsorption within the sampling system. This was accomplished by minimizing both sample flow rates and sample line length, using inert tubing, and heating the sample tubing and gas cell.

MagCorp injects the feed gas at six locations on the casting machine at a concentration of 0.4% SF_6, balance air/CO_2. The volume of the hood alone depletes the concentration of the feed gas by a factor of 10. Air Liquide concluded that approximately 33% of the total injected SF_6 could be recycled from the hood with only the top exhaust port. The species present during casting are shown below:

Table 1. Concentration of species present during casting.

Species	Concentration (ppm)
SO_2	200 – 1500
CO	5 – 20
HCl	5 – 10

Neither HF, F_2, or Cl_2 were detected in the casting hood. Particulate was filtered from the exhaust gas using an effective pore size of 10 microns. Testing found approximately 6.4 grams deposited over a 15-hour exposure at 60 scfm. The particles were composed of carbon, magnesium, oxygen, sulfur, and iron, ranging in size from 5 to 350 μm. Most of the particles formed magnesium compounds varying from traces to 12 wt%. From this experiment, it was concluded that a wet scrubber was not necessary because the particulate would sublime at temperatures below 200°F and the expected amount of SO_2 could be neutralized using an alkali scrubber filled with limestone.

The second part of Phase 2 involved optimization of the exhaust ports to maximize the amount of SF_6 "pulled" for recovery. MagCorp installed three additional exhaust ports on the casting hood, with one in the hot zone and two in the cooling zone. All of the added ports were installed below the upper conveyor molds to enhance the cover gas efficiency by forcing the cover gas through the conveyor and over the magnesium ingots. Air Liquide analyzed only for SF_6 using the ND-IR. It was concluded that the amount of SF_6 for recovery increased from 33% to approximately 46%.

FLOXAL SF_6 RECYCLING SYSTEM

Polymeric membranes have been used successfully in the refining and petrochemical sectors for many years to separate hydrogen from various hydrocarbon streams, and also to separate carbon dioxide from natural gas wells. More recently, membrane systems have opened a whole new spectrum of applications to industrial gas companies, because they offer on-site generation of low-cost nitrogen.

The transport of gas through a polymeric membrane is governed by a solution/diffusion mechanism. Gases first dissolve into the membrane polymer, then diffuse through it via an imparted pressure gradient. Transport rate is governed by the partial pressure differential across the membrane. A thin membrane film is very desirable, because the gas transport rate is inversely proportional to the thickness of the membrane-separating layer. Membranes are characterized by two parameters: flux and selectivity. Flux, the gas movement, is a measure of the amount of gas transported through a given area of membrane film per unit of time under a given partial pressure differential. Selectivity is the ratio of transport rates between gas species. Generally, flux and selectivity are inversely proportional, so an appropriate balance of properties must be considered in making a compromise between them. While flux is a strong determinant of membrane and capital cost, selectivity largely influences product purity and operation cost.

In air separation applications, nitrogen is the "slow," non-permeable gas and oxygen is the "fast," permeable gas. However, for the SF_6 capture application, both nitrogen and oxygen (i.e., air) are fast-permeating species. This is due to the fact that both nitrogen and oxygen have a much smaller kinetic diameter than SF_6 (Table 2). Furthermore, since sulfur hexafluoride is found in the exhaust streams at low concentrations under 1%, its partial pressure driving force through the membrane is minimal, and conversely, its recovery in the non-permeate stream of the membrane is very high. Another system advantage is that air is recovered in the permeate stream at nearly atmospheric pressure and can be vented without waste of compression energy. SF_6 is maintained at pressure in the non-permeate stream, which in turn facilitates its downstream mixing.

Table 2. Kinetic diameter of different gas molecules.

Name	Formula	Kinetic Diameter (A)
Oxygen	O_2	3.5
Nitrogen	N_2	3.7
Sulfur Hexafluoride	SF_6	4.9

Advances in technology allow production of extremely efficient hollow fiber separation systems. Hollow fibers lend themselves to high packing densities and can be operated at elevated pressures. High pressure can be fed either to the bore or to the shell side of the fiber, depending upon the application, while permeable gases migrate across the fiber wall as the gas travels through the permeator vessel. The fibers are assembled in a pressure vessel housing or “module” which contains a multitude of hollow fibers (e.g., 1 million) as shown in Figure 2.

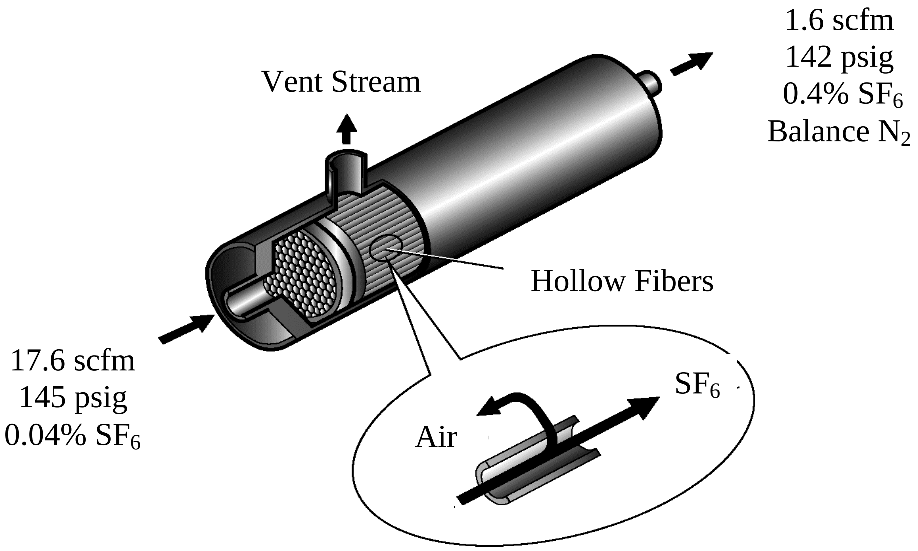

Figure 2. SF_6-containing exhaust gas is fed to the bore side of the fiber. Air permeates through the fiber wall and is vented at atmospheric pressure, while SF_6 remains under pressure inside the fiber bore.

The Floxal unit consists of four segments: pretreatment, compression, separation, and recycling, as is shown in the flow diagram of Figure 3. The choice of the pretreatment process depends upon the individual magnesium melting operation. Generally, it involves the removal of solid particulate and any corrosive gases, if they exist, in the SF_6-containing exhaust stream. This is achieved via conventional scrubbing and filtration operations. The outlet of the pretreatment process is then compressed in the range of 145 psig. This pressure is sufficient to reach good SF_6 capture efficiency, which allows the use of widely available machines commonly used for air compression. The compressed stream is then fed into the bore side of the membrane module. Gases, such as oxygen, carbon dioxide, argon, etc., permeate through the membrane to the shell side and exit at low pressure, while the SF_6 is retained at high pressure on the bore side. Leaving the membrane module, the concentrated SF_6 stream enters a gas-mixing unit, which adjusts the concentration of SF_6 to the composition of a protective atmosphere for magnesium melting.

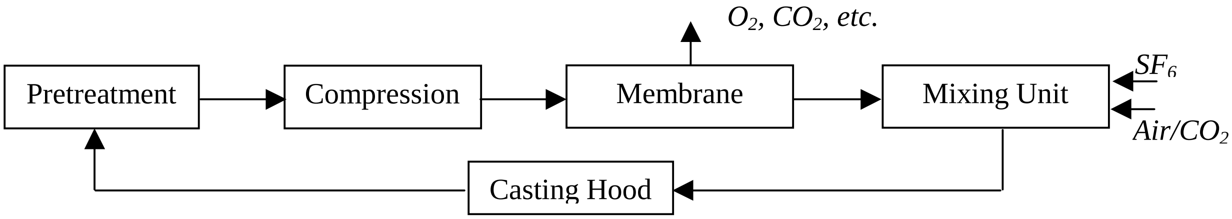

Figure 3. Schematic diagram for SF_6 on-site recycling system.

Figure 4 shows the pilot unit used at MagCorp, containing pretreatment, compression, and a membrane module. This unit was sized small for test purposes. The unit was used for over 650 hours and recycled on average 18 scfm of exhaust gas. The membrane produced on average 1.6 scfm of 0.4% SF_6/balance N_2 and 16.0 scfm of permeate (enriched oxygen). It was not necessary to pipe the product gas of the Floxal unit into the gas mixer, because the SF_6 concentration matched that of the feed gas. Table 3 summarizes the unit’s typical performance. Assuming a suction rate of 60 scfm and no escape losses, the Floxal unit has the capability of reducing the consumption of SF_6 on MagCorp’s primary cast machine by 41%. It should be noted that this limitation is much more a function of exhaust gas capture than limitations of the recovery unit. The capture system demonstrated that the SF_6 exhaust gas could be concentrated 10 times. This performance, depending on the hood dilution, matches or exceeds the feed gas concentration.

Figure 4. The Floxal unit used at MagCorp for over 650 hours.

Table 3. SF_6 capture rate and captured purity.

Streams	$[SF_6]$
Inlet Line	0.04%
Permeate, Vent Line	0.003%
Product Line	0.4%
SF_6 Recovery Rate	+90%

Two different membrane modules were available on the unit, a C-bundle and a G-bundle. The C-bundle, which was tested at MagCorp, contains more fibers that are smaller and less dense than those used for the G-bundle. Because of this difference, the C-bundle is supposed to have a lower recovery rate but a higher flow rate than the G-bundle. Time constraints did not allow this difference to be qualified at MagCorp in time for the presentation of this paper.

Membrane technology provides an extremely high SF_6 capture rate. Also, membrane systems are very effective dryers. The product stream from a membrane system is extremely dry, so it can be recycled directly back into the protective atmosphere. The membrane elements can operate unattended if they are protected from particulate matter with adequate filtration. Membrane systems are modular and easily expandable; additional compression machinery, as well as membrane modules, can be easily added to the system to provide increased system capacity.

Minor Issues

The pretreatment system consisted of a dry alkali scrubber (packed tower) filled with limestone used to neutralize any acidic gas, followed by a particulate filter (inlet filter) with effective pore size of 0.01 μm to catch any remaining particulate. The packed tower worked fairly well, except for plugging after 650 hours of operation. Blowing compressed air through the discharge of the tower decompressed the limestone and any sediment that deposited in the void space. Figure 5 shows the crusty deposit that formed at the top (inlet) of the packed tower. It was necessary to remove the top 1" layer after compressed air was blown through the discharge end of the packed tower multiple times. The tower completely plugged after a total of 677 hours of operation, making it necessary to replace the packing.

Figure 5. Pluggage of packed tower approximately 1" below the top surface.

In order for the membrane system to operate, the pressure drop across the pretreatment system has to be less than 8.8 psig. The membrane system operates at a minimum pressure of 85 psig, preset at the factory for optimum performance. When the packed tower plugged, the Floxal unit continued to run; the membrane system did not discharge the casting hood exhaust gas into the atmosphere, and the gas was not recycled.

The inlet filter was changed approximately every 150 hours of operation. The filter was sectioned and analyzed for calcium, magnesium, and sulfate. The results are seen below. This filter, like the packed tower, is capable of shutting the membrane system down if the pluggage exceeds the 8.8 psig drop. The cause of the pluggage has not been precisely determined. The likely suspect is airborne particulate originating in the casting facility.

Table 4. Analysis of inlet filter particulate for a 2" x 2" section.

Element	Concentration (ppm)
Mg	125
Ca	37
SO_4	295

Corrosion issues on the compressor arose when both the compressor outlet hose and fitting corroded and sprung a leak after 234 and 640 operating hours, respectively. It has yet to be determined whether this was caused by H_2SO_4 or H_2CO_3 forming from non-neutralized gas. The compressor condensate indicated an acidic pH with a low concentration of SO_4.

Ideas for design changes to the pretreatment have been proposed, but will not be finalized until Air Liquide examines and analyzes the Floxal unit's condition. A possible way to prevent the packed tower from plugging is to place the inlet filter before it to catch the particulate. Other alternatives specific to the packed tower include replacing major components with corrosion-resistant material, using a zeolite impregnated with $KMnO_4$, using activated carbon impregnated with NaOH or KOH, or using a wet scrubber using quicklime or caustic. Possible changes to the inlet filter include self-cleaning filters or the addition of an electrostatic precipitator. All of these options are expensive and need further review.

FUTURE EXPERIMENTATION

The exact amount of SF_6 recycled could not be empirically determined because MagCorp's current cover gas distribution does not allow for individual measurement of each cast machine. For investigational simplicity, the experimental setup did not capture the product gas into a surge tank where it would be available for future use. Instead, to allow the Floxal unit to run without interruption and prevent it from deadheading, the product gas was immediately recycled back into the casting hood. The product gas depleted over time, because the casting hood is not a perfectly sealed system and cover gas is used only during periods of castings. Piping changes are necessary to determine both the empirical reductions and generating an improved material balance. These modifications are planned for a future date.

Expanding the use of the Floxal unit is being considered for the other two casting machines, as well as the DC caster. The capture of cover gas on the DC caster is a more difficult task because of its configuration, as seen in Figure 6. Again, the suction will have to be designed to minimize disruption of the protective layer in order to prevent burning of the molten magnesium. The suction port would have to be located far above the SF_6 injection lines to prevent disturbance to the cover gas, and also to take advantage of the chimney effect described above.

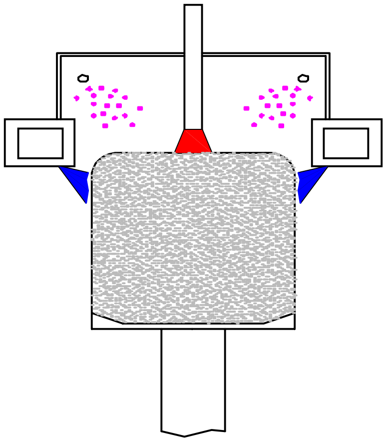

Figure 6. Direct chill casting of magnesium.

Modifications to Air Liquide's permanent system would be necessary for the Floxal unit to run without interruption. The cover gas operating parameters for each casting machine need to be independently adjustable due to different operational needs based on ingot size and type. If one Floxal unit were used for the entire cast house, the exhaust gas would be combined, would never reach steady state, and therefore would never provide a constant product concentration. Also, the use of a surge tank has its drawbacks when all the casting machines are not casting. There would be a risk of diluting the product gas and overpressurizing the surge tank if the Floxal unit were not shut off during this downtime.

CONCLUSION

The membrane-based SF_6 on-site recycling system is well suited for capturing highly diluted SF_6 in the exhaust lines due to its extremely high separation factors. From an operational standpoint, the unit was low maintenance and generally trouble free, requiring little intervention by operating personnel.

Using the C-bundle membrane, a 90% recovery or better was obtainable. This rate is expected to be higher with the G-bundle membrane: approximately 95% or better. The SF_6 concentration of the system output was increased by 10 times the concentration of the inlet gas (the casting hood exhaust gas).

Through the use of a correctly sized Floxal unit**,** with a suction rate of 60 scfm**,** MagCorp's SF_6 consumption is capable of being reduced by 41%. Expected improvements in SF_6 recovery will be gained by design changes to seal the casting hood tighter.

Surprisingly, analysis of the gas composition in MagCorp's casting hood did not detect any HF or F_2 gases, which are normal byproducts of the reaction between SF_6 and molten magnesium.

Based on the success of this project, MagCorp anticipates additional experimentation with alternate membrane bundles, different pretreatment steps, and future expansion of this system to other casting machines.

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