FINAL
TECHNICAL REPORT

SF_6 Replacement Evaluation in Magnesium Sand and Investment Casting
(Project 09-366)

Prepared for:

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and the California Environmental Protection Agency
Research Division
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ABSTRACT

Sulfur hexafluoride (SF_6) will not be allowed for use in magnesium casting after January 1, 2013 given its high global warming potential of 23,900, and the magnesium casting industry needs to find a suitable replacement. This study explored the use of Novec 612 on dry sand, green sand and investment magnesium casting as a replacement alternative. Three facilities with different melting and pouring practices participated in this investigation. The levels of Novec 612 gas used were high to determine feasibility and but not optimal parameters. Castings were subsequently processed per customer specifications and attrition rates due to gas cover related defects were assessed. Novec 612 provided adequate protection as a cover gas for the production of magnesium castings in sand and investment casting applications. The scrap rates were not higher than with the use of SF_6 gas protection. Mechanical properties were unchanged.

Novec 612 requires the purchase of gas evaporating, mixing and metering equipment. The price depends on the features necessary to successfully use the Novec 612 given operational differences. Based on the results of this study in today's prices there would be a net increase in production costs to the foundries from tens of thousands of dollars per year depending on the gas usage and specific equipment purchases related to the switch. However, it is important to note that this comparison is being made from optimized SF_6 gas delivery systems with non-optimized Novec 612 systems. It is expected that lower quantities of Novec 612 would produce successful castings, but these quantities are not yet known.

EXECUTIVE SUMMARY

Background:

Magnesium sand and investment casting requires a protective gas due to the very high reactivity of molten magnesium with atmospheric oxygen. Over the last few decades the protective or cover gas of choice has been SF_6. However, SF_6 is a very powerful greenhouse gas with a Greenhouse Warming Potential of 23,900 due to its high infrared absorption and long life in the atmosphere. For these reasons, a replacement technology is sought. Ideally, a new cover gas that has the advantages of SF_6 – molten metal protection, mold gas purging, non-toxicity, non-flammability, ease of use, and reasonable cost – can be found.

Cover gasses consist of an active gas and a carrier agent such as CO_2. The gas blends are used in three distinct functions: to cover the molten metal in the furnace during melting, to cover the molten metal during transportation and pouring, and lastly to purge the mold of atmospheric air with cover gas. Molten magnesium forms an oxide layer that is brittle and cracks and thus is permeable to further oxidation with atmospheric oxygen. Since magnesium oxidation is a very powerful exothermic reaction, if left unchecked the reaction will continue very violently. The cover gas reacts with the exposed liquid surface of the magnesium and thus limits the oxidation and violent reactions.

Historically two other technologies have been used to protect molten magnesium: SO_2 cover gas and fluxes. SO_2 is used in the same capacities as SF_6, that is, during melting, transportation and pouring of the molten metal as well as purging of the mold. The main drawback of SO_2 is that it is a criteria air pollutant under the Clean Air Act. Thus, it needs to be regulated and controlled. Fluxes are salt based granular materials that are used to cover the surface of the molten metal. Thus, they can be used during melting and pouring on the ladle. However, they can’t be used for purging of atmospheric air in the mold. For these reasons, SO_2 and fluxes are less than ideal substitutes.

Fluorinated ketones, specifically Novec 612 and HFC-134a have been explored for some applications as a replacement for SF_6. Novec 612 is being successfully used as a cover gas for ingot casting and die casting of magnesium. In addition, it is non toxic, non flammable, and has a Greenhouse Warming Potential of approximately 1 due to its short life in the environment. Novec 612 is more reactive than SF_6 and will break down faster at the processing temperatures of molten magnesium. There are significant differences between sand and investment casting and die and ingot casting. The first one is higher casting temperatures used in sand and investment casting which cause the Novec 612 to break down much faster. Thus, it is possible that the Novec 612 will not survive long enough to successfully protect the metal. The second difference is significantly higher exposure to the open atmosphere by the metal during melting and pouring than in the other processes. Thus, it will be necessary to use much higher levels of cover gas in sand casting than in die casting and ingot casting, greatly affecting the economics of the process.

The main objective of the project is to evaluate the possibility and implications of switching SF_6 with Novec 612 for sand and investment magnesium casting.

Methods:

The experiment was designed to incorporate the various methods of magnesium melting and pouring in dry and green sand and investment casting as practiced in California. The intent was to change the existing processes as little as possible in order to use Novec 612 as a replacement.

On the melting side, Novec 612 was used to protect during metal melting, pouring and mold flushing, and in combination with flux use according to existing practice. In melting, Novec 612 was used as a cover gas in conjunction with a covered crucible with a distribution manifold. These crucibles were also used to pour into the molds. A second method was used where the metal was melted under a cover of flux. Then the flux was removed and the gas was used to cover the metal during pour in a crucible without a lid. The third method used flux to protect the metal in the furnace and during pour, and the gas was used only to flush the mold.

39 molds were poured and 66 castings were produced. The pour weight per mold ranged from 4.5 Kg (10 lbs) to 163 Kg (360 lbs). The alloys used included AZ91and AZ91E (alloyed with aluminum and zinc) and ZE41 (alloyed with zinc, zirconium and rhenium) which due to containing rare earth elements are more susceptible to cover gas related defects. Castings were then processed and evaluated using standard methods.

Results:

All molding methods, both alloys, and all casting weights could be successfully poured with Novec 612 as cover gas. The only defective castings were due to lack of proper gas cover due to an assignable cause that would be expected to produce the same problems with SF_6. However, the different melting and metal handling practices need to be addressed separately.

The amount of Novec 612 used was conservatively high to test the possibility of casting with this gas. The crucibles that used lids and manifolds worked very well, and in fact it may be possible to lower the Novec 612 concentration in the gas in the future. For mold flushing, the concentration may be able to be significantly reduced as well. The crucible that was open to the atmosphere without flux presented more operational difficulties. While the castings from this process were acceptable, the metal smoked and slightly flared as some of the magnesium did oxidize more than desired. For this practice an improved method of delivery to the metal surface needs to be developed and/or a higher concentration of Novec 612 needs to be used.

At current prices of Novec 612, SF_6, and mixing equipment required for the Novec 612, there is a net increase in production cost for all facilities studied. The increase in operational cost can be in the order of tens of thousands of dollars per year. However, it should be noted that the comparison is between optimized SF_6 delivery vs. non-optimized Novec 612 delivery. Lower Novec 612 quantities could alter this equation.

Conclusions:

Novec 612 can be used as a replacement for SF_6 in sand and investment casting. Future work is necessary to optimize gas concentrations and delivery methods. The process economics are very sensitive to changes in the cost of the Novec 612 gas, SF_6 gas, usage patterns and equipment cost. Any changes in this area could lead to an overall significant increase in process cost.

INTRODUCTION

Background

The California Global Warming Solutions Act of 2006 (AB 32) creates a comprehensive, multi-year program to reduce greenhouse gas (GHG) emissions in California. As part of this commitment, the California Air Resources Board (ARB or Board) has developed a regulation to reduce sulfur hexafluoride (SF_6), a greenhouse gas with a global warming potential of 23,900, from non-semiconductor and non-utility applications. In February 2009, the regulation was approved by the Board. Included in the restrictions in the regulation, sulfur hexafluoride may no longer be used in magnesium casting after January 1, 2013.

There are four major types of magnesium casting: die, sand, and investment casting (producing parts), and ingot (primary and secondary pure magnesium and alloys used in the other part production). There are two types of magnesium casting in California: sand casting and investment casting. In the US, the most common magnesium casting process is die casting, but this process is no longer being done within California. All magnesium casting involves melting magnesium and pouring it into molds to create an end product such as an automotive or aircraft part. However, the strength and complexity needed in the final product requires different processes be used in the casting of different parts.

In die casting, the molten metal is not exposed to the open atmosphere (air) and is delivered to the mold under high pressure via a closed furnace system. The die pressure is maintained until the cast is solid.

In typical sand and investment casting, metal is melted in a crucible, which is then transported to the mold area where the molten metal is exposed to atmospheric air as it is poured into a mold. The purpose of the cover gas in magnesium casting is to protect molten magnesium from this atmospheric exposure. Due to gating systems (in-mold metal channeling systems) used in both sand and investment casting there is an opportunity for air entrainment and oxidation of the metal within the mold. Thus, it is necessary for the cover gas protection of the metal not only during the melting phase of the process, but also during molten metal handling including travel through air and within the mold. Due to the longer process and mold filling times, the temperatures also tend to be much higher for sand and investment casting than for die casting.

Ingot manufacturing is similar to the open processes of sand and investment casting but the final product does not require complex shapes or strength, which may necessitate different manufacturing parameters.

Most of the research on cover gas alternatives has been done in the context of die casting and ingot casting. Although the success in those industries is promising, there are some differences between those two processes and the sand and investment casting typical in California. Sand and investment casting involve higher temperatures (787^{o}C to 815^{o}C [1450^{o}F to 1500^{o}F] compared to 582^{o}C [1080^{o}F] for die casting) and a process more open to the atmosphere, which means not all options for alternatives available for die-casting are available for sand and investment casting.

In the sand and investment magnesium casting industry, the cover gas mixture contains approximately 0.2% to 0.5% by volume of SF_6 mixed with air and/or CO_2. Based on results of an ARB survey with a 100% response rate, emissions in California from magnesium casting are estimated at approximately 0.05 $MMTCO_2E$.[1]

<u>Protection Mechanism of SF_6</u>

SF_6 is used in magnesium casting as a cover gas to prevent the rapid oxidation (burning) of molten magnesium in the presence of air. This is accomplished when a small portion of the SF_6 reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. Without an effective cover gas, molten magnesium oxidizes with atmospheric oxygen, producing a lower quality product and increasingly, the risk of a fire incident. The magnesium reacts with atmospheric oxygen and forms a magnesium oxide layer that is permeable allowing magnesium vapor to escape and oxidize. The fluorine from SF_6 upon decomposition mixes with the remainder of the surface and "seals" the permeable parts of the oxide layer (figures 1 and 2). In figures 3 and 4, the difference between protected and unprotected pouring and melting operations is very evident.

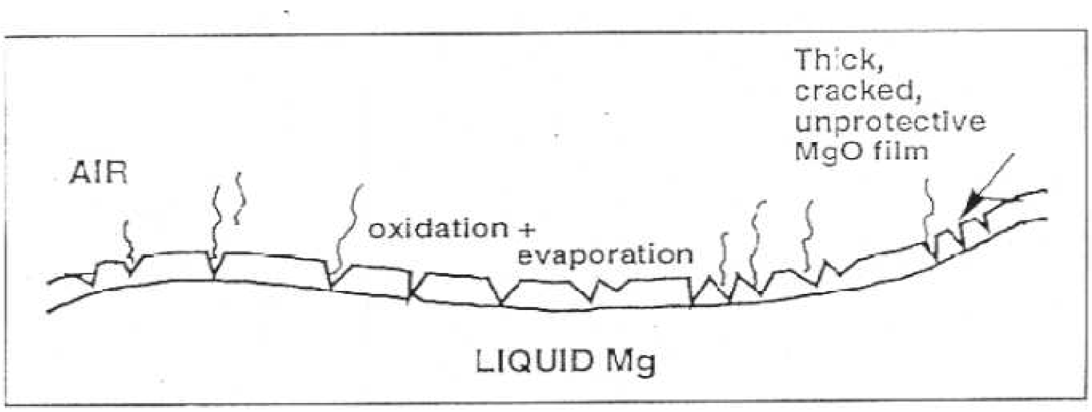

Figure 1: Surface of liquid magnesium.[2]

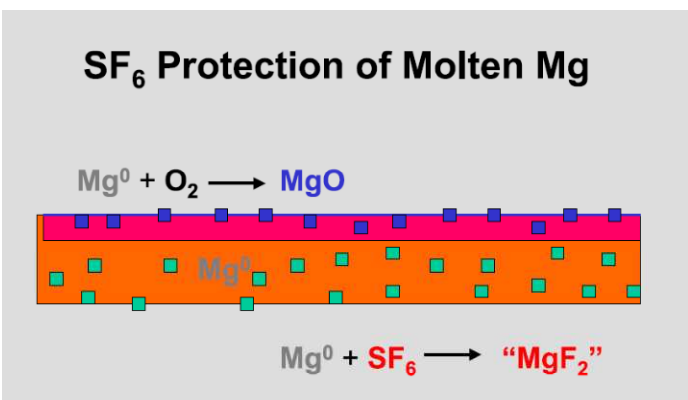

Figure 2: Development of film protection on the surface of magnesium[3]

Figure 3: Examples of unprotected and protected magnesium pouring. The figure on the left has significant amounts of magnesium oxide formation (smoke and flaring) and the figure on the right shows properly protected pouring. Courtesy Dean Milbrath.

Figure 4: Surfaces of molten magnesium showing oxidation. On left, surface film on molten magnesium with bright spots indicating minor oxidation. On the right, molten magnesium without protection in a small pan.

It is important to note that only a fraction of the SF_6 used in current practice is broken down to form the MgF_2 film, most of it remains unchanged.[4] One significant operational difference is that the available excess SF_6 is able to continue protecting should a disruption of the protective blanket occur. This makes the use of SF_6 a gas that is easy to work with and that makes the process quite reliable. Open casting generally uses 1-6% SF_6 concentration where 95% of the gas is emitted unchanged. Closed melting furnaces use a lower concentration of 0.2-1% but also emit over 90% of the SF_6 unchanged. Emissions for both cases depend upon specific conditions of gas distribution, alloy, humidity and other environmental conditions.[5]

Alternative Analysis

Alternative cover gases that have been tested and proven effective within magnesium casting as a whole include sulfur dioxide (SO_2), Novec™ 612 (a fluorinated ketone, $C_6F_{12}O$), HFC-134a ($C_2F_4H_2$), and frozen carbon dioxide (CO_2).[6] The alternative gases react in a similar manner as SF_6 in the presence of magnesium, producing a protective surface film. Although most testing has occurred in die-casting facilities, there have been limited successful tests in sand casting facilities for both SO_2 and the fluorinated ketone. Prior to this testing unfortunately only one of the tests has been documented and made public. The single documented test was done in Asia and there is no data on temperatures, use of cores, complexity of the casting, number of castings poured, and other critical variables. No documented tests using fluorinated ketone have been done for investment casting. However, tests with Novec 612 in other molten magnesium applications have been carried out successfully.[7]

Historically two technologies have been used to protect molten magnesium prior to the advent of SF_6: SO_2 cover gas and fluxes. SO_2 is used in the same capacities as SF_6, that is, during melting, transportation and pouring of the molten metal as well as purging of the mold. The main drawback of SO_2 is that it is a criteria air pollutant under the Clean Air Act. Thus, it needs to be regulated and controlled. Fluxes are salt based granular materials that are used to cover the surface of the molten metal. Thus, they can be used during melting and pouring in the ladle. However, they can't be used for purging of the mold. For these reasons, SO_2 and fluxes are less than ideal substitutes.

As mentioned earlier, sand and investment casting have different operating conditions that may limit the viability of available alternatives but SO_2 and the Novec 612 appear to be options for those facilities. HFC-134a may also be an option for some sand casting, though it is not examined in this project.

The alternatives are expected to produce at least a 98% reduction in greenhouse gas emissions. Table 1 provides the average emissions and reductions by alternative cover gas, based on a 2007 U.S. EPA measurement study at a die-casting facility.

Table 1 - Reduction of Greenhouse Gas Emissions for the Magnesium Die-Casting Industry[8]

Cover Gas Mixtures	Average GHGs by cover gas		Reduction from SF_6 (%)
	g CO_2E/hr	MTCO_2E/yr	
SF_6 with CDA	381,309	3340	-
Novec 612 with CO_2	2,790	24	99
HFC-134a with CDA	8,557	75	98
SO_2 with CDA	3	0.03	>99.9
Frozen CO_2	8,460	74	98

Note: CDA stands for Clean Dry Air

Operational requirements for a replacement are also a significant consideration. First, the replacement should have a competitive performance with SF_6 in terms of its protection effectiveness. It should be preferably non-toxic, and non-hazardous. It must also be non-flammable.[9]

The data available from die and ingot casting strongly suggest that the two practical alternatives to consider are SO_2 and Novec 612, a fluorinated ketone.[10]

Technical Considerations for SO_2

SO_2 is cited in a patent from 1934. It was extensively used with a combination of salt based fluxes until the advent of SF_6. SF_6 was preferred because SO_2 is toxic and corrosive. Due to its history, SO_2 is a proven and reliable technology. It also has the advantage that it does not contribute to global warming and it may be a cost effective solution. SO_2 is also widely available and its cost is less volatile than SF_6, since it is used in many applications such as food preservative, refrigerant, bleaching agent, disinfectant, etc.[11]

SO_2 protects magnesium by the formation of a protective layer due to the following reaction:
$Mg(l)+SO_2(g)+O_2(g) \rightarrow MgSO_4$
$MgSO_4(s)+Mg(l) \rightarrow MgO(s)+MgS(s)$ and this is the protective layer[12]

However the disadvantages include toxicity (2 ppm occupational exposure limit for 8 hours) and corrosiveness with potential acidic precipitation (H_2SO_4).[13] These issues lead to the need for personal protective equipment for workers and add training costs as well as environmental controls. In addition, SO_2 is regulated by local agencies (in the Los Angeles area by the South Coast Air Quality Management District - SCAQMD) and there are significant regulatory issues since it is a criteria air pollutant under the Clean Air Act. There are broader environmental issues such as contribution to acid rain and generally an unpleasant odor in the working environment. SO_2 is also more difficult to use than SF_6. SO_2 has a very low vapor pressure at room temperature so it requires external heating be effectively deployed, which is a challenge particularly in areas with cold weather. It also tends to freeze valves and condense in the lines. Lastly, SO_2 requires corrosion resistant materials making its implementation more expensive.

For these reasons, the project members wanted to look for a better alternative than SO_2, even though it has been successfully used in the past.

Technical Considerations for Novec 612

The physical and Environmental Health and Safety (EHS) properties of Novec 612 are given in Table 2:

Table 2: Physical and EHS Properties of Novec 612[14]

Physical Properties:		EHS Properties	
Boiling Point (^oC)	49	Atmospheric Lifetime (days)	<10
Freezing Point (^oC)	-108	Global Warming Potential	~1
Vapor Pressure @ 20^oC (kPa)	32.6	Flash Point	None
Liquid Density @ 20^oC (g/mL)	1.61	PEL (ppmV)	150
Gas Density @ 80^oC, 1 Atm (g/mL)	0.011	Acute LC 50 (ppmV)	>100,000

Reactions of Novec 612:
Novec 612 is a fluorinated ketone, $C_6F_{12}O$, which reacts more rapidly and completely with molten magnesium than SF_6. It thermally decomposes on the molten magnesium surface producing MgF_2 and CO_2 with few by products. This efficient reactivity also produces more surface protection since each molecule contains twice as many fluorine atoms as SF_6. Thus, Novec 612 can be used at a much lower concentration than SF_6 (0.015 to 0.4 volume % or 150 to 4000 ppmV compared to 0.7 to 6% SF_6).

However, because of the very high reaction efficiency of Novec 612, one area where it does not perform as well as SF_6 is in the accidental case of runaway oxidation. That is, when for any reason the molten metal begins to oxidize, it heats the environment around it. Typically, at the beginning of such a reaction it is easy to smother with SF_6 because there are more molecules available given the higher concentration use. In addition, SF_6 is more stable at higher temperatures so enough molecules are able to remain unchanged as they approach the surface of the magnesium. In the case of Novec 612, the molecules will break down faster at the higher temperatures and given the lower concentration of gas there will be less available for direct contact with the metal. The significantly higher amounts of Novec 612 needed to bring a runaway reaction under control are well beyond normal operating parameters (an emergency supply of flux is normally available for such situations).

The high efficiency of Novec 612 also requires tighter process control (precise Novec 612 concentration and uniform cover gas delivery) than SF_6.[15] In an operational sense it is “less forgiving”.

Environmental considerations:
Emitted gases and byproducts of the thermal breakdown of Novec 612 in casting applications include Novec 612, CO and traces of HF, C_3F_8, and C_2F_6. These have been detected in closed casting applications such as die casting and ingot casting.[16] Sand casting and investment casting being far more open are expected to yield very low concentrations of these gases in the environment.

Novec 612 Gas Preparation:
Novec 612 is a liquid at room temperature. In order to gasify it, dry air is typically passed through a bubbler with the Novec 612 liquid. This vaporizes Novec 612 which is then metered and mixed with a bulk carrier gas, typically CO_2, and sent to the casting line.[17] The composition of the gas is typically CO_2 bulk carrier gas with 5-20% dry air and Novec 612 in amounts from 150 ppmV (die casting) to 4000 ppmV (open casting) depending on the application. It is possible to use nitrogen as a carrier gas but it results in higher consumption of Novec 612 and

can result in higher formation of HF.[18] This gas bubbler method has the additional advantage of containing no moving parts. This is shown schematically on figure 5 and the actual mixing equipment used in the experiment in on figure 6.

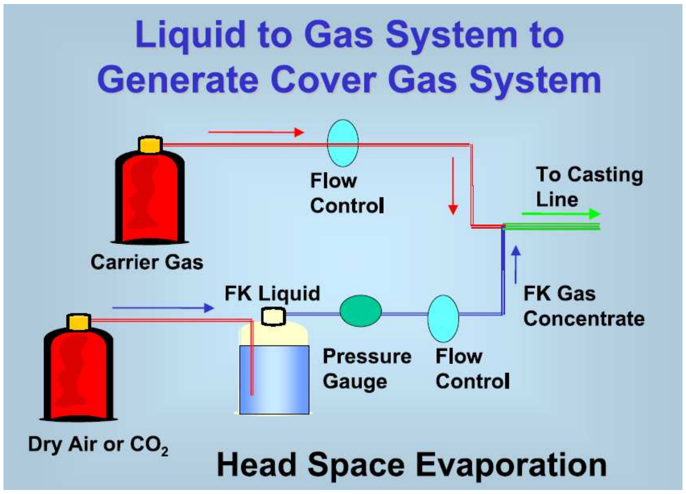

Figure 5: Schematic representation of the gasification process for Novec 612.


Figure 6: Experimental Novec 612 mixing and metering equipment.

Mixing equipment can range from fixed orifice, to volumetric, to compensated volumetric to massic (mass controlled) mixers. These mixing options increase in order of price and also in the accuracy of their mixing. The tight process controls desired to maintain optimum performance of the Novec 612 cover gas while minimizing usage require a massic mixer.[19] For this reason, the mixing and metering equipment can be very expensive, in the range of $55,000-$100,000 estimated for the sand and investment casting applications.

MTG Shield is a magnesium melt protection system that used Novec 612 as the primary protection agent. It used premixed Novec 612 in CO_2 carrier gas at concentrations of 1400 ppm in a system requiring no capital mixing equipment.[20] The system was sized for small applications and most of the demand was for large installations. MTG has since discontinued this product line for lack of interest in the market.

Delivery to molten metal:
The faster thermal breakdown of Novec 612 requires superior distribution compared to SF_6. SF_6 can travel longer distances to fully cover the molten metal because it is not as reactive as Novec 612. Thus, it is possible to use a single point source for SF_6 in the furnace and it will protect the entire melt. For more reactive gases like Novec 612, the breakdown of the gas is faster, thus by the time it reaches the edges of the crucible there is insufficient protective gas. This is schematically illustrated in figure 7.

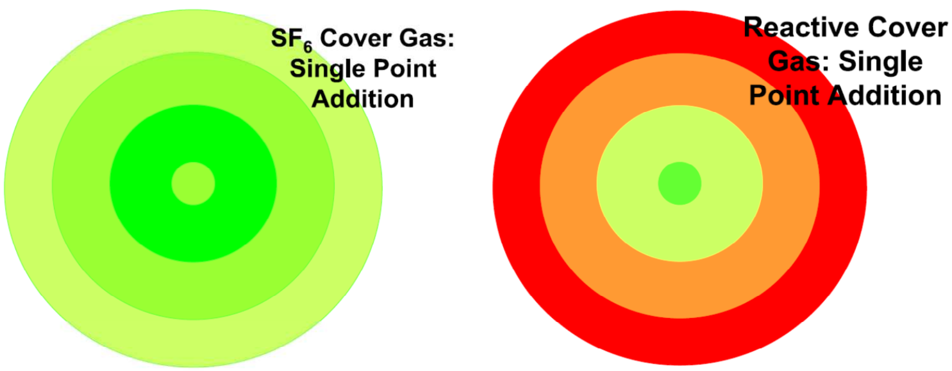

Figure 7: Single point addition effect of cover gas. The diagram indicates zones of adequate coverage (green, darker better) and inadequate coverage (red, darker worse). Single point addition is possible for SF_6 because there is sufficient protective gas reaching the edges of the crucible to protect the surface of the molten metal because it breaks down more slowly than reactive gasses. For the reactive gas, not enough molecules survive to the edge of the crucible to provide adequate protection.

Reactive gases thus require even distribution of the gas on the entire surface. This also leads to the opportunity to use less molecules as they are not being sacrificed to survive the travel to the edge of the crucible. This also leads to the possibility of using lower gas concentrations. This is schematically shown on figure 8.

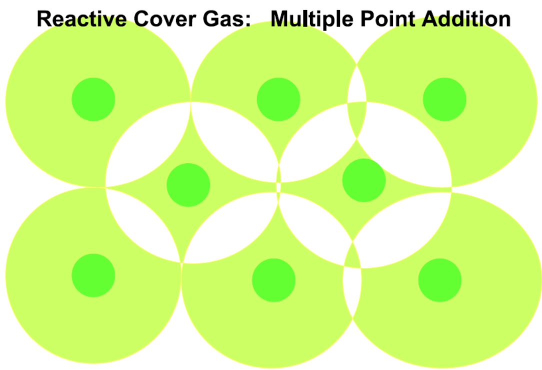

Figure 8: Multiple point addition of cover gas. With multiple points of addition the cover gas needs to travel less distance, thus it is possible to provide full coverage. The green areas indicate adequate coverage (darker, better). The white areas show overlap of protective gas for more successful cover.

Magnesium melting crucibles in foundries are predominantly round. A simple solution that allows for adequate gas distribution in this geometry is the use of a distribution manifold pipe in the shape of a ring. In addition to this, holes drilled at regular intervals should also be drilled at different angles to provide for full protection. In this manner multiple source points are provided over the entire melt allowing for superior coverage.[21] This is shown schematically on figure 9.

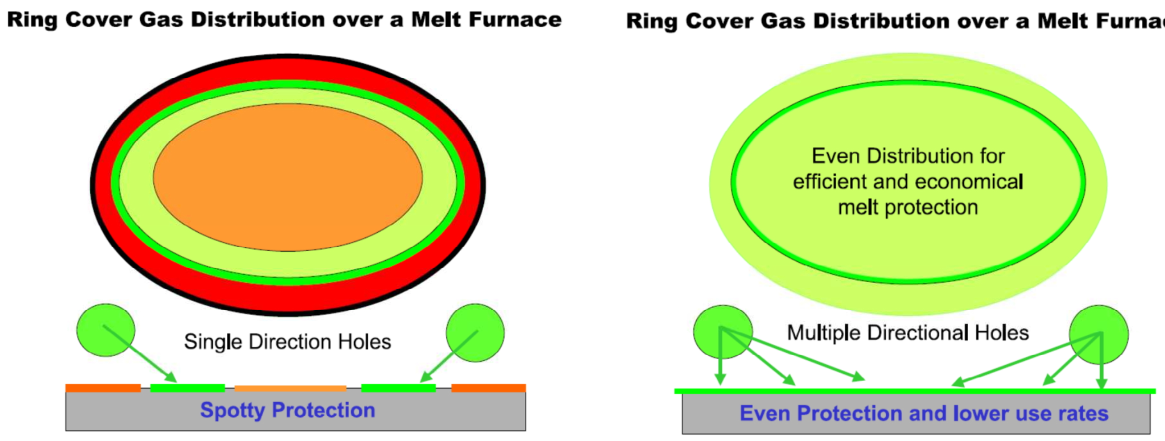

Figure 9: Comparison of ring type manifold coverage for protective gas. On the left, single angle holes provide inadequate coverage for reactive gasses since they form a ring of coverage, and as the gas travels across the surface of the molten metal it breaks down prior to fully covering all the metal. Thus, some of the metal is not protected. On the right, multiple directional holes provide more complete coverage of the melt by executing a distributed multipoint coverage pattern.

The ring manifold is applicable to crucibles with a fixed, unhinged lid. However, some facilities use hinged lids in their practice and a ring manifold is not practical. In this case, as part of the experiment a "D" shaped manifold with more holes aiming to the hinged portion of the crucible was used. In addition, a different practice is to pour with an open crucible. This was tested with an inverted funnel with a diffuser in it to direct the gas and help distribute it more uniformly across a wider area.

Delivery to mold:
Magnesium casting molds are flushed with SF_6 for a period of time prior to filling with molten metal. The goal is to continue having the protective atmosphere of the cover gas within the mold. The same practice works with Novec 612, and no changes would be required.

Project Objectives

The overall objective of the project is to determine the viability of promising cover gas alternatives through testing at California facilities. In addition, the research will result in best practices that can be communicated to and used by the industry as a whole. The project will test fluorinated ketone in various sand casting and investment casting situations, and determine settings for the key operational parameters.

PROCEDURE

Facilities participating in experiment:

Consolidated Precision Products - Pomona:
Address: 4200 West Valley Boulevard, Pomona, CA 91769.

Consolidated Precision Products (CPP) is a manufacturer of highly-engineered components and sub-assemblies, supplying the commercial aerospace, military and industrial markets with small-to-large "function" critical products. CPP-Pomona is the corporate headquarters for Consolidated Precision Products.

The Pomona facility is a leading manufacturer of medium to large dry sand Aluminum and Magnesium castings for the aerospace and military industries. CPP—Pomona's processes include Green Sand and Dry Sand Castings in aluminum and magnesium alloys.

CPP—Pomona's common aluminum alloys poured are: A201, A328, A356, A357, B201, B203, B206, B224, D357, C355, and Pure Al. Common Magnesium Alloys poured are: Pure Ingot 25#, ZE41 Ingot, AZ91E Ingot, WE43 Ingot, QE22, AZ91, AZ92, EZ33. The size range of products are up to 8 feet cubic envelope, and up to 2,000 lbs. net weight.

Magparts:
Address: 1545 Roosevelt Street, Azusa, CA 91702.

Magparts, operating in Azusa, is a manufacturer of high strength aluminum and magnesium castings, primarily for the aerospace industry. The company produces sand castings, permanent mold castings and investment castings.

Magparts has over 33,000 square feet of manufacturing space with melting capacity of up to 20,000 pounds per day. Molding systems include both dry sand and green sand molding systems. Other features are an automated dry sand conditioning and delivery systems. Core making capabilities include no-bake, cold box, and shell core methods. Castings as heavy as 125 pounds net weight and up to 6 feet in length or width can be produced.

Magparts casts many different aluminum alloys that include A201, A206, A356, 356, A357, C355, 319 and 535, and have developed significant mechanical strength advancements in the A201 alloy. For magnesium alloys, they cast AZ91C, AZ91E, AZ92A, EZ33A, and ZE41A. Magparts's services offered include integrated design support, in-house pattern and tooling construction, contour machining, anodize, paint and sub-assembly, heat treat, producing high quality ready to use products all certified to SO/AS9100/NADCAP and customer unique requirements.

(Note: Magparts was purchased by Consolidated Precision Products during the duration of this project.)

Magnesium Alloy Products
Address: 2420 N Alameda Street, Compton, CA 90222-2895

Magnesium Alloy Products (a.k.a. Magalloy) is located in Compton California. They produce complex, high strength aluminum and magnesium castings in the typical alloys for the military and aerospace industries. Their molding systems include both Dry Sand and Green Sand casting. Magnesium Alloy employs approximately 57 people. Casting sizes range from a few pounds to over 200 lbs net weight.

<u>Experimental design:</u>

- The study focused on establishing feasibility of Novec™612 as an SF_6 drop in substitute.

- Process: The processes tested included green sand, dry sand and investment casting.
    - Sand casting uses a replica of the part, called a permanent pattern that is placed inside a flask (akin to a box) where sand is then compacted and assumes the shape of the pattern. Then, the pattern is removed and leaves a cavity behind in the shape of the part to be produced. Then, metal is poured into this cavity obtaining the desired shape. In green sand casting the sand is a mixture of sand, clay, water and other additives that when compacted retain the shape of the pattern. Dry sand casting uses sand that is mixed with chemical adhesives that glue the sand grains together and in this manner they retain the shape of the part. Green sand and dry sand molds are shown in figure 10. The largest molds are made with dry sand exclusively as shown in figure 11 which shows the mold for the largest part in the trials.

Figure 10: Sand molds used in the experiment. Green (the black ones in color) sand molds on the left and dry sand (tan in color) molds on the right.

Figure 11: Largest mold poured in trials.

- o Investment casting, also known as lost wax casting, begins with an expendable part replica, called a wax pattern, that is coated with ceramic slurry which then hardens. Then the wax is melted out leaving a cavity in the shape of the part. Then the ceramic mold is heated to facilitate metal flow in very thin sections, the mold is filled with molten metal and this produces the part.
- The molds poured included typical geometric complexity and pour size. Design extremes were not targeted in this study.
- The alloys poured were AZ91 (alloyed with aluminum and zinc) and ZE41 (alloyed with zinc, zirconium and rhenium). The heats were a combination of 60% remelt and 40% ingot. Figure 12 shows a furnace charged with ingot and some material ready to be remelted.

Figure 12: Furnace charged with ingot and remelt alloy ready to load in furnace.

- The starting concentration of Novec™612 was based on the equipment manufacturer's recommendations, but was to be adjusted as deemed appropriate as the trials progressed. Cumulative information obtained from one trial was incorporated into the next trial.
- The pouring temperature for each/mold alloy was between 704^{o}C- 815^{o}C (1300^{o}F-1500^{o}F), based on current values used for these parts.

- Melting and molten metal handling procedures: Magnesium melting was performed in typical form with the exception that SF6 gas was replaced with Novec 612. Where fluxes are used in melting protection or for additional gas supplements during metal treatment such as during the addition of grain refiners, they continued to be used in the same manner. Flux melting is shown in figure 13.

Figure 13: Furnace with flux protection.

- Two different molten metal cover gas techniques were used at various parts of the process: Hinged crucible lid with “D” shaped ring, and inverted funnel with diffuser plates. Figure 14 shows a closed crucible with a hinged lid and an inverted funnel with diffuser plates.

Figure 14: Crucible with hinged lid and open crucible with inverted funnel and diffuser.

- Mold gas protection was done as typical with SF6 with the only difference that when possible the molds were flushed with ten volumes of protective gas within the mold cavity. Figures 15 and 16 show this procedure.

Figure 15: Molds being purged with cover gas. When only one or few molds are poured at one time, it is possible to flush the molds shortly before pouring.

Figure 16: A row of 18 molds being poured from a single heat. Note that the mold flushing was done just ahead of the pour.

- The gating/rigging system that governs the metal flow rate in the mold was the existing system. The foundries' customers own the patterns that were used in the experiment, thus the foundries do not have the authority to change the pattern and the owners are very unlikely to allow changes to a successful pattern. In addition, current magnesium gating practice is already optimized to minimize metal turbulence which will help in the success of the new cover gas.
- SF6 was available as a backup gas for safety considerations. The facility safety requirements and respective staff were relied upon to provide authority on whether or not to utilize a backup gas. As it turned out, this was not necessary.

<u>Indicators of feasibility:</u>

This study was a feasibility study to give an indication of whether the alternative is viable for the magnesium industry. These results are the first step to answering the question: Can Novec™612 provide proper coverage and protection in the magnesium sand or investment casting process? Indicators of viability were based on the following:

- Scrap rates after using the SF6 replacement are of similar magnitude or less than historical scrap rates for the castings. All testing was done using existing customer/facility procedures and specifications.
- Final alloy chemistry on heats/parts as appropriate to pass existing customer/facility requirements.
- Visual and dye penetrant evaluation were performed on all castings and measured against existing customer/facility procedures.
- Where appropriate, per customer specifications, mechanical and physical properties were examined and measured with existing customer/facility criteria.

Since this was a feasibility study and the sample size of molds was small, a definitive answer with statistically significant results was not the anticipated outcome. For example, scrap rates may be higher due to changing the operational parameters throughout the testing. However, the overall testing gave an indication of whether this will work and what changes need to be made to the delivery system or other components to ensure a successful transition.

This report was reviewed by the participants to make sure nothing proprietary (information or photos) is inadvertently included in the report. This is important because the magnesium facilities make flight critical components, aerospace parts, and other national defense components. Items and/or processes may be confidential to the facility or their customers.

RESULTS AND DISCUSSION

The function of the cover gas in magnesium melting and pouring is to prevent and minimize oxidation of the metal. The cover gas has no other function. Thus, mechanical properties such as strength, ductility, hardness, or other properties such as microstructure, chemical composition, or corrosion resistance are not directly affected by the use of gas. They are only enhanced by the prevention of defects due to the gas. Thus, it was expected that the mechanical properties would be satisfactory as long as there were no defects. In fact, the measured properties were typical.

Molding method analysis:

The sand molding methods used were green sand, dry sand and green sand in combination with dry sand. For the purposes of analysis they were separated as dry sand exclusively and molds that had green sand components. The third molding method is investment casting which uses a completely different ceramic system and thus will be treated separately. Tables 3, 4, and 5 separate the parts by the different processes. It is possible to see in these tables that there is no difference in the amount or concentration of cover gas by mold type.

Dry sand and green sand processes:

The green sand molding process uses clay and water to bind the sand grains together while the dry sand molding process uses a chemical binder to bond the sand grains together. Thus, the main difference is the presence of water in the green sand process. Dry sand is stronger than green sand, so the larger molds will tend to be made exclusively of dry sand. Also, parts that need greater dimensional accuracy or geometric intricacy will be molded exclusively with dry sand as well. Otherwise, both processes exhibit similar mold cavities and molten metal pathways. For this reason, the analysis will separate the molds that are dry sand and those that have green sand (and moisture) within them.

Table 3 presents the data for the production of magnesium castings in dry sand and table 4 in green sand. As can be seen, Novec 612 can provide adequate protection for dry sand and green sand molds as there were no rejects in either sample. In addition, the gas concentration and flow did not change between mold types.

Table 3: Results for dry sand molds.

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
E	4/4	17/37	Dry Sand	ZE41	Flux	NA	Novec 612, 2400 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 3000 ppmV, 85 LPM	Zero
D	3/3	27/60	Dry Sand	ZE41	Flux	NA	Novec 612, 2682 ppmV, 57 LPM, inverted funnel with diffuser	Novec 612, 2682 ppmV, 57 LPM	Zero
B	1/1	35/76	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
C	1/1	55/122	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
G	1/1	150/330	Dry Sand	ZE41	Flux	NA	Novec 612, 2600 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 4280 ppmV, 62 LPM	Zero
A	1/1	163/360	Dry Sand	ZE41	Novec 612, 4342 ppmV, 58.5 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 60 LPM	Zero

In green sand processes there is moisture present in the mold, and the castings also tend to be smaller and less intricate. It is also a cheaper process and is used whenever possible. In this case it is possible to see in Table 4 that the Novec 612 can provide adequate protection. No scrap castings were produced with green sand and a similar gas coverage was used as with dry sand molds.

Table 4: Results for molds with green sand.

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
H	18/18	5.2/11.4	Green Sand	AZ91	Flux	NA	Novec 612, 2300 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 2360 ppmV, 54 LPM	Zero
L	1/1	4.5/10	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero
F	4/4	17/37	Dry Sand in Green Sand	ZE41	Flux	NA	Novec 612, 2600 ppm, 72 LPM, inverted funnel with diffuser	Novec 612, 4500 ppm, 60 LPM	Zero
M	1/1	18/40	Dry Sand in Green Sand	AZ91E	Novec 612, 3050 ppmV, 52 LPM	D Ring in crucible	Novec 612, 3050 ppmV, 30 LPM	Novec 612, 3050 ppmV, 30 LPM	Zero
K	1/1	23/50	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero

Investment Casting:

Table 5 shows the results of the two investment casting molds produced. This is the only process that produced scrap castings due to gas cover issues. The scrap castings were the result of inadequate cover gas in the mold. For investment casting the molds are preheated in a furnace and are then taken to a pouring station. There they are poured as quickly as possible to minimize mold cooling. In magnesium casting, where it is necessary to flush the mold with cover gas while it is cooling it is imperative to have a high flow rate of cover gas. The nature of the equipment was unable to deliver that much gas in the first of the three molds poured, but had stabilized for the second and third molds. Thus, even though there was scrap in this process, the reasons for it can be overcome and an SF_6 comparison with the same difficulties would have yielded similar results.

Table 5: Results for investment casting molds:

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
I	1/10	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 30 LPM	Zero
J	2/20	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 20 LPM	3/20 15%*

*Mold movement was rushed and this led to the rejects. This same problem would have occurred with SF_6.

Alloy:

Alloys AZ91 and the minor variant AZ91E as well as ZE41 were poured. This was done to test the conditions with the more robust alloy (AZ91 and AZ91E) and with more sensitive rare earth containing alloys (and ZE41). While there are other alloys that are more sensitive, they were not used in this study but the facilities feel that these alloys could be successfully used with these techniques. Tables 6 and 7 present the parts separated by alloy type poured. As can be seen in these tabes, there is no pattern to the amount of gas required that is determined by alloy.

Table 6: AZ91 and AZ91E alloy results.

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
H	18/18	5.2/11.4	Green Sand	AZ91	Flux	NA	Novec 612, 2300 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 2360 ppmV, 54 LPM	Zero
L	1/1	4.5/10	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero
M	1/1	18/40	Dry Sand in Green Sand	AZ91E	Novec 612, 3050 ppmV, 52 LPM	D Ring in crucible	Novec 612, 3050 ppmV, 30 LPM	Novec 612, 3050 ppmV, 30 LPM	Zero
K	1/1	23/50	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero
I	1/10	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 30 LPM	Zero
J	2/20	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 20 LPM	3/20 15%*

*Mold movement was rushed and this led to the rejects. This same problem would have occurred with SF_6.

The ZE41 alloy is the most common rare earth alloy poured. As can be seen in table 7, they can be successfully protected by Novec 612, with no difference in the gas cover requirement with respect to AZ91.

Table 7: ZE41alloy results.

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
F	4/4	17/37	Dry Sand in Green Sand	ZE41	Flux	NA	Novec 612, 2600 ppmV, 72 LPM, inverted funnel with diffuser	Novec 612, 4500 ppmV, 60 LPM	Zero
E	4/4	17/37	Dry Sand	ZE41	Flux	NA	Novec 612, 2400 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 3000 ppmV, 85 LPM	Zero
D	3/3	27/60	Dry Sand	ZE41	Flux	NA	Novec 612, 2682 ppmV, 57 LPM, inverted funnel with diffuser	Novec 612, 2682 ppmV, 57 LPM	Zero
B	1/1	35/76	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
C	1/1	55/122	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
G	1/1	150/330	Dry Sand	ZE41	Flux	NA	Novec 612, 2600 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 4280 ppmV, 62 LPM	Zero
A	1/1	163/360	Dry Sand	ZE41	Novec 612, 4342 ppm, 58.5 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 60 LPM	Zero

<u>Cover gas composition:</u>

The gas used in the trials was a mixture of 95% CO_2, 5% dry air, and between 2000 and 4500 ppmV of Novec 612. The trials were initially conducted with high levels of Novec 612 and as success was seen, the concentration was dropped in subsequent heats with the intent to find the limits at which the gas began to be unsuccessful. Of all the conditions tested only the open ladle configuration with reverse funnels and diffusers proved to reach marginal conditions. Thus, for this practice either a higher concentration of gas, or higher flow rate (both of which would place more Novec 612 on the magnesium) or significantly improved distribution of the gas would be necessary. In all other cases, the gas distribution was more than sufficient and it may be possible to further reduce the amount of gas utilized.

With regards to molding process, for investment casting better coordination of the pouring process will be required. If this does not prove sufficient, it may be aided by increasing the amount of Novec 612 in the mold (either by increasing concentration and/or flow rate). At this point it seems that the defective parts were due to testing anomalies rather than process performance.

Part size:
Parts studied in this project ranged from small with pour weights of 5.2 Kg (11.4 lbs) for 10 parts to 163 Kg (360 lbs) per part. The Novec 612 cover gas performed adequately in all instances, with the exceptions noted in the tables due to procedural failures..

Gas distribution method:
Two operational differences were tested for the gas distribution method on the crucible: One was with a crucible covered with a hinged lid and a "D" shaped distribution diffuser under the lid. The other one was with an open crucible. The results of each method are shown in tables 8 and 9. Note that the covered crucible required significantly lower gas flow rates and concentrations of Novec 612.

In figure 17 an illustration of a covered crucible with an internal "D" manifold.   Note that there is no smoke emitting from the crucible.

Figure 17: Crucible with hinged lid. Note the lack of smoke.

As can be seen in table 8 using a covered crucible with a D ring diffuser produces acceptable results. Figure 17 also shows the lack of smoke produced with this protection method. Table 8 shows that it is possible to drop the concentration of Novec 612 gas down to as little as 2200 ppmV. In addition, note that total cover gas flow was also successful as low as 30 LPM.

Table 8: Molds poured with a covered crucible with a hinged lid and a D ring manifold.

Part	**Number of Molds/ Parts**	**Mold Pour Weight (Kg/ lbs)**	**Molding Process**	**Alloy**	**Melt Protection**	**Gas Distribution On Melt**	**Pour Protection**	**Mold Protection**	**Rejects due to gas**
L	1/1	4.5/10	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero
M	1/1	18/40	Dry Sand in Green Sand	AZ91E	Novec 612, 3050 ppmV, 52 LPM	D Ring in crucible	Novec 612, 3050 ppmV, 30 LPM	Novec 612, 3050 ppmV, 30 LPM	Zero
K	1/1	23/50	Dry Sand in Green Sand	AZ91E	Novec 612, 2200 ppmV, 52 LPM	D Ring in crucible	Novec 612, 2200 ppmV, 30 LPM	Novec 612, 2200 ppmV, 30 LPM	Zero
B	1/1	35/76	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
C	1/1	55/122	Dry Sand	ZE41	Novec 612, 3426 ppmV, 57 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 57 LPM	Zero
A	1/1	163/360	Dry Sand	ZE41	Novec 612, 4342 ppmV, 58.5 LPM, closed crucible	D Ring in crucible	Novec 612, 2682 ppmV, 57 LPM closed crucible	Novec 612, 2682 ppmV, 60 LPM	Zero

As can be seen in figure 18 (and contrasting with figure 17) casting without a lid and with funnels to provide protection cover gas produced a lot of smoke and magnesium oxide. This indicates that the protection was at the lowest acceptable operational limit. In fact, it was a surprise that none of these castings were scrapped. This can be remedied by designing the delivery equipment to deliver more gas to the crucible resulting in even higher gas consumption or modifying the process for improved delivery distribution.

Figure 18: Open crucible with inverted funnels with diffusers. On the left, note the smoke emanating from the molten metal indicating less than optimal coverage. On the right, pouring the metal in the mold. Note the bright spots indicating oxidation on the surface of the metal.

As can be seen in Table 9 Novec 612 can provide adequate coverage when used without a lid or manifold. However, note that the amount of gas used was the maximum possible with the experimental mixing equipment, resulting in higher Novec 612 consumption.

Table 9: Molds poured with an open crucible.

Part	Number of Molds/ Parts	Mold Pour Weight (Kg/ lbs)	Molding Process	Alloy	Melt Protection	Gas Distribution On Melt	Pour Protection	Mold Protection	Rejects due to gas
H	18/18	5.2/11.4	Green Sand	AZ91	Flux	NA	Novec 612, 2300 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 2360 ppmV, 54 LPM	Zero
F	4/4	17/37	Dry Sand in Green Sand	ZE41	Flux	NA	Novec 612, 2600 ppmV, 72 LPM, inverted funnel with diffuser	Novec 612, 4500 ppmV, 60 LPM	Zero
E	4/4	17/37	Dry Sand	ZE41	Flux	NA	Novec 612, 2400 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 3000 ppmV, 85 LPM	Zero
D	3/3	27/60	Dry Sand	ZE41	Flux	NA	Novec 612, 2682 ppmV, 57 LPM, inverted funnel with diffuser	Novec 612, 2682 ppmV, 57 LPM	Zero
G	1/1	150/330	Dry Sand	ZE41	Flux	NA	Novec 612, 2600 ppmV, 112 LPM, inverted funnel with diffuser	Novec 612, 4280 ppmV, 62 LPM	Zero
I	1/10	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 30 LPM	Zero
J	2/20	5.4/12	Investment	AZ91E	Flux	NA	Flux	Novec 612, 2200 ppmV, 20 LPM*	3/20 15%

*Mold movement was rushed and this led to the rejects. This same problem would have occurred with SF_6.

<u>Mold flushing:</u>

Mold flushing varied with the molds being poured each heat. Foundries will run standard heats of a certain amount of molten metal given their equipment. This may be enough to fill only one large mold, or several smaller molds. The range of molds poured per heat ranged from one mold per heat, in which case there was plenty of time to flush the mold to 18 molds per heat, in which case the molds were flushed immediately ahead of pouring. Lastly, investment casting molds require very careful coordination to be fully flushed while minimizing the amount of time between taking them out of the preheat furnace and pouring them.

Economic Analysis:

There are several variables that need to be taken into account to evaluate the economic impact of switching from SF_6 to Novec 612 cover gas. They include the cost of the gas which is determined by supply and demand for SF_6 and by production costs and pricing policies of the only producer for Novec 612. Also, the amount of cover gas used, which is determined by the process that each facility uses. This process dictates the duration of cover gas application as well as the concentrations used. Lastly, the cost of the gasification and mixing equipment required for Novec 612. Other considerations, such as new piping that would be required are considered to be small and negligible in the analysis.

Cost of gas:

SF_6 is a commodity and the prices are determined by market forces. As such, over the last few years the cost of SF_6 has varied from $13.20/Kg to $44.00/Kg ($6-$20/lb). Currently, SF_6 cost was quoted to Cal Poly Pomona at $23.14/Kg ($10.52/lb)[22] and one of the facilities at $25.50/Kg ($11.59/lb). The economic analysis will hinge on what direction prices take in the future, but as this is unknowable, current range of recent prices will be used in the analysis.

Novec 612 is a gas that is produced exclusively by 3M. 3M provided a cost range of Novec 612 is in the $44-55/Kg ($20-25/lb) range for the USA, affected by the volume demands for each customer. They also indicated that pricing is impacted by the cost of electricity, HF and nickel and hydrocarbon feedstocks.[23] The price used for comparative analysis was the midpoint of the range given $49.50/Kg ($22.50/lb).

Amount of gas used by each facility:

The amount of gas used by each facility is directly related to their process. There are three stages at which cover gas can be used: Melting protection, metal transportation and pouring, and mold flushing.

For melting protection flux can be used instead of cover gas and one facility exclusively used flux at melting (no cover gas usage), another facility used flux in some instances and cover gas in other instances, and the last facility used cover gas exclusively. Thus, for the facility that used flux exclusively for melting there is no gas usage at this stage. The facilities that use gas cover during melting take from 70 to 150 minutes to melt the metal under the cover of gas for each batch produced. During this time the metal is in a crucible with a lid and there is a steady stream of gas going into it.

For transportation and pouring all facilities used cover gas for metal protection. Transportation is the act of moving the crucible with the metal to the pouring location in the foundry. Pouring is actually transferring the liquid metal from the crucible to the mold, a step where the stream of molten metal requires protection. In this case there were two methods used at the facilities: a crucible with a lid and a crucible that is open to the atmosphere. The crucible with a lid keeps the gas within the crucible, preventing it to freely escape to the atmosphere. The open crucible allows for more gas to dissipate to the atmosphere and thus requires a higher amount of the active cover gas to provide adequate protection. The facilities that used a crucible with a lid use a 2% SF_6 mixture with CO_2 carrier which resulted in a usage of 0.129 Kg/hr (0.283 lbs/hr) of SF_6 [from purchasing and production records]. The open crucible facility used a 6% SF_6 mixture in CO_2 at a higher flow rate to compensate for the difference in techniques and this resulted in a consumption of 0.906 Kg/hr (1.994 lbs/hr) of SF_6 [from purchasing and production records]. These values will be used for the low and high consumption comparisons.

The values of Novec 612 in the experiment for the crucibles that used a lid ranged from 2200 ppm and 52 SLPM to 4342 ppm and 60 SLPM. The lower values will be used in the economic analysis as the castings were successful and these yield a Novec 612 flow rate of 0.127 Kg/hr (0.280 lbs/hr).

For the open crucible, the Novec 612 concentrations ranged from 2300 ppm at 112 SLPM to 4500 ppm at 54 SLPM and this range proved to be marginal coverage. The number that will be used in the analysis is 4342 ppm at 60 SLPM, which was the highest amount of Novec 612 used and equaled 0.205 Kg/hr (0.450 lbs/hr) of gas consumed because the protection is marginal and higher levels of gas usage would have been used had the experimental equipment been capable of it. It is important to note that the experiment was set to determine feasibility of the Novec 612 for protection, not optimization of the parameters.

Mold flushing with cover gas is typically begun a few minutes prior to pouring with a sequence beginning when the metal is ready to be transported to the pouring site. The mold flushing is done with the same equipment that is used to protect the metal during transportation (same concentrations and flow rates). In the experiment, when the Novec was used simultaneously to protect the metal and flush the mold, the gas supply was split for each function. Thus, for the economic analysis the time component for the mold flushing will be the same as that for transportation and pouring of the metal. The gas concentrations and flow rates were also the same.

Gasification and mixing equipment:
The implementation of Novec 612 into the production system of these foundries would require the purchase of at least one gasification and mixing piece of equipment at a cost per unit of \$55,000 to \$75,000.[24] The range is dependent on the various features that the facility would like to implement in the unit. It is noteworthy that a unit was quoted to one of the participant facilities in 2009 at \$100,000.[25] It seems that at this point it may be possible to have one mixer per facility, with some perhaps needing two. Currently, SF_6 is largely moved around in cylinders prefilled by the supplier but this option will not be available for the Novec 612 because it is not possible to bottle the gas at the required concentrations.

Cost comparison:
The amount of gas used depends on the concentration rate, the flow rate, and the amount of time that each facility uses cover gas. The economic estimate will be developed in dollars of cost of active cover gas per hour of use. In this way it will be possible to incorporate the different amounts of time in different steps of the process and at different concentrations and flow rates at

which the various facilities would use the gas. The net present worth (NPW) was then calculated in terms of how many hours the facilities would expect to run the gas per year per the formula:

NPW=PW (future savings or expenses) – Initial Cost of Equipment
Note: For simplification purposes, positive values will be savings or income and negative values will be expenses.

For the crucible with a lid, the Novec 612 gas usage of 0.127 Kg/hr at $49.50/Kg of gas results in a cost per hour of $6.29/hr. SF_6 gas at a usage of 0.129 Kg/hr and a cost of $25.50/kg, gives a cost per hour of $3.29/hr. Thus, using Novec 612 would result in an increased expense of $3.00/hr of application with a covered crucible. It is necessary to note that the comparison will suffer from the fact that the SF_6 practice has evolved and improved over a long time. The Novec 612 values are based only on feasibility, not optimized values. It is anticipated that as the Novec 612 is used, it will also be optimized. At this point it is not possible to know what these usage levels will be. The foundry that uses a 100% gas process uses gas for approximately 8000 hrs/yr (4 furnaces per shift/one shift per day). This gives an annual increased gas expense of $24,000. Given the different possible estimates of the cost of equipment a present worth value was calculated at each equipment price threshold. The interest rate used is 7% with an amortization period of seven years[26] of depreciable life.

The present worth values obtained are presented in Table 10. Note that the results for the net present worth calculation are also presented at recent high and low prices for SF_6.

Table 10: Present Worth for covered crucible and high gas volume foundry at 7% interest and 7 year amortization.

Equipment Cost ($)	SF_6 Cost @ $13.20 Kg (recent low)		SF_6 Cost @ $25.50 Kg (current price)		SF_6 Cost @ $44.00 Kg (recent high)	
	Annual Increased Gas Cost ($)	Net Present Worth ($) ($SF_6$@ $13.20/Kg)	Annual Increased Gas Cost ($)	Net Present Worth ($) ($SF_6$@ $25.50/Kg)	Annual Increased Gas Cost ($)	Net Present Worth ($) ($SF_6$@ $44.00/Kg)
55,000	36,704	-252,801	24,000	-184,441	4935	-81,596
75,000	36,704	-272,801	24,000	-204,441	4935	-101,596
100,000	36,704	-297,801	24,000	-229,441	4935	-126,596

Thus, the switch to Novec 612 would result in an increase in operating costs ranging from $184,441 to $229,441 over seven years, at current SF_6 prices and the Novec 612 levels used in this study. Note that even at the historical high price for SF_6 savings are not realized. Again, further optimization of the use of Novec 612 is likely in order to reduce the amount of gas necessary for successful magnesium casting.

For the open crucible, the Novec 612 gas usage of 0.205 kg/hr would result in a cost of $10.07/hr. The SF_6 at a usage rate of 0.906 kg/hr would result in a cost of $29.96/hr. The savings by using Novec 612 instead of SF_6 are $19.89/hr. However, this facility uses flux melting and has a much lower production volume. Thus, they only use gas for an estimated 173 hrs/year. This yields a savings in the gas cost of $2261/yr. The net present worth analysis is presented in Table 11. Note that the results for the net present worth calculation are also presented at recent high and low prices for SF_6. Again, improvements in practice are likely to reduce the amount of Novec 612 required for successful casting in this method.

Table 11: Present Worth for open crucible and lower gas volume foundry at 7% interest and 7 year amortization.

Equipment Cost ($)	SF_6 Cost @ $13.20 Kg (recent low)		SF_6 Cost @ $25.50 Kg (current price)		SF_6 Cost @ $44.00 Kg (recent high)	
	Annual Increased Gas Savings ($)	Net Present Worth ($) ($SF_6$@ $13.20/Kg)	Annual Savings in Gas Cost ($)	Net Present Worth ($) ($SF_6$@ $25.50/Kg)	Annual Increased Gas Cost ($)	Net Present Worth ($) ($SF_6$@ $44.00/Kg)
55,000	328	-53,232	2,256	-42,838	5158	-27,201
75,000	328	-73,232	2,256	-62,838	5158	-47,201
100,000	328	-98,232	2,256	-87,838	5158	-72,201

Thus, the switch to Novec 612 would result in lower annual operating costs of 2,256 per year. However, this is insufficient to pay for the initial equipment cost, and thus, the net present worth results in a net increase in expenditures ranging from $42,838 to $87,838 over seven years, at current SF_6 prices and the Novec 612 levels used in this study. Again, even at the historical high prices for SF_6 the net result is still a net increase in production cost.

(Authors note: In conversations with the open crucible facility, based on the observations during the experiment, opportunities to greatly reduce their use of SF_6 gas were observed. Since, this facility indicates changes in their process for a preliminary drop in use of SF_6 of approximately 60%. The same techniques could be used to reduce Novec 612, but the economic effect is unclear due to lack of exact data. However, as the overall gas usage would be decreased for both practices, the amount of gas savings would decrease, thus making it harder to pay back the original equipment cost.)

Magnesium casting facilities outside of California are not required to comply with a ban of SF_6. Thus, they are not subject to the increase in cost associated with the transition to other cover gasses. This could give California foundries an incentive to leave the state. However, the International Magnesium Association has been actively pursuing replacements to SF_6 globally which could affect this incentive.

CONCLUSIONS

Based on the experimental results Novec 612 has the potential of substituting for SF_6 in magnesium sand casting and investment casting applications. Novec 612 provided adequate protection as a substitute for SF_6. In the case of dry and green sand molds, no scrap was produced that was due to cover gas issues. The only problem presented itself with investment casting in one of three molds, and it is felt that this can easily be overcome with adequate equipment and procedures. There was no difference on the gas cover practice for the two alloy families tested, AZ91 & AZ91E and ZE41. Castings from one kilogram to over 160 kilograms were successfully produced. Scrap rates were at or below historical rates.

The gas cover method provided a significant difference in the amount of gas used. The covered crucible with an internal manifold required much lower gas flow rates and Novec 612 gas concentrations than the open crucible method. However, both produced successful castings.

The values for flow rates and concentrations of cover gas can still be improved. This study was a feasibility study not an optimization study. As such, the amount of gas cover used was conservative in that it aimed to overprotect the castings. It may be possible with additional research to reduce the amount of Novec 612 used in the operation, perhaps by separately optimizing the concentrations and flows of the individual process steps (melting, transport and pouring), though this may require the use of additional equipment at extra expense.

Significant operational and equipment changes need to be made to switch to Novec 612 and the transition will likely significantly increase the production costs of magnesium castings. The main driver of this cost increase depends on how the facility uses the cover gas: for the facility that used the gas 8000 hours per year, they already had a relatively optimized process for the use of SF_6, and thus, the change in the cost of the gas was the main driver. However, the gasifying, mixing and metering equipment added significantly to this expense. In the case of the foundry that used an open crucible, the gas cost was driven down with the use of Novec 612. However, the need to purchase gasifying, mixing and metering equipment erased any savings and resulted in a net increase in cost. While optimization values for the use of Novec 612 are yet to be determined, it is unlikely that they will be low enough to justify switching cover gas purely on economic benefits. In fact, the switch to Novec 612 will result in increases in production costs of tens of thousands of dollars per year. This will make California based foundries less competitive in the open market versus other foundries that are not required to switch cover gasses.

The purchase price estimates of gasifying, mixing and metering equipment ranged from $55,000 to $100,000. This cost is a major driver of the increase in cost for the process. The foundries can lower the overall cost increase of conversion by carefully evaluating what equipment needs they really have and purchasing very basic equipment. However, these savings are unlikely to offset the economics of the switch from a net increase in cost to a net saving.

RECOMMENDATIONS:

1) Pursue optimization of gas concentration and total flow rate required for casting production. It is possible that significant savings are possible in the processes that used a covered crucible by simply changing the concentrations and flow rates of the gas. In the open crucible, better delivery methods will be necessary to lower the consumption of Novec 612, and these should be pursued.

2) Optimize manifolds used in gassing molds and in crucibles to reduce the use of gas and improve the protection it provides.

3) Carefully determine necessary characteristics required and desired in gas mixers in order to potentially reduce cost. This cost is a significant economic driver hampering the implementation of Novec 612.

4) Directly measure, not estimate or calculate, the current use of SF_6 using flow meters to get a very accurate analysis of the true costs and a more accurate comparison of the economic aspects versus the use of Novec 612.

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