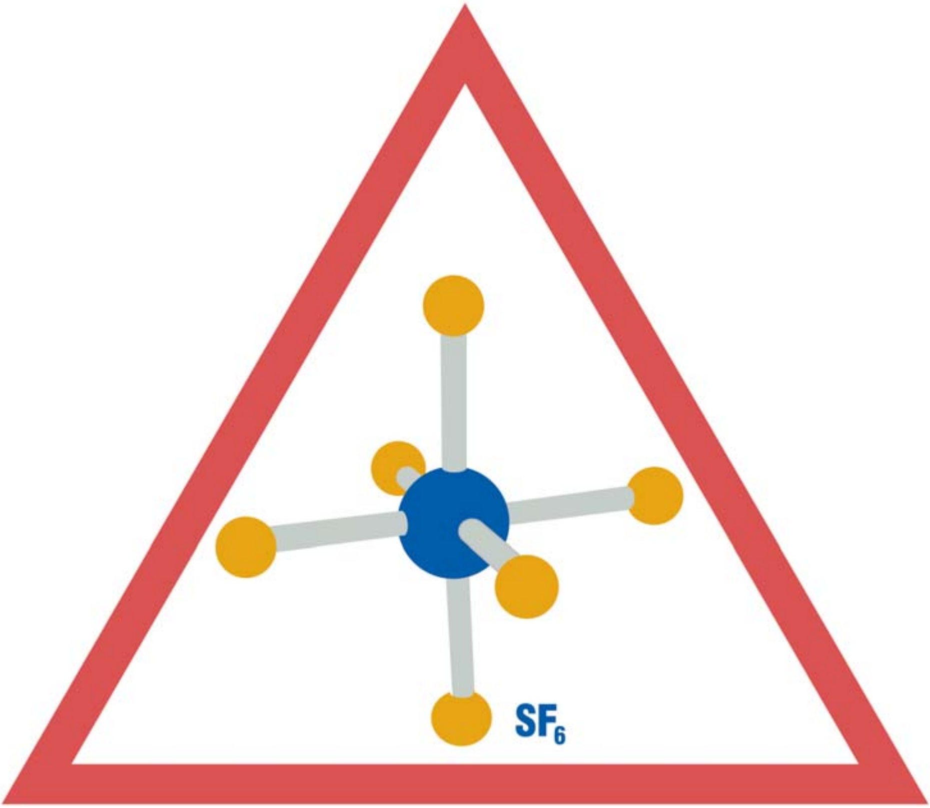
Alternatives to SF_6 for Magnesium Melt Protection



United States Environmental Protection Agency

SF_6 Emission Reduction Partnership for the Magnesium Industry

International Magnesium Association
The Global Voice for Magnesium

Japan Magnesium Association

China Magnesium Association

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中国有色金属工业协会镁业分会
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United States Environmental Protection Agency

EPA-430-R-06-007

The environmental benefits provided by lightweight and recyclable magnesium have the potential to grow significantly in the future as consumers, businesses, and national governments seek to reduce greenhouse gas emissions. The global magnesium industry is working together with governments to demonstrate its environmental stewardship and eliminate SF_6 emissions. New melt protection technologies are cleaner and cost effective, and will help further improve the industry's environmental performance.

Photo courtesy of Mark S. Johnson Photography; www.msjphotography.com

Alternative (non-SF_6) melt protection can provide:

- **Excellent performance**
- **Potential cost savings**
- **Worker safety and environmental benefits**

Why Does Molten Magnesium (Mg) Need Protection?

Today's automobiles, aerospace technologies, and portable electronics all use magnesium (Mg) for its advantageous light weight and structural properties. While being produced and when used in manufacturing other products, molten Mg will oxidize (burn) on contact with ambient air. Therefore Mg producers and parts manufacturers use melt protection on the metal's surface to prevent burning. In the past, salt fluxes or concentrated sulfur dioxide (SO_2) gas were used for this purpose. While these chemicals provided adequate melt protection, they also reduced the quality of the metal, corroded equipment, and presented workplace and environmental hazards. Since the 1970s, the international magnesium industry has largely used SF_6 for melt protection for its nontoxic, nonflammable, and non-corrosive characteristics. China's rapidly growing Mg industry employs sulfur powder for melt protection but is transitioning to SF_6 cover gas systems to improve product quality.

Molten Mg without melt protection

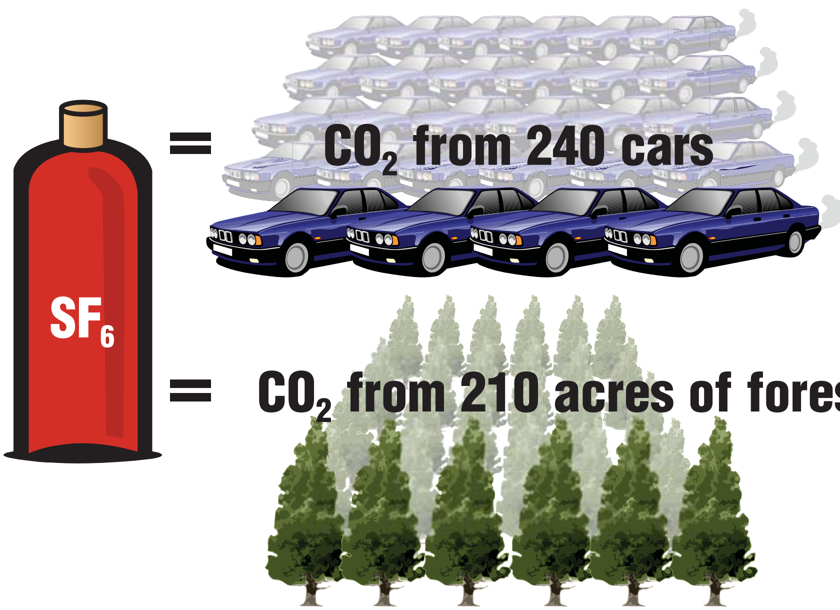
Molten Mg with melt protection

Photos courtesy of 3M™ Company

Why Eliminate SF_6?

Although it is an effective Mg cover gas, SF_6 is a very potent and persistent greenhouse gas,[1] which means its release to the atmosphere contributes to global warming for thousands of years. Many national governments and companies around the world are seeking to reduce or eliminate SF_6 use in molten Mg processes. For example in the United States, members of the SF_6 Emission Reduction Partnership for the Magnesium Industry have committed to voluntarily eliminate SF_6 emissions by 2010. Also, the European Union will prohibit the use of SF_6 in Mg die-casting beginning in 2008, except when used in quantities less than 850 kg per year.

Many end users of Mg worldwide will continue to demand consistently high-quality Mg products and will seek improved environmental conditions that alternative flux-less melt protection other than SF_6 can provide.

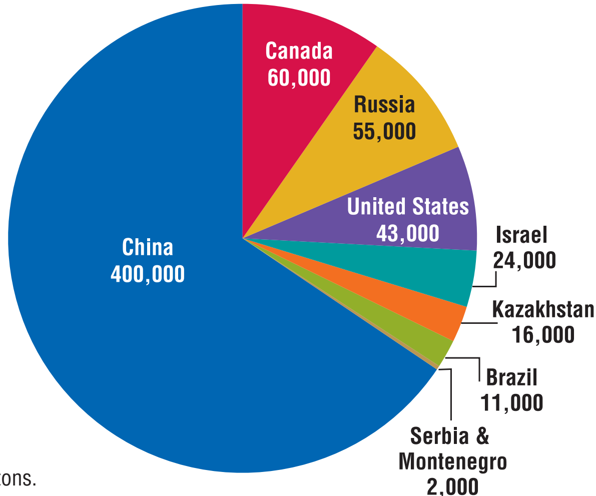


One standard 52 kg (115 lb) cylinder of SF_6 is equivalent to 1,243 tonnes of CO_2. Therefore, the climate benefit of eliminating emissions of one standard cylinder is similar to eliminating CO_2 emissions from 240 U.S. passenger cars for one year or planting roughly 210 acres of forest land.[2]

[1] SF_6 has a 100-year global warming potential of 23,900 and an atmospheric lifetime of 3,200 years. *Climate Change 1995: The Science of Climate Change*. Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press, Cambridge, U.K.

[2] EPA ENERGY STAR conversion factor (11,560 lbs CO_2 / U.S. car), http://www.energystar.gov

2004 Estimated Worldwide Mg Primary Production/Capacity[a]



[a] Reported in metric tons.
Source: U.S. Geological Survey and Hydro Magnesium estimates.
U.S. Geological Survey – URL: http://minerals.er.usgs.gov/minerals/pubs/commodity/magnesium/mgmetmcs05.pdf
Hydro Magnesium – *Magnesium Supply and Demand 2004*, IMA Annual Conference, Berlin 22-24.5.2005

China's magnesium industry presents a unique opportunity for climate protection in the world's fastest growing production center. The magnesium industry in China is opening new plants and beginning to transition from flux-based melt protection to cover gas technologies. Instead of using the potent global warming gas SF_6 for melt protection, these firms can "leapfrog" beyond SF_6 and choose the more environmentally friendly options discussed in this brochure. By adopting alternative melt protection technologies, China has an opportunity to avoid releasing annual greenhouse gas emissions equal to roughly 9.6 million metric tons of carbon dioxide ($MMTCO_2$)—more than three times the total emissions released by the entire U.S. Mg industry, production and casting combined, in 2004.[3]

[3] Based on U.S. Geological Survey estimates of China's 2004 primary Mg production of 400 kt. See URL: http://minerals.er.usgs.gov/minerals/pubs/commodity/magnesium/mgmetmcs05.pdf. Assumes 1 kg SF_6/mt of Mg produced.

What Alternatives to SF_6 are Available for Mg Melt Protection?

Several alternative melt protection technologies are commercially available that provide comparable performance to SF_6. The most technically proven alternatives to date include:

- **AM-cover™—**Patented fluorine-based blended gas technology consisting of an active gas (such as HFC-134a) and a carrier gas such as nitrogen or carbon-dioxide.
- **Novec™ 612 Magnesium Protection Fluid—**Patented blended liquid-to-gas system using a fluorinated ketone as the active ingredient and a carrier gas such as carbon dioxide or nitrogen and dry air.
- **Dilute SO_2—**An approximately 1.5% SO_2 mixture that uses nitrogen, carbon dioxide, and/or dry air as a carrier gas.

Other alternatives have been developed but are not currently commercialized or readily available. One technique known as "COOLCOM" generates solid CO_2 (i.e., dry ice) for melt protection.[4] Another technique is a boron trifluoride (BF_3) system that uses solid fluoroborate as a feedstock to generate a small amount of BF_3 gas in-line when needed for melt protection.[5] A third technique under investigation uses SO_2F_2 for melt protection.

What are the Benefits of Mg Melt Protection Alternatives to SF_6?

By using fluxless melt protection other than SF_6, the global Mg industry can benefit from improved metal quality, potential cost savings, and increased workplace safety while reducing greenhouse gas emissions.

Potential Cost Savings

Companies can potentially reduce their costs using Mg melt protection other than SF_6. Using alternative fluorine-based blended melt protection in place of an SF_6-based cover gas process can reduce metal loss (% dross) due to oxidation and provide associated cost savings, as shown in the hypothetical example in the graph on page 5. This example also shows that as the incoming Mg raw material price increases, the resulting cost savings also increase.

When considering dilute SO_2 systems, the cost of SO_2 per kg is usually less than the cost of SF_6; however, equipment and process upgrades often must be made to safely use sulfur-based systems, and associated worker safety and environmental risks

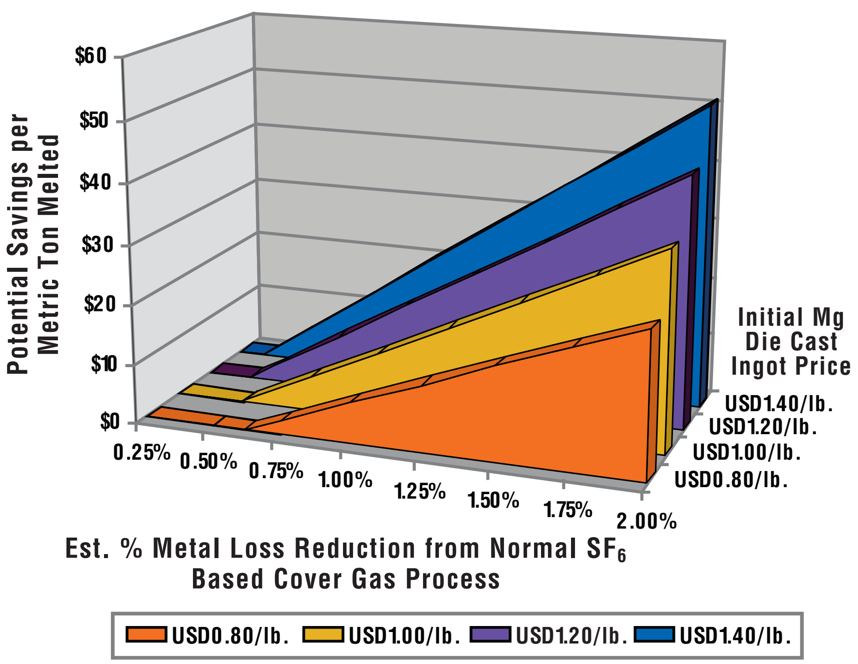
[4] Bach et al, 2005. See URL: www.tms.org/Meetings/Annual-05/AM05-TechProg.pdf
[5] Revankar et al, no date. See URL: http://www.hatch.ca/Light_Metals/Articles/

are necessary considerations. Dilute SO_2 systems also do not reduce metal loss, and thus may not offer the additional cost savings possible with fluorine-based systems shown in the graph below.

Mg producers or casters should note that the potential for the cost savings shown in the graph depends on the use of appropriate gas distribution systems, furnace lid designs and maintenance, and other production factors. Also, magnesium melt protection costs depend on many factors, including the price of Mg raw materials, the cost of a specific melt protection, the ratio of blended gas used, and the flow rate needed.

Potential Cost Savings from Reducing Metal Losses: Alternative fluorine-based melt protection vs. SF_6 cover

% Metal Loss Reduction Vs. Die Cast Ingot Price
(Die Cast Process Only)



Workplace Safety and Environmental Benefits

Alternative non-SF_6 Mg melt protection can provide important workplace safety and environmental benefits. These systems:

- Produce less smoke and fumes—making the workplace safer for workers' health
- Are non-flammable
- Reduce or eliminate greenhouse gas emissions—A typical diecasting facility that processes 2,000 tonnes of Mg per year using alternative melt protection other than SF_6 may reduce greenhouse gas emissions by over 60,000 tonnes of CO_2 equivalent emissions per year compared to an SF_6-based system.
- Do not deplete stratospheric ozone

The alternative melt protection technologies can potentially produce toxic or corrosive byproducts, as does SF_6 (see Table 1). However, if these technologies are managed and operated correctly, the byproducts can be maintained at acceptable levels.

Photo courtesy of CAST and American Magnesium

Mg casting operation using SF_6; alternative fluorine-based melt protection may substantially reduce the workplace fume and smoke emissions shown above.

Table 1. Summary of Magnesium Melt Protection Options

	Compound	Atmospheric Lifetime[a] (yrs)	Global Warming Potential (GWP)[a] (100 yrs)	Potential Climate Benefit (% reduction in overall global warming vs. SF_6)[b]	Selected Potential Byproduct Emissions of Concern[c]	Equipment and Process Upgrades (from SF_6 system)
Commercially Available Technologies	SF_6	3,200	23,900	--	SO_2[d], HF[e]	--
	FK (Novec™ 612)	0.014	~1[f]	95-99%	HF[e], PFIB[g], PFCs[h]	Moderate (e.g., same as "minimal" plus liquid processing equipment & monitoring)
	HFC-134a (AM-cover)	14.6	1,300	95-99%	HF[e], PFCs[h]	Minimal (e.g., recalibrate mixing units; possibly add entry point to improve distribution)
	Dilute SO_2	Several days	0	NA	SO_2[d]	Significant (e.g., replace all mixing equipment & distribution system piping with stainless steel/corrosion-resistant materials; monitoring)
Technologies Under Investigation	BF_3	?	Not measured	?	BF_3[i]	Moderate (see above)
	SO_2F_2[j]	?	~1	?	SO_2[d], HF[e]	Significant[j] (see above)

[a] Global Warming Potential (GWP) reflects the potential for contributing to the heating of the earth's atmosphere over a specified time frame. CO_2 has a GWP of 1. The GWP figures listed above are from: *Climate Change 1995: The Science of Climate Change.* Intergovernmental Panel on Climate Change (IPCC), Cambridge University Press, Cambridge, U.K.

[b] Potential Climate Benefits are from: *Characterization of Cover Gas Emissions from U.S. Magnesium Die Casting*, U.S. EPA, May 2004, pp. ES-4, ES-5, 5-7. EPA430-R-04-004, www.epa.gov/highgwp/magnesium-f6/pdf/covergas_may2004.pdf

[c] This category does not reflect a comprehensive list of potential byproduct emissions, but rather those most commonly identified; other byproduct emissions may also be produced.

[d] SO_2 must be used with care. It is toxic to humans at 2 parts per million (ppm) (based on American Conference of Governmental Industrial Hygienists Threshold Limit Values) and can corrode steel equipment. At levels produced in the magnesium industry, it contributes minimally to acid rain.

[e] HF (hydrogen fluoride) is toxic at low levels and can accelerate corrosion of equipment. HF levels may be minimized to acceptable levels by using good operating practices.

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

[g] PFIB (perfluorisobutylene) is toxic; good operating practices can eliminate PFIB byproduct emissions.

[h] PFCs (perfluorocarbons) are potent greenhouse gases and have long atmospheric lifetimes ranging from 1,000 to 50,000 years (see www.ipcc.ch//press/SPM.pdf). Adding oxygen to the cover gas mixture can minimize PFC production to non-detectable levels (see www.epa.gov/highgwp/electricpower-sf6/pdf/milbrath.pdf).

[i] BF_3 (boron trifluoride) gas is highly reactive, toxic (1 ppm workplace exposure limit, U.S. DOL/OSHA), and corrosive; good operating practices may maintain BF_3 at acceptable levels.

[j] SO_2F_2 is toxic and thus poses potential workplace hazards; these hazards must be addressed with the use of alarms or odorization, equipment upgrades, and establishment of a safe supply chain.

Retrofitting for Alternative Melt Protection Technologies

In most cases, conversion from an SF_6-based or (older) SO_2-based system to a non-SF_6 alternative melt protection system is relatively easy. It is important that melt protection users carefully follow the manufacturer's recommended best practices to achieve good performance, maintain product quality, and achieve workplace and environmental improvements. Table 1 (previous page) briefly summarizes the environmental and operational concerns. When installing a new melt protection technology, companies should use careful advance planning and good operating practices, such as:

- **Proper choice and grade of carrier gases—**Pay attention to the final blended product (active ingredient plus carrier gas) and how efficiently it is applied to the molten Mg surface. For example, some alternatives perform better in carrier gas mixtures of nitrogen or carbon dioxide rather than dry air alone.

- **Correct concentrations and flow rates—**Know exactly how much of the final product has been delivered; consider the need for improving current gas blending equipment. With some alternatives, Mg is best protected at lower concentrations and higher flow rates than those used with SF_6.

- **Good distribution systems and practices—**Available melt protection alternatives are more reactive and thus less thermally stable than SF_6, making good gas distribution essential.

- **Appropriate operating conditions—**Monitor process parameters such as molten metal level, and variations in temperature and alloy chemistry.

The detailed information needed to convert a facility to use an alternative melt protection technology is available from the respective technology providers – please see the list of suppliers' contact information on the back cover.

Globally, the magnesium industry can avoid annual greenhouse gas emissions equal to more than 15 million metric tons of CO_2 by eliminating SF_6 emissions. The environmental benefit from choosing climate-friendly Mg melt protection technologies is equivalent to the CO_2 absorbed by planting 2.5 million acres (10,117 km^2) of forest[a], an area larger than the United States Yellowstone National Park.

[a] Assumes 1 kg SF_6 /mt of Mg (global primary production only) and an average of 6 mt CO_2 per acre of forest per year. Source: R. Birdsey, 1996, USDA Forest Service.

Photo of Yellowstone National Park courtesy of U.S. National Park Service

Contact Information:

U.S. EPA:	www.epa.gov/magnesium-sf6
IMA:	www.intlmag.org
CMA:	www.chinamagnesium.org www.chinamagnesium.org/english.htm
JMA:	www.kt.rim.or.jp/~ho01-mag

Product Information:

AM-cover:	www.am-technologies.com.au/metal.htm
Novec™ 612:	www.3M.com; dsmilbrath@mmm.com mixing equipment: christian.domanyi@rauch-ft.com (outside N. America) kurt.brissing@rauch-ft.com (N. America) www.tn-sanso.co.jp/en/index.html (Japan)
Dilute SO_2 (Europe):	www.aski-gasetechnik.de
Dilute SO_2 (N. America):	www.polycontrols.com
COOLCOM:	www.linde-gas.com
SO_2F_2:	www.halidegroup.com