A Replacement for SF_6: The MagShield System

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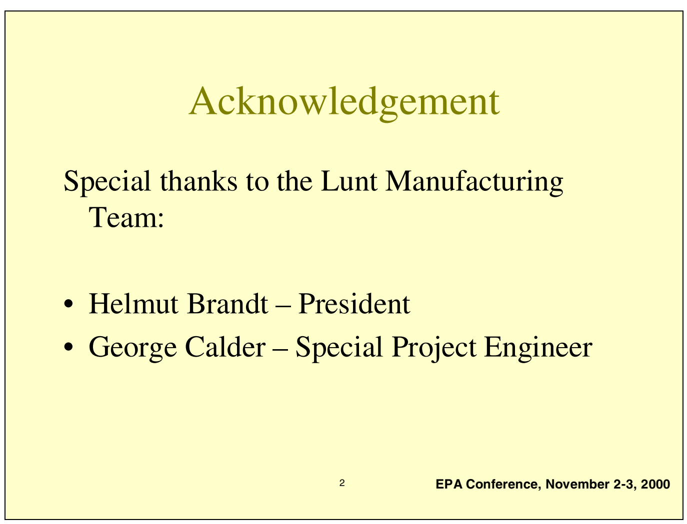
Introduction:

The greatest challenge facing the global metallurgical industry in the first decade of the new millennium may be its ability to reduce greenhouse gas (GHG) emissions while maintaining economically viable production. In the magnesium industry, the use of sulfur hexafluoride gas contributes more to the total GHG emissions than any other single source.

The MagShield system developed by HATCH is an economical, novel in-line protective gas generation system that carries no greenhouse gas liability and affords superior performance while maintaining a safe and odor-free work environment.

This paper outlines the MagShield process and reviews the results of industrial trials carried out at Lunt Manufacturing.

Parts of this paper have been presented at the annual conference of the International Magnesium Association in Vancouver, Canada, in May 2000. Since that time we have continued our work on the system and the presentation will include the most updated data and information.



We would like to thank Lunt Manufacturing Company for providing the facilities to carry out the highly successful MagShield industrial trials. Our special thanks to Mr. Helmut Brandt, president, and Mr. George Calder, special project engineer, of Lunt for their enthusiasm, active participation and support.

Presentation Overview

- Magnesium protection – prior art
- Use and limitations of SF_6
- The MagShield System
- Industrial trials - results
- Conclusions
- Future Plans

3 EPA Conference, November 2-3, 2000

This figure is an overview of the presentation. In this presentation we will briefly discuss the history of various methods used for magnesium protection including SF_6. We will then focus on the new MagShield technology. The presentation then discusses the results and conclusions of the industrial trials. This is followed by comments on the system's present status and Hatch's plans for the technology.

Magnesium Protection History

- 1910's - Present
  - Salt fluxes
- 1948
  - Addition of 0.0005% Be
- 1930's - Present
  - SO_2
- 1970's - present
  - SF_6

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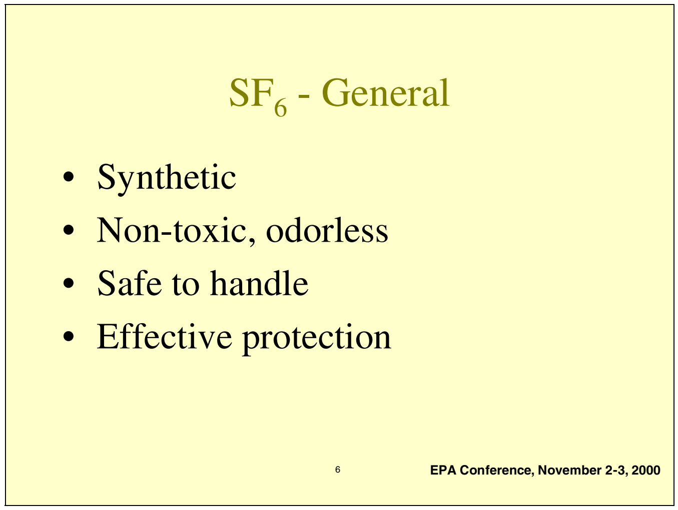
The magnesium industry has followed numerous paths and methods to reduce the impact of oxidation. As early as the late 1920's, gases that formed protective films on the surface of magnesium had been identified.

A 1934 US Patent by Riemers cited some of these gases, among them SF_6, BF_3, and SO_2.

The extensive work of Hanawalt et al. in the late 60's and early 70's formed the basis for the industrial application of fluoride compounds for melt protection. Battelle in 1977 successfully demonstrated fluxless melting using SF_6.

This figure also indicates that salt fluxes, SO_2, and SF_6 gases are presently in use for protecting molten magnesium. The majority of the magnesium industry uses SF_6 gas because it is assumed to be inert and safe.



As mentioned above, SF_6 gas is presently used by a majority of industries that process magnesium. It is a synthetic gas, heavier than air, colorless, odorless, non-flammable and non-toxic. It is thermally stable up to 800°C and does not react with water unless at high temperature (>600°C), whereupon it will form HF, and thus requires very dry air for blending purposes.

SF_6 protects molten magnesium when mixed with dry-air and/or CO_2 at a concentration of 0.5 vol.% or less. When SF_6 is used, the oxidation of the magnesium is reduced due to the formation of a fluoride-oxide film barrier. Recently, however, SF_6 has been cited as being a significant contributor to global warming and as such has come under increasing pressure.

Over the last several years, the magnesium industry has used gas mixtures containing SF_6 to protect molten magnesium from oxidation as a replacement for flux and SO_2. Until recently the method has been considered to be environmentally sound both for the workplace and in the environment. Studies have now shown that SF_6 in the atmosphere has an extremely high global warming potential relative to CO_2. A report by the US World Resources Institute reported that the global warming potential for SF_6 is 23,900 relative to CO_2. This means that 1 kilogram of SF_6 in the atmosphere gives approximately the same contribution to the greenhouse effect as 24 tonnes of CO_2. At typical consumption rates this means that SF_6 contributes the equivalent of 24 tonnes of CO_2 per tonne of magnesium smelted.

The lifetime of SF_6 in the atmosphere is estimated to be 3,200 years. This gas is the dominant greenhouse contributor for magnesium smelters and die casters. Due to these environmental problems, it is expected that the future use of SF_6 will be limited and many countries and end users plan to phase out SF_6 use completely by the year 2005.

Why Not BF_3?

- BF_3 is equally effective in protecting molten magnesium BUT:
  - SF_6 availability
  - Toxicity/corrosiveness concerns
  - Dry carrier gas requirements
  - Compressed gas – costly/special storage
  - Storage – potentially serious hazard

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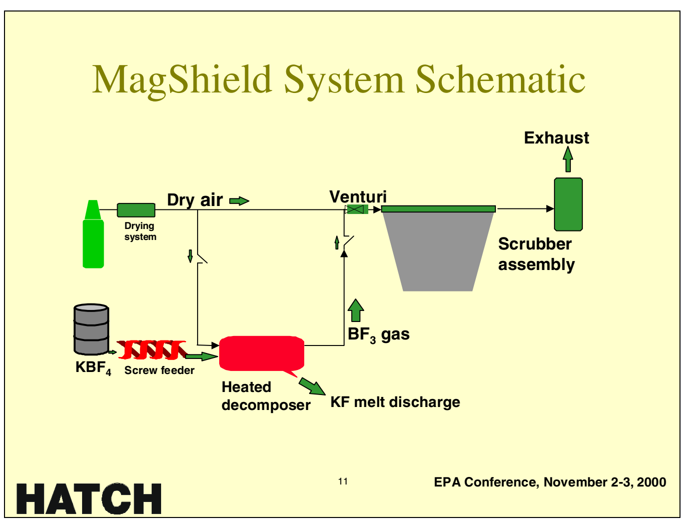
Why hasn't BF_3 been used previously? Firstly, BF_3 purchased as a manufactured compressed gas is very costly. Secondly, BF_3 when stored as a concentrated, highly compressed gas is potentially hazardous due to the risk of cylinder or line rupture.

BF_3 decomposes in moist air to form corrosive acids. It can also react with common metals to release hydrogen.

BF_3, SF_6 and SO_2 gases are effective for protecting molten magnesium. However, costs and safety are also issues deciding which cover gas to use. Also important is the fact that BF_3 is not a greenhouse gas, and fugitive emissions can be easily and effectively removed by scrubbing, if needed.

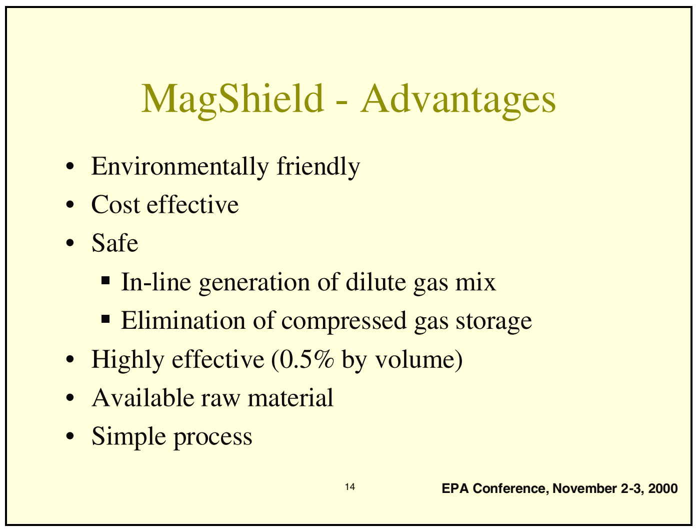
A novel way of preventing the excessive gas handling, transportation, storage, and corrosion issues associated with the use of BF_3 is by using an in-line fluoride gas generation method. This can be achieved by the controlled thermal decomposition of certain fluoride compounds. MagShield uses this simple principle to generate only the small amount of BF_3 required and in dilute concentrations. According to our test results, using a fluoroborate in-line decomposition process, a small amount of generated BF_3 easily protects molten magnesium.



This is the basic schematic of our system. The main parts of the system are a solid feeder, air dryer, decomposer and a scrubber assembly. This last piece of equipment was not required in the industrial trials.

A precision powder feed system delivers a special prepared solid fluoroborate into the decomposition furnace. Liberated BF_3 gas is carried from the furnace in a side stream of the main dry air carrier gas stream. The main carrier gas stream dilutes the liberated BF_3 gas. The mixture control is by adjustment of the powder feed rate and by adjustment of the carrier gas dilution ratio.

In our system, KBF_4 decomposes in-situ to generate the protective gas and an inert glassy fluoride compound, which is removed as solid or liquid. BF_3 generation begins at around 350°C and increases with temperature.



This figure provides an overview of the advantages associated with the MagShield system. This is a simple, cost-effective, environmentally safe and patented technology. The new system can generate the protective gas as and when needed for the operation. The system gas generation can be completely stopped by simply shutting off the heat supply or the raw material feed. The system is very compact; therefore the gas has to travel a very short distance and can be generated next to its intended application. The raw material is inexpensive and readily available.

Most magnesium processing industries have a plan to remove SF_6 and possibly return to the use of SO_2. This encouraged us to develop a system based on the in-line decomposition of an innocuous compound.

➢ ***Amount used and toxicity***: The BF_3 and SO_2 required are approximately 0.7% and 1.5%, respectively, in air. The TLV level for BF_3 and SO_2 gas is 1 ppm and 2 ppm respectively. The SO_2 must be stored as a compressed gas or liquid; thus, in case of an accidental release, the volume is so large that the concentration far exceeds the TLV limit. In the case of MagShield, however, heat is required to generate BF_3 from the fluoroborate so a major "spill" is virtually impossible.

➢ ***Gas generation and storage***: An elaborate handling, storage, piping, and safety system is necessary with SO_2. This is avoided with our novel system. The BF_3 gas is generated on an as-needed basis, thereby requiring limited safety systems.

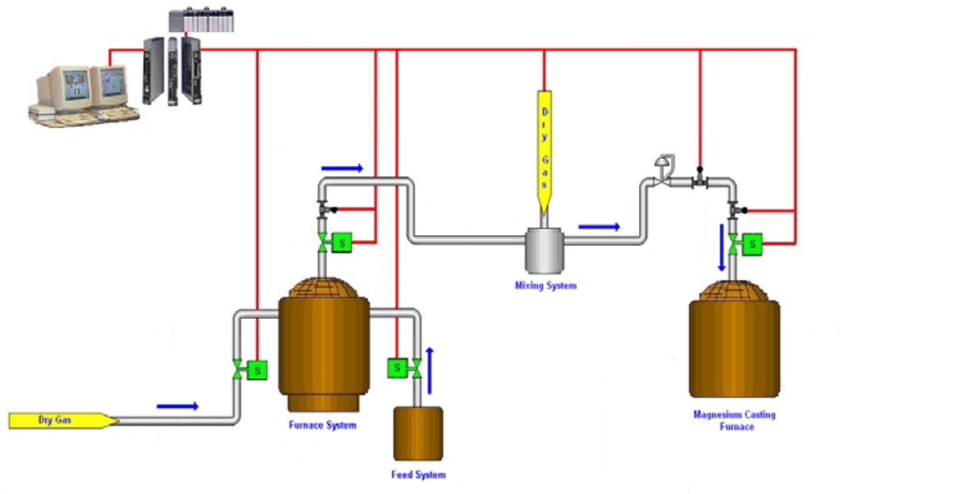
- ➢ ***Fugitive gas scrubbing***: BF_3 can be easily scrubbed using water, whereas SO_2 is more difficult to scrub. The resultant slurry is easily neutralized. The efficient scrubbing of BF_3 will allow the industry to meet “applicable environmental standards” (if necessary).

  Potassium fluoroborate is not listed as a hazardous substance and can easily be stored. Price and availability are not problems. It is a stable compound and only starts to decompose above 350ºC.

- ➢ ***System/installation design***: Regardless of the gas used, emissions must be controlled so that work place levels do not exceed TLV limits. Compared with SO_2, safe BF_3 concentrations are more easily obtained due to the lower concentrations required. Actual measured data from our recent industrial trials at Lunt are reviewed later.

The primary objectives of the industrial trial program carried out at Lunt were, firstly, to validate the MagShield process as effective in an industrial environment; secondly, to evaluate its operation with respect to ergonomics; and thirdly, to quantitatively assess the health and safety impact of the process. Secondary objectives were to refine and improve the design of the process equipment, and to confirm that end products produced using MagShield were, in all measurable respects, equal in quality to those produced under conventional cover gas.

Technology Description



MagShield System

The use of the MagShield system in a furnace adjacent to the die-casting machine operation is very simple. The gas is generated in line adjacent to the furnace and then utilized at the appropriate concentration.

The gas-mixing ratio of the protective gas is essential in order to obtain a safe and efficient protection; therefore a gas-mixing unit, which controls concentration and flow rate, has been employed. The mixer is also equipped with an air compressor and an integrated air dryer.

This shows the actual MagShield prototype system that was utilized at Lunt. The photo shows the furnace, feeder, and the dry air system.

The furnace was resistance heated and AM60B alloy was held at 1310ºF. The furnace was used continuously to die-cast automotive parts. Any gas that escaped through the cover was exhausted. No scrubber was employed. The MagShield system was connected to the furnace using a T-joint connection on the SF_6 gas supply line.

It is important to control the BF_3 concentration at the melt surface. The gas volume above the melt should be minimal. This is a typical operating mode in any magnesium operation. The gas was supplied to the crucible through several nozzles with enough velocity to ensure a homogeneous concentration in the atmosphere above the melt. Such a distribution tube is fixed underneath the lid of the crucible. The velocity in the nozzle should exceed or compensate for the high buoyancy in the air above the melt. The crucible system was generally well sealed to reduce any gas leakage.

The melt was protected with varying amounts of BF_3 (0.1 – 0.7 vol.%) gas in dry air. During the trials, the protection was excellent with little or no sparking or burning, even with vigorous agitation. The oxide/fluoride skin on the melt surface stayed bright and shiny when the BF_3 concentration was greater than 0.5%, but when the concentration was less than about 0.5% the skin or film turned light tan. Unlike SO_2 and SF_6, the reactivity of BF_3 with the magnesium also increases with temperature providing good protection at all operating temperatures.

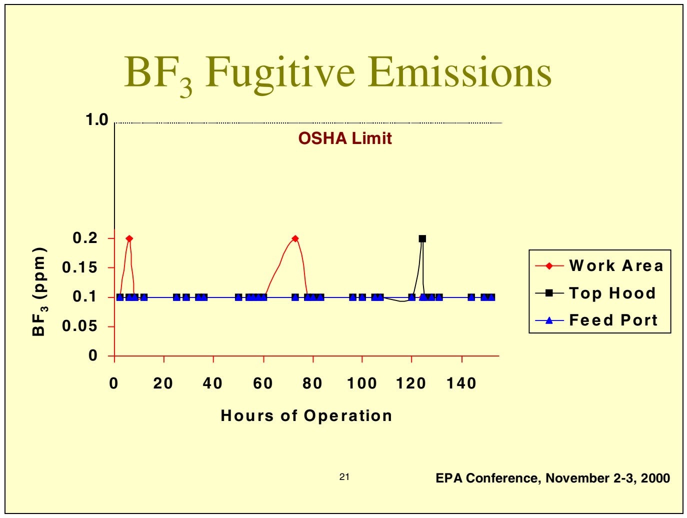
The amount of BF_3 required per tonne magnesium varied between 0.6 to 0.8 kg during these trials. This may not be optimum.

The ratio of waste residue to BF_3 generated is less than one. Thus for a die casting plant that melts 5,000 tonnes annually, less than 1 drum of waste per month is generated. This material is not hazardous and can be landfilled.

The protection with BF_3 was tested under various operational modes at Lunt. For example, we conducted the trials with a simulated power failure. We switched off the power to the system as well as the gas flow to the furnace. Full protection was observed even after 45 minutes, compared with only 30 minutes with SF_6 according to Lunt.

During all the trials we carried out continuous emission analyses and assessed the operation continuously for safety. Emissions were measured near the furnace, work area, and the lid. Emissions were generally less than 0.1 ppm while maintaining the same plant ventilation. No corrosion problems were noted, and no fumes or odors were emitted.

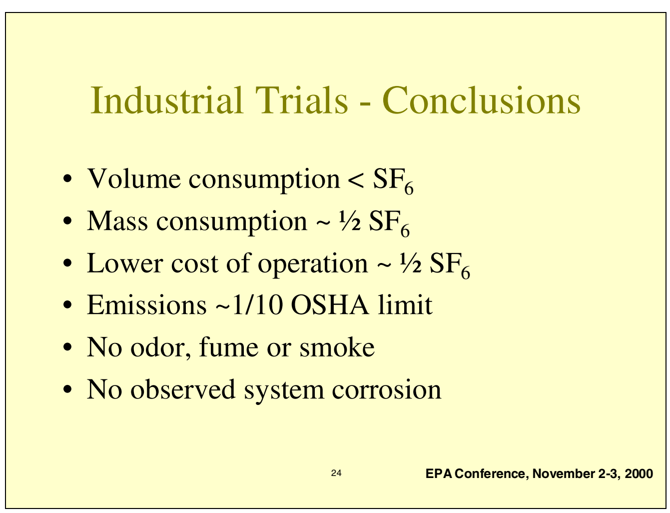
BF_3 concentration was monitored at various locations. This photograph shows the gas measurement at the exhaust port.



The BF_3 gas emissions were continuously monitored during our trials and the results are shown in this slide. The equipment used was the Enmet analyzer calibrated for 0-10 ppm level. A hood was provided over the work area and the hood exhaust gas concentration was measured. During all testing, gas concentrations were observed to be generally 10 times lower than the OSHA limit. The maximum concentration observed at any given time was approximately 0.2 ppm.

The metal feed rate was maintained in the same manner as that with SF_6. The operation was carried out with the same output parameters for SF_6 (shot weights). The process worked well without any technical problems. The system was observed for dross and sludge accumulation. It appears that the amount of sludge and dross generated may be less than that produced using SF_6. Additional trials are required to verify this observation. Lunt analyzed the parts cast using BF_3 per their procedures and no problems were noted.

Mechanically the system has been shown to be robust but additional minor modifications will be incorporated in the commercial unit.



The MagShield industrial trials were carried out using a similar amount of BF_3 in dry air as with SF_6. In several cases the trials were conducted using less than 0.5 volume percent. The lowest concentration necessary for continuous operations is yet to be optimized. The concentration of BF_3 was continuously monitored in and around the furnace/work area. Throughout testing, BF_3 emissions were generally observed to be under one-tenth of the OSHA limit. In conclusion:

- ➢ Volumetrically, the consumption of BF_3 is less than or equal to that of SF_6.
- ➢ The mass consumption of BF_3 is approximately half of SF_6.
- ➢ The cost of BF_3 gas generation is less than half of SF_6.
- ➢ The workplace emissions are almost 10 times lower than the OSHA requirement.

Hatch has finalized the engineering design and the issues involving commercialization of our MagShield system.