Concept for the Reduction of SF_6 Emissions in Magnesium Foundries

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Abstract

The “concept for the reduction of SF_6 emissions in magnesium foundries” from Solvay Fluor und Derivates is a possibility for magnesium foundries to be included in the SF_6 ReUse Concept. It describes the efforts that have to be taken to switch to sulphur dioxide (SO_2), but how to keep the door open for continuous operating with SF_6. This four-step process allows the magnesium foundry to decide on a fundamental database what will be their “tailor made” solution for reducing the SF_6 emissions. These four steps are: determining the leaks and the quantities; installations of adequate gas suction systems; installation of an SF_6 recovering system including filters for decomposition products; and giving the concentrated exhausted gases back to Solvay Fluor und Derivate. Solvay Fluor und Derivate will decide if the gas quality can be reclaimed or has to be destroyed through incineration.

Introduction

Solvay Fluor started producing SF_6 in the 1960s and has since become a leading global supplier. Already at the beginning of 1990, Solvay developed the ReUse Concept for SF_6; this was primarily designed for products coming from electrical equipment, where most of the worldwide SF_6 production is used.

In the years since then, the ReUse Concept has been widely adopted by the industry and is today an established procedure for minimising SF_6 emissions from electrical equipment.

Solvay has now developed a concept to include the magnesium industry in this already existing SF_6 ReUse procedure and is currently introducing it to magnesium producers.

A less favourable characteristic of SF_6 is namely a comparatively high global warming potential due to its persistence in the atmosphere. There is e.g. for magnesium cross car beam production, which is mainly induced by SF_6 and, to a smaller extent by CO_2 emissions from the magnesium alloy production; it is not possible to reach a break even within a reasonable mileage of less than 200.000 km. Without SF_6 emissions, as a further result of improved magnesium production and processing, the break even would then be in the range of 67.000 km to 109.000 km, depending on the fuel-saving factor [1]. This makes it essential to keep SF_6 in closed cycles as far as possible in order to minimise emissions by utilising recycling and reuse potential.

Concept To Reduce SF_6 Emissions

There is a big difference in the application of SF_6 used in electrical equipment and magnesium foundries. In electrical equipment, pure SF_6 concentrations are used compared to 0,04 vol% to 0,4 vol.% SF_6 in the magnesium industry [2]. These low concentrations make it obligatory to concentrate the SF_6 first and transport these gas mixtures from foundries to reclaiming companies afterwards.

In the past, there were tendencies in the magnesium foundries to replace SF_6 with SO_2. The magnesium foundries accept the health risks of SO_2 and the disadvantages for the magnesium process (e.g., sulphur dome effect) in order to gain environmental advantages for the diecasted magnesium [3]. Solvay's SF_6 ReUse Concept assists the magnesium foundries in reducing SF_6 emissions and makes the SF_6 technology environmentally more competitive. The concept is developed for foundries that are investing money in a gas management system for SO_2. Solvay Fluor und Derivate will be your partner and will help you decide what will be the individual solution. The concept includes a four-stage process to reduce the SF_6 emissions by more than 90%.

First Stage - Determination of Exhaust Gas Quality and Quantity

The first stage is to evaluate all SF_6 emission sources, including all possible decomposition products. There are a lot of different gaseous reaction products possible (e.g., SO_2, hydrogen fluoride (HF), thionyl fluoride (SOF_2), sulphuryl fluoride (SO_2F_2)) depending on the conditions [2]. Analogous to the SF_6 ReUse Concept for electrical equipment, Solvay offers analytical services to detect the SF_6 leaks and the possible reaction products. The methods used are mobile gas chromatograph and HF monitor onsite the melting pot. If the reaction compounds are not completely detectable onsite, a sample bottle will be filled and analysed at the SFD laboratories.

If a database on the quality of emission sources is established and combined with the flow rates of each emission source, a sufficient database for an exhaust gas treatment is given. Now the magnesium foundry can decide if a local or a central exhaust gas treatment or even a combination of both is the most efficient system. Besides the freights of each leakage, the treatment technology must be adopted. There are several technologies available on the market: e.g., gas scrubber, membranes and adsorber technology in combination with prefiltering steps. Prefiltering steps are necessary to prolong or save the treatment technology used afterwards from by-products that occurred during the melting process.

Second Stage - Exhaust Gas Suction

In the second stage, a system is installed to collect the air/CO_2 mixture contaminated with SF_6. There are several companies in the market offering these services.

Third Stage - Filter System for the Decomposition Products

The filter system or decomposition treatment used depends on the exhaust gas management. In principle, there are two different solutions feasible: a local treatment system and a complete treatment system. Local treatment systems like adsorbers have the advantage of being selective and requiring less space. There are disadvantages like limited capacity and an additional recharging process.

A complete decomposition product treatment system could be an alkaline gas scrubber. The advantages of such a complete system is a higher capacity and no recharge processing, because of continuos dosing of alkaline compounds. There are disadvantages like introduction of humidity into the system and additional chemicals and waste.

It depends on the gas management of each company to determine which will be the best solution.

Fourth Stage - A Pressure Swing Adsorption Plant Recovers the SF_6 from the Air.

Selective molecular sieves (adsorbers) are commonly used for gas separation in pressure swing adsorption processes—e.g., removing chlorinated organic compounds from air. There are also molecular sieves that adsorb SF_6 and have already been described by Daniel Berg and William M. Hickam in 1961 (13X molecular sieve) [4]. Molecular-sieve zeolites are crystalline aluminosilicates of elements from group IA and group IIA such as sodium, potassium, magnesium, and calcium. Chemically, they are represented by the empirical formula:

$$M_{2/n}O.Al_2O_3.ySiO_2.wH_2O \quad [5].$$

These zeolites with a specific pore size and a specific module (ratio on SiO_2/Al_2O_3) are able to adsorb SF_6. This becomes clear when comparing the molecule diameters of SF_6 and N_2.

	d_m	l	w	h
SF_6	0.522	0.58	0.5	0.49
N_2	0.258	0.33	0.23	0.23

Table 1: Dimensions of penetrant molecules (in nm) [6]

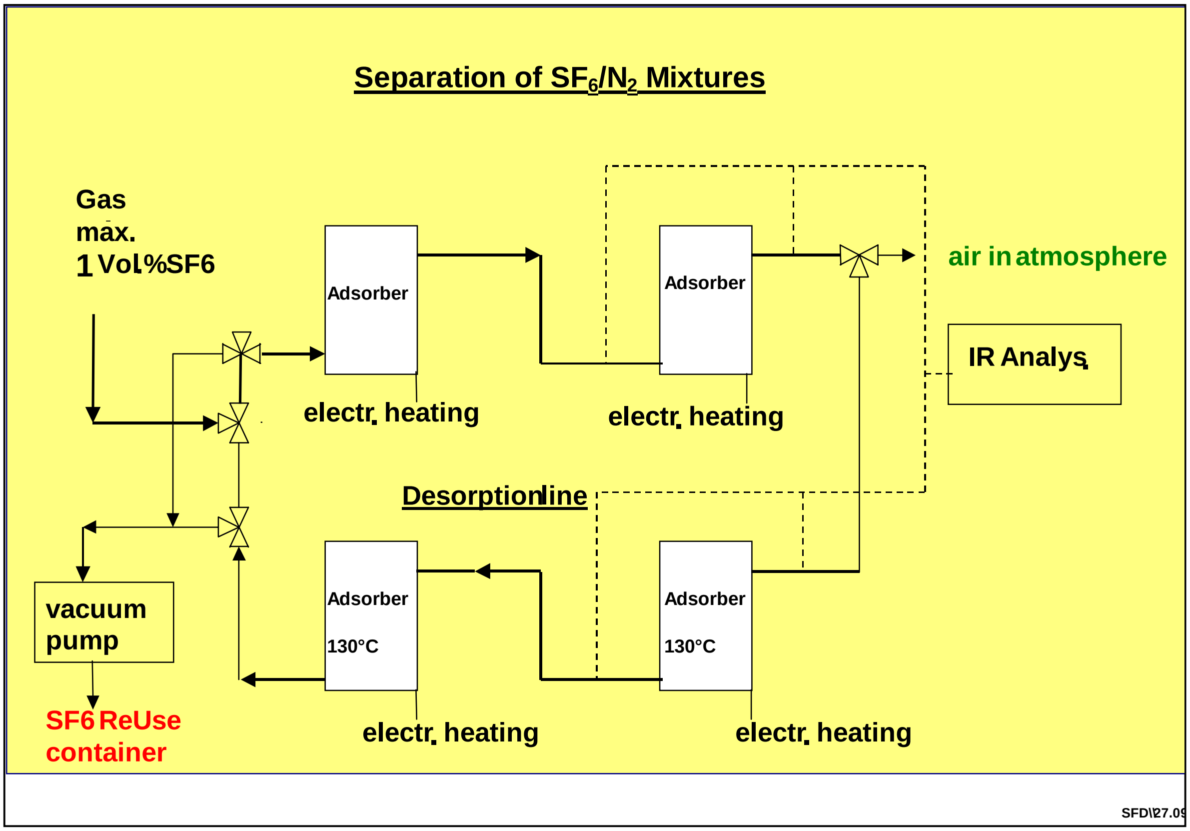
The comparison of the dimensions shows that a molecular sieve that adsorbs SF_6 and allows N_2 to pass must be used.

In the past, the commercially available zeolites were mainly hydrophilic due to their lower SiO_2 content. Modern production processes for zeolites have made it possible to reduce the Al_2O_3 content in the zeolites. These SiO_2-rich zeolites have hydrophobic characteristics [7]. With these zeolites, SF_6 can be removed from N_2 down to a level of 10 ppm and the zeolites can be regenerated by thermal desorption.

The resulting concentration of the reclaimed SF_6 could easily be more than 90% by weight, depending on the parameters (like temperature and vacuum) and the zeolite.

The concentration of SF_6 delivered by the molecular sieves depends on the other gases present in the mixtures. Therefore, other gases like CO_2 are in competition with SF_6, which means that they adsorb and release under the same process parameters.

The capacity of the molecular sieve ranges from 1% to 3% by weight. Consequently, for 1 kg of 100% SF_6 between 40 and 100 kg of molecular sieve is necessary (corresponds to a molecular sieve volume of 28–70 l).



Picture 3: Molecular sieve process

Picture 3 shows a molecular sieve process with two adsorber lines in parallel. This modification allows a continuous adsorption process. While one adsorber line is working, the other is regenerated. The whole process is controlled by means of an infrared (IR) analyser. This IR analyser on-line monitors the SF_6 concentration downstream of each adsorber. If, for example, the SF_6 value at MS4 is above 10 ppmv, the analyser sends a signal to the automatic valves to switch to the other adsorber line. The regeneration of an adsorber line is a two-step process. In the first step, a vacuum pump removes the residual gas mixture from the plant. This gas mixture will not be released, but is reintroduced into the other adsorption line. In the second step, the electrical heating increases the temperature of the adsorber material to a level above 130°C. During this heating process, the adsorbed SF_6 is desorbed and filled into a storage vessel or ReUse container by means of a vacuum pump and a compressor. If the vacuum pump reaches a certain value, (e.g., 50 mbar), the desorption process is finished. A temperature of 130°C is necessary to prevent moisture from building up in the adsorber. This process is preferably used for low SF_6 concentrations (i.e., 2 vol.% of SF_6 or lower) and reasonable flow rates, if a mobile separation concept is required.

Example for the Magnesium Industry

The technical parameters recommended by IMA for one square meter of melt surface with an enclosure volume of 100 liters are 10 L/min gas flow including 0,2 vol.% SF_6 [2]. These values are corresponding to 20 ml/min SF_6 = 1,2 l/h SF_6 (100 vol.%) or 9,6 l/d SF_6 (8h a d). Calculating the corresponding mass of SF_6 introduced per day is 59,4 g/d (density 6,18 g/l at 1 bar and 15°C) or 297 g per week.

At ambient pressure, the adorber material has an adsorption coefficient between 2,5 and 3%. The total amount of adsober material necessary for one week is approximately 11 to 12 kg (for above-mentioned application).

The SF_6 release after this purification is 10 ppmv. If two adsorber lines are used in parallel, one can be recharged per week via pressure swing technology. There is almost no co-adsorption of air but some co-adsorption of zeolites tested by Solvay Fluor. All trials were performed on a laboratory scale with synthetic gas mixtures. Solvay now has experience in practical tests with gas originating from a melting pot.

The first **three stages** as described above also have to be implemented if a magnesium foundry wishes to switch to $SO_{2.}$ However, the toxicological risk of SO_2 is not eliminated by doing so.

The enriched (more than 80 vol%) SF_6 gas stream is then filled into the SF_6 ReUse cylinder provided by Solvay. The SF_6 gas in the ReUse cylinders coming from magnesium foundries is either subsequently fed back into the SF_6 production plant's purification process or goes into an incineration plant. Through incineration, the SF_6 gas mixture is decomposed into HF and SO_2, and both gases can easily be adsorbed via gas alkaline scrubbers. The conditions for taking back used SF_6 are similar to those applicable for the electrical industry.

This SF_6 ReUse Concept for magnesium foundries from Solvay Fluor allows the magnesium industry to minimise SF_6 emissions without affecting the quality of the molten magnesium metal. In addition, the ReUse Concept helps improve the environmental competitiveness of magnesium against other light metals.

Literature:

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