New technologies for protective cover gas mixing help reduce emissions and production cost

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Abstract

The magnesium industry is in a deep period of transformation. The arrival of new players who have access to cheaper labor as well as the increase of the environmental pressure forces them to reduce their GWP gas emissions at the same time as reducing their production costs.

In order to examine solutions offered to this industry, this paper illustrates the evolution of technologies used to produce molten magnesium protective cover gas, the benefits associated with each of these, the capital expenditures and the production costs required by these technologies and finally, their capacity to handle new cover gas alternatives.

Evolution of technologies for molten magnesium protective cover gas

Up to the mid 80’s, gas mixers with fixed orifices were largely used for the protection of molten magnesium. These mixers, simply constituted from a specific-sized hole in a ‘T’, produced non-adjustable mixtures and were strongly influenced by any process variation such as load variations¹, pressure drops and temperature changes. Moreover, fixed orifice mixers were only based on theoretical calculations, which did not reflect the real world, and they did not allow any readout. Thus, to obtain a fair security margin against any of these process variations, the users had no other choice than to operate at a very

¹ The load variation is a function of the quantity of furnaces in operation and the mode of operation (cleaning, production or standby) of each of those.
high SF$_6$ ratio (approximately 5%). Figure 1.1 presented at the appendix illustrates this situation.

The new economic environment created in the 90’s by the rise of SF6 prices, the troubles associated with the high concentration of fluorine and the lack of gas mixer control limited the use of fixed orifices as gas mixers. The need for volumetric gas mixers was created. This new generation of gas mixing equipment allowed basic readings, adjustment and diagnostics. In addition, volumetric gas mixers are less, but still, influenced by process variations related to load, pressure and temperature variations$^2$. In spite of their fair performance, the user had the possibility of producing mixtures at lower concentration ($\approx 1\%$) while preserving an acceptable margin of security against process variations.

Within this period, the magnesium industry also saw a derivate of the previous volumetric mixer, the compensated volumetric mixer. Those mixers, designed with a more stable flow path and pressure compensated rotameters$^3$, are allowing readout in standard conditions. Standard condition compensated rotameters have the benefit of offering a readout more closely related to the amount of mass of gases mixed together. Consequently, compensated volumetric gas mixers are less influenced by process variations than the previous volumetric generation. Once again, this advancement offered the user the possibility of producing mixtures at lower concentration ($\approx 0.5\%$) while preserving an acceptable margin of security. Figure 1.3 illustrates this improvement.

In the last decade, the requirements for cover gases have changed again. The increase of global environmental concerns and the arrival of new alternative cover gases, with a need of gas mixtures with controls as low as 0.01%, do not allow any more magnesium cover gas to operate in excess of protection. These new challenges, accentuated by the urgent

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$^2$ Please refer to figure 1.2 for further information

$^3$ Rotameters who offer readout in standards condition are compensated in pressure, temperature and viscosity. They are characterized by the letter ‘S’ place before the flow unit (Example: slpm, sgpm and scfh)
need to reduce manufacturing costs, are factors that increase the demand for mixers capable of producing more efficient cover gases with lower mix ratios as well as multiple gas types.

To satisfy this new requirement, massic gas mixers have been developed. This newest generation of mixers directly measures the mass, just as a weigh scale. Unlike volume, mass is unaffected by changes in pressure, temperature, viscosity and density. Mass measurement is also directly correlated to the chemical reaction requested. Moreover, new massic measurement is 10 times less influenced by load variations than the volumetric instruments used in the previous generation of mixers. Thus, mass measurement is a major advancement for the magnesium industry which is – or should be – more interested in measuring mass rather than volume to ensure the tightest control and the right amount of fluorine in the cover gases. The massic mixer finally provides the opportunity to lower the mix ratio while increasing the immunity against process variations. Figure 1.4 illustrates this improvement.

**Capital expenditures and production cost reductions**

In today’s context of global markets, companies must focus on reducing their production cost. Gas usage optimization and tighter controls are two avenues offered to the magnesium industry to achieve this goal.

*The gas usage optimization.*

Gas usage optimization can be illustrated by comparing operation costs associated with each of the technologies presented before. Table 1 illustrates these.

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4 A molecule of gas always weighs the same mass. So, if you mix a constant massic ratio of two gases, you are assured to always obtain the same quantity of molecule of each gas. This is not true for a volumetric ratio of gas because the volume of each gas is a function of its pressure and temperature and in most cases, the relation is not linear (the Ideal Gas Law cannot be applied).
Table 1 – Gas usage optimization and associated payback

<table>
<thead>
<tr>
<th>Technology</th>
<th>Acquisition costs</th>
<th>Operation costs</th>
<th>Return on investment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed orifice</td>
<td>1000$</td>
<td>310,178$</td>
<td>----</td>
</tr>
<tr>
<td>Volumetric</td>
<td>8000$</td>
<td>61,962$</td>
<td>12 days</td>
</tr>
<tr>
<td>Compensated volumetric</td>
<td>12000$</td>
<td>30,981$</td>
<td>141 days</td>
</tr>
<tr>
<td>Massic mixer</td>
<td>25000$</td>
<td>12,397$</td>
<td>184 days</td>
</tr>
</tbody>
</table>

Note: The calculations are showed in appendix (page 8).

The analysis of operation costs revealed two different things. The first one is the fact that the gas ratio security margin requested by old technologies, like fixed orifices and volumetric mixers, increase considerably the production costs and, consequently, the GWP emissions. The second one is the fact that the production cost economy associated with the use of a more recent technology, like massic or compensated volumetric, is higher than the acquisition cost of the technology.

Therefore, even if we do not consider the dross economy related to a more efficient use of protective cover gas, the upgrade from volumetric to compensated volumetric or massic technologies offers a less-than-a-year return on investment. Thus, the gas usage optimization is not only a environment issue, but it’s also a fast and effective way of decreasing production cost and being more competitive in a global market place.

*The benefits of a tighter control*

Massic mixers incorporate electronic controls, which allow a better mixing precision and advanced management tools. Electronic control allows the use of smart digital valves. Unlike older manual or analogue valves, this new generation of valves allows more than sixteen thousand stages of adjustment and correct themselves within less than a second.

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5 Production cost base on gas consumption only, do not include economy related to dross reductions and rework costs
This improvement allows us to adjust the mixture at more than an hundredth of a percent. Therefore, the user can now optimize his mix ratio and run at 0.175%, instead of running at the theoretical value of 0.20% and improving a SF$_6$ cylinder life expectation by another 15%.

In addition, massic mixers offer advance management tools. As a flight computer which always evaluate the most economical way to achieve a certain goal while optimize the fuel usage, massic mixers come with optimization software. This Ethernet software allows to reduce gas consumption and emissions by finding the right balance between the mix concentration and the flow rate used.

Moreover, massic mixers include preprogrammed algorithms to monitor plant wide gas consumption, detect any unusual situations, avoid premature cylinders replacement, and eliminate last minute shortages. When used with gas distribution boxes, plant wide mixers also calculate the cost of operation of each individual furnace and control the gas consumption for each of them. Thus, instead of always running at full flow, the mixer can automatically choke the gas consumption of a furnace in standby condition and push more flow in the ones that are in cleaning mode. Pulsing of flow rates is also available for various operation modes such as door opening.

**New alternative cover gas**

With new alternative cover gases, the magnesium industry can no longer run with excess of protection. When used in excess of protection, those new solutions produce excessive...
cost of operation, high GWP emissions or in some cases health threatening emissions. Moreover, some of these new alternative cover gas require extremely low concentration that cannot be obtained with conventional volumetric mixers. Thus, as illustrated at the figure 2.1, massic technology is the most suitable technology for this type of application because it:

- Functions at a specific point of operation without any excess or lack of protection
- Allows very low mixture adjustment at more than an thousandth of a percent and as low as 0.001%
- Is the least expensive to operate
- Gives the higher security margin against process variations
- Is easily upgradeable to new alternative cover gases like AMCover™ and Novec 612™.

**Conclusion**

Since the mid 80’s, protective cover gas technologies have significantly evolved. The need to reduce manufacturing costs, the increase of global environmental concerns and the arrival of new alternative cover gases have increase the demand for mixers capable of producing more efficient cover mixtures.

A new generation of mixers capable of directly measuring the mass have been developed to meet this need. Those mixers provide the opportunity to lower the mix ratio, increase the immunity against process variations and optimize gas usage. Moreover, they are also the most viable alternative for the new cover gas, which cannot be used in excess ratio anymore.
<table>
<thead>
<tr>
<th>Technology</th>
<th>Performance characteristic</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1 Fixed orifice mixers</td>
<td><img src="image1.png" alt="Image" /> Immunity against process variations of Fixed orifice mixers</td>
<td>To obtain a fair security margin against any of these process variations, the users had no other choice than to operate at a very high SF6 ratio, which was acceptable up to the 90’s</td>
</tr>
<tr>
<td>Figure 1.2 Volumetric mixers</td>
<td><img src="image2.png" alt="Image" /> Immunity against process variations of Volumetric mixers</td>
<td>Costs of running in excess were more important in the 90’s but users begin to have the possibility of producing mixtures at lower concentration (≈ 1%) while preserving an acceptable margin of security.</td>
</tr>
<tr>
<td>Figure 1.3 Compensated volumetric mixer</td>
<td><img src="image3.png" alt="Image" /> Immunity against process variations of Volumetric compensated mixers</td>
<td>Compensated volumetric gas mixers are less influenced by process and load variations. This advance offered the possibility of producing mixtures at a lower concentration (≈ 0.5%)</td>
</tr>
</tbody>
</table>
Mass measurement provides the opportunity to lower the mix ratio while significantly increasing the immunity against process variations.

**Figure 2 – New alternative cover gas**

<table>
<thead>
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<th>Performance characteristic</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>New alternative cover gas</td>
<td>New alternative cover gas must be mixed at the requested point of operation, without any derivation due to process variation. This point of operation can be very low</td>
</tr>
</tbody>
</table>

**Table 1– Cost of operations and return on investment calculations**

Table 1 presents the cost of operation and the return on investment for a facility using 4 medium casting machines which each require 20 slpm (≈42 scfh) of SF6 mixture. The SF6 prices have been established at 23$/kg (1200 USD for 115 lb cylinder) and the absolute density of SF6 at 21ºC used is 0.006406 kg/l

**Cost of operation of a fixed orifice mixer (5% SF6 ratio)**

Total volume of SF6 consumed per minute = 4 furnaces x 20 slpm x 5% ratio
  = 4 slpm of SF6 per minute

Total volume of SF6 consumed per year = 4 slpm x 60 min. x 24 hrs x 365 days
  = 2,102,400 liter of SF6 per year
Total mass of \( \text{SF}_6 \) consumed per year = \( 2,102,400 \times 0.006406 \text{ Kg/l} \)
= 13,468 kg

Total cost of operation of fixed orifice = \( 13,486 \text{ kg} \times 23\$/kg \)
= 310,178$

**Cost of operation of a volumetric mixer (1% \( \text{SF}_6 \) ratio)**

Total volume of \( \text{SF}_6 \) consumed per minute = 4 furnaces x 20 slpm x 1% ratio
= 0.8 slpm of \( \text{SF}_6 \) per minute

Total volume of \( \text{SF}_6 \) consumed per year = 0.8 slpm x 60 min. x 24 hrs x 365 days
= 420,480 liter of \( \text{SF}_6 \) per year

Total mass of \( \text{SF}_6 \) consumed per year = 420,480 l x 0.006406 Kg/l
= 2,694 kg

Total cost of operation of fixed orifice = 2,694 kg x 23$/kg
= 61,962$

**Cost of operation of a compensated volumetric mixer (0.5% \( \text{SF}_6 \) ratio)**

Total volume of \( \text{SF}_6 \) consumed per minute = 4 furnaces x 20 slpm x 0.5% ratio
= 0.4 slpm of \( \text{SF}_6 \) per minute

Total volume of \( \text{SF}_6 \) consumed per year = 0.4 slpm x 60 min. x 24 hrs x 365 days
= 210,240 liter of \( \text{SF}_6 \) per year

Total mass of \( \text{SF}_6 \) consumed per year = 210,240 l x 0.006406 Kg/l
= 1,347 kg

Total cost of operation of fixed orifice = 1,347 kg x 23$/kg
= 30,981$

**Cost of operation of a massic mixer (0.2% \( \text{SF}_6 \) ratio)**

Total volume of \( \text{SF}_6 \) consumed per minute = 4 furnaces x 20 slpm x 0.2% ratio
= 0.16 slpm of \( \text{SF}_6 \) per minute

Total volume of \( \text{SF}_6 \) consumed per year = 0.16 slpm x 60 min. x 24 hrs x 365 days
= 84,096 liter of \( \text{SF}_6 \) per year

Total mass of \( \text{SF}_6 \) consumed per year = 84,096 l x 0.006406 Kg/l
Total cost of operation of fixed orifice = 539 kg x 23$/kg = 12,397$

*Payback generated by switching from fixed orifice to volumetric technologies*

\[\text{SF}_6 \text{ economy per year} = 310,178$ - 61,962$\]
\[= 248,216$/ \text{year}\]

\[\text{SF}_6 \text{ economy per day} = 248,216$/365 \text{ days}\]
\[= 680.04$/ \text{day}\]

Number of days required to achieve the payback = \(\frac{8000 \text{ $ investment}}{680.04$/ \text{day}}\)
\[= 11.76 \text{ days}\]

*Payback generated by switching from volumetric to compensated volumetric technologies*

\[\text{SF}_6 \text{ economy per year} = 61,962$ - 30,981$\]
\[= 30,981$/ \text{year}\]

\[\text{SF}_6 \text{ economy per day} = 30,981$/365 \text{ days}\]
\[= 84.88$/ \text{day}\]

Number of days required to achieve the payback = \(\frac{12000 \text{ $ investment}}{84.88$/ \text{day}}\)
\[= 141.38 \text{ days (≈ 4.5 month)}\]

*Payback generated by switching from volumetric to massic technologies*

\[\text{SF}_6 \text{ economy per year} = 61,962$ - 12,397$\]
\[= 49,565$/ \text{year}\]

\[\text{SF}_6 \text{ economy per day} = 49,565$/365 \text{ days}\]
\[= 135.79$/ \text{day}\]

Number of days required to achieve the payback = \(\frac{25000 \text{ $ investment}}{135.79$/ \text{day}}\)
\[= 184.11 \text{ days (≈ 6.2 month)}\]