The Impact of Carrier Gas Selection on SO2 and SF6 Melt Protection in a Simulated Magnesium Dosing Furnace

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A Change to $\text{SO}_2$ – WHY?

- Reduced corrosion of furnace steel crucibles
  - $\text{SF}_6$ at 0.2-0.3% in $\text{N}_2$ attacks crucible
  - $\text{SF}_6$ at less than 0.10 – 0.15% leads to excessive magnesium oxidation
- Fewer rejected/returned castings due to MgO inclusions
- Reduced environmental impact – an issue with customers – a growing issue in China.
Fewer Rejected/Returned Parts

Areas of turbulence and Oxide Accumulation in the Rauch Dosing System

N₂ – SF₆

Areas of Turbulence & Oxide

Dosing Furnace

Melt Chamber

Pump Chamber

Die Cast Machine
Fewer Rejected/Returned Parts

- Oxides accumulate in pump and transfer pipe of Rauch dosing units using SF₆-N₂
- These periodically wash into shot chamber and parts producing internal Hard spots!
Reduced Environmental Impact
- an issue with customers - a growing issue for China!

- \( \text{SF}_6 \) is most potent Greenhouse gas known today.
- 1Kg of \( \text{SF}_6 \) = 24 TONS of \( \text{CO}_2 \).
Why Change to $\text{SO}_2$?

- Reduced costs
  - $\text{SO}_2$ has been estimated to be about $1/10$ the cost of $\text{SF}_6$ for the gas alone.
  - Reduced crucible replacement costs
  - Reduced losses due to returned/rejected parts
  - Reduced risk of losing customers due to quality problems
IMA Program for SF6 Alternatives

- 1999 - IMA initiated a development program seeking alternatives to SF$_6$ due to environmental impact.
- 2000 – 2003 The program at SINTEF, a Norwegian Research Institute, evaluated other fluorine containing compounds.
- SO$_2$ was not considered due to historical issues associated with poor usage practices.
- N$_2$ was not considered as a carrier gas because the researchers & advisors felt it produced inferior surface films with SF$_6$.
IMA Program for SF\textsubscript{6} Alternatives

- 2004 – Summary presentation* was made which identified three compounds as good alternatives to SF\textsubscript{6} based on a commercial scale trial in Porsgrunn, Norway
  - **AM-Cover** – F134A, the std. refrigerant for auto Air Conditioners.
  - **HFE7100** – a fluorinated ether used for electronics degreasing. (a 3M product)
  - **Novec 612** – a fluoroketone used as a replacement for Halon in fire extinguishers for electrical equipment. (a 3M product)

IMA Commercial Scale Trial -
NH, Porsgrunn, Norway/September 2 – 13, 2002

• **Gases** – SF6 & AM-Cover/F-134a; HFE 7100; Novec 612 @ 500ppm in *dry air* or *CO2* +5% air

• **Gas Flows** - varied 2.5, 5, 10, & 20 nl/min

• **Furnace** – 500 kg “bath tub”, 0.5 m² surface area

• **Melts** – AM50 and ZE41/RZ5 @ 680 & 710 °C

• **Performance** - Monitored by Video & Digital Image

• **Melt surface** – quiescent, no turbulence present

➔ The trials demonstrated the benefit of CO2 blends
Freon 134a - different carriers; AM50 @ 710 °C

- Air – 1200 nl/hr
  Not Acceptable!

- CO₂+ 5% Air – 300 nl/hr
  Acceptable!
SO2 + dry air, N2, or CO2

- SO₂ (0.8 – 2%) has been successfully used with N₂ or dry air in Rauch units in Europe for years.
- But - can the protection achieved with SO₂ be improved with the use of CO₂ as with SF₆, & the alternative fluorocarbons?
- Better melt quality may be obtained without corrosion and with lower SO₂ levels.
Test Set-Up With Pumping
Test Set-Up With Pump & Mixer

• Rauch Gas Mixing Unit for SO2 + N2/Air & CO2

• The mixed gas is analyzed by Varian Portable Gas Chromatograph
Carrier Gases & Blends Tested

- 100% Nitrogen
- 75% Nitrogen + 25% Carbon Dioxide
- 50% Nitrogen + 50% Carbon Dioxide
- 90% Carbon Dioxide + 10% “Dry” Air
- 50% Carbon Dioxide + 50% Dry Air
- 100% Dry Air (less than -30 C dew point)
Test Procedure

- Molten AZ91D @ 690° C.
- Clean melt surface, T-pipe, & Lid.
- Equilibrate test atmosphere for minimum of 10 minutes prior to initiation.
- Pump metal for 1 minute every 5 minutes.
- Repeat for a period of 1 hour.
- Observe melt surface protection and oxide build-up on lid bottom and T-pipe.
Initial SF₆ Trials Without Pumping

10 Min (left) + 1 hour (right) exposure to est. 0.06% SF₆ + N₂ @ 800 Nl/hr

Temp = 690 deg C

Very Protective - BUT!
0.2% SF$_6$ in 100% N$_2$ @ 800 Nl/Hr. with pumping!

- Surface after one hour test.
- Heavy oxide Build-up on lid & melt surface
- Most of surface protected
- Smoke generated during run
0.1% $\text{SF}_6$ in 100% $\text{N}_2$ @ 800 Nl/Hr.

- Surface burning after one hour test.
- Note heavy oxide build-up on lid.
- Smoke generated during run.
0.1% SF$_6$ in 100% N$_2$ @ 800 NL/Hr.

Smoke just before 12$^{th}$ pump

Smoke just after 12$^{th}$ pump
0.1% SF₆ in 100% N₂ @ 800 Nl/Hr.

Heavy oxide build-up on T-pipe and covers!
Taiyuan Dosing Pump - Production

- Oxides in pump and transfer pipe of Rauch dosing units, which periodically wash into shot chamber and parts!
With $\text{CO}_2$ much different result -
0.1% $\text{SF}_6$ in 25% $\text{CO}_2 + 75\% \text{N}_2$

- Excellent surface protection
- No oxide build-up on lid or T-pipe
- Note ball of skins that has been pushed up

Surface after one hour test period.
With CO$_2$ much different result -

0.1% SF$_6$ in 25% CO$_2$ + 75% N$_2$

No smoke just before 12$^{th}$ pump

No smoke just after 12$^{th}$ pump
With CO$_2$ much different result -
0.1% SF$_6$ in 25% CO$_2$ + 75% N$_2$

No oxide build-up after one hour run
Different result – even at lower SF6
0.06% SF₆ in 25% CO₂ + 75%N₂

- Excellent surface protection
- No smoke or oxide build-ups
- Note skin ball that has been pushed up

Surface after one hour test period.
2% SO₂ in 100% N₂ – hour with pumping

- Performance better than 0.2% SF6 in 100% N₂
- Still much oxide on cover and T-pipe & smoke
With CO$_2$ again different result - 1% SO$_2$ in 50% CO$_2$ + 50% N$_2$

- Little or no oxide build in pipe & on covers
- Melt surf shiny oxide but oxide in large ball
Protective even to low levels of \( \text{SO}_2 \) -
0.05% \( \text{SO}_2 \) in 50% \( \text{CO}_2 \) + 50%\( \text{N}_2 \)

- At 0.05% no smoke
- Little or not oxide build
- Thin oxide skin on melt
- Oxide in smaller ball form
SF₆ in 80% CO₂ + 20% “Dry” Air

@ 800 NL/Hr- 1hour pumping
Why the difference?

- Why the difference in 100% N2, with and without stirring?
- Why the difference in behavior with stirring between 100% N2 & N2+CO2 or dAir?
Mag Surface in 100% N2

- N2 does not react at normal melt temperature
- Leaked Air forms Oxide film
- But film is full of holes
  Mg vapor escapes and reacts with leaked air = SMOKE/FIRE

Mg metal -- O2 → SMOKE
Oxide -- O2 → FIRE
In 100% N₂ + SF₆/SO₂

For quiescent melt -

- Addition of SF₆ or SO₂ acts to fill holes in Oxide
- No burning!
- No Smoke!

Mg metal -->

Oxide --

+ SF₆, + SO₂ → MgF₂/MgS--
In 100% N₂ + SF₆/SO₂

With mechanical agitation

• The film is torn and broken

• Leaked O₂ is not sufficient to repair and prevent Mg vapor escaping

• Smoke and/or FIRE result

Mg vapor + O₂ = Smoke

Mg metal -- O₂
Oxide -- MgF₂/MgS-- O₂

MgO smoke
MgO and fire!!
Test Furnace + Rauch Pump
- with 100% N2: Particulate oxide & Smoke

N₂ + SF₆/SO₂

Escaping Mg vapor encounters O₂ in gases above melt -> smoke particles

Particulate Oxide forms on moving surface sinks, then floats in mass

Molten Mag
Test Furnace + Rauch Pump
- elastic film with CO2 or Air – No Smoke

N₂/CO₂ +SF₆/SO₂

Continuous elastic oxide skin sinks, then floats in mass

Molten Mag
Conclusions

- SF$_6$, or SO$_2$ in N$_2$ protect a quiescent melt surface to very low levels of 0.03 – 0.06% of either agent.
- With the turbulence of a cycled dosing pump however the protection was less than adequate with both SF$_6$ and SO$_2$, even at normally effective concentrations of 0.2% and 2%, respectively.
- The protective film on the surface of the quiescent melts must be the result of leaked air in the dosing furnace.
Conclusions

- When CO$_2$ blends with N$_2$ or dry air are employed with the agents smoke and oxide deposits in the vapor space are eliminated with both SF$_6$ and SO$_2$ to very low levels of each.

- With CO2 blends, while the smoke & oxide deposits in the vapor space are eliminated, the oxide is still present but contained in a ball on the melt surface.
Conclusions

- It was observed that as the concentration of the agent was decreased the volume of oxides accumulated in the ball decreased as well. This is consistent with observations of thickened skins at higher concentrations of inhibitors in the cover gas.
- These observations suggest that SO2 can be as effective as SF6 for melt protection of magnesium.
- With the use of CO2 blends, significantly lower concentrations of the agents are effective. Reducing the thickness or volume of oxide skins produced.
The End

Thank You!