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

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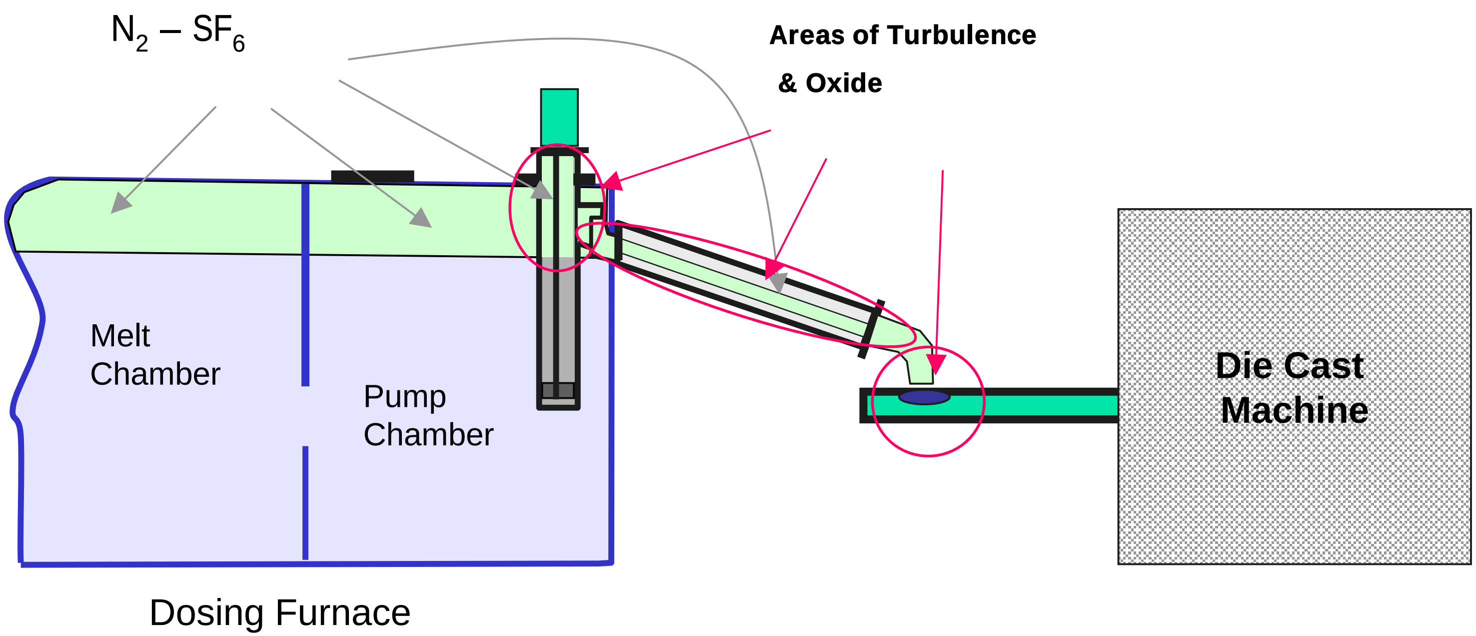
A Change to SO_2 – WHY?

- Reduced corrosion of furnace steel crucibles
  - SF6 at 0.2-0.3% in N_2 attacks crucible
  - SF6 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



Fewer Rejected/Returned Parts

- Oxides accumulate in pump and transfer pipe of Rauch dosing units using SF_6-N_2
- These periodically wash into shot chamber and parts producing internal Hard spots!

Reduced Environmental Impact

– an issue with customers – a growing issue for China!

- SF_6 is most potent Greenhouse gas known today.
- **1Kg** of SF_6 = ***<u>24 TONS of CO_2.</u>***

Why Change to SO_2?

- Reduced costs
  - SO_2 has been estimated to be about 1/10 the cost of 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.
- SO2 was not considered due to historical issues associated with poor usage practices.
- N2 was not considered as a carrier gas because the researchers & advisors felt it produced inferior surface films with SF_6

IMA Program for SF_6 Alternatives

- 2004 – Summary presentation* was made which identified three compounds as good alternatives to SF_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)

* G. Trannell, et al., Proceedings of the IMA, New Orleans, 2004.

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 m^2 surface area
- ***Melts*** – AM50 and ZE41/RZ5 @ 680 & 710 ^oC
- ***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

AM50 - HFC 134a / Air - 20 l/min - 710 ºC

Air – 1200 nl/hr

Not Acceptable!

AM50 - HFC 134a / CO_2 + Air - 5 l/min - 710 ºC

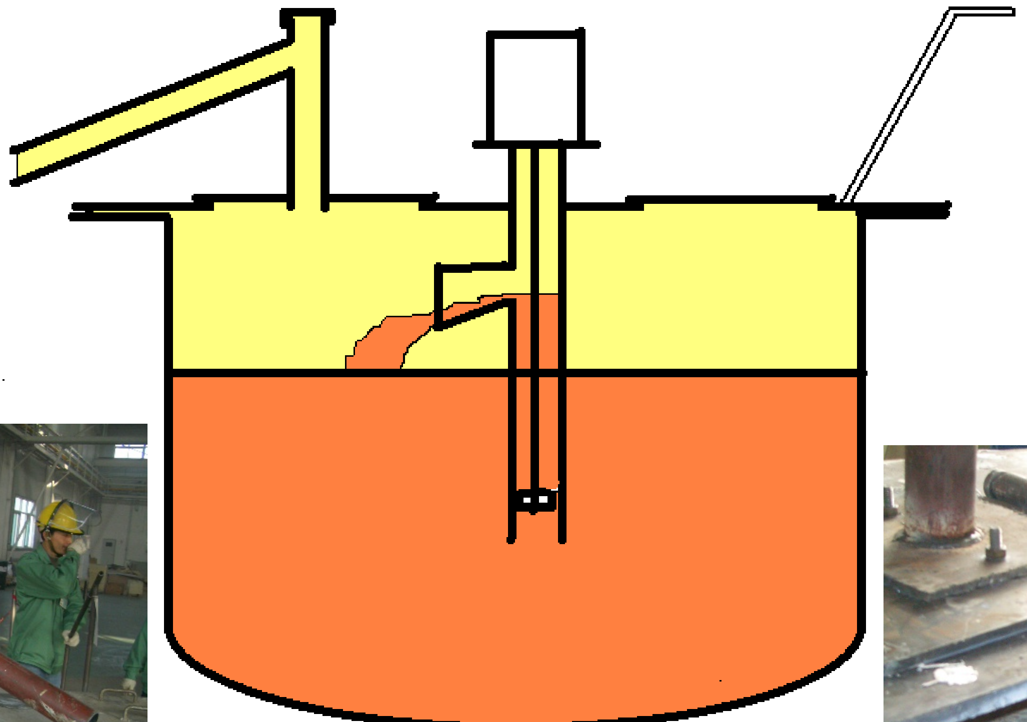
CO_2+ 5% Air – 300 nl/hr

Acceptable!

SO2 + dry air, N2, or CO2

- **SO_2 (0.8 – 2%) has been successfully used with N_2 or dry air in Rauch units in Europe for years.**
- **But - can the protection achieved with SO_2 be improved with the use of CO_2 as with SF6, & the alternative fluorocarbons?**
- **Better melt quality may be obtained without corrosion and with lower SO_2 levels.**

Test Set-Up With Pumping



Test Set-Up With Pump & Mixer

- Rauch Gas Mixing Unit for SO_2 + N_2/Air & CO_2

- 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 SF_6 Trials Without Pumping

Photo # 5576

Photo # 5579

- 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% SF_6 in 100% 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 12th pump

Smoke just after 12th pump

0.1% SF_6 in 100% N_2 @ 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 CO_2 much different result - 0.1% SF_6 in 25% CO_2 + 75%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

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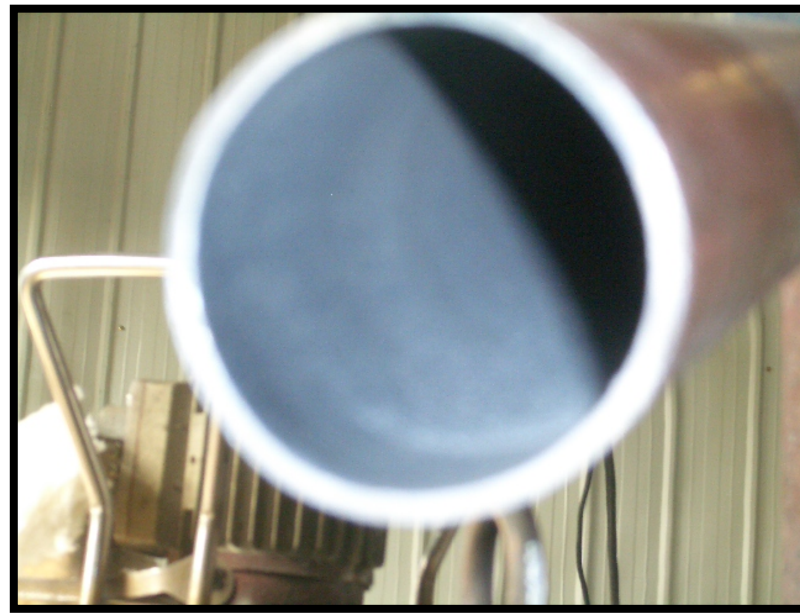


No oxide build-up after one hour run

Different result – even at lower SF6

0.06% SF_6 in 25% CO_2 + 75%N_2

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

Surface after one hour test period.

$2\%SO_2$ in $100\%N_2$ – hour with pumping

- Performance better than 0.2% SF6 in 100% N_2
- Still much oxide on cover and T-pipe & smoke

With CO_2 again different result -
1% SO2 in 50% CO_2 + 50%N_2

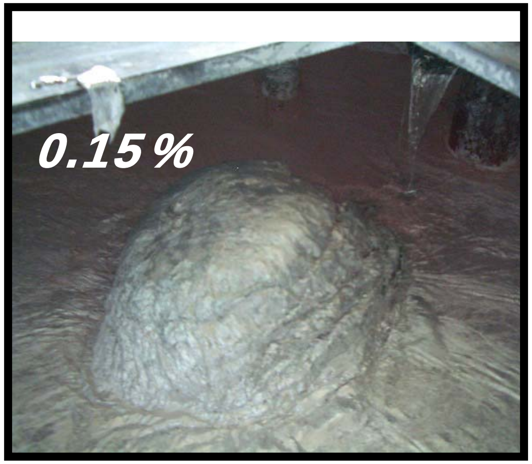
- Little or no oxide build in pipe & on covers
- Melt surf shiny oxide but oxide in large ball

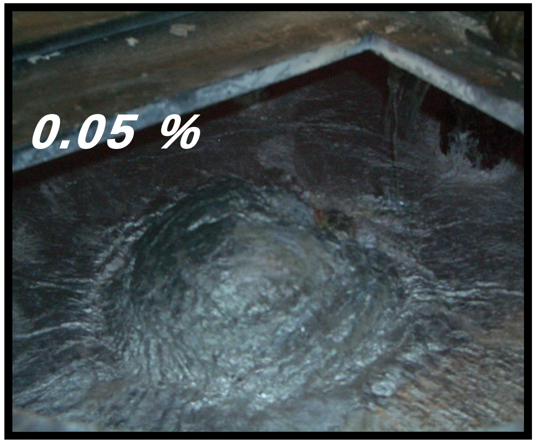
Protective even to low levels of SO_2 - 0.05% SO2 in 50% CO_2 + 50%N_2

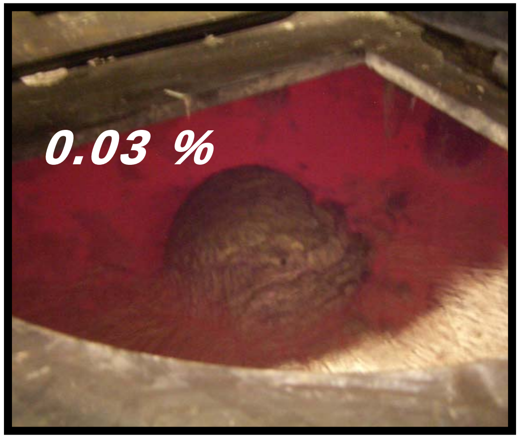
- At 0.05% no smoke
- Little or not oxide build
- Thin oxide skin on melt
- Oxide in smaller ball form

SF_6 in 80% CO_2 + 20% "Dry" Air

@ 800 Nl/Hr- 1hour pumping





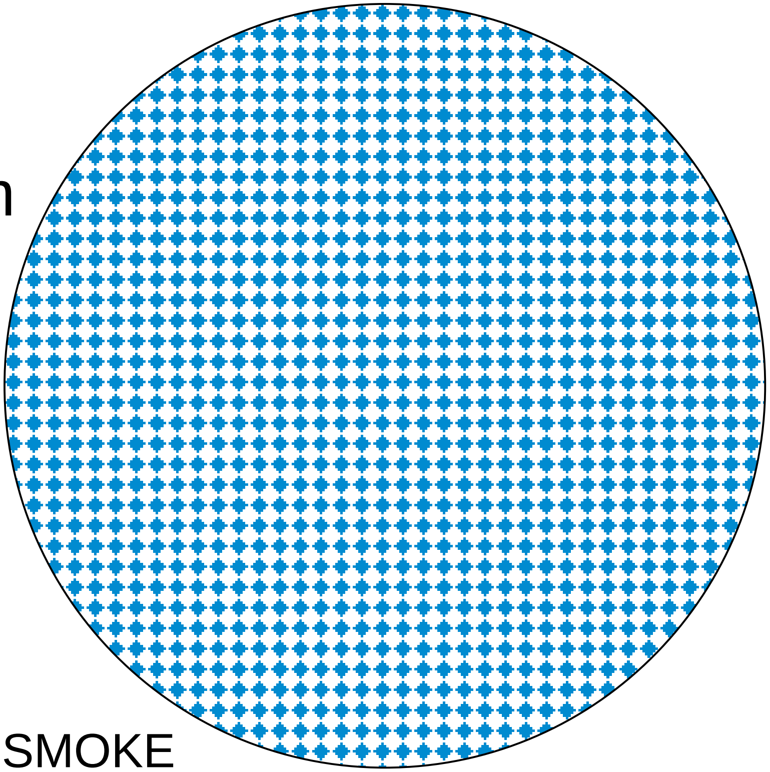


Why the difference?

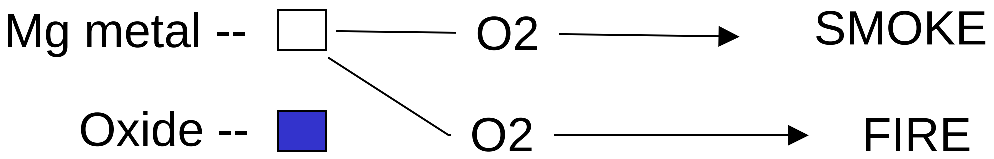
- Why the difference in 100% N_2, with and with out stirring?
- Why the difference in behavior with stirring between 100% N_2 & N_2+CO_2 or dAir?

Mag Surface in 100% N_2

- N_2 does not react at normal melt temperature
- Leaked Air forms Oxide film



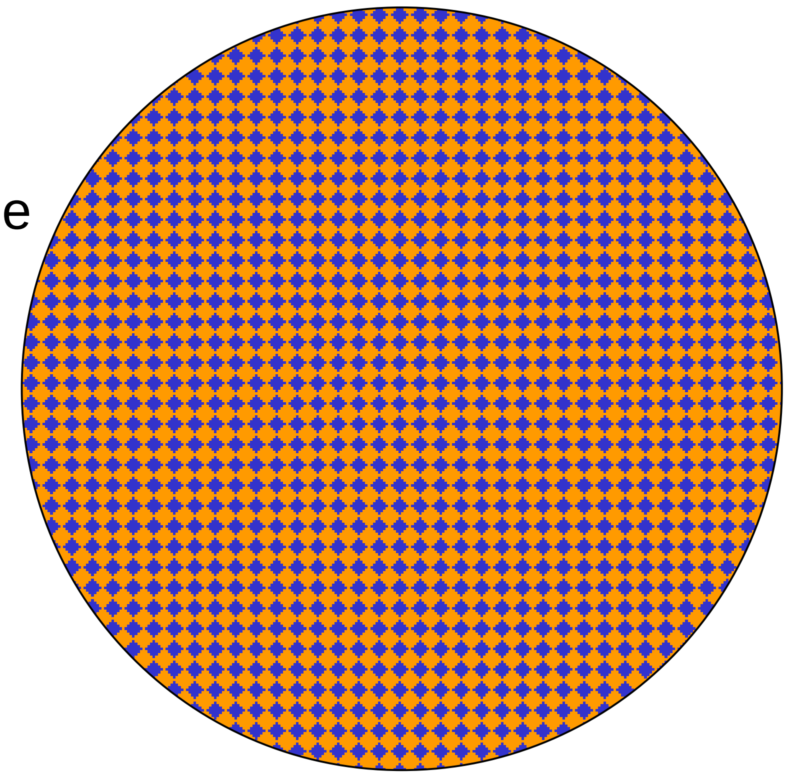
- But film is full of holes Mg vapor escapes and reacts with leaked air = SMOKE/FIRE



In 100% N_2 + SF_6/SO_2

For quiescent melt -

- Addition of SF_6 or SO_2 acts to fill holes in Oxide
- No burning!
- No Smoke!



Mg metal --

Oxide --

+ $SF_{6,}$

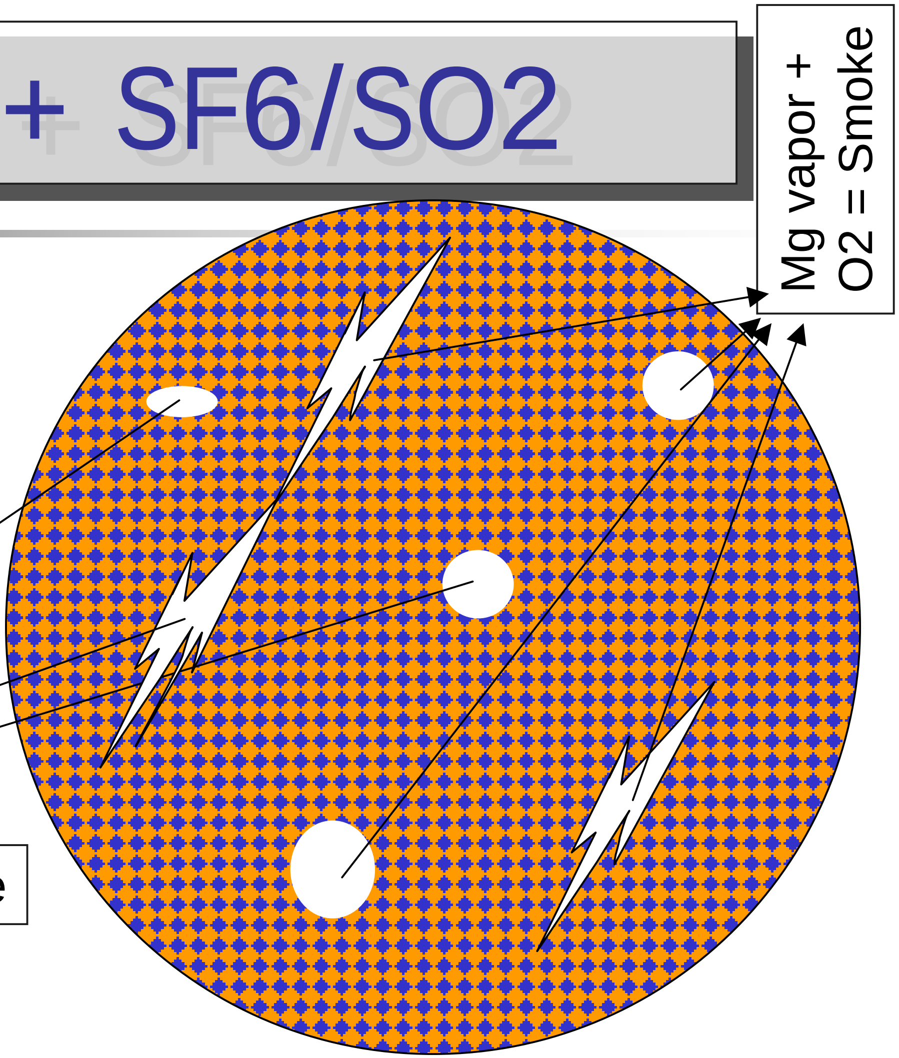
+ SO_2

MgF2/MgS--

In 100% N_2 + SF_6/SO_2

With mechanical agitation

- The film is torn and broken
- Leaked O_2 is not sufficient to to repair and prevent Mg vapor escaping
- Smoke and/or FIRE result



Mg vapor + O_2 = Smoke

Mg metal --

Oxide --

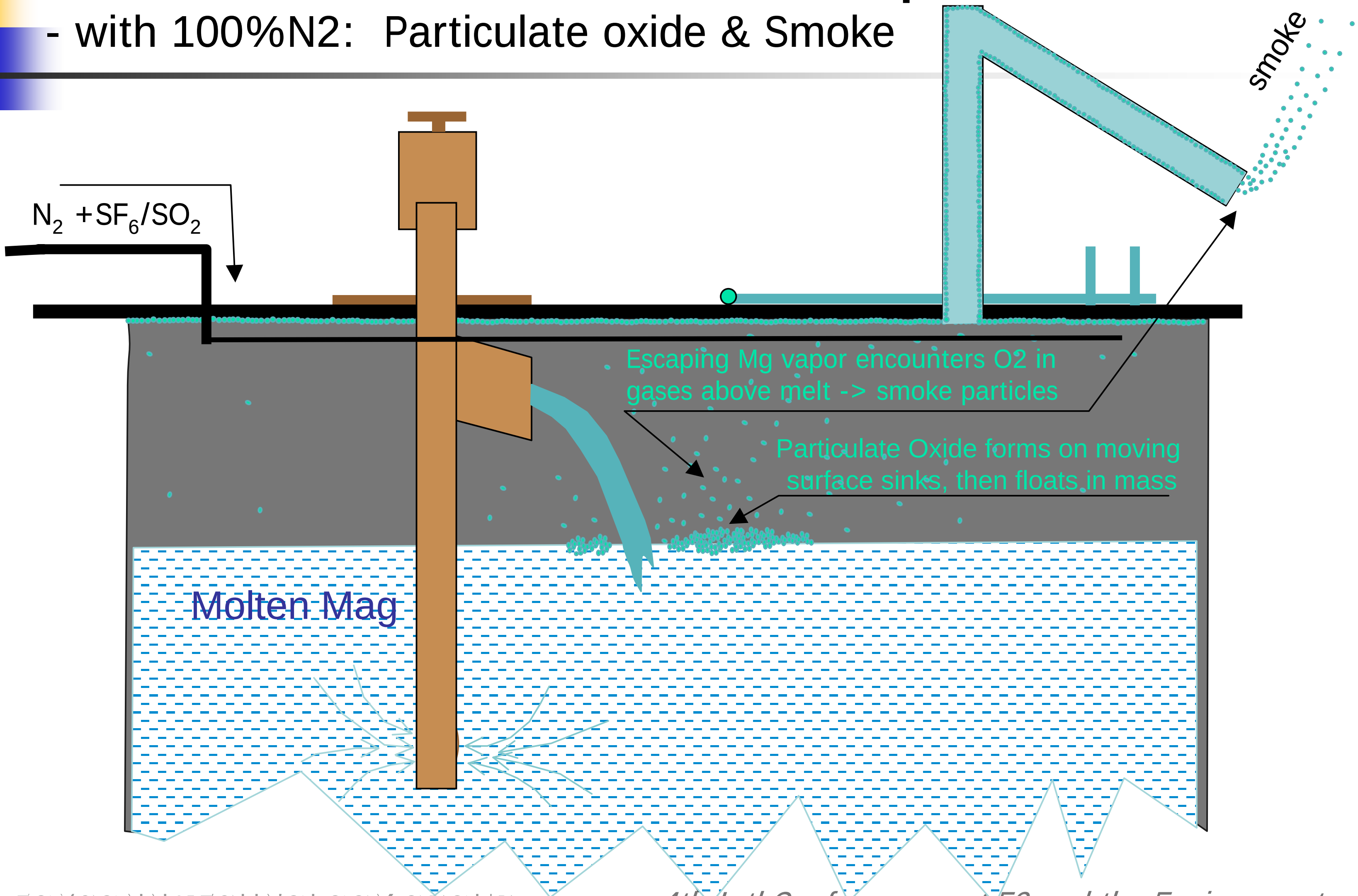
MgF_2/MgS--

O_2 → MgO smoke

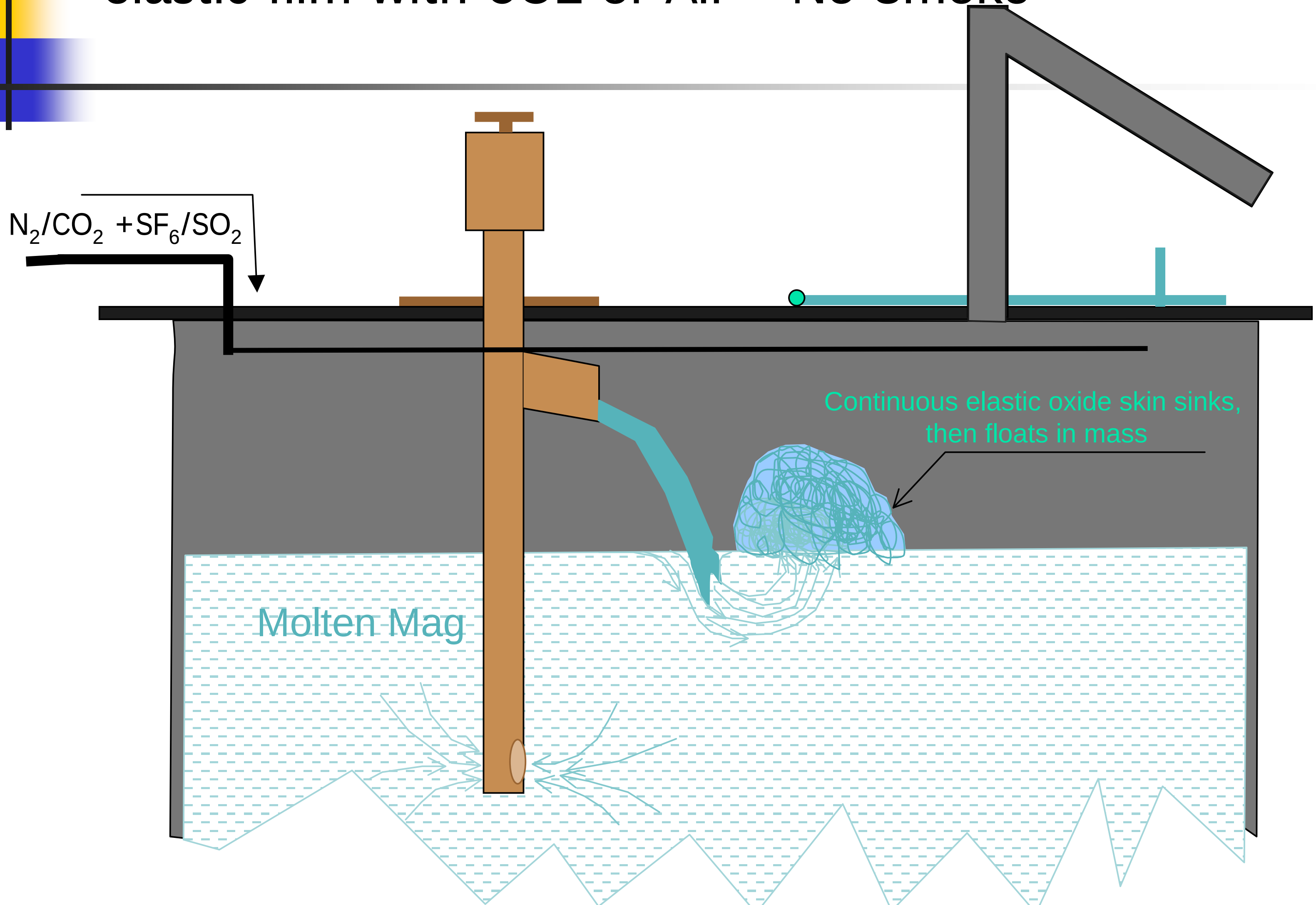
O_2 → MgO and fire!!

Test Furnace + Rauch Pump

- with 100%N2: Particulate oxide & Smoke



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



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!