3M™ Novec™ 612 Magnesium Protection Fluid

Dean S. Milbrath

3M Industrial Chemicals, EMMD

International Conference of SF_6 and the Environment

December 1-3, 2004

- **How much SF_6 is lost?**
- **How is Novec™612 different from SF_6?**
- **How do you use Novec™ 612 in casting operations**
  - **Carrier gas, mixing**
  - **Concentrations, Flow rates**
  - **Gas distribution**
- **How expensive is it use Novec™ 612 as a cover gas?**

SF_6 Emissions

Open Casting

Generally 1-6% SF_6 at high flow rates used

>95% emitted unchanged

- Open casting (not contained)
- Large thermal air currents (over 900°F temp difference)
- Minimal hot surface for reaction
- Emission depend upon gas distribution, alloy, and cooling efficiencies

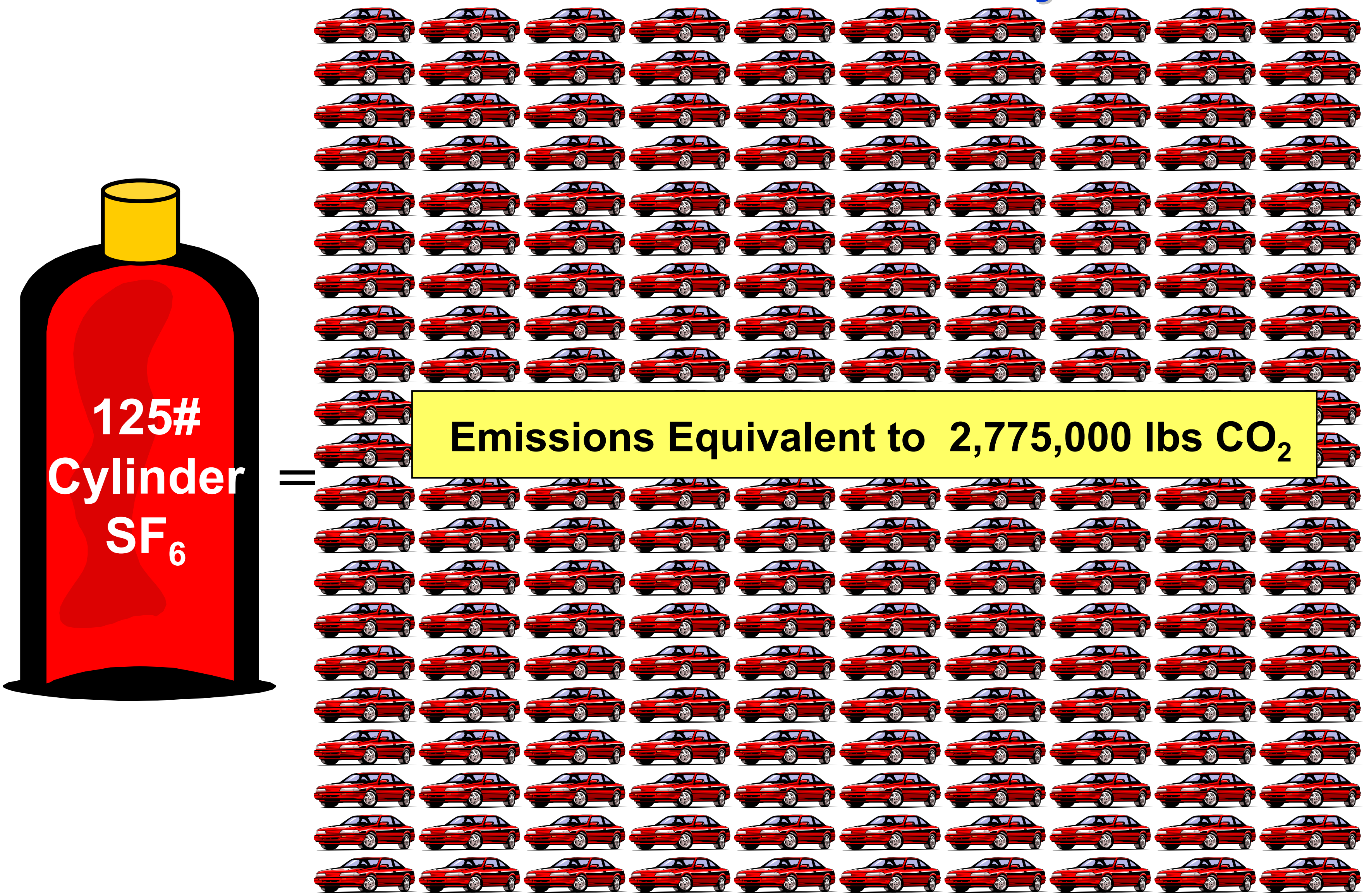
Melt Furnaces

Generally 0.2-1.0% SF_6 at low flow rates used

About 90% emitted unchanged

- Contained atmosphere, longer contact with hot surfaces
- Emissions depend upon equipment, alloy and process operations

Greenhouse Gas Emissions from 1 Cylinder of SF_6



Annual CO_2 emissions from 263 U.S. passenger cars

Requirements for an SF_6 Replacement Cover Gas

- ✓ Protect molten pure and alloyed Mg
- ✓ Low GWP and no ODP
- ✓ Safe, nontoxic at RT
- ✓ Nonflammable
- ✓ Minimal (or manageable) toxic thermal decomposition products
- ✓ Cheaper than SF_6

Global Warming Potentials

Compound	Lifetime (yrs)	GWP (100 Yr ITH)	
CO_2	100-150	1	
SF_6	3200	22,200	
C_3F_8	2600	8,600	PFCs
C_4F_{10}	2600	8,600	PFCs
C_6F_{14}	3200	9,000	PFCs
CF_3CH_2F	13.6	1,600	HFCs
CF_3CHF_2	32.6	3,800	HFCs
CHF_3	243	14,800	HFCs
$C_3F_7C(O)C_2F_5$	**0.014**	**~1**	**FKs**

Novec™ 612 Comparison

Environmental Properties	SF_6	SO_2	HFC-134a	Novec™ 612 Agent
Ozone depletion Potential (ODP)	0	0	0	0
Atmospheric Lifetime (years)	3200		140	0.014
Global Warming Potential (GWP)	22,200	1	1300	1

Greenhouse Gas Emissions for Novec™ 612

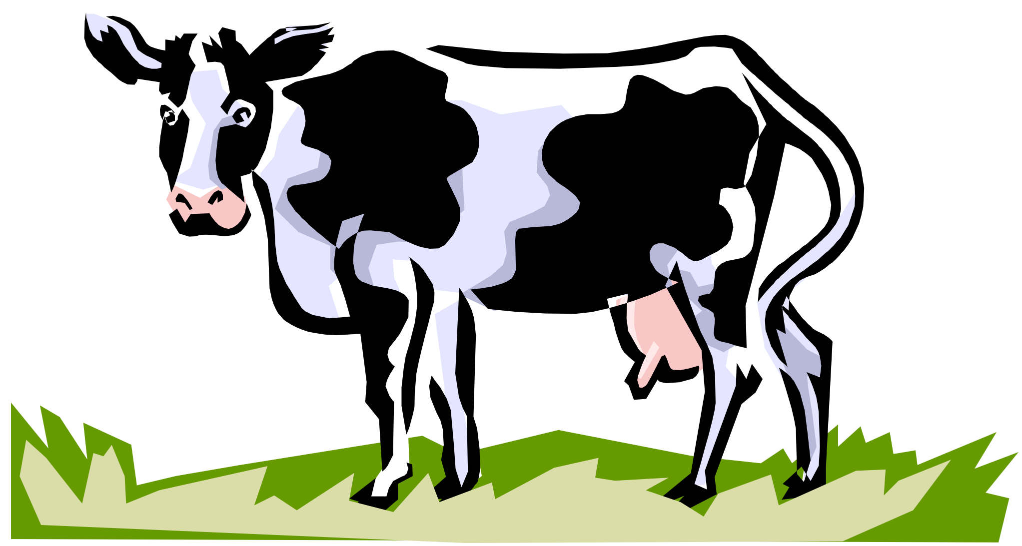
Equivalent to a 125 Pound Cylinder of SF_6

0.003 Car-Years or

1 Cow-Day Equivalent

Equivalent
Novec™
612

=



Fluorinated Ketone Physical and Environmental, Safety and Health Properties

Physical Properties	
Boiling Point °C	49
Freezing Point °C	-108
Viscosity, liquid @ 20°C, cSt	0.042
Vapor Pressure @ 20°C, kPa	32.6
Gas Phase Thermal Stability	<575 C
Gas Density @ 80°C - 1 Atm, g/mL	0.011

EHS Properties	
Atmospheric lifetime, days	<10
Global Warming Poteintial	1
Flash Point	None
PEL, ppmV	150
Acute LC50, ppmV	>100,000

History of Novec 612 Agent

- Fluoroketone chemistry in use in other large scale applications
- Safety and environmental sustainability established
- Mg cover gas development started in late 2000
- Studied thermal degradation, reactions with Mg, and formulation of cover gases
- Numerous commercial trials in open casting and die casting equipment
- Novec™ 612 Fluid is an effective cover gas agent

Commercial Trials

- Open casting: >150 mTons of pure and alloyed Mg cast
- Tested on hot and cold chamber die casting cells
- Limited sand casting
- Pure, AM50, AM60, AZ91, WE-42, RZ-5, AJ-52, AJ-62, Mg-Ca and Mg-Sr alloys cast
- Tests done in US, Canada, Germany, Austria, Norway, and Japan

Basics of Using Novec™612 Cover Gases

- Cover Gas Formulation
- Cover Gas Distribution
- Equipment and process variation
- Dynamic flow control
- Process Economics

Cover Gas Formulation

Novec™ 612 cover gas process window is smaller than SF_6

Protection/economics depend upon carrier gas used

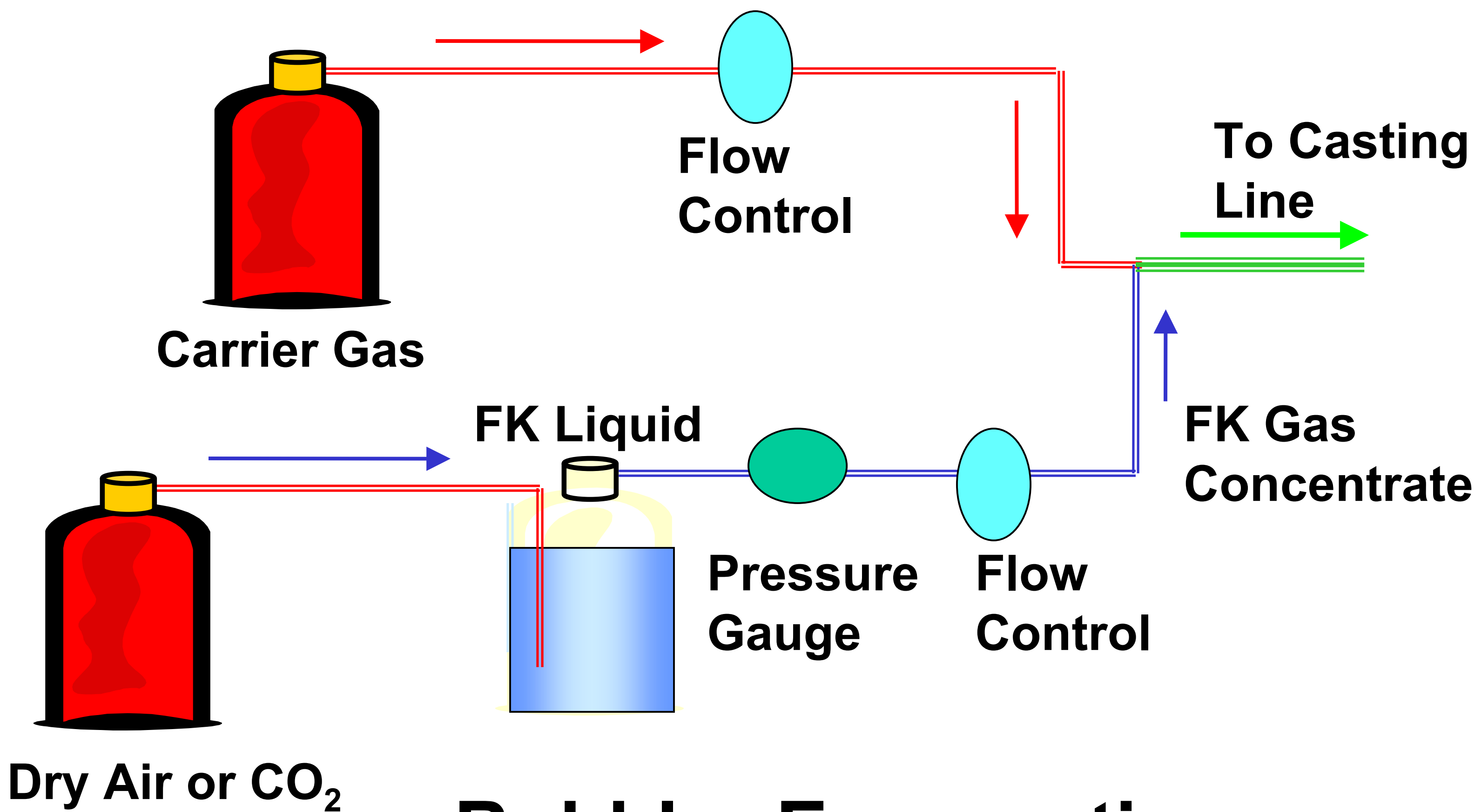
- **CO_2 Carrier gas with 5-20% dry air**
  - **Nitrogen/5-20% dry air also works**
    [Higher 612 consumption and HF emission]
  - **Also used in up to 50:50 CO_2/dry air**
    Higher HF emission and 612 use rates
  - **100% Dry air carrier is <u>not recommended</u>**

Cover Gas Preparation

Evaporate Novec™612 into a carrier gas stream

- Direct evaporation works, but requires precision pumps with computer controls
- Nippon Sanso system provides a concentrated Novec 612 in CO_2 stream
- Gas bubbler method is reliable with no moving parts

Liquid to Gas System to Generate Cover Gas System



Bubbler Evaporation

Cover Gas Formulation

- Novec™612 liquid is converted to a concentrated gas stream (similar to SF_6 cylinder output)
- Novec™612 Concentrate stream is then diluted to working concentrations
- Gas mixing equipment just like SF_6
  - Requires recalibration for 612
    - (about 1.25 denser than air)
- *Commercial units available [Contact 3M for details]*

Typical Novec™ 612 Cover Gas: Concentration/Flow Rates

- Open casting: Pure Mg, AM-50, AZ-91
- Concentration: 0.2 - 1.0% (in CO_2 w/10% dry air)
- Flow Rates: 50 to 180 SCFH
- Typical thermal dilution about 30-100 fold with thermal air currents
- Emitted gases: Novec 612 and CO with traces of HF and C_3F_8

Typical Novec™ 612 Cover Gas: Concentration/Flow Rates

Die Casting: AM-60, AZ-91

Concentration: 0.015 to 0.05% in CO_2 with 15% dry air or

0.03 to 0.075 % in N_2 with 15% dry air

Flow rate: 20 to 50 SLPM at idle conditions

Gases Emitted: Novec™ 612, CO, HF with traces of C_3F_8 and C_2F_6.

Gas Distribution: *Frying Pan Analogy*

Choices in adding oil to a frying pan

-Pour it on: Slow to spread evenly without mechanical assistance (High conc, low flow rate)

-Pour around the edge: better, but still slow (High conc, increased flow rate)

-Spray it on: Fast and efficient (Low conc, high flow rate)

More oil used when poured than when it is sprayed

Cover Gas Distribution

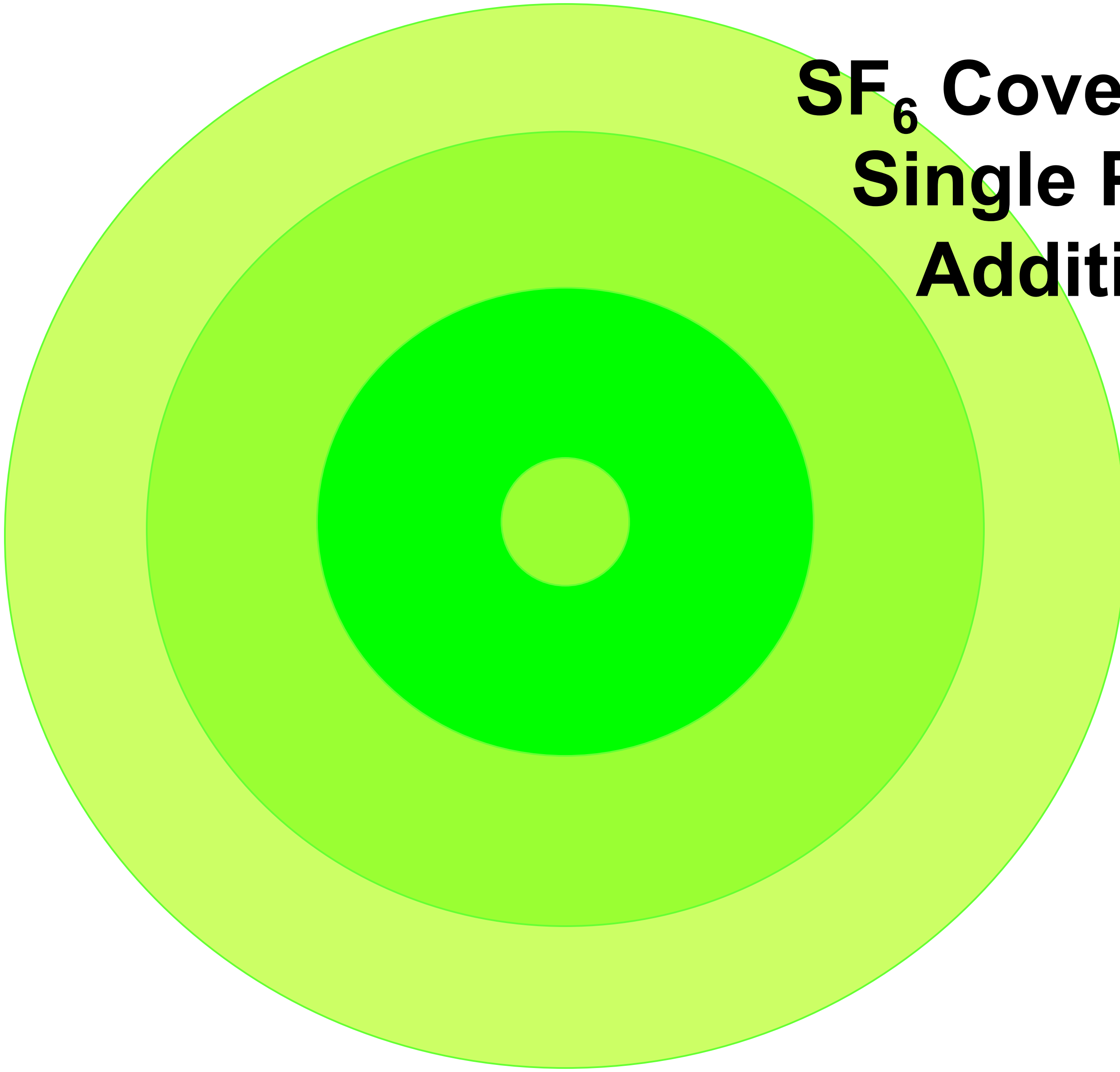
<u>Even</u> distribution of cover gas is very important for all SF_6 substitutes

– Much more reactive, limited carry

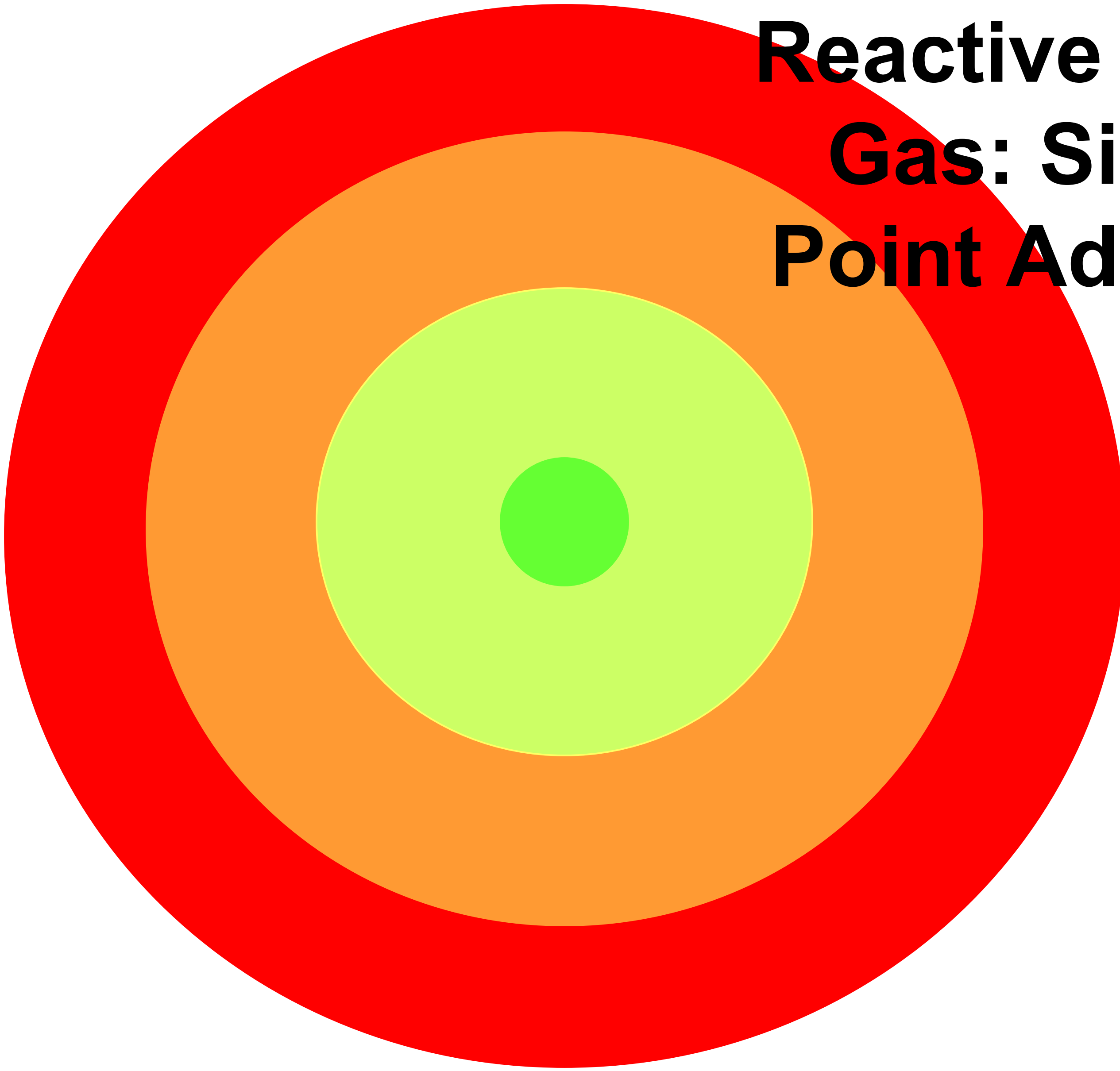
<u>Uneven</u> distribution requires high concentration and high flow rates

– Higher emissions of HF, carbonyl fluoride and trace PFCs

SF_6 Cover Gas: Single Point Addition



Reactive Cover Gas: Single Point Addition



Reactions of Novec™ 612

$$C_2F_5\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}C_3F_7 \xrightarrow[>575\ C]{-CO} {}^*C_2F_5 + {}^*C_3F_7$$

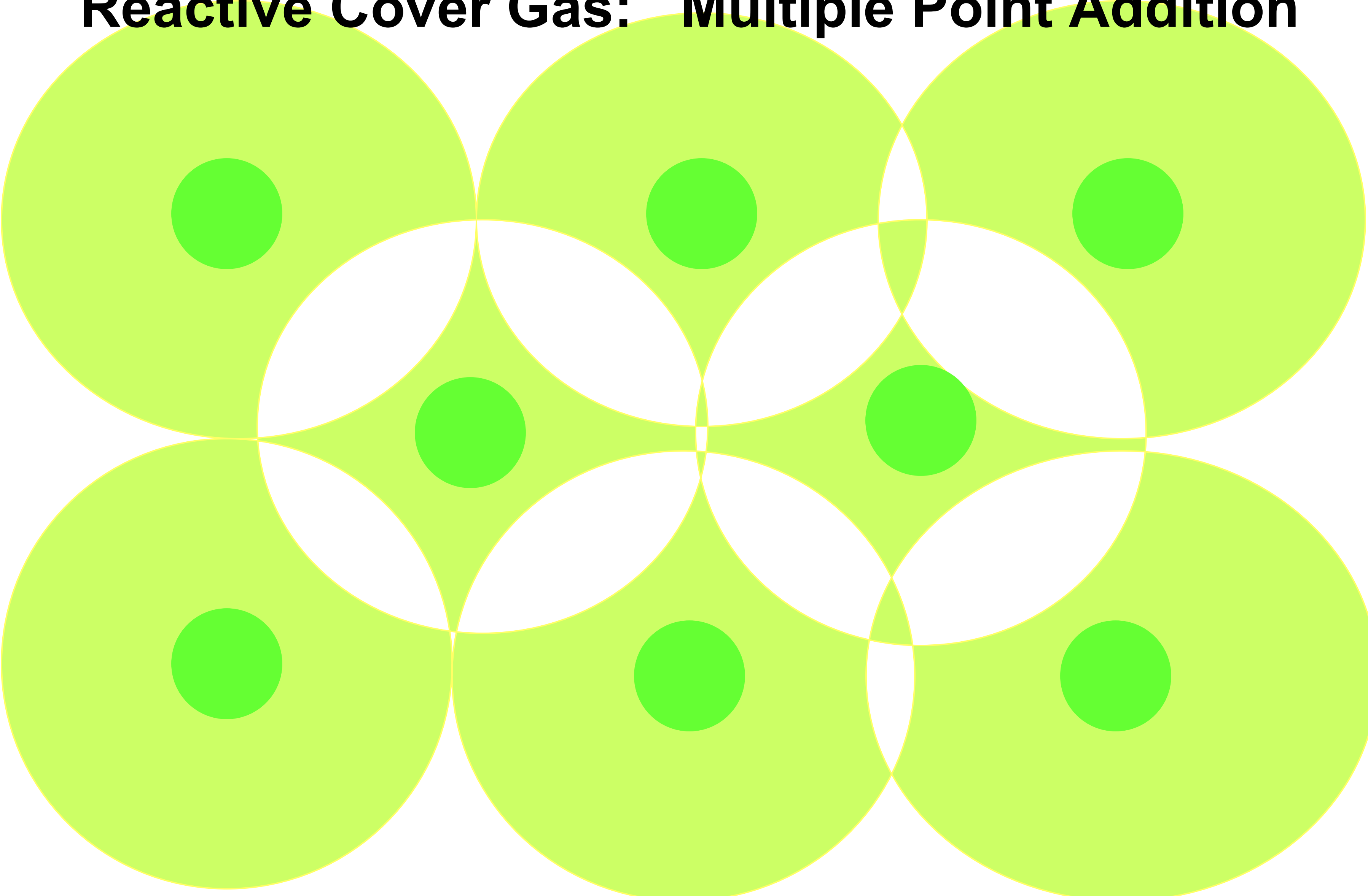
$${}^*C_2F_5 + {}^*C_3F_7 \xrightarrow{Mg^0} \text{“}MgF_2\text{”} + CO_2$$

$${}^*C_2F_5 + {}^*C_3F_7 \xrightarrow{O_2} CO_2 + HF + TFA$$

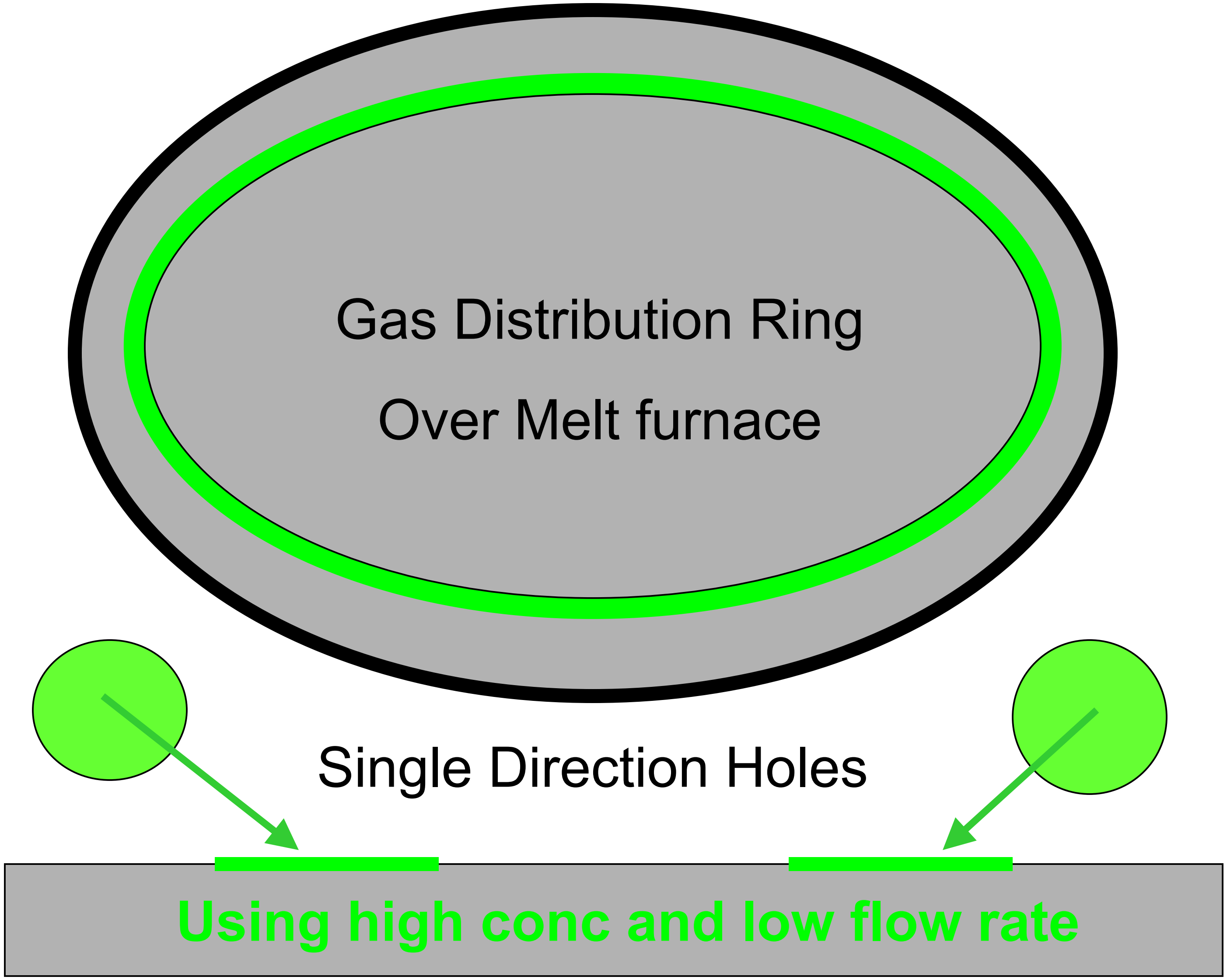
${}^*C_2F_5 + {}^*C_3F_7 \rightarrow$ ~~PFCs~~

${}^*C_2F_5 + {}^*C_3F_7 \rightarrow$ ~~PFCs + F-Olefins~~

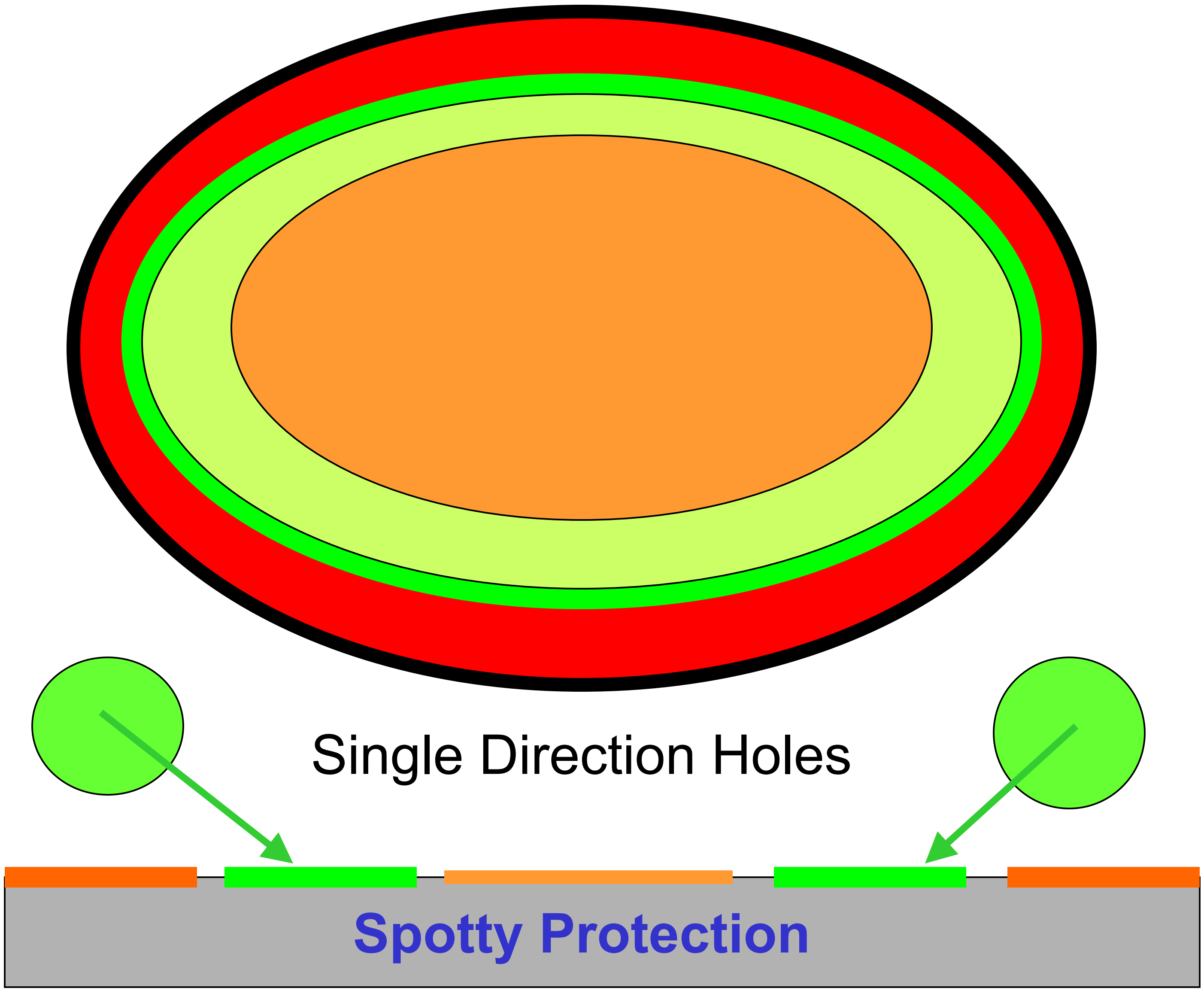
Reactive Cover Gas: Multiple Point Addition



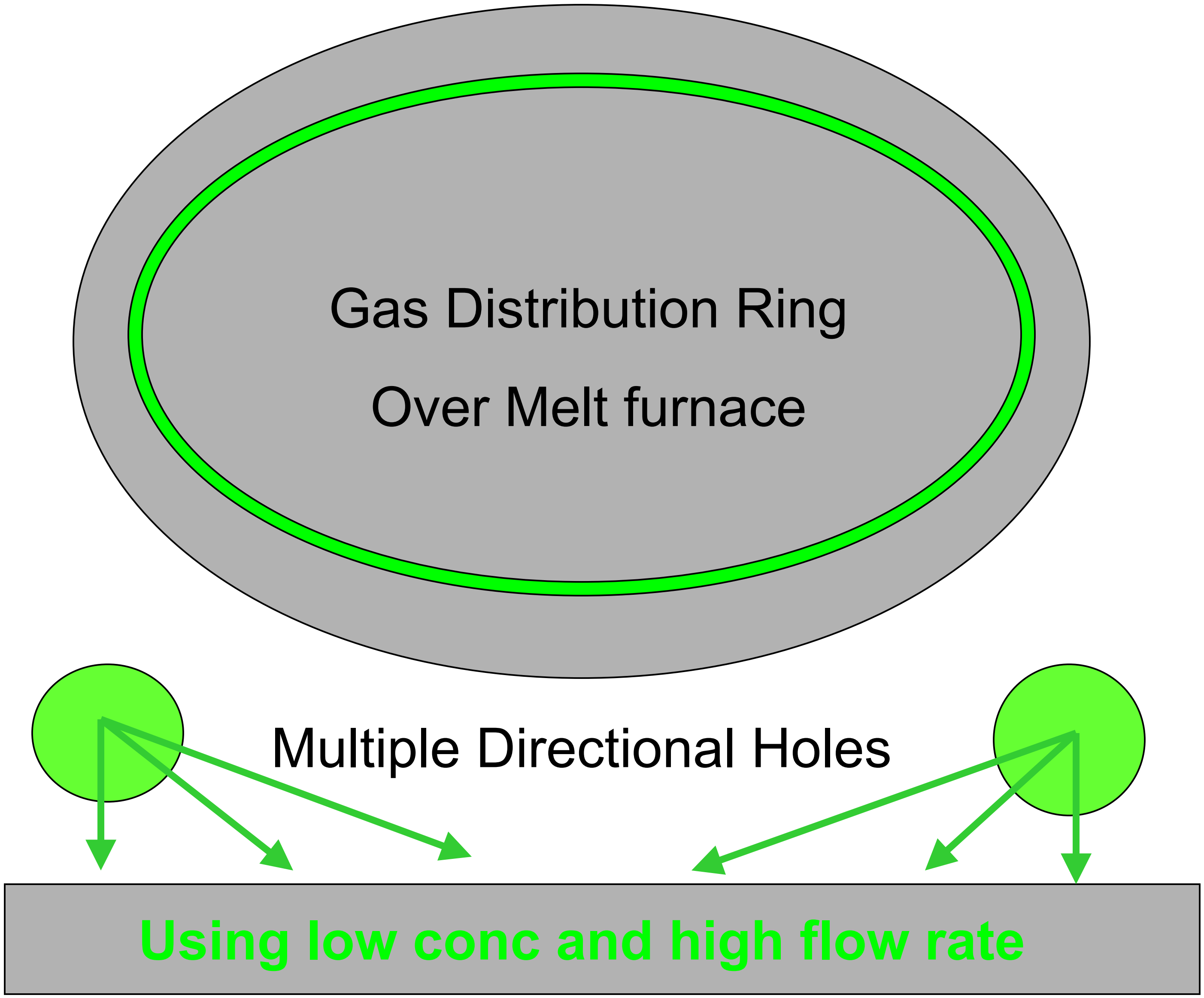
Ring Cover Gas Distribution over a Melt Furnace



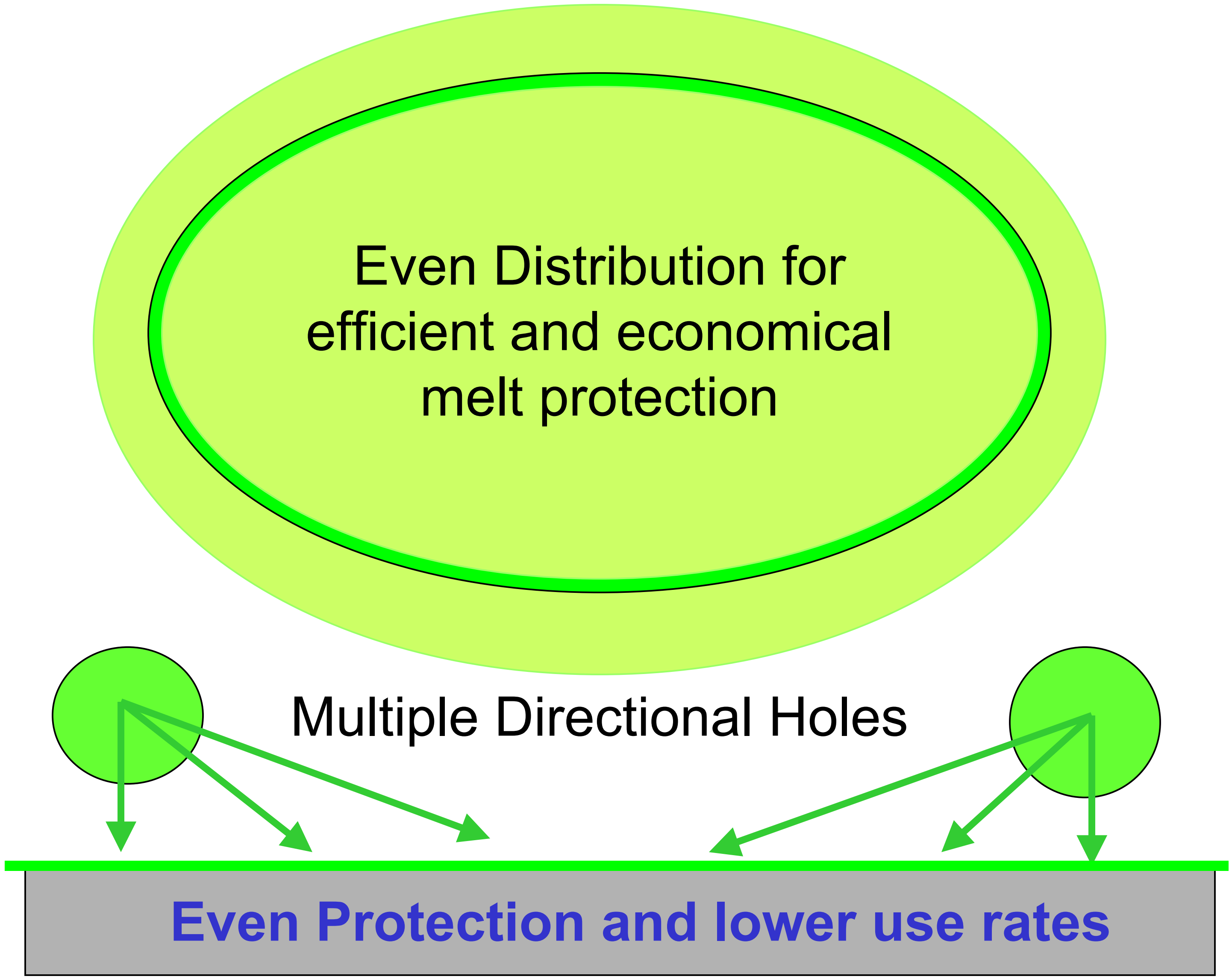
Ring Cover Gas Distribution over a Melt Furnace



Ring Cover Gas Distribution over a Melt Furnace



Ring Cover Gas Distribution over a Melt Furnace



Equipment/Process Variation

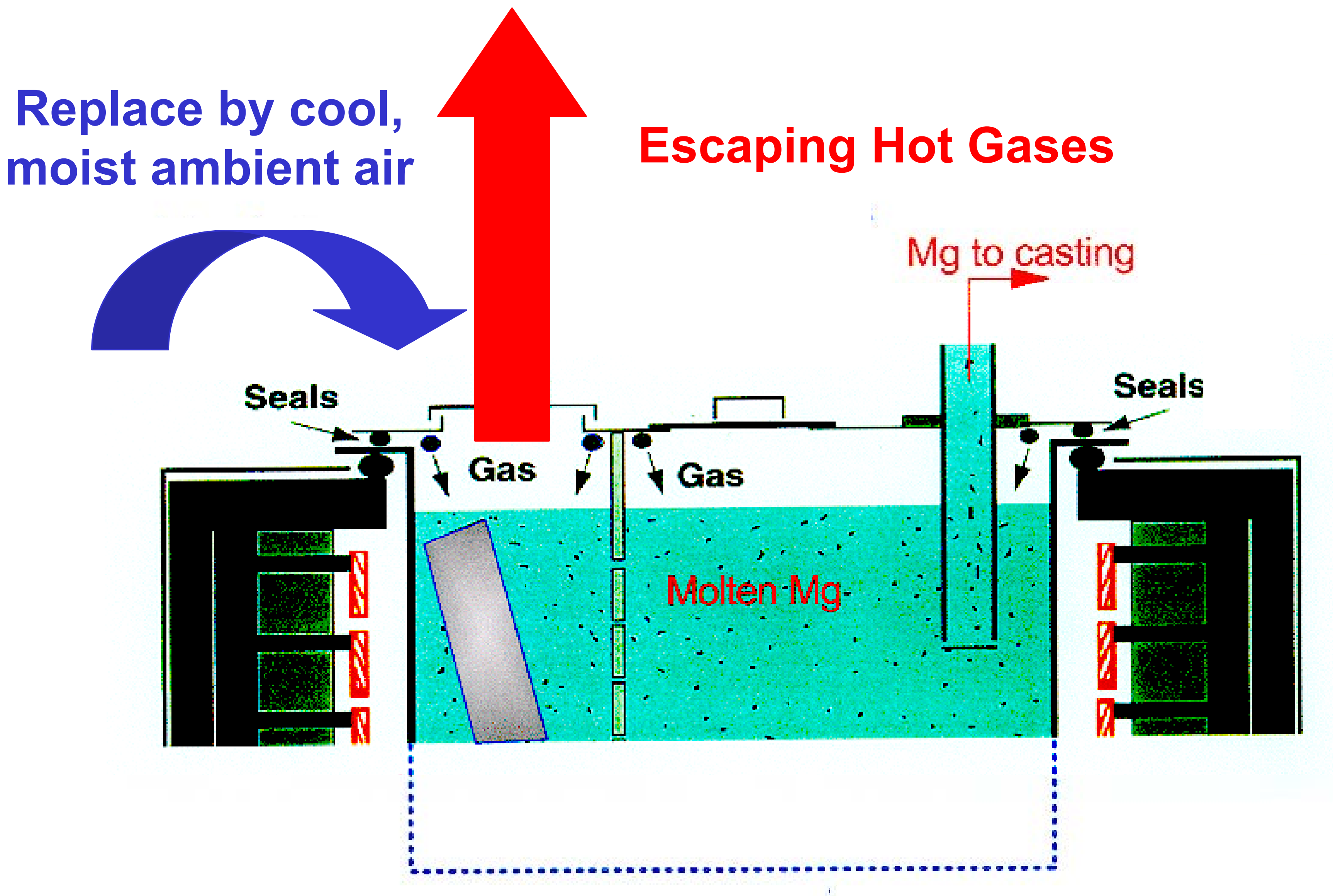
Variables affecting cover gas performance

- Alloy, type of casting process
- Surface temperature (casting process and furnace heating geometry)
- Operating procedures (cleaning methods and frequency)
- Cover gas distribution and flow control

Gas Flow Basics

- Hot gas is less dense than cold gas
- Hot gases rise, Cold gases sink
- Headspace gases are 300 to 500 C hotter than incoming cover gas
- Headspace gases are about ¼ to ½ the density of incoming cover gas

Opened Furnace Hatch

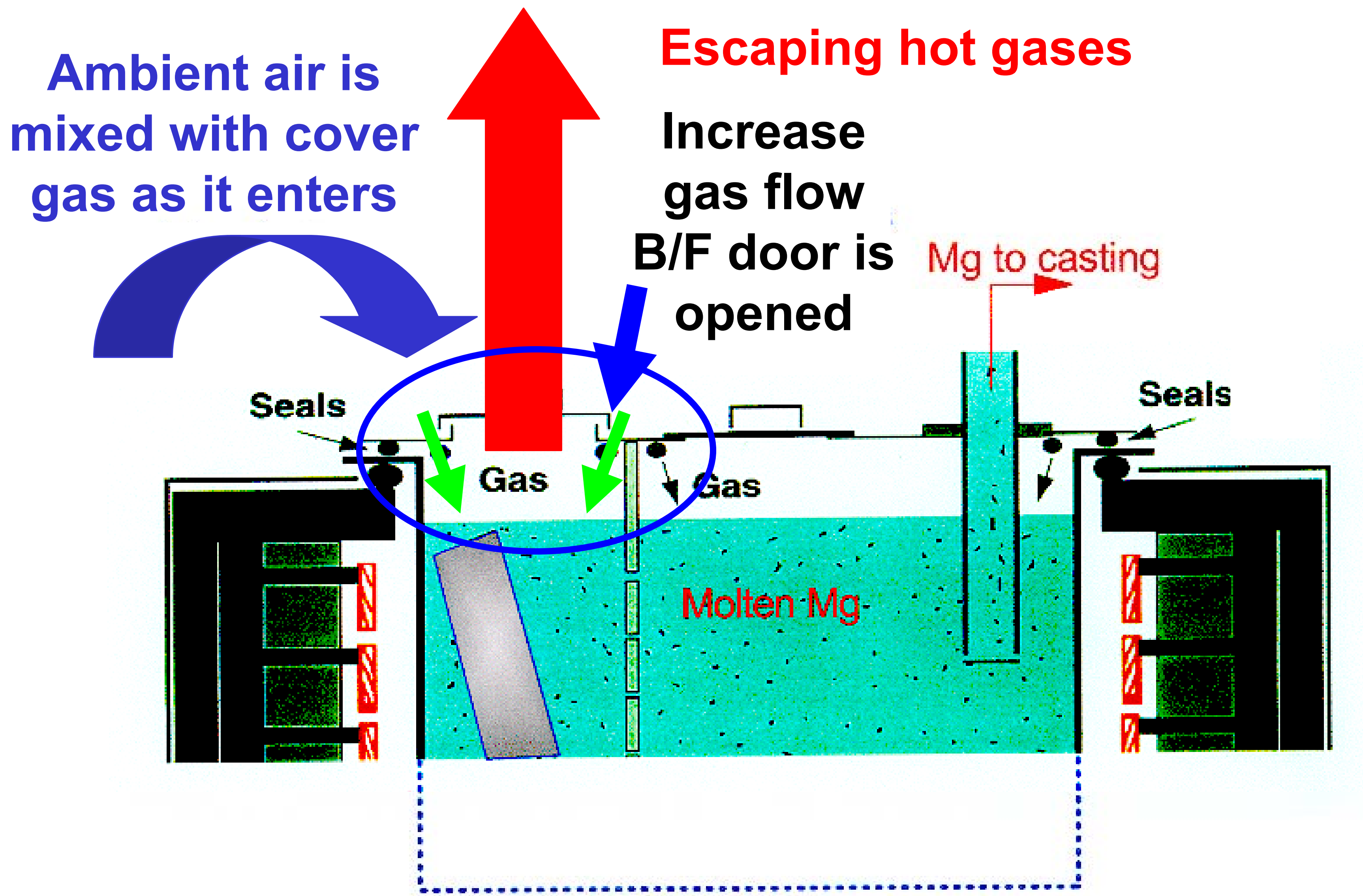


Dynamic Flow Control

Opening furnace hatches introduces large amounts of ambient air into furnace headspace

- **Added moisture produces HF, metal oxides**
- **Cover gas recovery to stable state takes a lot of time**
- **Old Solution: Set cover gas use high to accommodate open hatch condition.**

Opened Furnace Hatch



Dynamic Flow Control

New Solution:

-Set cover gas use for closed furnace

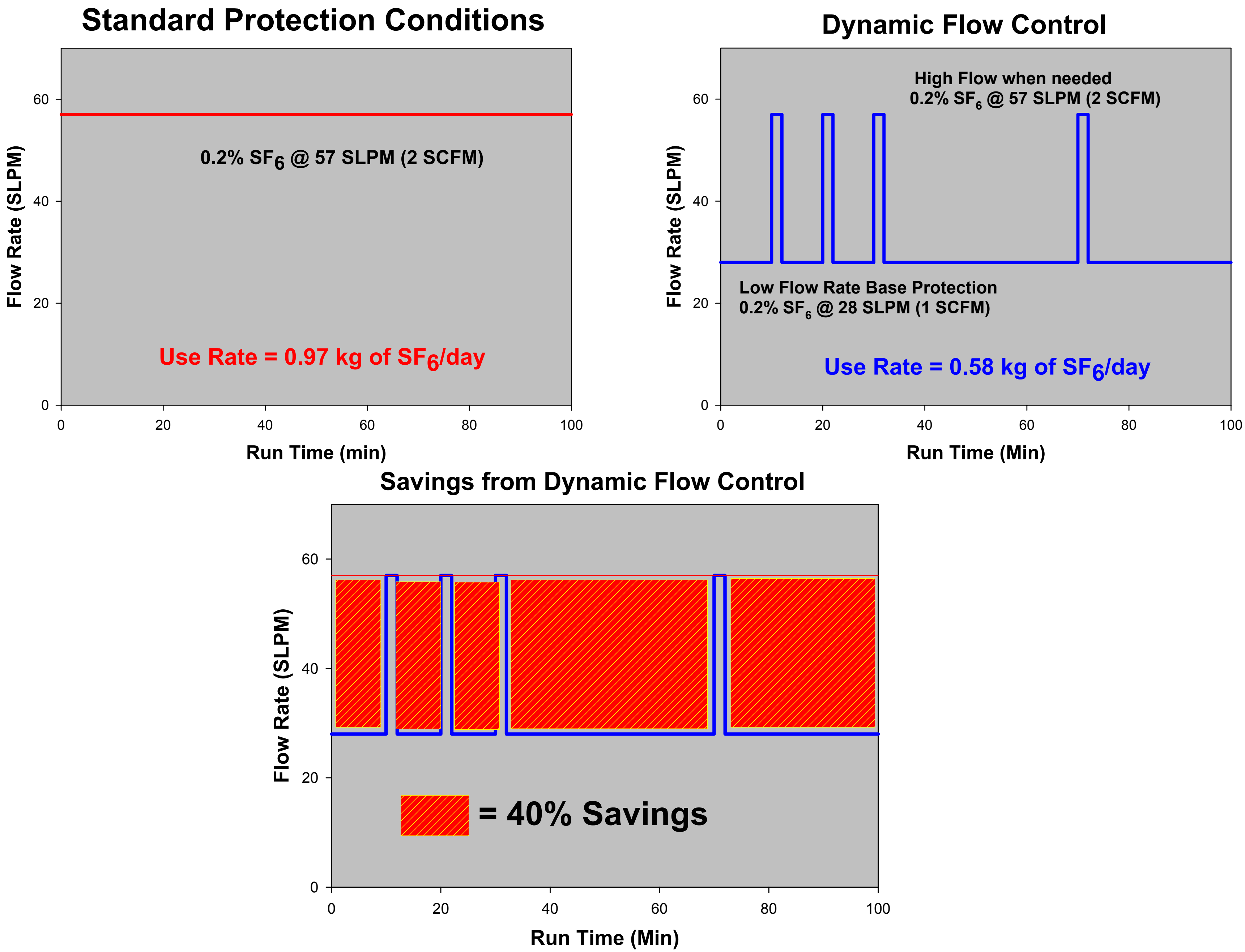
-Increase flow rates automatically as doors are opened

Ambient air is diluted with cover gas and recovery time is reduced,

Effect of moisture intrusion is less (less HF)

A more stable melt is produced

More economical use of cover gases



Standard Protection Conditions
0.2% SF6 @ 57 SLPM (2 SCFM)
Use Rate = 0.97 kg of SF6/day
Flow Rate (SLPM)
Run Time (min)
Dynamic Flow Control
High Flow when needed
0.2% SF6 @ 57 SLPM (2 SCFM)
Low Flow Rate Base Protection
0.2% SF6 @ 28 SLPM (1 SCFM)
Use Rate = 0.58 kg of SF6/day
Flow Rate (SLPM)
Run Time (Min)
Savings from Dynamic Flow Control
= 40% Savings
Flow Rate (SLPM)
Run Time (Min)

Dynamic Flow Control

Flow Control Strategy:

- Use cover gas agent concentration and flow rate to protect an idling furnace
- Increase flow rate during open operations, e.g. ingot addition, dosing pump operation, drossing and furnace cleaning

Can make use of existing process controls

Results: Lower agent use rates, lower emissions, more economical process

Process Economics

Generally use rates are 25 to 30% that of SF_6 (direct substitution) [Costs below SF_6]

Lower use rates with changes to recommended CO_2 cover gas formulations [Savings]

Additional savings with improved gas distribution and dynamic flow control [Significant savings]

Novec™ 612 Magnesium Protection Fluid

Virtually eliminates GHG from cover gas

Commercially proven and viable

Uses existing gas-mixing equipment with modifications

Even gas distribution is very important

Dynamic cover gas flow control will reduce cover gas use, emissions and costs