

# Ultra Low GWP Cover Gas for Magnesium Alloy Die-casting

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# New Gas / Excellent Environmental Properties

- **Chemical Name**

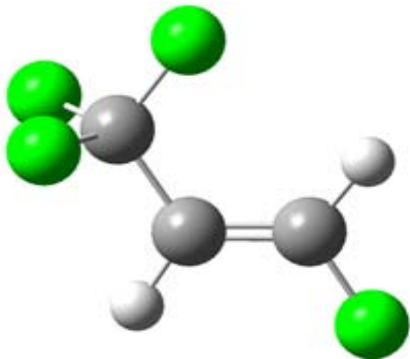
*trans*-1,3,3,3-tetrafluoropropene

- **Usage Name**

1234ze / OF-1234ze

- **Chemical Formula**

$\text{CF}_3\text{CH}=\text{CFH}$



- **ODP = 0**

- **100 year GWP = 9**

**(SF<sub>6</sub> = 23,900)**

- **Atmospheric Lifetime = 20days**

**(SF<sub>6</sub> = 3,200years)**

# Toxicity / Physical Properties

## Toxicity

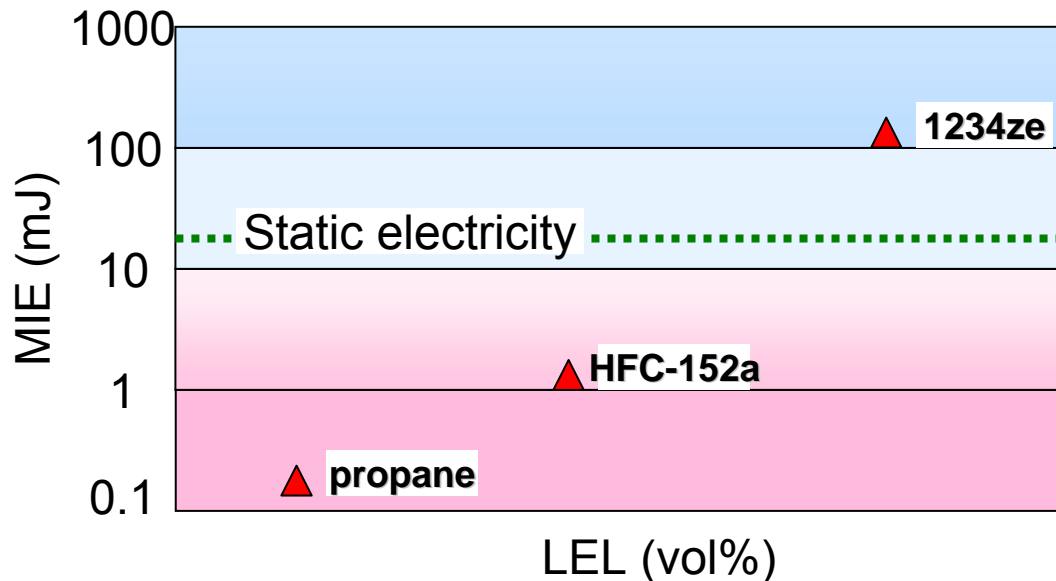
- Ames : Negative
- Acute toxicity : No effect level
- Chromosomal ab. : Negative
- Partition coefficient : no problem
- 28days (rat) : No effect level

## Physical Properties

- Boiling point : -19°C
- Vapor Density : 4.66 (Air=1)
- Specific Gravity : 1.098 (48°C)
- Vapor pressure : 0.5MPa (25°C)
- **Flammability : Slightly Flammable**

# Flammability Properties

	LEL* (vol%)	UEL* (vol%)	MIE (mJ)
Propane	2.3	9.5	0.31
HFC-152a	3.7	19.6	1.25
1234ze	5.6	14.4	>123



LEL : 5.6vol%

Concentration of 1234ze as a cover gas : <1.0vol%



No ignition

MIE : >123mJ

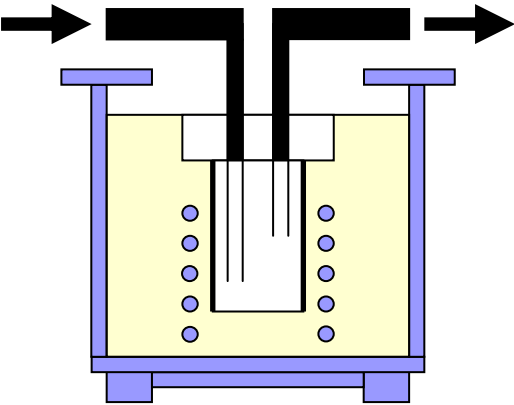
Static electricity from human : 30mJ



More difficult to ignite

# Thermal decomposition

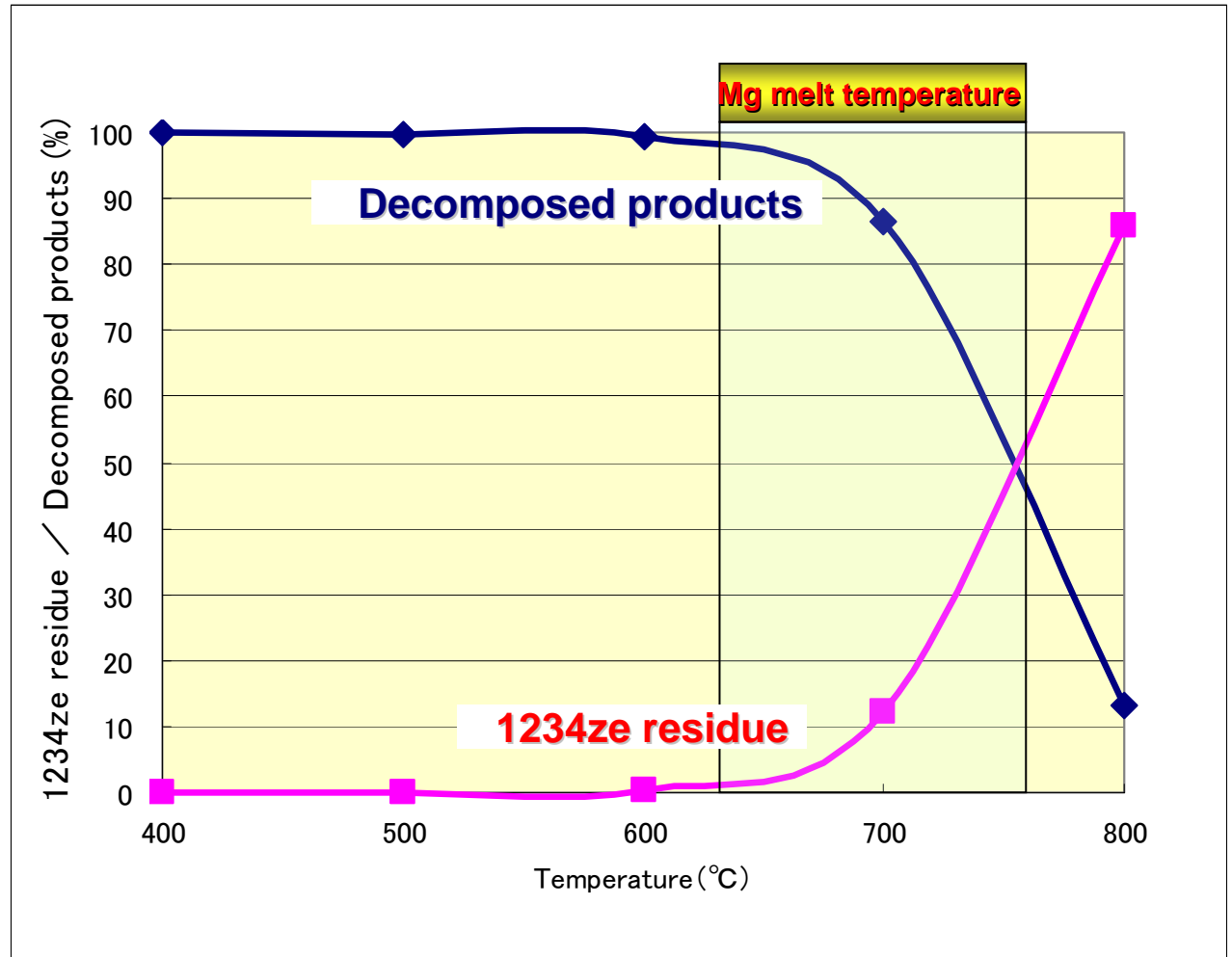
1234ze



SUS vessel: 50mm  $\phi$   $\times$  250mm

Surface area: 19.6

Retention time: 13.7min



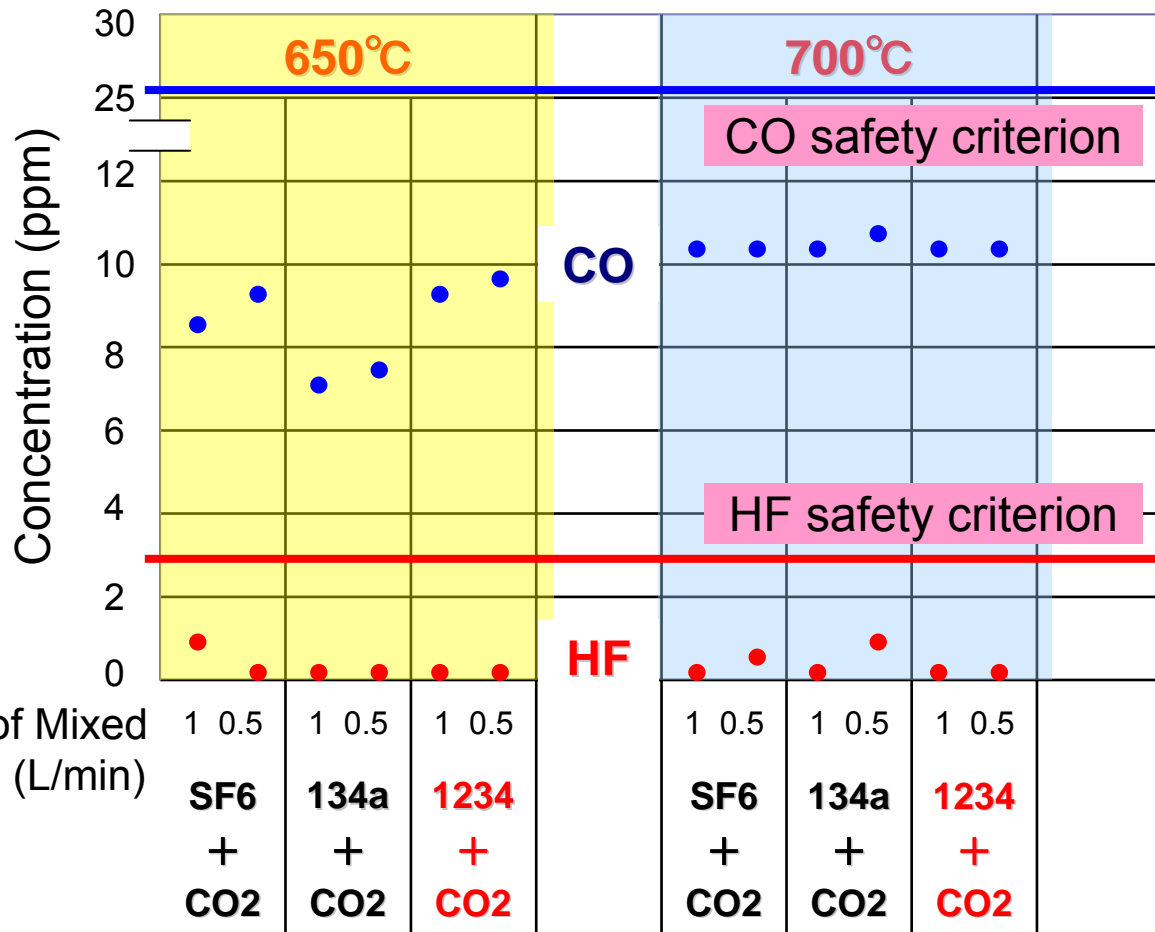
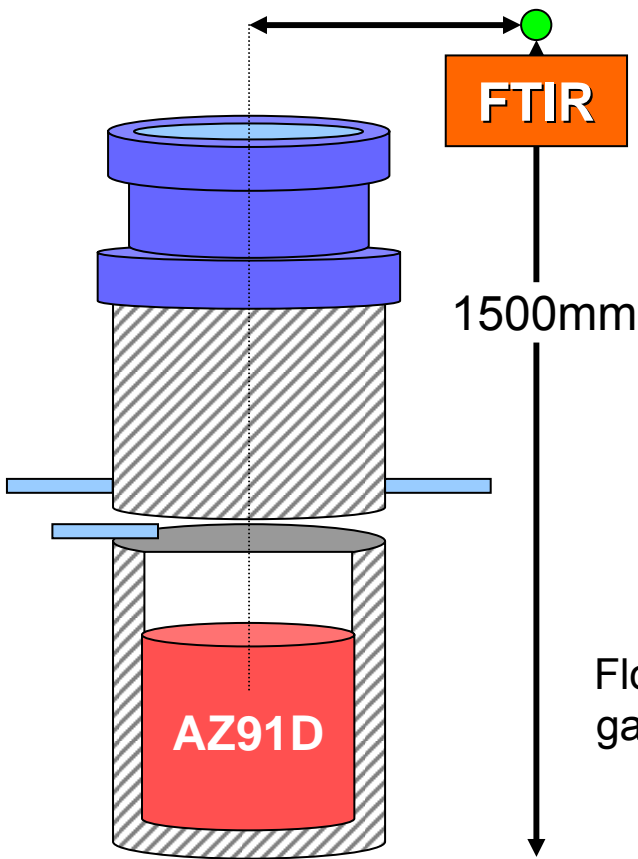
Mg melt temperature

Decomposed products

1234ze residue

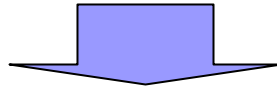
# Safety Evaluation of Occupational Surroundings

Data : Nagaoka University of Technology



# Summary I

- **We had conducted preliminary experiments and confirmed that 1234ze had excellent performance as a cover gas.**



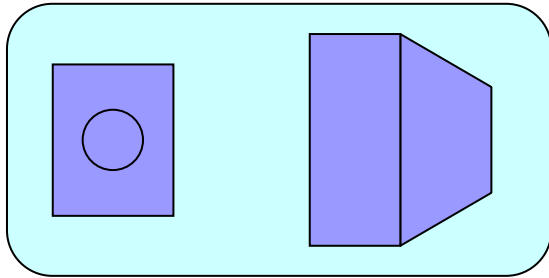
- **We need to conduct trial experiments at die-casters.**

# Trial experiments at die-casting in Japan

	Corporate name	Casting Machine	Evaluation	Status
<b>1</b>	<b>AHRESTY</b>	<b>COLD</b>		
<b>2</b>	<b>TOSEI</b>	<b>HOT</b>		
<b>3</b>	<b>NIKKIN MgCAST</b>	<b>HOT</b>		
4	A	COLD		
<b>5</b>	<b>B</b>	<b>HOT/COLD</b>		
6	C	COLD		
<b>7</b>	<b>D</b>	<b>COLD</b>		
8	E	RECYCLE		
9	F	HOT/COLD		
10	G	HOT/COLD		
11	H	HOT		
12	I	COLD		
13	J	COLD		
14	K	HOT		
15	L	COLD		



# Trial experiment at die-casting I — 1

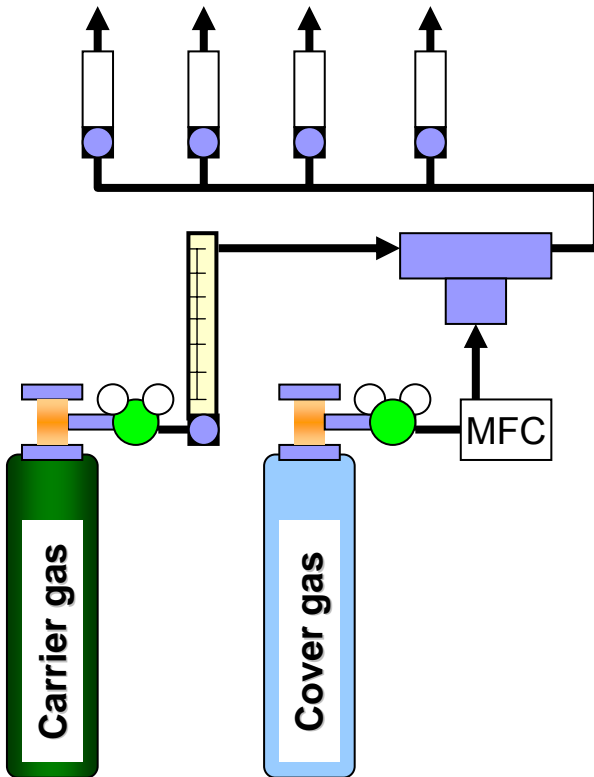


Corporate name: Nikkin Mg Cast CO.,LTD

Address: Fukuoka

Business outline: Magnesium die-casting

Trial Date: 2007, Oct 29 — Oct 31



= TEST CONDITIONS =

1. Casting Machine: HOT

2. Mg Alloy: AZ91D

3. Surface Area: 0.5m<sup>2</sup>

4. Temperature: 630°C



• CENTRAL GLASS

# Trial experiment at die-casting I – 2

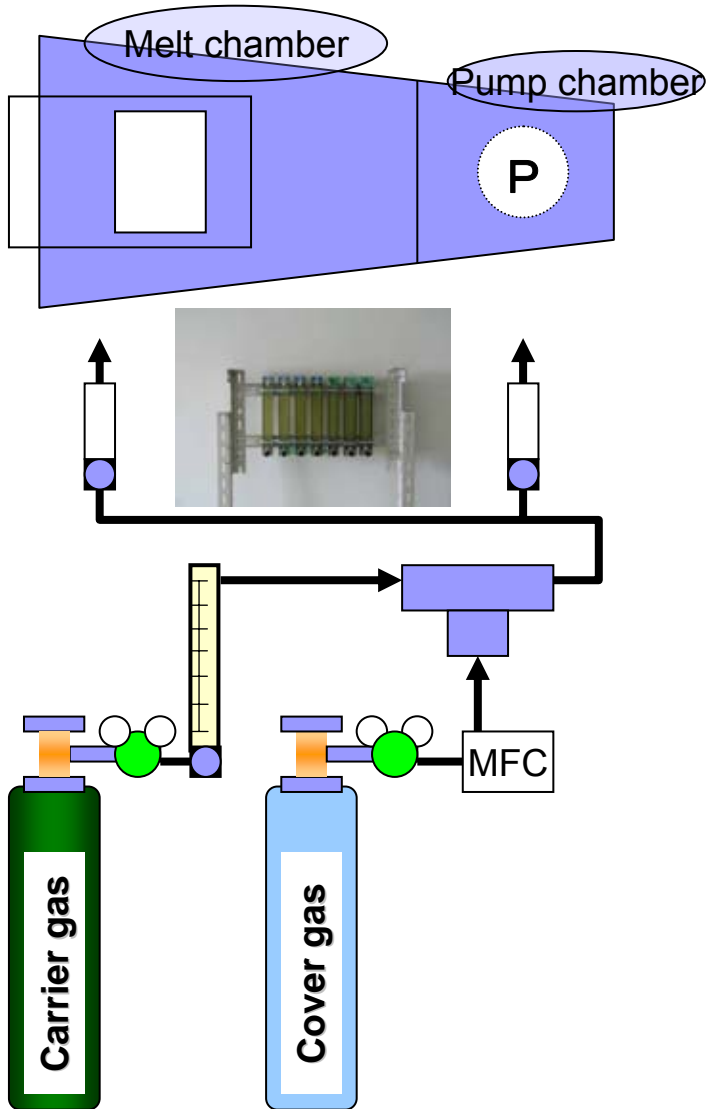
	Flow of mixed gas		Cover gas	Time to ignition		Evaluation
	N2(L/min)	SF6(L/min)	VOL %	Sec	Place	
SF6-1	—	≒40	100	53	Back	○
SF6-2	—	≒40	100	9	Back	○
	CO2(L/min)	1234(mL/min)				
1234ze-1	10	40	0.4	12	Back	○
1234ze-2	10	60	0.6	14	Back	○
1234ze-3	20	40	0.2	22	Back	○
	N2(L/min)	1234(mL/min)				
1234ze-1	30	60	0.2	80	Back	◎
1234ze-2	30	30	0.1	35	Side	○
<b>1234ze-3</b>	<b>20</b>	<b>40</b>	<b>0.2</b>	<b>57</b>	<b>Back</b>	<b>◎</b>

## ■ Measurement of decomposition gases (human worker

	Result	Limitation of detector	TWA
HF	ND	<0.1 ppm	3 ppm
CO	ND	<1 ppm	25 ppm
NH3	ND	<0.5 ppm	25 ppm

It is now proven to reduce more than 99.9% of CO2 emission by introducing 1234ze.

# Trial experiment at die-casting II — 1

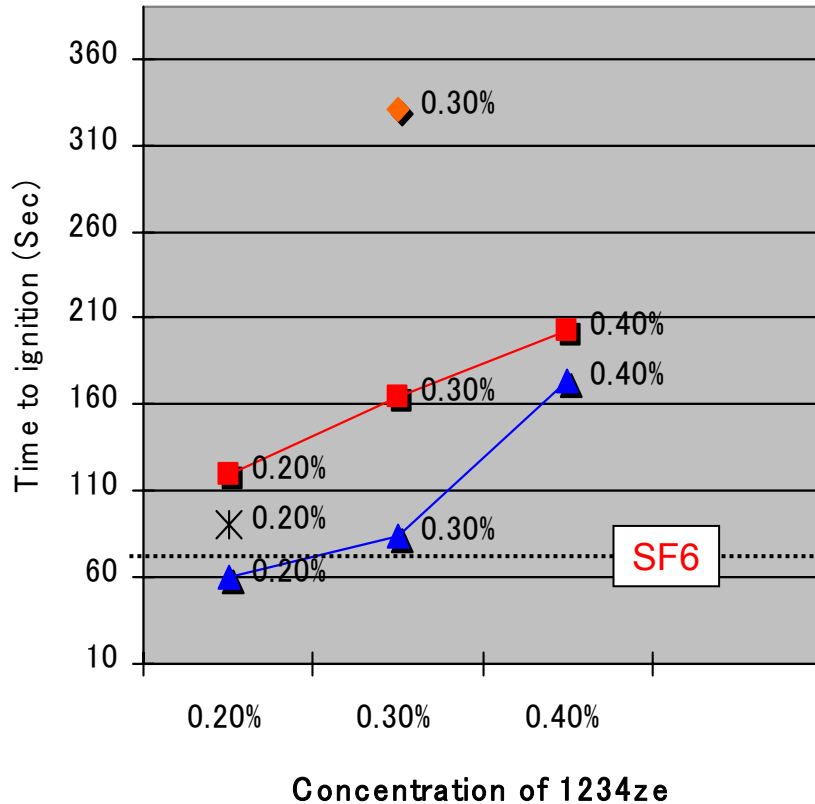


Corporate Name	D (anonymity)
Casting machine	COLD
Surface area	0.50m <sup>2</sup> (Pump:0.13,Melt:0.37)
Temperature	Pump: 690°C、Melt: 685°C
Mg alloy	AM60B

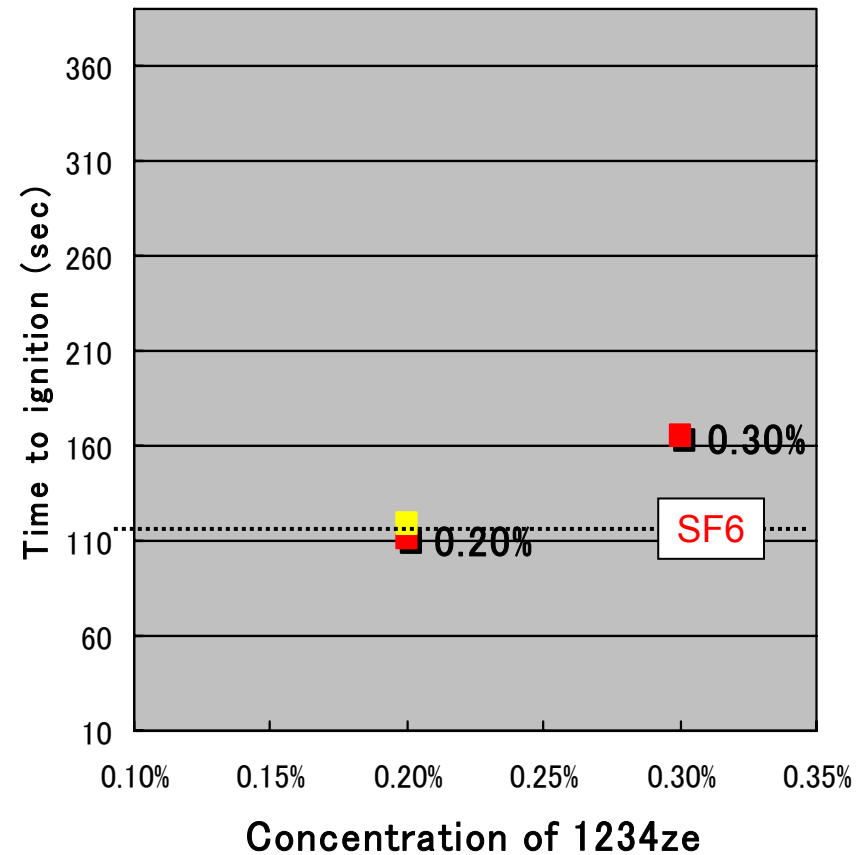
Mixed gas	Flow of Mixed gas (L/min)	Flow of cover gas (ml/min)	Concentration of cover gas
SF6 + N2	11	22	0.2%
1234ze + N2	25	75	0.3%
1234ze + N2	25	50	0.2%
1234ze + N2	20	80	0.4%
1234ze + N2	20	60	0.3%
1234ze + N2	20	40	0.2%
1234ze + N2	15	60	0.4%
1234ze + N2	15	45	0.3%
1234ze + N2	15	30	0.2%
SF6 + N2	11	22	0.2%

# Trial experiment at die-casting II – 2

Melt Chamber

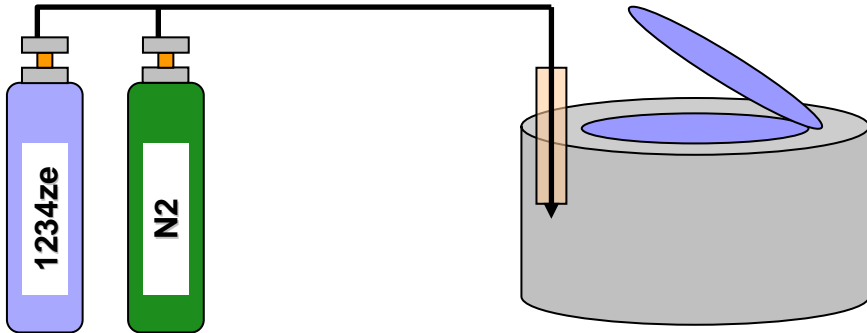


Pump Chamber



▲ : 15L/min    
 ■ : 20L/min    
 ◆ : 25L/min

# Trial experiment at die-casting III



Corporate name: B (anonymity)  
 Experimental furnace (Surface area: 0.44m<sup>2</sup>)  
 Mg alloy: AZ91D  
 1234ze: 0.16% (20ml)  
 Carrier Gas (N2) : 13L/min



1234ze + N2



Ignition

Temperature	Time to ignite
630°C	9min 55sec
640°C	4min 55sec
637°C	3min 05sec
680°C	2min 00sec

- Thin surface layer
- Take time to ignition



Good evaluation



Stop introducing mixture gas for 10min



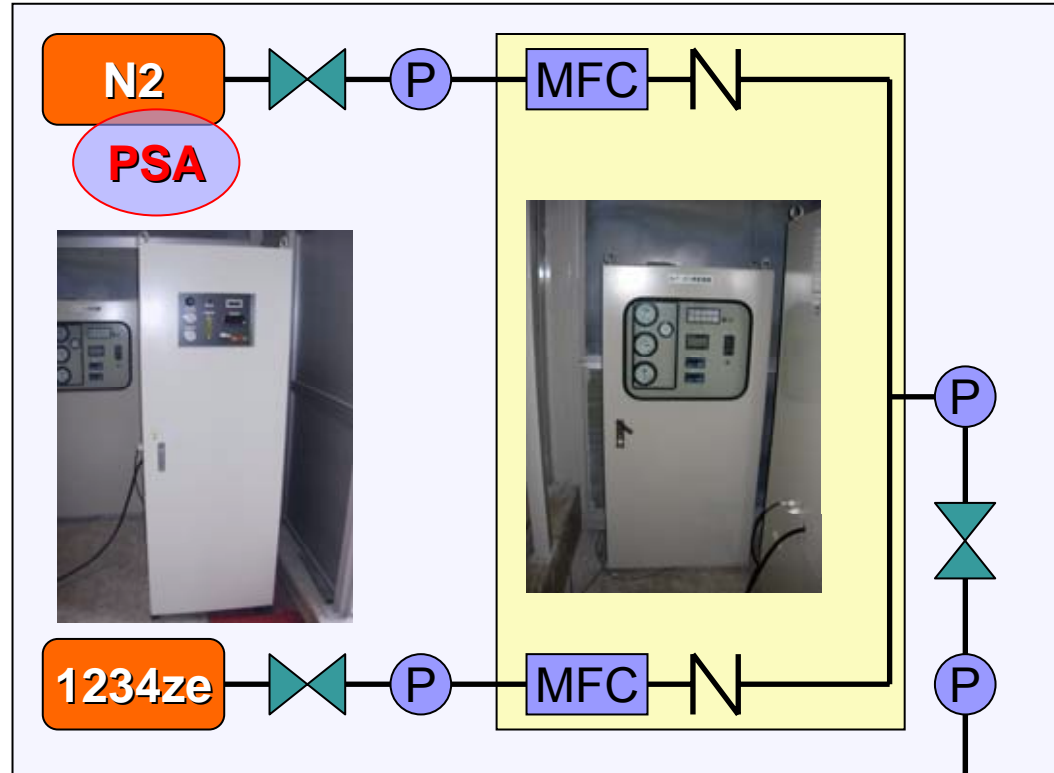
1234ze was sprayed into the casting hood for 2min with a lid closed.



Fire was extinguished

# Introduction on TOSEI I

- Corporate Name: TOSEI
- Address: Shizuoka
- Business Outline: Mg die-casting



□ Casting machine: HOT

□ Mg Alloy: AZ91D

□ Temperature: 630°C



# Introduction on TOSEI II



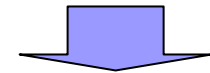
Surface area: 0.5m<sup>2</sup>

Temperature: 630°C

Mg Alloy: AZ91D

Cover Gas: 0.15%

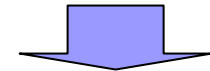
Carrier Gas (N<sub>2</sub>): 15L/min



No ignition

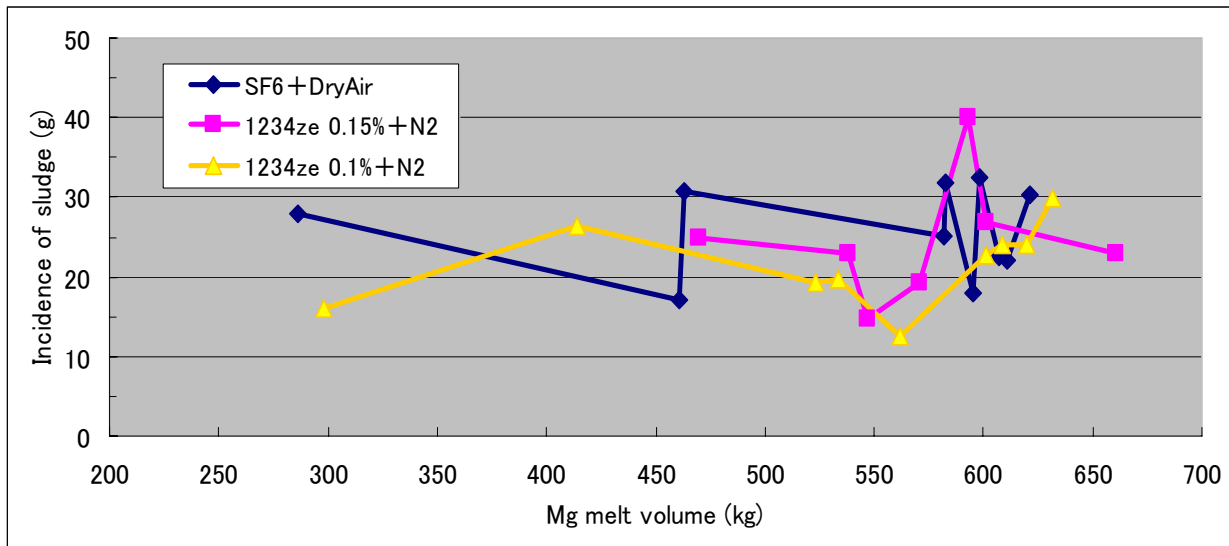
Surface of molten Mg is stable

Decrease of sludge



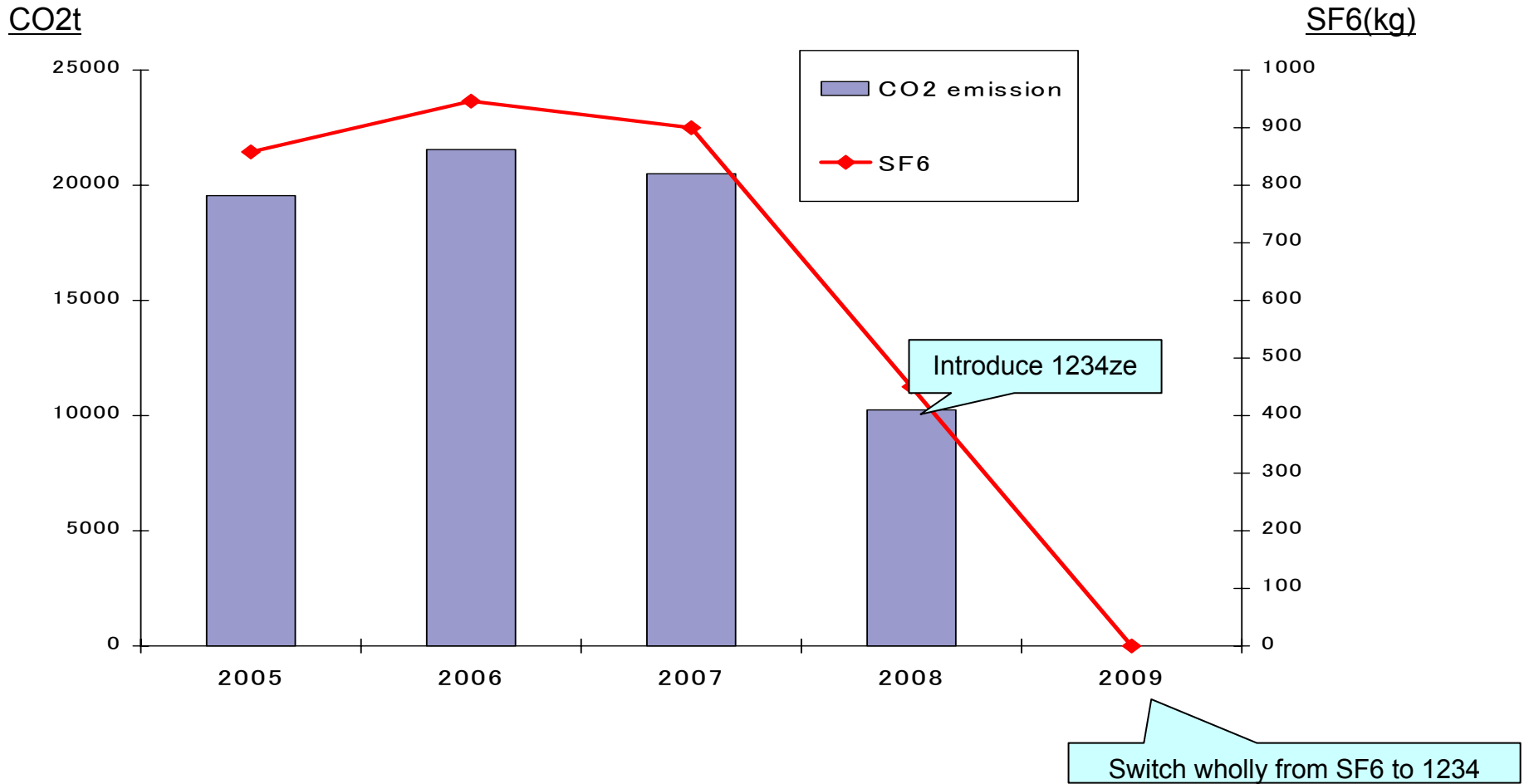
Cover Gas: 0.10%

Carrier Gas (N<sub>2</sub>): 10L/min



# Introduction on TOSEI III

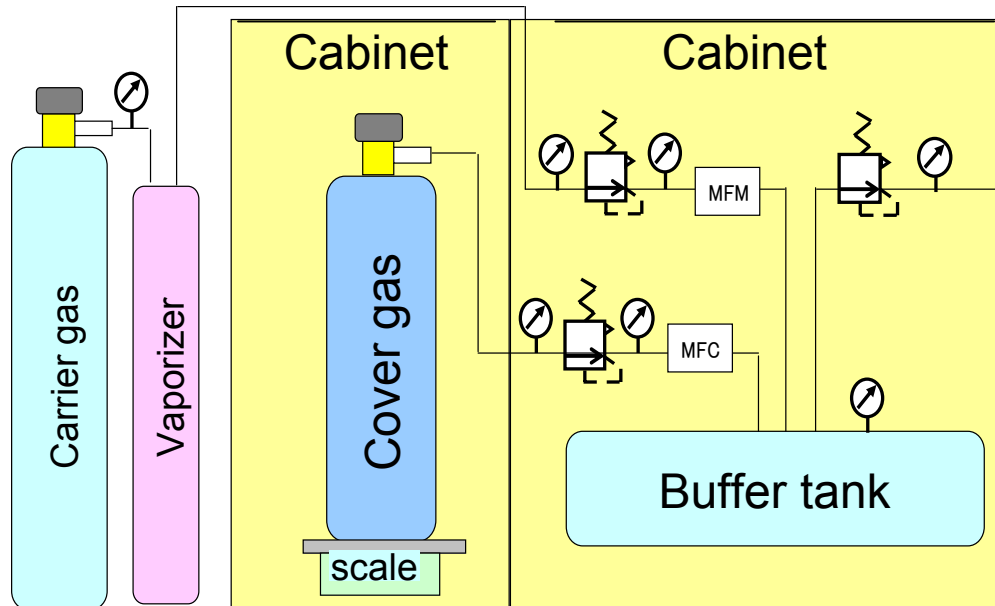
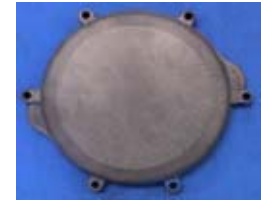
## CO2 emission





# Introduction on AHRESTY I

- Corporate Name: AHRESTY
- Address: Tochigi
- Business Outline: Die-casting



**Casting machine: COLD**

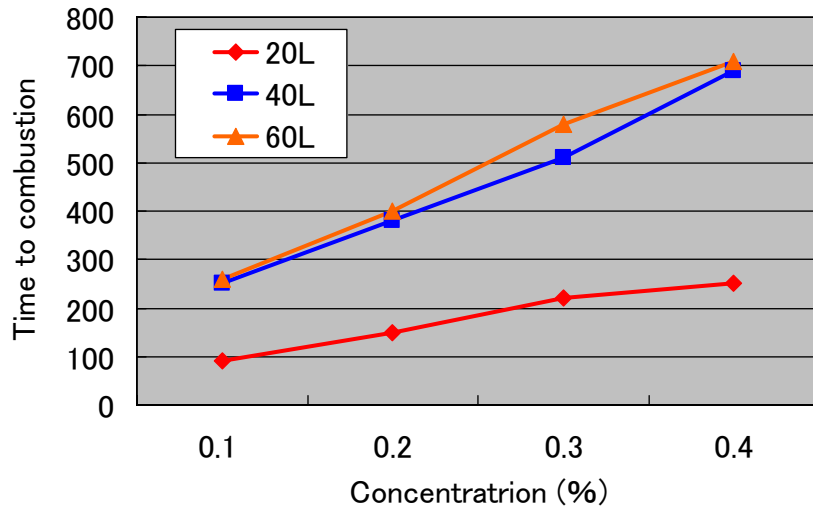
**Mg Alloy: AZ91D**

**Temperature: 650°C**

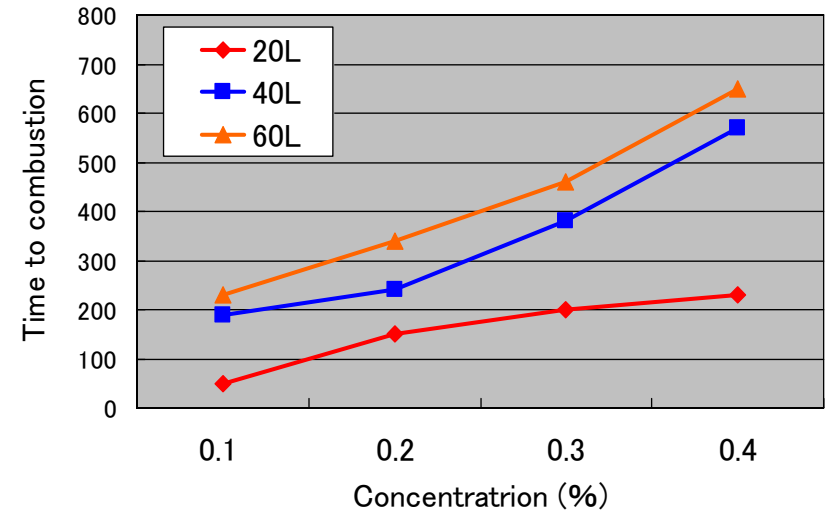
**Surface area: 0.8m<sup>2</sup>**

# Introduction on AHRESTY II

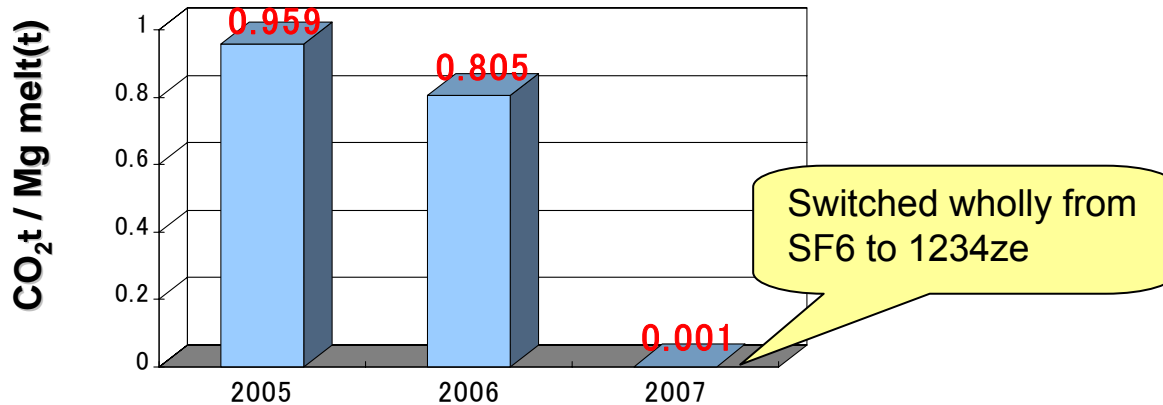
**SF6+CO2**



**1234+CO2**



**CO<sub>2</sub> emission**



# Trial experiments at die-casting in Japan

		Casting Machine	Evaluation	Status
1	AHRETTY	COLD	Good	Introduced
2	TOSEI	HOT	Good	Introduced
3	NIKKIN MgCast	HOT	Good	Introduce until 2009
4	A	COLD	Good	Introduce until 2009
5	B	HOT/COLD	Good	Introduce until 2009
6	C	COLD	Good	Introduce until 2009
7	D	COLD	Good	Planning to introduce
8	E	RECYCLE	Good	
9	F	HOT/COLD	Now conducting	Planning to introduce
10	G	HOT/COLD	Good	Planning to introduce
11	H	HOT	—	Studying
12	I	COLD	—	Studying
13	J	COLD	—	Studying
14	K	HOT	—	Studying
15	L	COLD	—	

# Summary II

- It is now proven that 1234ze has almost the same ability of SF<sub>6</sub> through many trial experiments at die-casters.
- In compliance with Kyoto protocol, Japan has to reduce 6% of CO<sub>2</sub> emission.
- We are required to provide many customers with 1234ze in order to reduce CO<sub>2</sub> emission in the Mg industry.
- We are now planning to built a 1234ze manufacturing plant.



**Thank you for your attention.**