New sustainable flame retardants and smoke suppressants in unplasticized PVC compounds

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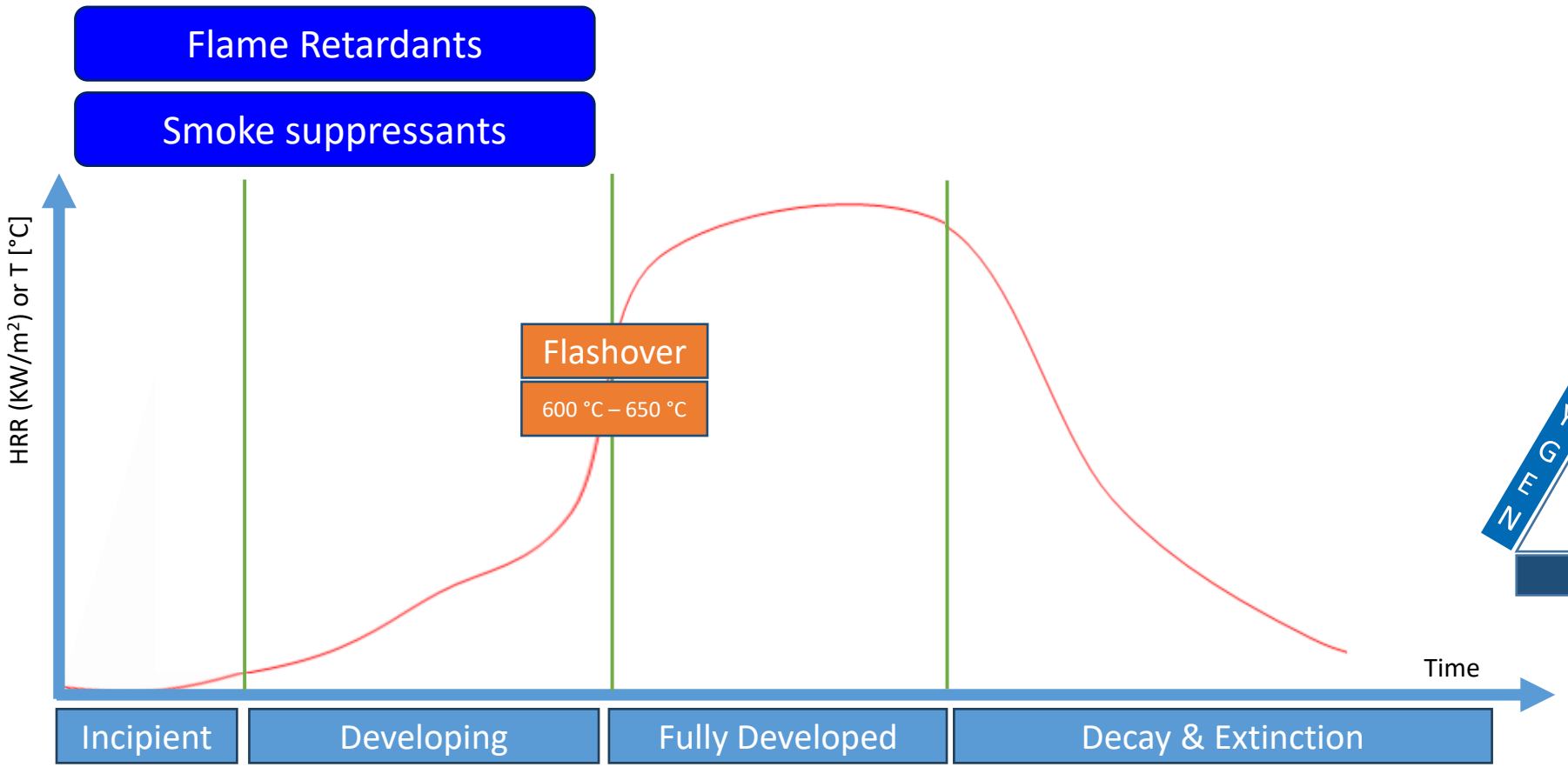
Reagens Group

- A privately owned, independent company, founded in the early 1950's.
- Consolidated group turnover of about € 250 million, underpinned by a solid financial structure.
- A global-scale manufacturer of specialty chemicals for PVC and other thermoplastics with headquarters in Bologna, Italy.
- The broadest PVC stabilizers product portfolio, manufactured in most of the key world regions, in modern, safe and efficient facilities.

The aim of flame retardants and smoke suppressants

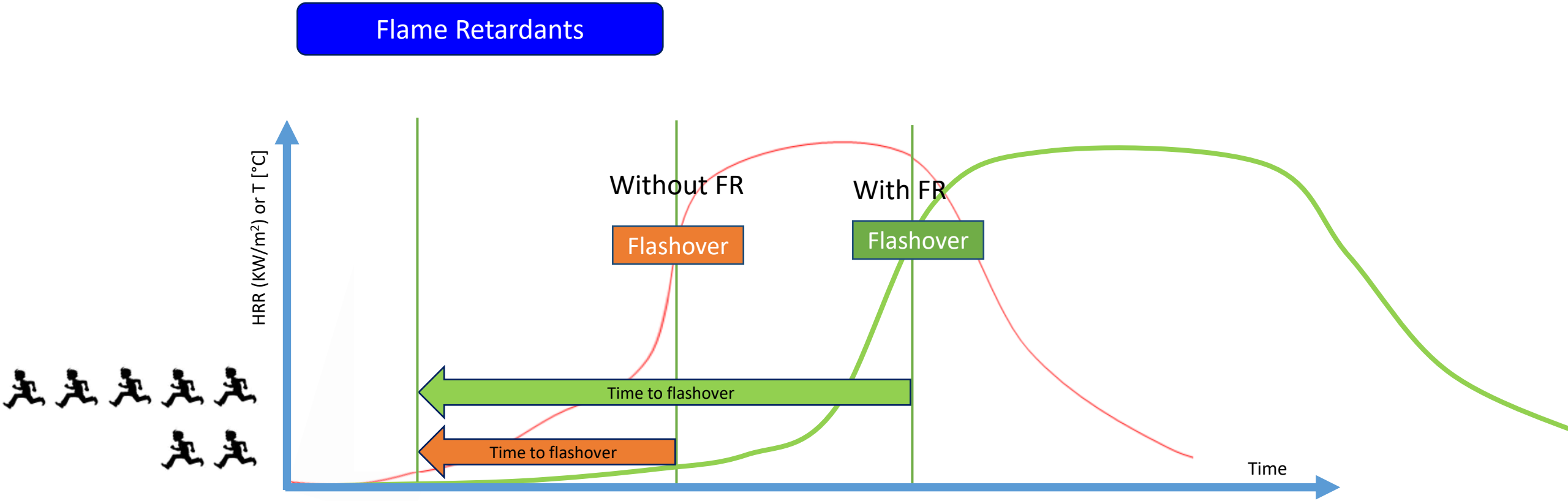
Scheme of a compartment fire



[1][2][3]

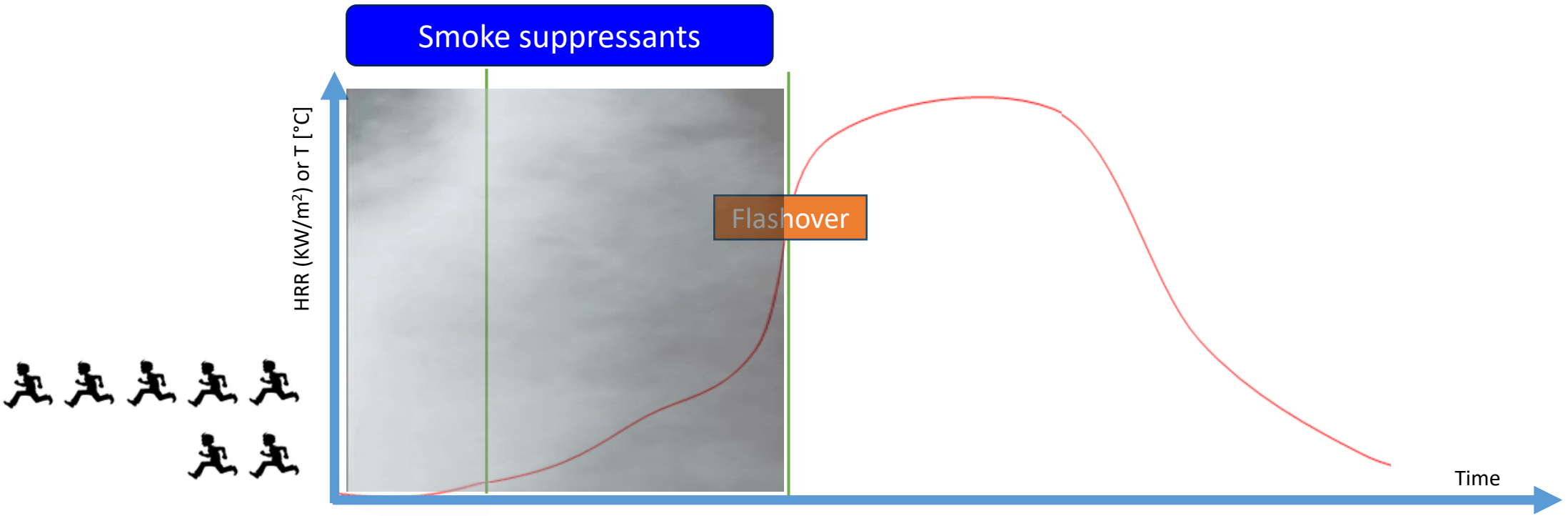
The aim of flame retardants and smoke suppressants

Scheme of a compartment fire



The aim of flame retardants and smoke suppressants

Scheme of a compartment fire

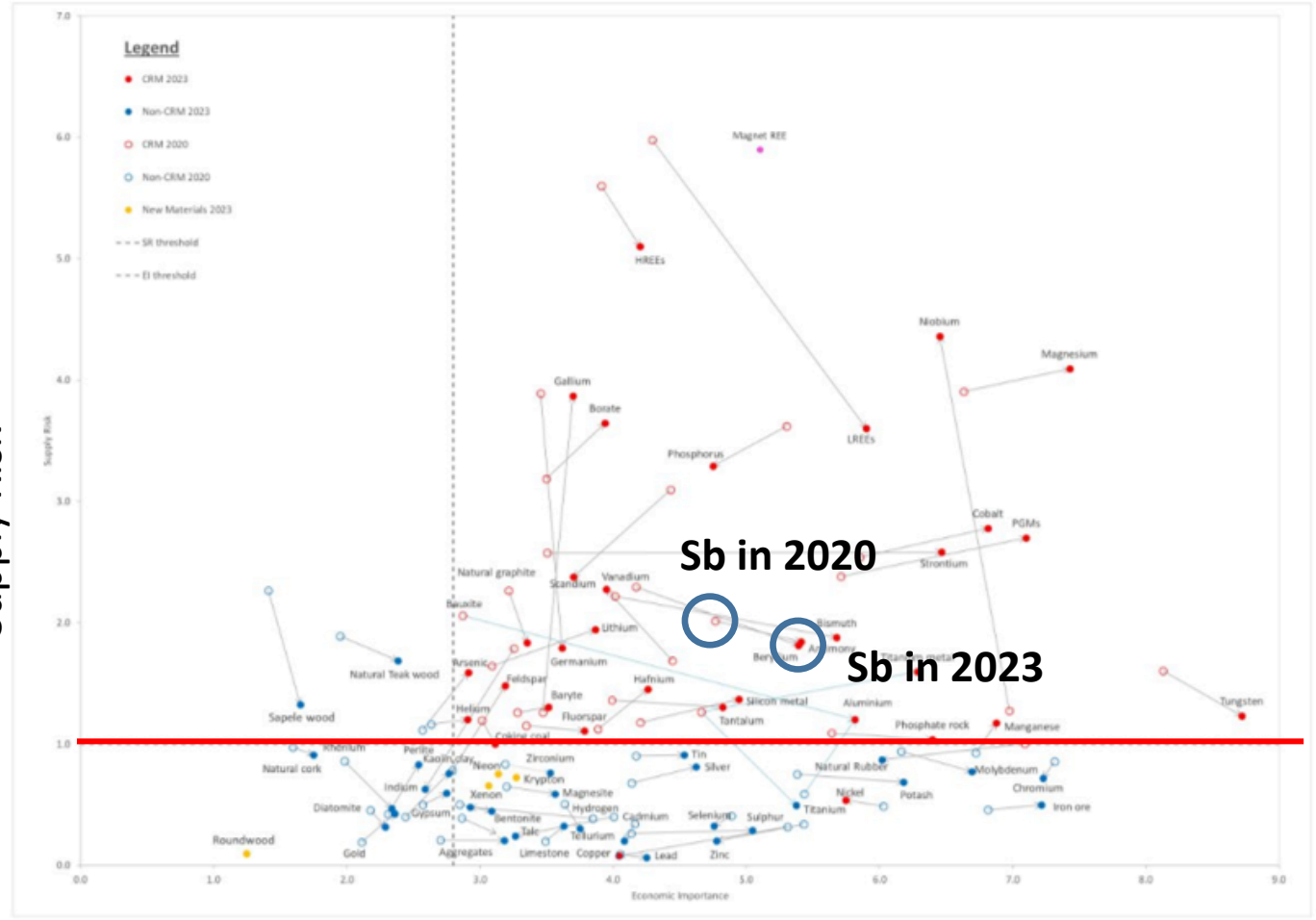


Drivers for Antimony Trioxide (ATO) substitution

1) Bad classification

- In the EU, on 12/03/2020, ECHA asked the registrants for new toxicological tests to verify if the classification "H350 1b - May cause cancer by inhalation" can be met. [4]
- ATO is included with other FRs in the action “The use of PVC in the context of not toxic environment” (Risk of restriction is specific application).
- ATO (with others FRs) has been included in the “Regulatory strategy for flame retardants issued by ECHA”. It regards halogenated and organophosphorus FRs, but in non halogenated plastics brominated FR are used in combination with ATO.

Drivers for Antimony Trioxide (ATO) substitution



2) Critical supply risk

ATO is **produced** exclusively **by unwrought Sb**.

Sb is a metal with **vast economic importance** but with a **critical supply risk**.

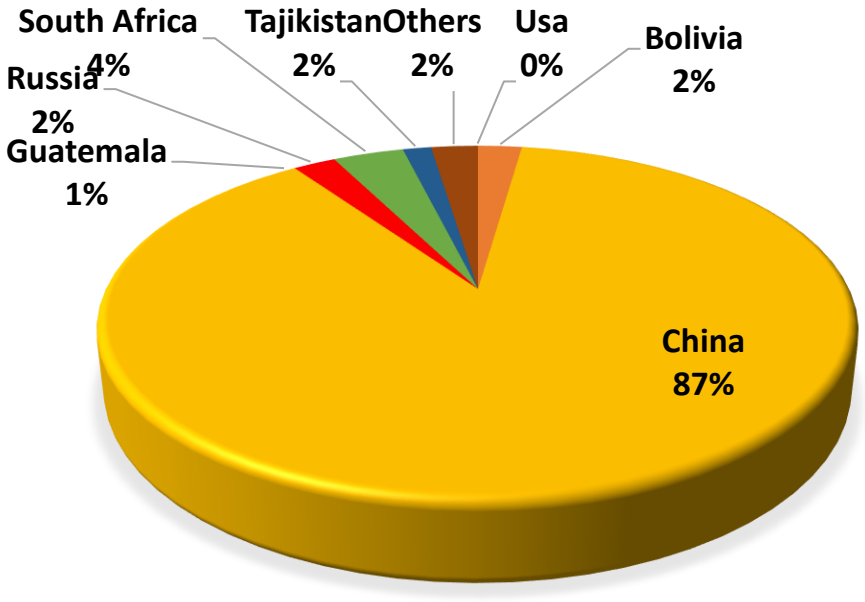
China processes more than 70 % of worldwide Sb: reserves + importations of ores from Bolivia, Australia, and Russia.

Sb has been enlisted as critical raw material in the EU (**CRM reports** from 2011, 2014, 2017, and 2020, 2023) and it is present in 35 critical minerals list in the US.

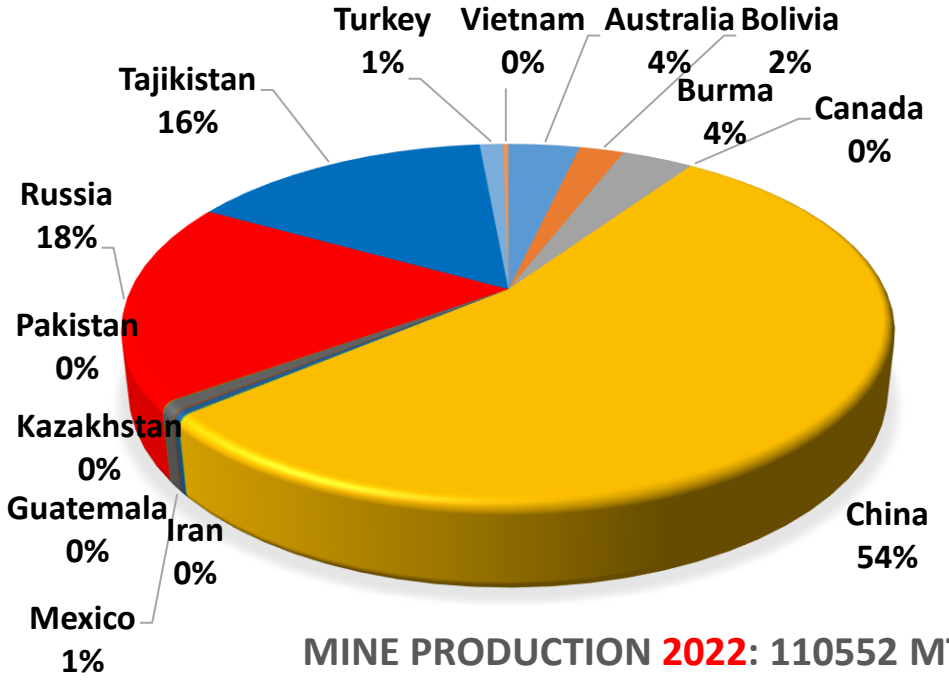
Figure 1: Reference: CRM list 2023_Final Report

Drivers for Antimony Trioxide (ATO) substitution

2) Critical supply risk



MINE PRODUCTION **2007**: 137000 MT [5]



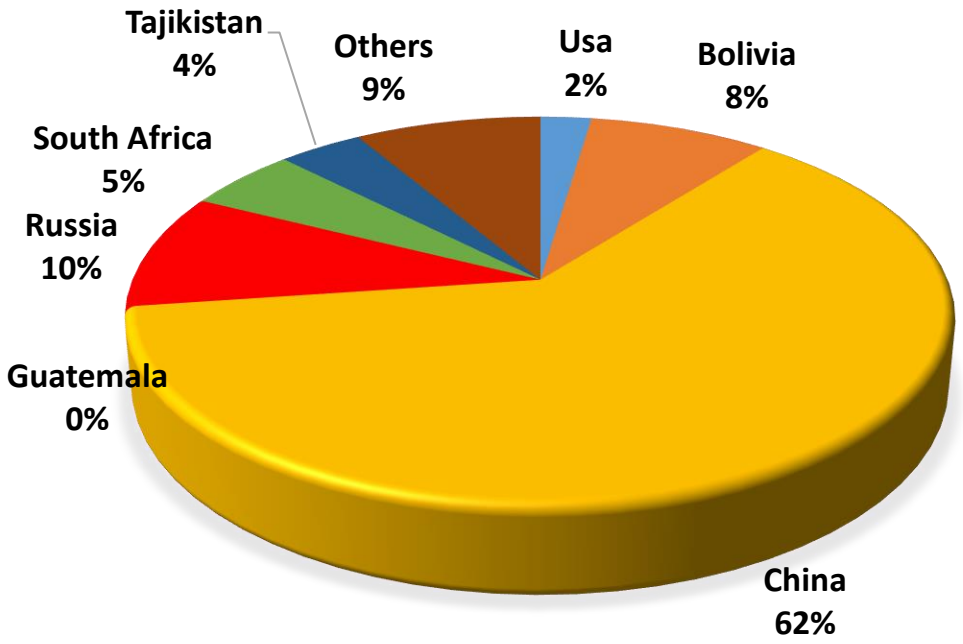
MINE PRODUCTION **2022**: 110552 MT [6]

The **EU** and US are 100 / 90 % dependent by other countries.

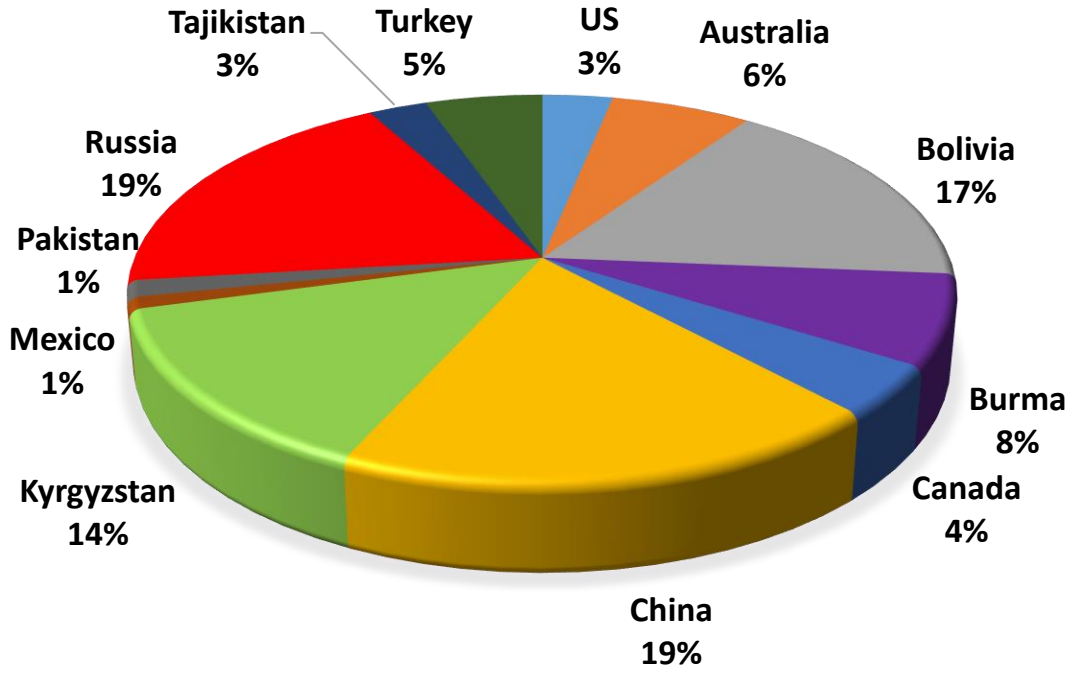
Drivers for Antimony Trioxide (ATO) substitution

2) Critical supply risk

RESERVES 2007: 3860000 MT [5]



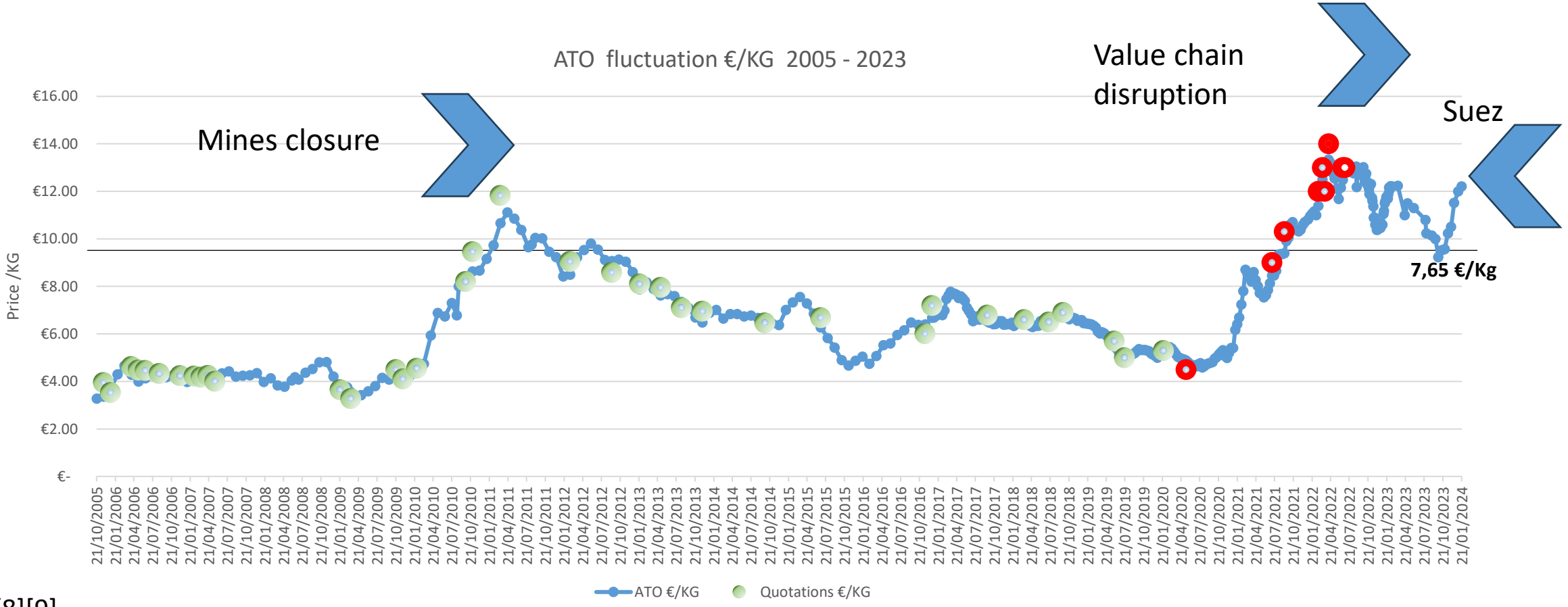
RESERVES 2023: 2000000 MT [6]



The **European Union** (EU) has **no Sb reserves**.
US has reserves but **no production** yet.

Drivers for Antimony Trioxide (ATO) substitution

2) Critical supply risk

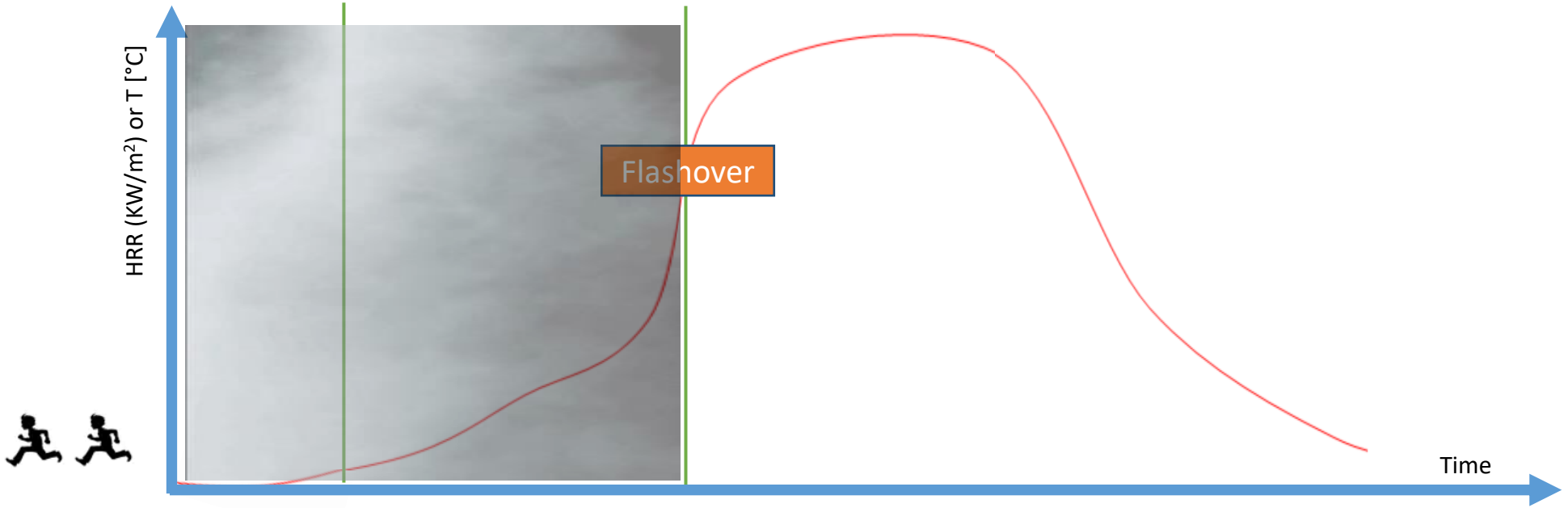


[7][8][9]

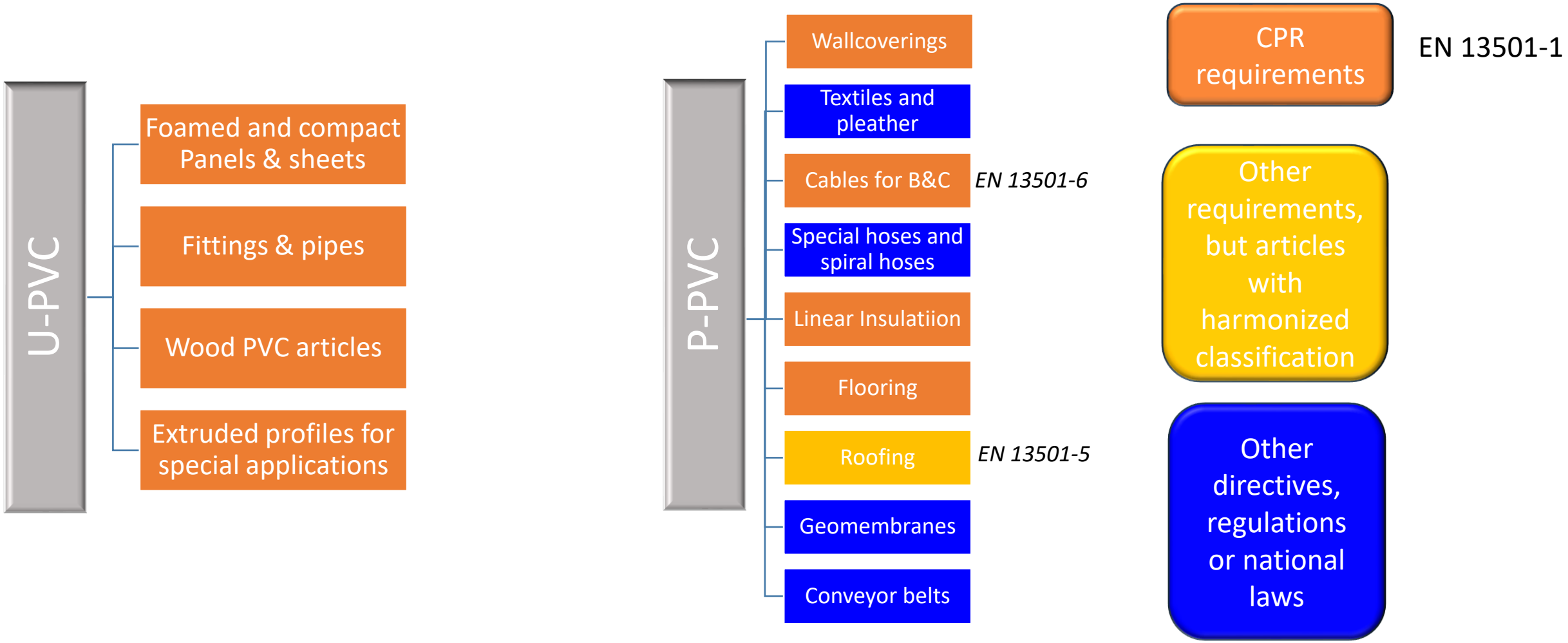
Drivers for Antimony Trioxide (ATO) substitution

3) Black and dense smoke

ATO cannot be used in low-smoke PVC compounds



B&C Regulatory context

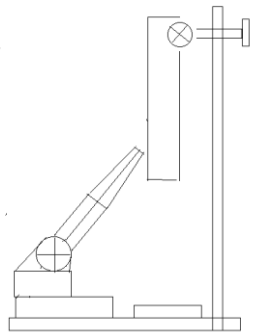


CPR Standards and requirements for PVC-U pannels

EN 13501-1 rules the classification of linear pipe thermal insulation (l), flooring (fl) and construction product excluding l or fl **in terms of reaction to fire**.
This involves also U-PVC panels installed permanently in buildings.

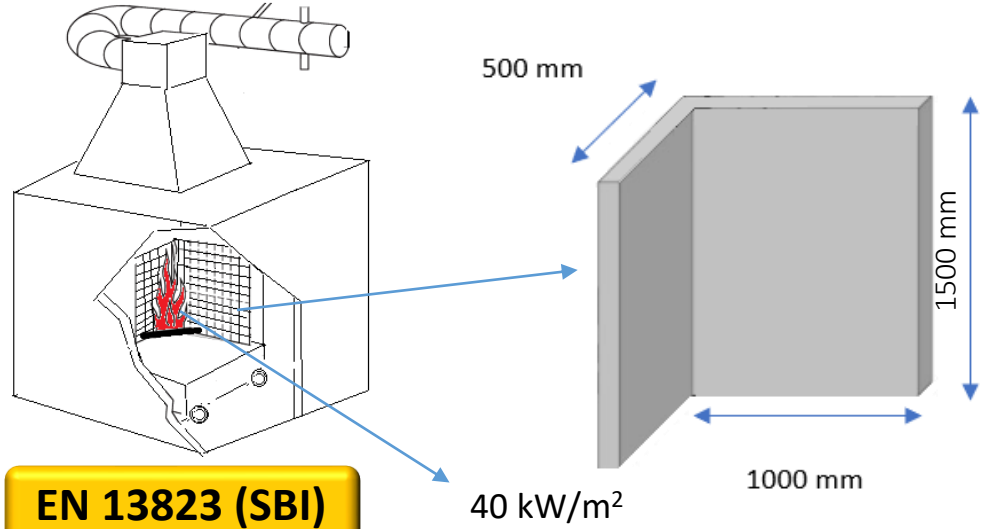
The required standards for giving them a CPR classification are:

Bench-scale test



EN ISO 11925-2

Large-scale test



EN 13823 (SBI)

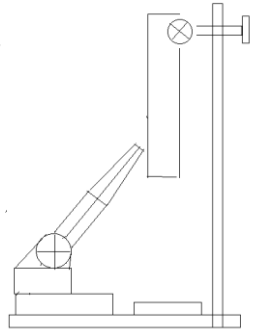
Less performant

Class	Test method(s)	Classification criteria	Additional classification
A1	EN ISO 1182 (1); *and*	ΔT ≤ 30°C; *and* Δm ≤ 50%; *and* t_f = 0 (i.e. no sustained flaming)	-
	EN ISO 1716	PCS ≤ 2.0 MJ.kg^{-1} (1); *and* PCS ≤ 2.0 MJ.kg^{-1} (2) (2a); *and* PCS ≤ 1.4 MJ.m^{-2} (3); *and* PCS ≤ 2.0 MJ.kg^{-1} (4)	
A2	EN ISO 1182 (1); *or*	ΔT ≤ 50°C; *and* Δm ≤ 50%; *and* t_f ≤ 20s	
	EN ISO 1716; *and*	PCS ≤ 3.0 MJ.kg^{-1} (1); *and* PCS ≤ 4.0 MJ.m^{-2} (2); *and* PCS ≤ 4.0 MJ.m^{-2} (3); *and* PCS ≤ 3.0 MJ.kg^{-1} (4)	
	EN 13823 (SBI)	FIGRA ≤ 120 W.s^{-1}; *and* LFS < edge of specimen; *and* THR_{600s} ≤ 7.5 MJ	Smoke production(5); *and* Flaming droplets/ particles (6)
B	EN 13823 (SBI); *and*	FIGRA ≤ 120 W.s^{-1}; *and* LFS < edge of specimen; *and* THR_{600s} ≤ 7.5 MJ	Smoke production(5); *and* Flaming droplets/ particles (6)
	EN ISO 11925-2(8): *Exposure = 30s*	Fs ≤ 150mm within 60s	
C	EN 13823 (SBI); *and*	FIGRA ≤ 250 W.s^{-1}; *and* LFS < edge of specimen; *and* THR_{600s} ≤ 15 MJ	Smoke production(5); *and* Flaming droplets/ particles (6)
	EN ISO 11925-2(8): *Exposure = 30s*	Fs ≤ 150mm within 60s	
D	EN 13823 (SBI); *and*	FIGRA ≤ 750 W.s^{-1}	Smoke production(5); *and* Flaming droplets/ particles (6)
	EN ISO 11925-2(8): *Exposure = 30s*	Fs ≤ 150mm within 60s	
E	EN ISO 11925-2(8): *Exposure = 15s*	Fs ≤ 150mm within 20s	Flaming droplets/ particles (7)
F	No performance determined		

CPR Standards and requirements **for class B s_2 d_0**

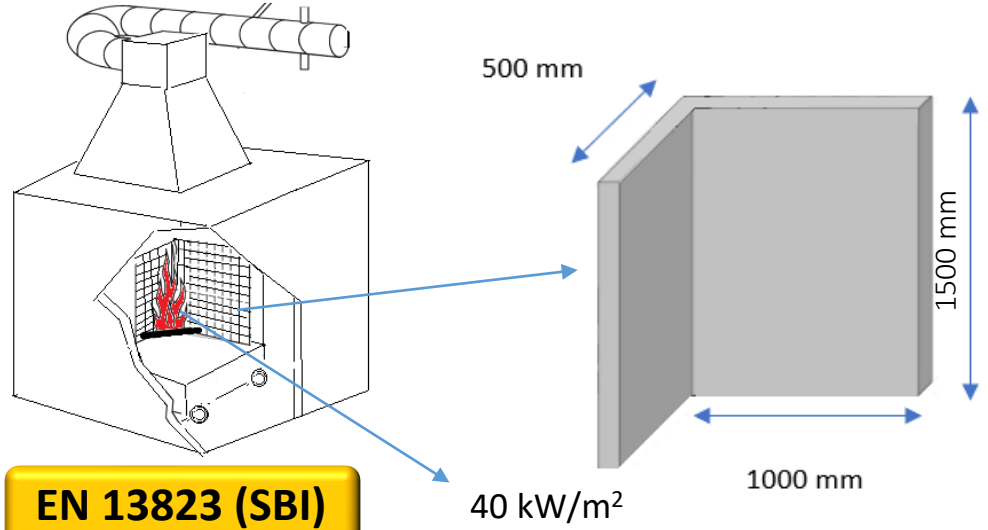
	Class B	Flaming droplets	Smoke
EN ISO 11925-2 *(exposure for 30 s)*	**FIGRA ≤ 120 Ws^{-1}** **LFS < edge of specimen** **THR_{600s} ≤ 7.5 MJ**	d2 if paper in bottom is ignited *(if not be evaluated with EN ISO 13823)*	
EN ISO 13823 *(test lasts 600s)*	**Fs ≤ 150 mm within 600 s**	**d0: no flaming droplets** d1: 10 s of flaming droplets in 600 s d2: not d1, not d2	s1: SMOGRA ≤ 30 m^2/s^2; TSP ≤ 50 m^2 **s2: SMOGRA ≤ 180 m^2/s^2; TSP ≤ 200 m^2** s3: if not d1 not d2

Bench scale test



EN ISO 11925-2

Large scale test

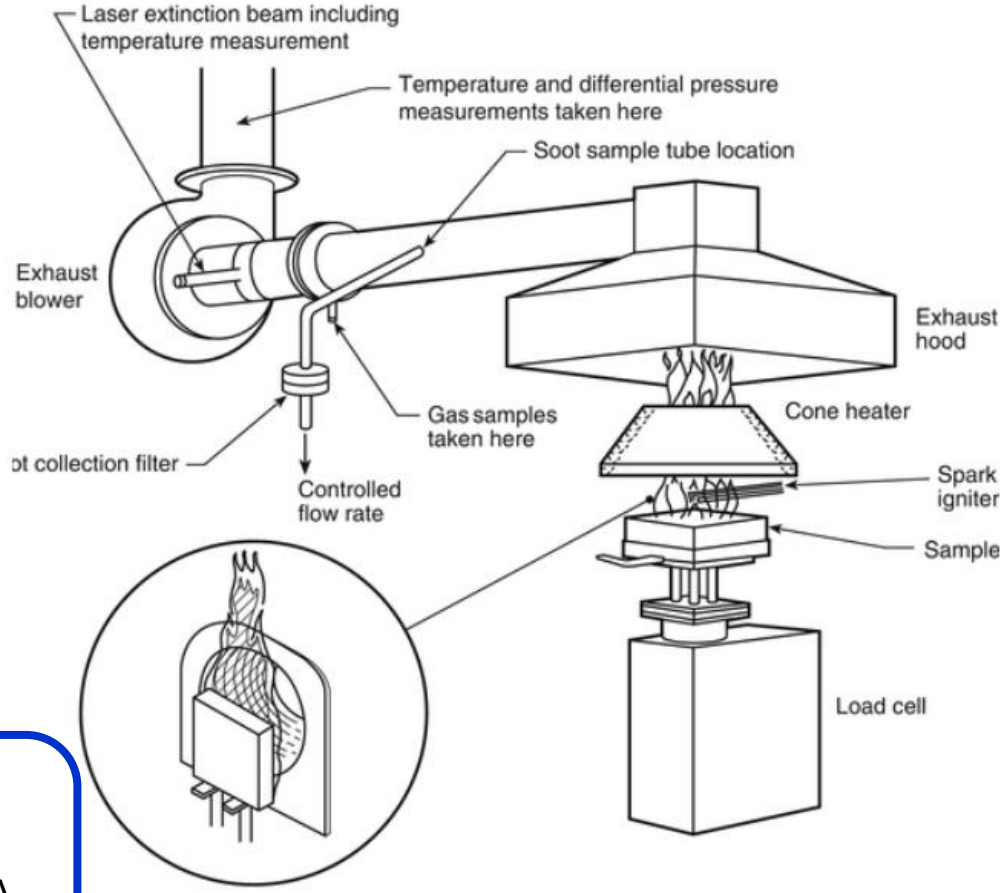


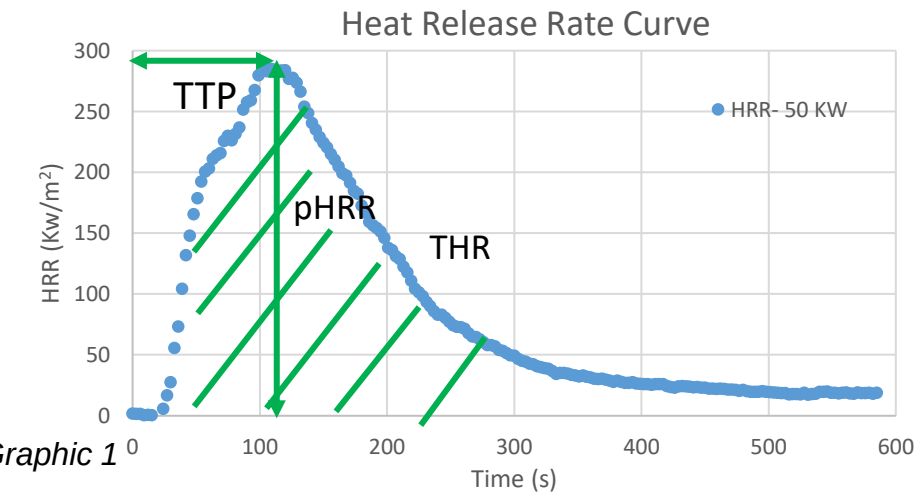
EN 13823 (SBI)

Small lab scale tests for modeling the large scale tests

Cone calorimetry ISO 5660 / ASTM E 1354

Heat evaluation	
peak HRR (kW/m²)	Peak of HRR curve
t peak HRR (s)	Time to peak
THR a 600 s (MJ/m²)	Total Heat Release at 600 s
THR a 1200 s (MJ/m²)	Total Heat Release at 1200 s
FIGRA (W/s)	Fire Growth Rate Index
Smoke Emission	
peak SPR (m²/s)	Peak of SPR curve
TSP a 600 s (m²)	Total smoke production at 600 s
TSP a 1200 s (m²)	Total smoke production 1200 s





Graphic 1

A good FR has got

- ↓ pHRR, THR, FIGRA
- ↑ TTP

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THR a 600 s (MJ/m²)	Total Heat Release at 600 s
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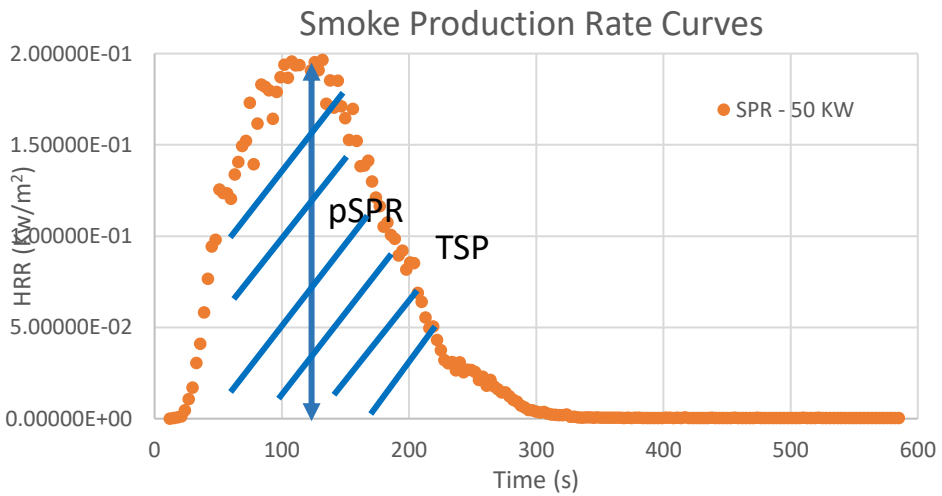
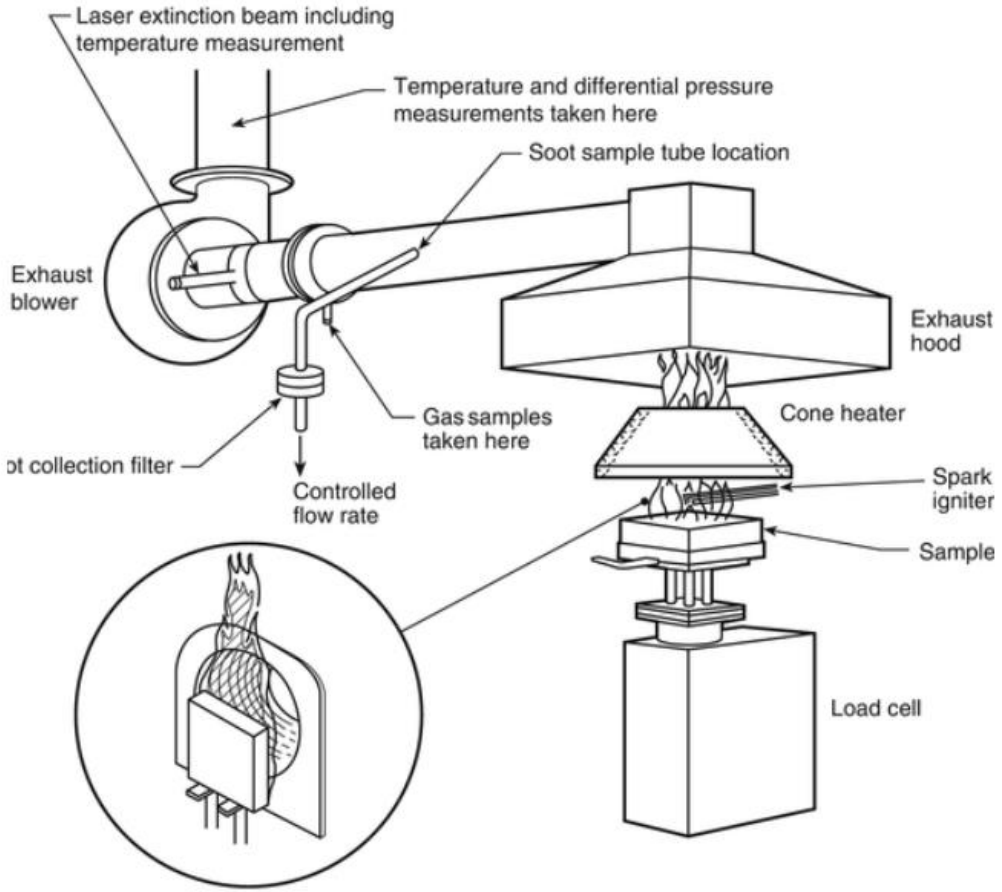
FIGRA (W/s)	Fire Growth Rate Index
Smoke Emission	
peak SPR (m²/s)	Peak of SPR curve
TSP a 600 s (m²)	Total smoke production at 600 s
TSP a 1200 s (m²)	Total smoke production 1200 s
SMOGRA (m²/s²)	Smoke Growth Rate Index

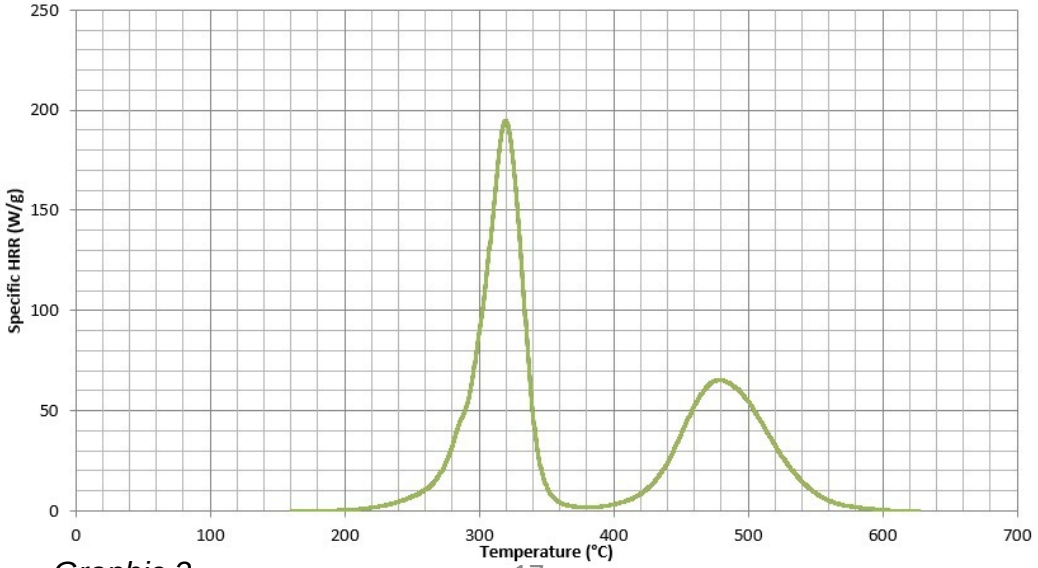




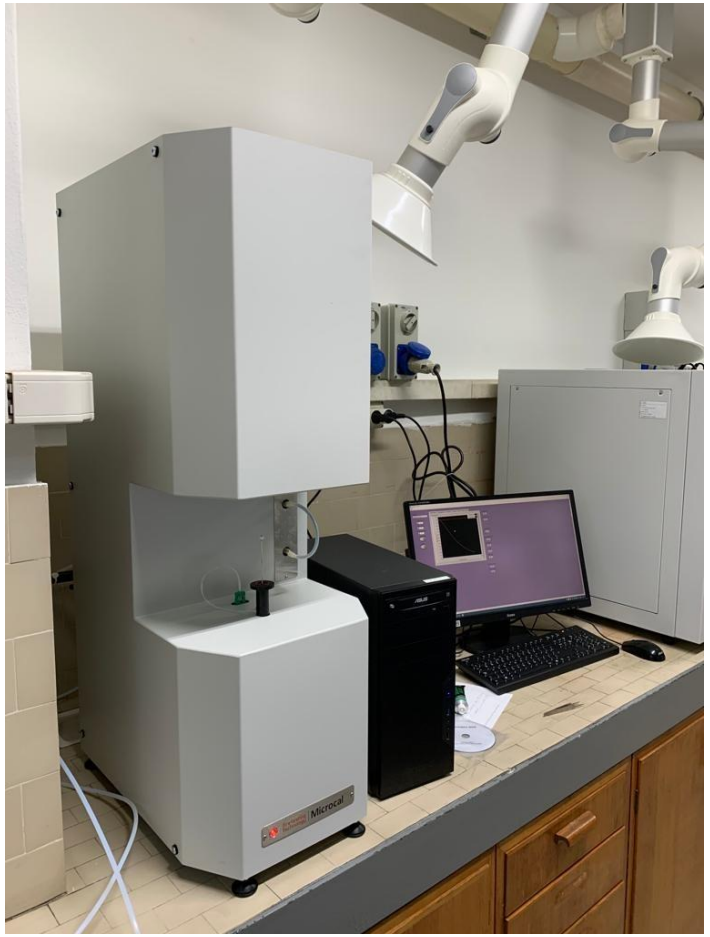
Small lab scale tests for modeling the large scale tests

Micro Combustion Calorimetry (MCC) according to ASTM D 7309

Heat evaluation	
FGC kW/g-K]	Fire Growth Capacity
ηc	Heat release capacity
Q max [kW/g-K]	Maximum specific heat release rate
Tmax [K]	Heat release temperature
hc [J/g]	Specific (total) Heat Release
Yp [g/g]	Yield of pyrolysis residue
hc gas [J/g]	Specific heat of combustion of fuel gases



Graphic 2



MCC in Reagens Lab

MCC test apparatus A test specimen between 5 mg and 50 mg is weighted and pyrolyzed in a specific range of temperatures. The gases are collected and burnt in oxygen and the specific heat release rate curve is measured. That give us the possibility to measure parameters like heat release capacity and the fire growth capacity to evaluate the fire performances of the material

[10]

ATO free solutions for PVC-U

The product name of ATO alternative is: Reaguard B-FR/9100

1) It is not classified according to CLP.

2) It has more stable price in comparison to ATO.

3) It is a flame retardant acting in condensed phase, but also a strong smoke suppressant.

4) It boosters thermal stability

5) It shows a good synergism with FR fillers as aluminum trihydroxide (ATH), and magnesium hydroxide (MDH) etc.

Formulations

Not Thermoformable Sheet	3 mm thickness	**FP0**	**FP1**	**FP2**	**FP3**
PVC NORVINYL S 6030	PVC Resin Suspesion K60	100	100	100	100
KANE ACE FM 50	Acrylic Impact Modifier	2,5	2,5	2,5	2,5
Realube ORI	Castor Oil	1	1	1	1,0
REAPAK G-LE/6010	Thermal Stabilizer	3,5	3,5	3,5	3,5
Kronos 2220	TiO2	0,8	0,8	0,8	0,8
HYDROCARB 95 T	Calcium Carbonate (Fine GCC)	15	-	-	-
Ecopyren 3,5 C	Magnesium hydroxide (Brucite)	-	15	15	15
RI002	Antimony Trioxide	6	-	-	-
Reaguard B-FR/9100	Flame retardant and smoke suppressant	-	6	9	11

Cone calorimetry results

		FP0	FP1	FP2	FP3
Heat flux	**50 kW/m²**	**ATO 6 phr**	**REA 6 phr**	**REA 9 phr**	**REA 11 phr**
Heat evaluation					
peak HRR (kW/m²)	Peak of HRR curve	**116**	**88**	**90**	**87**
t peak HRR (s)	Time to peak	**280**	**240**	**275**	**375**
THR a 600 s (MJ/m²)	Total Heat Release at 600 s	**24,79**	**28,27**	**29,79**	**24,76**
THR a 1200 s (MJ/m²)	Total Heat Release at 1200 s	**37,47**	**41,54**	**44,96**	**39,76**
FIGRA (W/s)	Fire Growth Rate	**397**	**369**	**355**	**261**
Smoke Emission					
peak SPR (m²/s)	Peak of SPR curve	**0,136**	**0,084**	**0,070**	**0,066**
TSP a 600 s (m²)	Total smoke production at 600 s	**20,99**	**12,81**	**13,38**	**11,85**
TSP a 1200 s (m²)	Total smoke production 1200 s	**20,99**	**12,81**	**13,38**	**11,85**
SMOGRA (m²/s²)	Smoke Growth Rate	**6,57**	**< LOQ**	**< LOQ**	**< LOQ**

Cone calorimetry results

	FP0	FP1	FP2	FP3
Heat flux	**ATO 6 phr**	**REA 6 phr**	**REA 9 phr**	**REA 11 phr**

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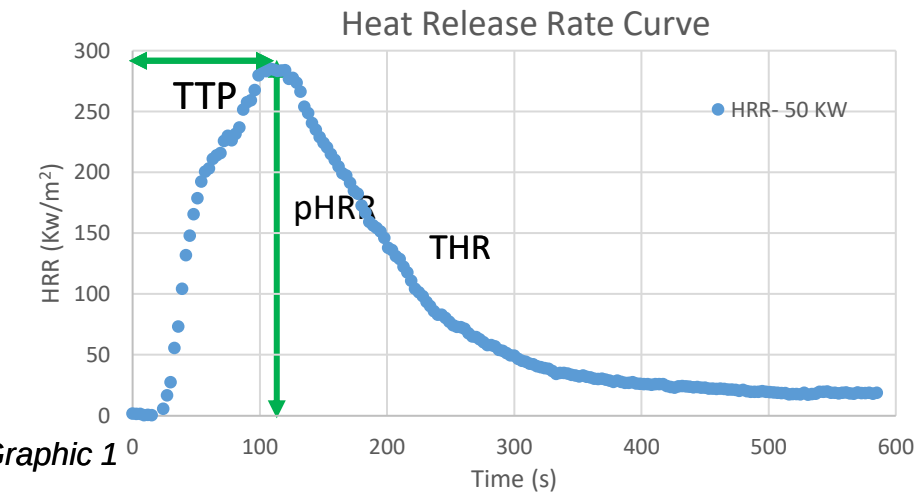
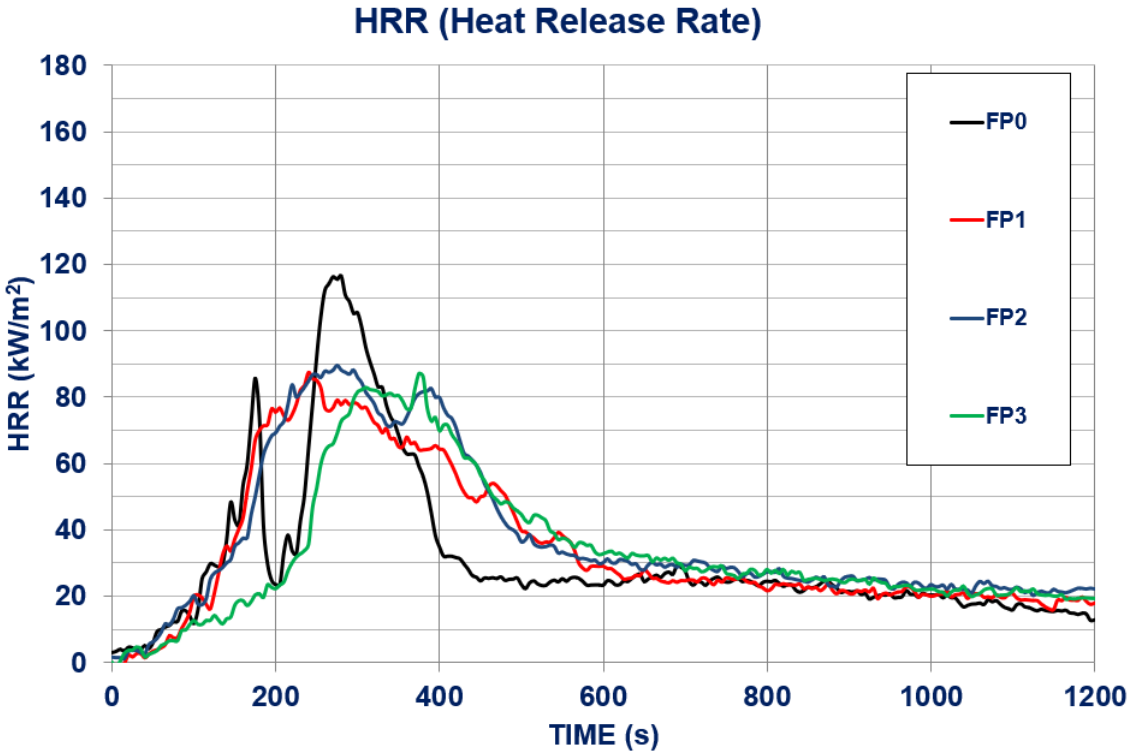
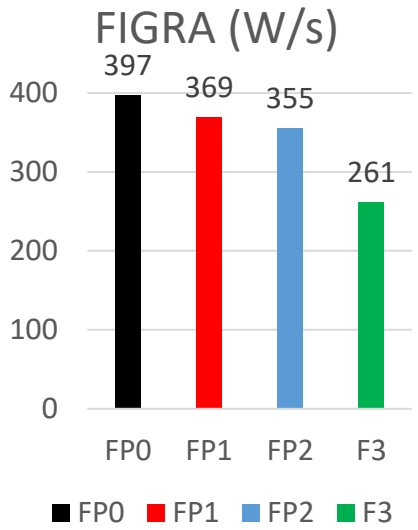


Graphic 1





A good FR has got

- pHRR, THR, FIGRA ↓
- TTP ↑

Cone calorimetry results

	FP0	FP1	FP2	FP3
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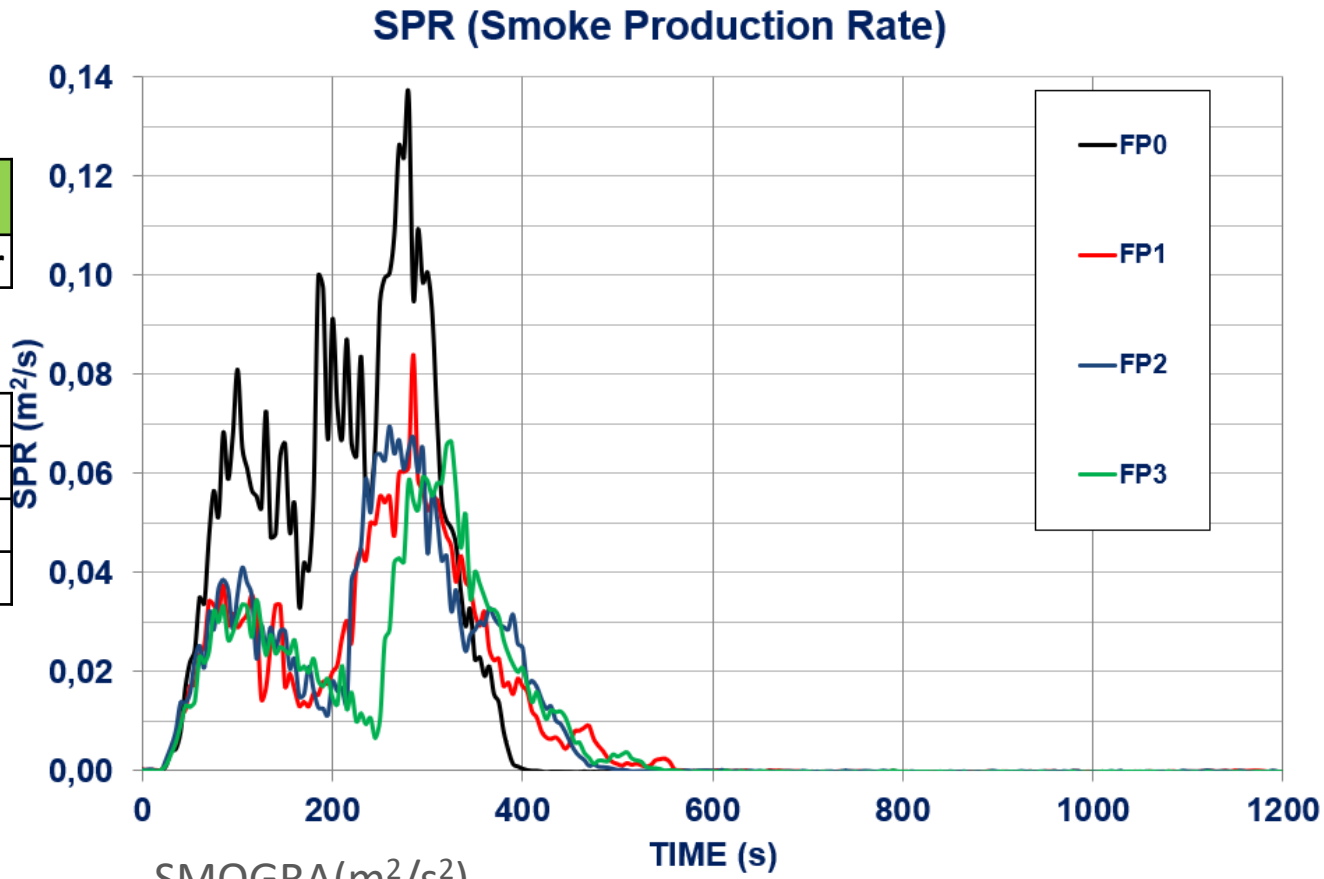
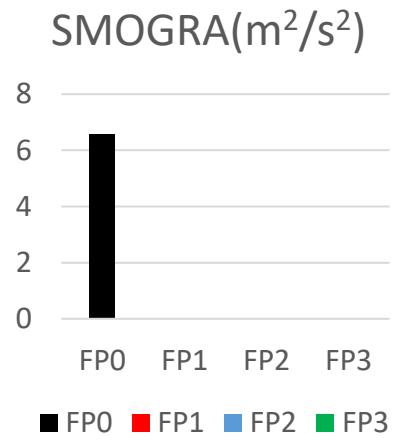
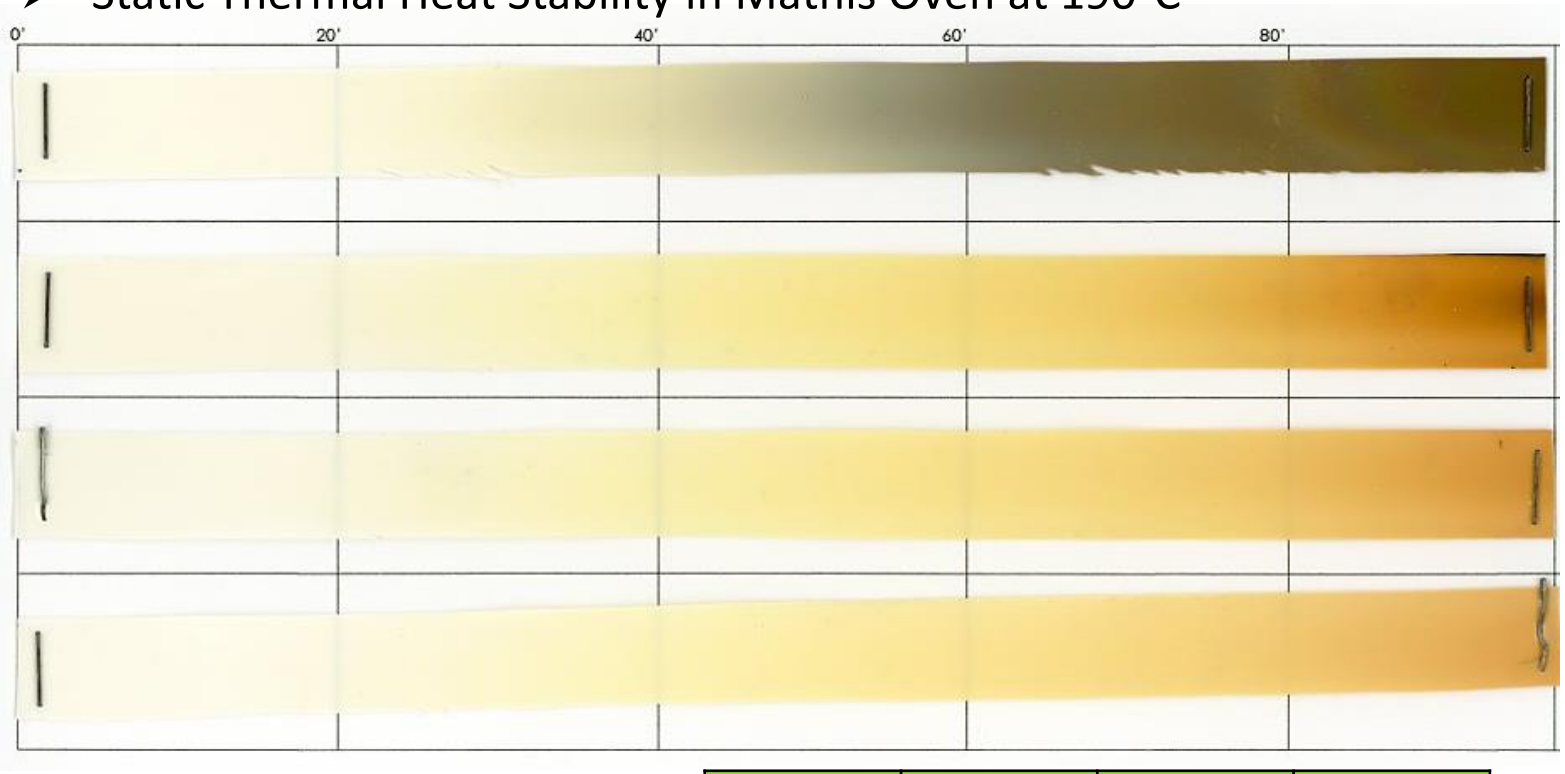
TSP a 1200 s (m^2)	**20,99**	**12,81**	**13,38**	**11,85**
SMOGRA (m^2/s^2)	**6,57**	**< LOQ**	**< LOQ**	**< LOQ**





Main characteristics, heat stability & color hold

- Static Thermal Heat Stability in Mathis Oven at 190°C



FP0
ATO @ 6 phr

FP1
B-FR/9100 @ 6 phr

FP2
B-FR/9100 @ 9 phr

FP3
B-FR/9100 @ 11 phr

Pressed kneader plate	FP0	FP1	FP2	FP3
L*	89,70	88,13	89,80	91,07
a*	-1,28	-2,10	-1,83	-1,77
b*	11,26	13,34	11,97	10,82
CR [min] (EN 60811-405)	59	77	86	91

Comments

- ATO is under ECHA “magnifying glass”. Parallelly, it will suffer more and more of shortage ↔ price fluctuations.
- Reagens is able to model the behavior of a fire on a small scale test (through CC and MCC) highlighting key parameters such as smoke emitted and heat released.
- REAGUARD B-FR/9100 can be a valid alternative to ATO both in terms of performance and of competitive price.
- The CC evidences that REAGUARD B-FR 9100 act in condensed phase 1) smothering the flame 2) reducing heat emission and especially 3) reducing smoke emission.
- A low smoke emission can do the difference b/w life/death: people can escape unharmed from the fire scenario or be rescued by firefighters.
- In the context of CPR, the reduction of smoke emission allows PVC-U B&C products to be in class s_1 or s_2.

Bibliography

[1] C. E. Wilkes, J. W. Summers, C. A. Daniels, Mark T. Berard. (2005). "PVC Handbook". (1st ed.). Hanser.

[2]Hirschler, M. Interscience Communications, London, UK, 14–15 February 2006.

[3] V. Babrauskas, R. D. Peakock. Fire Safety Journal, 1992, 18(3), 255 – 272.

[4] LAST UPDATE: DECISION ON SUBSTANCE EVALUATION: ECHA dated 12/03/2020

[5] Mineral Commodity Summaries; 2007

[6] Mineral Commodity Summaries; 2023

[7] Blu line and dots. ATO price calculated by Sb quotation + extra costs as AMC applies;

[8] Green dots ATO prices applied by main players in Europe;

[9] Red dots. Customer Interviews about ATO price level during visits, formalized in VR or telephone interviews to customers

[10] Bassi, I.; Delchiaro, F.; Bandinelli, C.; Mazzocchetti, L.; Salatelli, E.; Sarti, G. A New Perspective on Hydrogen Chloride Scavenging at High Temperatures for Reducing the Smoke Acidity of PVC Cables in Fires, IV: The Impact of Acid Scavengers at High Temperatures on Flame Retardance and Smoke Emission. *Fire* **2023**, *6*, 259. https://doi.org/10.3390/fire6070259