Development of Flame Retardant Formulation for Cables

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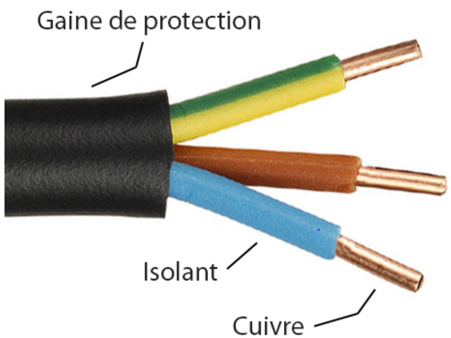
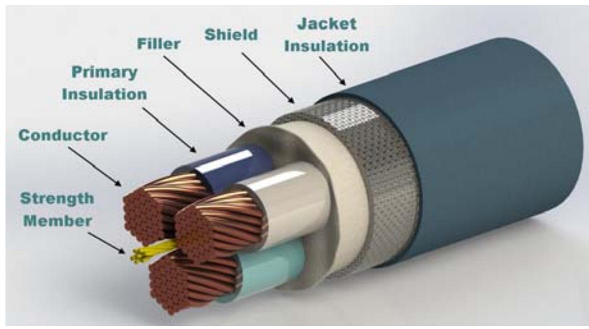
Cables are a major concern for fire safety in building

- ✓ 100 m² of office contain 200 kg of cable
- ✓ 48% of residential fires are attributed to electrical distribution systems between 2007-2011 (US) and in 30 % of the cases, a cable/wire was the source of ignition
- ✓ Cables can spread fires in particular due to cables tray in building - Propagation of the fire through floors and doors
- ✓ Cables are complex





Fire retardancy or fire protection?

Fire retardancy

- Why?
  - To save lifes
- How?
  - Delaying the fire growth
- Means?
  - Decreasing the fire kinetics

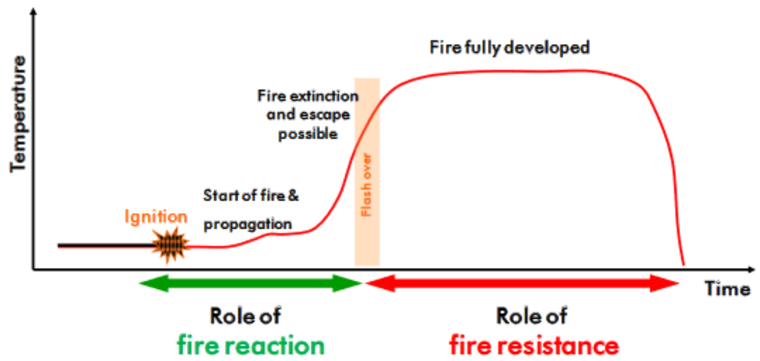
Fire protection

- Why?
  - To save lifes
- How?
  - Limiting the progressing of fire from one to another area
- Means?
  - Using fireproof barriers to compartment the fire areas

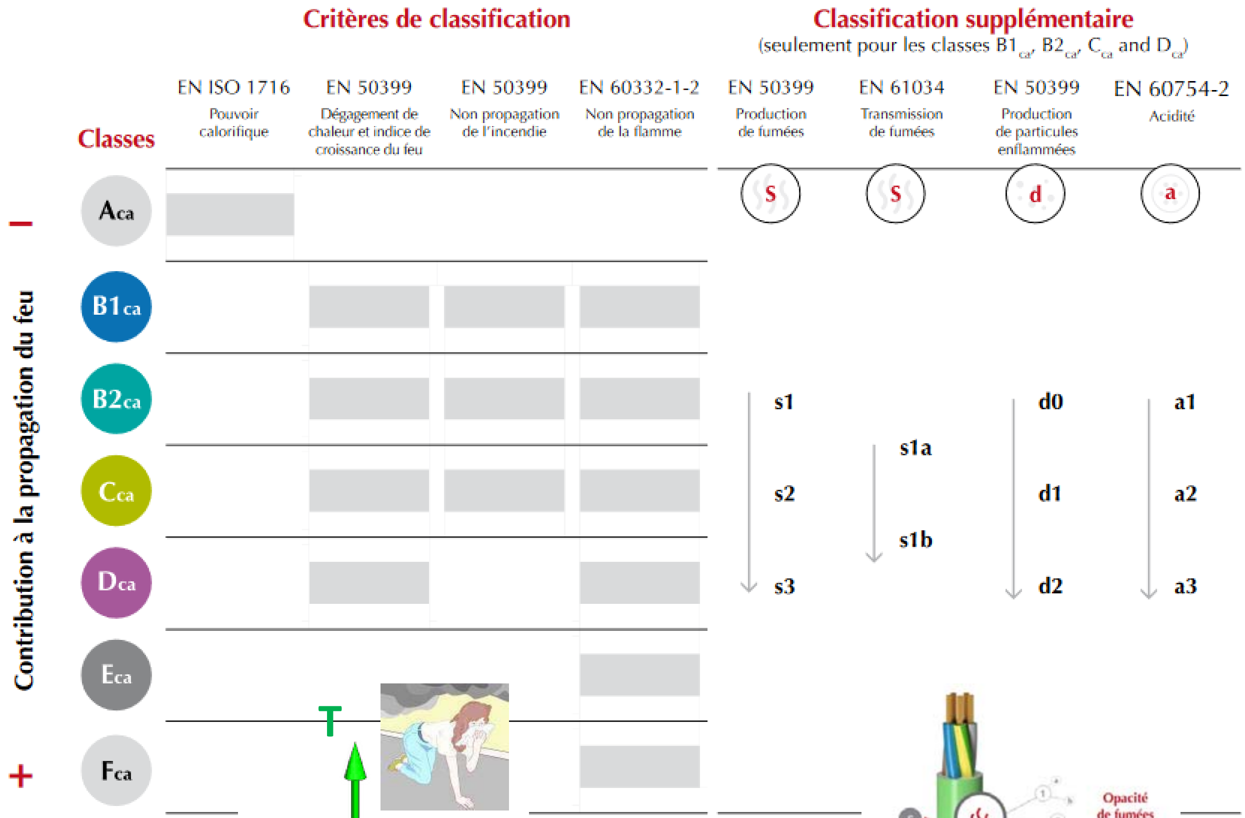
Cables

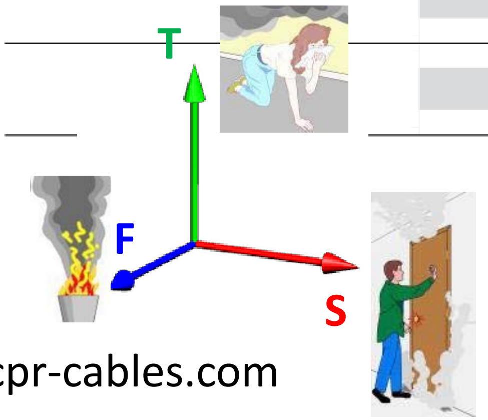
will continue to operate normally in the presence of prolonged fire for a specified time under defined conditions

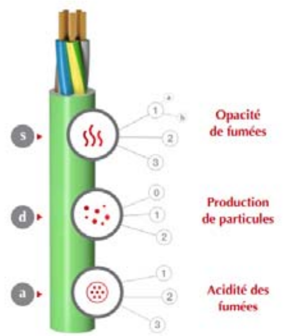
will resist the propagate of fire into a new area



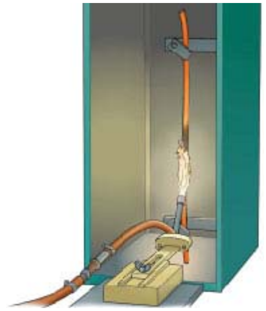
Fire retardancy : Euroclass







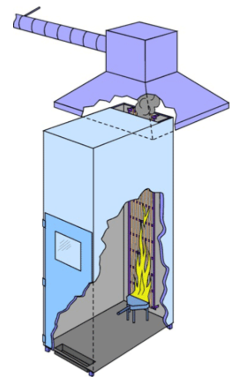
http://cpr-cables.com



EN 60332-1-2

Small scale method:

- 1 kW burner
- 0.5 m of cable

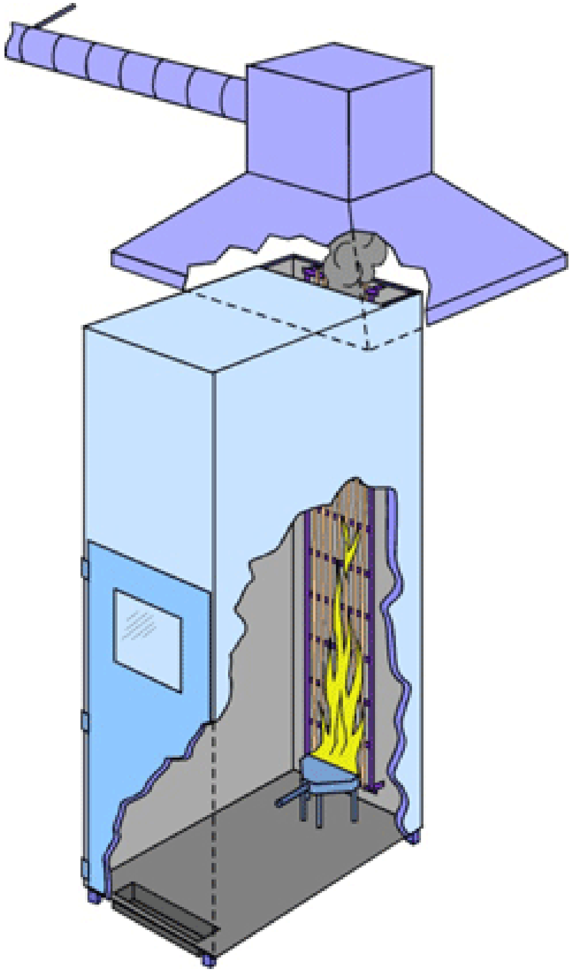


EN 50399

Large scale method:

- 20.5 or 30 kW burner
- > 20 m of cable

EN 50399



- Box size : 1 x 2 x 4 m / Specimen = 17*3,5 m long cables
- Burner : 20.5 or 30 kW (different scenario)
- Measure HRR, THR SPR, flame spread,

Fire Growth Rate Index → FIGRA = max (HRR/t)

- Main differences with classical tests (cone, etc.):
  - Based on cables → multi component system / complex geometry
  - → More complex – larger scale
  - Burner is applied during all the test (20 min)
  - → ≠ than UL-94 test
  - Study of flame spread
  - → ≠ than cone experiment

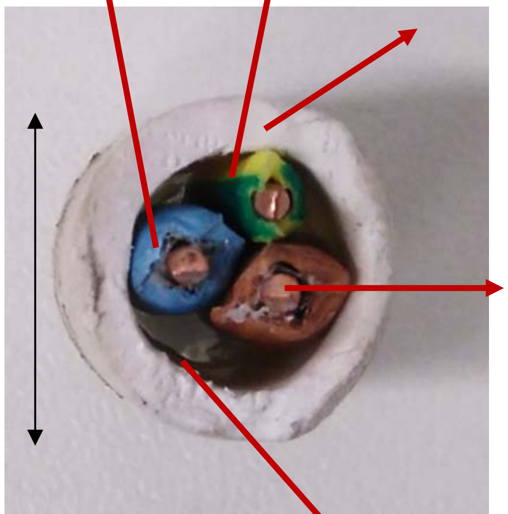
→ No correlation between classical test and standards

Development of FR Cable : Our approach

Insulation
Flame retarded thermoplastic

Insulation
Non-FR thermoplastic

Sheathing/Jacket
PE / ATH
EVA / ATH
+ synergists

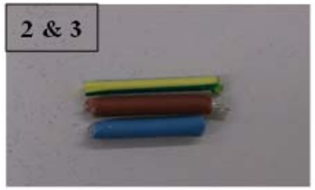


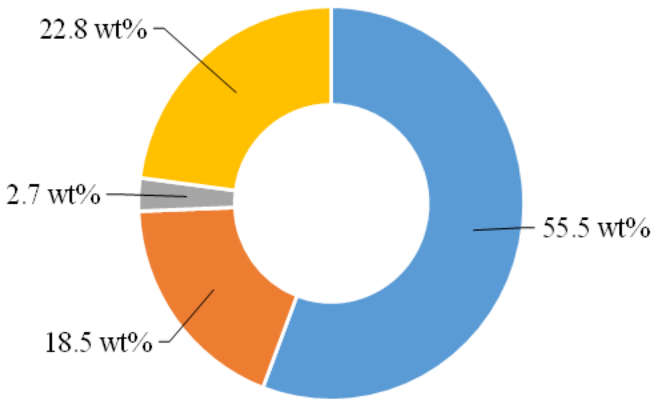
12mm

Copper core

Tape

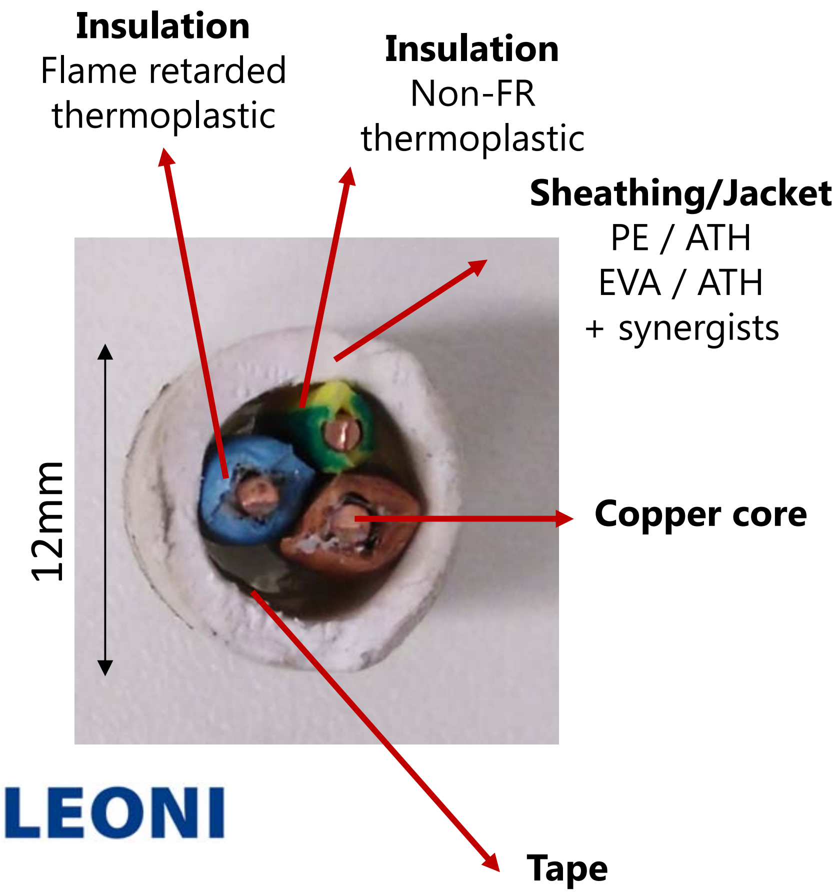
LEONI

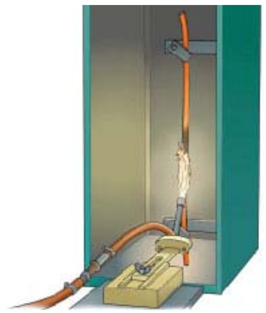




1 - Sheathing 2 - HFFR insulator 3 - Non-FR insulator 4 - Conductors

Development of FR Cable : Our approach





EN 60332-1-2

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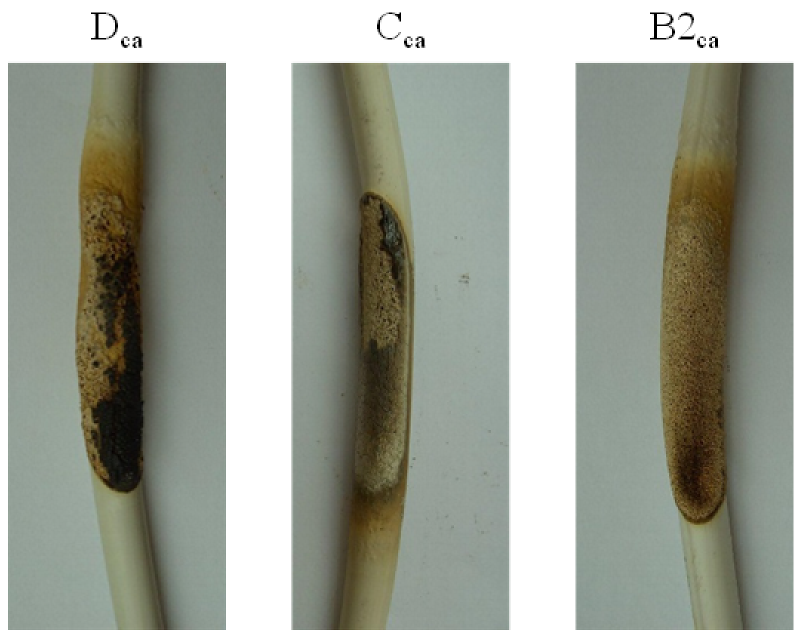
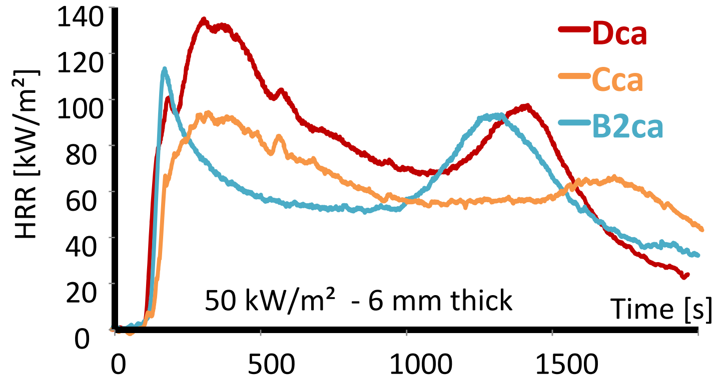
- 0.5 m of cable



Development of FR Cable : Our approaches

LEONI

		D_{ca}	C_{ca}	$B2_{ca}$
Cone on raw materials e.h.c [MJ/kg]	Sheating	24.5	20.0	20.6
	HFFR Insulator	25.3	25.3	25.3
	No-FR Insulator	38.2	38.2	38.2
Cone on sheating	TTI [s]	83	113	147
	pHRR [kW/m²]	137	98	119
	THR [MJ/m²]	131	95	111



	Ca_D_{ca}_Be1	Ca_C_{ca}_Be1	Ca_$B2_{ca}$_Be1
1 – Sheathing	71 %	66 %	68 %
2 – HFFR insulator	24 %	28 %	26 %
3 – Non-FR insulator	5 %	6 %	6 %
Total Heat Released [MJ/m_{cable}]	3.47	3.02	3.18

Development of FR Cable : Our approaches

LEONI

- Sheathing :
  - 65-75% of the heat released when a cable burns
  - Protect the underlying material

  → **Key component in cable design**

- Idea of the test:

  Study flame spread on a whole cable

Study flame spread on a thin sheathing material

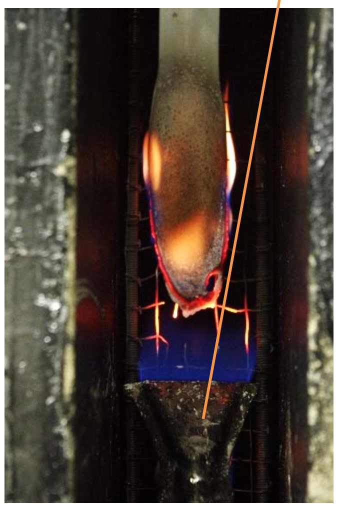
→ Avoids cable production

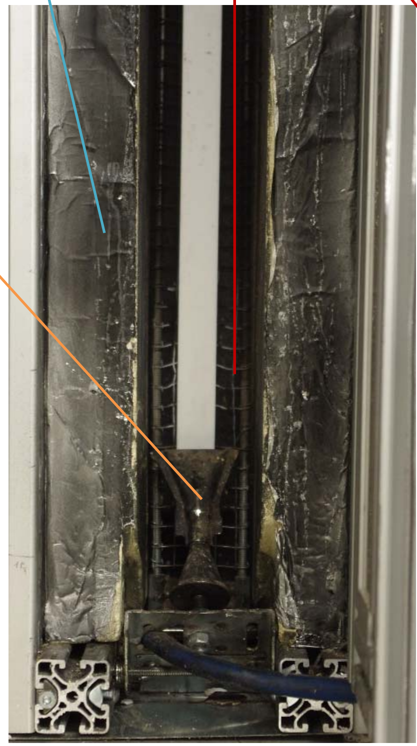
→ Lower amount of material for test specimen

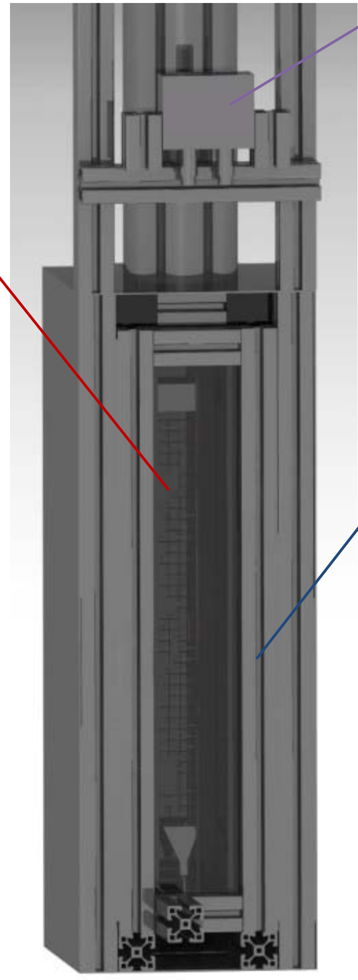
→ More suitable screening tool

Small scale test apparatus

- ≈1/8 scaled down enclosure of EN 50399
- Parameters observed:
  - Flame spread
  - HRR, THR, FIGRA

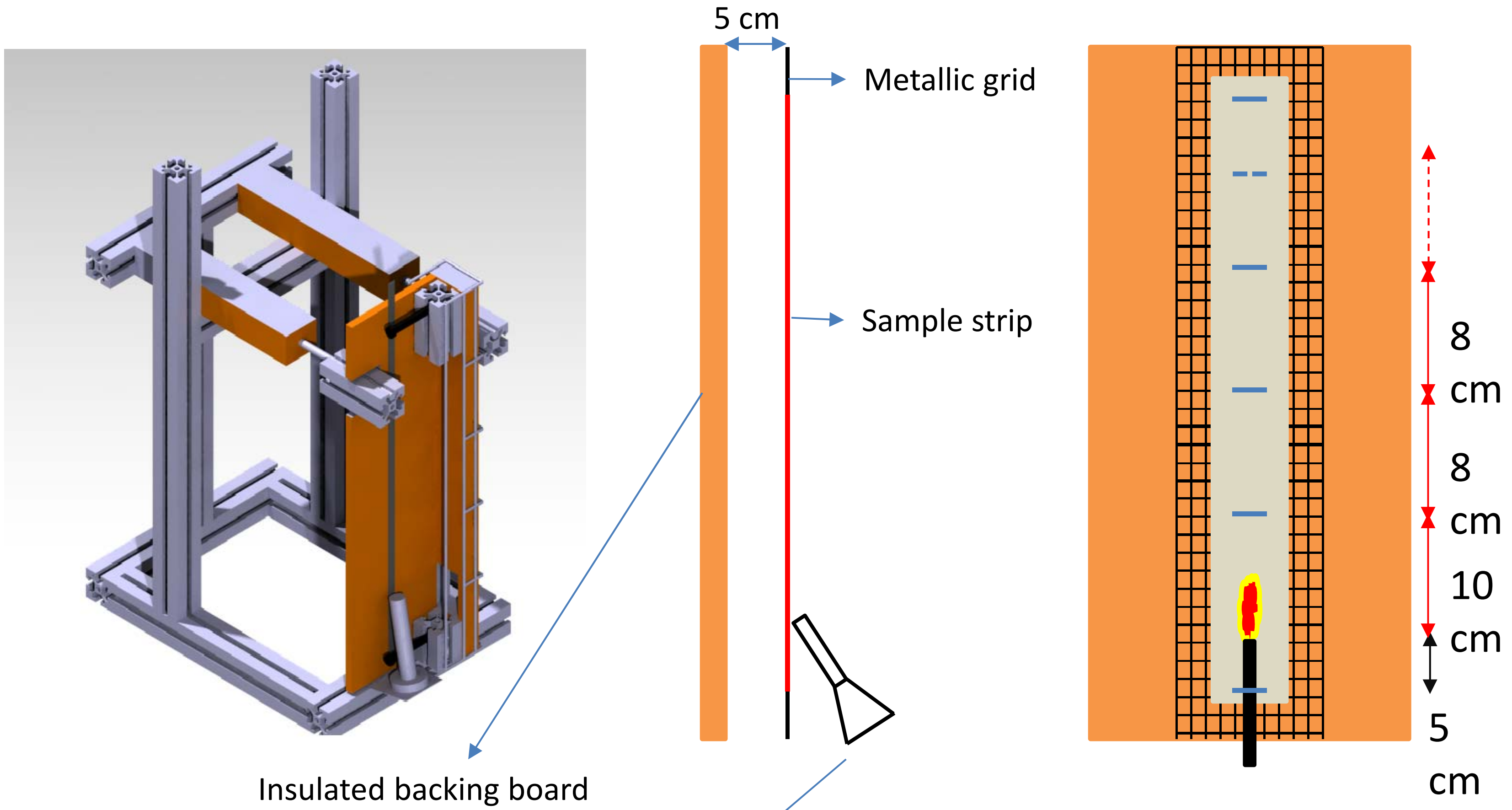






$$\dot{q}(t) = E(\dot{m}^0_{O_2} - \dot{m}^t_{O_2})$$

Small scale test apparatus

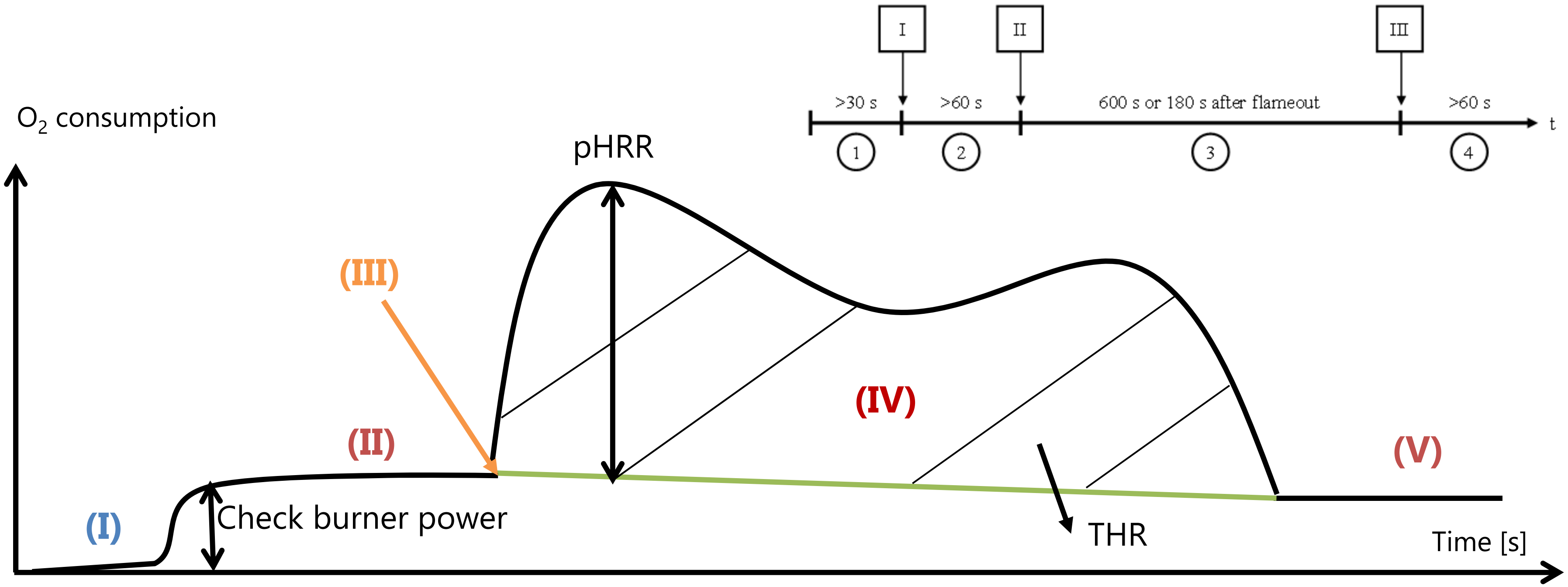


50 W burner
Flame is applied during all the duration of the test

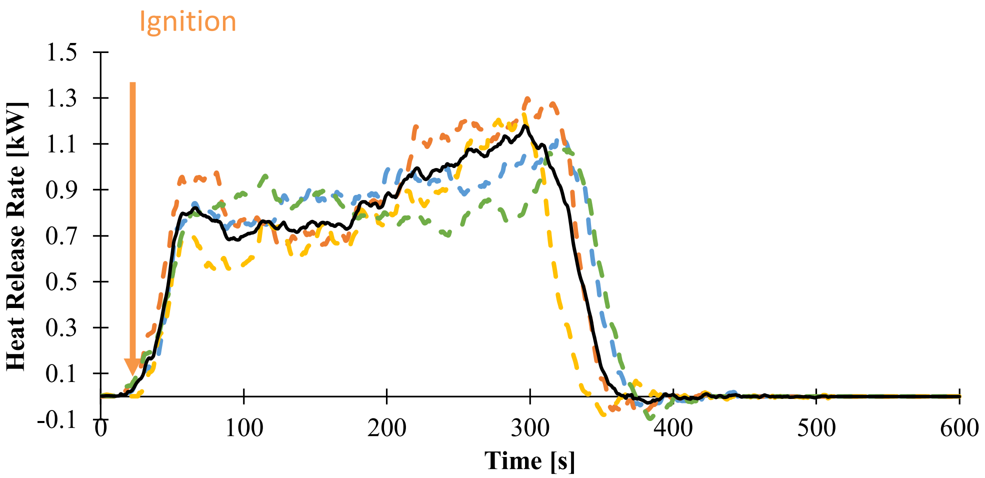
- Time to ignition/flameout ?
- Flame Spread ?
- “Strength” of the residue ?

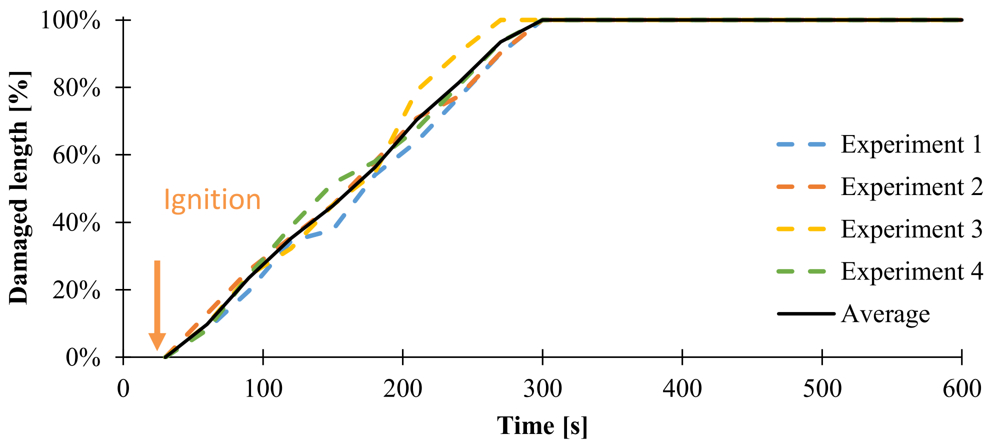
Test protocol

- Collect background for O_2 analyzer <u>without</u> burner **(I)**
- Collect background for O_2 analyzer <u>with</u> burner **(II)**
- Application of the burner on the sample **(III)**
- Measurement of HRR by oxygen depletion and Flame Spread by visual observation **(IV)**
- After flame out, baseline <u>with</u> burner to check if no drift of the burner power **(V)**



Repeatability of the measurement



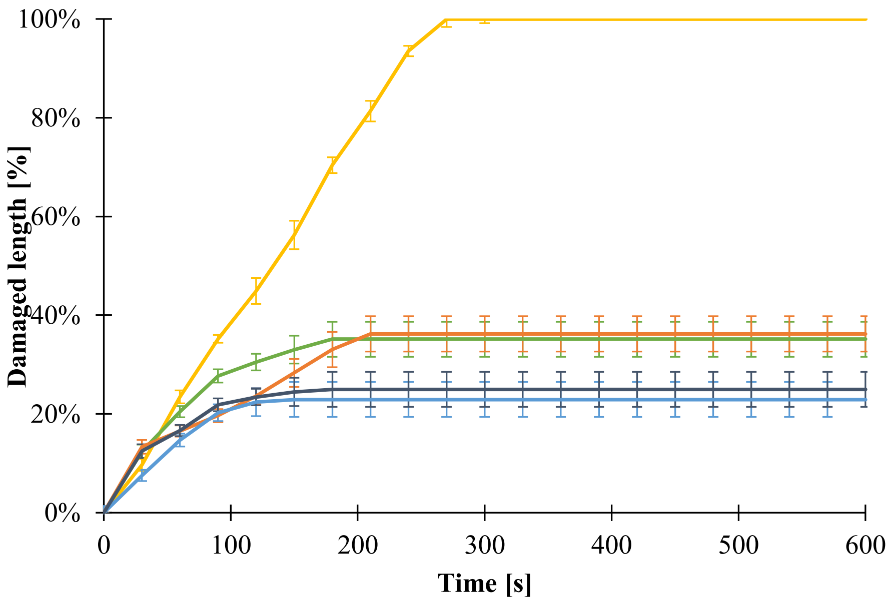


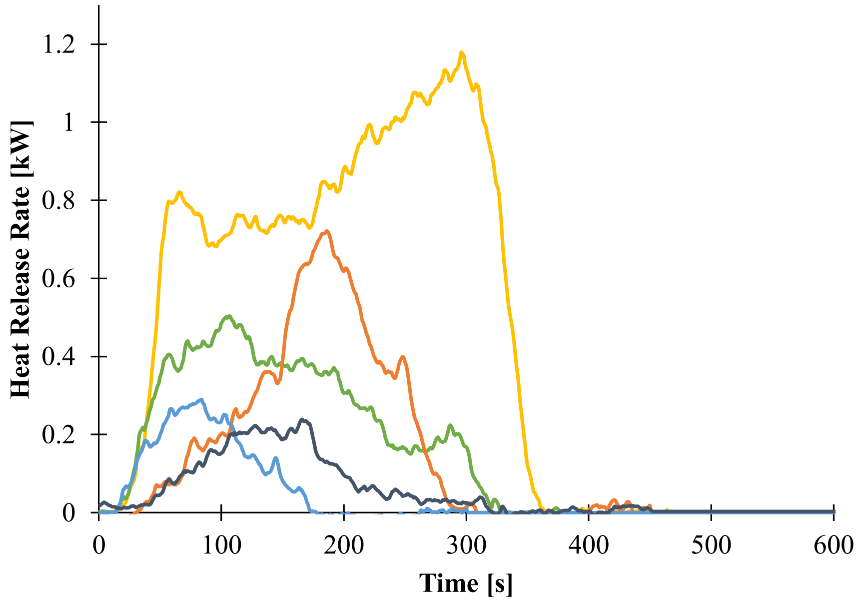
- For a cable classified D_{ca}
  - FS = 100 % (flame spread completely)
  - pHRR = 1,31 kW ± 3,7%
  - FIGRA = 7,22 W/s ± 8,5%
  - THR = 260 kJ ± 5,1%
- Good repeatability of HRR measurement

Flame spread results on benchmark cables

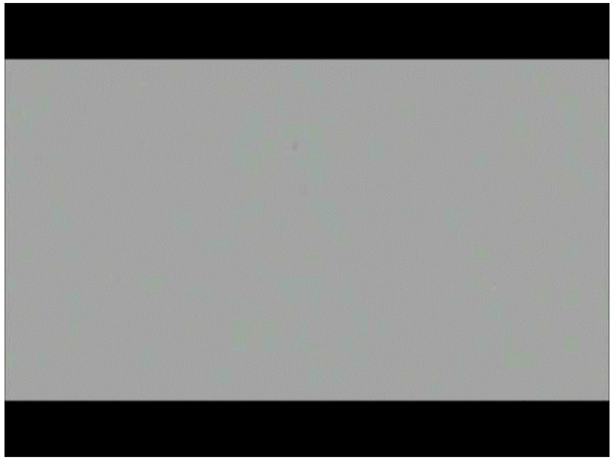
- Selection of 5 different benchmark materials
  - 1 Euroclass D_{ca}
  - 2 Euroclass C_{ca}
  - 2 Euroclass $B2_{ca}$

Fire classification using the bench scale test follows the same trend as in the EN 50399 apparatus





Flame spread results on benchmark cables



CBL2-MOD2-001 – Euroclass D

Time to ignition	40’’
Dripping	2’ 15’’
Time to reach the clamp	6’ 30 ‘’
Time to flameout	7’

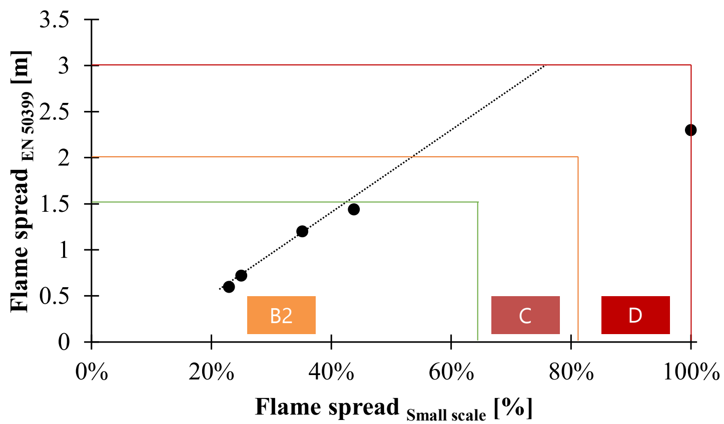
CBL2-MOD2-001 – Euroclass B2

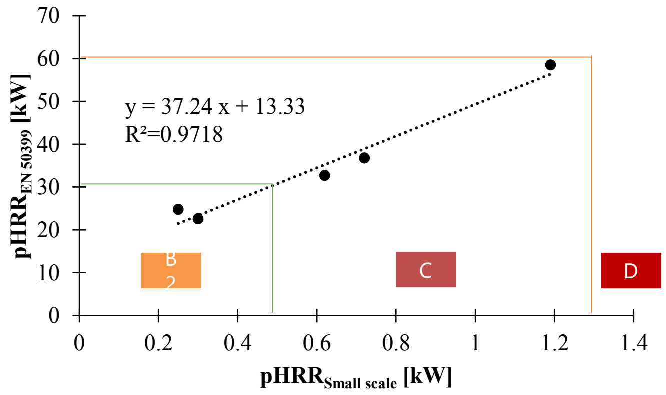
Time to ignition	1’ 10’’
Time to flameout	1’ 50’’
Apparition of a white residue	2’ 40’’
Breaking of the white residue	No

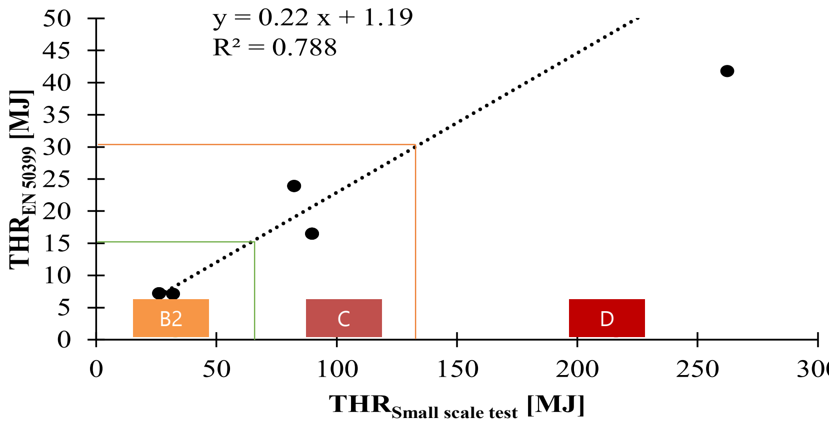
→ **Correlation ?**

Correlation bench-scale test – EN50399

- Search for possible correlations → Plot of test Parameter$_{EN50399}$ vs. Paramater$_{small\ scale}$





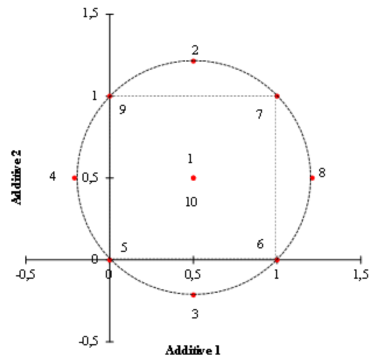


Euroclass	EN 50399	Small scale test
$B2_{ca}$	Damaged length < 1.5 m	Damaged length < 44.2 %
	THR < 15 MJ	THR < 63 kJ
	pHRR < 30 kW	pHRR < 0.45 kW
C_{ca}	Damaged length < 2.0 m	Damaged length < 56.5 %
	THR < 30 MJ	THR < 133 kJ
	pHRR < 60 kW	pHRR < 1.25 kW
D_{ca}	-	Damaged length > 56.5 %
	THR < 70 MJ	THR > 133 kJ
	pHRR < 400 kW	pHRR >1.25 kW

Materials screening

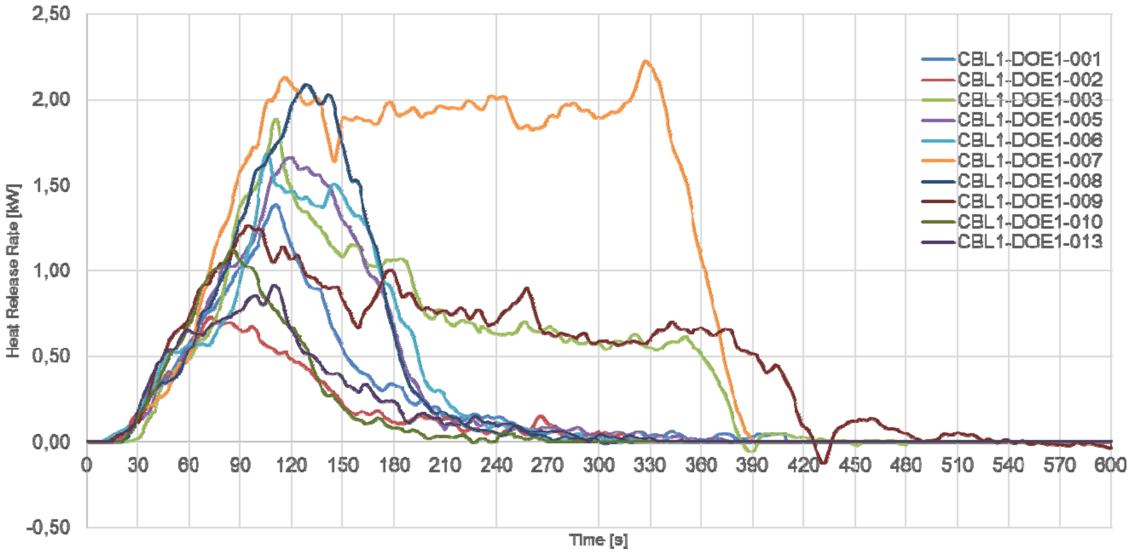
Use of Design of Experiments (surface response)

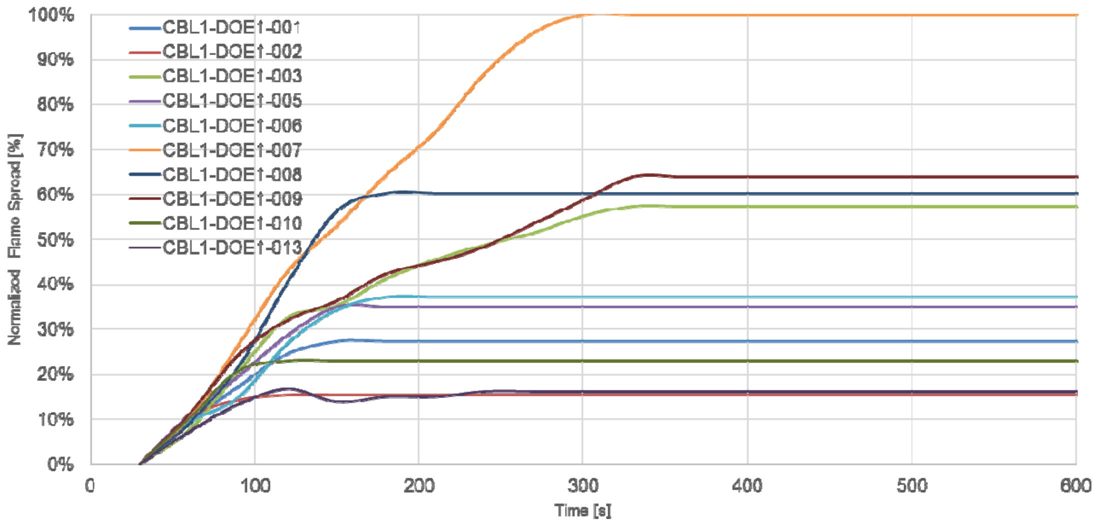
→10 materials
→Small scale test and cone test for comparison



Sample name	Additive 1	Additive 2	ATH	EVA
CBL1_DOE01_001	0,8	5,0	59,2	35
CBL1_DOE01_002	0,8	10,0	54,2	35
CBL1_DOE01_003	0,8	0,0	64,2	35
CBL1_DOE01_004	0,8	5,0	59,2	35
CBL1_DOE01_005	0,0	5,0	60	35
CBL1_DOE01_006	0,2	1,5	63,3	35
CBL1_DOE01_007	1,3	1,5	62,2	35
CBL1_DOE01_008	0,8	5,0	59,2	35
CBL1_DOE01_009	1,3	8,5	55,2	35
CBL1_DOE01_010	1,5	5,0	58,5	35
CBL1_DOE01_011	0,8	5,0	59,2	35
CBL1_DOE01_012	0,8	5,0	59,2	35
CBL1_DOE01_013	0,2	8,5	56,3	35

Materials screening

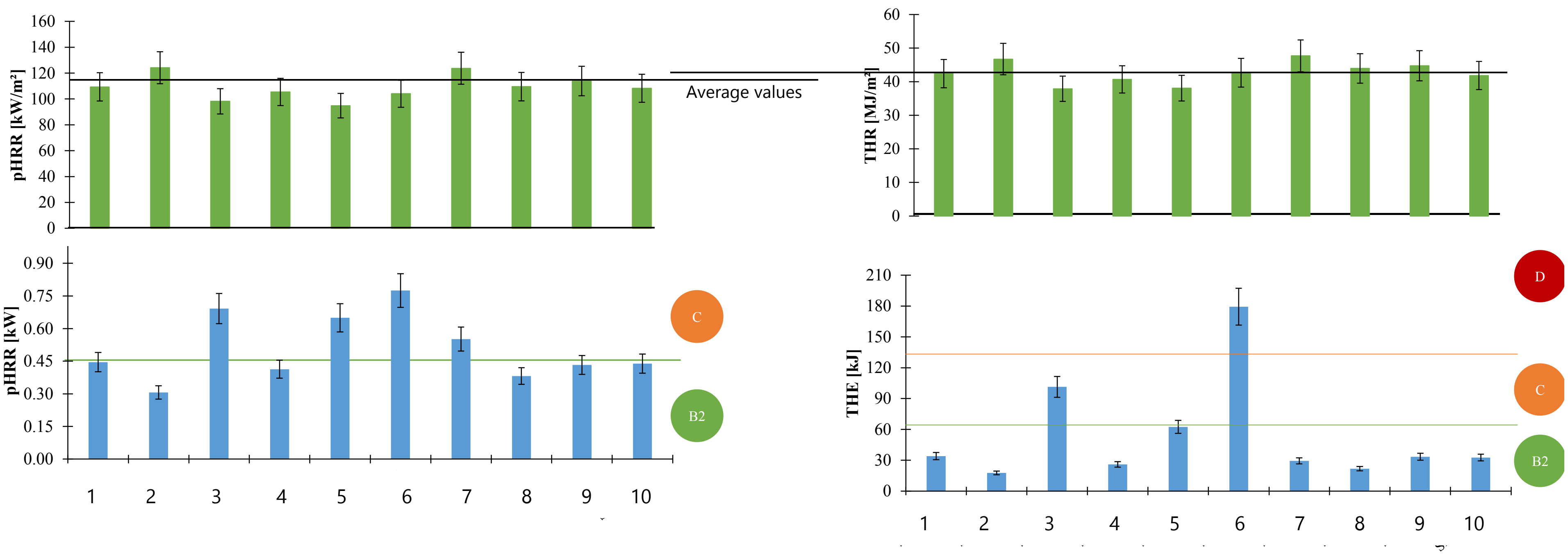




Sample name	Predicted EUROCLASS
CBL1_DOE01_001	C
CBL1_DOE01_002	B2
CBL1_DOE01_003	C
CBL1_DOE01_004	/
CBL1_DOE01_005	C
CBL1_DOE01_006	C
CBL1_DOE01_007	D
CBL1_DOE01_008	D
CBL1_DOE01_009	C
CBL1_DOE01_010	B2
CBL1_DOE01_011	/
CBL1_DOE01_012	/
CBL1_DOE01_013	B2

Materials screening

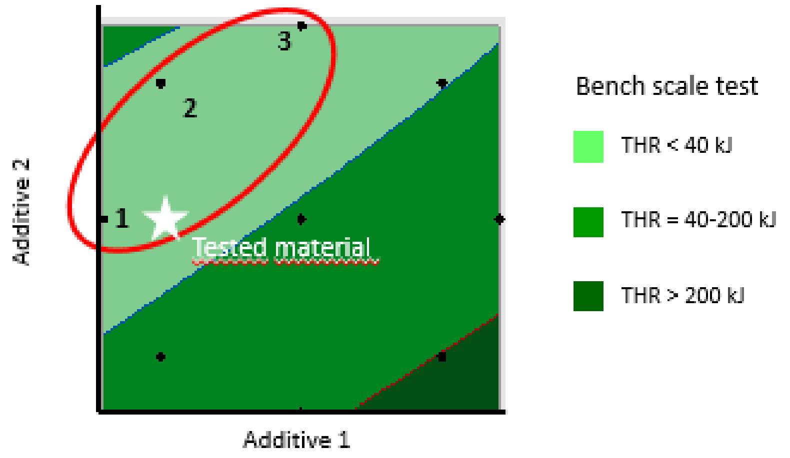
- Cone testing
  - → All the formulation behaves similarly
  - → No indications about flame spread
- Small scale testing
  - → Differences can be observed



→ **Validation ?**

New materials screening

- Choice of the formulation to be tested at the large scale test



	Small scale test	EN 50399 predicted	EN 50399 experiment
Damaged length	34.2 ± 6.1 %	0.84-1.06 m	0.66 m
pHRR	0.43 ± 0.02 kW	28-30 kW	15 kW
THR	25 ± 8 kJ	4.9-8.4 MJ	6 MJ
Classification		$B2_{ca}$	$B2_{ca}$

Conclusion about small scale testing

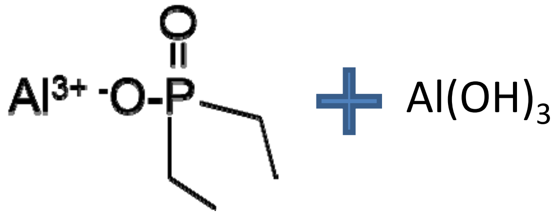
- Development of a small scale test based on large scale standard test
  - Possible to evaluate flame spread and HRR parameters
  - Repeatable measurements
  - Down scaling conserve the Euroclass classification
  - Linear correlations were found

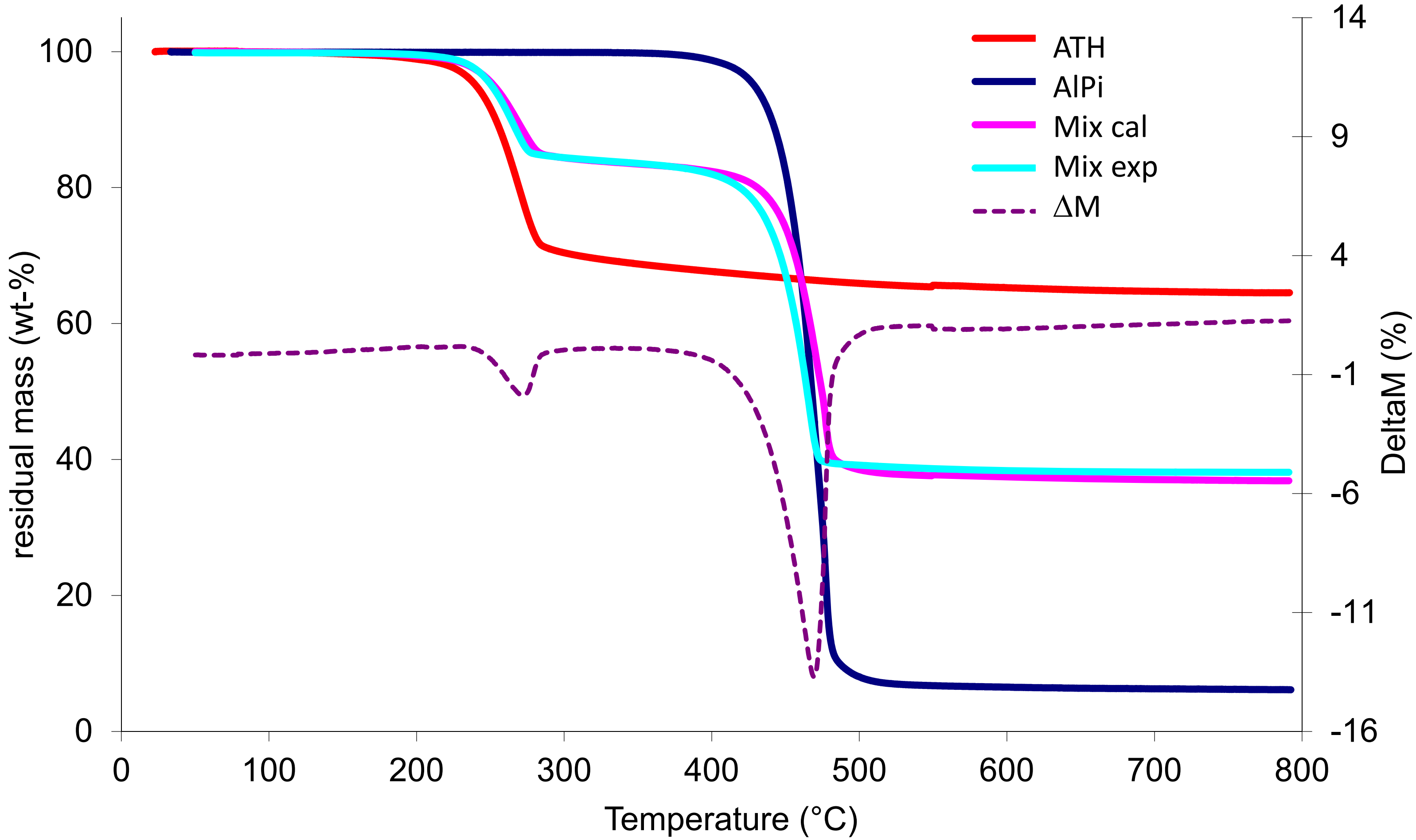
→ Helped to develop a new formulation – Good prediction of the EN50399 results

→ **Mode of action ?**

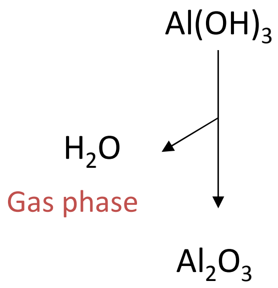
→ **Model System EVM/ATH/AlPi**

Mechanism of action???

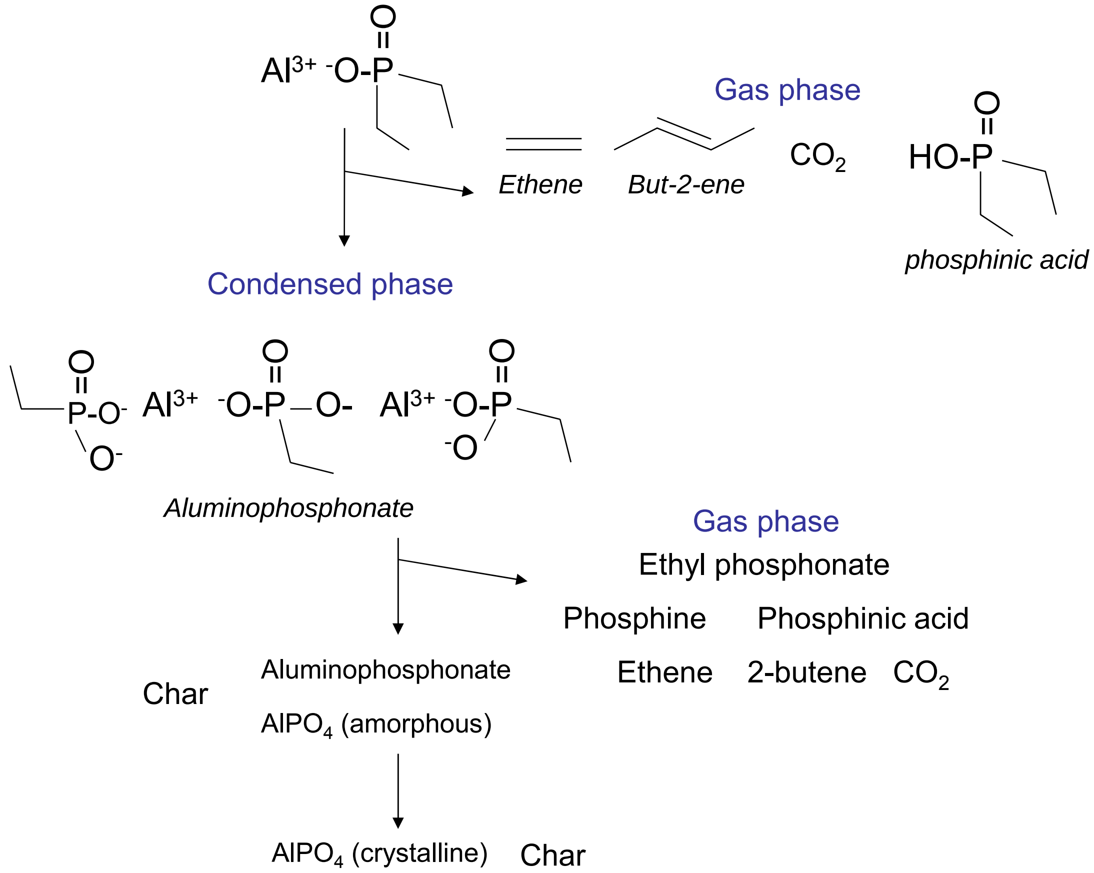




Mechanism of action???



Interactions?



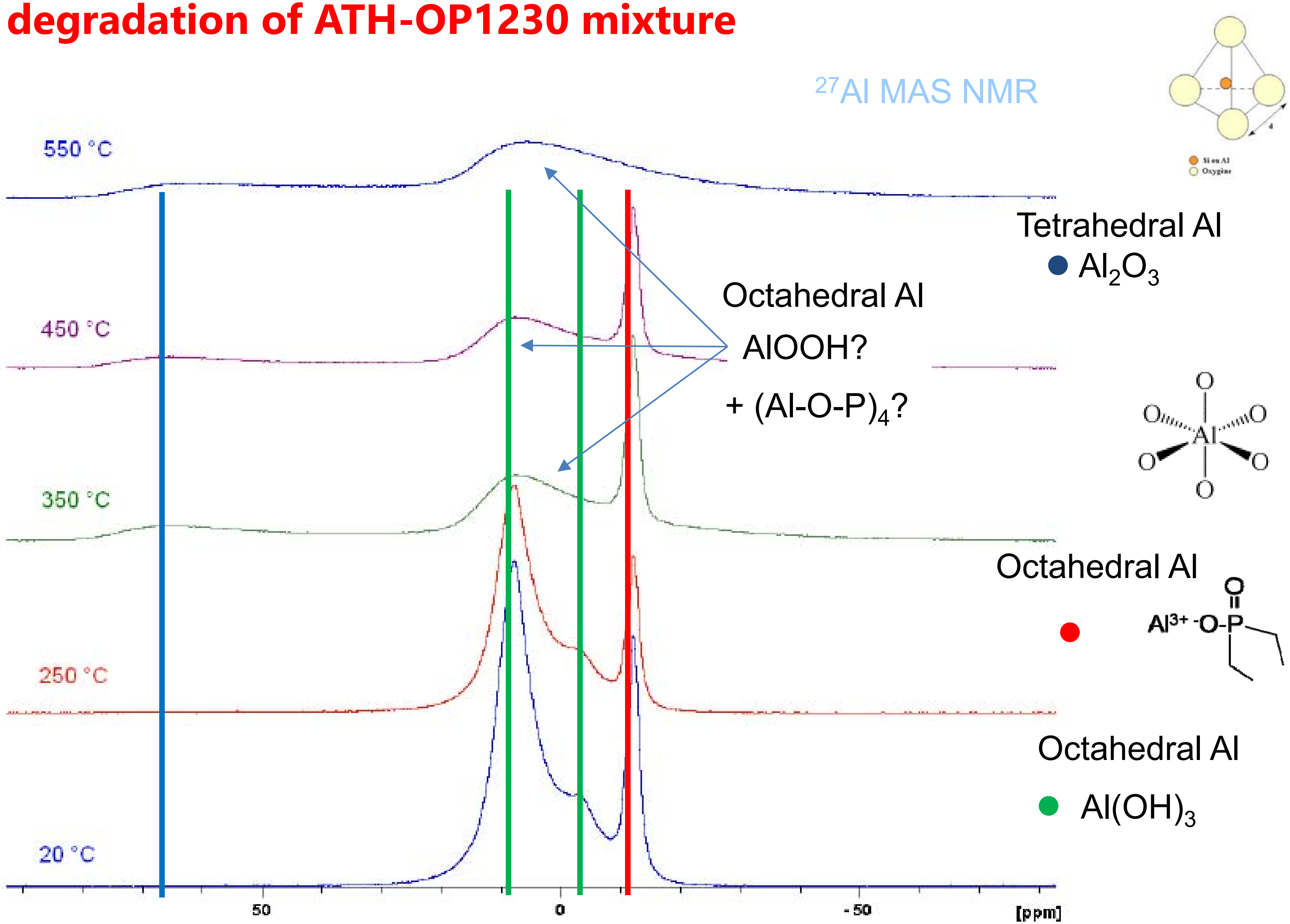

HTT, 250°C,-9.5%


HTT, 350°C,-12%


HTT, 450°C,-27%


HTT, 550°C,-58%

Thermal degradation of ATH-OP1230 mixture



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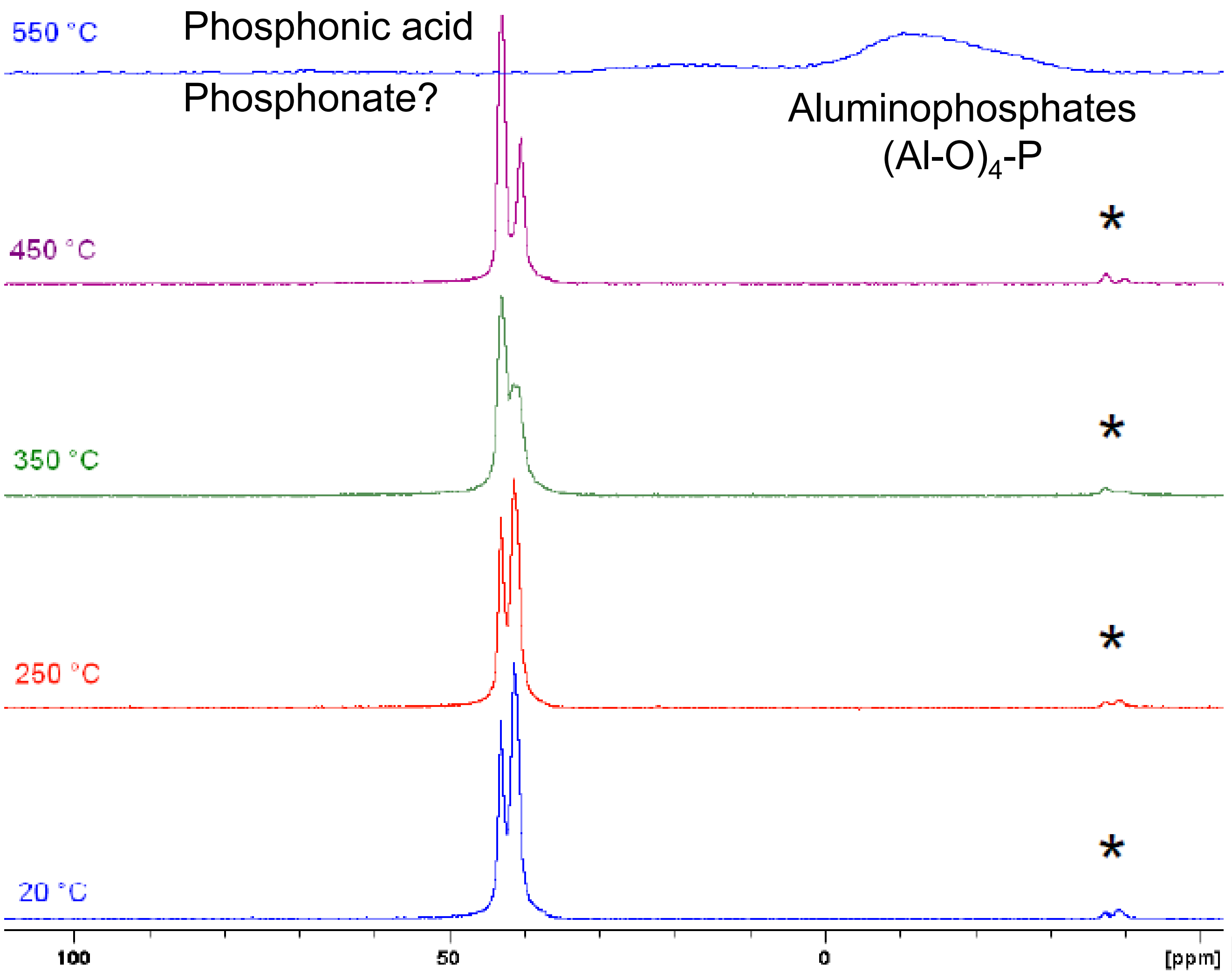
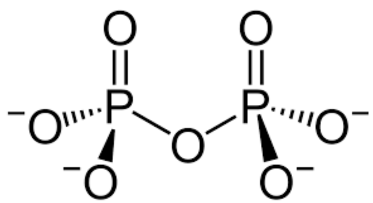
Thermal degradation of ATH-OP1230 mixture

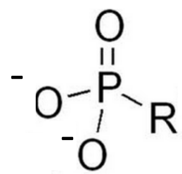
^{31}P MAS NMR



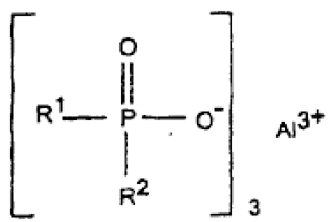
Pyrophosphate



Phosphonate



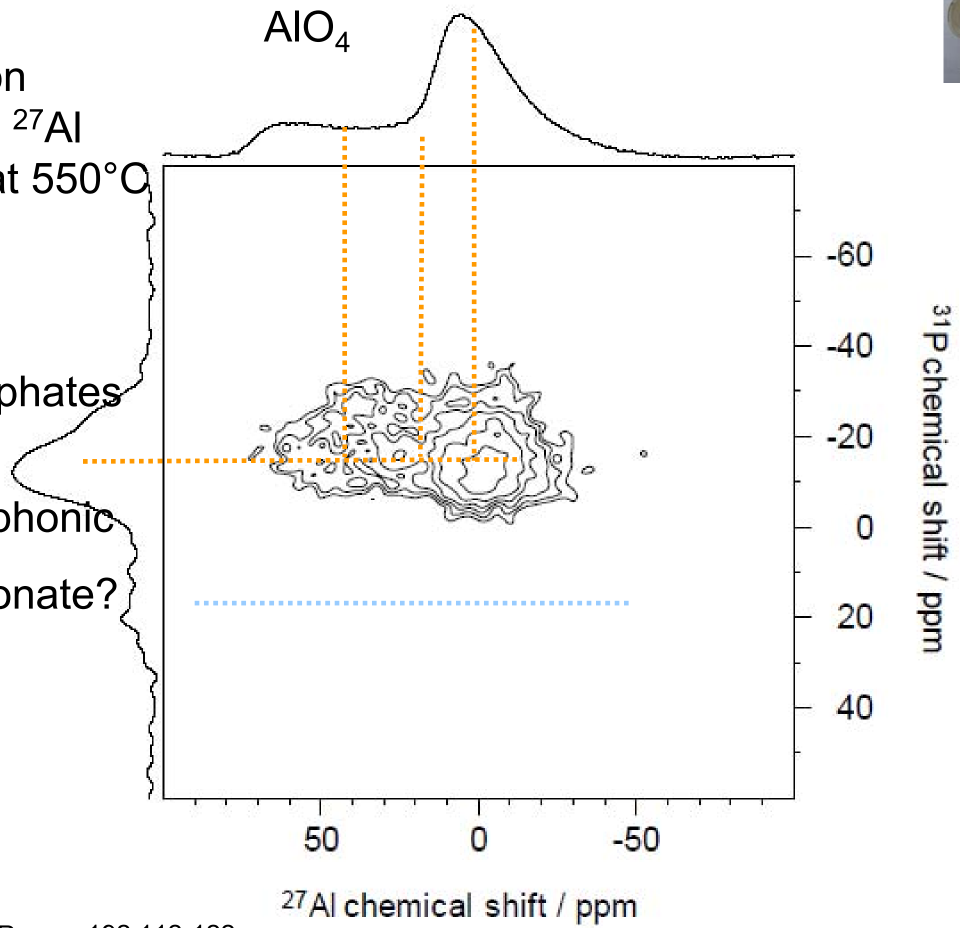
Phosphinate



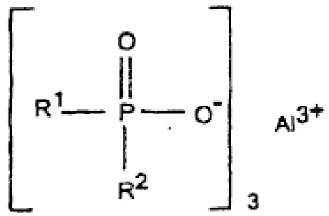
Thermal degradation of ATH-OP1230 mixture

2D MAS-NMR D-HMQC (Dipolar Heteronuclear Multiple Quantum Coherence)

Spatial correlation between ^{31}P and ^{27}Al
Sample treated at 550°C



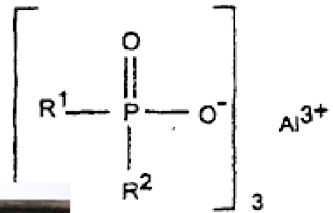
$Al(OH)_3$ +



Aluminophosphates

Organic phosphonic acid

~~Char~~



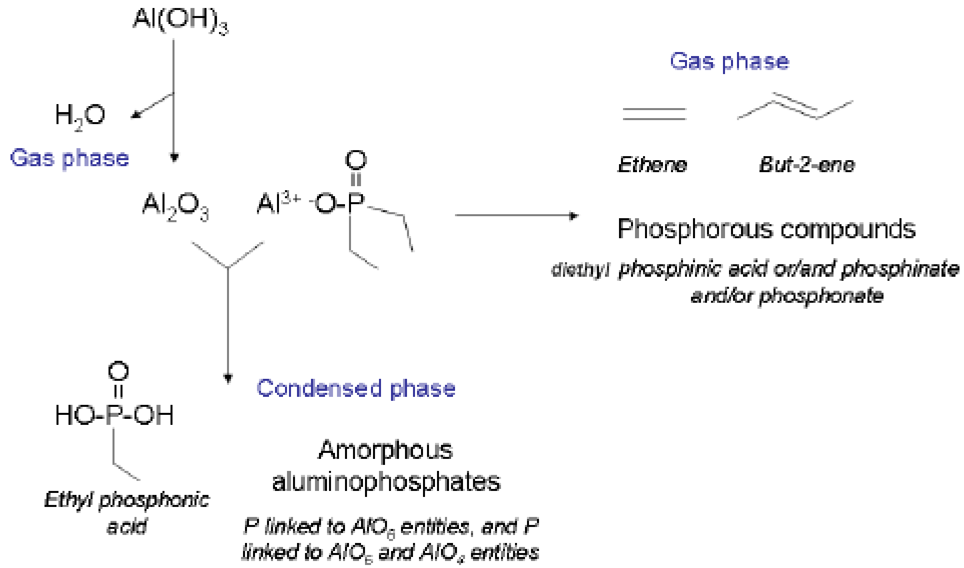
Aluminophosphonate

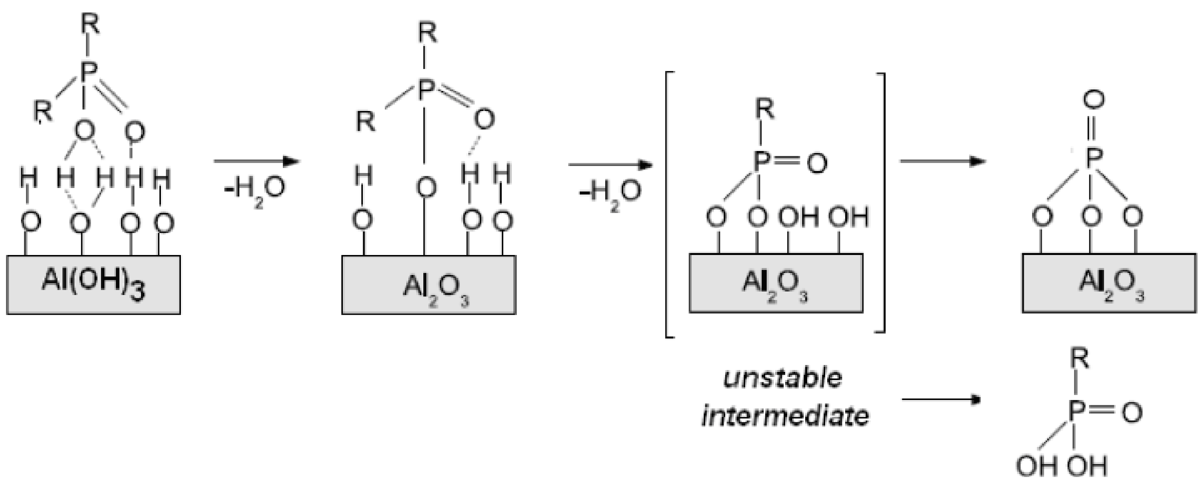
Aluminophosphate

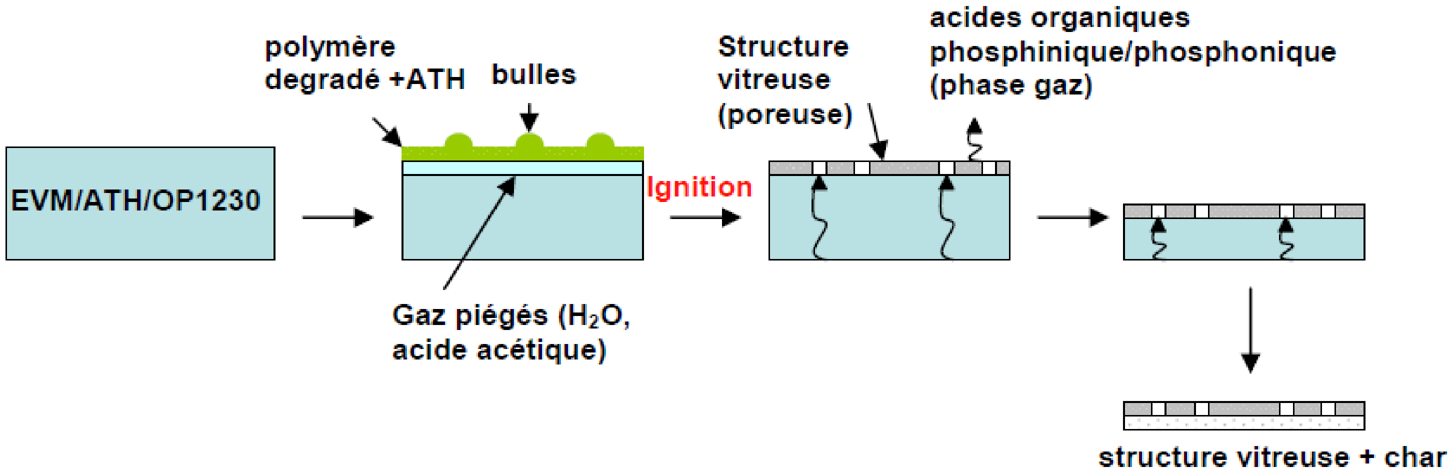
Char

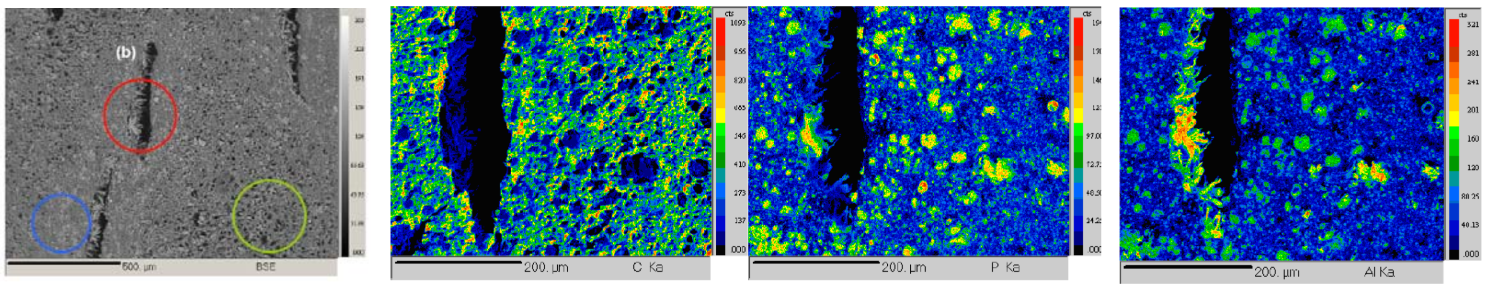
*Hu B. et al. *Journ. Magn. Reson.* 192:112-122

Thermal degradation of ATH-OP1230 mixture

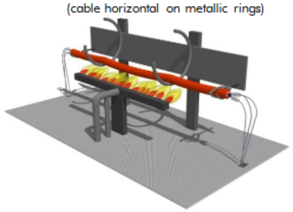








IEC 60331-11 & -21 & -23
(cable horizontal on metallic rings)

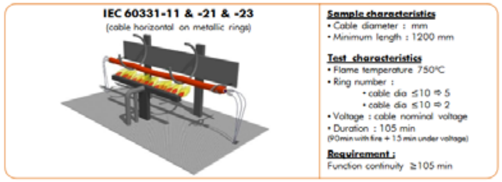


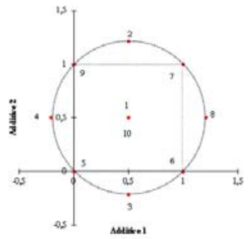
Sample characteristics
- Cable diameter : mm
- Minimum length : 1200 mm

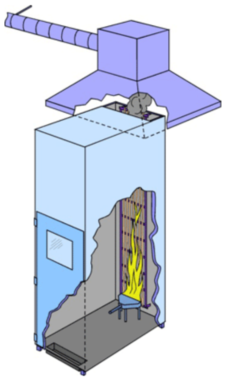
Test characteristics
- Flame temperature 750°C
- Ring number :
  - cable dia ≤10 ⇒ 5
  - cable dia ≤10 ⇒ 2
- Voltage : cable nominal voltage
- Duration : 105 min
(90min with fire + 15 min under voltage)

Requirement :
Function continuity ≥105 min

Conclusion



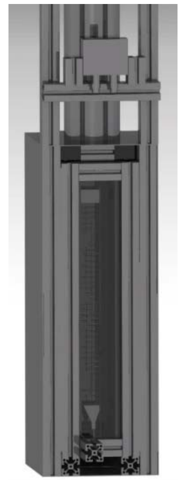




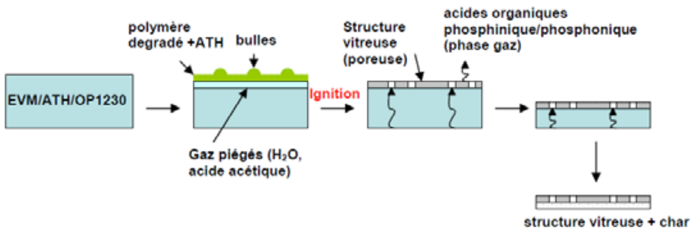
Development of FR formulations

Large Scale Fire Testing

Lab scale testings: Adapted



Mode of action



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