Investigation of the Thermal Behavior of Bitumen and Model Bituminized Waste Products

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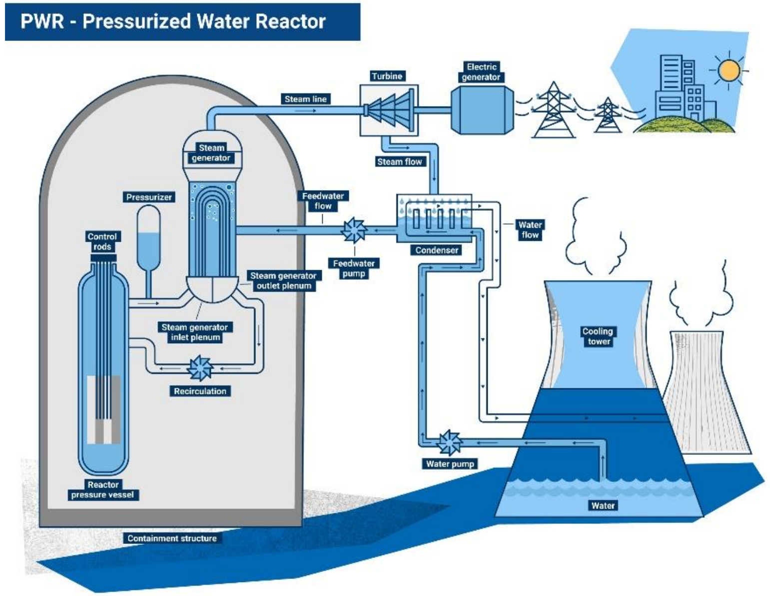
CEA: French Alternative Energies and Atomic Energy Commission
LNE: National metrology and testing laboratory

1. General introduction

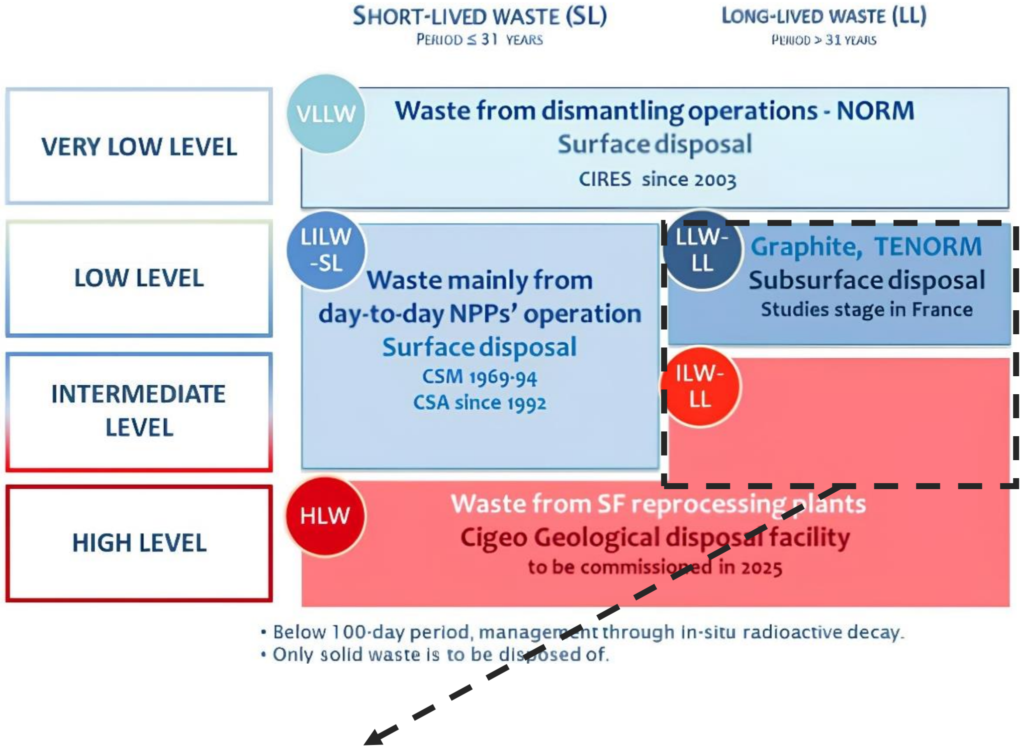
Context:

Energy need → nuclear energy (≈ 70% of energy production in France)



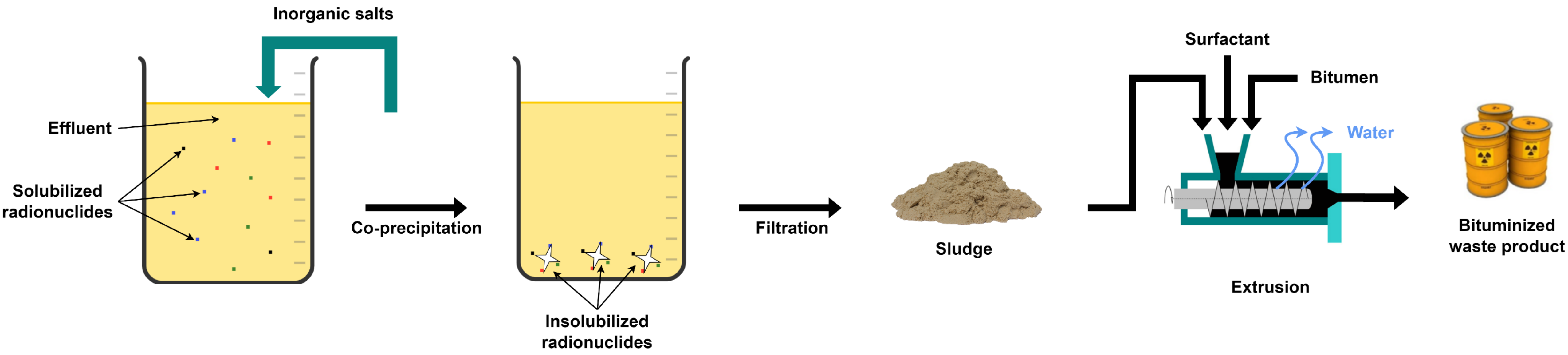
Waste production

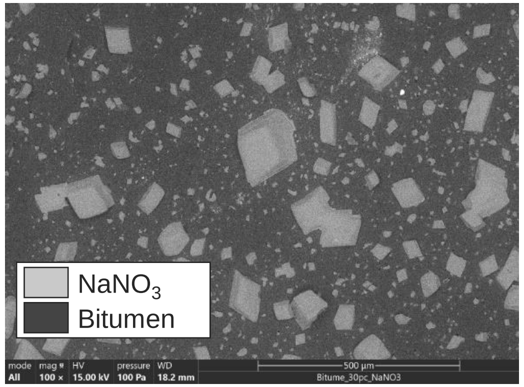
Waste classification



Bituminization (1960): bitumen was chosen as a matrix for encapsulating

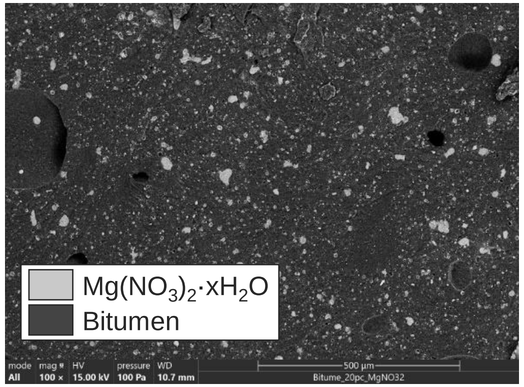
Context:





Bitumen containing 30% $NaNO_3$

Model BWP



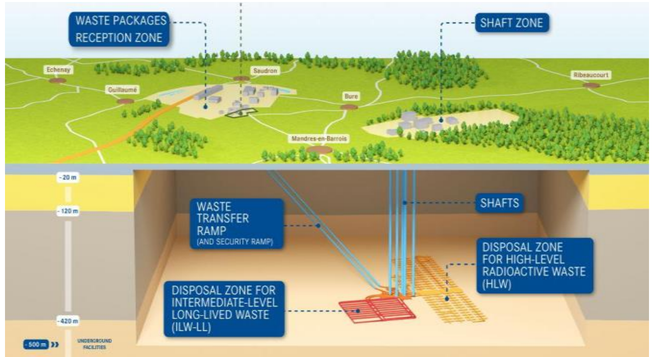
BWP containing 20% $Mg(NO_3)_2{\cdot}xH_2O$

Context:

What is the motivation to study bituminized waste products (BWP)?

Marcoule (62.000 drums)	La Hague (13.000 drums)

BWP temporary storage



Cigéo facility

- **Disposal facility:**

Final disposal facility for BWPs is planned to be a 500 meters underground storage (Cigéo facility)

- **Problematic:**

Acceptability of BWP's at Cigéo currently questioned regarding behavior in accidental fire scenario

Bitumen → flammable material | potential exothermic reactions between bitumen and salts

- **Research objectives:**

Study of the thermal and burning behavior of BWP

Reinforce the safety strategy and fire risk control of BWPs in a fire scenario

Methodology & PhD. scope:

Materials

BWP composition → considerable complexity (bitumen + >10 inorganic phases)


Pure Bitumen

Step-by-Step Approach to describe real BWP

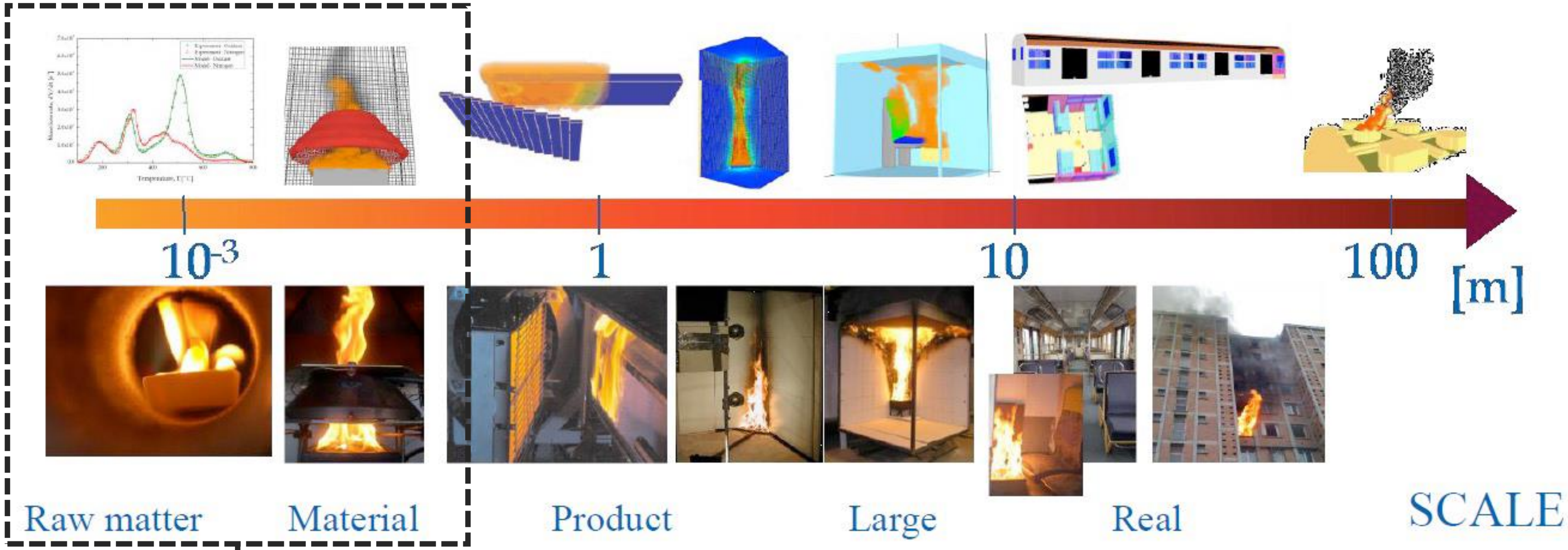
- **Starting Point: Pure Bitumen**
  - Primary component of BWP

- **Progressive Complexity (model BWP)**
  - Bitumen + 20% $Mg(NO_3)_2 \cdot xH_2O$
  - Bitumen + 30% $NaNO_3$
  - ...toward realistic BWP composition

Nitrates: Main constituents in sludge ~30%
Major contributors to BWPs thermal reactivity

Methodology & PhD. scope:

Multi scale approach



1. Matter scale

Study of the thermal behavior and chemical reactivity (TGA, DTA, SEM, FTIR, XRD…)

Propose a robust predictive kinetic model for the mass loss

2. Material scale

Heat transfer mechanisms and burning behavior (controlled atmosphere cone calorimeter “CACC”)

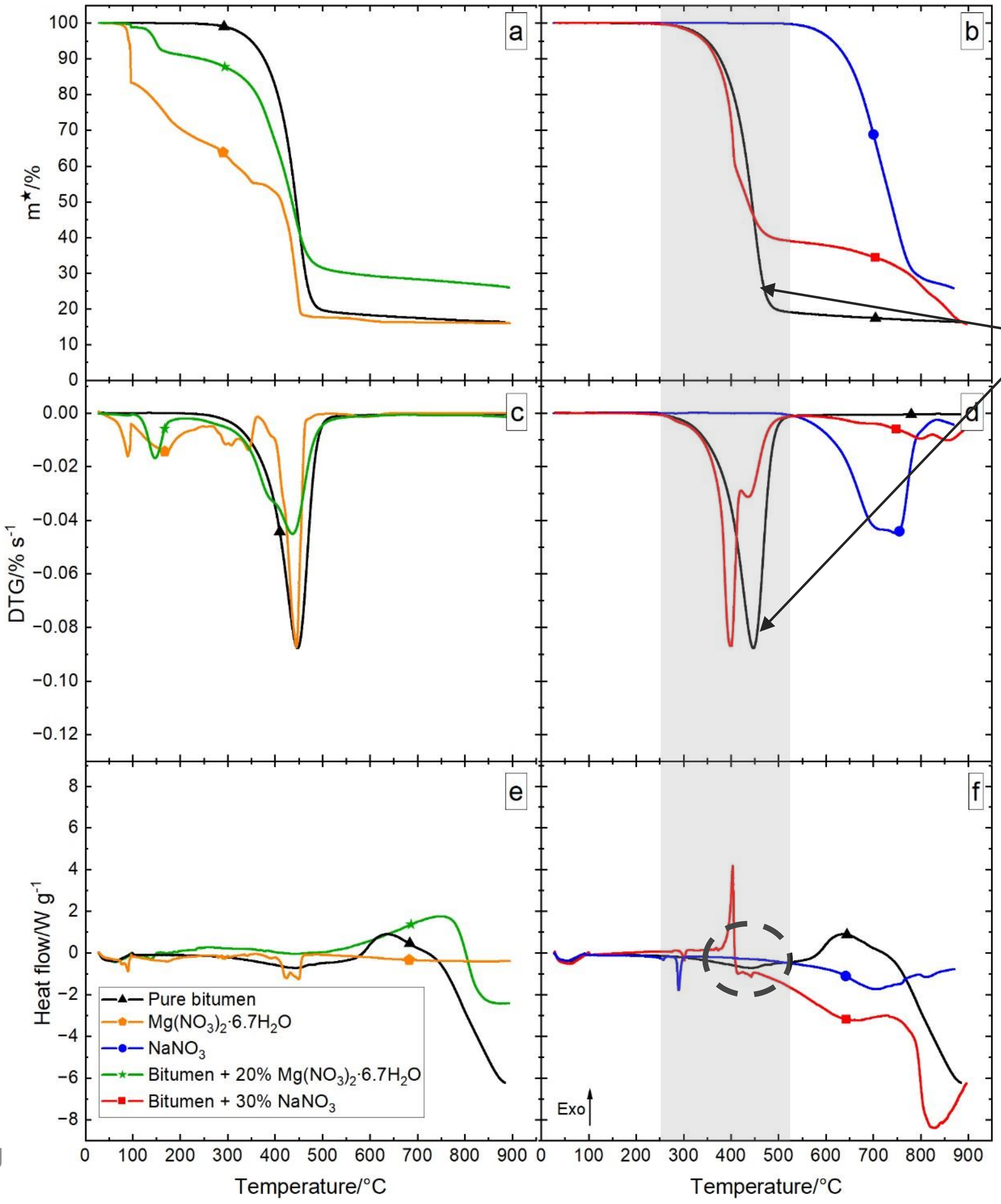
Developing a predictive **heat transfer pyrolysis model** coupled with **kinetic sub-model**.

2 Matter scale

Chemical reactivity and kinetic modelling

Thermal analysis: Pure bitumen

G. MATTA, Thermochim. Acta, Jun. 2023



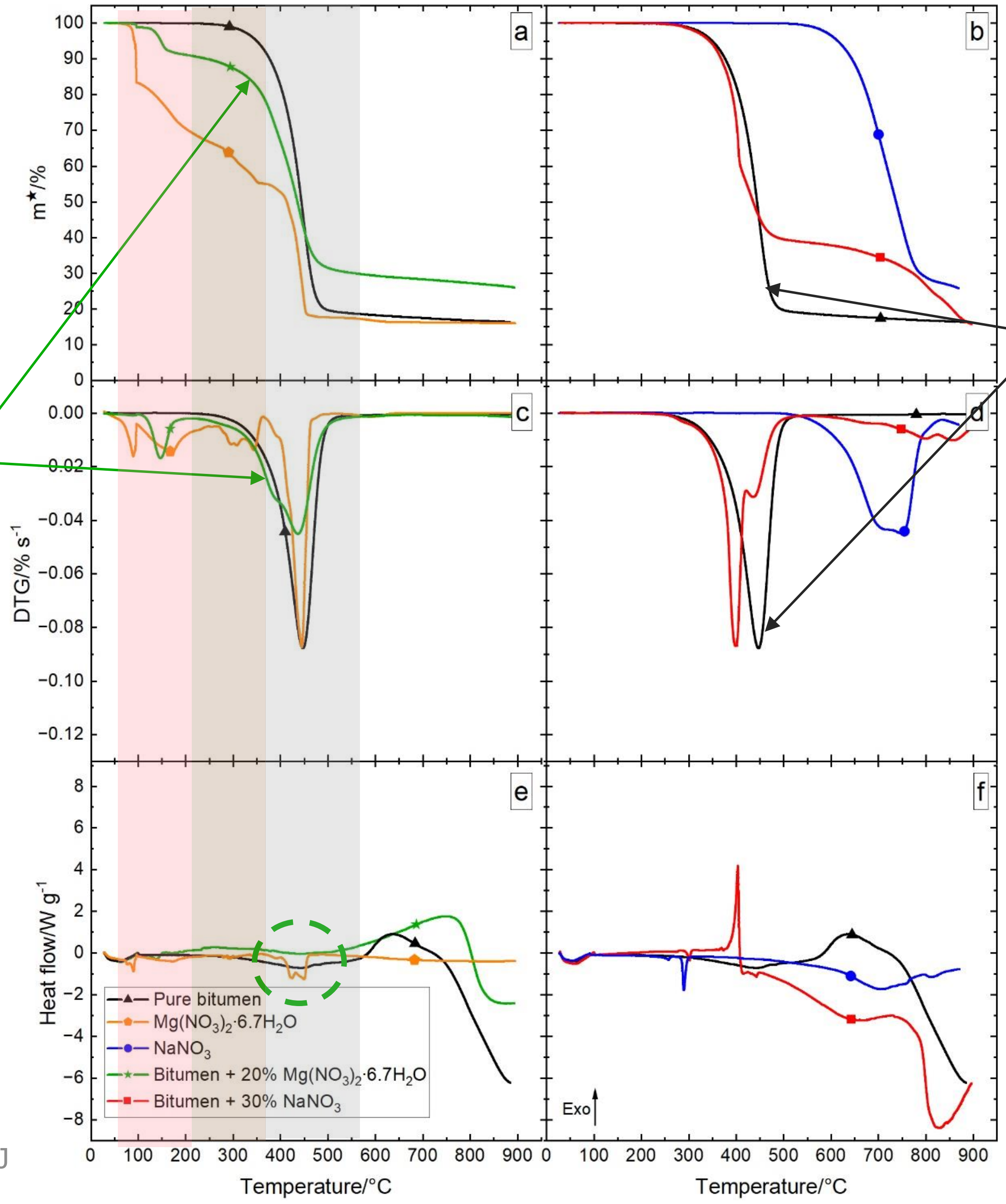
- 1 mass loss identified with final mass loss of 83%
- 435.60°C: endothermic event corresponding to bitumen pyrolysis

TGA-DTA conditions:
β: 5 °C.min^{-1}
Gas: 50 mL.min^{-1} N_2
m_0 sample ≈ 10mg

Thermal analysis: Bitumen + 20% $Mg(NO_3)_2 \cdot xH_2O$

G. MATTA, Thermochim. Acta, Jun. 2023

- Water free and physisorbed
- Bound water, beginning of bitumen pyrolysis and interactions
- Bitumen pyrolysis, salts decomposition, interactions



- 1 mass loss identified with final mass loss of 83%
- 435.60°C: endothermic peak corresponding to bitumen pyrolysis

TGA-DTA conditions:

β: 5 °C.min^{-1}

Gas: 50 mL.min^{-1} N_2

m_0 sample ≈ 10mg

Thermal analysis: Bitumen + 30% $NaNO_3$

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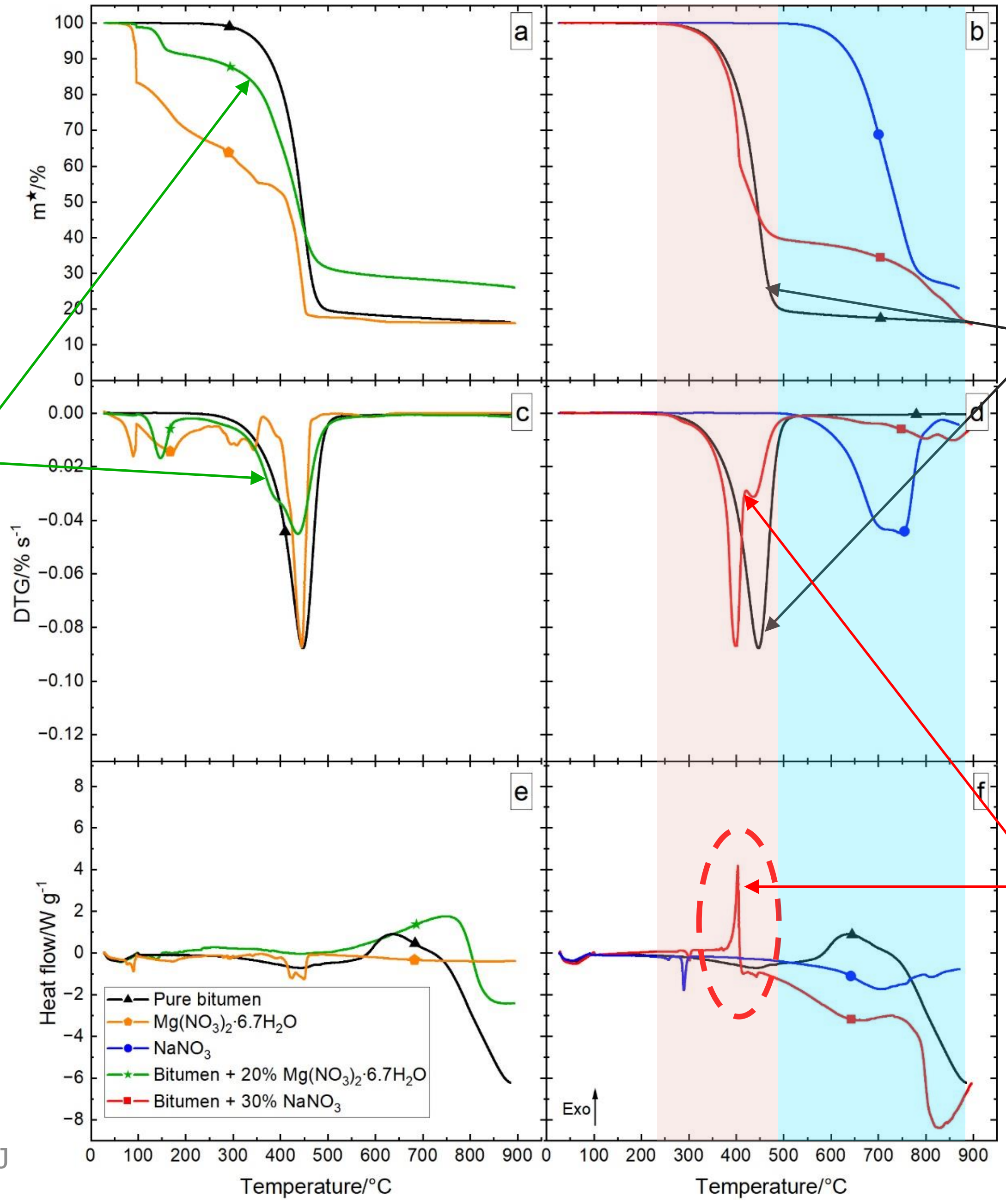


- 1 mass loss identified with final mass loss of 83%
- 435.60°C: endothermic peak corresponding to bitumen pyrolysis

- 380-420°C: an exothermic peak corresponding to the interaction between $NaNO_3$ and bitumen

TGA-DTA conditions:
β: 5 °C.min^{-1}
Gas: 50 mL.min^{-1} N_2
m_0 sample ≈ 10mg

Kinetic model: Distribution Activation Energy Model

(V. Vand, Proc. Phys. Soc, May 1943)

Devolatilization reactions
- Numerous
- Parallel & irreversible
- 1st order

$A_i e^{\frac{-E_i}{RT}}$, rate constant

Decomposition rate of each reaction i is: $\frac{\partial v_i(t)}{\partial t} = k_i\left(v_i^{\infty} - v_{i(t)}\right)$

$$\text{Time integration: } v_i^{\infty} - v_{i(t)} = v_i^{\infty} \exp\left(-\int_{to}^{t} A_i e^{\frac{-E_i}{RT(t)}} dt\right)$$

DAEM assumes that all reactions share the same frequency factor A_i and that the number of reactions is large enough to permit the activation energies to be expressed as a continuous distribution $f(E)$

$$x(t) = \frac{v_{(t)}}{v^{\infty}} = 1 - \int_{0}^{\infty} \exp\left(-\int_{to}^{t} A e^{\frac{-E}{RT(t)}} dt\right) f(E) dE$$

Integral form of conversion

Parameter identification was based on the optimization of the objective function, residual sum of squares (RSS) between experimental and calculated conversion rates of all data: $OF = \sum_{1}^{N_{exp}} \sum_{t_0}^{t_f} (X_{exp}(t) - X(t))^2$

(P. Perré et al., Fuel, Mar. 2021.)

Kinetic model: Distribution Activation Energy Model

Materials:
1. **Pure bitumen**
2. **Bitumen + 20% magnesium nitrate hexahydrate**
3. **Bitumen + 30% sodium nitrate**

Intrinsic thermo-kinetic study

Thermogravimetric experiments

DAEM

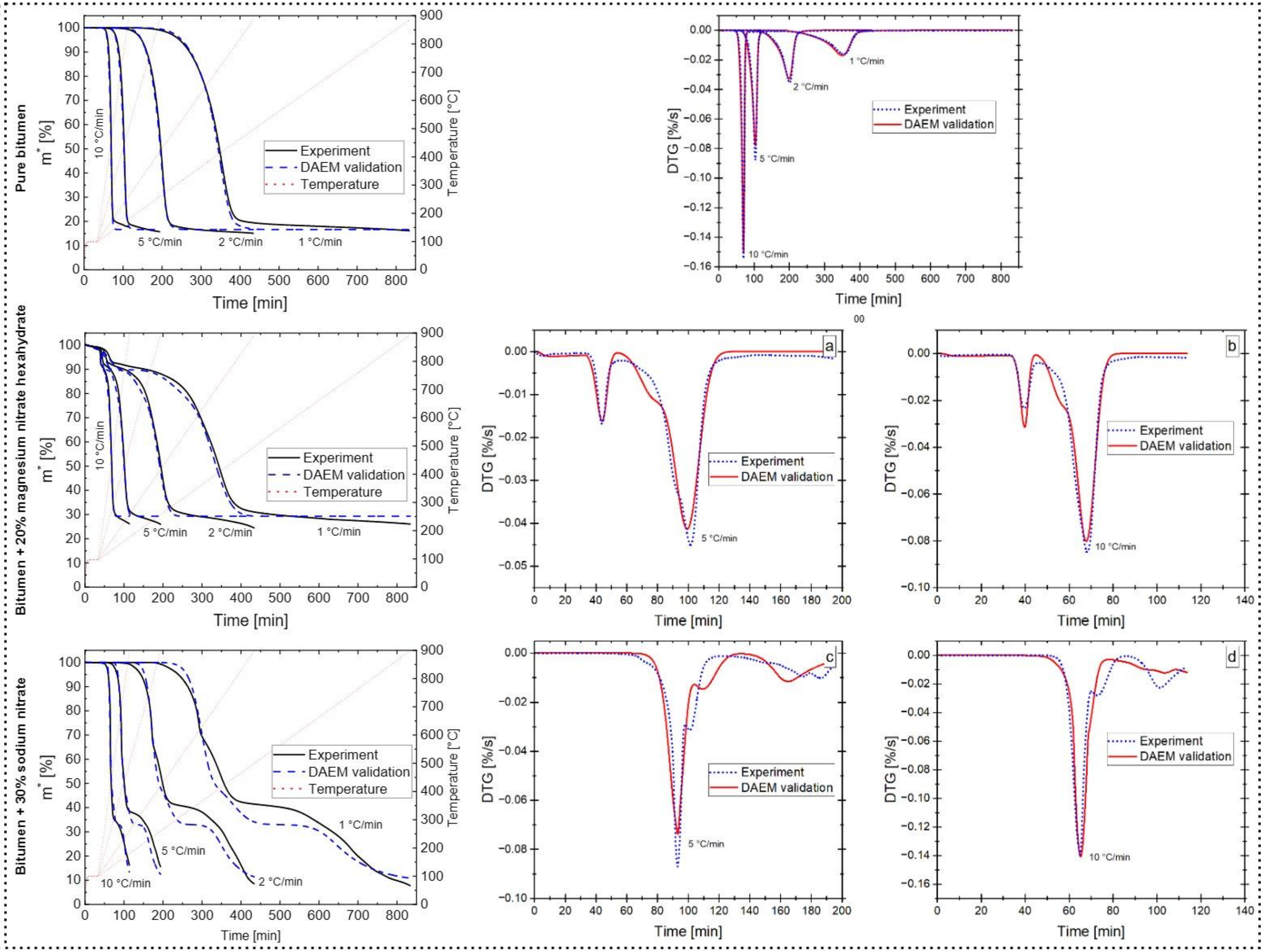
Isothermal tests (Learning database) → Identification →

Identification:
Distribution number and shape determination
1. Gaussian / multi-Gaussian
2. Gamma

↓ Kinetic parameters ↓

Validation:
- Kinetic predictions
- Model evaluation
- Predictive accuracy

← Prediction ← **Dynamic tests** (Validation database)



3. Material scale

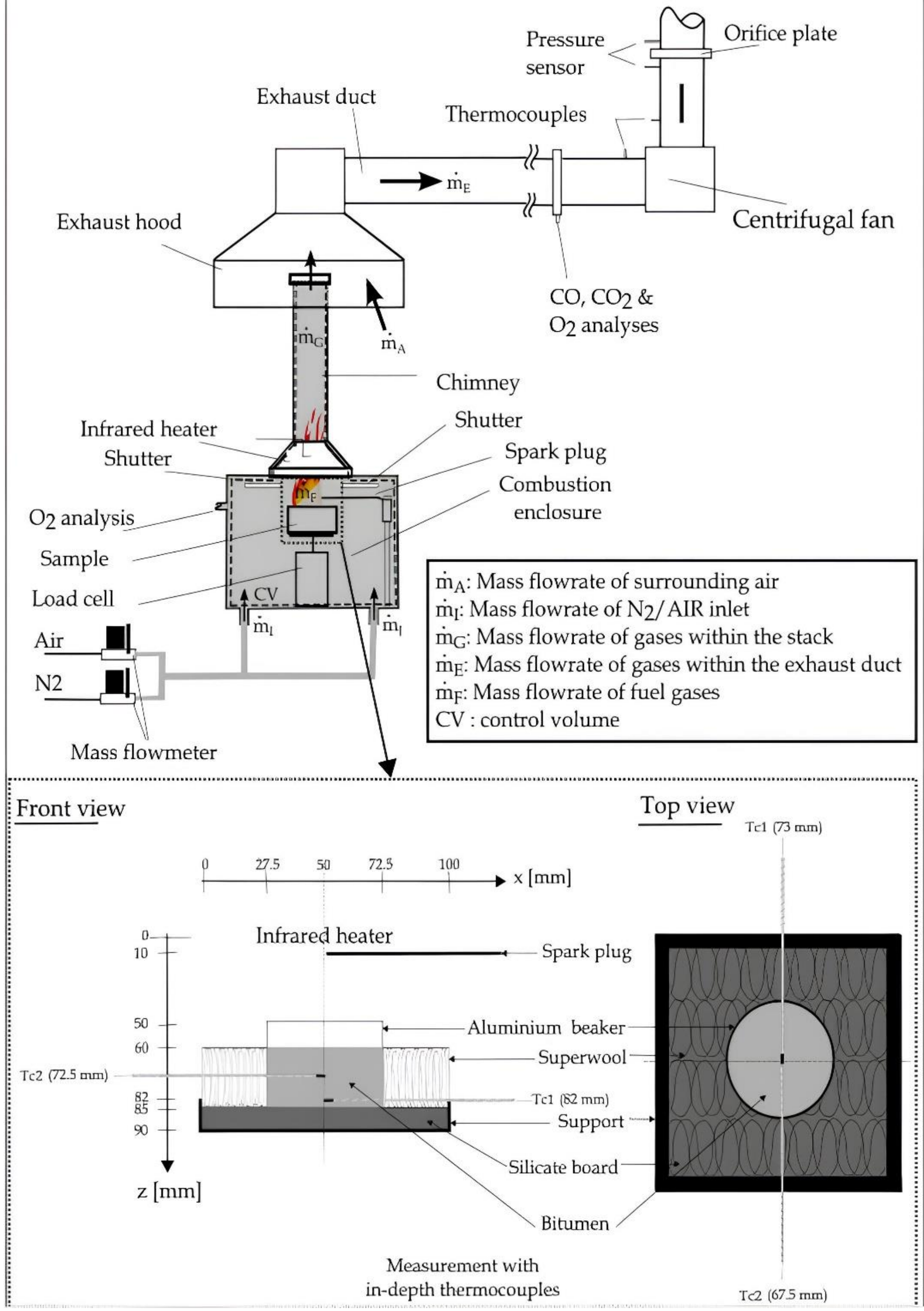
Burning behavior under CACC

Cone calorimeter:

Experiments:

	25 kW/m²	30 kW/m²	35 kW/m²
Under nitrogen: effect of heat flux	*Mass loss rate* ($\dot{m}$") Heat release rate ($\dot{Q}$") Temperature (T)		
Under air: effect of heat flux			

	21% O_2	18% O_2	15% O_2	12% O_2	10% O_2	8% O_2	<1% O_2
Under 30 (kW/m²) : effect of O_2 depletion	$\dot{m}$" $\dot{Q}$" T						



3.1. Material scale

Pure bitumen under CACC

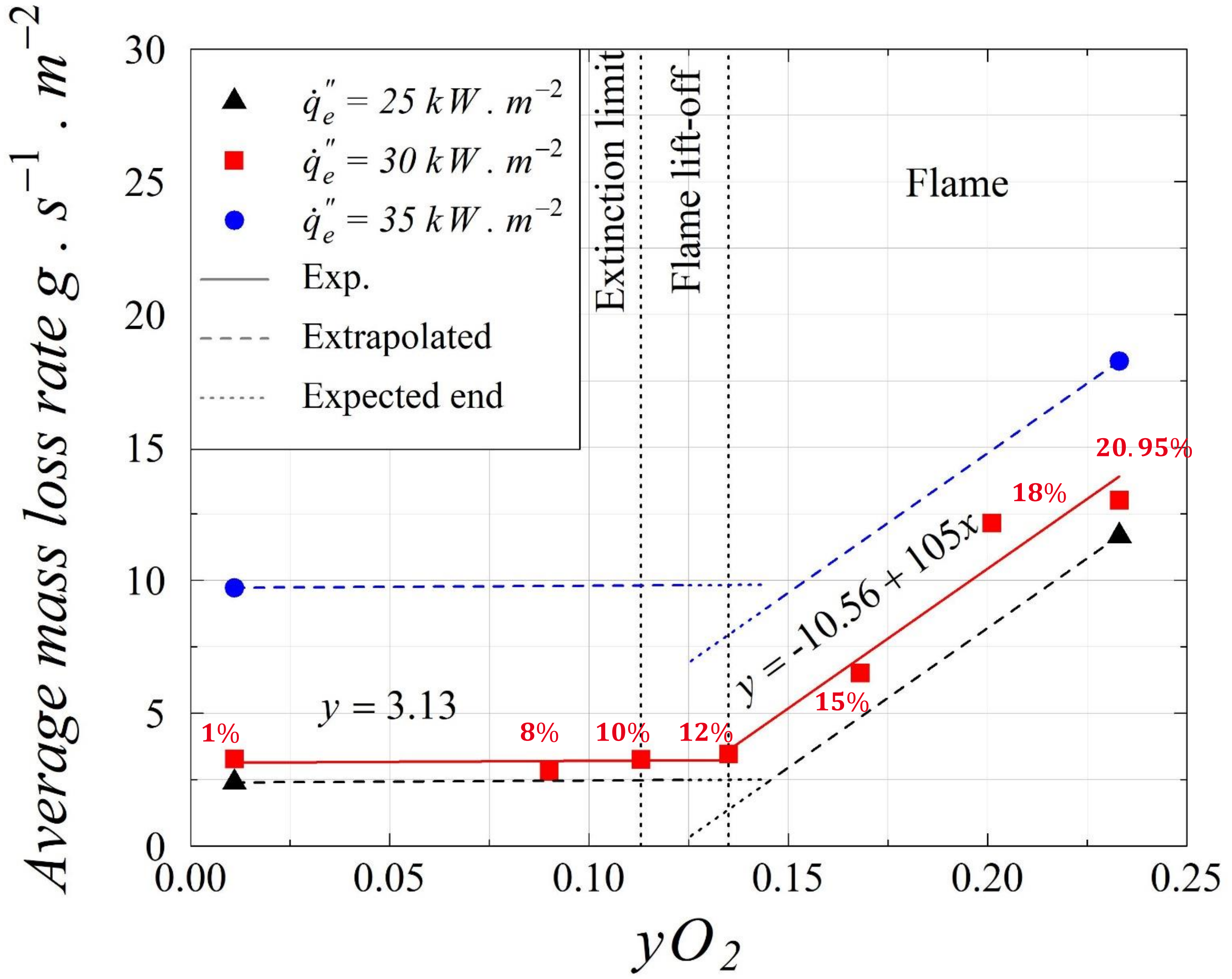
Comparison of bitumen under different O_2 level

- **Under incident flux of 30 $kW.m^{-2}$**

$y_{O_2} = 20.95\% \ (air)$	$y_{O_2} = 18\%$	$y_{O_2} = 15\%$	$y_{O_2} = 12\%$
			
High-intensity flame Over flow and flame spread	Lower-intensity flame	Low-intensity flame with intermittent flame flashes	Flame lift-off Intermittent flame

Comparison of bitumen under different O_2 level

- **Under incident flux of 30 $kW.m^{-2}$**



Flaming zone:

y_{O_2} ↓ → flame intensity ↓

Flame intensity ↓ → flame feedback ↓

Flame feedback ↓ → mass loss rate ↓

Oxygen level directly affect flame (gas phase) and indirectly solid phase.

Non-flaming +flame lift-off zones:

y_{O_2} directly affects thermo-oxidative reactions

y_{O_2} ↓ → no effect on mass loss rate

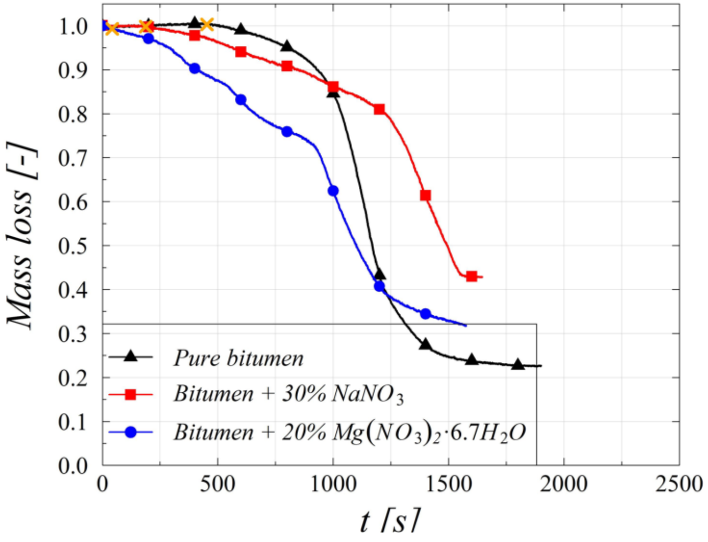
No significant thermo-oxidative reactions or gas production overcomes oxygen diffusion.

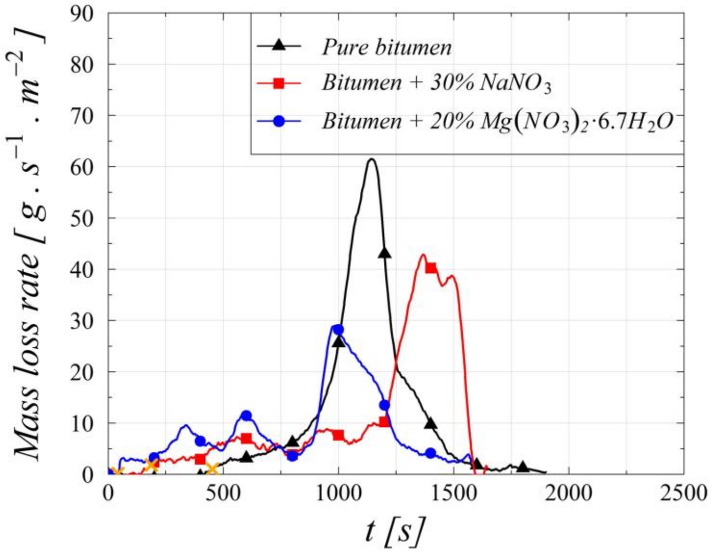
3.2. Material scale

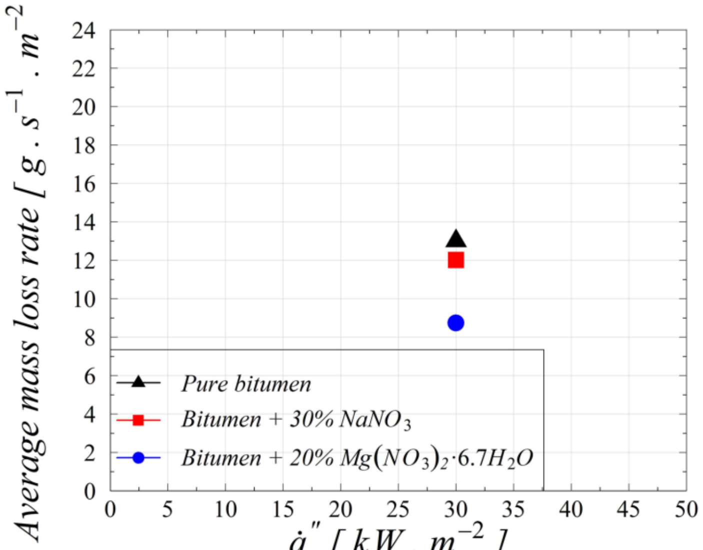
Model BWP under CACC

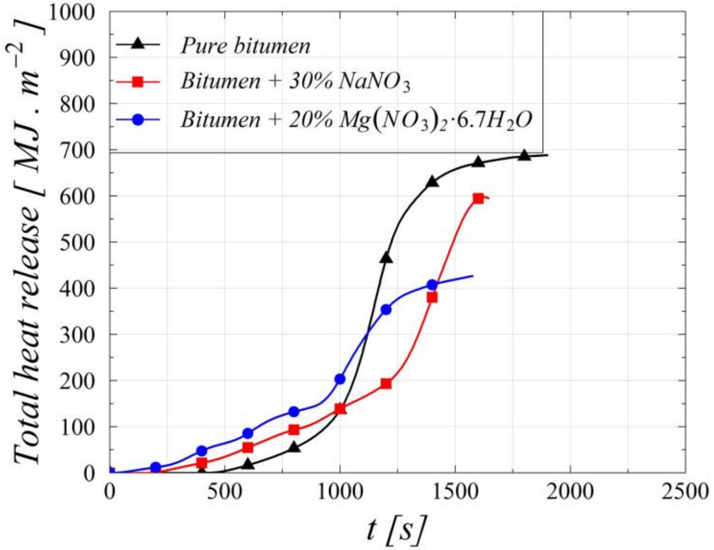
Comparison of bitumen and model BWPs

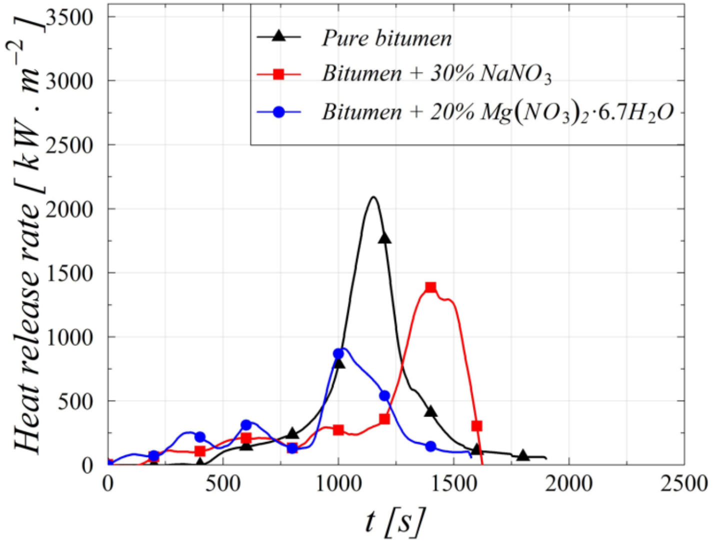
- under air ($y_{O_2} = 21\%$) at 30 $kW.m^{-2}$











Among all samples, the bitumen containing 20% magnesium nitrate hexahydrate ignited the fastest.

Bitumen demonstrated the highest energy release among tested materials.

4. Conclusion & Perspective

General Conclusion

- ✓ **Thermal behavior of pure bitumen, bitumen-20% $Mg(NO_3)_2 \cdot 6.7H_2O$, and bitumen-30% $NaNO_3$ was investigated under TGA and CACC.**
- ✓ **Kinetic and heat transfer models developed to predict thermal degradation**

- **Matter scale (scale of TGA):**
  1. Full investigation of thermal behavior and reactivity. Degradation and exothermic event was identified and discussed.
  2. Kinetic model developed (DAEM) has significant predictive potential with satisfactory uncertainties.

- **Material scale (scale of CACC):**
  1. Full investigation of burning behavior. Bitumen exhibited the highest energy output among all tested materials. Exothermic behavior observed at the matter scale did not manifest at the material scale.
  2. Development of 1D heat transfer model (in final stage).

Perspective

1D Thermo-Kinetic Cone Simulation

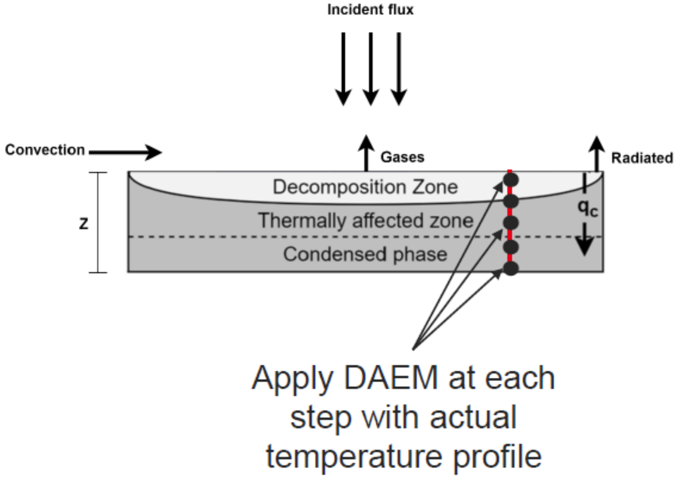
Simulates 1D transient heat conduction in a bitumen under external heat flux (cone calorimeter).

Couples heat transfer with thermal decomposition kinetics (virgin → char+gas).

Updates temperature, density fields, and material properties in time.

Computes mass, mass loss rate (MLR), and compares to experimental data.

$$\underbrace{\rho(T)\,c_p(T)}_{\substack{\text{density} \times \text{specific heat} \\ = \text{thermal inertia}}} \cdot \underbrace{\frac{\partial T(x,t)}{\partial t}}_{\substack{\text{rate of} \\ \text{temperature change}}} = \underbrace{\frac{\partial}{\partial x}\left[k(T)\,\frac{\partial T(x,t)}{\partial x}\right]}_{\substack{\text{heat conduction (Fourier's law)} \\ \text{diffusion of heat in x-direction}}} - \underbrace{\sum_i H_i\,\frac{\partial \alpha_i(x,t)}{\partial t}}_{\substack{\text{heat absorbed/released} \\ \text{by pyrolysis reactions}}}$$



THANK YOU

Q & A

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