



**HAL**  
open science

## Thermal analysis of a large geopolymer mortar monolith (2.7 m<sup>3</sup>) in an industrial waste container

Pascal Girardin, Gilles Cardinal, Mickaël Marchand, Matthew Moinard, Elodie Nilly, Pascal Antonucci, Arnaud Poulesquen

### ► To cite this version:

Pascal Girardin, Gilles Cardinal, Mickaël Marchand, Matthew Moinard, Elodie Nilly, et al.. Thermal analysis of a large geopolymer mortar monolith (2.7 m<sup>3</sup>) in an industrial waste container. Technical Meeting on the Status and Use of Geopolymers to Immobilize Radioactive Waste, Apr 2022, Vienne (virtuel), Austria. , 2022. cea-04836677

**HAL Id: cea-04836677**

**<https://cea.hal.science/cea-04836677v1>**

Submitted on 13 Dec 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The logo for the Alternative Energies and Atomic Energy Commission (CEA), consisting of the lowercase letters 'cea' in a white, sans-serif font, positioned above a horizontal green line.

From research to industry

## Thermal analysis of a large geopolymer mortar monolith (2.7 m<sup>3</sup>) in an industrial waste container

5 april 2022

Pascal GIRARDIN

Traitement and conditionning of  
radioactive waste



## Summary

- ▶ Mortars based on geopolymers have been proposed for the conditioning of magnesium-alloy scraps. The qualification of the immobilization process requires the confirmation that, during the setting of the geopolymer matrix, the temperature in the waste container would not exceed a threshold where adversarial consequences could be observed, such as increased scrap corrosion (accompanied with hydro-gen production) or structural matrix disorders.
- ▶ An experimental campaign has culminated in 2020 with the pouring of a large geopolymer mortar quantity (2.7 m<sup>3</sup>) in an industrial-size cubic container, and the monitoring of the ensuing temperature transient inside the mortar and on the package walls. We present a numerical thermal model based on finite elements, we justify the hypothesis and adopted material parameters, and we compare the obtained numerical simulation with the experimental result.
- ▶ The comparison between the measured temperatures and the calculated ones is rather acceptable. The agreement regarding the maximum temperature inside the mortar is especially satisfactory. Sensibility analyses have shown that the temperature peak is not dependent on the external cooling fluxes (irradiance and atmospheric convection), but only on the mortar thermal properties.



## Context – Issue - Objective

- ▶ **Context : More than 1600 tons of magnesium-alloy scraps are currently stored in interim repositories at Marcoule, waiting for a definitive conditioning and disposal**
  - Included, 600 tons with the status {Low-Medium activity, Short Life}, to be definitely stored in a surface repository, after immobilization inside a 2.7 m<sup>3</sup> cubic container
- ▶ **Issue : Mg is highly reactive : contact with cementitious matrices leads to H<sub>2</sub> production**
  - Geopolymer mortars appear to be advantageous candidates
  - During setting, heat generation and temperature increase, which activates corrosion and H<sub>2</sub> production
  - Laboratory tests suggest an admissible temperature ceiling of 60 °C
  - Requirement to guarantee this maximal temperature in a range of operating and incidental situations, in large monoliths
- ▶ **Objectives : to build and validate a numerical thermal model of the monolith setting**
  - Definition of a thermo-kinetic model of the setting heat generation, and to investigate its parameters
  - Preparation of a 3-D finite element model
  - Validation of the model through the available experimental results, and analyze of the thermal transient

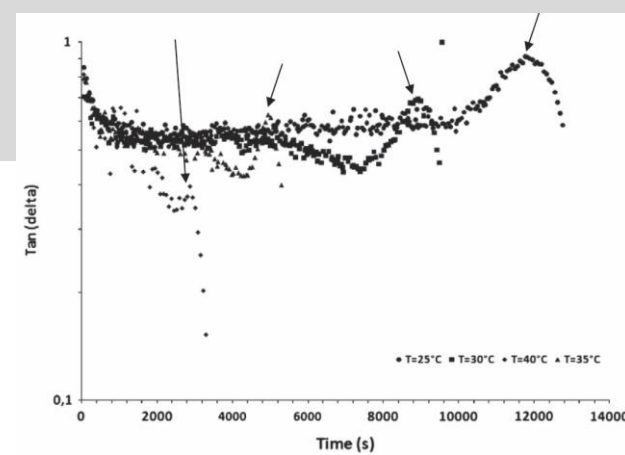


## Experimental program

### ► Experimental program addressing several operational issues

- Many technical topics being investigated : preparation of the activation solution, mortar mixing, transfer, pouring and filling, rheology, sedimentation, geometrical stability, impact of the solid waste on the filling, .., and the setting thermal peak
- Outline :
  - 2012- : Solidification tests in small instrumented canisters (120 l, 220 l)
  - 2013/10 : Solidification of a 1 m<sup>3</sup> monolith
  - 2020/09 : Manufacturing of an industrial-sized 2,7 m<sup>3</sup> monolith, inside its container





## Modelling the setting heat

### ► The setting of the geopolymer matrix

- A mix of reactions : dissolution-rearrangement of polymers-precipitation
- As for cementitious materials, a usual way to model this reaction mix is to aggregate them :
  - Definition of an apparent reaction advancement, based on the generated heat
  - Definition of three parameters : apparent activation energy, affinity function, specific enthalpy

$$\xi(t) = q(t)/q(\infty)$$

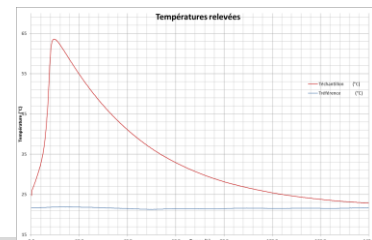
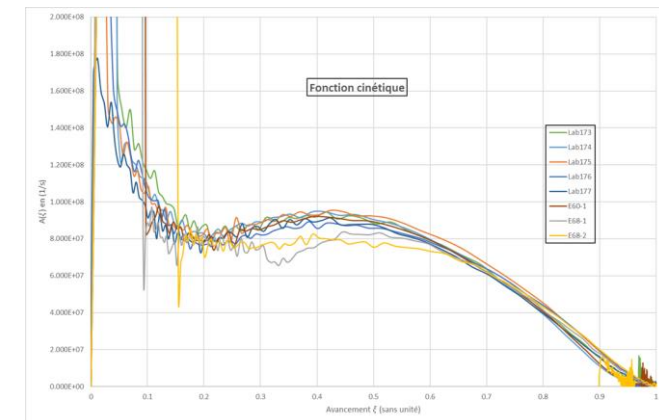
$$\Theta_{volumic} = \rho_{mortar} \cdot H_{specific} \cdot \frac{d\xi}{dt} = \rho_{mortar} \cdot H_{specific} \cdot \tilde{A}(\xi) \cdot e^{\left(-Ea(T,\xi)/RT\right)}$$

### ► Evaluation of the activation energy $Ea$ with dynamic rheology

- Observation of the elastic modulus  $G'$  and viscous modulus  $G''$  during the setting of a geopolymer paste (without sand), at different temperatures (by a team lead by Dr A. Poulesquen, CEA)
- Plotting of the time necessary to reach the maximum of the loss function  $\tan(\delta) = G''/G'$
- Conclusion :  $Ea \sim 74.5 \text{ kJ/mol}$

### ► Evaluation of $H_{specific} \cdot \tilde{A}(\xi)$ with calorimetric test

- Reference mortar :  $H_{specific} \sim 78 \text{ kJ/kg}$

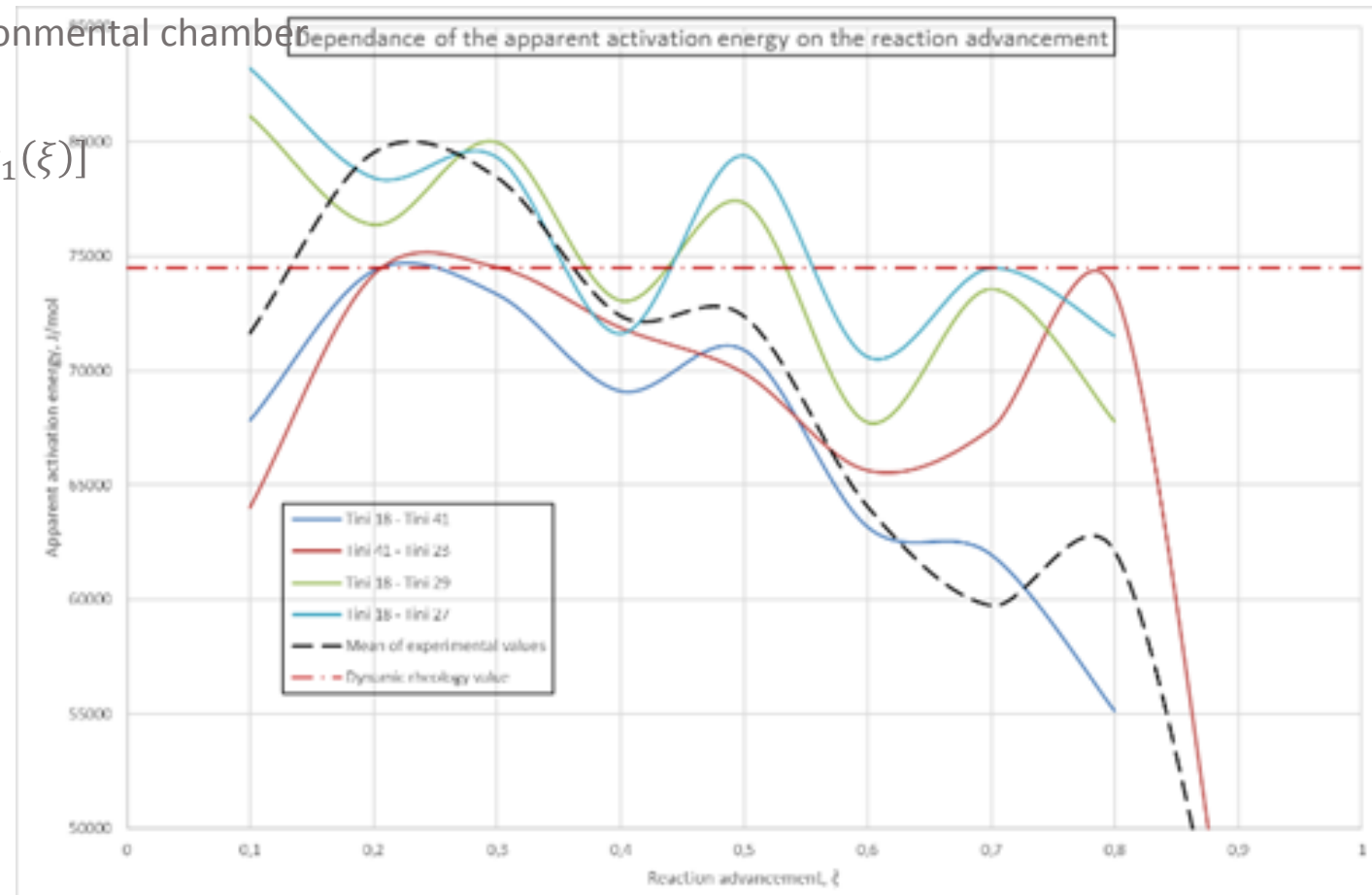


## Apparent activation energy $Ea(T, \xi)$

### ► Vindication of the considered value $Ea \sim 74.5 \text{ kJ/mol}$

- Calorimetric measurements, at different temperature conditions in an environmental chamber
- For each pair  $\{T_1, T_2\}$ , estimation

$$Ea(\xi) = \frac{-R}{\left(\frac{1}{T_2(\xi)} - \frac{1}{T_1(\xi)}\right)} \text{Ln}[\dot{q}_2(\xi) / \dot{q}_1(\xi)]$$



## Evaluation of material characteristics

### ► Thermal conductivity

- Measured by R&D team at INSA-Rennes led by Aveline Darquennes (associated R&D project 'DECIMAL'), with a 'Hot disk' device
- On the solidified mortar, but still wet :  $\lambda_{mortier} = 1.87 \text{ W/K/m}$

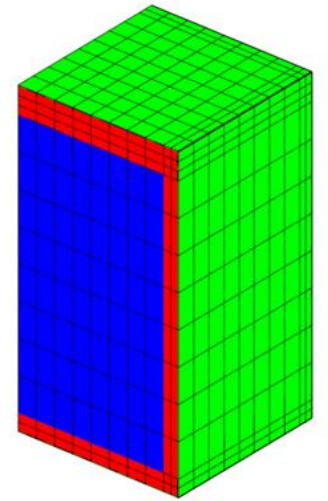
### ► Specific heat

- Measured here at the CEA/LCBC, with a microcalorimetric device
- On the solidified mortar, but still wet :  $C_{p\_mortier} = 1515 \text{ J/K/kg}$

### ► Specific enthalpy

- Measured here at the CEA/LCBC, with a Langavant calorimeter, on several instances
- Nominal value  $H_{specific} \sim 78 \text{ kJ/kg}$ , but Minimal value  $H_{specific} \sim 76 \text{ kJ/kg}$ , and Maximal value  $H_{specific} \sim 90 \text{ kJ/kg}$
- Impact of input material properties, mixing method and duration, ...

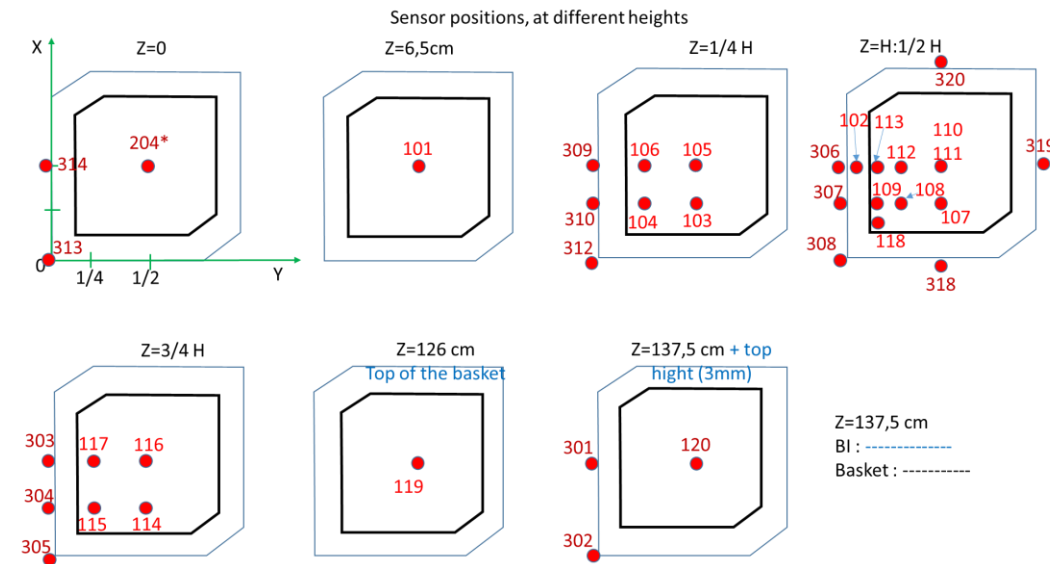
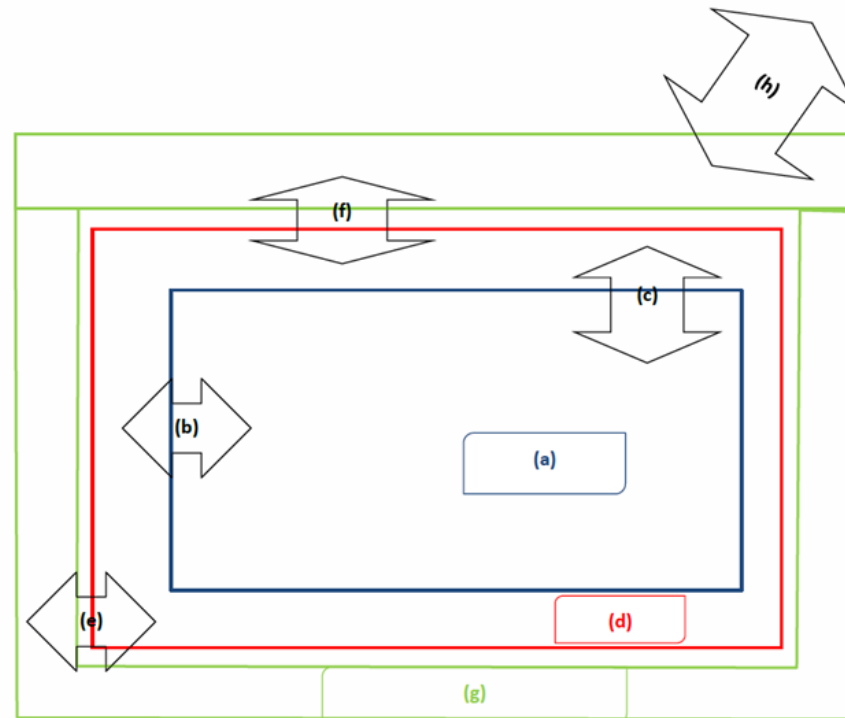
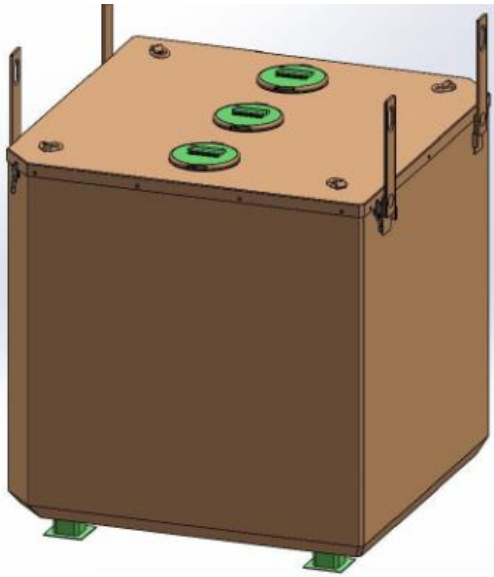




## Geometrical and thermal modelling of the 2020 industrial size experiment

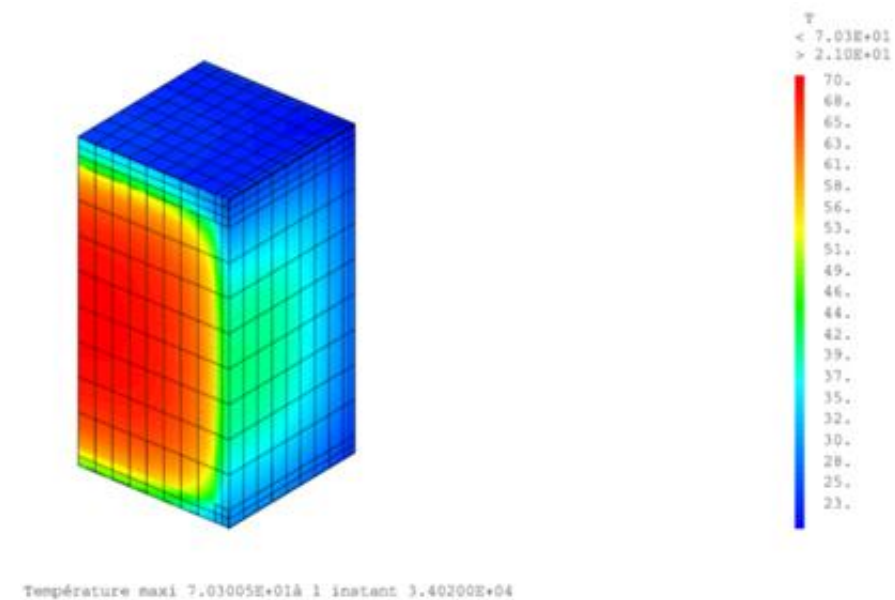
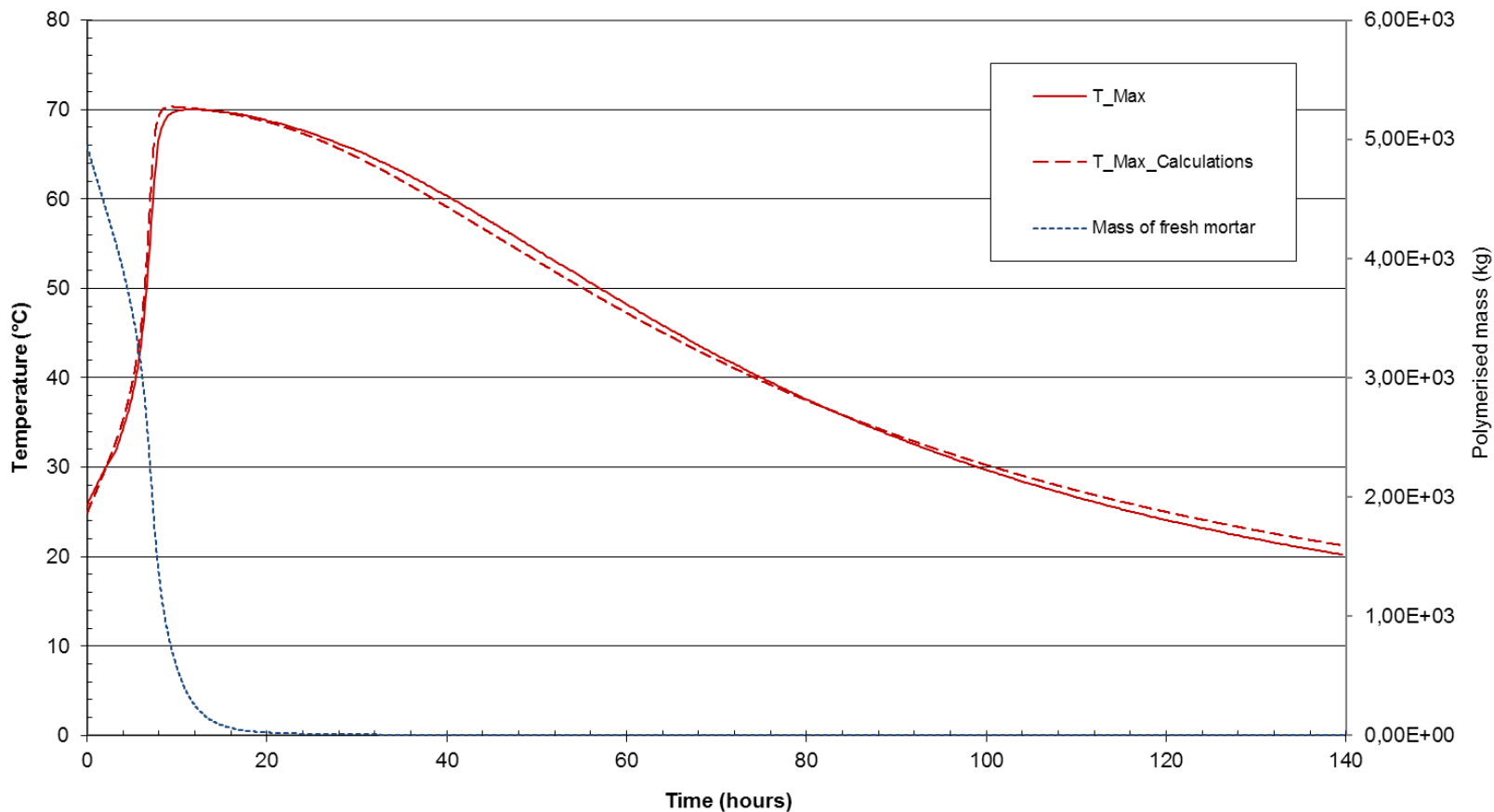
### ► Thermal modeling with the CEA Cast3M software

- Geometrical details (inside the box) : air gap at the apex, internal basket
- 10125 nodes, 180-hour transient, 37 thermal sensors, inside and outside the box
- Thermal conduction, heat generation, external fluxes (atmospheric convection, radiative transfer)



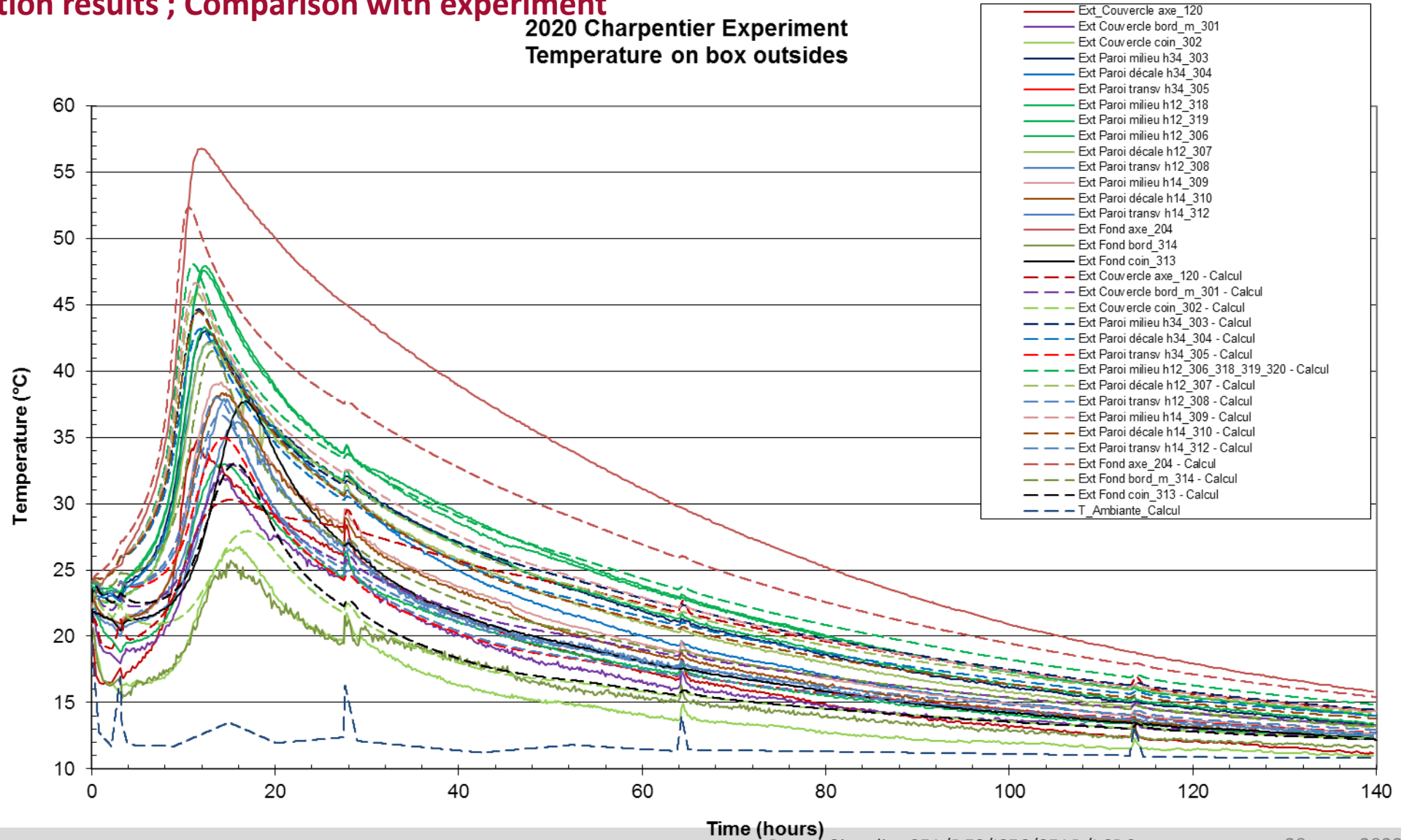
## Simulation results ; Comparison with experiment

- Temperature peak at 09:30  
Maximal temperature



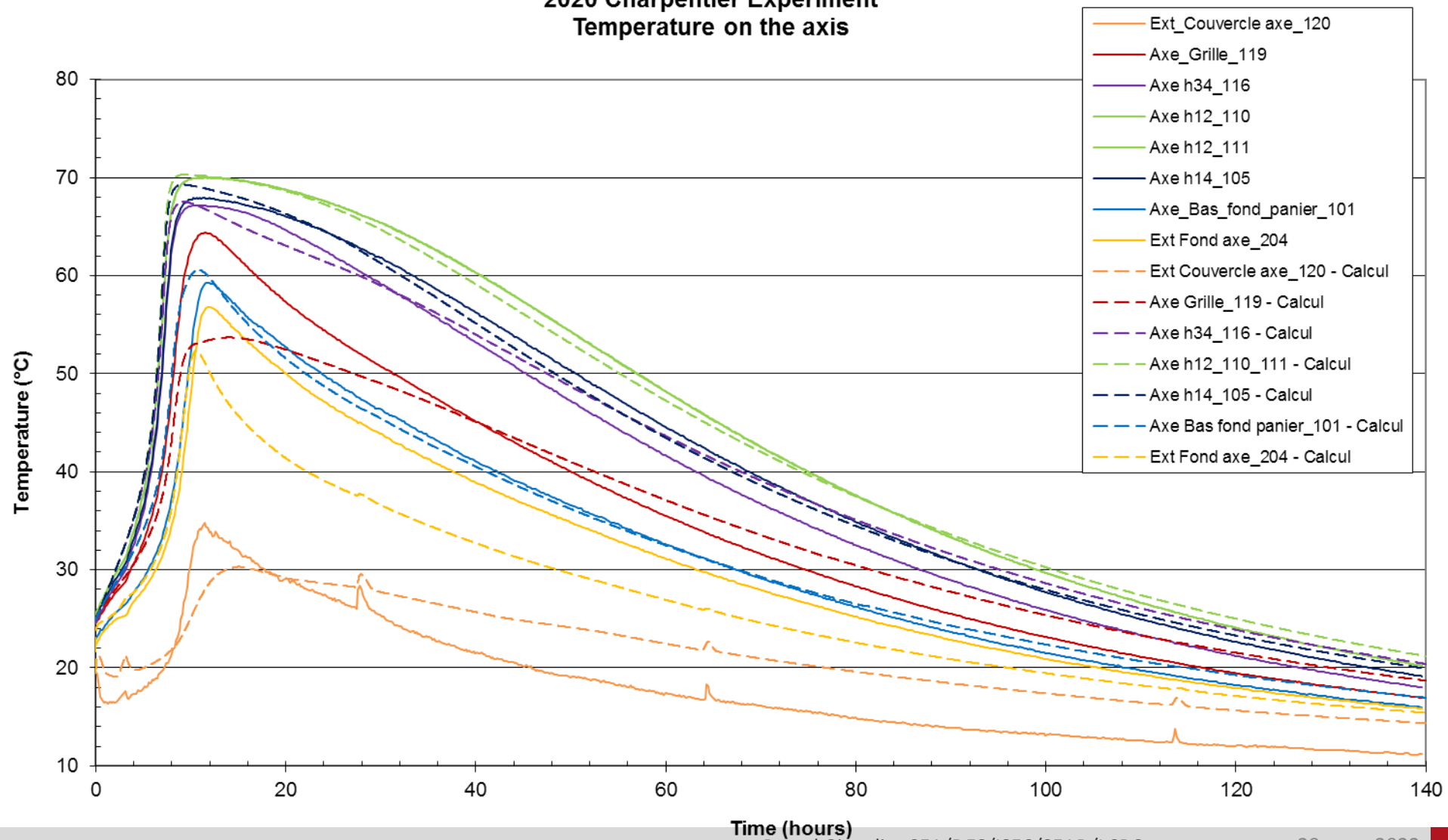
## Simulation results ; Comparison with experiment

2020 Charpentier Experiment  
Temperature on box outsides

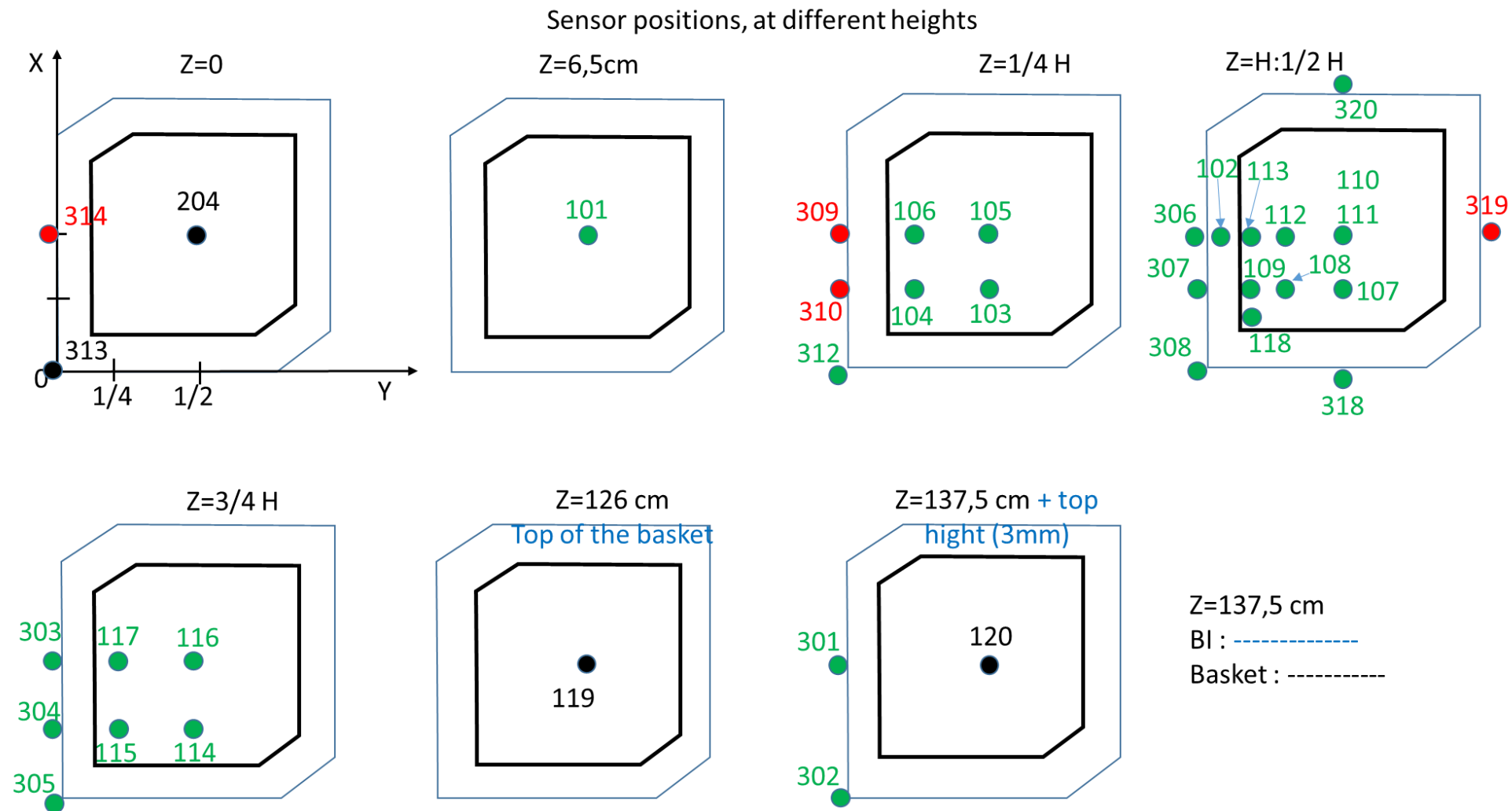


## Simulation results ; Comparison with experiment

2020 Charpentier Experiment  
Temperature on the axis



## Simulation results ; Comparison with experiment



## Sensitivity analysis

### ► Parameters

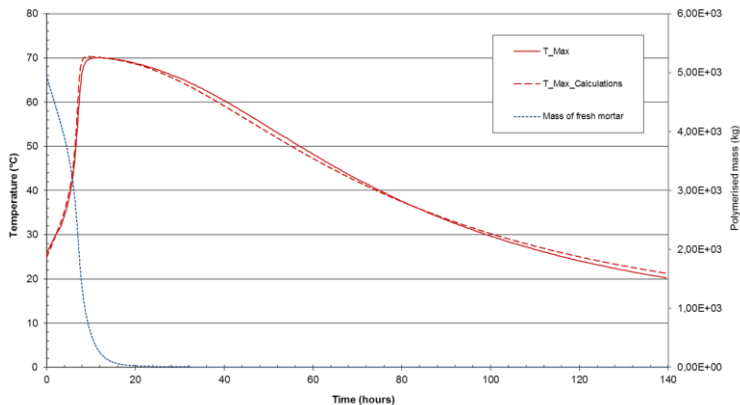
- Emissivity
- External temperature
- $h$  : internal thermal transfert efficiency
- Apparent activation energy
- Specific enthalpy

Parameter	Maximal temperature in the mortar (°C)	Deviation from the nominal temperature (simulation) (°C)
Experimentation measurement	70.0052	-0.2953
Simulation, nominal values	70.3005	--
Emissivity $\epsilon = 0.75$	70.3074	0.0069
Emissivity $\epsilon = 1.0$	70.2988	-0.0017
$T_{air} = 10\text{ °C}$	70.2638	-0.0367
$T_{air} = 25\text{ °C}$	70.3674	0.0669
$h_{apex} = 8\text{ W/m}^2/\text{K}$	70.3009	0.0004
$h_{apex} = 20\text{ W/m}^2/\text{K}$	70.2988	-0.0017
$h_{contact} = 100\text{ W/m}^2/\text{K}$	70.3056	0.0051
$h_{contact} = 2000\text{ W/m}^2/\text{K}$	70.3001	-0.0004
$h_{pehd} = 40\text{ W/m}^2/\text{K}$	70.3114	0.0109
$h_{pehd} = 150\text{ W/m}^2/\text{K}$	70.2883	-0.0122
$h_{grille} = 40\text{ W/m}^2/\text{K}$	70.3087	0.0082
$h_{grille} = 250\text{ W/m}^2/\text{K}$	70.2961	-0.0044
$Ea = 65\text{ kJ/mol}$	70.2184	-0.0821
$Ea = 84\text{ kJ/mol}$	70.4165	0.116
$H_{massique} = 75000\text{ J/kg}$	68.5398	-1.7607
$H_{massique} = 92000\text{ J/kg}$	78.6093	8.3088

## Some conclusions of the experimental/numerical campaign

- ▶ Confirmed peak temperature in a 2.7 m<sup>3</sup> waste-free form at 70°C
  - Peak temperature (with waste) should be smaller but close to the 60°C limit
- ▶ Industrial size heat transient : The peak temperature is independant of the outside cooling phenomena (convection, irradiance)
- ▶ Usefulness of the sensitivity analysis, to prioritize the parameter precision needs
- ▶ Impact of the geometrical scale : issues at small scale (120 l, 220 l) can be very different than those at large scale (irradiance, ...)

Maximal temperature



## Next steps and investigations

### ► Thermal impact of the metallic waste

- Evaluation of an homogenized thermal conductivity (with the help of the Mori-Tanaka method)

$$\lambda_{mortier} = 1.87 \text{ W/K/m} , \text{ estimated } \lambda_{enrobé} = 2.47 \text{ W/K/m}$$

### ► Improvement of our knowledge about the enthalpy fluctuations (depending on the input material properties)

### ► Evaluation of the H<sub>2</sub> generation in the waste container due to the heat peak







# Thank you for your attention

Speaker : Pascal Girardin\*

In collaboration with Gilles Cardinal, Mickaël Marchand, Matthew Moinard, Elodie Nilly, Pascal Antonucci, Arnaud Poulesquen

CEA, DES, ISEC, DE2D, Univ Montpellier, Marcoule, BP 17171, 30207 Bagnols-sur-Cèze cedex, France

\* Corresponding Author, E-mail: [pascal.girardin@cea.fr](mailto:pascal.girardin@cea.fr)

With the support of Jennifer Doriguzzi (CEA, DES, DDSD, URDM)

The authors are thankful to Aveline Darquennes (INSA-Rennes) and all the participants of the R&D 'DECIMAL' project