The Use of Thermal Analysis in the Development and Characterisation of Materials for Energy Storage

-**Thermochemical Energy storage**

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Introduction - Purpose

- **26%** of all the UK's energy consumption used specifically for;
    - Domestic Space Heating (DSH)
    - Domestic Hot Water (DHW)
- **88%** of energy for DHW + DSH comes directly from **gas** and **oil**
- **2%** of energy for DHW + DSH comes from **Renewables**
- **Thermochemical Energy Storage** offers a renewable solution to store excess solar irradiance and release the heat almost **loss free** when required

Introduction

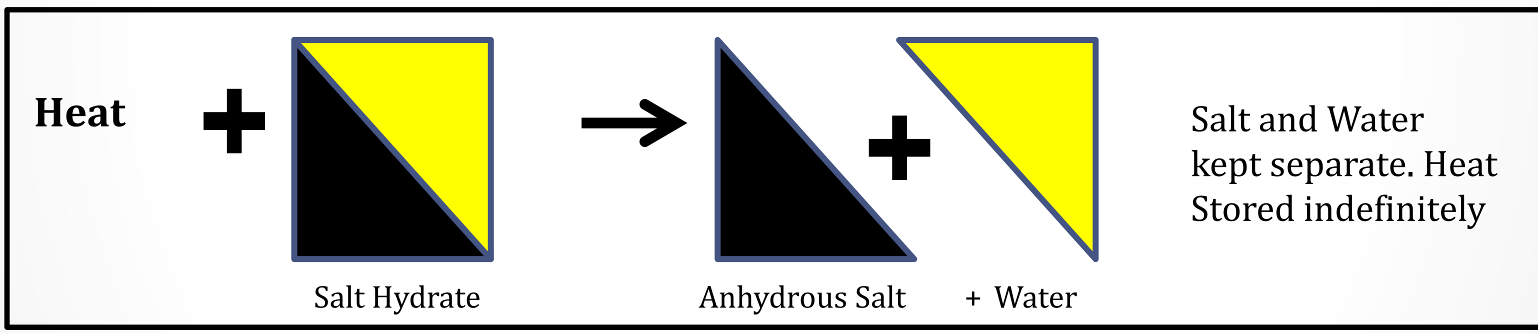
- What is Thermochemical Energy Storage?
- What is $MgSO_4$
- What do I use TA's TGA and DSC for;

1. Energy storage potential of Thermochemical Energy Storage Materials (TCESM).
2. Slow dehydration (charging) kinetics
3. The hydration of salt hydrates within porous host materials.

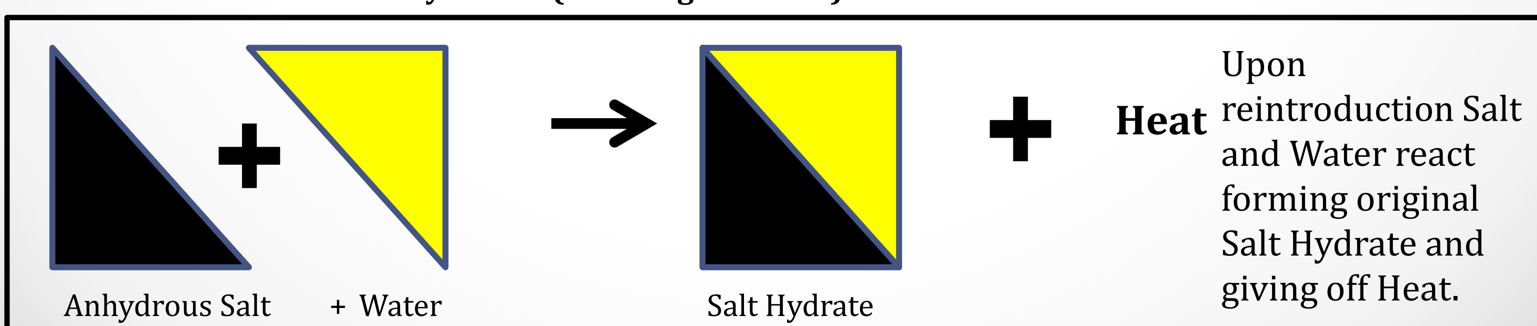
What is TCES?

- Target : Develop a Thermochemical Energy Storage (TCES) material for domestic interseasonal heat storage.
  - Charge in summer – using solar thermal collector
  - Discharge in winter.

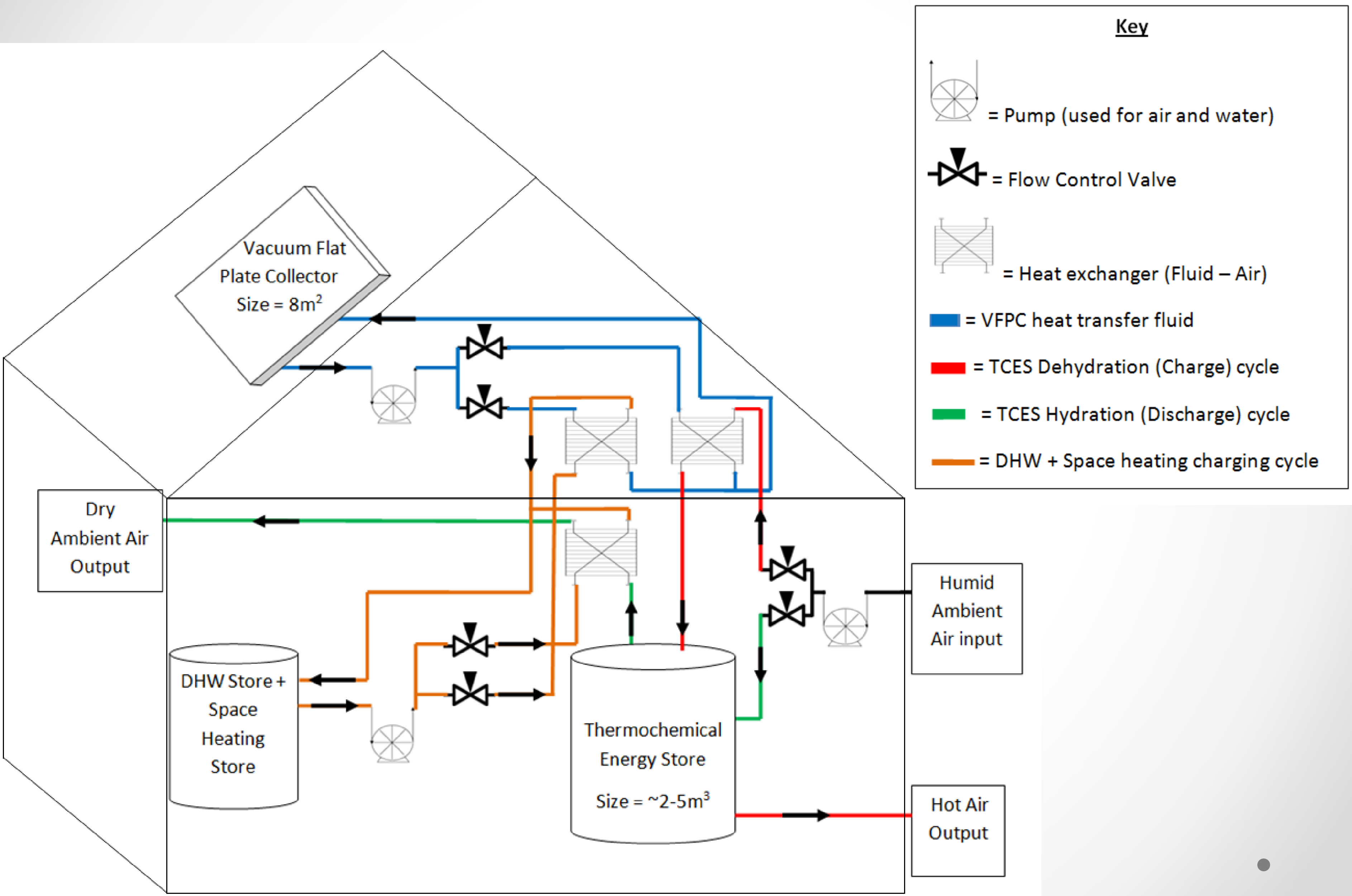
Dehydration (Charging Process)



Re-hydration(Discharge Process)



Possible TCES integration



$MgSO_4.7H_2O$

Requirements;

- Dehydrate (charge) below 150˚C, High energy density (*target 277kWh/m³*), Safe materials, Competitive kWh price (*i.e. <10p/kWh*).

$MgSO_4.7H_2O$ = Great potential for domestic inter-seasonal heat storage.

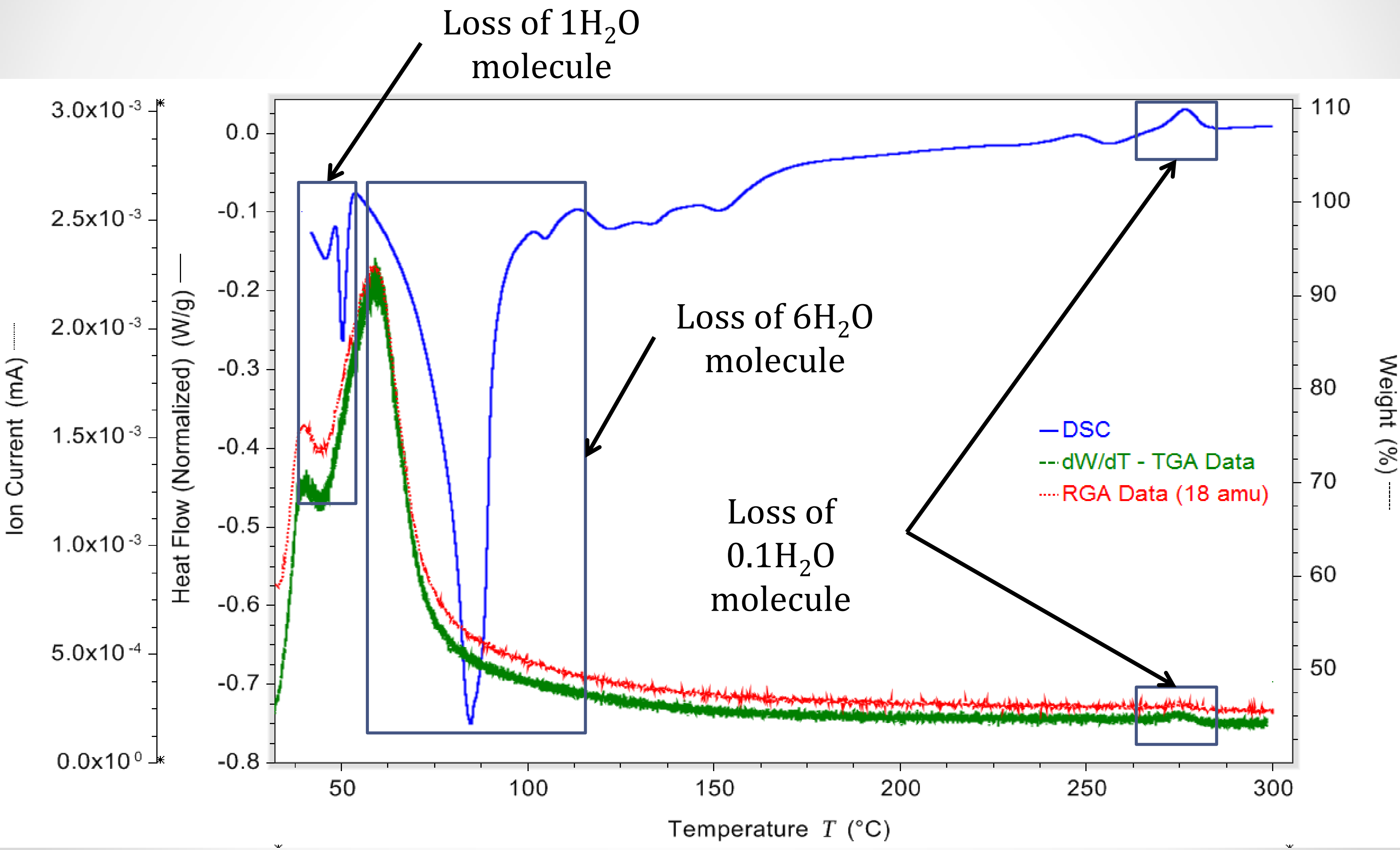
Cost effective (£61/Ton), Widely available, High energy density 2.8GJ/m^3 (778kWh/m^3), Non-Toxic.

Problems – Material difficult to work with in powder form, agglomeration occurs reducing cycle stability, permeability and power output. Sensitivity to high heating rates.

- Solution? – Develop a composite material (**possible using an absorbent**) to enhance the poor characteristics of $MgSO_4$ and extract as much energy as possible while meeting the above targets.

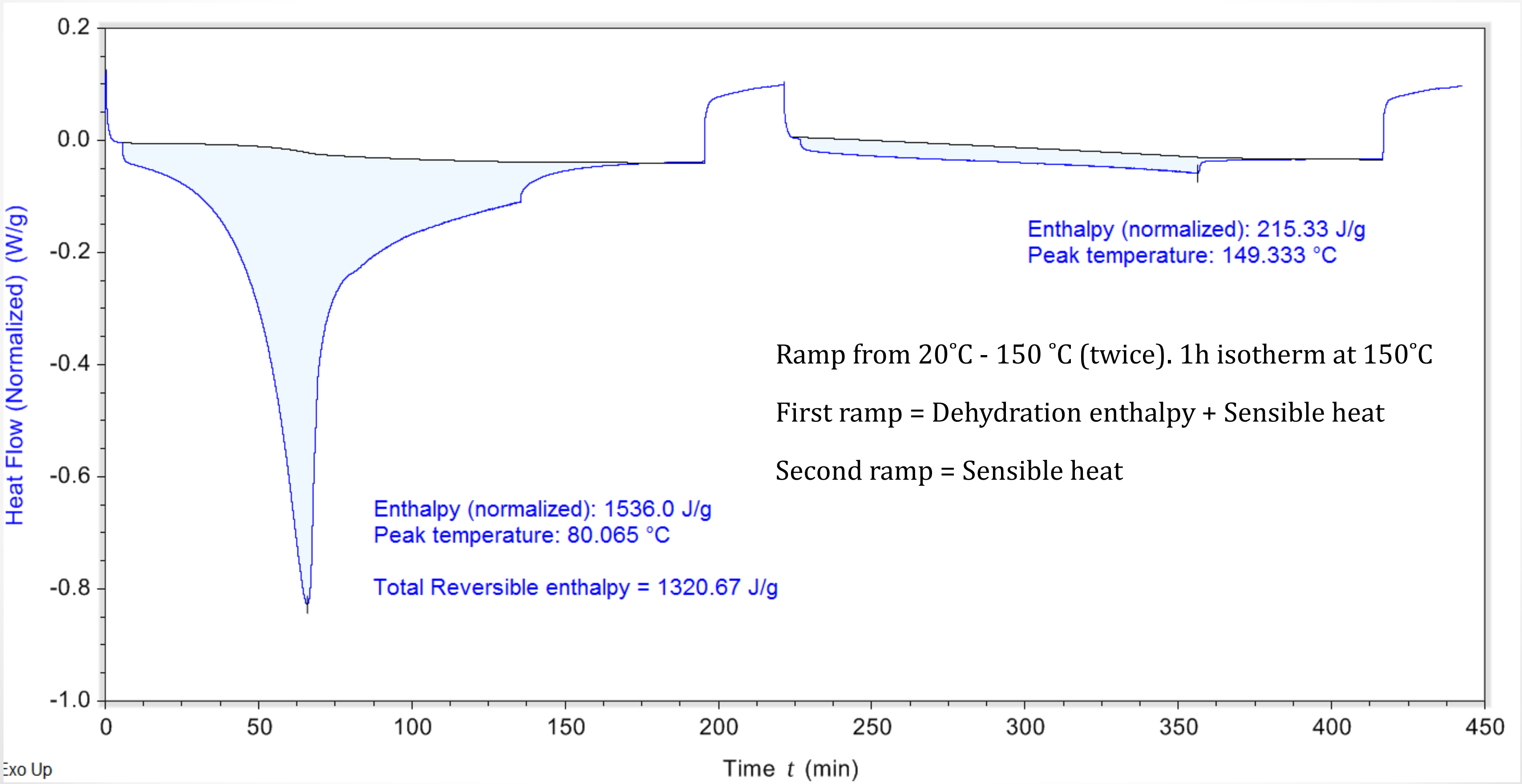
$MgSO_4.7H_2O$ Dehydration

•DSC, TGA and RGA used to characterise and assess potential of TCES materials for Domestic use.



1. Energy Storage potential of TCESM

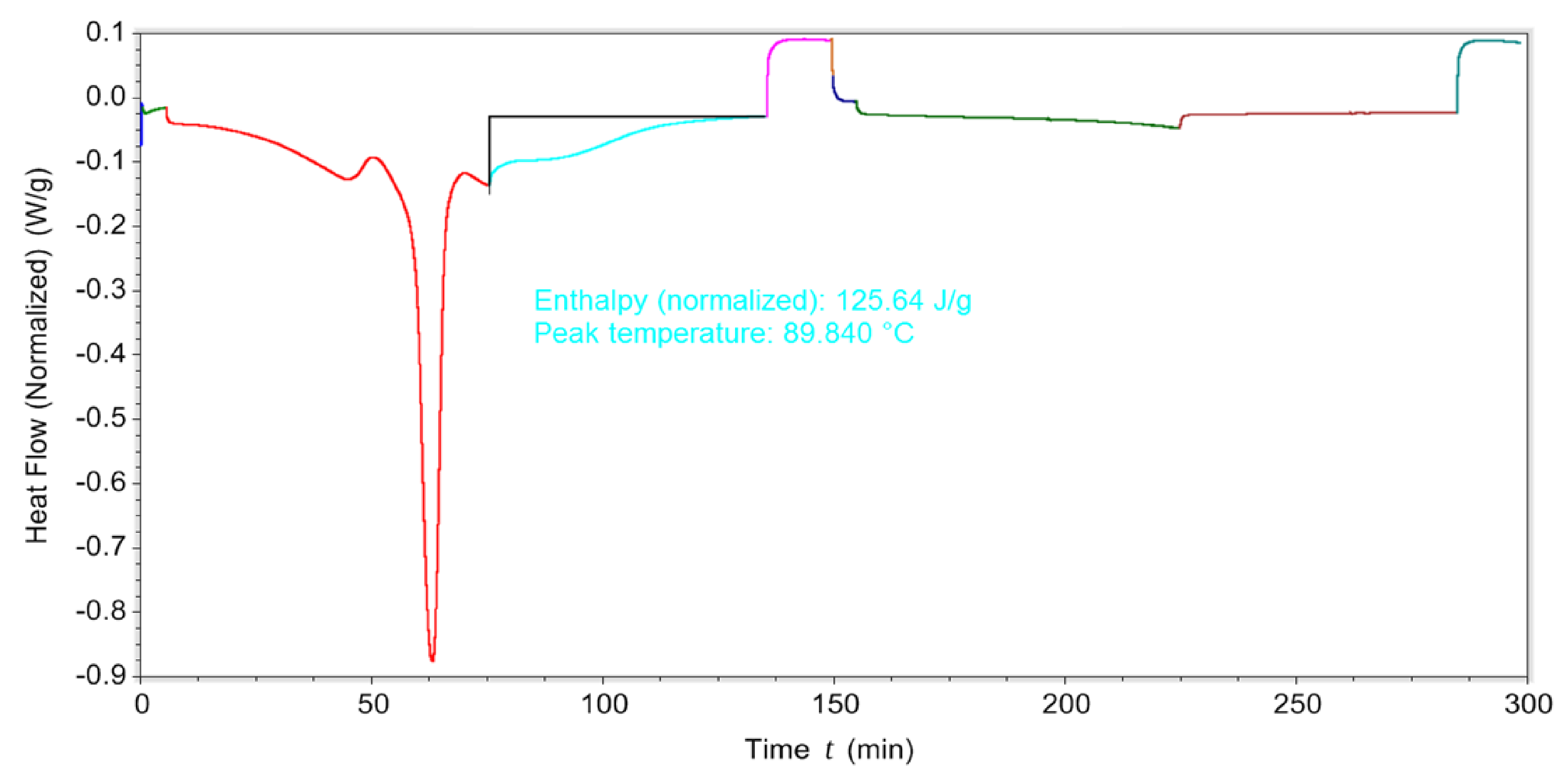
- DSC to analyse the dehydration enthalpy - vital for energy storage potential.
  - Analyse overall energy required for each charge cycle (J/g)
  - Assess temperatures at which energy is stored



Average after 8 cycles = ~1200J/g = $MgSO_4$
Water =~335J/g Concrete =~ 120J/g

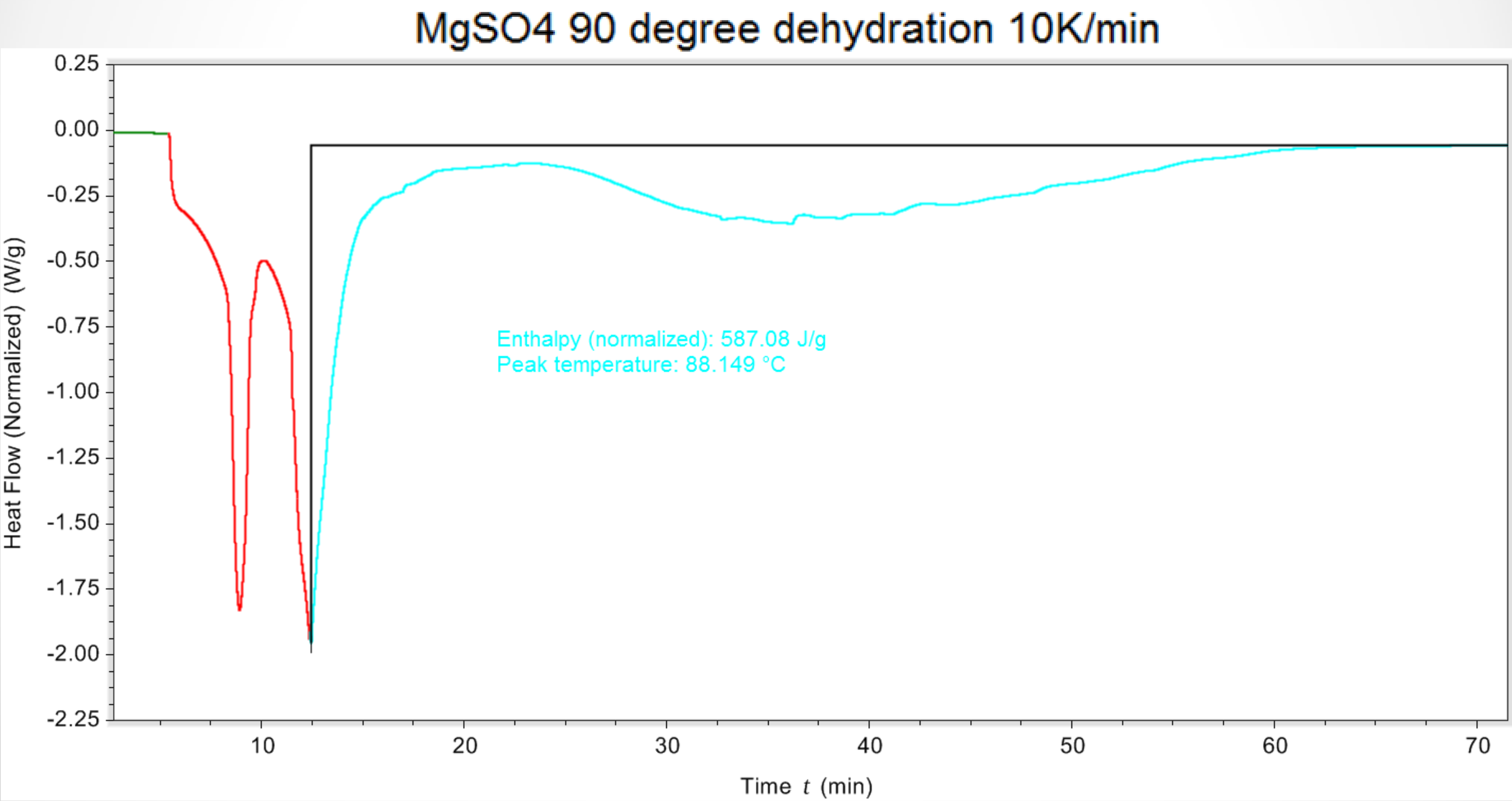
2. $MgSO_4$ Slow Dehydration Kinetics

- DSC and TGA used for assessing the dehydrating (charging) kinetics of the $MgSO_4$.
- The DSC is used to evaluated the isothermal dehydration enthalpy of each sample with varying heating rate.
- The heating rate used for the dehydration (charging) of $MgSO_4$ impacts the temperature at which energy is stored and water is lost.
- Below shows $MgSO_4$ dehydrated to 90˚C and held isothermally with the isothermal segment integrated.



2. $MgSO_4$ Slow Dehydration Kinetics

- Graph shows $MgSO_4$ dehydrated using 10K/min
- Notice the endothermic peak in the isothermal period.



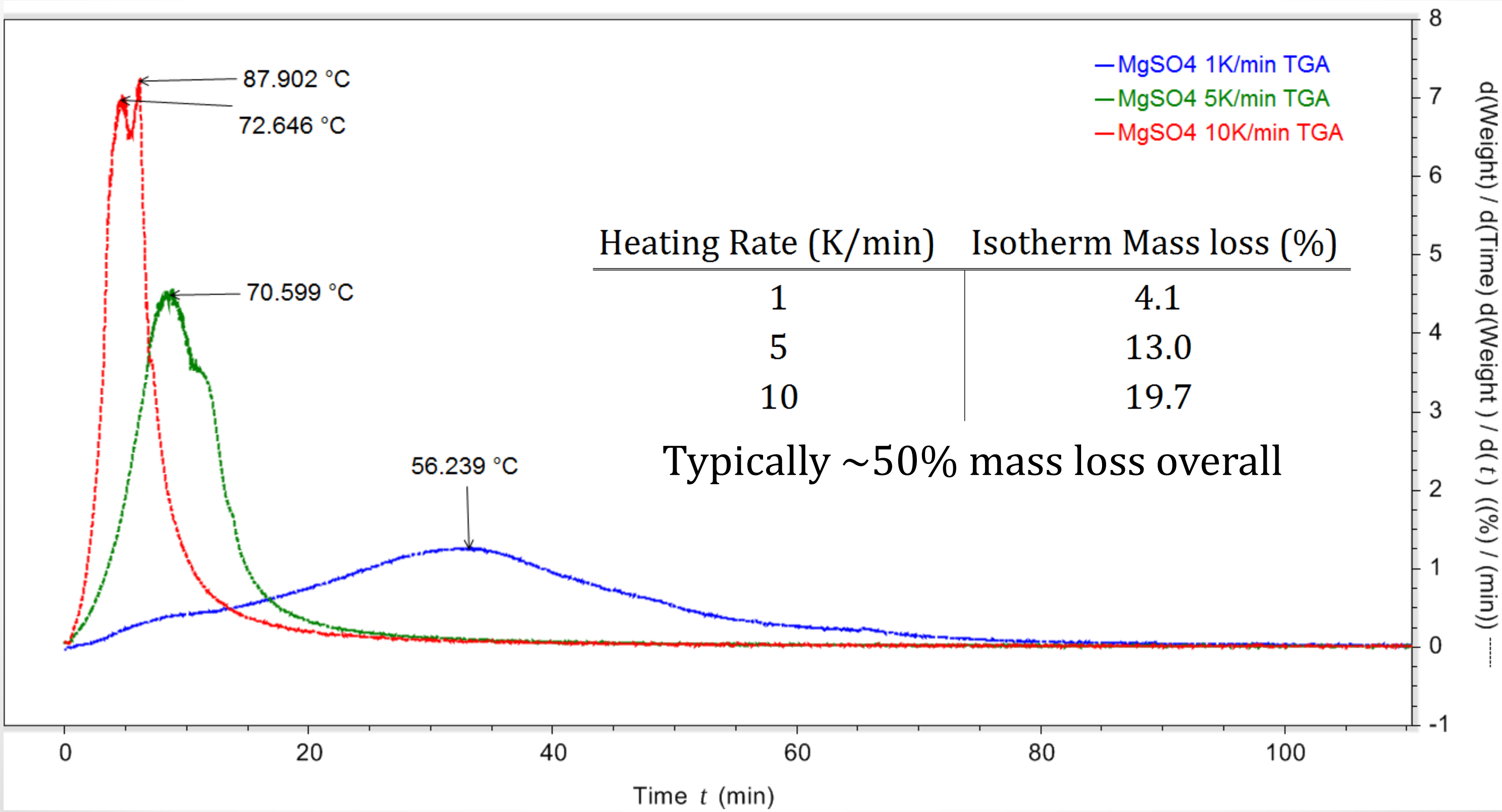
2. $MgSO_4$ Slow Dehydration Kinetics

- After integration of the isotherm period clearly the endothermic heat flow increases with increasing dehydration temperature.
- Causes a delay in the dehydration “charging” of the $MgSO_4$ material.

		Heating Rate (K/min)		
		1	**5**	**10**
Cycle 1	Isotherm Enthalpy (J/g)	77	337	481
	Iso / Dehy (%)	12	57	69
Cycle 2	Isotherm Enthalpy (J/g)	119	261	372
	Iso / Dehy (%)	20	54	61

2. $MgSO_4$ Slow Dehydration Kinetics

- The TGA is used in a similar way for assessing the peak dehydration temperature and also the mass loss in the isothermal period.
- With increasing heating rate the peak dehydration temperature and isotherm mass loss increases.

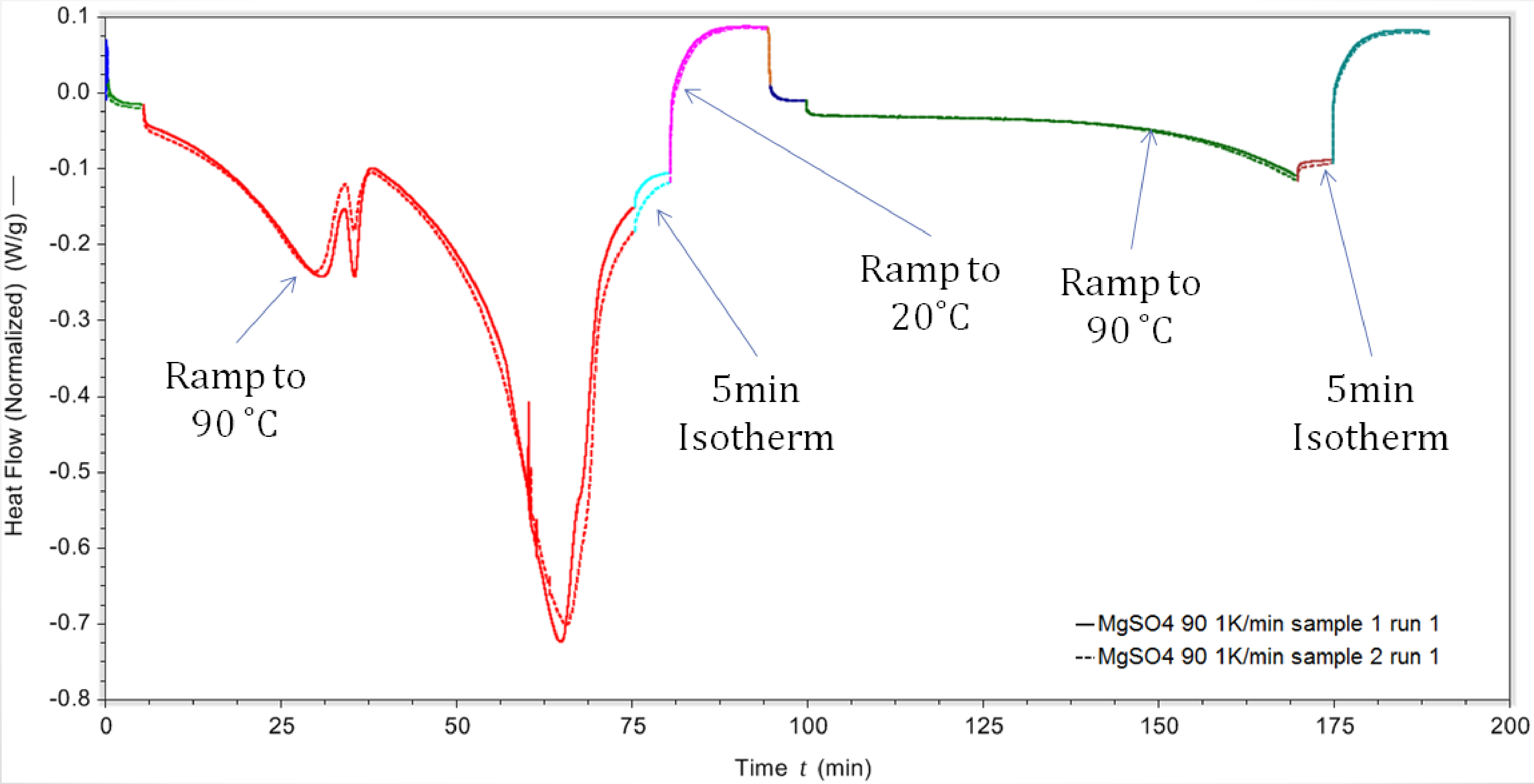


Heating Rate (K/min)	Isotherm Mass loss (%)
1	4.1
5	13.0
10	19.7

Typically ~50% mass loss overall

2. $MgSO_4$ Slow Dehydration Kinetics

- The $MgSO_4$ doesn't always reach the same level of dehydration if a higher heating rate is used. The isothermal period is an important consideration when considering different heating rates



Average dehydration enthalpy (including ramp to 20˚C) = **955 J/g**

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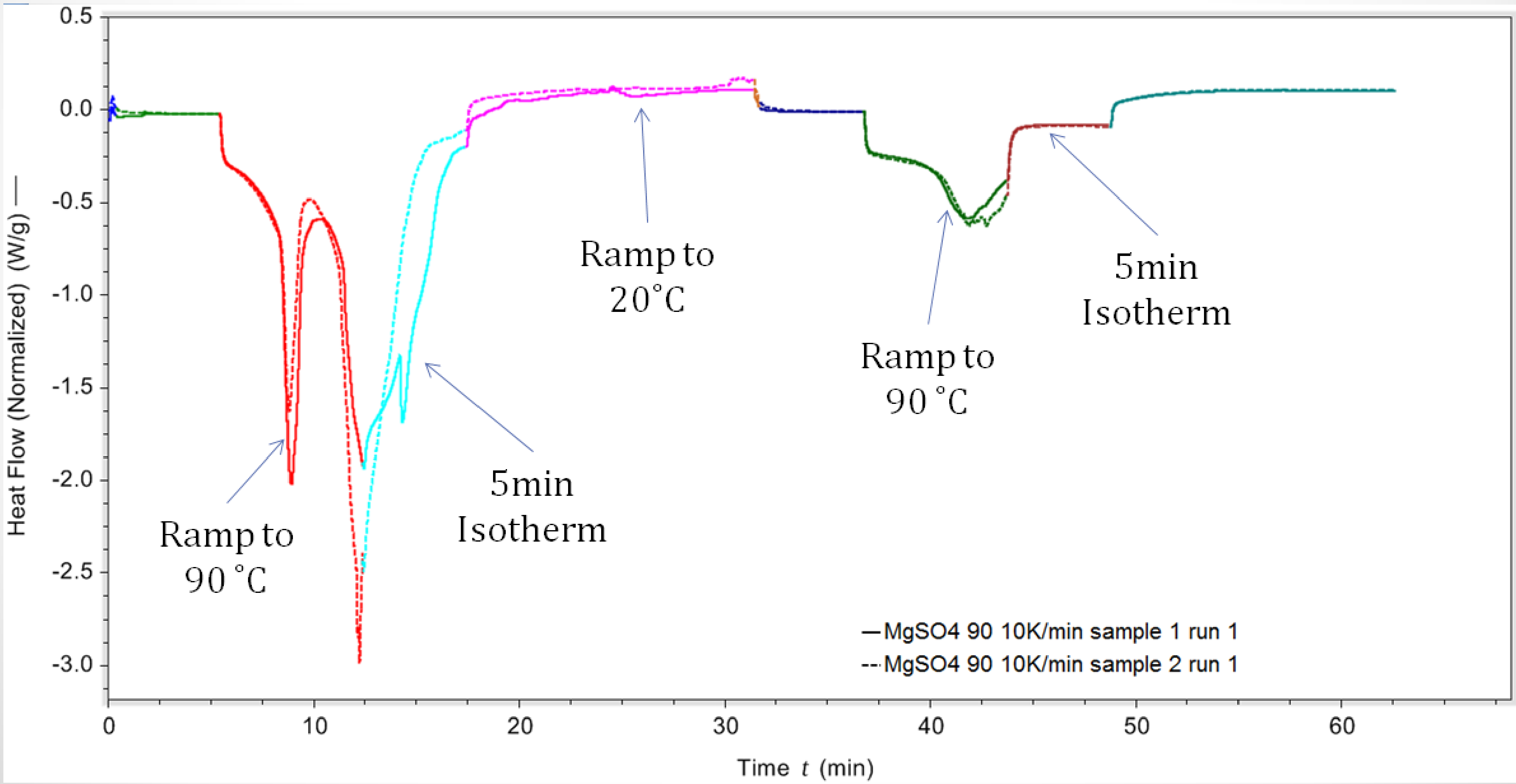

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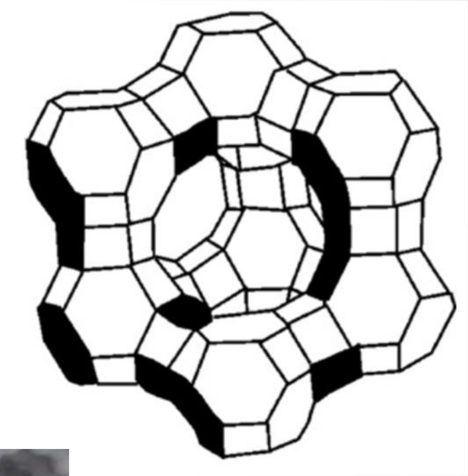
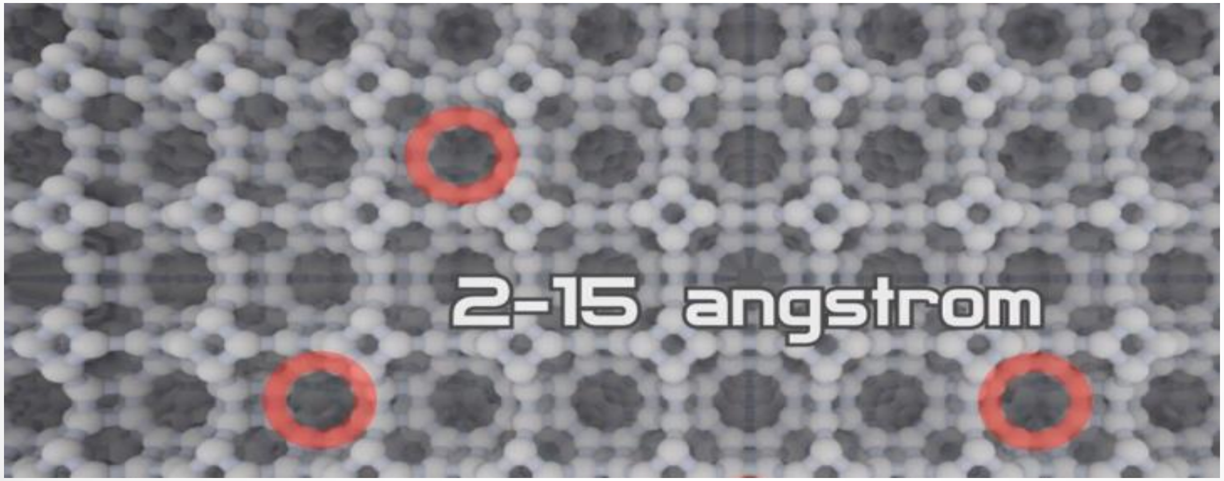
3. Hydration within Porous hosts

<u>13x molecular sieve</u> (AKA Zeolite)

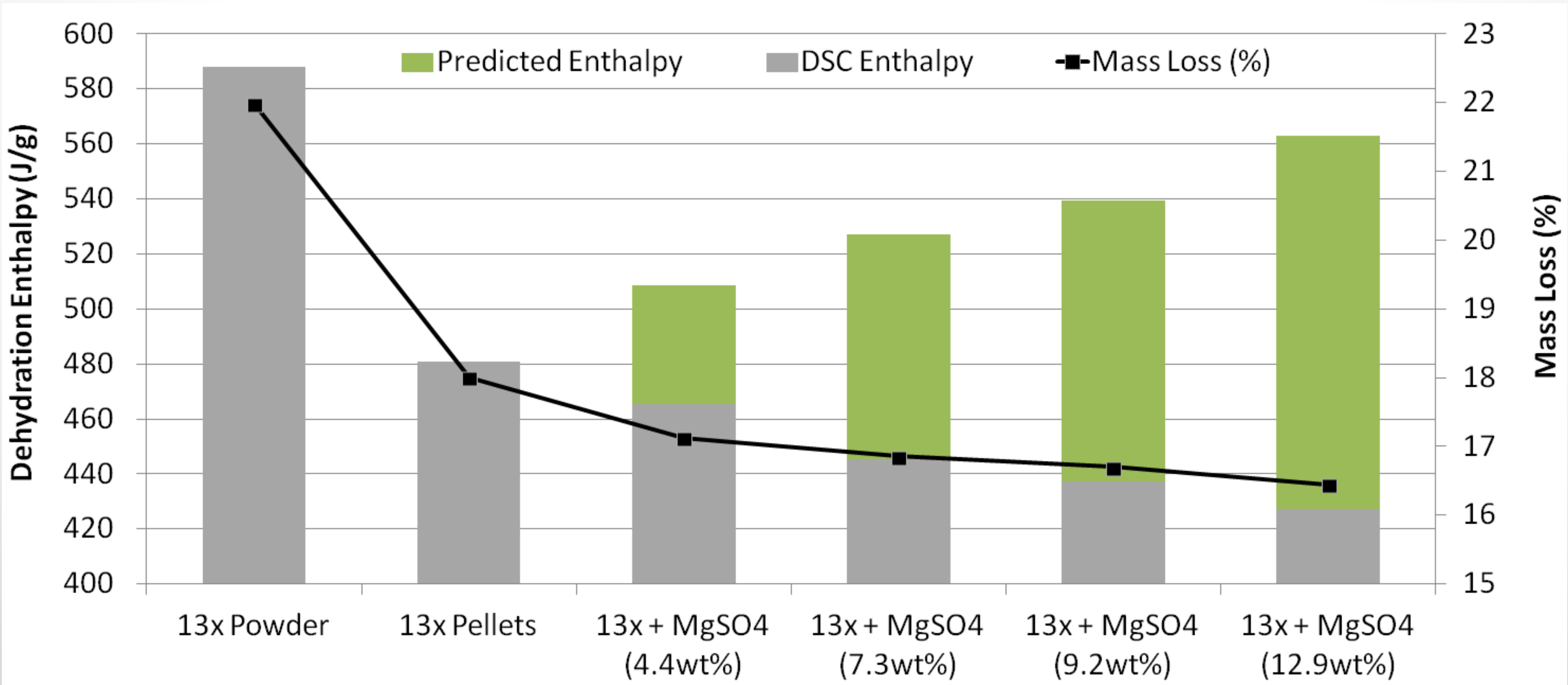
- Absorbent material with uniform “cage like” 3D alumina silicate crystal structure.
- Could potentially be used to store heat.
- The structure has uniformed pores.
- Potentially ideal for $MgSO_4$ impregnation.





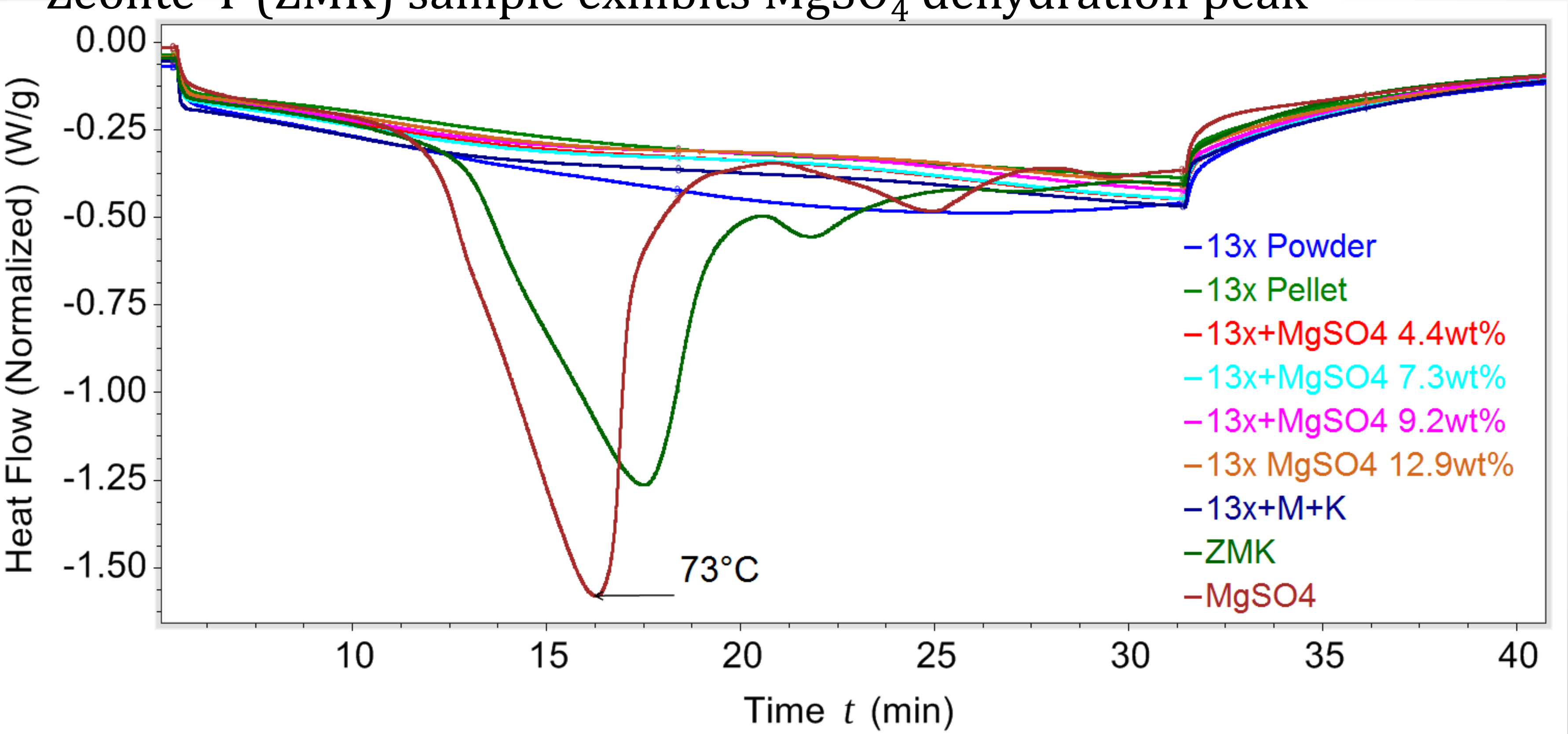
3. Hydration within Porous hosts

- Graph showing mass loss %, DSC dehydration enthalpy and predicted DSC dehydration enthalpy of each 13x sample (created using wetness impregnation) tested.
- Decreasing dehydration enthalpy with increasing $MgSO_4$ wt%
- Suggests Lack of $MgSO_4$ hydration within 13x material



3. Hydration within Porous hosts

- Graph shows DSC dehydration plots for each sample tested.
- All 13x sample's show no $MgSO_4$ dehydration peak
  - Using two different preparation methods
  - Not good for $MgSO_4$ host
- Zeolite-Y (ZMK) sample exhibits $MgSO_4$ dehydration peak



Summary

TA's Thermal analysis devices (DSC and TGA) used for;

1. Identifying the energy storage potential of thermochemical energy storage materials.
    1. Temperature material is charged
    2. Peak charging "zones"
2. Understanding the slow dehydration (charging) kinetics of thermochemical materials.
3. Establishing the hydration of salt hydrates within host materials
    1. Identifying know dehydration peaks

Using standard calorimetry to characterize phase change materials

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Introduction

- A fifth of the UK's final energy demand in 2015 was used for conventional heating applications using natural gas [1];
- To decarbonize the space heating sector, heat pumps are viable candidates;
  - To minimize both carbon intensity and electrical peak load demands, their usage should be restrained to off peak times;
- Phase change materials can effectively increase the storage capacity of common sensible heat storage systems for daily heat storage applications;

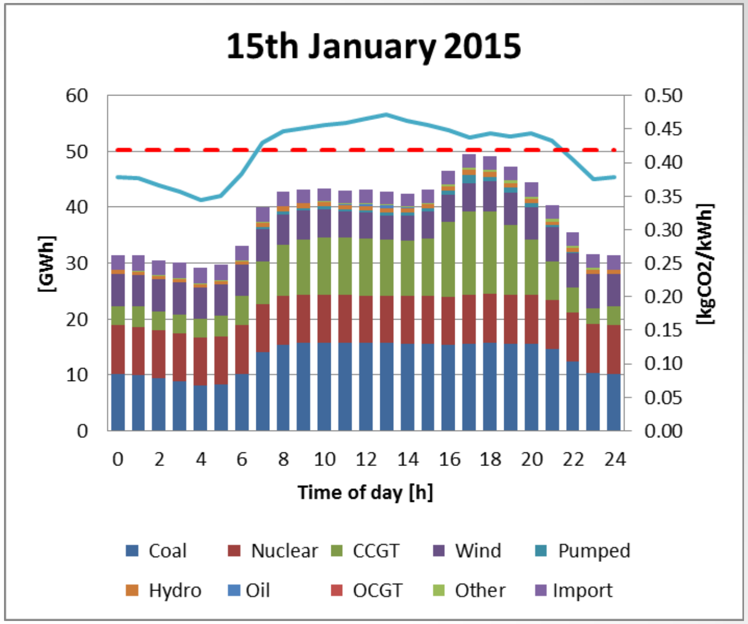


Figure 1-Hourly variation of CO2 emissions associated with the electricity supplied by the UK national grid.

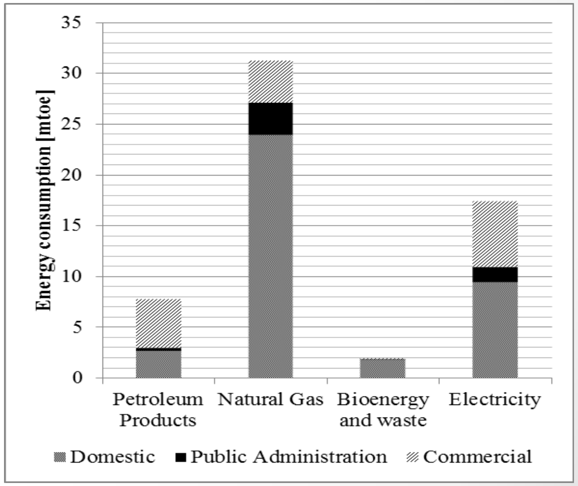


Figure 2 - The UK's final energy consumption aggregated values for 2014 by source in the Domestic, Commercial and Public Administration sectors.

[1] - K. Harris, A. Annut, and I. MacLeay, *Digest of United Kingdom Energy Statistics 2015*, vol. b. 2015.

i-STUTE

Thermal energy storage

- Phase change Materials can store large amounts of heat within a narrow temperature range;

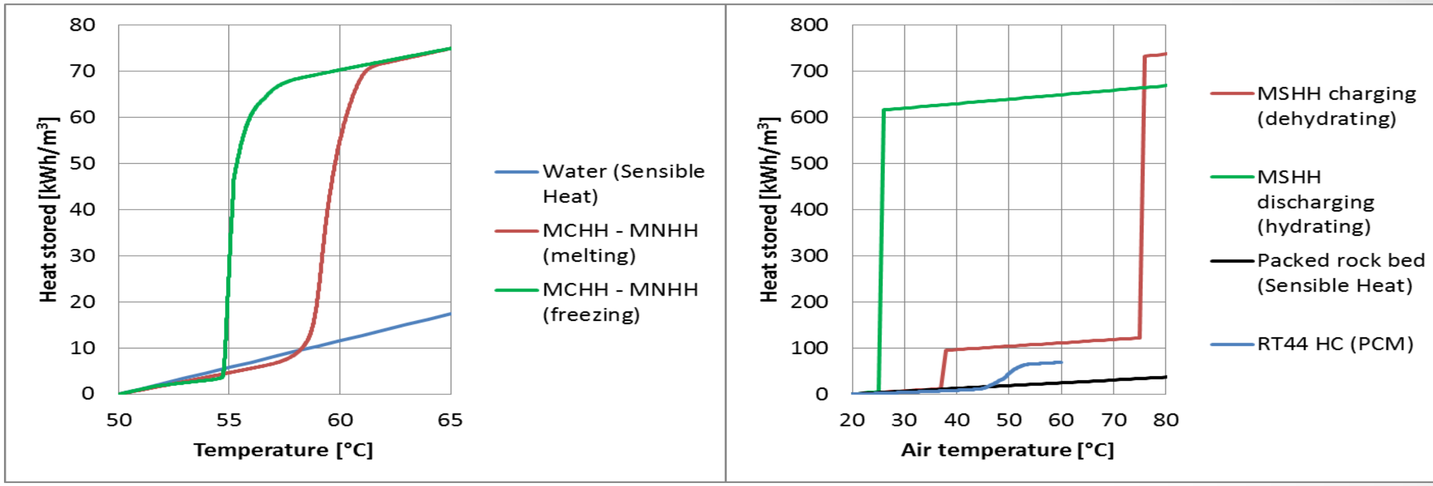


Figure 3 – Enthalpy-Temperature diagrams comparing sensible, latent and thermochemical heat storage.

- Proven technology, less denser than thermochemical heat storage;

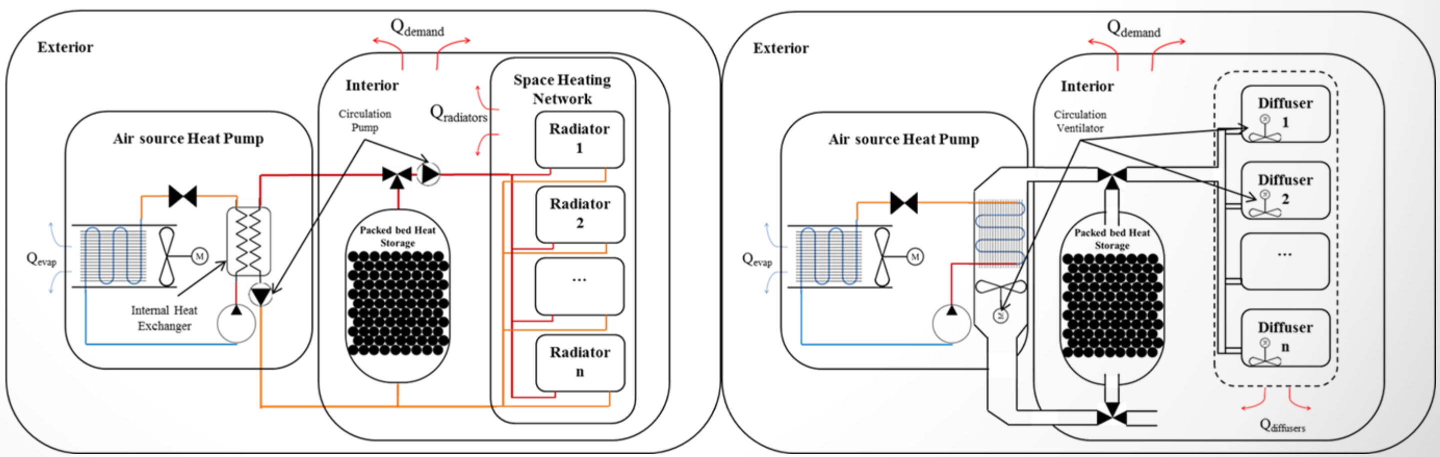


Figure 4 – Integrating heat storage into a conventional space heating and centralized ventilated heating network.

Thermal Analysis

- Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are common devices used to used to rapidly access the PCMs:
  - Thermal stability;
  - Cycle repeatability;
  - Sub cooling prior to solidification;
  - Latent heat of fusion;
  - Heat capacities;

Figure 5 – Discovery DSC from TA instruments.

Figure 6 – Discovery TGA from TA instruments

TGA analysis

Thermal stability

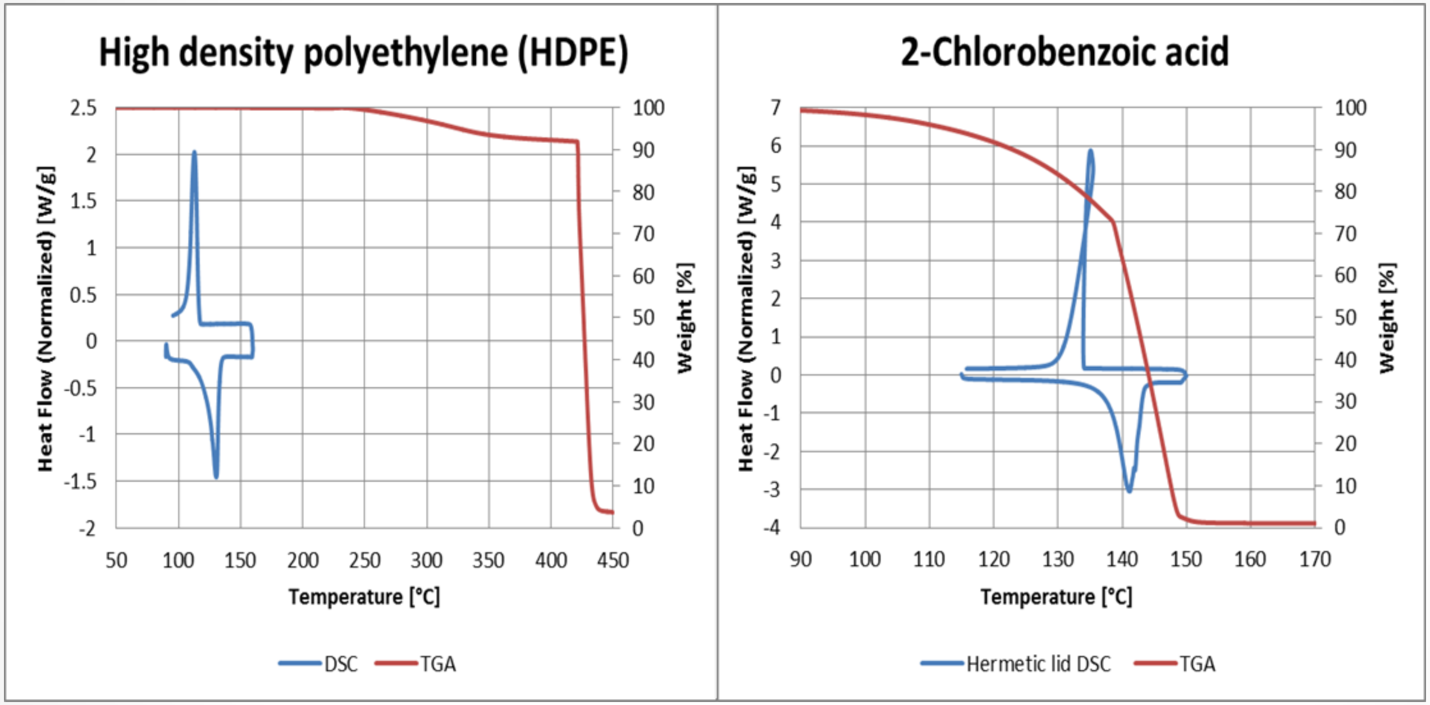


Figure 7 – Overlay of the DSC and TGA result for two a stable PCM and a unstable PCM.

- Ramp rates below 3˚C/min and sample sizes below 5mg improves the TGA measurement temperature accuracy;
- A 30 to 60 ˚C plateau prior to the melting point indicated some stability in the molten state;

DSC analysis

Cycle repeatability

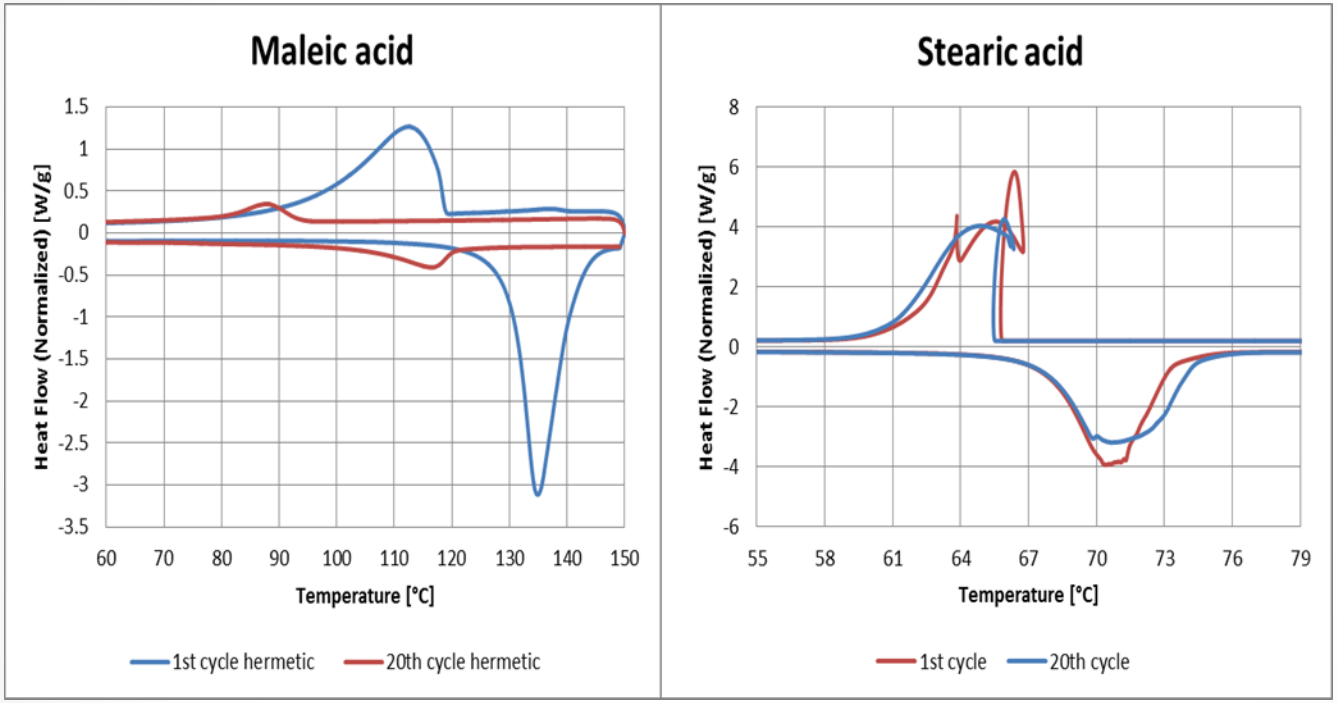


Figure 8 –DSC cycling results for a PCM with a irreversible and a reversible phase change.

- DSC cycling results are a useful tool to quickly determine the reversibility of a phase change;

DSC analysis

Sub cooling

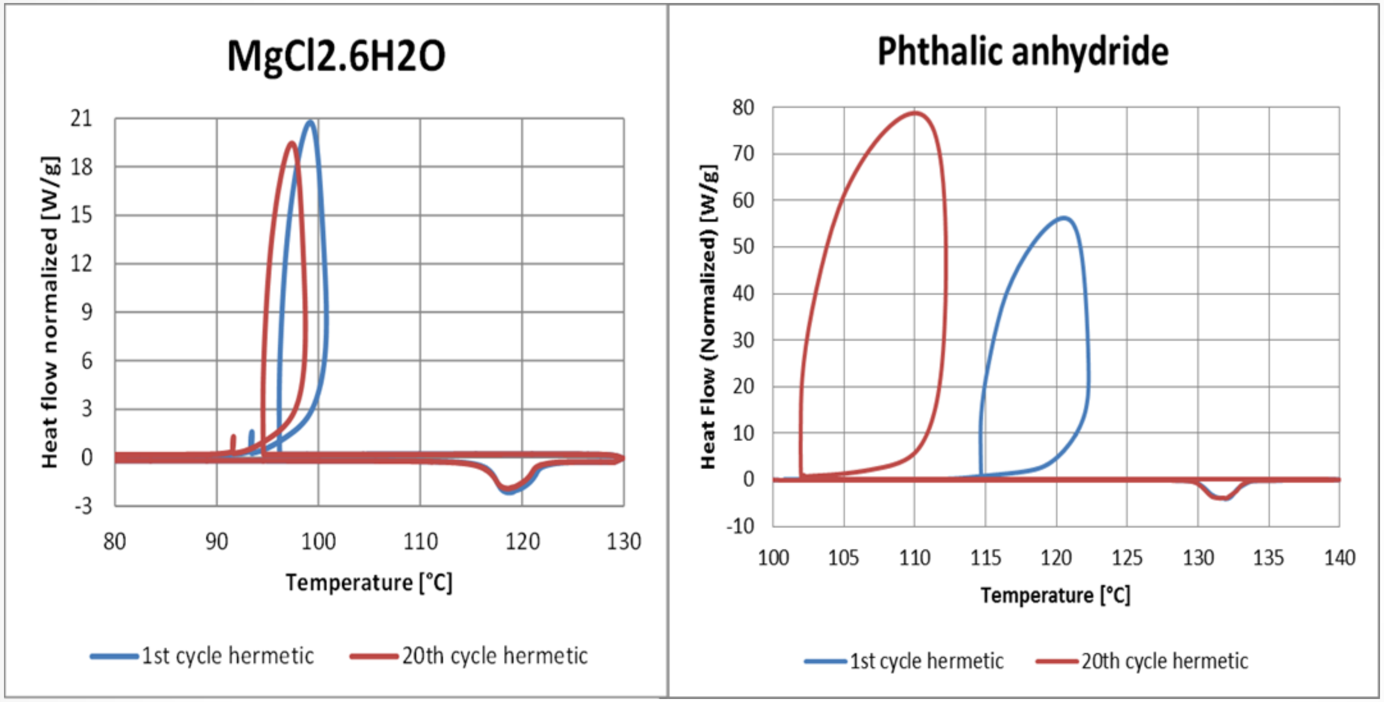


Figure 9 –DSC measurement results for two PCMs with sub cooling in the onset of their crystallization.

- Difficulty in starting to nucleate the first solid crystals among the molten PCM;
- Main limitation for standard DSC analysis;
- Dependent on the sample size;

DSC analysis

Latent heat of fusion

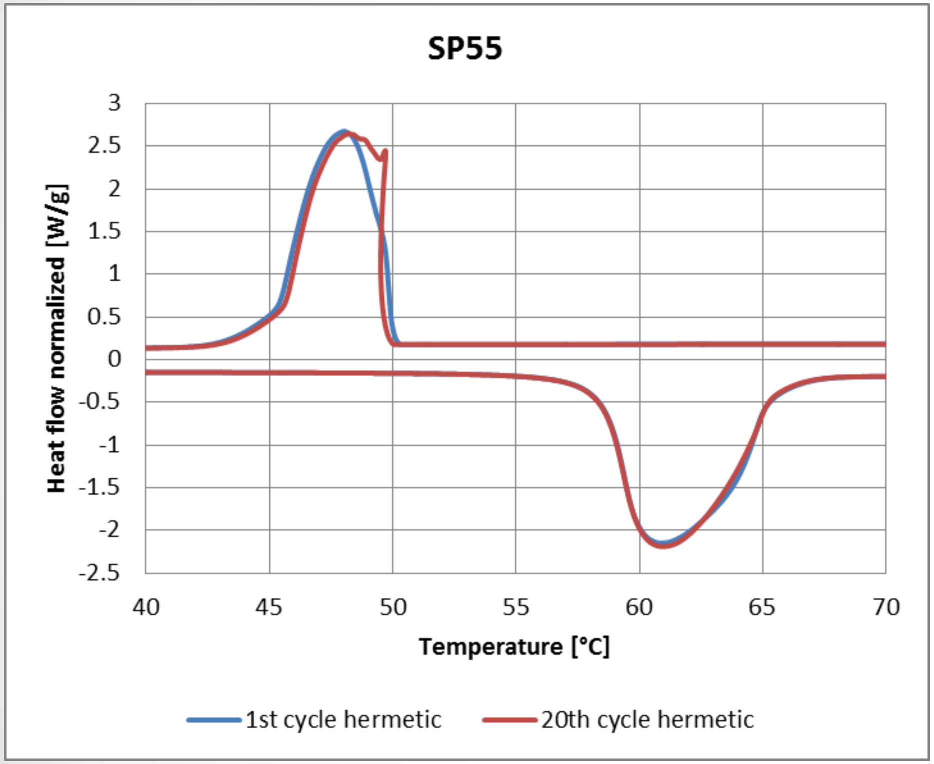
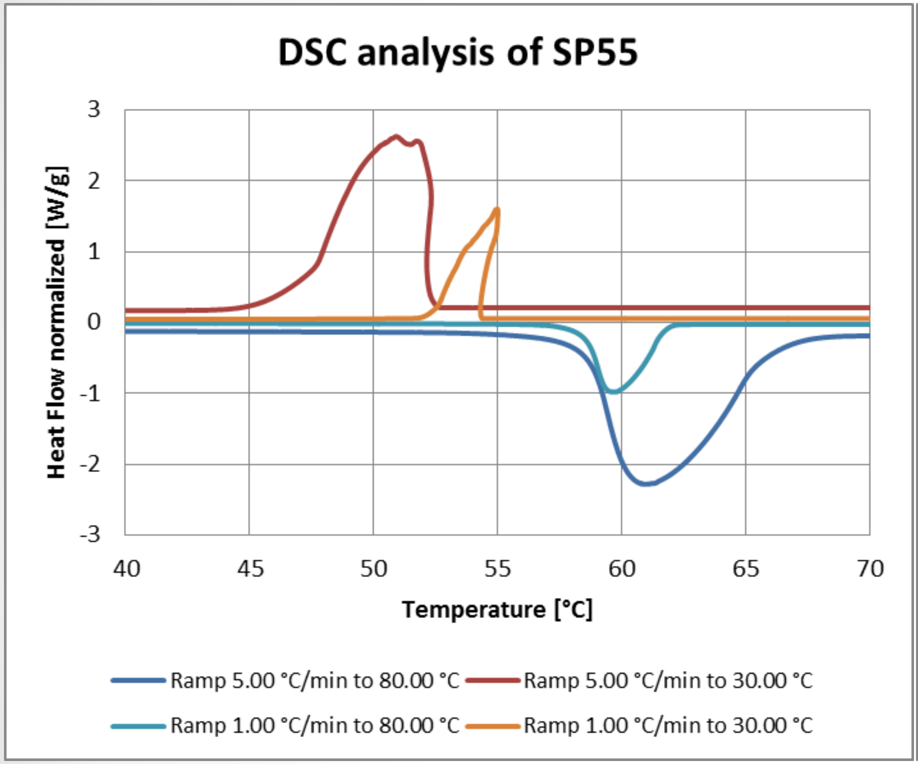


Figure 10 – DSC measurement results for a eutectic mixture containing 59% Mg(NO3).6H2O and 41% MgCl2.6H2O (%wt).

- Using as baseline the lower heat flow signal;
- Accounting the enthalpy absorbed between the baseline and the local heat flow signal;
- Obtains reliable values with reduced sample sizes (<=10mg);

DSC analysis

Heat capacity curves



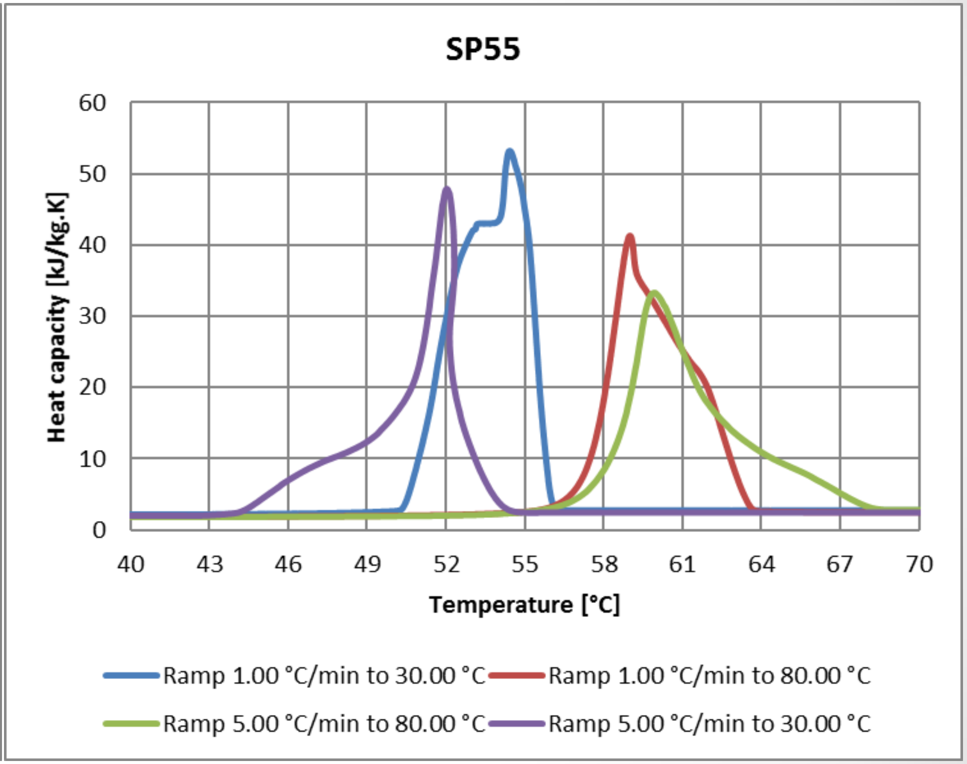


Figure 11 – DSC measurement results for a eutectic mixture containing 59% Mg(NO3).6H2O and 41% MgCl2.6H2O (%wt).

- Lower heat rates give more accurate results of the material's thermal response;
- Heat rates lower than 1 K/min in a standard DSC are very sensitive to noise;

Materials screening and characterization

- Salt hydrates eutectic mixture presented the most interesting properties;
  - High storage density;
  - Relatively good thermal conductivity;
  - The system would need to operate up to 65°C to fully melt the PCM;

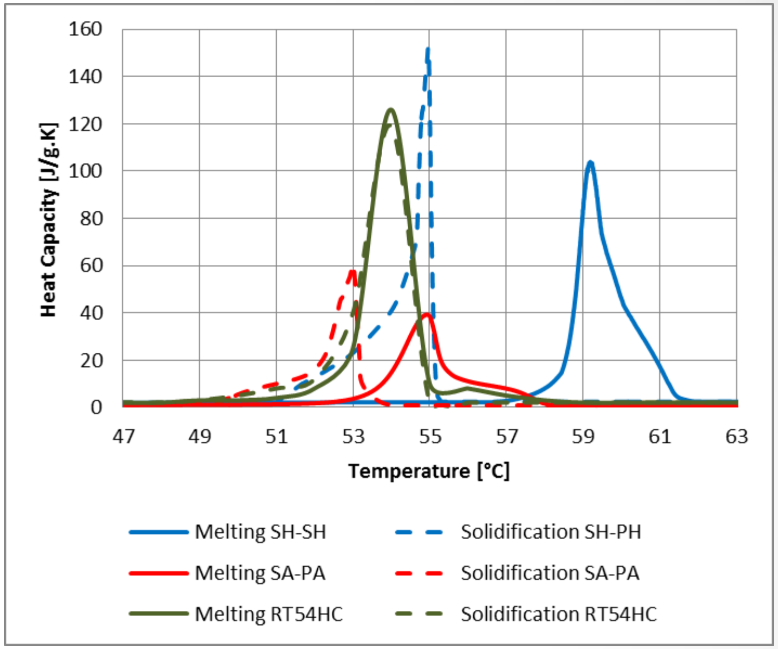


Figure 12 - Overlay of the heat capacity curves of the 3 candidate PCMs

Table 1 – Material properties of selected candidate PCM's.

PCM Candidates	T_{melt}	H_{melt}	λ	ρ_s	$E_{density}$ (from 40 to 65 °C)		Price	
	°C	kJ/kg	w/m.K	kg/m³	kWh/m³	to water	£/m³	£/kWh
Paraffin Wax (RT54HC)	53	150	0.200	880	55	1.92	421	7.63
SA - PA	54	178	0.260	971	61	2.14	351	5.72
SP55 (SH-SH)	58	150	0.610	1610	83	2.90	92	1.19

Thank You for the attention!

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