Material selection and prototype design of a double-fluid circulation PCM storage for SHIP applications

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Project objective

- To demonstrate that SHIP is reliable, flexible, robust and cost-competitive
  - At temperatures between 200°C and 300°C
  - Industrial sectors such as textile, plastics, wood, metallurgy, and chemistry

Thermal storage need

- To ease the integration of SHIP in an existing process
- A unique component with the following functions:
  - Heat storage from the solar field
  - Excess heat storage from the industrial process
  - Heat release to the industrial process
  - Direct heat transfer between solar and process loops using different HTFs

Thermal storage solution:

**Combined Heat Storage (CHS)**
## PCM review, selection and testing

### Selected material
- **Stability and performances OK**
- **Thermo physical characteristics**
  - **Highly Hygroscopic**
  - **High density**

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>ΔH_{sol/liq} (J/g)</th>
<th>T_{f} (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic Mixture</td>
<td>Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;—KNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>70</td>
<td>152</td>
<td>Affordable, highly hygroscopic</td>
</tr>
<tr>
<td>Eutectic Mixture</td>
<td>NaNO&lt;sub&gt;3&lt;/sub&gt;-Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;—KNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Very low</td>
<td>180</td>
<td>Affordable, highly hygroscopic</td>
</tr>
<tr>
<td>Sugar and sugar alcohol</td>
<td>d-Mannitol</td>
<td>294-341</td>
<td>165-168</td>
<td>High supercooling and stability issues</td>
</tr>
<tr>
<td>Eutectic mixture</td>
<td>LiNO&lt;sub&gt;3&lt;/sub&gt;-NaNO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>233</td>
<td>156</td>
<td>High Cost, highly hygroscopic</td>
</tr>
<tr>
<td>Eutectic mixture</td>
<td>LiNO&lt;sub&gt;3&lt;/sub&gt;-KCl</td>
<td>272</td>
<td>160</td>
<td>High Cost, highly hygroscopic, corrosion issues</td>
</tr>
<tr>
<td>Eutectic mixture</td>
<td>HCOONa-HCOOK</td>
<td>175</td>
<td>176</td>
<td>Scarce existing data, corrosion issues</td>
</tr>
<tr>
<td>Inorganic salt</td>
<td>Potassium thiocyanate</td>
<td>112-114</td>
<td>157-177</td>
<td>Low cycling stability, corrosion issues, toxicity</td>
</tr>
<tr>
<td>Fatty acid</td>
<td>Adipic acid</td>
<td>239-252</td>
<td>152</td>
<td>Flammable at temperatures &gt;170°C, corrosion issues</td>
</tr>
<tr>
<td>Amide</td>
<td>Benzanilide</td>
<td>129-139</td>
<td>161</td>
<td>Produce CMR and flammable gas upon decomposition</td>
</tr>
<tr>
<td>Phenolic acid</td>
<td>Salicylic acid</td>
<td>199</td>
<td>157-159</td>
<td>Low cycling stability, highly flammable</td>
</tr>
<tr>
<td>Aromatic hydrocarbon</td>
<td>Hydroquinone</td>
<td>179-235</td>
<td>160-173</td>
<td>Low cycling stability, highly flammable, CMR?</td>
</tr>
<tr>
<td>Sugar and sugar alcohol</td>
<td>Dulcitol</td>
<td>246-257</td>
<td>167-185</td>
<td>Low cycling stability, supercooling</td>
</tr>
</tbody>
</table>
Material characterization - binary mixture

Proportions mixed and heated 4h @ 250°C, then characterized

\[ T_{\text{onset}} = 152°C, \quad H_f = 70 \text{ J/g}, \quad H_{[140-180]} = 130 \text{ J/g} \]

Density:
- Solid @ 22°C: 2 151 kg/m³
- Liquid @ 185°C: 2 074 kg/m³

Source: Chartan et al., 2019, The Journal of Chemical Thermodynamics, 2019
Material characterization - effect of humidity

Ca(NO\textsubscript{3})\textsubscript{2} not available as anhydrous salt

- Only Ca(NO\textsubscript{3})\textsubscript{2}-4H\textsubscript{2}O in standard conditions

Ca(NO\textsubscript{3})\textsubscript{2}-4H\textsubscript{2}O:
- Start dehydration below 40°C
- Fully dehydrated above 160°C
- Total mass loss: 30%wt

Effect of humidity on binary mixture and impact on the storage unit?

1°C/min, 66mg
Influence of humidity on the binary material

- 50g bulk anhydrous binary mixture left 3 weeks at 17°C/47%Hr in an open container

Water molecules modify the binary nitrate and make it unusable for heat storage

Is it possible to regenerate it?
Influence of humidity on the binary material

Anhydrous binary salt, grinded left 3 weeks at 17°C/47%Hr

Melting/solidification temperature increases as humidity drops → binary nitrate « regenerates »
PCM storage design: state of the art

✓ PCM storage prototypes for CSP application
  ✓ Shell and tube design
  ✓ A unique HTF

Source: Garcia et al., 2020 SolarPACES Conference
Prototype integration & Design parameters

✓ Prototype tested on two facilities

<table>
<thead>
<tr>
<th>HTF type</th>
<th>CHS Lab tests</th>
<th>SHIP200 prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>From FRIENDSHIP heat producers</td>
<td>Pressurized water</td>
<td>Thermal oil</td>
</tr>
<tr>
<td>From / To existing process heat consumers</td>
<td>Steam</td>
<td>Pressurized water</td>
</tr>
</tbody>
</table>

✓ Design conditions

<table>
<thead>
<tr>
<th></th>
<th>Charge</th>
<th>Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Transfer Fluid</td>
<td>Wacker Helisol XLP</td>
<td>pressurized water</td>
</tr>
<tr>
<td>Charging/discharging time</td>
<td>4 h</td>
<td>2 h</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>200°C</td>
<td>140°C</td>
</tr>
<tr>
<td>Pressure level – Nominal</td>
<td>5 bara</td>
<td>20 bara</td>
</tr>
<tr>
<td>Mean HTF temperature</td>
<td>178.2°C</td>
<td>148.2°C</td>
</tr>
<tr>
<td>HTF mass flow</td>
<td>156 g/s</td>
<td>354 g/s</td>
</tr>
</tbody>
</table>
Design selection methodology

Heat transfer assessment (0D)
Flow maps (HTF) & CFD (MCP)

Inputs:
- Storage capacity
- PCM
- Charge/discharge time
- Thermal performances specifications

Heat Exchanger geometry:
- Option #1
- Option #2
- …
- Option #n

PCM Storage capacity, Charge/discharge time
- N_{tubes}(i), L_{tube}(i)
- N_{tubes}(j), L_{tube}(j)

Heat Exchanger geometry:
- N_{tubes}(i), L_{tube}(i)

Power design (1D dynamic model)

Energy design
- With constraints on tube number, standards, height, …

∞ of designs

30 designs

15 designs

if NOK:
- N_{tubes}
- L_{tube}

3 possible options
Possible two-fluid designs

- A wide range of possible designs
  - Aluminium heat exchanger tubes: would need enhanced thermomechanical resistance and corrosion tests
  - Extrusion limits for aluminium inserts
  - Standard finned tubes only

**Concentric Tubes**
- Without inserts
- With inserts
  - Aluminium tubes

**Parallel Tubes**
- Without inserts
- With inserts
  - Hexagonal path
  - Square path
  - Aluminium tubes

**Additional information**
- Steel tube
- Aluminum tube
- Circular fins
- Longitudinally finned tube
- SHIP HTF
- Process HTF

- Low thermal performances
- Lab tests only
- Difficult to extrude
Sizing results

<table>
<thead>
<tr>
<th>Design</th>
<th>Option A</th>
<th>Option B</th>
<th>Option C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{in}/D_{out}$ charge tube (mm)</td>
<td>13.65 / 19.05</td>
<td>13.65 / 19.05</td>
<td>10.48 / 15.88</td>
</tr>
<tr>
<td>$D_{in}/D_{out}$ discharge tube (mm)</td>
<td>32.7 / 38.1</td>
<td>32.7 / 38.1</td>
<td>10.48 / 15.88</td>
</tr>
<tr>
<td>$D_{out}$ fins (mm)</td>
<td>63.5</td>
<td>63.5</td>
<td>34.88</td>
</tr>
<tr>
<td>Tube spacing (mm)</td>
<td>96</td>
<td>70</td>
<td>88</td>
</tr>
<tr>
<td>Number of double fluid tube</td>
<td>29</td>
<td>61</td>
<td>37</td>
</tr>
<tr>
<td>Tube length (m)</td>
<td>3.64</td>
<td>3.52</td>
<td>3.87</td>
</tr>
<tr>
<td>[CFD] $\Delta T_{max}$ end of discharge (K)</td>
<td>4.0</td>
<td>2.6</td>
<td>9.3</td>
</tr>
<tr>
<td>[1D model] Charged energy*</td>
<td>85% ▲</td>
<td>95% ▲</td>
<td>82% ▲</td>
</tr>
<tr>
<td>[1D model] Discharged energy*</td>
<td>98% ○</td>
<td>107% ○</td>
<td>87% ○</td>
</tr>
</tbody>
</table>

Source: Metais & Eckert *Journal of Heat Transfer* 86 295-6 1964
Conclusions & Outlook

✓ CHS prototype design
  ✓ A wide range of geometries considered
  ✓ CFD models to evaluate heat transfer in PCM+fins(+inserts) volume
  ✓ 1D modelling to assess thermal performances in rated charge/discharge cases
  ✓ Ongoing engineering study with promising designs for the 3 options

✓ PCM selection and characterization
  ✓ Not a lot of choice in this temperature range! Very few data in literature
  ✓ Low cost and non corrosive PCM found
  ✓ Ongoing work on humidity management and filling procedures

✓ Perspectives
  ✓ CHS storage adapted to numerous storage applications: district heating, Carnot batteries, waste heat recovery, ...
  ✓ Concentric designs show high heat transfer rates and can be used as heat exchangers
Thanks for your attention!

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