# Synthesis and evaluation of composite materials for thermochemical energy storage

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## Introduction

- Industrial waste heat is available at various temperatures, typically ranging from 30°C to 160°C, and the re-use of industrial waste heat has the potential to offer significant energy savings, with the annual market potential for recoverable heat within the UK estimated to be between 10TWh and 40TWh. **[1]**
- The reaction kinetics of some salt-fluid combinations promise great potential for **high density thermal energy storage**. However, salts must be held on a substrate in order to allow volumetric expansion whilst providing efficient heat and mass transfer.
- The use of composite materials containing **Expanded Natural Graphite** (ENG) can greatly improve the heat and mass transfer of sorbent materials, as well as enhancing material integrity. In addition to its high thermal conductivity and low price, ENG is also highly permeable, permitting easy mass transfer of the working fluid. **[2]**

## Experimental methods

### 1. Composite synthesis

- Warmed ENG-$CaCl_2$ slurry was compressed to a rectangular block and cut perpendicular to the direction of compression to allow the thermal conductivity to be measured axially.

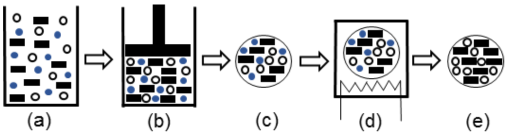

**Figure 1 — Manufacturing process of $CaCl_2$-ENG composites. (a) Homogenous ENG/$CaCl_2$ slurry; (b) compressed slurry block; (c) compressed slurry cylinder (cut perpendicular to compression direction); (d) drying; (e) final sample containing only $CaCl_2$ and ENG**

### 2. Determining thermal properties

- Thermal conductivity (k) of samples was calculated using the Guarded Heat Flow Meter technique, with an Anter Quickline-10™ machine.

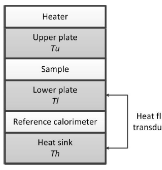

**Figure 2 —Anter Quickline™ machine**

- From temperatures $T_u$, $T_l$ and $T_h$ (see *Fig. 2)* and equations **(1)** and **(2)**, k was then determined. Reference samples of steel and Vespel© with known k values were first used to create a calibration line.

$$R_{th} = \frac{(T_u - T_l)}{Q} - R_{th,int} = \frac{F \cdot (T_u - T_l)}{(T_l - T_h)} - R_{th,int} = F \cdot \left(\frac{\Delta T_s}{\Delta T_r}\right) - R_{th,int} \quad \textbf{(1)}$$

$$k = \frac{d}{R_{th}} \quad \textbf{(2)}$$

### 3. $NH_3$ uptake and cycle stability

- Selected samples exposed to $NH_3$ in **Large Temperature Jump** (LTJ) rig. Once fully ammoniated, samples experienced a step temperature change from 10°C to 90°C, causing 50% desorption. The physical characteristics of the samples post-cycling was also observed.

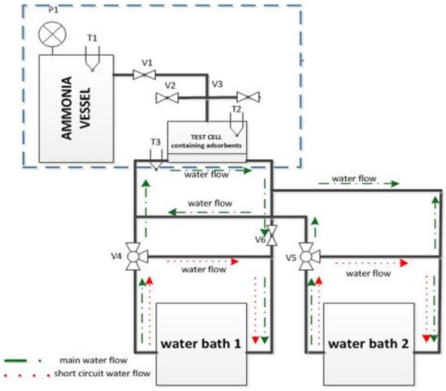

**Figure 3 —LRT schematic. $NH_3$ vessel and test cell insulated within a controlled isothermal container.**

## References

**[1]** https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/294900 element_energy_et_al_potential_for_recovering_and_using_surplus_heat_from_industry.pdf

**[2]** Wang, L., Tamainot-Telto, Z., Metcalf, S., Critoph, R. and Wang, R. (2010). Anisotropic thermal conductivity and permeability of compacted expanded natural graphite. *Applied Thermal Engineering*, 30(13), pp.1805-1811.

**[3]** Wang, K., Wu, J., Wang, R. and Wang, L. (2006). Effective thermal conductivity of expanded graphite-$CaCl_2$ composite adsorbent for chemical adsorption chillers. *Energy Conversion and Management*, 47(13-14), pp.1902-1912.

## Thermal conductivity results

- ENG content kept constant per sample, at ~6.0g or 76.5kgm$^{-3}$.
- Substantial increase in thermal conductivity with >40% salt content (6.4Wm$^{-1}$K$^{-1}$) compared with $CaCl_2$ powder alone (0.31 - 0.39 Wm$^{-1}$K$^{-1}$) **[3]**.
- Thermal conductivities of ~3.5Wm$^{-1}$K$^{-1}$ recorded when salt content >81% of total mass.

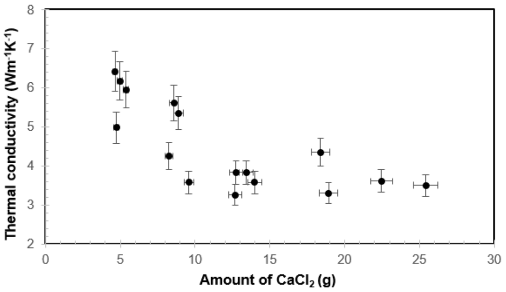

**Figure 4 — Axial thermal conductivity vs $CaCl_2$ content, with ENG density held constant at 76.5 kgm$^{-3}$**

## LTJ results

- Selected samples were cycled (see *Table 1)*, adsorbing to $CaCl_2 \cdot 8NH_3$ and desorbing to $CaCl_2 \cdot 4NH_3$ during each cycle.
- Samples behaved as expected, showing no loss in $NH_3$ adsorption/desorption as number of cycles increased.
- Denser samples took less time to adsorb/desorb.
- Results indicate more salt present in all samples, as actual $\Delta NH_3$ differed from theoretical $\Delta NH_3$ between 7% and 23%.

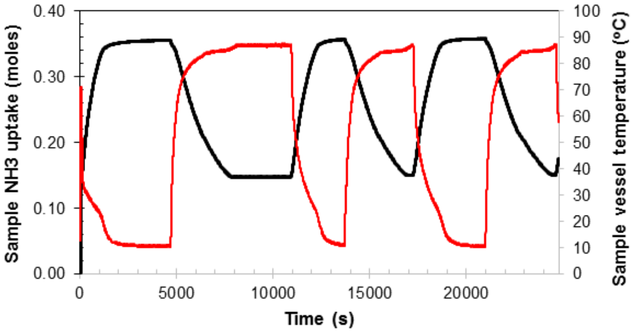

**Figure 5 (above) —NH3 uptake (black) and Sample vessel temperature (red) vs time [Sample C]**

**Table 1 (below) - LRJ output data**

| Sample | $CaCl_2$ content (g) | ENG content (g) | Ratio of $CaCl_2$:ENG | Thermal conductivity, k (Wm$^{-1}$K$^{-1}$) | Measured $\Delta NH_3$ (moles) | Cycles |
|---|---|---|---|---|---|---|
| A | 4.67 | 3.08 | 1.52 | 1.68 | 0.208 | 3 |
| B | 8.25 | 6.10 | 1.35 | 6.17 | 0.205 | 4 |
| C | 18.39 | 6.11 | 3.01 | 5.35 | 0.345 | 2 |

### Sample stability

- The level of sample deformation increased with the $CaCl_2$ content of each sample.
- Sample C (containing most salt) deformed significantly more than others.


A


B


C

## Conclusions

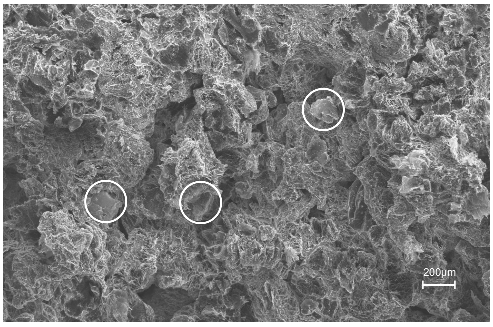

**Figure 6 —SEM image of sample with ENG density 75.8kgm$^{-3}$ and a $CaCl_2$:ENG ratio of 3.13, with likely salt crystals circled.**

- The method trialled for synthesising composites and evaluating their axial thermal conductivity produced strong durable samples.
- The presence of $CaCl_2$, while crucial, reduced the overall stability of the samples.
- Composites displayed thermal conductivities of between 3 Wm$^{-1}$K$^{-1}$ and 7 Wm$^{-1}$K$^{-1}$, whilst the maximum stable solid adsorbent density was found to be 52 kgm$^{-3}$ after cyclic exposure to ammonia.

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