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-CaCl₂ slurry was compressed to a rectangular block and cut perpendicular to the direction of compression to allow the thermal conductivity to be measured axially.

2. Determining thermal properties

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

From temperatures $T_{in}$, $T_{out}$, and $T_{s}$ (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.

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R_{th} = \frac{(\theta_{in} - \theta_{out})}{Q} = R_{th,int} + \frac{F(\theta_{in} - \theta_{s})}{Q} = R_{th,int} - F \cdot \left(\frac{\Delta T}{\Delta L}\right) \cdot R_{th,ext} \quad (1)
\]

\[
k = \frac{d}{R_{th}} \quad (2)
\]

3. NH₃ uptake and cycle stability

- Selected samples exposed to NH₃ 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 ENG content kept constant per sample, at ~6.0g or 75.6kg m³.

Substantial increase in thermal conductivity with >40% salt content (6.4 W m⁻¹ K⁻¹) compared with CaCl₂ powder alone (0.31 - 0.39 W m⁻¹ K⁻¹) [3].

Thermal conductivities of ~3.5 W m⁻¹ K⁻¹ recorded when salt content >61% of total mass.

Thermal conductivity results

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LTJ results

- Selected samples were cycled (see Table 1), adsorbing to CaCl₂ - 4NH₃ and desorbing to CaCl₂ - 4NH₂ during each cycle.
- Samples behaved as expected, showing no loss in NH₃ 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 ΔNH₃ differed from theoretical ΔNH₃ between 7% and 23%.

Sample stability

- The level of sample deformation increased with the CaCl₂ content of each sample.
- Sample C (containing most salt) deformed significantly more than others.

Conclusions

- The method trialled for synthesising composite and evaluating their axial thermal conductivity produced strong durable samples.
- The presence of CaCl₂, while crucial, reduced the overall stability of the samples.
- Composites displayed thermal conductivities of between 3 W m⁻¹ and 7 W m⁻¹, whilst the maximum stable solid adsorbent density was found to be 52 kg m⁻³ after cyclic exposure to ammonia.

References