MERITS
Preparation & characterization of sodium sulfide hydrates for application in thermochemical storage systems

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0. Background: Thermochemical heat storage system

- **System level**
  - Supply & demand simulations
  - Dimensioning heat & power
  - Open/closed system?
  - Vacuum/atmospheric?

- **Component level**
  - HX implementation
  - HX corrosion prevention
  - Evap/Cond implementation
  - Reservoir implementation

- **Material level**
  - TCM type
  - Composite TCM development
  - Cycling stability

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1. AJ de Jong et al, SHC 2013
2. C. Hoegaerts et al, SHC 2014
3. This presentation
0. Background Cycle depiction

\[ \text{Na}_2\text{S.nH}_2\text{O} \]

(1) 40°C hydration

(2) 80°C dehydration

\[ \text{Na}_2\text{S.5H}_2\text{O} (s) \Leftrightarrow \text{Na}_2\text{S.} \frac{1}{2}\text{H}_2\text{O} (s) + 4.5 \text{H}_2\text{O} (g) \]

storage capacity = 2.6 GJ/m³

De Boer et al 2003
1. Preparation of salt hydrate crystals

- $\text{Na}_2\text{S}.9\text{H}_2\text{O}$ elevated temp $\Rightarrow$ 20°C
- $\text{Na}_2\text{S}.5\text{H}_2\text{O}$ elevated temp $\Rightarrow$ >50°C
- Penta-hydrate crystals: more elongated / angular than nona-hydrate crystals

*Penta-hydrate: yellow mother liquor and white crystals (settled)*
2. Cycling test – set-up and method

- **Aim**: to cycle between Na$_2$S penta-hydrate and hemi-hydrate
- **Cycling period**: 2 hours 80°C + 2 hours 40°C
- **Temperature evaporator / condenser**: 7°C
- **Duration**: 1 week = 42 cycles
- **Control by computer + monitoring of temperatures**
2. Cycling test - observations

\[ \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O (s)} \Leftrightarrow \text{Na}_2\text{S} \cdot \frac{1}{2}\text{H}_2\text{O (s)} + 4.5 \text{H}_2\text{O (g)} \]

\( \text{Na}_2\text{S} \) becomes yellow during dehydration.

Power failure: "Over-hydration" of \( \text{Na}_2\text{S} \) (melting)
3. Characterization
   a. Chemical stability

1. **H₂S formation**: \( \text{Na}_2\text{S} + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{H}_2\text{S} \)
   - Detection of dissolved H₂S in water phase
     - HACH LANGE Kuvettentest LCK653 detection method
   - All reproducible experiments: \( \text{H}_2\text{S} < \text{detection limit!} \)
     - Detection limit = 0.1 mg H₂S/L
   - Verification/: no detection with GC method

2. **SO₃²⁻ formation**: \( 2 \text{Na}_2\text{S} + 3 \text{O}_2 \rightarrow 2 \text{Na}_2\text{SO}_3 \)
   - Not expected, but observed 0-15 wt% with pXRD
   - Correlation with sample age & purging with air (O₂)
   - Handling advice: N₂ blanket
3. Characterisation of salt hydrates

Before cycling – SEM images

- Surface covered with pores
- Surface covered by layer of other material, probably dried up mother liquor, forming 9H₂O crystals
3. Characterisation of salt hydrates

*After cycling 42 times, removal at 40°C - SEM*

- Sponge-like porous structure

0.9\(\text{H}_2\text{O}\)

0.5\(\text{H}_2\text{O}\)
3. Characterisation of salt hydrates

*After cycling 42 times, removal at 80°C - SEM*

- Sponge-like porous structure

9H$_2$O

5H$_2$O
3. Characterisation

*After cycling – powder diffraction*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na$_2$S.9H$_2$O</th>
<th>Na$_2$S.5H$_2$O</th>
<th>Na$_2$S.2H$_2$O</th>
<th>Na$_2$S.0H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S.9H$_2$O before cycling</td>
<td>100</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$S.9H$<em>2$O 42 cycles; $T</em>{\text{out}}$ = 40°C</td>
<td>25</td>
<td>71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$S.9H$<em>2$O 42 cycles $T</em>{\text{out}}$ 80 °C</td>
<td>3</td>
<td>36</td>
<td>~10</td>
<td>42</td>
</tr>
<tr>
<td>Na$_2$S.5H$_2$O before cycling</td>
<td>5</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$S.5H$<em>2$O 42 cycles; $T</em>{\text{out}}$ 40 °C,</td>
<td>11</td>
<td>89</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$S.5H$<em>2$O 42 cycles $T</em>{\text{out}}$ 80 °C</td>
<td>4</td>
<td>50</td>
<td>~10</td>
<td>22</td>
</tr>
</tbody>
</table>

Cycling with two hour time periods: conversion not complete
NB Accuracy pXRD hampered by inhomogeneity of initial samples
4. Preparation of cellulose stabilized salt hydrates

**Suspension**-crystallization: Water added, with stirring

**Melt** solidification: No water added, no stirring

- **Result**: free flowing composite crystals ~mm size
- **Melt solidification** appears evenly distributed salt / cellulose
5. Characterisation of cellulose / salt composites

After cycling 42 times, removal at 40°C – SEM

- Sponge-like porous structure

9H₂O with cellulose

5H₂O with cellulose
5. Characterisation

*After cycling – powder diffraction*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na$_2$S.9H$_2$O</th>
<th>Na$_2$S.5H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S.9H$_2$O before cycling</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Na$_2$S.9H$_2$O + cellulose before cycling</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Na$_2$S.9H$<em>2$O 42 cycles; $T</em>{out} = 40^\circ$C</td>
<td>25</td>
<td>71</td>
</tr>
<tr>
<td>Na$_2$S.9H$_2$O + cellulose 42 cycles</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>Na$_2$S.5H$_2$O before cycling</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>Na$_2$S.5H$_2$O + cellulose before cycling</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>Na$_2$S.5H$<em>2$O 42 cycles; $T</em>{out} 40^\circ$C</td>
<td>11</td>
<td>89</td>
</tr>
<tr>
<td>Na$_2$S.5H$_2$O + cellulose 42 cycles</td>
<td>38</td>
<td>62</td>
</tr>
</tbody>
</table>

- Presence of cellulose does not influence (chemical) composition
5. Bed volume change during cycling

- Bed height measured with camera stills
- Bed volume change up to 10-15% during cycling
- Cold stage: increase in bed height
- Hot stage: decrease in bed height.
5. Mechanical bed stability test

- Salt bed compressed by weight in closed cylinder
- Cylinders in oven
- Temperature gradually increased (10°C every hour)
- Height decreases with increasing temperature
Summary (1)

Preparation:
• Methods available for:
  - well defined crystals of Na$_2$S pentahydrate and nonahydrate
  - composite of salt with cellulose (stabilizer)
• Temperature cycling of samples at reduced pressure to mimic operation in a thermochemical system.
• Samples characterized by microscopic imaging, SEM and pXRD

Chemical stability:
• Na$_2$S hydrate salt reacts with O$_2$ from air forming Na$_2$SO$_3$
• During cycling no detectable quantity of H$_2$S in set-up
Summary (2)

Physical stability

- pXRD:
  - samples at 40°C mostly 5\(\text{H}_2\text{O}\) (>60%) and 9\(\text{H}_2\text{O}\),
  - samples at 80°C partially 0\(\text{H}_2\text{O} / 2\text{H}_2\text{O}\) (‘\(\frac{1}{2}\text{H}_2\text{O}\)’) and 5\(\text{H}_2\text{O}\)
- SEM images: morphology change from well-defined angular crystal to highly porous, sponge-like shape
- Material goes through stage with both pentahydrate and solution present
  - in presence of excess water also nonahydrate forms
- Cellulose stabilized crystals similar behaviour

Mechanical stability

- Salt bed 10-15% volume change during cycling.
- Mechanical salt bed strength test:
  height decreases with increasing temperature
Recommendations

› Do not expose Na$_2$S hydrates to air, use nitrogen blanket.
› During cycling monitor conversion rate of penta-hydrate to hemi-hydrate
› When going through stage were salt and solution are present follow change of cellulose/salt composite material
› To assess effect of porous sponge like crystal shape on mass transfer of water vapour during (de)hydration
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