

Material and Component Development for Thermal Energy Storage

**Subtask 3T - TCM
measuring procedures
and testing under
application conditions**



Material and Component Development for Thermal Energy Storage

This is a report from SHC Task 58 / ES Annex 33: Subtask 3T “TCM measuring procedures and testing under application conditions”

Daniel Lager, Lia Kouchachvili, Xavier Daguenet

15.06.2021

Report number: D3T DOI: 10.18777/ieashc-task58-2021-0004

The contents of this report do not necessarily reflect the viewpoints or policies of the International Energy Agency (IEA) or its member countries, the IEA Solar Heating and Cooling Technology Collaboration Programme (SHC TCP) members or the participating researchers.

Solar Heating and Cooling Technology Collaboration Programme (IEA SHC)

The Solar Heating and Cooling Technology Collaboration Programme was founded in 1977 as one of the first multilateral technology initiatives (“Implementing Agreements”) of the International Energy Agency.

Our mission is “*Through multi-disciplinary international collaborative research and knowledge exchange, as well as market and policy recommendations, the IEA SHC will work to increase the deployment rate of solar heating and cooling systems by breaking down the technical and non-technical barriers.*”

IEA SHC members carry out cooperative research, development, demonstrations, and exchanges of information through Tasks (projects) on solar heating and cooling components and systems and their application to advance the deployment and research and development activities in the field of solar heating and cooling.

Our focus areas, with the associated Tasks in parenthesis, include:

- Solar Space Heating and Water Heating (Tasks 14, 19, 26, 44, 54)
- Solar Cooling (Tasks 25, 38, 48, 53, 65)
- Solar Heat for Industrial and Agricultural Processes (Tasks 29, 33, 49, 62, 64)
- Solar District Heating (Tasks 7, 45, 55)
- Solar Buildings/Architecture/Urban Planning (Tasks 8, 11, 12, 13, 20, 22, 23, 28, 37, 40, 41, 47, 51, 52, 56, 59, 63, 66)
- Solar Thermal & PV (Tasks 16, 35, 60)
- Daylighting/Lighting (Tasks 21, 31, 50, 61)
- Materials/Components for Solar Heating and Cooling (Tasks 2, 3, 6, 10, 18, 27, 39)
- Standards, Certification, and Test Methods (Tasks 14, 24, 34, 43, 57)
- Resource Assessment (Tasks 1, 4, 5, 9, 17, 36, 46)
- Storage of Solar Heat (Tasks 7, 32, 42, 58)

In addition to our Task work, other activities of the IEA SHC include our:

- SHC Solar Academy
- *Solar Heat Worldwide*, annual statistics report
- SHC International Conference

Our members

| | | |
|---------------------|------------------------------------|----------------|
| Australia | European Copper Institute | Slovakia |
| Austria | France | South Africa |
| Belgium | Germany | Spain |
| Canada | International Solar Energy Society | Sweden |
| CCREEE | Italy | Switzerland |
| China | Netherlands | Turkey |
| Denmark | Norway | United Kingdom |
| EACREEE | Portugal | |
| ECREEE | RCREEE | |
| European Commission | SACREEE | |

For more information on the IEA SHC work, including many free publications, please visit www.iea-shc.org.

Contents

| | |
|---|-----------|
| Contents | |
| 1 Contributor/Authors | 1 |
| 2 Introduction | 2 |
| 3 Deliverables | 3 |
| 4 List and description of available and needed TCM characterization procedures for the identified material and reaction properties (D3T1) | 4 |
| 5 D3T2: Result of a round robin test of a TCM candidate (D3T2) | 5 |
| 5.1 Introduction..... | 5 |
| 5.2 Salt Hydrate Round Robin Tests..... | 5 |
| 5.2.1 Preliminary Test Method for the 2nd Round Robin (SrBr ₂ *nH ₂ O)..... | 5 |
| 5.2.2 Final Test Method for the 2nd Round Robin (SrBr ₂ *nH ₂ O)..... | 7 |
| 5.2.3 Evaluation of the specific heat capacity cp(T) of SrBr ₂ ·6H ₂ O, SrBr ₂ ·1H ₂ O and SrBr ₂ based on heat flow Differential Scanning Calorimetry (hf-DSC)..... | 10 |
| 5.3 The Zeolite 13X Round Robin Tests..... | 13 |
| 5.3.1 1st and 2nd zeolite 13X round robin..... | 13 |
| 5.3.2 3rd zeolite 13X round robin..... | 14 |
| 6 Description of a harmonized measurement procedure for the TCM performance under realistic application conditions (D3T3) | 15 |
| 6.1 Procedure..... | 16 |
| 6.1.1 Thermal energy storage type – “classification”..... | 16 |
| 6.1.2 Conservation laws and transfer functions..... | 16 |
| 6.1.3 Measurement parameters and analysis..... | 16 |
| 6.1.4 Measurement temperatures - scenarios..... | 17 |
| 6.2 Experimental..... | 18 |
| 6.2.1 Sorbent and sorbate..... | 19 |
| 6.2.2 Lab scale storage unit..... | 19 |
| 6.3 Results..... | 20 |
| 6.3.1 Data, figures, tables and Diagrams..... | 20 |
| 6.3.2 Uncertainty estimation..... | 21 |
| 6.4 Discussion and assessment..... | 21 |
| 6.5 Considerations about scaling-up..... | 21 |
| 7 Acknowledgment | 22 |
| 8 References | 22 |
| APPENDIX A | 23 |
| Goal of this document..... | 23 |
| Procedure for salt hydrate materials (e.g. SrBr ₂)..... | 23 |
| Definition of the Scenarios..... | 23 |
| Pretreatment / Dry Mass Detection..... | 23 |
| Measurement of equilibrium points..... | 24 |

| | |
|--|-----------|
| Definition of equilibrium state | 26 |
| Delivery of results (values, format, units)..... | 26 |
| APPENDIX B..... | 30 |
| Goal of this document: | 30 |
| Procedure for salt hydrates (e.g. SrBr ₂) | 30 |
| Definition of the Scenarios..... | 30 |
| Pretreatment / Dry Mass Detection | 30 |
| Measurement of equilibrium points..... | 31 |
| Definition of equilibrium state | 34 |
| Measuring the heat (of adsorption)..... | 34 |
| Delivery of results (values, format, units)..... | 34 |
| APPENDIX C..... | 37 |
| Goal of this document | 37 |
| Procedure for porous materials (e.g. zeolite) | 37 |
| Definition of the Scenarios..... | 37 |
| Pretreatment / Dry Mass Detection | 37 |
| Measurement of equilibrium points..... | 38 |
| Definition of equilibrium state | 39 |
| Measuring the heat (of adsorption)..... | 39 |
| Delivery of results (values, format, units)..... | 40 |
| Literature | 41 |
| APPENDIX D: Results report of the 3rd Zeolite 13X Round Robin..... | 42 |
| APPENDIX E: Measurement protocol for the evaluation of specific heat capacity $c_p(T)$ of SrBr₂·nH₂O and SrBr₂ based on heat flow differential scanning calorimetry | 43 |
| Differential Scanning Calorimetry - DSC..... | 43 |
| Measurement principle | 43 |
| Calibration | 43 |
| Temperature calibration..... | 43 |
| Heat flow calibration | 44 |
| Specific heat capacity measurements | 44 |
| Measurement procedure..... | 45 |
| Temperatures:..... | 45 |
| Calibration | 46 |
| Specific heat capacity measurements | 46 |
| Symbols and subscripts | 48 |
| References..... | 48 |

1 Contributor/Authors

- Alenka Ristic - National Institute of Chemistry - SI
- Andrea Frazzica – ITAE - IT
- Andreas Hauer – ZAE - DE
- Annelies Vandersickel – TU München - DE
- Benjamin Fumey – EMPA - CH
- Bernhard Zettl – FH Oberösterreich - AT
- Candida Milone – University Messina - IT
- Daniel Lager - AIT Austrian Institute of Technology (Author section: 1 – 4, 5.2.3, 5.3.1, APP E) - AT
- Danny Mueller – TU Wien - AT
- Eric Laurenz - Fraunhofer ISE - DE
- Fabian Fischer – ZAE - DE
- Gayaneh Issayan – FH Oberösterreich - AT
- Georg Gravogl – TU Wien - AT
- Henner Kerskes – Universität Stuttgart - DE
- Jonathon Elvins – Swansea University - UK
- Jusitn Searle – Swansea University - UK
- Kevyn Johannes – INSA Lyon - FR
- Lia Kouchachvili - NRCan (Author section: 5.1, 5.2.1-5.2.2, 5.3.2, APPENDIX A,B,C,D) - CA
- Paul Gantenbein - University of Applied Sciences Rapperswil - CH
- Phil Eames - Loughborough University - UK
- Pim Donkers – TNO - NL
- Raffaele Liberatore – ENEA - IT
- Reda Djebbar - CanmetENERGY, NRCan - CA
- Ruud Cuypers – TNO - NL
- Sara Walsh - Swansea University - UK
- Thomas Aigenbauer - FH Oberösterreich - AT
- Thomas Herzog – TH Wildau - DE
- Wim van Helden – AEE INTEC - AT
- Xavier Daguenet - University of Applied Sciences Rapperswil (Author section: 6, 7, 8) – CH

2 Introduction

This Subtask aims to have reliable thermal analysis methods/protocols and procedures for the characterization of material and reaction properties for sorption and chemical reactions of thermal energy storage (TES) applications. One goal is an inventory of already standardized measurement procedures for TCM as well as of needed characterization procedures.

One challenge in the development of thermochemical storage systems is the difference between tests on micro scale and on laboratory scale, as has been found in many instances in practice. In order to have reliable tools for optimisation of storage materials for a given TES application, both the dependencies of the final storage performance on the actual material properties must be investigated and testing under operation conditions given by the application should be performed

The main objectives of Subtask 3T are therefore:

- Establishing common procedures for measuring material properties (starting with reaction equilibrium and including all material properties in the end)
- Testing of novel TCM under application conditions

One of the first tasks was to collect the already used methods/protocols especially for caloric information like enthalpy changes. A list with relevant literature existing of new publications, standards, etc. was established during the activities which is still a living document.

The biggest part of all activities in this subtask was to develop a common sense for enthalpy and mass change measurements of sorption and thermochemical materials as well as a procedure to compare results on lab scale. Different round robin tests on a zeolite and salt storage material were conducted and evaluated. These results were used to further develop the measurement procedures.

3 Deliverables

According to the objectives and the defined work plan, following deliverables were defined:

- D3T1: List and description of available and needed TCM characterization procedures for the identified material and reaction properties
- D3T2: Result of a round robin test of a TCM candidate (e.g. Zeolite 13X)
- D3T3: Description of a harmonized measurement procedure for the TCM performance under realistic application conditions

The next sections summarize the outputs for each deliverable.

4 List and description of available and needed TCM characterization procedures for the identified material and reaction properties (D3T1)

A list with relevant literature existing of new publications, standards, etc. was established during the activities which is still a living document. A file server was set up so that all participants can upload their literature or references.

Table 1: Extract from the reference list created

| Nr | Title | Type | Year | Author |
|----|---|---------|------|-----------------|
| 1 | Thermal Properties of Materials for Thermo-chemical Storage of Solar Heat | Report | 2005 | Ch. Bales et al |
| 2 | Thermophysical analysis of sorption materials for thermal energy storage | Poster | 2015 | D. Lager |
| 3 | Round Robin Test on Enthalpies of Redox Materials for Thermochemical Heat Storage | Paper | 2016 | J. González-Ag |
| 4 | High-Temperature Energy Storage: Kinetic Investigations of the CuO/Cu ₂ O Reaction Cycle | Paper | 2017 | M. Deutsch et |
| 5 | Experimental approaches to analyse thermophysical properties of thermochemical heat storage materials | Present | 2017 | D. Lager |
| 6 | Thermochemical heat storage – from reaction storage density to system storage density | Paper | 2016 | A.J. de Jong et |
| 7 | Preparation & characterization of sodium sulfide hydrates for application in thermochemical storage systems | Paper | 2015 | M. Roelands e |
| 8 | A review on properties of salt hydrates for thermochemical storage | Paper | 2014 | F. Trausel et a |

The file server is still available for all contributors and the list can still be updated with new relevant literature references regarding characterization techniques for TCMs.

The most important outcome is, that there is no standardized procedure to evaluate caloric and mass information (enthalpy and mass change) on sorption and salt hydrate candidates at application conditions. This new developed procedures and defined application conditions for sorption materials and chemical reactions are documented in D3T2.

5 D3T2: Result of a round robin test of a TCM candidate (D3T2)

5.1 Introduction

Materials' testing and characterisation procedures for the SrBr₂*nH₂O and the Zeolite 13X as well as the measurement results from the participating laboratories is summarised in this report.

5.2 Salt Hydrate Round Robin Tests

The material samples for SrBr₂*nH₂O used by all the participating laboratories was provided by INSA-Lyon

5.2.1 Preliminary Test Method for the 2nd Round Robin (SrBr₂*nH₂O)

The proposed measuring procedure is given in Appendix A. The testing equipment by the participating laboratories as well as some of the testing conditions are summarized in Table 1_1.

Table 1_1. Participants' laboratory equipment and specific variables

| Participants | Instruments | crucible | Cooling method/cooling rate | Initial sample mass [mg] | Carrier gas | Period of measurement [hours] |
|--------------|---------------------------|--------------------------------|-----------------------------|--------------------------|----------------|-------------------------------|
| CanmetENERGY | STA Netzsch | Al ₂ O ₃ | Air (3K/min) | 27.16 | N ₂ | 33 |
| CETHIL-INSA | Sensys Evo TG-DSC Setaram | SiO ₂ | N ₂ (1K/min) | 4.3 | He | 63 |

The measured sample mass obtained by the two participating laboratories for all measurement points 1 to 8 is summarised in Table 1_2

Table 1_2. Sample mass (absolute) for all measurement points 1 to 6.

| Point # | Symbol | Sample Mass [mg] | |
|---------|----------------|------------------|-------------|
| | | CanmetENERGY | CETHIL-INSA |
| P 1 | $m_{dry/P1}$ | 26.07 | 3.016 |
| P 2 | $m_{Ads2'/P2}$ | 34.00 | 4.216 |
| P 3 | $m_{Des1/P3}$ | 25.84 | 3.194 |
| P 4 | $m_{Ads1/P4}$ | 33.72 | 4.223 |
| P 5 | $m_{Des2/P5}$ | 21.60 | 3.203 |
| P 6 | $m_{Ads2/P6}$ | 31.02 | 4.221 |
| P7 | $m_{dry/P7}$ | 19.79 | 3.014 |
| P8 | $m_{Hyd4/P8}$ | 26.52 | 4.217 |

The measured water uptake during hydration: Hyd₁, Hyd₂, Hyd₃ and Hyd₄ achieved by the different laboratories is summarised in Table 1_3

Table 1_3. Water uptake between Hyd₁, Hyd₂, Hyd₃ and Hyd₄

| Description | Symbol | Water uptake [g/g] | | Standard Deviation | Water uptake [mol H ₂ O/mol SrBr ₂] | | Standard Deviation |
|--|---------------|--------------------|--------------|--------------------|--|--------------|--------------------|
| | | Canmet ENERGY | CETHI L-INSA | | Canmet ENERGY | CETHI L-INSA | |
| Uptake after Hyd1 related to dry mass $m_{dry/P1}$ | ΔX_1 | 0.30 | 0.398 | 14% | 4.564 | 5.472 | 9% |
| Uptake after Hyd2 related to mass Deh1 $m_{Deh1/P3}$ | ΔX_2 | 0.30 | 0.322 | 3.5% | | | |
| Uptake after Hyd3 related to mass Deh2 $m_{Deh2/P5}$ | $\Delta X_1'$ | 0.43 | 0.319 | 14.8% | | | |
| Uptake after Hyd4 related to dry mass $m_{dry/P7}$ | $\Delta X_2'$ | 0.34 | 0.399 | 7.9% | 4.676 | 5.484 | 8% |

The measured hydration heat during the four-hydration steps Hyd₁, Hyd₂, Hyd₃ and Hyd₄ is summarized in Table 1_4.

Table 1_4. Measured hydration heat

| Description | Symbol | CETHIL-INSA | | CanmetENERGY | | Standard Deviation |
|----------------------------|------------|----------------------|------------|----------------------|------------|--------------------|
| | | Hydration time [min] | Heat [J/g] | Hydration time [min] | Heat [J/g] | |
| Hydration Heat during Hyd1 | H_{Hyd1} | $t_{Hyd1/P2} = 540$ | 838.06 | $t_{Hyd1/P2} = 240$ | 486 | 26.6% |
| Hydration Heat during Hyd2 | H_{Hyd2} | $t_{Hyd2/P4} = 420$ | 727.85 | $t_{Hyd2/P4} = 240$ | 490.6 | 19.5% |
| Hydration Heat during Hyd3 | H_{Hyd3} | $t_{Hyd3/P6} = 355$ | 730.90 | $t_{Hyd3/P6} = 240$ | 690.5 | 2.8% |
| Hydration Heat during Hyd4 | H_{Hyd4} | $t_{Hyd4/P8} = 520$ | 844.69 | $t_{Hyd4/P8} = 240$ | 433.75 | 32% |

It was agreed by the participants to not pursue the preliminary test method for the 2nd round robin for the SrBr₂ any further.

5.2.2 Final Test Method for the 2nd Round Robin (SrBr₂*nH₂O)

The proposed final test method for the 2nd Round Robin is given in Appendix B. The testing equipment by the participating five laboratories as well as some of the testing conditions are summarized in Table 2_1.

Table 2_1. Participants' Specific Variables

| Participants | Instruments | crucible | Cooling method/cooling rate | Pre-treatment time at 120oC, hr | Pre-treatment time at 180oC, hr | Period of measurement |
|----------------|---------------------------|--------------------------------|-----------------------------|---------------------------------|---------------------------------|-----------------------|
| TNO | Setaram TG/DSC | Al | N ₂ (2K/min) | 24 | 12 | 4 days |
| TUe | Mettler Toledo TGA/DSC 3+ | Al | (1K/min) | 6 | 3 | |
| CanmetENERGY | STA Netzsch | Al ₂ O ₃ | Air (3K/min) | 10 | 3 | 32 hours |
| CETHIL-INSA | Sensys Evo TG-DSC Setaram | SiO ₂ | N ₂ (1K/min) | 6 | 8 | 96 hours |
| Fraunhofer ISE | Setaram SETSYS EVOLUTION | Pt | | 40 | 10 | ~ 7 days |

The measured test sample mass by the different laboratories for points 1 to 6 is summarised in Table 2_2

Table 2_2. Sample mass (absolute) for all measurement points 1 to 6.

| Point # | Symbol | Sample Mass [mg] | | | | |
|---------|----------------|------------------|-------|--------------|-------------|----------------|
| | | TNO | TUe | CanmetENERGY | CETHIL-INSA | Fraunhofer ISE |
| P 1 | $m_{dry/P1}$ | 20.88 | 4.556 | 4.60 | 2.516 | 15.171 |
| P 2 | $m_{Ads2'/P2}$ | 21.05 | 4.587 | 4.85 | 2.515 | 15.672 |
| P 3 | $m_{Des1/P3}$ | 20.97 | 4.588 | 4.85 | 2.511 | 15.673 |
| P 4 | $m_{Ads1/P4}$ | 27.70 | 5.995 | 6.36 | 3.285 | 20.44 |
| P 5 | $m_{Des2/P5}$ | 19.60 | 4.294 | 4.51 | 2.333 | 14.707 |
| P 6 | $m_{Ads2/P6}$ | 21.02 | 4.585 | 4.80 | 2.496 | 15.666 |

The measured water uptake during Des₁/Ads₁ and Des₂/Ads₂ is summarised in Tables 2_3 and Table 2_4. The standard deviation of the measured water uptake by the different participating laboratories is within 4% confirming the reliability of the test procedure used.

Table 2_3. Water uptake between Des1 / Ads1 and Des2 / Ads2

| Description | Symbol | Sample Mass [g/g] | | | | | Standard Deviation |
|---|---------------|-------------------|--------|---------------|-------------|----------------|--------------------|
| | | TNO | TUe | Canmet ENERGY | CETHIL-INSA | Fraunhofer ISE | |
| Uptake between Des1 / Ads1 related to dry mass | ΔX_1 | 0.322 | 0.3088 | 0.328 | 0.308 | 0.314 | 2.4% |
| Uptake between Des2 / Ads2 related to dry mass | ΔX_2 | 0.068 | 0.0643 | 0.0630 | 0.065 | 0.063 | 2.8% |
| Uptake between Des1 / Ads1 related to mass Des2 | $\Delta X_1'$ | 0.343 | 0.3277 | 0.335 | 0.332 | 0.324 | 1.95% |
| Uptake between Des2 / Ads2 related to mass Des2 | $\Delta X_2'$ | 0.072 | 0.0678 | 0.064 | 0.07 | 0.065 | 4.4% |

Table 2_4. Water uptake between Des₂ / Ads₂ relative to dry mass at P₅

| Participants | Mass at P ₅ | | Uptake between Des ₂ / Ads ₂ related to mass Des ₂ (P ₅) | |
|--------------------|------------------------|--------------|---|--|
| | [mg] | [mole] | [g/g] | [mole H ₂ O/ mole SrBr ₂] |
| TNO | 19.6 | 0.0000792 | 0.072 | 0.9959596 |
| TUe | 4.294 | 0.0000173544 | 0.068 | 0.93348085 |
| CanmetENERGY | 4.51 | 0.0000182 | 0.064 | 0.88461538 |
| CETHIL-INSA | 2.333 | 0.000009429 | 0.069 | 0.96086542 |
| Fraunhofer ISE | 14.707 | 0.00005944 | 0.0652 | 0.89670256 |
| Standard Deviation | | | 4.4% | 4.38% |

The measured heat of salt hydration during the four hydration steps Hyd₁, Hyd₂, Hyd₃ and Hyd₄ is summarized in Table 2_5.

Table 2_5. Heat of salt hydration between Des₁ / Ads₁ and Des₂ / Ads₂. Unit is J/g.

| Description | Symbol | Heat of adsorption [J/g] | | | | | Standard Deviation |
|---|-------------|--------------------------|------|---------------|-------------|----------------|--------------------|
| | | TNO | TUe | Canmet ENERGY | CETHIL-INSA | Fraunhofer ISE | |
| Heat of Adsorption (material specific) Des ₁ / Ads ₁ | H_{Ads1} | 970 | 883 | 830 | 690.0 | 713 | 18% |
| Heat of Adsorption (material specific) Des ₂ / Ads ₂ | H_{Ads2} | 256 | 184 | 177.2 | 43.0 | 172 | 41% |
| Heat of Adsorption (adsorbate specific) Des ₁ / Ads ₁ | H'_{Ads1} | 3000 | 2858 | 2530 | 2240.3 | 3060 | 11% |

| | | | | | | | |
|---|-------------|------|------|--------|-------|------|-------|
| Heat of Adsorption (adsorbate specific) Des ₂ / Ads ₂ | H'_{Ads2} | 3765 | 2875 | 2812.7 | 661.5 | 2810 | 39.7% |
|---|-------------|------|------|--------|-------|------|-------|

Results of the heat of hydration shows a considerable gap between the reported values from the different laboratories. Further refinement of the test method is required.

5.2.3 Evaluation of the specific heat capacity $c_p(T)$ of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 1\text{H}_2\text{O}$ and SrBr_2 based on heat flow Differential Scanning Calorimetry (hf-DSC)

The objective of this round robin test was the evaluation of the specific heat capacity of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 1\text{H}_2\text{O}$ and SrBr_2 based on heat flow Differential Scanning Calorimetry (hf-DSC). This task was split in two subtasks:

- Definition of a measurement protocol based for DSC measurements
- Evaluation of the measured data

The definition of the measurement protocol was developed within the participants, the resulting procedure can be found in the section: "Measurement protocol for the evaluation of specific heat capacity $c_p(T)$ of $\text{SrBr}_2 \cdot n\text{H}_2\text{O}$ and SrBr_2 based on heat flow differential scanning calorimetry".

3 Institutes were joining the first run:

- National Resources Canada NRC - Innovation and Energy Technology – CanmetENERGY
- Fraunhofer - Institute for Solar Energy Systems - ISE
- Austrian Institute of Technology AIT – Center for Energy – Sustainable Thermal Energy Systems

In the following tables and figures the results of the three participating institutes are represented. The shown numbers represent the institute and are assigned randomly.

Used devices and operating conditions

| | 1 | 2 | 3 |
|---------------------|----------|-------------------------|-------------------------|
| System | DSC | NETZSCH STA | NETZSCH DSC 204 F1 |
| Crucible | | Al; d = 5 mm; h = 2mm | Al; 40 μ l |
| Gas | | N2 40 ml/min | N2 40 ml/min |
| Reference | | Sapphire m = 21.55mg | Sapphire m = 21.10mg |
| Heating Rate | 10 K/min | 10 K/min | 10 K/min |
| Tmin | 25 | 20 | 0 |
| Tmax | 190 | 40 | 190 |

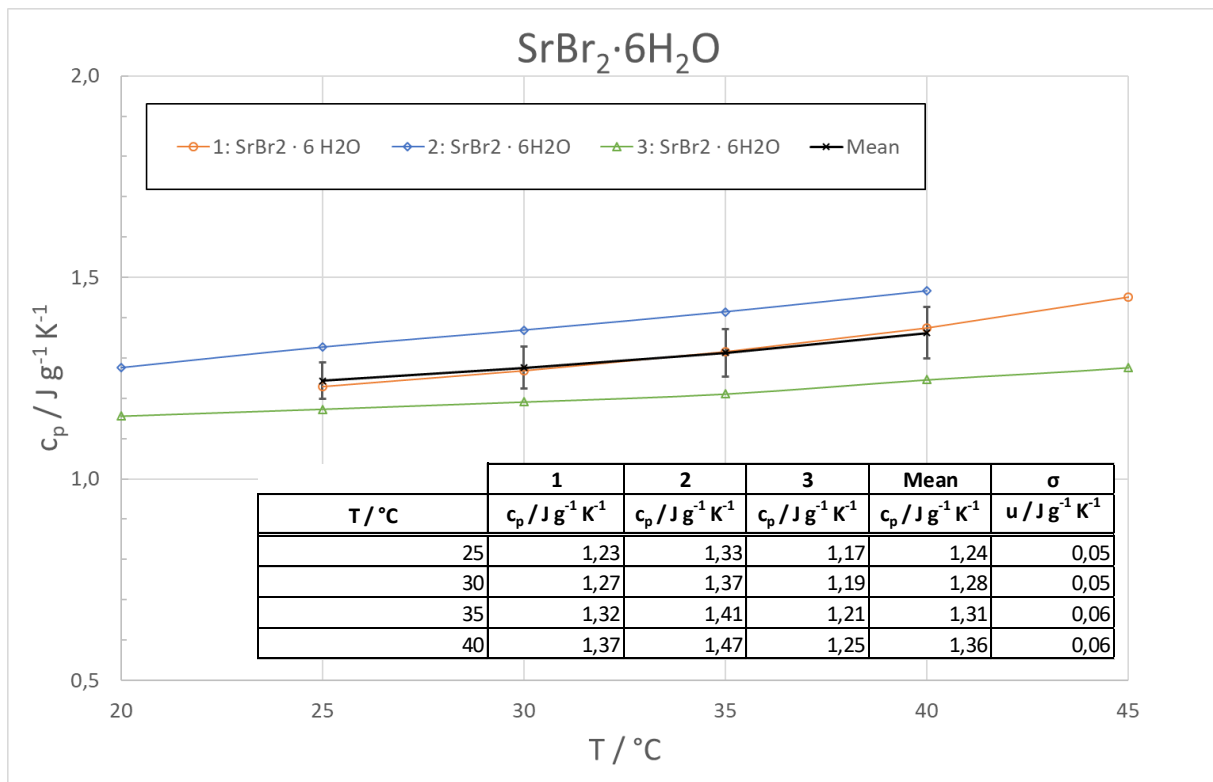


Figure 1: Specific heat capacity results of SrBr₂·6H₂O

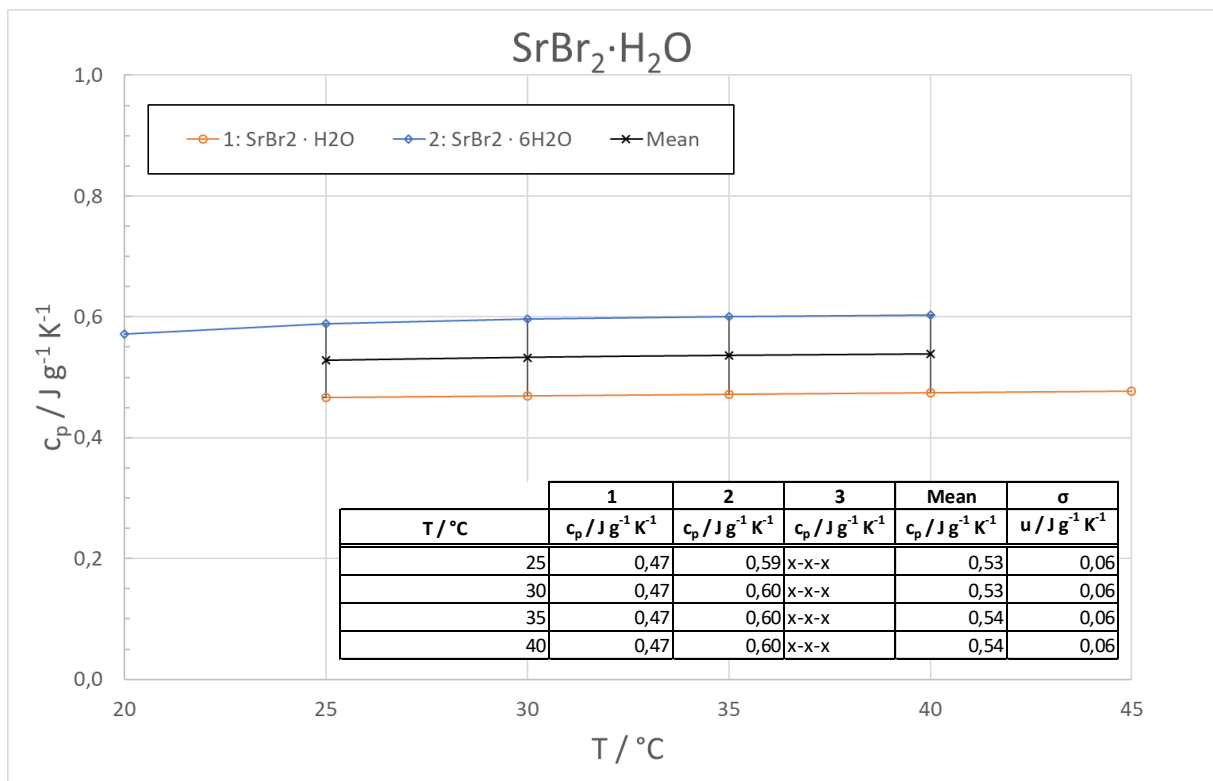


Figure 2: Specific heat capacity results of SrBr₂·6H₂O

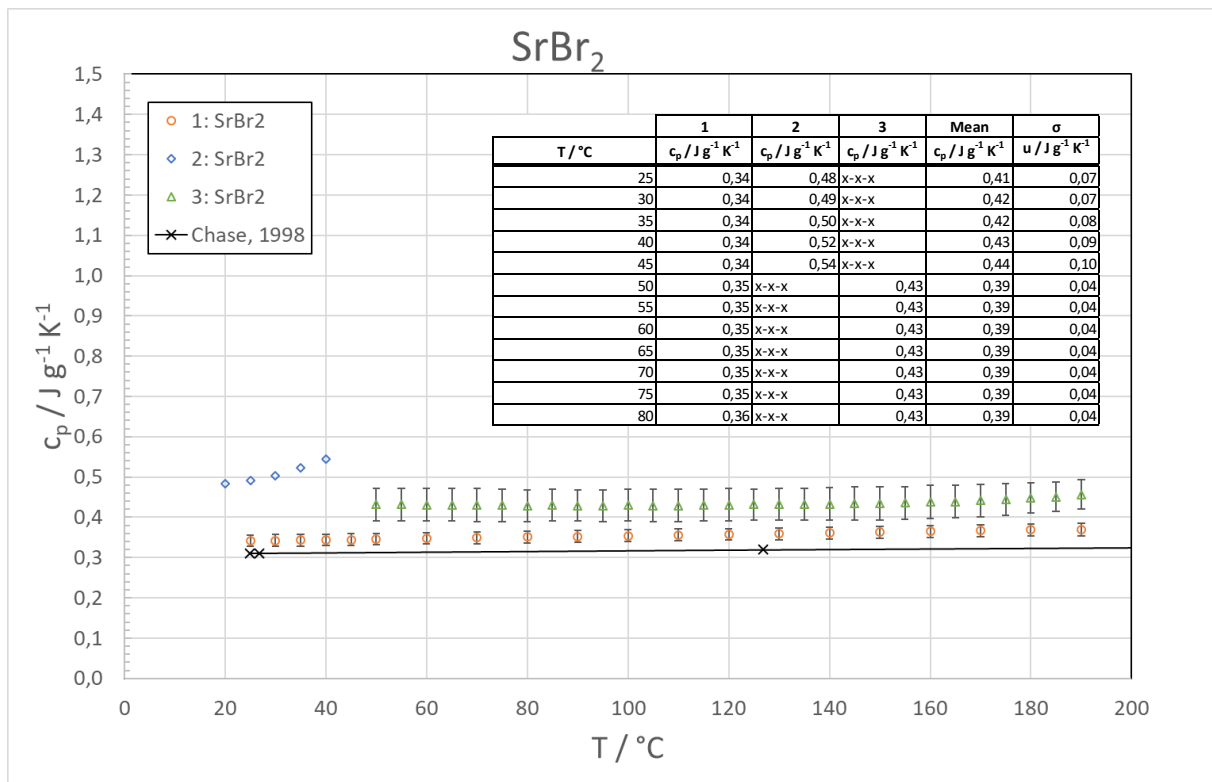


Figure 3: Specific heat capacity results of SrBr₂

Because this round robin was in a first round executed at the end of the overall project, there are still open questions about the reasons of the displayed deviations. A possible explanation lies in the different ways of sample preparation. s

This would be a starting point for further activities in a follow-up project to further improve the measurement procedure in a second round

5.3 The Zeolite 13X Round Robin Tests

5.3.1 1st and 2nd zeolite 13X round robin

The results of the first round robin showed large deviations between the measured water uptake and enthalpy based on already defined measurement protocols which were not clearly defined. Especially the procedure for the detection of the dry mass was not clearly defined.

The second round robin described already a more detailed measurement procedure for the TCM performance under realistic application conditions. Following table shows the discussed boundary conditions for the measurement:

| Point # | Label | Sample Temperature [°C] | Vapor pressure [mbar] | Corresp. Dew point [°C] |
|---------|-------------------------|-------------------------|-----------------------|-------------------------|
| P 1 | Pretreatment / Dry mass | 350 | < 1 e-3 | < -150 |
| P 2 | Adsorption 2' | 55 | 8.7 | 5 |
| P 3 | Desorption 1 | 130 | 56.3 | 35 |
| P 4 | Adsorption 1 | 35 | 17.1 | 15 |
| P 5 | Desorption 2 | 180 | 17.1 | 15 |
| P 6 | Adsorption 2 | 55 | 8.7 | 5 |

Improvements compared to 1st Round Robin:

- Clear defined measurement procedure and sent around as a document
- Developed a results report sheet and sent around as a document
- Temperatures close to realistic applications
- A second reference point was included for those who can't detect the dry sample mass (due to apparatus limitations)

The results showed still deviations in water uptake and heat of adsorption. The lessons learned from this round robin was, that

- the definition of a reference mass in addition to dry mass shows a positive effect, however not the most important point
- The definition of a measurement procedure helped all participants
- There is still potential for improvement regarding:
 - Heat of adsorption should be measured from desorption point to adsorption point and not vice versa
 - Calculating vs. measuring the heat of adsorption must be discussed

These results lead to a new procedure for the third round robin with:

- A simplified measurement procedure (only one water vapor pressure for the whole procedure)
- Measurement of the heat of adsorption from a desorption point to an adsorption point and not vice versa
- Same scenarios and temperatures for the salt and the zeolite round robin
- Scenarios should fit the application conditions for domestic

5.3.2 3rd zeolite 13X round robin

The proposed measuring procedure for the 3rd zeolite 13X round robin is given in Appendix C. The material samples, NaMSX zeolite is a 13X type zeolite with binder, used by all the participating laboratories was provided by ZAE – Bayern.

The reported sample mass at the different test points (P₁-P₆) measured by the participating laboratories is summarized in Table 3_1

Table 3_1. Sample mass (absolute) for all measurement points 1 to 6

| Point # | Symbol | Sample Temperature [°C] | Sample Mass [mg] | |
|---------|---------------|-------------------------|------------------|--------------|
| | | | ZAE | CanmetENERGY |
| P 1 | $m_{dry/P1}$ | 350 | 197.6035 | 32.01 |
| P 2 | $m_{Ads2/P2}$ | 65 | 240.316 | 38.82 |
| P 3 | $m_{Des1/P3}$ | 95 | 232.638 | 37.54 |
| P 4 | $m_{Ads1/P4}$ | 35 | 247.431 | 40.065 |
| P 5 | $m_{Des2/P5}$ | 180 | 209.7705 | 33.85 |
| P 6 | $m_{Ads2/P6}$ | 65 | 240.501 | 38.875 |

The water uptake measured by the laboratories during Des₁ / Ads₁ and Des₂ / Ads₂ is summarized in Table 3_2. The standard deviation of the measured water uptake by the different participating laboratories is within 3% confirming the reliability of the test procedure used.

Table 3_2. Water mass uptake between Des1 / Ads1 and Des2 / Ads2

| Description | Symbol | Uptake [g/g] | | Standard Deviation |
|---|---------------|--------------|--------------|--------------------|
| | | ZAE | CanmetENERGY | |
| Uptake between Des1 / Ads1 related to dry mass | ΔX_1 | 0.0749 | 0.0789 | 2.6% |
| Uptake between Des2 / Ads2 related to dry mass | ΔX_2 | 0.1555 | 0.157 | 0.5% |
| Uptake between Des1 / Ads1 related to mass Des2 | $\Delta X_1'$ | 0.07055 | 0.0746 | 2.8% |
| Uptake between Des2 / Ads2 related to mass Des2 | $\Delta X_2'$ | 0.14645 | 0.14845 | 0.7% |

The measured heat of adsorption between Des₁ / Ads₁ and Des₂ / Ads₂ by the participating laboratories is summarized in Table 3_3. These reported results from only two participating laboratories cannot be conclusive. Additional participation is required.

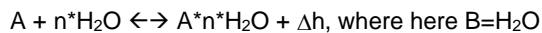
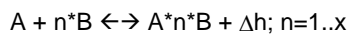
Table 3_3. Heat of adsorption between Des1 / Ads1 and Des2 / Ads2. Unit is J/g.

| Description | Symbol | Heat [J/g zeolite] | | Standard deviation |
|---|-------------|--------------------|--------------|--------------------|
| | | ZAE | CanmetENERGY | |
| Heat of Adsorption (material specific) Des1 / Ads1 | H_{Ads1} | 230.1 | 295.5 | 12.45% |
| Heat of Adsorption (material specific) Des2 / Ads2 | H_{Ads2} | 530.85 | 549.35 | 1.7% |
| | | [J/g water] | | |
| Heat of Adsorption (adsorbate specific) Des1 / Ads1 | H'_{Ads1} | 3073.5 | 3745.92 | 9.9% |
| Heat of Adsorption (adsorbate specific) Des2 / Ads2 | H'_{Ads2} | 3413.4 | 3499.12 | 1.24% |

6 Description of a harmonized measurement procedure for the TCM performance under realistic application conditions (D3T3)

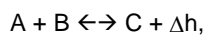
The contributors to this Task 58 Annex 33 focus on laboratory scale thermo-chemical energy storages (TES) where phase transitions and thermo-chemical reactions contain the energy potential.

In an adsorption or absorption storage, the following exothermic (discharging)¹ and endothermic (charging) reactions of components A plus B are taking place:



where A can be a zeolite, silica gel (adsorption) or base or salt solution (absorption) and in most of the applications B is water (H₂O) or water vapour, respectively.

For a thermo-chemical storage, the simplest reaction equation is given by:



where the reaction of A plus B ends in a new component C plus the heat Δh .

For the assigned application, the thermo-physical properties of the materials have to be known. The materials quality and possible impurities will influence the power and energy performance of the TES unit through the physical parameters.

Thermal energy storage components are designed to foster the task of keeping and delivering thermal energy in the power and capacity range needed for application. If the storage material selection or development is done, then the question is how to transfer the material thermo-physical properties to a storage component with an optimal operation function. This means, depending on the concept, to design a heat and mass transfer unit and thus a power unit and a materials container (tank) unit, the capacity unit. The storage component itself is a part of a storage system containing several additional technical parts. In this deliverable D3T3, the focus is on adsorption-based storage concepts, which means the sorbent is a solid and the sorbate is a gas (vapour, e.g. water vapour), but could also be a liquid.

Therefore, the material properties determined for example in a TGA- DSC measurement have to be transferred to a heat and mass exchanger lab scale component – on multi-particle level of several hundred grams² - to determine the heat transfer coefficient α and the mass transfer coefficient β in a combined experiment. This experiment has to be designed to optimally use/convert the advantageous properties of the storage material to an energy output. To do so, a heat and mass transfer experimental concept similar to the aimed large scale (power and capacity described in T4D1 of the task) unit has to be defined as part of the storage component development process. Out of this development process, a small scale experimental setup can be built and a simulation model could be defined. In this experimental setup, the temperature level of the heat sources and heat sinks have to reach the measurement temperatures of the TGA-DSC apparatus. For future scaling reasons, ideally the experimental power of this unit is in the range of several hundred Watts up to 1 kW. Using the experimental results, the simulation model (if there is any) will be validated within the measured parameter range and scaling correlations are resulting (dimensionless correlations). If the fundamental heat and mass exchange properties – the collective phenomena – do not change, a scaling to a higher power of several kW is possible. This means that the task of transfer (to transfer the process) into the aimed application is possible – which in other simple words means – the development of “engineering relations” for the design and scaling of the storage component is possible.

In the following sections a “**harmonized measurement procedure**” - *Description of a harmonized measurement procedure for the TCM performance under realistic application conditions* – is presented.

¹ The main processes of a thermal energy storage are charging and discharging.

² With the aim of a certain type of storage concept.

6.1 Procedure

The experimental work performed in the thermal energy storage projects contributing to the IEA Task 58 ECES Annex 33 has the target of transferring the know-how to the application areas. These areas can be the building sector for heating and cooling, process industry, transportation or any other technology where thermal energy storages are technically feasible, economically profitable and are contributing to sustainability. This aim implies the challenge of **scaling up** the small or medium **lab scale experiments to higher power and capacity**.

At the current level of effort and as unwritten agreement, the IEA work groups pursue a “**harmonised measurement procedure**” for the “lab storage performance assessment”. **This procedure and the measurements performed based in it is linked to the D3T2 relating the temperature scenarios.**

6.1.1 Thermal energy storage type – “classification”

A variety of thermo-chemical storage laboratory designs are on the research level. Based on the solid sorbent and sorbate flow and treatment processes, a “classification” in “**types of thermal energy storage**” is proposed³. This “classification” comprises 4 adsorption storages:

open: A) *fixed sorbent bed air and sorbate flow reactor*
B) *continuous moving sorbent bed air and sorbate flow reactor*
C) *mixed sorbent batch air and sorbate flow reactor*

closed: D) *fixed sorbent bed sorbate flow reactor*

In this “classification”, *absorption* is not considered because the *sorbent is liquid*. And a *zeolite molecular sieve* (see section 3.1 sorbent and sorbate) is rather not a reactant of a chemical reaction and therefore *chemical reactions* are at this stage of document not included here. But the author has to decide whether the fundamental exothermic process is a phys-sorption or a chemi-sorption.

6.1.2 Conservation laws and transfer functions

In the field of thermal energy storage R&D and technology, the power (W) and the capacity (Wh) of the storage units are the key “dimensions” or “figures”. Like in all other process technology areas, the conservation laws of **mass, momentum and energy** are the base frame for a comprehensive and complete assessment of the relevant storage versions. And with the boundary conditions of the (laboratory) system comprising of heat sources, heat sinks (their power and temperature level) and the storage unit, the knowledge of the steady state or part load operation is required. In other words, “the transfer functions of power and temperature have to be known”. Furthermore, the knowledge of the start-up and switching off behaviour in function of time is required. The list below is a summary (presume: *conservation of geometry*):

- *mass (sorbent, sorbate, fluid, container)*
- *momentum (sorbent, sorbate, fluid)*
- *power and energy / enthalpy*
- *steady state behaviour in function of power and temperature*
- *part load behaviour*
- *start-up /switching off behaviour*

6.1.3 Measurement parameters and analysis

For the analysis of the laboratory storage unit it is obvious that the physical parameters have to be measured in an appropriate precision as well as in time and geometrical resolution. The measurement data uncertainty estimation gives a hint for sensor precision and, if necessary, an idea of improvement. In case a simulation model (CFD) will be developed or is available, a validation will be possible. A validated model will allow the reduction of the experimental effort.

³ *Main criteria are: operation condition, temperature level and heat transport, residence time, “phase arrangement” (gravimetric separation), mass flow in heterogeneous systems and external reactions.*

As a requirement of this deliverable D3T3 a round-robin TGA-DSC measurement campaign with Zeolite 13X (SrBr₂) was done and described in D3T2 (Lia Kouchachvili, Reda Djabbar, 2019). The amount of 13X (SrBr₂) material is in the g (gram) range and thus the sorbate (water) uptake lays in the sub-gram range. The TGA-DSC measurements serves quasi as one of the «Single Particle» experiments.

With the assumption of the available thermo-physical properties of the storage material – the sorbent-sorbate combination - as well as of the container material (storage material, heat transfer fluid etc.), the following list contains the parameters to be or may be measured and deduced thereof:

- *mass m (kg) & mass flow dm/dt (kg/s, kg/h) (sorbent, sorbate, heat transfer fluids)*
- *volume flow rate (m^3/s , m^3/h) (sorbent, sorbate, heat transfer fluids)*
- *temperature T (°C; K) (sorbent, sorbate, heat transfer fluids)*
- *time t , time step Δt / time resolution (s)*
- *pressure p (mbar, Pa) (sorbent, sorbate, heat transfer fluids)*
- *enthalpy h (J/kg) & enthalpy flow dh/dt (J/kg*s)*
- *input and output power (W) & input and output energy (J)*
- *auxiliary power (W) & energy (J)*

6.1.4 Measurement temperatures - scenarios

In the application of a sorption (ad- and ab-) thermal energy storage, the boundary conditions are of the heat sinks and sources are required for the power (W) and the temperature level (°C, K). As there is a broad variety of TES types, it is challenging to restrict to a common heat sources and sinks parameter range in this Task 58 Annex 33 working group.

But to keep the temperatures in the TGA-DSC measurements (Round Robin Test – Zeolite 13X) and following the **4 temperatures approach the desorption (des) – adsorption (ads) process steps** - for the 13X sorbent material should be done at 2 scenarios:

- Scenario 1: **95 °C (des) / 10 °C condensation & 35 °C (ads) / 10 °C evaporation.**
- Scenario 2: **180 °C (des) / 10 °C condensation & 65 °C (ads) / 10 °C evaporation.**
- Scenario 2b: **130 °C (des) / 10 °C condensation & 35 °C (ads) / 10 °C evaporation** (if scenario 2 not useful).

Nevertheless, air-conditioning (room heating and/or cooling and hot tap water) is mentioned in all contributions as one of the application areas. Within this application area, the remaining common parameter - the **dependent parameter** (variable) - is the “output” **temperature T** (and power) level of the storage:

- Application **temperature range T = 35 °C** (heating) **to 65 °C** (ads +5 K to reach 60 °C DHW).

All other **independent parameters** (variables like air humidity – open storage – and/or water vapour pressure – closed storage) have to be chosen and adjusted to reach the above mentioned temperature range.

6.2 Experimental

In the Kick Off meeting from Lyon it was agreed to use as sorbent material the zeolite molecular sieve KÖSTROLITH® NaMSXK with a particle size of 1.6 to 2.5 mm (supplied by Fabian Fischer of ZAE Bayern). Further information about the sorbent materials is given in Table 2. Water will be used as sorbate because of the excellent thermodynamic properties. Figure 4 and Figure 5 are showing the vapour pressure curves of water and the combination of water and zeolite (from literature).

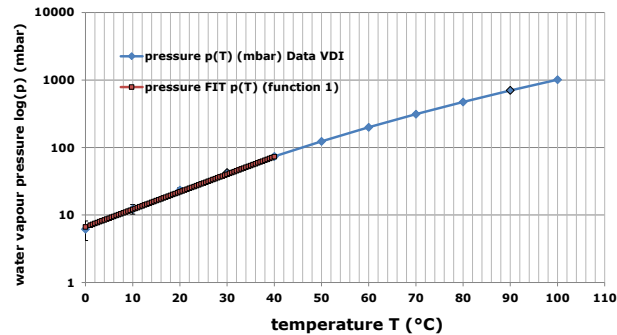


Figure 4 Water vapour pressure p curve in function of temperature T . VDI data and a fit function in the range of $T=0^{\circ}\text{C}$ to 40°C . This figure will be replaced by a “complete” figure $p(T, c)$, see **Figure 5**.

Figure 5 Van-'t Hoff or vapour pressure p curves ($1/T - \log(p)$ diagram) of a sorbent in function of temperature and load c/c_0 . Adopted from literature. I would like to have this curves for zeolite molecular sieve KÖSTROLITH® NaMSXK (1.2 – 2.5 mm).

6.2.1 Sorbent and sorbate

Table 2 Specifications for the used sorbent: zeolite molecular sieve KÖSTROLITH® NaMSXK (1.2 – 2.5 mm), chemical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot m \text{SiO}_2 \cdot n \text{H}_2\text{O}$

| | Method | NaMSXK (1.2 – 2.0 mm) | NaMSXK (1.6 – 2.5 mm) |
|---|----------|-----------------------|-----------------------|
| Beads Size Range (nominal, mm) (approx. mesh size) | | 1.2 – 2.0 10 x 16 | 1.6 – 2.5 8 x 12 |
| Bulk Density (compacted, g/l) | CWKM-118 | 680 - 725 | 680 - 725 |
| Attrition (% wt.) | CWKM-122 | max. 0.2 | max. 0.2 |
| Crush Strength (N/bead) | CWKM-108 | min. 10 | min. 25 |
| Moisture Content (as delivered, % wt.) | CWKM-408 | max. 1.0 | max. 1.0 |
| Water Adsorption Capacity* (55 % rel. hum., 20 °C, % wt.) | CWKM-403 | min. 26.5 | min. 26.5 |
| CO ₂ Adsorption Capacity* at 2.4 mbar CO ₂ pressure (cm ³ (STP) / g) | CWKM-409 | min. 24.0 | min. 24.0 |

6.2.2 Lab scale storage unit

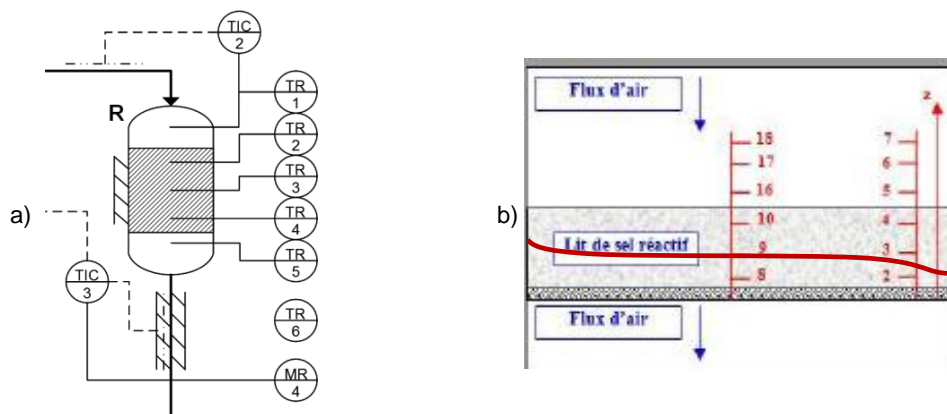


Figure 6: Examples of storage component type/class a), “fixed sorbent bed air and sorbate flow reactor”. Adopted from Thomas Nonnen et al., 2016. R=reactor, TIC=temperature indicator/controller, TR=thermocouple / temperature sensor, MR=moisture sensor. b) Temperature profile from F. Marias, 2014. The numbers 2 to 18 indicate temperature sensor positions.

Table 3 Range of the independent parameters in the experiment to reach (measure) the dependent variable temperature T: most of you already have done this section

| |
|--|
| Geometry: maybe you already have done this section |
| Material: Container material thermo-physical properties |
| Geometry: particle size see Table 2 (distribution) |
| Mass: Sorbent mass or mass range: m_{\min} to m_{\max} , Sorbate mass range: m_{\min} to m_{\max} |
| Etc. |

6.3 Results

6.3.1 Data, figures, tables and Diagrams

Measurement results are figures, graphs, tables and if fit functions were use eventually equations. The analysis and interpretation of the results follows. Assessment: see section 5 below. An example (Steffen Beckert, Silvie Rougé) is shown in Figure 7. The heat transfer zone (temperature) and their time dependent development in function of position can be seen in Figure 14.

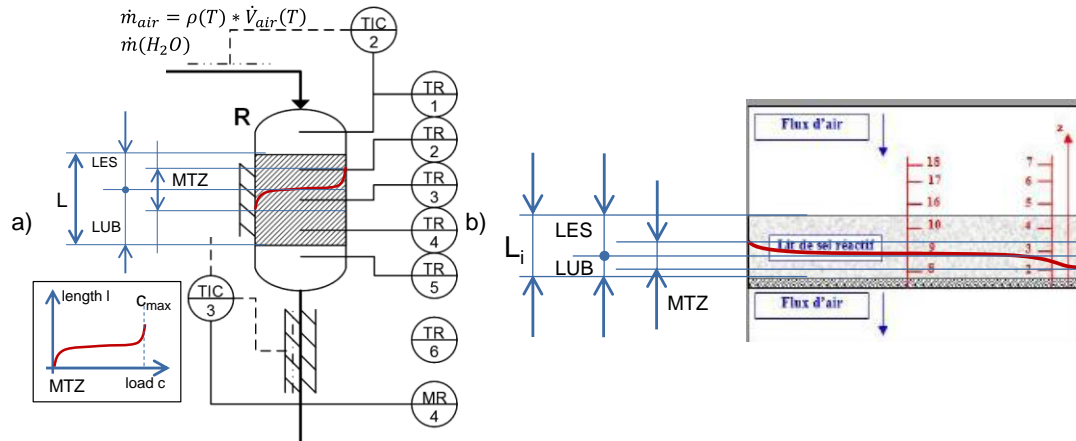


Figure 7 Measured mass transfer zone: examples of storage component type/class A) “fixed sorbent bed air and sorbate flow reactor”. a) left, adopted from Thomas Nonnen et al, 2016. R=reactor, TIC=temperature indicator/controller, TR=thermocouple / temperature sensor, MR=moisture sensor. L=length of the fixed sorbent bed, LES= length of equilibrium part, MTZ=mass transfer zone, LUB=length of unused bed. Insert: MTZ graph with maximum load c_{max} and arbitrary units. b) right, Adopted from F. Marias, 2015.

Possible presentation of measurement results of an open system are the outlet air conditions in a **psychrometric chart or Mollier Diagram**. Or, like in Figure 8, the temperature $T(t, z)$ in function of time t and position z in the solid sorbent bed.

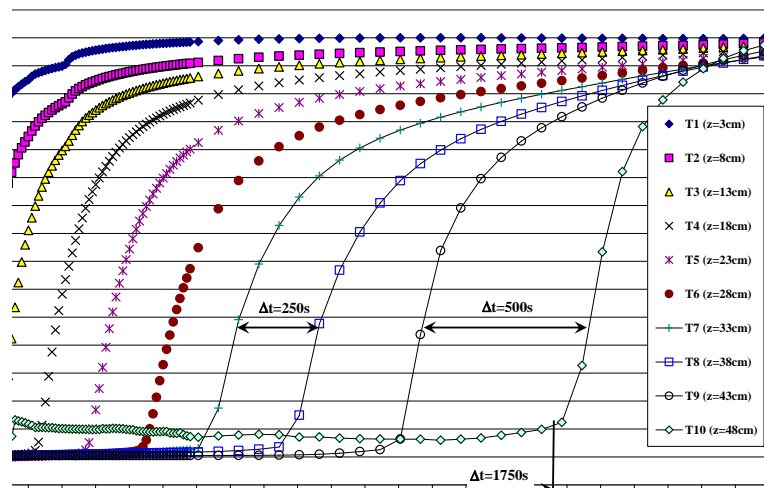


Figure 8 Evolution of the sorbent bed temperatures T1 to T10 (normalised) in function of time t and position z during the water vapour adsorption process. Adopted from own measurements.

6.3.2 Uncertainty estimation

Contributors: Please do an uncertainty estimation of your experimental results. Follow for example NIST Technical Note 1297 or JCGM 100:2008 (Barry N. Taylor and Chris E. Kuyatt, 1994, Joint Committee for Guides in Metrology, 2008) or ISO 21748:2017 (Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty evaluation, 2017) or appropriate methods.

6.4 Discussion and assessment

Contributor – laboratory experiment: Each experiment of a contributor and the results are discussed by you. In this way, the comparison with other experiments (which may have totally different geometric dimensions etc.) can/could be easier done.

One of the more obvious performance indicator is the maximal temperature lift achievable during the discharging process. This temperature difference is measured between the temperature level at which the heat can be delivered and the low temperature heat source. By increasing this temperature difference, the delivered output power usually decreases until reaching the equilibrium point (null output power).

Depending on the boundary condition, the discharging power ($Q_{discharging}$) can be used to calculate the discharging efficiency ($\eta_{discharging}$) according to following equation:

$$\eta_{discharging} = \frac{Q_{discharging}}{Q_{thermochemical}}$$

with $Q_{thermochemical}$ based on the sorbent status

In the same way, a charging efficiency ($\eta_{charging}$) can be defined:

$$\eta_{charging} = \frac{Q_{charging}}{Q_{thermochemical}}$$

Allowing determining the system global efficiency (η_{global}):

$$\eta_{global} = \frac{Q_{discharging}}{Q_{charging}} = \eta_{discharging} \cdot \eta_{charging}$$

This efficiency calculated on a lab scale prototype should stay unchanged for a demonstrator using the same technology and is a major output to get an assessment of the storage density (kWh/m³) – the storage energy per used volume. In fact, the aim for high energy density storages is the reduction of the foot-print or just the reduction of the volume.

6.5 Considerations about scaling-up

The system characterisation is described in Deliverable D4T1 (Benjamin Fumey et al.). Nevertheless, scaling from lab scale processes to the system (of real application, one or two orders higher, or more) is a challenge. In this task, inputs from the measurements done on the lab scale prototype (like dimensionless numbers) may be used for the modelling. In fact, generally, the measurement results are analysed in dimensionless presentation like $T(t)/T_{max}$, $p(t)/p_{max}$, etc. Furthermore, in heat and mass transfer process scaling, the dimensionless numbers (heat transfer) like $Nu = Nu(Re, Pr)$ and (mass transfer) $Sh = Sh(Sc, Pr)$ play an important role.

7 Acknowledgment

This research in the section "Description of a harmonized measurement procedure for the TCM performance under realistic application conditions" was supported by the Swiss Federal Office of Energy in the frame of the ABSTOREX project, by the Commission of Technology and Innovation in the frame of SCCER Heat and Electricity Storage as well as by the University of Applied Sciences of Rapperswil.

8 References

- ISO 21748:2017(en). Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty evaluation.
- Barry N. Taylor and Chris E. Kuyatt, Guidelines for Evaluation and Expressing the Uncertainty of NIST Measurement Results. NIST National Institute of Standards and Technology, United States Department of Commerce, NIST Technical Note 1297 Edition 1994.
- Foivos Marias, 2015. Analyse, Conception et expérimentation de procédés de stockage thermique résidentiel de longue durée par réaction thermochimique à pression atmosphérique. Thermique [physics.class-ph]. Université Grenoble Alpes, 2015.
- Foivos Marias, Pierre Neveu, Gwennyn Tanguy, Philippe Papillon, 2014.
- JCGM 100:2008, 2008. Joint Committee for Guides in Metrology (JCGM/WG 1). Evaluation of measurement data – Guide to the expression of uncertainty in measurement; 2008.
- Lia Kouchachvili, Reda Djabbar, Summary of the Round Robin Tests for SRBr2 and 13X, 2019. Thermodynamic analysis and experimental study of solid/gas reactor operating in open mode. Energy 66 (2014) 757-765.
- Thomas Nonnen et al. 2016. A Thermochemical Long-Term Heat Storage System Based on a Salt/Zeolite Composite. Chem. Eng. Technol. 2016, 39, No. 12, 2427-2434.

APPENDIX A

(September 9th, 2018)

IEA Task 58 / Annex 33 Subtask 3T

Measurement Procedure for the 2nd Salt Hydrate Round Robin ($\text{SrBr}_2 \cdot n\text{H}_2\text{O}$)

Goal of this document

By applying and following this procedure, reproducible and comparable measurement results of hydration/dehydration potential, enthalpy of hydration /dehydration as well as the characterization of the cyclic stability for salt hydrate thermochemical materials (TCM) will be produced, to predict the material performance under particular boundary conditions of an application.

Procedure for salt hydrate materials (e.g. SrBr_2)

The applied methods include gravimetric analyzers with vapor or humidity conditioning, optional with calorimetric extension (TG, TG-DSC, STA). The procedure consists of a pretreatment of the sample, and several hydration- and dehydration points, while all of them have to reach equilibrium state.

Definition of the Scenarios

Three (3) scenarios of salt hydration shall be applied in order to characterize the hydration potential of the salt, which are derived from boundary conditions in typical applications, and are in good agreement with the temperatures for domestic heating and cooling sent in a document (Temperatures_Buildings) by Benjamin Fumey.

Pretreatment / Dry Mass Detection

A standardized pretreatment is necessary for comparable salt hydration calculations, as the dry mass will serve as one of the reference masses. There is no known existing unified test method at this time for salt hydrate pretreatment. The following proposed sample pretreatment for the present 2nd round robin shall be as follows.

- The optimal sample pretreatment temperature T_{max} should be selected considering and well below the melting point of the considered salt hydrate. For the case of SrBr_2 , the proposed $T_{\text{max}}=200^\circ\text{C}$ is well below the melting temperature of SrBr_2 , which is about 657°C as per the Handbook of Inorganic Compounds
- The sample shall be heated starting from laboratory ambient conditions to T_{max} with a heating rate of $1\text{K}/\text{min}$ followed by an isothermal drying step for another 1 hour (see Figure 1). The total pretreatment time shall be about 3 hours.

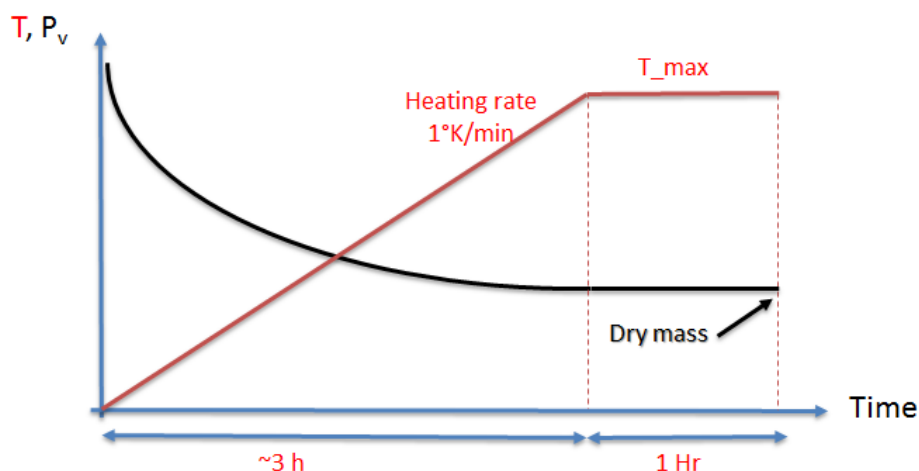


Figure 9: Proposed pretreatment procedure

Comments to Round-Robin participants of IEA/Annex 58/33: For the case that the measurement setup is not capable of supplying complete dry air during the pretreatment as well as during the dehydration experiments, please indicate this together with the measurement results.

Measurement of equilibrium points

In the following steps, three hydration and two dehydration equilibrium points along with two pretreatment steps are defined in order to characterize the hydration/dehydration properties and cyclic stability of salt hydrate. The three dew points representative of typical winter ambient water evaporation source conditions include 5, 7 and 10 °C corresponding to water vapor pressures of 8.7, 10 and 12.3 mbar and sample temperatures of 25, 95 and 200 °C. Hydration transition steps are represented in green arrows on Figure 2. Dehydration transitions are represented in bleu arrows and the two pretreatment transitions are represented by black arrows. These points are motivated by applications addressed with salt hydrate TCM's, and take care of the chosen reference sample for the round robin test (SrBr₂).

Table 4: Temperatures and vapor pressure/dew point Test Points

| Point # | Label | Sample Temperature [°C] | Vapor Pressure [mbar] | Corresp. Dew point [°C] |
|---------|----------------------------|-------------------------|-----------------------|-------------------------|
| P1 | Pretreatment / Dry Mass 1 | 200 | < 1 e-3 | -150 |
| P2 | Hydration 1 | 25 | 8.7 | 5 |
| P3 | Dehydration 1 | 95 | < 1 e-3 | -150 |
| P4 | Hydration 2 | 25 | 10 | 7 |
| P5 | Dehydration 2 | 95 | < 1 e-3 | -150 |
| P6 | Hydration 3 | 25 | 12.3 | 10 |
| P7 | Pretreatment / Dry Mass 2 | 200 | < 1 e-3 | -150 |
| P8 | Cycling test / Hydration 4 | 25 | 8.7 | 5 |

For all heating dehydration and pretreatment transitions, a heating rate of 1K/min is defined. For all cooling phases to bring the sample hydration reference temperature $T_{Hyd_Ref}=25^{\circ}\text{C}$. Possible cooling rates are dependent on available laboratory equipment and shall be defined and reported. The procedure is defined step-by-step as follows:

Initial Pretreatment (P 1):

Reference mass detection; please choose temperatures according to chapter (b) as 200 °C, and water vapor pressure < 1 e-3 mbar, heating rate as 1 K/min. When reaching T_{max} , keep constant temperature and lowest water vapor pressure possible for at least 1 Hour.

The mass detected during at the end of this initial and first pretreatment is the initial denoted as mass $m_{in/P1}$ and serving as one of the reference masses for salt hydration potential calculations.

Comparing $m_{dry/P1}$ to the initial sample at the start of the testing m_{start} shall confirm whether the salt has reached the anhydrous state of the salt.

Hydration 1 (P 2):

Sample Temperature of 25 °C corresponding to the Test hydration Reference mass T_{Hyd_Ref} , dew point of 5 °C corresponding to 8.7 mbar ; this hydration point serves as the most stringent test for characterizing the hydration suitability of the salt; the mass detected is labelled as $m_{Hyd1/P2}$ and will be used for reproducibility of the salt cycling suitability check. The time to reach equilibrium $t_{Hyd1/P2}$ shall be reported

Dehydration 1 (P 3):

Sample Temperature of 95 °C corresponding to the Test dehydration temperature T_{Dehd_Ref} and water vapor pressure < 1 e-3 mbar, heating rate as 1 K/min, constant temperature and pressure level for at least 1 Hour; the mass detected is labelled as $m_{Deh1/P3}$. The mass detected in reaching this first dehydration cycle will be compared and used as one of the reference masses for salt hydration calculations. The time to reach equilibrium $t_{Deh1/P3}$ shall be reported

Hydration 2 (P 4):

Sample Temperature of 25 °C, dew point of 7°C corresponding to 10 mbar ; this hydration point serves as an intermediary winter ambient condition test for the hydration suitability of the salt; the mass detected is labelled as $m_{Hyd2/P4}$ and will be used for reproducibility of the salt cycling suitability check. The time to reach equilibrium $t_{Hyd2/P4}$ shall be reported

Dehydration 2 (P 5):

Sample Temperature of 95 °C and water vapor pressure < 1 e-3 mbar, heating rate as 1 K/min, constant temperature and pressure level for at least 1 Hour; the mass detected is labelled as $m_{Deh2/P5}$;

The mass detected in reaching this first dehydration cycle will be compared and used as one of the reference masses for salt hydration calculations. The time to reach equilibrium $t_{Deh2/P5}$ shall be reported

Hydration 3 (P 6):

Sample Temperature of 25 °C, dew point of 10°C corresponding to 12.3 mbar ; this hydration point serves as a maximum winter ambient condition test for the hydration suitability of the salt; the mass detected is labelled as $m_{Hyd3/P6}$ and will be used for reproducibility of the salt cycling suitability check. The time to reach equilibrium $t_{Hyd3/P6}$ shall be reported

2nd Pretreatment (P 7):

In order to confirm the cyclic suitability of the salt and confirm whether the salt retains its original properties, the first dehydration/hydration cycle shall repeated exactly as was executed at the start of the testing.

After completion of Hydration 3 phase, the salt 2nd pretreatment should be performed similar to P1. Please choose temperatures according to chapter (b) as 200 °C, and water vapor pressure < 1 e-3 mbar, heating rate as 1 K/min, constant temperature and vapor pressure level for at least 1 Hour.

The mass detected during this 2nd pretreatment is the second mass $m_{2/P7}$ serving as one of the reference masses for salt hydration potential calculations.

Comparing $m_{dry/P7}$ to the initial sample at the start of the testing m_{start} shall confirm whether the salt has reached the anhydrous state and shall be compared to $m_{dry/P1}$ for assessing the salt cycling suitability

Hydration 4 (P 8):

Sample Temperature of 25 °C, dew point of 5°C corresponding to 8.7 mbar ; this hydration point will be compared to P2; the mass detected is labelled as $m_{Hyd4/P8}$ and will be used for assessing the salt cycling suitability. The time to reach equilibrium $t_{Hyd4/P8}$ shall be reported

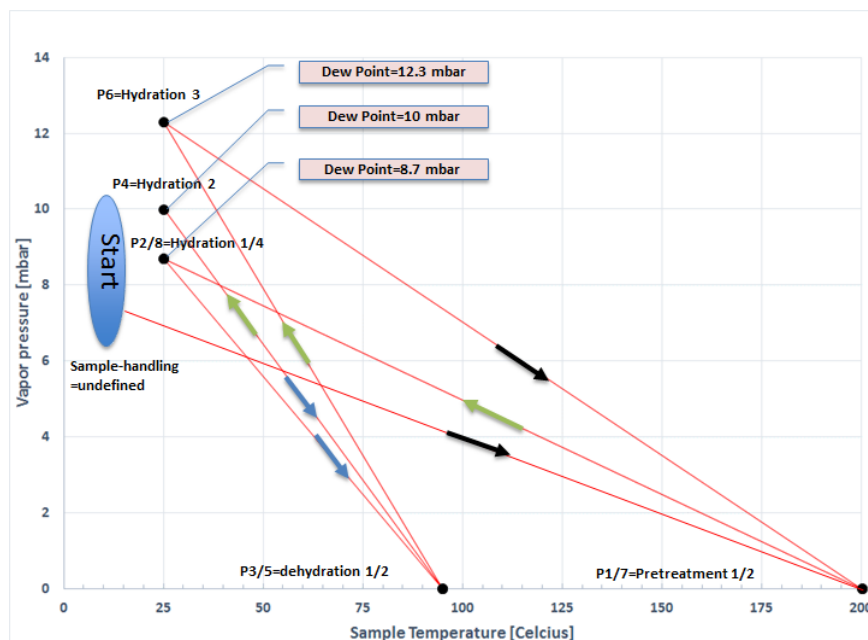


Figure 10: Scheme of the measurement procedure as plotted in the grid of sample temperature and vapor pressure.

Definition of equilibrium state

Depending on the measurement setup, salt hydration/dehydration in the segment and kinetics, the time for reaching equilibrium varies severely from several hours to more than a day. An appropriate equilibrium is reached, when there is only balance-related noise left, without any significant tendency of the signal.

A guideline for estimating equilibrium is in progress.

Measuring the heat (of hydration/dehydration)

For this Round Robin, there will be one option, and the consistency of results and applied method for the future will be discussed in the next Task/Annex meeting.

Direct measurement with STA / TG-DSC:

According to the procedure, the heat release during hydration can be measured for all of P2, P4, P6 and P8. The heat gain during dehydration can be measured for both P3 and P5. The sensible heat of the adsorption material has to be subtracted. This can be done either by performing and subtracting a blank measurement under inert gas atmosphere, or by post-processing of the data (when T-dependent $c_{p, SrBr_2}$ values are available).

Calculation from the SrBr₂ characteristic curve:

The heat of adsorption can be calculated by models like.....

If you report values for the heat, please indicate if they are measured or calculated by applying a model and which model was used.

Delivery of results (values, format, units)

For comparing the results and for detecting the reasons for deviations, please follow the instructions for delivery of the data in the following. It is proposed to repeat the measurements to ensure repeatable results. Please use the Results Report Sheet which will be sent out with the procedure and use a separate sheet for each measurement run. Please state the uncertainty of each measured value. For the analyzation of the results it would also be interesting to indicate the uncertainties of the used apparatus. For this purpose, an additional table is included in the Result Report Sheet. Please choose the fields in the table which are relevant for your apparatus. If the pretreatment of your sample is conducted externally, you can indicate the uncertainty of the external balance in the field "Dry mass determination".

In the following, you find further information for doing the data analysis:

- Sample mass (absolute) for all measurement points 1-8, (please subtract sample holder/crucible), Units [mg]
- Hydration mass uptake of the salt are measured during P2, P4, P6 and P8 equilibrium points, and are compared to the mass of dehydrated salt detected during the preceding dehydrated points (P1, P3, P5 and P7) and dehydration steps 1 and 2, Units [g/g dry mass]

$$\Delta m_1 = \frac{m_{Hyd1/P2} - m_{dry/P1}}{m_{dry/P1}}$$

$$\Delta m_2 = \frac{m_{Hyd2/P4} - m_{Deh1/P3}}{m_{Deh1/P3}}$$

$$\Delta m_3 = \frac{m_{Hyd3/P6} - m_{Deh2/P5}}{m_{Deh2/P5}}$$

$$\Delta m_4 = \frac{m_{Hyd4/P8} - m_{dry/P7}}{m_{dry/P7}}$$

- Hydration heat release of the four-hydration test processes Hyd1, Hyd2, Hyd3 and Hyd4. Unit is J/g of dehydrated mass of salt at the start of the hydration phase; Units [J/g_{salt, dehydrated}]
Calculation according to

$$H_{Hyd1} = \frac{\int_{Hyd1_i}^{Hyd1_f} \dot{Q} dt}{m_{dry/P1}} \quad H_{Hyd2} = \frac{\int_{Hyd2_i}^{Hyd2_f} \dot{Q} dt}{m_{Deh1/P3}}$$

$$H_{Hyd3} = \frac{\int_{Hyd3_i}^{Hyd3_f} \dot{Q} dt}{m_{deh5/P1}} \quad H_{Hyd4} = \frac{\int_{Hyd4_i}^{Hyd4_f} \dot{Q} dt}{m_{dry/P7}}$$

(Please note: \dot{Q} as exothermal is negative; i and f relate to the start and finish of the hydration process)

- Dehydration heat gain of the two-hydration test processes Deh1, Deh2. Unit is J/g of dehydrated mass of salt measured at the end of the dehydration p; Units [J/g_{salt, dehydrated}]

Calculation according to:

$$H_{Deh1} = \frac{\int_{Deh1_i}^{Deh1_f} \dot{Q}' dt}{m_{Deh1/P3}} \quad H_{Deh2} = \frac{\int_{Deh2_i}^{Deh2_f} \dot{Q}' dt}{m_{Deh2/P5}}$$

(Please note: \dot{Q} as endothermal is positive)

- Cyclic behavior of the salt is measured in terms of the reproducibility of dehydrated mass during the two dehydration processes Deh1 and Deh2 when considering the reference application dehydration temperature, T_{Deh_Ref} , which in this case is assumed 95°C. It is also measured in terms of the reproducibility of dry mass during the two pretreatment processes Dry1 and Dry2 when considering $T_{max} = 200^\circ C$, Units [g/g]

$$\Delta m_1 = \frac{m_{Deh2/P5} - m_{Deh1/P3}}{m_{Deh1/P3}}$$

$$\Delta m_2 = \frac{m_{dry/P7} - m_{dry/P1}}{m_{dry/P1}}$$

Cyclic behavior of the salt is also measured by comparing the heat hydration heat release after the pretreatment up to $T_{max} = 200^\circ C$ of the salt sample H_{Hyd1} and H_{Hyd2}

Good luck with the measurements!

Questions / comments / improvement of the procedure, please send an email to Reda.Djebbar@Canada.ca

When you have performed the measurements and processed the data, please send it to the same email address (using the Results Report Sheet).

References:

- Dale L. Perry, Handbook of Inorganic Compounds, Second Edition

Results report of the Salt Hydrate ($\text{SrBr}_2 \cdot n\text{H}_2\text{O}$) 2nd Round Robin

| | |
|------------------------|---|
| Lab: | |
| Operator: | |
| Measurement Apparatus: | |
| Measurement Mode: | <input type="checkbox"/> static (pure water vapor atmosphere) <input type="checkbox"/> dynamic (pure water vapor atmosphere) <input type="checkbox"/> dynamic with carrier gas: |
| Pretreatment: | <input type="checkbox"/> Vacuum with final pressure: <input type="checkbox"/> other: |
| Heat of Adsorption | <input type="checkbox"/> measured <input type="checkbox"/> calculated, applying model: |
| Period of Measurement: | |

Uncertainty of apparatus (datasheet values). Please choose the fields, which are relevant for your apparatus.

| | | | | | |
|------------------|-----------------|-----------------------|-----------------------------|--------------|--|
| Temperature [°C] | Pressure [mbar] | Relative Humidity [%] | Saturation Temperature [°C] | Balance [mg] | Dry Mass Determination (external) [mg] |
| | | | | | |

1. Sample mass (absolute) for all measurement points 1 to 8. Please also report here the mass of the salt sample at the very start of the testing m_{start} in [mg] Unit is mg.

| Point # | Symbol | Sample Temperature [°C] | Vapor Pressure [mbar] | Equilibrium time [min] | Sample Mass [mg] | Uncertainty [mg] |
|---------|----------------------|-------------------------|-----------------------|------------------------|------------------|------------------|
| P0 | m_{start} | NA | NA | NA | | |
| P 1 | $m_{\text{dry}/P1}$ | 200 | < 1 e-3 | As per Section b | | |
| P 2 | $m_{\text{Hyd1}/P2}$ | 25 | 8.7 | | | |
| P 3 | $m_{\text{Deh1}/P3}$ | 95 | < 1 e-3 | | | |
| P 4 | $m_{\text{Hyd2}/P4}$ | 25 | 10 | | | |
| P 5 | $m_{\text{Deh2}/P5}$ | 95 | < 1 e-3 | | | |
| P 6 | $m_{\text{Hyd3}/P4}$ | 25 | 12.3 | | | |
| P7 | $m_{\text{dry}/P7}$ | 200 | < 1 e-3 | As per Section b | | |
| P8 | $m_{\text{Hyd4}/P8}$ | 25 | 8.7 | | | |

2. Hydration mass gain during Hyd1, Hyd2, Hyd3 and Hyd4 equilibrium . Unit is g/g dry mass.

| Description | Symbol | Uptake [g/g] | Uncertainty [g/g] |
|---|--------------|--------------|-------------------|
| Uptake after Hyd1 related to dry mass $m_{\text{dry}/P1}$ | Δm_1 | | |
| Uptake after Hyd2 related to mass Deh1 $m_{\text{Deh1}/P3}$ | Δm_2 | | |
| Uptake after Hyd3 related to mass Deh2 $m_{\text{Deh2}/P5}$ | Δm_3 | | |
| Uptake after Hyd4 related to dry mass $m_{\text{dry}/P7}$ | Δm_4 | | |

3. Dehydrated and Dry mass change after the dehydration and the pretreatment cycles. Unit is g/g.

| Description | Symbol | Uptake [g/g] | Uncertainty [g/g] |
|--|--------------|--------------|-------------------|
| Dehydrated mass change between Deh1 and Deh2 | Δm_1 | | |
| Dry mass change between Dry1 and Dry2 | Δm_2 | | |

4. Hydration Heat of the four-hydration test processes Hyd1, Hyd2, Hyd3 and Hyd4. Unit is J/g of dehydrated mass of salt at the start of the hydration phase.

| Description | Symbol | Hydration time [min] | Heat [J/g] | Uncertainty [J/g] |
|----------------------------|------------|----------------------|------------|-------------------|
| Hydration Heat during Hyd1 | H_{Hyd1} | $t_{Hyd1/P2} =$ | | |
| Hydration Heat during Hyd2 | H_{Hyd2} | $t_{Hyd2/P4} =$ | | |
| Hydration Heat during Hyd3 | H_{Hyd3} | $t_{Hyd3/P6} =$ | | |
| Hydration Heat during Hyd4 | H_{Hyd4} | $t_{Hyd4/P8} =$ | | |

5. Dehydration Heat of the two-hydration test processes Deh1, Deh2. Unit is J/g of dehydrated mass of salt measured at the end of the dehydration cycle.

| Description | Symbol | Dehydration time [min] | Heat [J/g] | Uncertainty [J/g] |
|------------------------------|------------|------------------------|------------|-------------------|
| Dehydration Heat during Deh1 | H_{Deh1} | $t_{Deh1/P3} =$ | | |
| Dehydration Heat during Deh2 | H_{Deh2} | $t_{Deh2/P5} =$ | | |

APPENDIX B

(January 14th, 2019) Measurement Procedure for Water Uptake Evaluation of TCMs
IEA Task 58 / Annex 33 Subtask Final Round Robin Procedure for SrBr₂

Goal of this document:

By applying and following this procedure, reproducible and comparable measurement results of water vapor uptake for thermochemical materials (TCM) will be produced, to predict the material performance under particular boundary conditions of an application.

Procedure for salt hydrates (e.g. SrBr₂)

The applied methods include gravimetric analyzers with vapor or humidity conditioning, optional with calorimetric extension (TG, TG-DSC, STA) [1]. The procedure consists of a pretreatment of the sample, and several hyd- and dehydration points, while all of them have to reach equilibrium state.

Definition of the Scenarios

As performed in the first round robin, two scenarios will be applied, which are derived from boundary conditions in typical applications, and are in good agreement with the temperatures for domestic heating and cooling sent in a document (Temperatures Buildings) by Benjamin Fumey.

Pretreatment / Dry Mass Detection

A standardized pretreatment is necessary for comparable uptake calculations, as the dry mass will serve as one of the reference masses. Please follow the following procedure presented below:

(It must be performed under 1 mbar corresponding of 3.2 % R.H.)

The optimal sample pretreatment temperature T_{\max} of 120°C was selected

The sample is heated starting from ambient conditions with a heating rate of 1K/min followed by an isothermal drying step

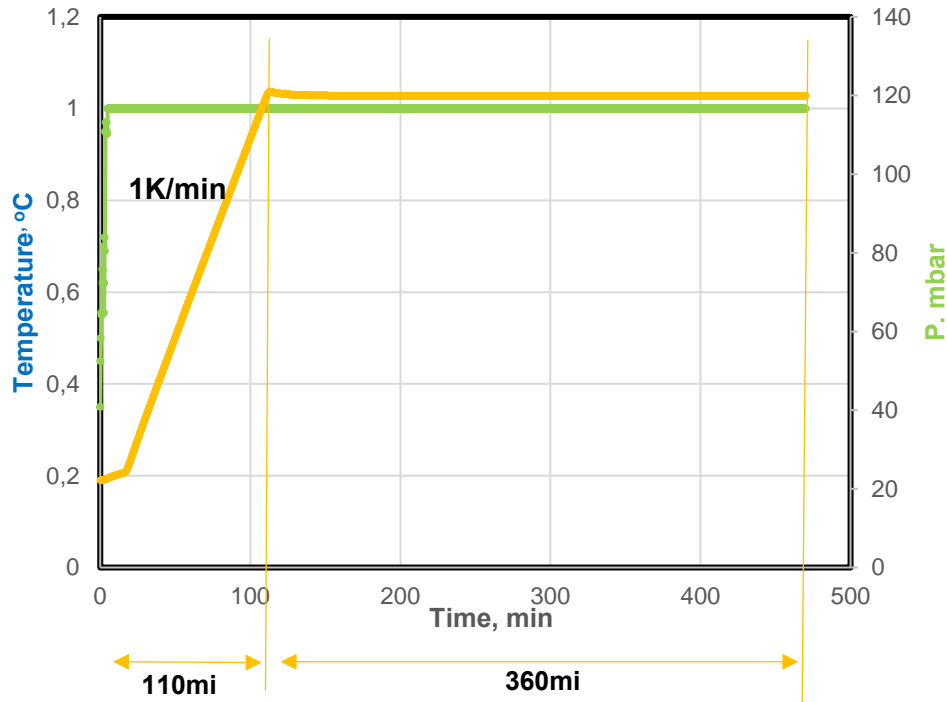


Figure 8: Proposed pretreatment procedure

Measurement of equilibrium points

In the following steps, two hydration and dehydration points are carried out, all with a dew point of 10 °C, which corresponds to water vapor pressure of 12.3 mbar, and sample temperatures of 35, 65, 95 and 180 °C). These points are motivated by applications addressed with TCM's, and take care of the chosen reference sample for the round robin test (SrBr₂).

For all heating phases, a heating rate of 1K/min is defined.

Table 5: Temperatures and vapor pressure/dew point, according to scenario 1 (Deh1, hyd1) and 2 (Deh2, Hyd2)

| Point # | Label | Sample Temperature [°C] | Vapor pressure [mbar] | Corresp. Dew point [°C] |
|---------|-------------------------|-------------------------|-----------------------|-------------------------|
| P 1 | Pretreatment / Dry mass | 120 | 1 | -20.1 |
| P 2 | Hydration 1 | 65 | 12.3 | 10 |
| P 3 | Dehydration 1 | 95 | 12.3 | 10 |
| P 4 | Hydration 2 | 35 | 12.3 | 10 |
| P 5 | Dehydration2 | 180 | 12.3 | 10 |
| P 6 | Hydration 3 | 65 | 12.3 | 10 |

The procedure is defined step-by-step:

Pretreatment (P 1):

Dry mass detection; please choose temperatures according to chapter as 120 °C, and pressure level 1 mbar, heating rate as 1 K/min, constant temperature and pressure level for at least 6 h.

The mass detected during pretreatment is the dry mass $m_{dry/p1}$ serving as one of the reference masses for uptake calculations.

Hydration 1 (P 2):

Sample Temperature of 65 °C, dew point of 10 °C corresponding to 12.3 mbar; this hydration point serves as intermediate step, so that the following dehydration can be approached in dehydration direction, and the two

following pairs can measure the heat in hydration mode; the mass detected is labelled as $m_{hyd1/P2}$ and can be used for reproducibility check

Dehydration 1 (P 3):

Sample Temperature of 95 °C (heating rate 1K/min), dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Deh1/P3}$

Hydration 1 (P 4):

Sample Temperature of 35 °C, dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{hyd2/P4}$

Dehydration 2 (P 5):

Sample Temperature of 180 °C (heating rate 1K/min), dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Deh2/P5}$;

In addition to the dry mass detected during pretreatment, the mass detected at Dehydration 2 $m_{Deh2/P5}$ will serve as a second reference mass for uptake calculations.

Hydration 2 (P 6):

Sample Temperature of 65 °C, dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{hyd3/P6}$

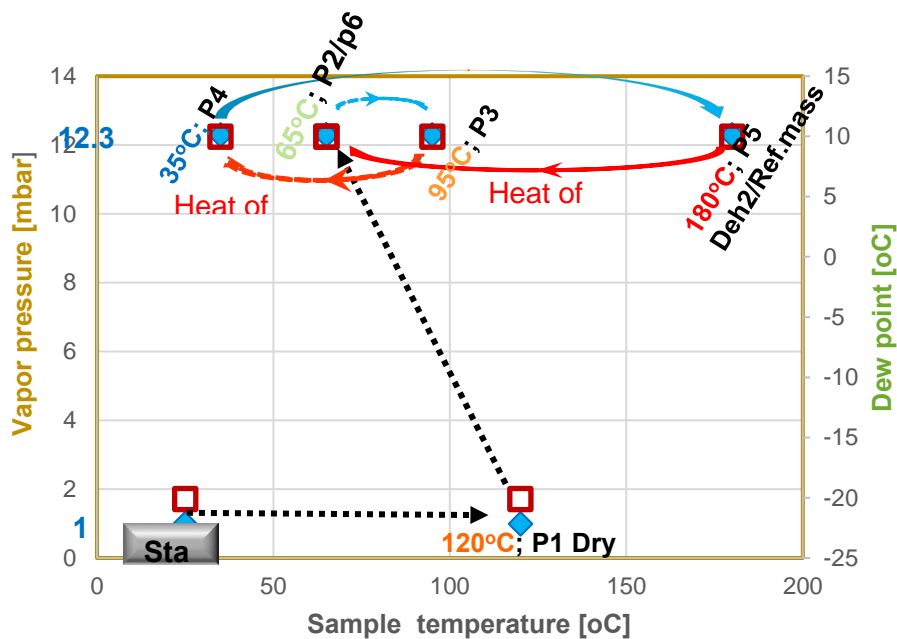
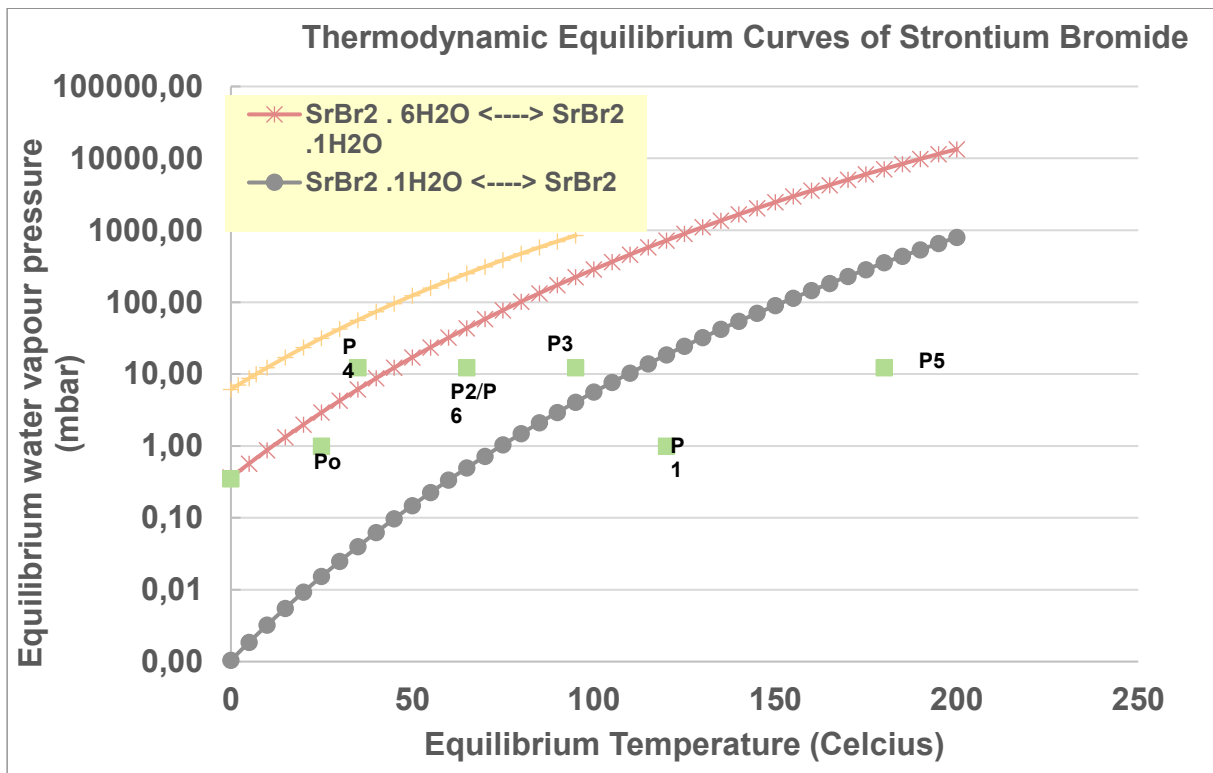


Figure 11: Scheme of the measurement procedure as plotted in the grid of sample temperature and vapor pressure/dew point; the red arrows indicate the transitions with measurement of the heat signal for the heat of hydration detection.



Definition of equilibrium state

Depending on the measurement setup, water uptake in the segment and kinetics, the time for reaching equilibrium varies severely from several hours to more than a day. An appropriate equilibrium is reached, when there is only balance-related noise left, without any significant tendency of the signal.

In a supplementary document a guideline for estimating equilibrium, or needed time to reach respectively, is delivered in advance of the Task meeting, to be discussed there.

Measuring the heat (of adsorption)

For the first iteration of the Round Robin, there will be two options, and the consistency of results and applied method for the future will be discussed in the Task/Annex meeting in Ljubljana.

Direct measurement with STA / TG-DSC:

According to the procedure so far, the heat (during adsorption) can be measured between Des1 and Ads1, and between Des2 and Ads2. The sensible heat of the adsorption material has to be subtracted (see Heat of Adsorption). This can be done either by performing and subtracting a blank measurement under inert gas atmosphere, or by post-processing of the data (when T-dependent $c_{p\ 13X}$ values are available).

Calculation from 13X characteristic curve:

The heat of adsorption can be calculated by models like Clausius-Clapeyron or Dubinin Potential Theory. If you report values for the heat, please indicate if they are measured, or calculated by applying a model, and which model was used.

Delivery of results (values, format, units)

For comparing the results, and to detect the reasons for deviations may appear, please follow the instructions for delivery of the data in the following. Please use the Results Report document, which will be sent out with the procedure.

- Sample mass (absolute) for all measurement points 1-6, (please subtract sample holder/crucible), Units [mg]
- Uptake between Ads1 / Des1 and Ads2 / Des2, related to dry mass detected in pretreatment (P1), Units [g/g]

$$\Delta X_1 = \frac{m_{Ads1/P4} - m_{Des1/P3}}{m_{dry/P1}}$$

$$\Delta X_2 = \frac{m_{Ads2/P6} - m_{Des2/P5}}{m_{dry/P1}}$$

- Uptake between Ads1 / Des1 and Ads2 / Des2, related to reference mass detected in Des2 (P5), Units [g/g]

$$\Delta X_1' = \frac{m_{Ads1/P4} - m_{Des1/P3}}{m_{Des2/P5}}$$

$$\Delta X_2' = \frac{m_{Ads2/P6} - m_{Des2/P5}}{m_{Des2/P5}}$$

- Heat of Adsorption (material) detected between Des1 and Ads1, as well as between Des2 and Ads2; Units [J/g_{Sorbent, dry}]

Calculation according to

$$H_{Ads1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_{p\ 13X} dT}{m_{dry/P1}}$$

$$H_{Ads2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_{p\ 13X} dT}{m_{dry/P1}}$$

(Please note: \dot{Q} as exothermal is negative)

- Heat of Adsorption (adsorbate) detected between Des1 and Ads1, as well as between Des2 and Ads2;
Units [J/g_{Adsorbate / water}]
Calculation according to

$$H'_{Ads1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_{p\ 13X} dT}{m_{dry/P1} * \Delta X_1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_{p\ 13X} dT}{m_{Ads1/P4} - m_{Des1/P3}}$$

$$H'_{Ads2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_{p\ 13X} dT}{m_{dry/P1} * \Delta X_2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_{p\ 13X} dT}{m_{Ads2/P6} - m_{Des2/P5}}$$

with ΔX_1 and ΔX_2 as defined above

If you report values for the heat, please indicate if they are measured, or calculated by applying a model, and which model was used.

Good luck with the measurements!

Questions / comments / improvement of the procedure, please send an e-mail to Markus.Fink@ait.ac.at

If you have performed the measurements and processed the data, please send it to the same mail address (using the Results_report sheet).

Results report of the Final SrBr₂ Round Robin

| | |
|------------------------|--|
| Lab: | |
| Operator: | |
| Measurement Apparatus: | |
| Measurement Mode: | <input type="checkbox"/> static (pure water vapor atmosphere) |
| | <input type="checkbox"/> dynamic (pure water vapor atmosphere) |
| | <input type="checkbox"/> dynamic with carrier gas: |
| Pretreatment: | <input type="checkbox"/> Vacuum with final pressure: |
| | <input type="checkbox"/> other: dynamic with N ₂ |
| Heat of Adsorption | <input type="checkbox"/> measured |
| | <input type="checkbox"/> calculated, applying model: |
| Period of Measurement: | |

Uncertainty of apparatus (datasheet values). Please choose the fields which are relevant for your apparatus.

| Temperature [°C] | Pressure [mbar] | Relative Humidity [%] | Saturation Temperature [°C] | Balance [mg] | Dry Mass Determination (external) [mg] |
|------------------|-----------------|-----------------------|-----------------------------|--------------|--|
| 0.1 | | | | | |

1. Sample mass (absolute) for all measurement points 1 to 6. Unit is mg.

| Point # | Symbol | Sample Temperature [°C] | Vapor Pressure [mbar] | Sample Mass [mg] | Uncertainty [mg] |
|---------|----------------|-------------------------|-----------------------|------------------|------------------|
| P 1 | $m_{dry/P1}$ | 120 | 1 | | |
| P 2 | $m_{Ads2'/P2}$ | 65 | 12.3 | | |
| P 3 | $m_{Des1/P3}$ | 95 | 12.3 | | |
| P 4 | $m_{Ads1/P4}$ | 35 | 12.3 | | |
| P 5 | $m_{Des2/P5}$ | 180 | 12.3 | | |
| P 6 | $m_{Ads2/P6}$ | 65 | 12.3 | | |

2. Uptake between Des1 / Ads1 and Des2 / Ads2. Unit is g/g.

| Description | Symbol | Uptake [g/g] | Uncertainty [g/g] |
|---|---------------|--------------|-------------------|
| Uptake between Des1 / Ads1 related to dry mass | ΔX_1 | | |
| Uptake between Des2 / Ads2 related to dry mass | ΔX_2 | | |
| Uptake between Des1 / Ads1 related to mass Des2 | $\Delta X_1'$ | | |
| Uptake between Des2 / Ads2 related to mass Des2 | $\Delta X_2'$ | | |

3. Heat of Adsorption between Des1 / Ads1 and Des2 / Ads2. Unit is J/g.

| Description | Symbol | Heat [J/g] | Uncertainty [J/g] |
|---|-------------|------------|-------------------|
| Heat of Adsorption (material specific) Des1 / Ads1 | H_{Ads1} | | |
| Heat of Adsorption (material specific) Des2 / Ads2 | H_{Ads2} | | |
| Heat of Adsorption (adsorbate specific) Des1 / Ads1 | H'_{Ads1} | | |
| Heat of Adsorption (adsorbate specific) Des2 / Ads2 | H'_{Ads2} | | |

APPENDIX C

Measurement Procedure for the 3rd Zeolite 13X Round Robin

IEA Task 58 / Annex 33 Subtask 3T

Goal of this document

By applying and following this procedure, reproducible and comparable measurement results of adsorbate uptake for thermochemical materials (TCM) will be produced, to predict the material performance under particular boundary conditions of an application.

Procedure for porous materials (e.g. zeolite)

The applied methods include gravimetric analyzers with vapor or humidity conditioning, optional with calorimetric extension (TG, TG-DSC, STA) [1]. The procedure consists of a pretreatment of the sample, and several ad- and desorption points, while all of them have to reach equilibrium state.

Definition of the Scenarios

As performed in the previous round robin, two scenarios will be applied, which are derived from boundary conditions in typical applications, and are in good agreement with the temperatures for domestic heating and cooling sent in a document (Temperatures_Buildings) by Benjamin Fumey.

Pretreatment / Dry Mass Detection

A standardized pretreatment is necessary for comparable uptake calculations, as the dry mass will serve as one of the reference masses. Please follow the procedure according to reference [2]. It must be performed under continuous evacuation (vacuum level: $< 1e-3$ mbar).

The optimal sample pretreatment temperature T_{max} should be selected according to the following classification.

•Strongly hydrophilic zeolites (4A, 13X): pre-treatment $T = 350^{\circ}C$.

The sample is heated starting from ambient conditions with a heating rate of 1K/min followed by an isothermal drying step for another 8 hours (Figure 1).

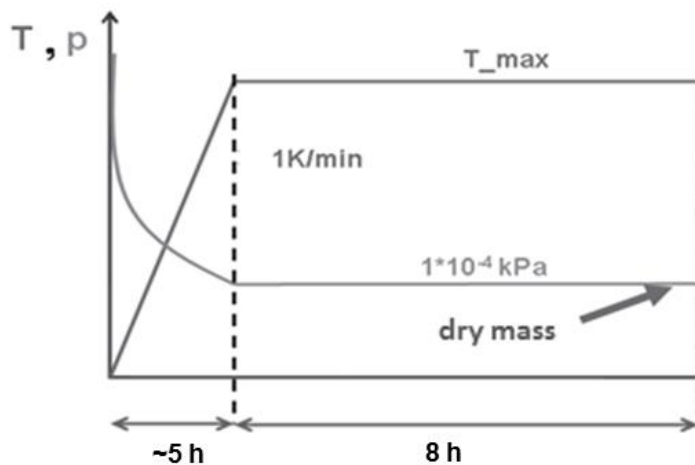


Figure 12: Proposed pretreatment procedure

Comment to Round-Robin participants of IEA/Annex 58/33: For the case that the measurement setup is not capable of applying vacuum, please indicate this together with the measurement results. To overcome deviations caused by differing partial pressures during pretreatment, an additional reference point will be introduced (see chapter Desorption 2 (P5)).

Measurement of equilibrium points

In the following steps, two ad- and desorption points are carried out, all with a dew point of 10 °C, which corresponds to water vapor pressure of 12.3 mbar, and sample temperatures of 35, 65, 95 and 180 °C (see Figure 2). These points are motivated by applications addressed with TCM's, and take care of the chosen reference sample for the round robin test (13X). For all heating phases, a heating rate of 1K/min is defined.

Table 6: Temperatures and vapor pressure/dew point, according to scenario 1 (Des1, Ads1) and 2 (Des2, Ads2)

| Point # | Label | Sample Temperature [°C] | Vapor pressure [mbar] | Corresp. Dew point [°C] |
|---------|-------------------------|-------------------------|-----------------------|-------------------------|
| P 1 | Pretreatment / Dry mass | 350 | < 1 e-3 | < -150 |
| P 2 | Adsorption 2' | 65 | 12.3 | 10 |
| P 3 | Desorption 1 | 95 | 12.3 | 10 |
| P 4 | Adsorption 1 | 35 | 12.3 | 10 |
| P 5 | Desorption 2 | 180 | 12.3 | 10 |
| P 6 | Adsorption 2 | 65 | 12.3 | 10 |

The procedure is defined step-by-step:

Pretreatment (P 1):

Dry mass detection; please choose as 350 °C, and vacuum level < 1e-3 mbar, heating rate as 1 K/min, constant temperature and pressure level for at least 8 h.

The mass detected during pretreatment is the dry mass $m_{dry/P1}$ serving as one of the reference masses for uptake calculations.

Adsorption 2' (P 2):

Sample Temperature of 65 °C, dew point of 10 °C corresponding to 12.3 mbar; this adsorption point serves as intermediate step, so that the following desorption can be approached in desorption direction, and the two following pairs can measure the heat in adsorption mode; the mass detected is labelled as $m_{Ads2'/P2}$ and can be used for reproducibility check.

Desorption 1 (P 3):

Sample Temperature of 95 °C (heating rate 1K/min), dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Des1/P3}$;

Adsorption 1 (P 4):

Sample Temperature of 35 °C, dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Ads1/P4}$;

Desorption 2 (P 5):

Sample Temperature of 180 °C (heating rate 1K/min), dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Des2/P5}$;In addition to the dry mass detected during pretreatment, the mass detected at Desorption 2 $m_{Des2/P5}$ will serve as a second reference mass for uptake calculations.

Adsorption 2 (P 6):

Sample Temperature of 65 °C, dew point of 10 °C corresponding to 12.3 mbar; the mass detected is labelled as $m_{Ads2/P6}$;

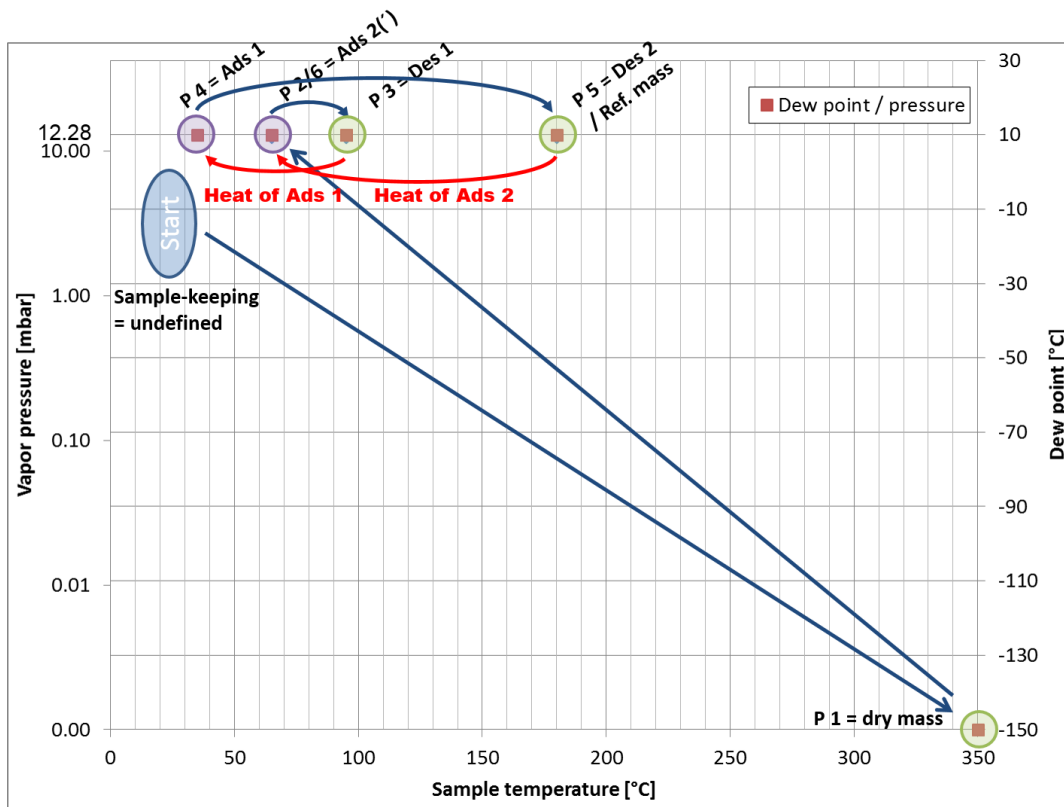


Figure 13: Scheme of the measurement procedure as plotted in the grid of sample temperature and vapor pressure/dew point; the red arrows indicate the transitions with measurement of the heat signal for the heat of adsorption detection.

Definition of equilibrium state

Depending on the measurement setup, water uptake in the segment and kinetics, the time for reaching equilibrium varies severely from several hours to more than a day. An appropriate equilibrium is reached, when there is only balance-related noise left, without any significant tendency of the signal.

A guideline for estimating equilibrium is in progress.

Measuring the heat (of adsorption)

For this Round Robin, there will be two options, and the consistency of results and applied method for the future will be discussed in the next Task/Annex meeting.

Direct measurement with STA / TG-DSC:

According to the procedure so far, the heat (during adsorption) can be measured between Des1 and Ads1, and between Des2 and Ads2. The sensible heat of the adsorption material has to be subtracted (see chapter Heat of Adsorption). This can be done either by performing and subtracting a blank measurement under inert gas atmosphere, or by post-processing of the data (when T-dependent $c_{p, 13X}$ values are available).

Calculation from 13X characteristic curve:

The heat of adsorption can be calculated by models like Clausius-Clapeyron or Dubinin Potential Theory.

If you report values for the heat, please indicate if they are measured or calculated by applying a model and which model was used.

Delivery of results (values, format, units)

For comparing the results and for detecting the reasons for deviations, please follow the instructions for delivery of the data in the following. It is proposed to repeat the measurements to ensure repeatable results. Please use the Results Report Sheet which will be sent out with the procedure and use a separate sheet for each measurement run. Please state the uncertainty of each measured value. For the analyzation of the results it would also be interesting to indicate the uncertainties of the used apparatus. For this purpose, an additional table is included in the Result Report Sheet. Please choose the fields in the table which are relevant for your apparatus. If the pretreatment of your sample is conducted externally, you can indicate the uncertainty of the external balance in the field "Dry mass determination".

In the following, you find further information for doing the data analysis:

- Sample mass (absolute) for all measurement points 1-6, (please subtract sample holder/crucible), Units [mg]
- Uptake between Ads1 / Des1 and Ads2 / Des2, related to dry mass detected in pretreatment (P1), Units [g/g]

$$\Delta X_1 = \frac{m_{Ads1/P4} - m_{Des1/P3}}{m_{dry/P1}}$$

$$\Delta X_2 = \frac{m_{Ads2/P6} - m_{Des2/P5}}{m_{dry/P1}}$$

- Uptake between Ads1 / Des1 and Ads2 / Des2, related to reference mass detected in Des2 (P5), Units [g/g]

$$\Delta X_{1'} = \frac{m_{Ads1/P4} - m_{Des1/P3}}{m_{Des2/P5}}$$

$$\Delta X_{2'} = \frac{m_{Ads2/P6} - m_{Des2/P5}}{m_{Des2/P5}}$$

- Heat of Adsorption (material) detected between Des1 and Ads1, as well as between Des2 and Ads2; Units [J/g_{Sorbent, dry}]
Calculation according to

$$H_{Ads1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_p 13X dT}{m_{dry/P1}}$$

$$H_{Ads2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_p 13X dT}{m_{dry/P1}}$$

(Please note: \dot{Q} as exothermal is negative)

- Heat of Adsorption (adsorbate) detected between Des1 and Ads1, as well as between Des2 and Ads2; Units [J/g_{Adsorbate / water}]
Calculation according to

$$H'_{Ads1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_p 13X dT}{m_{dry/P1} * \Delta X_1} = \frac{\int_{Des1}^{Ads1} \dot{Q} dt - \int_{T_{Des1}}^{T_{Ads1}} c_p 13X dT}{m_{Ads1/P4} - m_{Des1/P3}}$$

$$H'_{Ads2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_p 13X dT}{m_{dry/P1} * \Delta X_2} = \frac{\int_{Des2}^{Ads2} \dot{Q} dt - \int_{T_{Des2}}^{T_{Ads2}} c_p 13X dT}{m_{Ads2/P6} - m_{Des2/P5}}$$

with ΔX_1 and ΔX_2 as defined above

Good luck with the measurements! Questions / comments / improvement of the procedure, please send an email to fabian.fischer@zae-bayern.de

When you have performed the measurements and processed the data, please send it to the same email address (using the Results Report Sheet)

Literature

- 1 *Henninger SK, Schmidt FP, Henning H-M.* Water adsorption characteristics of novel materials for heat transformation applications. *Applied Thermal Engineering* 2010; 30 (13): 1692–1702
- 2 *Henninger SK, Freni A, Schnabel L et al.* Unified water adsorption measurements procedure for sorption materials. In: *Proceedings ISHPC 2011*: 513–522

APPENDIX D: Results report of the 3rd Zeolite 13X Round Robin

| | |
|------------------------|---|
| Lab: | |
| Operator: | |
| Measurement Apparatus: | |
| Measurement Mode: | <input type="checkbox"/> static (pure water vapor atmosphere) <input type="checkbox"/> dynamic (pure water vapor atmosphere) <input type="checkbox"/> dynamic with carrier gas: |
| Pretreatment: | <input type="checkbox"/> Vacuum with final pressure: <input type="checkbox"/> other: |
| Heat of Adsorption | <input type="checkbox"/> measured <input type="checkbox"/> calculated, applying model: |
| Period of Measurement: | |

Uncertainty of apparatus (datasheet values). Please choose the fields which are relevant for your apparatus.

| Temperature [°C] | Pressure [mbar] | Relative Humidity [%] | Saturation Temperature [°C] | Balance [mg] | Dry Mass Determination (external) [mg] |
|------------------|-----------------|-----------------------|-----------------------------|--------------|--|
| | | | | | |

1. Sample mass (absolute) for all measurement points 1 to 6. Unit is mg.

| Point # | Symbol | Sample Temperature [°C] | Vapor Pressure [mbar] | Sample Mass [mg] | Uncertainty [mg] |
|---------|----------------|-------------------------|-----------------------|------------------|------------------|
| P 1 | $m_{dry/P1}$ | 350 | < 1 e-3 | | |
| P 2 | $m_{Ads2'/P2}$ | 65 | 12.3 | | |
| P 3 | $m_{Des1/P3}$ | 95 | 12.3 | | |
| P 4 | $m_{Ads1/P4}$ | 35 | 12.3 | | |
| P 5 | $m_{Des2/P5}$ | 180 | 12.3 | | |
| P 6 | $m_{Ads2/P6}$ | 65 | 12.3 | | |

2. Uptake between Des1 / Ads1 and Des2 / Ads2. Unit is g/g.

| Description | Symbol | Uptake [g/g] | Uncertainty [g/g] |
|---|---------------|--------------|-------------------|
| Uptake between Des1 / Ads1 related to dry mass | ΔX_1 | | |
| Uptake between Des2 / Ads2 related to dry mass | ΔX_2 | | |
| Uptake between Des1 / Ads1 related to mass Des2 | $\Delta X_1'$ | | |
| Uptake between Des2 / Ads2 related to mass Des2 | $\Delta X_2'$ | | |

3. Heat of Adsorption between Des1 / Ads1 and Des2 / Ads2. Unit is J/g.

| Description | Symbol | Heat [J/g] | Uncertainty [J/g] |
|---|-------------|------------|-------------------|
| Heat of Adsorption (material specific) Des1 / Ads1 | H_{Ads1} | | |
| Heat of Adsorption (material specific) Des2 / Ads2 | H_{Ads2} | | |
| Heat of Adsorption (adsorbate specific) Des1 / Ads1 | H'_{Ads1} | | |
| Heat of Adsorption (adsorbate specific) Des2 / Ads2 | H'_{Ads2} | | |

APPENDIX E: Measurement protocol for the evaluation of specific heat capacity $c_p(T)$ of $\text{SrBr}_2 \cdot n\text{H}_2\text{O}$ and SrBr_2 based on heat flow differential scanning calorimetry

$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ is a promising thermochemical energy storage material which was already analysed in the IEA TASK 55 / ECES Annex 33 to determine the phase change and reaction enthalpies based on calorimetric and thermogravimetric measurements. Nevertheless, also the sensible heat or specific heat capacity $c_p(T)$ of the salt hydrates $\text{SrBr}_2 \cdot n\text{H}_2\text{O}$ and the pure SrBr_2 salt is needed to describe the enthalpy change for further applications. This document describes a measurement procedure based on a heat flow Differential Scanning Calorimeter (hf-DSC) to evaluate these material properties. The general information in this document are from the dissertation "*Evaluation of thermophysical properties for thermal energy storage materials - determining factors, prospects and limitations*" [1]. For more detailed information the reader is referred to this document.

Differential Scanning Calorimetry - DSC

Measurement principle

According [2] the following definition applies for DSC: "*Differential Scanning Calorimetry means the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program*". There are two different basic types of DSC, the heat flux and the power compensated DSC. In this work, the heat flux DSC with disk type sensor is described, which was also used for the further experiments. If the reader is interested on other calorimetry instrumentations please refer to [2,3].

Calibration

In case of DSC calibration, this would mean that measurement standards or certified reference materials are needed for the measured quantities temperature T , heat Q and heat flow Φ . In the standard document [4] several points are listed, which are influencing the calibration result. Some of these points are:

- heating and cooling rates
- type and size of the used crucibles
- position of the sample in the sample crucible
- mass and size of the sample
- thermal contact between crucible and sensor

Temperature calibration

Temperature calibration in the heating segment of a DSC is done by melting calibration substances in a crucible on the sample side of the DSC sensor. As recommended by [2] at least 3 fixed points of the calibration materials defined in the International Temperature Scale of 1990 (ITS-90) [5] should be used to calibrate temperature in the desired temperature range.

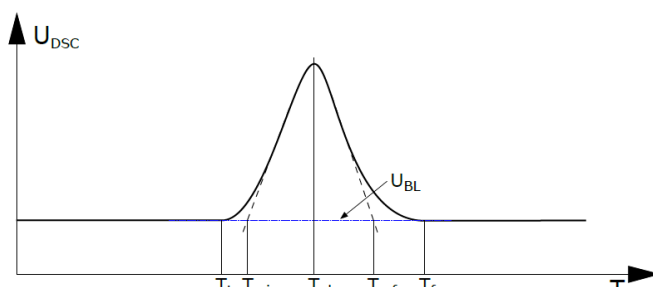


Figure 14: DSC Voltage U_{DSC} versus T during a transition with the characteristic temperatures

Since a DSC experiment is no static method, a phase transition measurement results in a peak. The shape of the measured peak is changing with different system setup, measurement or sample parameters. For temperature calibrations, the extrapolated initial temperature $T_{e,i}$ is used to compare the measured temperature to the fixed temperature point of the calibration standard.

Heat flow calibration

A heat flow calibration identifies the relation between the measured voltage U_{DSC} and the true heat flow Φ by measuring a reference material with known specific heat capacity $c_p(T)$ as shown in the following equation.

$$S_{DSC}(T) = \frac{U_{Ref}(T) - U_0(T)}{m_{Ref} c_{p,Ref}(T) \beta}$$

To do a heat flow calibration at least two measurement runs are necessary:

1. a zero-line measurement U_0 with empty crucibles to eliminate system related influences (e.g. asymmetric sensor, different crucible masses)
2. a standard reference measurement with a known $c_p(T)$ in the temperature range of interest

In case of the heat flow calibration, the sensitivity $S_{DSC}(T)$ is valid for the measured temperature range in the temperature resolution of $c_p(T)$ of the standard reference material.

Specific heat capacity measurements

According to [6,7] $C_p(T)$ is the amount of heat required to raise the temperature of a substance by 1 K at constant pressure without a first-order phase transition. To evaluate $c_p(T)$ from an already calibrated and zero-line corrected heat flow Φ of a DSC, the mass m and the heating rate β are needed as shown in the following equation

$$c_p(T) = \frac{C_p(T)}{m} = \frac{\phi(T)}{m \beta}$$

As described by [2], $c_p(T)$ is only valid in the absence of transitions or reactions (peaks) and it describes the amount of heat needed, to raise the temperature of a substance. According to the German Institute for Standardization (DIN) 51007 standard [6], at least three measurement runs are needed to evaluate $c_p(T)$ of a substance:

- a zero-line measurement with empty crucibles,
- a standard reference measurement (e.g. α -Al₂O₃ Sapphire standard)
- and a sample measurement.

The temperature program starts with an isothermal segment followed by a dynamic heating segment and ends again with an isothermal segment at the maximum temperature. The recommended heating rate is $\beta = 10 \text{ K min}^{-1}$.

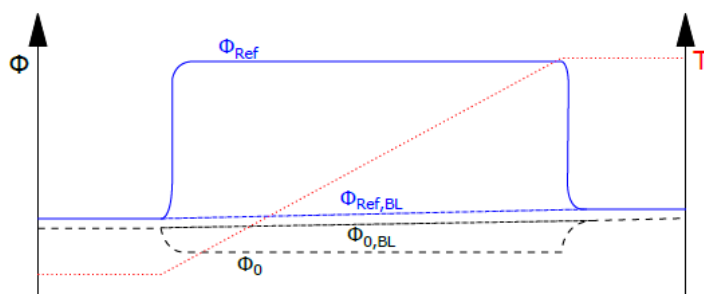


Figure 15: DSC signals for Φ_{Ref} and Φ_0 to evaluate the calibration factor $K(T)$ for $c_p(T)$ measurements

A dimensionless calibration factor $K(T)$, as shown in the following equations is used to calibrate the heat flow and to subtract a baseline construction between the isothermal segments of $\Phi_0(T)$ and $\Phi_{Ref}(T)$. This baseline construction allows a correction if there is an offset of the heat flow Φ between the isothermal segments.

$$K(T) = \frac{C_{p,Ref}(T) \beta}{[\phi_{Ref}(T) - \phi_{Ref,BL}(T)] - [\phi_0(T) - \phi_{0,BL}(T)]}$$

$$c_{p,S}(T) = \frac{K(T) [\phi_S(T) - \phi_0(T)]}{\beta m_S}$$

In the standard DIN European Standard (EN) International Organization for Standardization (ISO) 11357-4 [7] another procedure for the evaluation of $c_p(T)$ is mentioned as shown in the following equations. As described before, again three measurements are needed to evaluate $c_{p,S}(T)$.

$$c_{p,S}(T) = c_{p,Ref}(T) \frac{m_{Ref}}{m_S} \frac{\phi_S(T) - \phi_0(T)}{\phi_{Ref}(T) - \phi_0(T)}$$

$$c_{p,S}(T) = c_{p,Ref}(T) \frac{m_{Ref}}{m_S} \frac{U_S(T) - U_0(T)}{U_{Ref}(T) - U_0(T)}$$

The main difference between these two standards is that in DIN EN ISO 11357-4 no additional baseline construction between the isothermal segments is needed. Additionally, a starting temperature 30 K below the first evaluated $c_{p,S}(T)$ is recommended. This is due to the time needed to reach a constant heating rate starting from an isothermal segment.

Measurement procedure

Temperatures:

Thermogravimetric results of the $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ at dry nitrogen gas flow have shown, that dehydration and mass loss already occur at temperatures $T > 25^\circ\text{C}$. Furthermore, the reaction shows a strong dependency on the heating rate as shown in **Error! Reference source not found.**

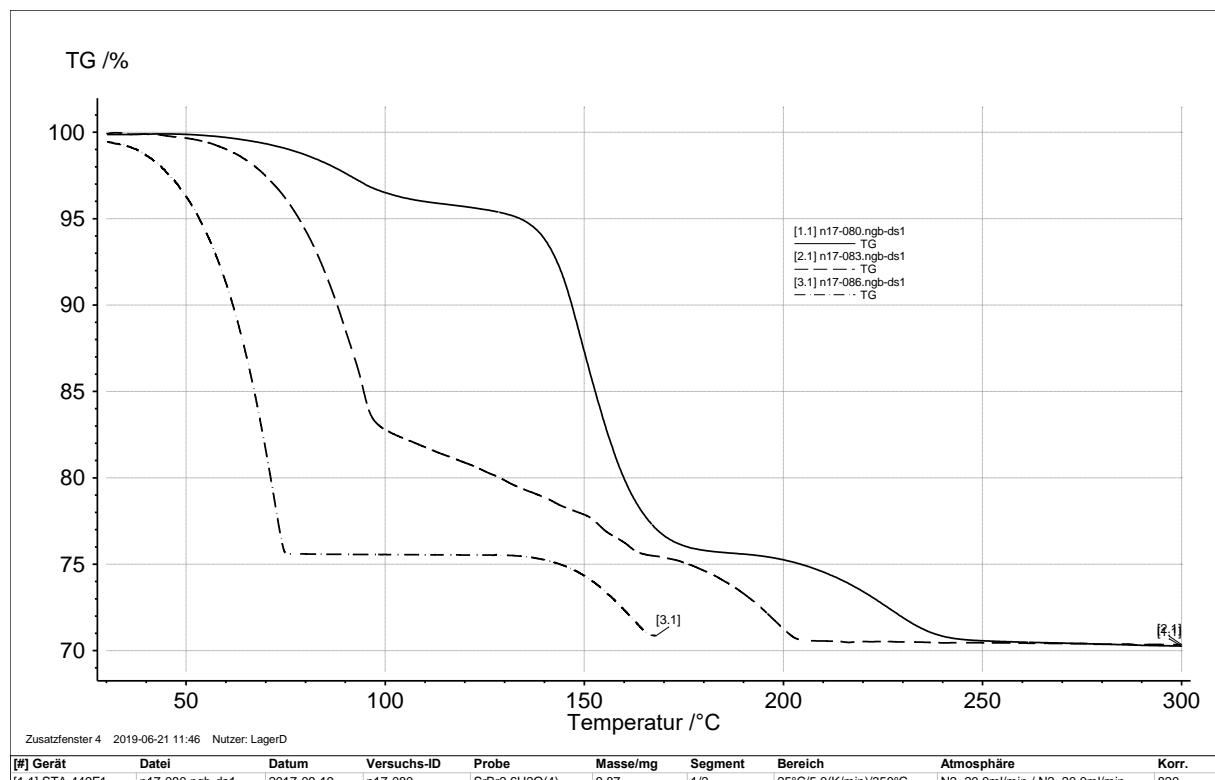


Figure 16: Thermogravimetric results at $\beta = 0.2, 1$ and 5 K min^{-1} of $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ up to $T = 300^\circ\text{C}$

Based on the DSC measurements with a dry N₂ gas flow following temperature boundaries were defined:

- For the evaluation of $c_p(T)$ at $T = 25\text{ °C}$ of SrBr₂·6H₂O it is necessary to start the experiments at least at -5 °C as recommended by ISO 11357-4. Furthermore, at dry N₂ gas flow SrBr₂·6H₂O dehydration starts already at $T = 25\text{ °C}$ that would not allow to evaluate $c_p(T)$ beyond this temperature.
- To evaluate the specific heat capacity of the first product (apparently the SrBr₂·1H₂O) in a bigger temperature interval, the max. temperature is limited with $T \approx 125\text{ °C}$ due to the next dehydration step to the pure SrBr₂ salt at dry N₂ gas flow conditions.
- Due to that, a minimum temperature range of $T = -5\text{ to }200\text{ °C}$ is needed to measure at least one measurement point for SrBr₂·6H₂O and several for SrBr₂·1H₂O and the pure SrBr₂.

Due to the dehydration reaction depending on the actual gas conditions it is recommended to prepare the sample in the wished hydrated form (SrBr₂·6H₂O; SrBr₂·1H₂O and SrBr₂) and hermetically seal them in the used crucible system before the DSC measurement runs.

Calibration

- Calibrate the temperature. Possible calibration substances are:
 - Hg; H₂O; Ga; In; Sn; Zn
 -

Specific heat capacity measurements

Due to the simplicity of the ISO 11357-4 in comparison to the DIN 51007 (no baseline construction, no heat flow calibration needed), the following procedure is based on this standard.

Samples and crucibles

- The crucibles for all measurements should not differ more than $\Delta m = 0,1\text{ mg}$
- Due to the high thermal conductivity, aluminium crucibles are recommended
- Prepare the wished hydrated form of the salt sample by applying a suitable method, e.g.
 - **Expose & wait:** Expose the sample in the open crucible to controlled conditions (temperature and vapour pressure) where the wished hydration level is the stable form and wait for equilibrium to settle. This can be done e.g. in a TG or a desiccator. Caution, for some hydration reactions, like SrBr₂·H₂O → SrBr₂·6H₂O, this might take very long time (weeks). Larger distance (in terms of pressure and/or temperature) to the equilibrium lines usually speeds up the process. It is also possible that the reaction speed depends on the direction, e.g. reaching SrBr₂·6H₂O by dehydrating oversaturated SrBr₂·6H₂O (mixture of sat. solution and SrBr₂·6H₂O) might be faster than by hydrating SrBr₂·H₂O.
 - **Dry, fill up & cure:** Determine the sample anhydrous mass by heating the open crucible under controlled humidity (e.g. 180 °C, 10 mbar) for several hours while controlling the weight (TG/heating station). From the anhydrous mass calculate the amount of SrBr₂ and from there the mass of the wished hydrate (target mass). Add DI water into the crucible until reaching the target mass e.g. using a micro pipette. Caution: Some of the required water will be taken from humid ambient air by spontaneous hydration/deliquescence; only fill up to target mass. Eventually (after sealing) the wished hydrate will form as the most stable phase. This curing process can be slow and might be faster at higher temperatures. Complete curing has occurred if c_p -measurement results are reproducible over several cycles.
- Seal the crucible hermetically quickly right after preparing the sample to the required hydration level/stoichiometry and check by weighing afterwards. Avoid hydration/dehydration from ambient while sealing as much as possible.
- As reference material, use an α -Al₂O₃ (synthetic sapphire) with a purity degree of 99,9 % or higher

- Choose the sample mass according your crucible volume and specific heat of your reference
- ($C_{p;Ref} \approx C_{p;S}$)
 - Check the mass before and after the measurement run, discard measurements if mass changes significantly

Temperature program

- The temperature program is depending on the used DSC furnace and cooling system. The minimum temperature can be chosen according the DSC system possibilities. The first evaluated c_p value should be 30 °C higher than the starting temperature.
- The heating rate β is depending on the sensitivity of the DSC sensor. A recommended $\beta = 10 \text{ K min}^{-1}$.
- The minimum temperatur T_{min} can be chosen depending on your cooling possibilities.
- The maximum temperatures are defined with:
 - 100 °C for $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$
 - 200 °C for $\text{SrBr}_2 \cdot 1\text{H}_2\text{O}$
 - 200 °C for SrBr_2
- Run the program subsequent for several (e.g. four) times and compare c_p by cycle and phase (heating/cooling) to check sample stability/complete sample preparation

Gas conditions

A dynamic, dry inert gas flow is recommended (e.g. 20 ml/min N_2) to fulfil reproducible gas conditions over all measurements.

Reproducibility and uncertainty evaluation

Several measurements are needed to evaluate an uncertainty of the $c_p(T)$ evaluation. Please refer to the “Guide to the Expression of Uncertainty in Measurement (GUM)” to express your uncertainty of the $c_p(T)$ results. The document is free available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.

Results

Material: (e.g. $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 1\text{H}_2\text{O}$ or SrBr_2)

DSC System: Manufacturer, Model and Type (e.g. NETZSCH, DSC 404C, hf-DSC)

Crucible: material, shape, dimensions, lid (e.g. Al, cylindric, $d = 6 \text{ mm}$; $h = 2 \text{ mm}$; cold welded)

Gas conditions: (e.g. N_2 ; 50 ml/min)

Calibration substances: Type and mass (e.g. Sapphire, $m = 60 \text{ mg}$)

Number and mass of samples before and after measurement: (e.g. 3 Samples, $m_1 = 10,2 \text{ mg}$, $m_2 = 10,3 \text{ mg}$, $m_3 = 10,1 \text{ mg}$)

Temperature program: (e.g. $T_{\text{start}} = 25 \text{ }^\circ\text{C}$; $T_{\text{end}} = 300 \text{ }^\circ\text{C}$; $\beta = 10 \text{ K/min}$)

Please use following table as representation of your $c_p(T)$ evaluation:

| $T / ^\circ\text{C}$ | $c_p(T) / \text{J g}^{-1} \text{K}^{-1}$ | $u_{c_p(T)} / \text{J g}^{-1} \text{K}^{-1}$ |
|----------------------|--|--|
| 25 | | |
| 30 | | |
| 35 | | |
| ... | | |

A temperature step of $5 \text{ }^\circ\text{C}$ is sufficient for the result table. Please use the unit $\text{J g}^{-1} \text{K}^{-1}$ for the evaluated mean of the specific heat data $c_p(T)$ out of at least three measurements. The uncertainty $u_{c_p(T)}$ can be expressed as defined in the GUM.

Symbols and subscripts

| Symbol | Description | Unit | Subscript | Description |
|-----------|--|---------------------------------|-----------|-----------------------------------|
| T | Temperature | $^\circ\text{C}$ | e | Extrapolated |
| c_p | Spec. heat capacity at constant pressure | $\text{J g}^{-1} \text{K}^{-1}$ | i | Initial |
| U | Voltage | V | f | Final |
| C_p | Heat capacity at constant pressure | J K^{-1} | DSC | Differential Scanning Calorimetry |
| Φ | Heat flow rate | W | Ref | Reference |
| u_{c_p} | Uncertainty of c_p | $\text{J g}^{-1} \text{K}^{-1}$ | S | Sample |
| m | mass | kg | 0 | Zero-line |
| β | Heating rate | K s^{-1} | BL | Baseline |
| S | Sensitivity | V W^{-1} | | |

References

- [1] Lager D. Evaluation of thermophysical properties for thermal energy storage materials - determining factors, prospects and limitations. Dissertation. Wien; 2017.
- [2] Höhne GWH, Hemminger WF, Flammersheim H-J. Differential Scanning Calorimetry. Berlin, Heidelberg: Springer Berlin Heidelberg; 2003.
- [3] Sarge SM, Höhne GWH, Hemminger W. Calorimetry: Fundamentals, instrumentation and applications. Weinheim, Germany: Wiley-VCH Verlag; 2014.

- [4] International Organization for Standardization. Plastics -- Differential scanning calorimetry (DSC) - Part 1: General principles;83.080.01; 2016; Available from: <https://www.iso.org/standard/70024.html>.
- [5] Blanke W (ed.). Die internationale Temperaturskala von 1990: (ITS-90). Braunschweig: Physikal.-Techn. Bundesanst; 1989.
- [6] DIN 51007:2019-04, Thermische Analyse_(TA)_- Differenz-Thermoanalyse_(DTA) und Dynamische Differenzkalorimetrie_(DSC)_- Allgemeine Grundlagen. Berlin: Beuth Verlag GmbH. doi:10.31030/3025544.
- [7] International Organization for Standardization. Plastics – Differential scanning calorimetry (DSC) – Part 4: Determination of specific heat capacity (ISO 11357-4:2014);;83.080.01; 2014; Available from: <https://www.iso.org/standard/65087.html>.