INSTITUT FÜR ENERGIETECHNIK UND THERMODYNAMIK
Institute for Energy Systems and Thermodynamics

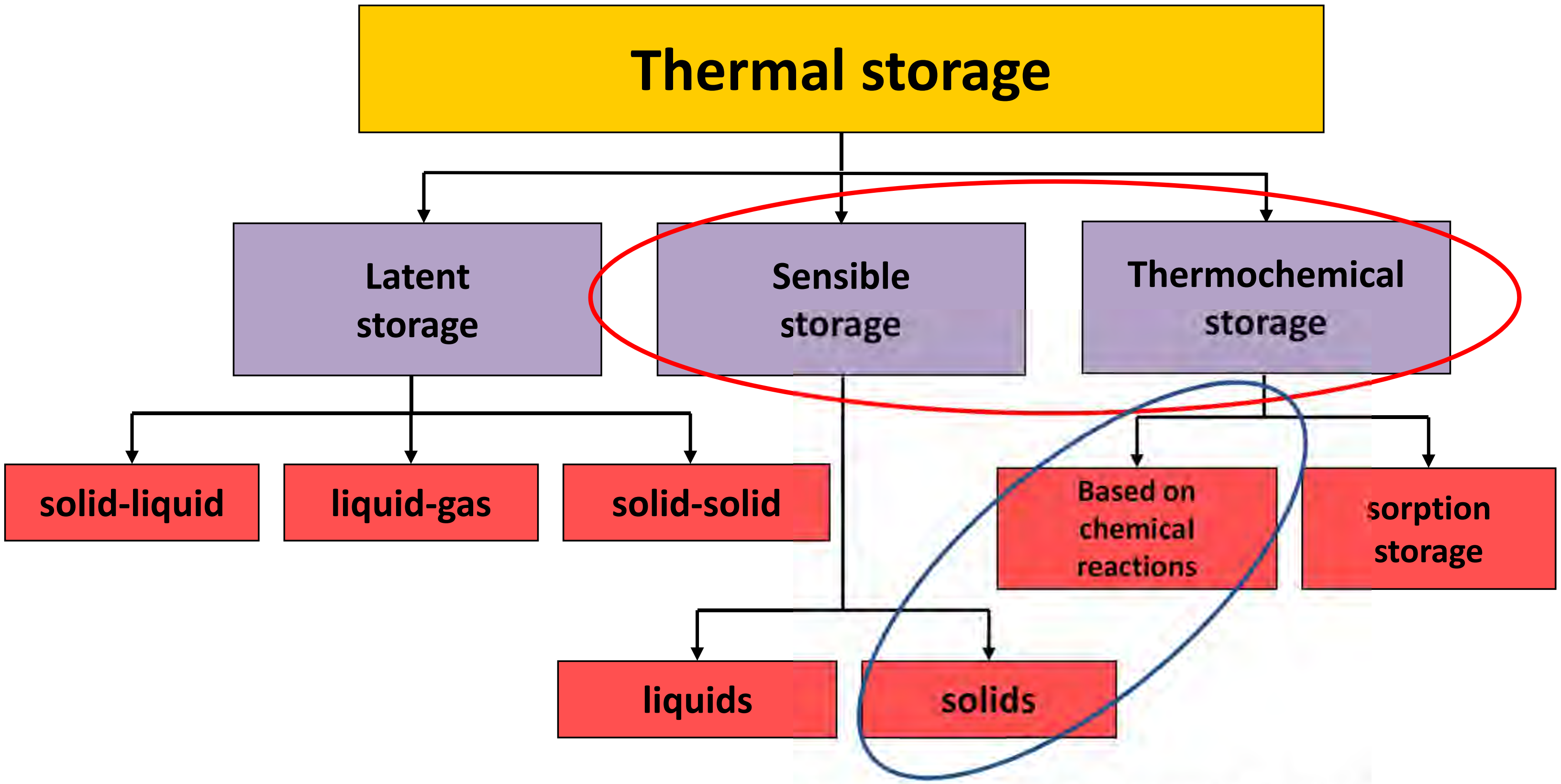
HANNOVER MESSE
1.– 5. April
2019

Compact high performance heat storage

High efficient use of waste heat from industry and power plants
from 150° to 850°C

Heimo WALTER and Andreas WERNER

Thermal energy storage
Which possibilities are available?



Solid-solid: heat energy will be stored at the transformation from one crystal structure to another.

Sensible energy storage

2 developed technologies

- **"SandTES" heat exchanger technology**
- **"Fluidization based particle -TES" heat exchanger technology**

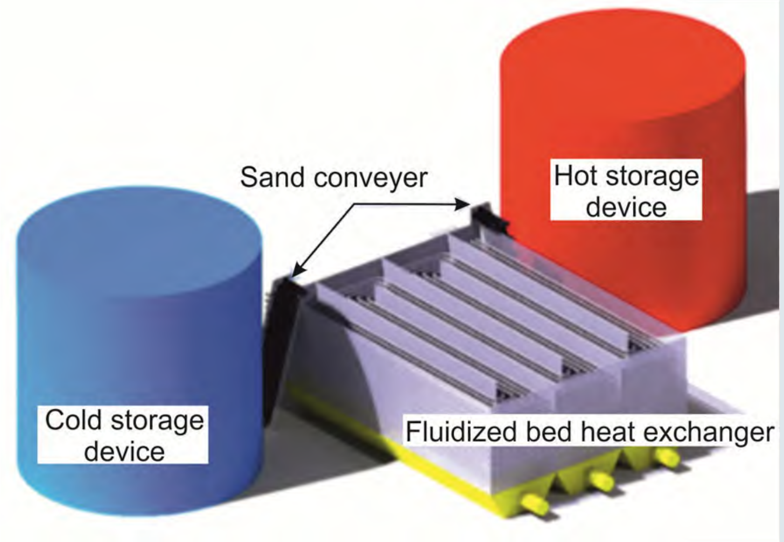
SandTES – heat exchanger technology

SandTES – heat exchanger technology

- **Storage of high temperature thermal energy with natural occurring material powder**
  - **low investment cost,**
  - **material sufficient available,**
  - **harmless handling possible,**
  - **operation under ambient pressure**
  - **good scalability**

SandTES – heat exchanger technology

- **Storage of high temperature thermal energy with powder [50-100 µm]**
  - Sand, corundum, ash, bauxite, magnesium oxide, …
- **Aktive storage technology**
  - Primary heat transfer medium & storage medium will be transported
  - Stationary operation, high thermal efficiency
- **SandTES – fluidized bed heat exchanger**
  - Tube bundle in a stationary fluidized bed
  - Counter current heat exchanger design
  - Natural- or once through power plants, industrial processes
- **Decoupling of storage capacity from heat capacity**



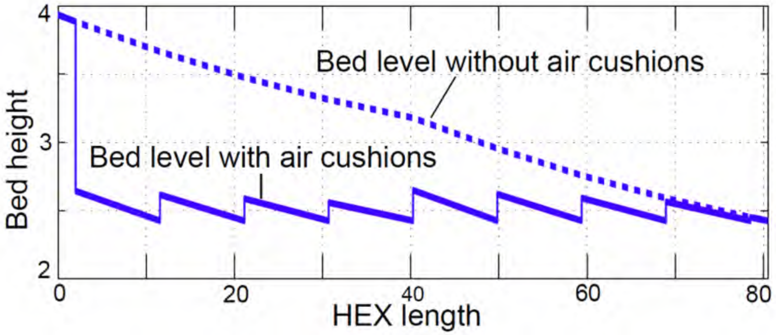
SandTES – heat exchanger technology

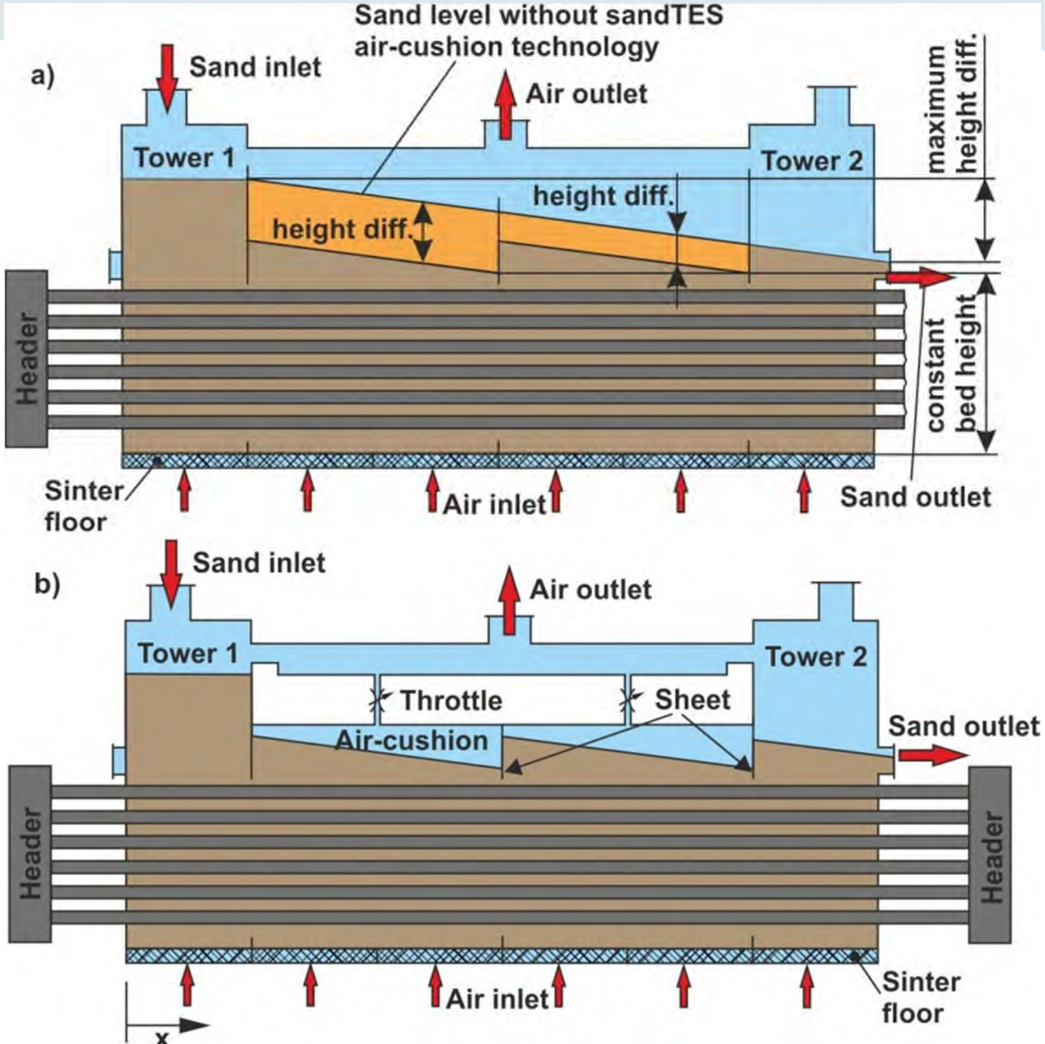
sandTES air-cushion principle

horizontal pressure gradient of viscous sand suspension:

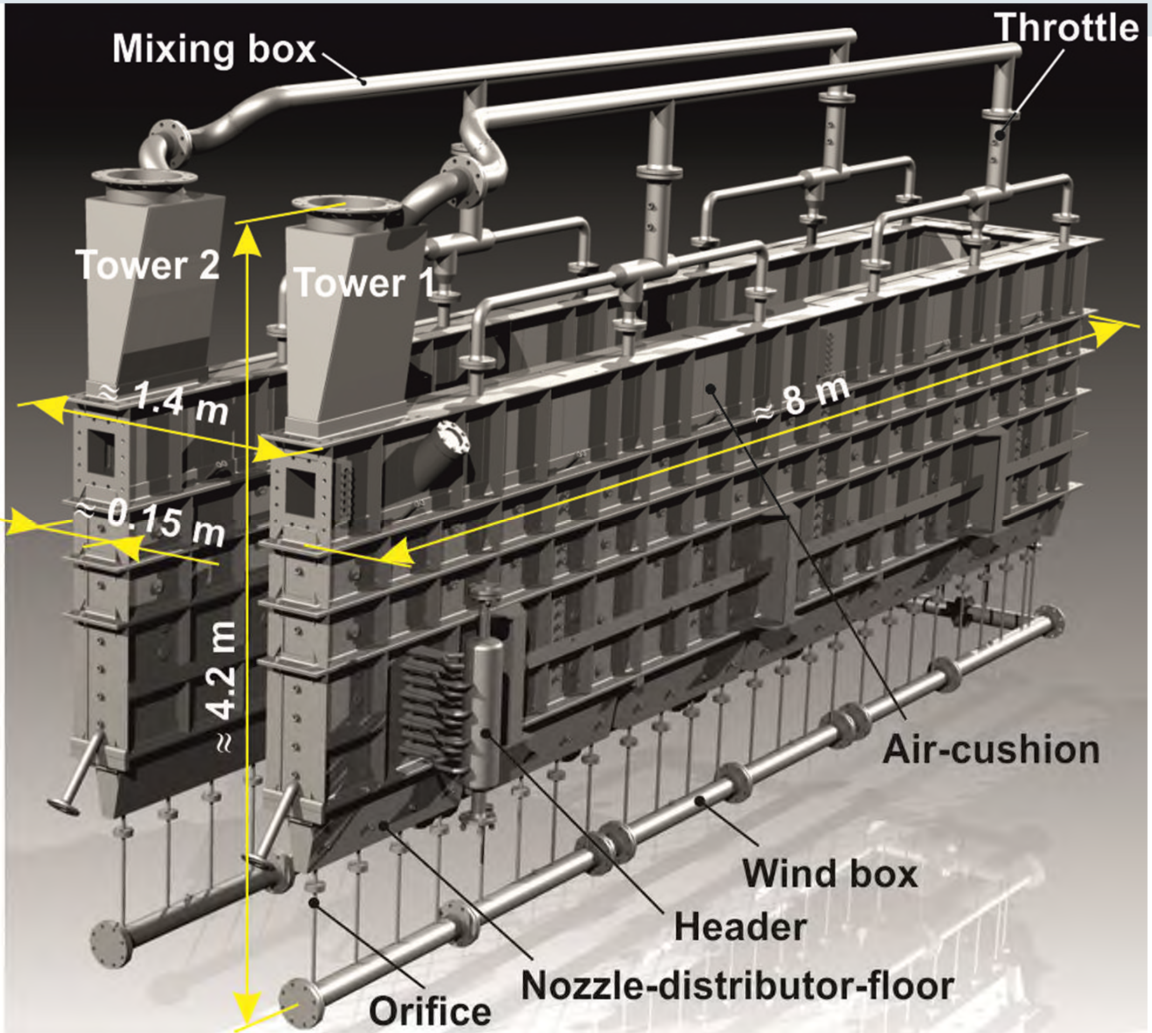
$$\frac{\partial p_{fb}}{\partial x} = \underbrace{(1-\varepsilon)}_{\text{porosity}} \underbrace{(\rho_p - \rho_f) g \frac{\partial h(x)}{\partial x}}_{\text{bouyancy force}}$$

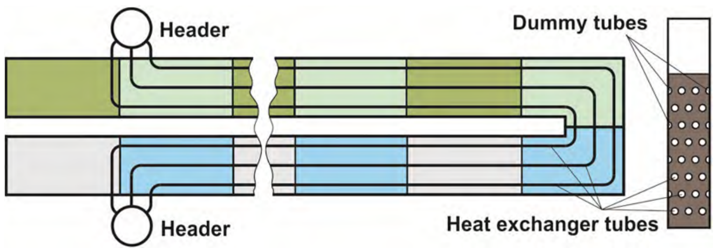
Compound pressure drop Δp_{HEX} has to be equal at every cross section along the particle's flow direction



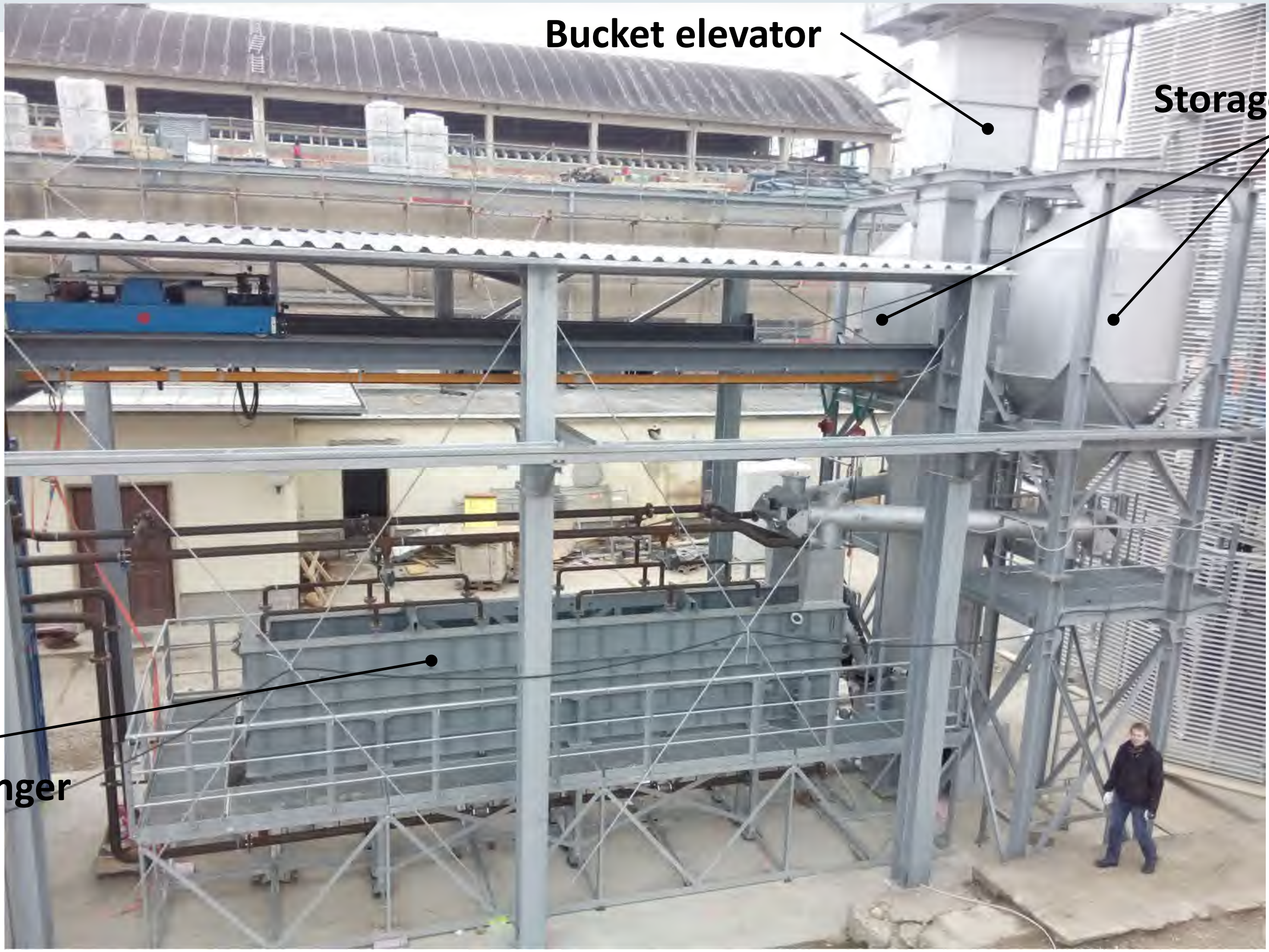


SandTES – test rig





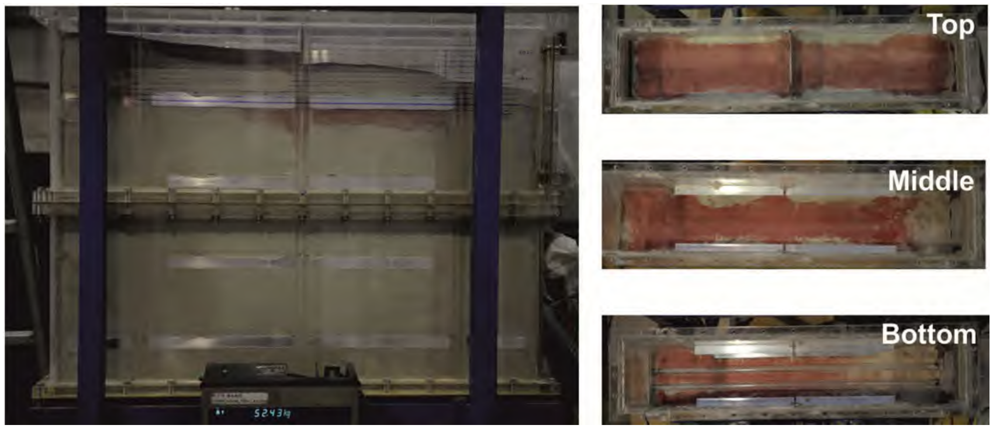
SandTES – test rig

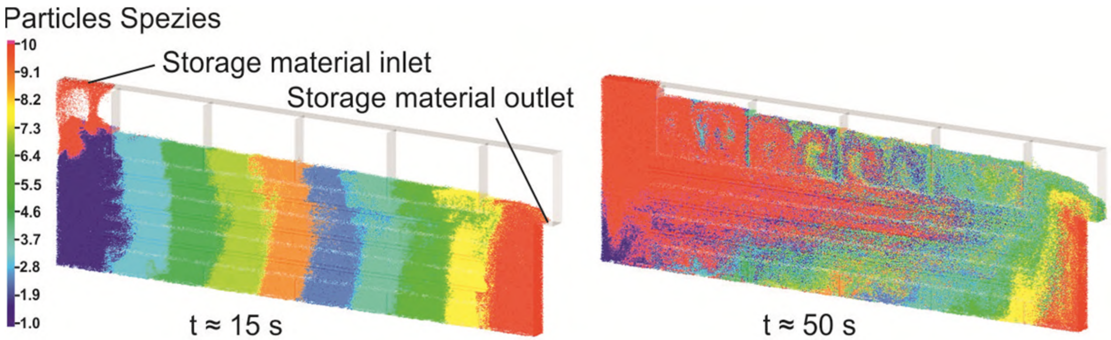


SandTES – heat exchanger technology

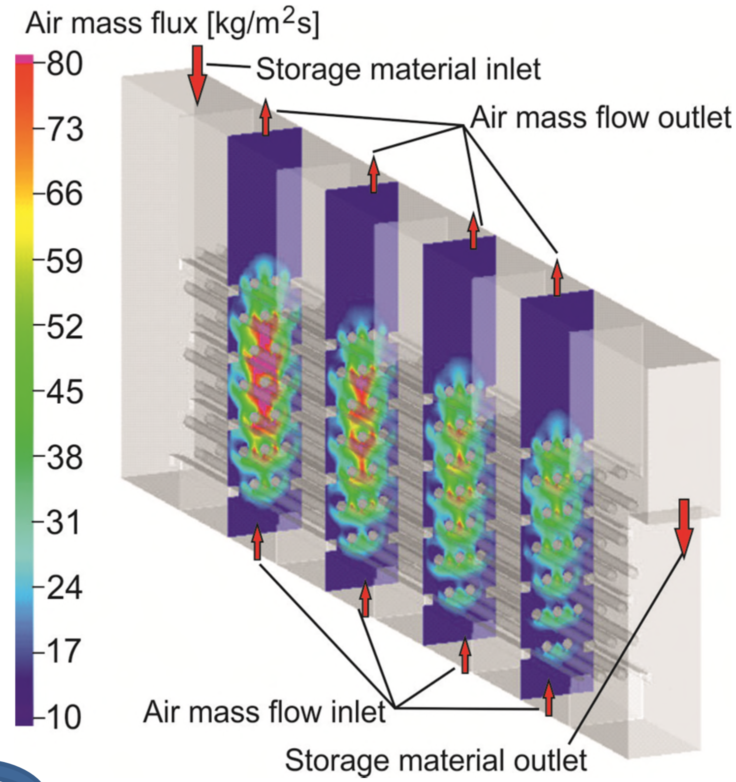
Experimental and numerical investigation

Mixing behavior, verification of the concept:





Flow behavior of the storage material within the tube bundle:



Fluidisation based particle – TES Technologie

Fluidisation based particle – TES technology

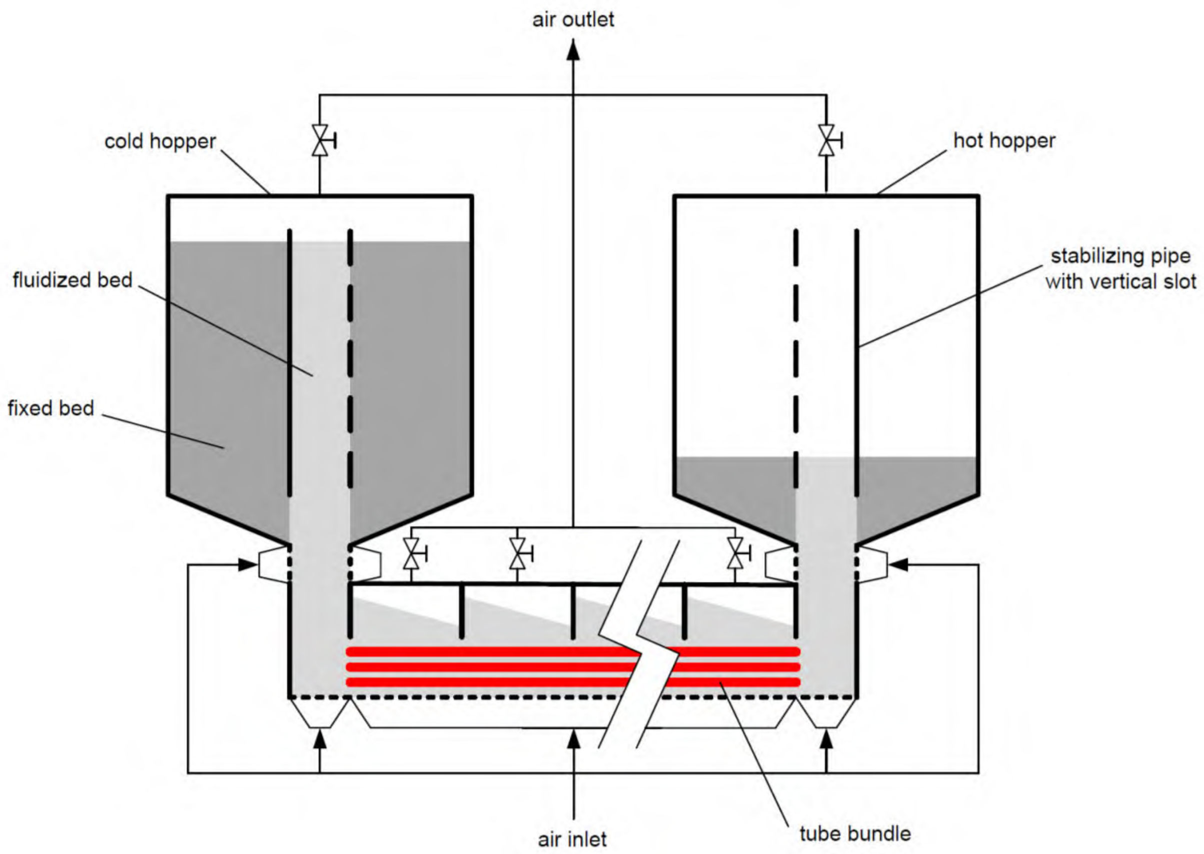
Further development of the SandTES-technology for short or middle storage times and –capacities.

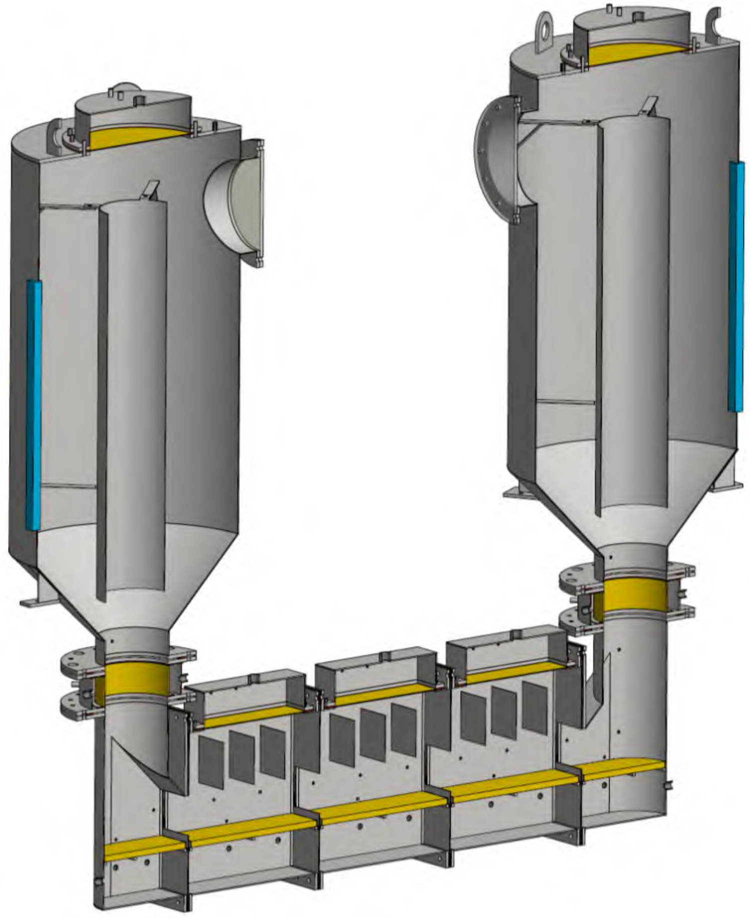
Appropriate for Particle diameter of 70 – 100 µm
Operation temperature up to approx. 800°C

technology concept without rotating components, like

- **bucket elevator**
- **screws**

FP – TES: test rig

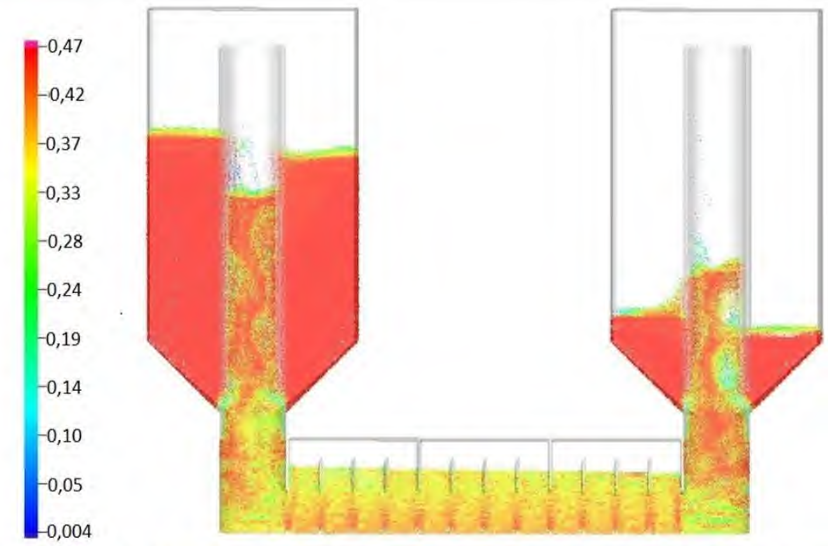


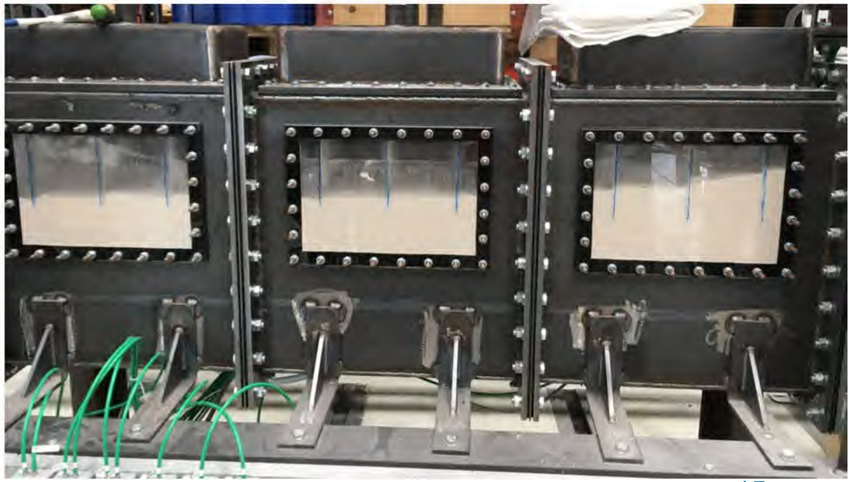


Channel cross section of 250 mm x 190 mm
Hoppers: 800 kg silica sand

FP – TES: test rig

Experimental and numerical investigations





FP – TES: maximum dimensions

The maximum design of the FP-TES depends on the hopper design.

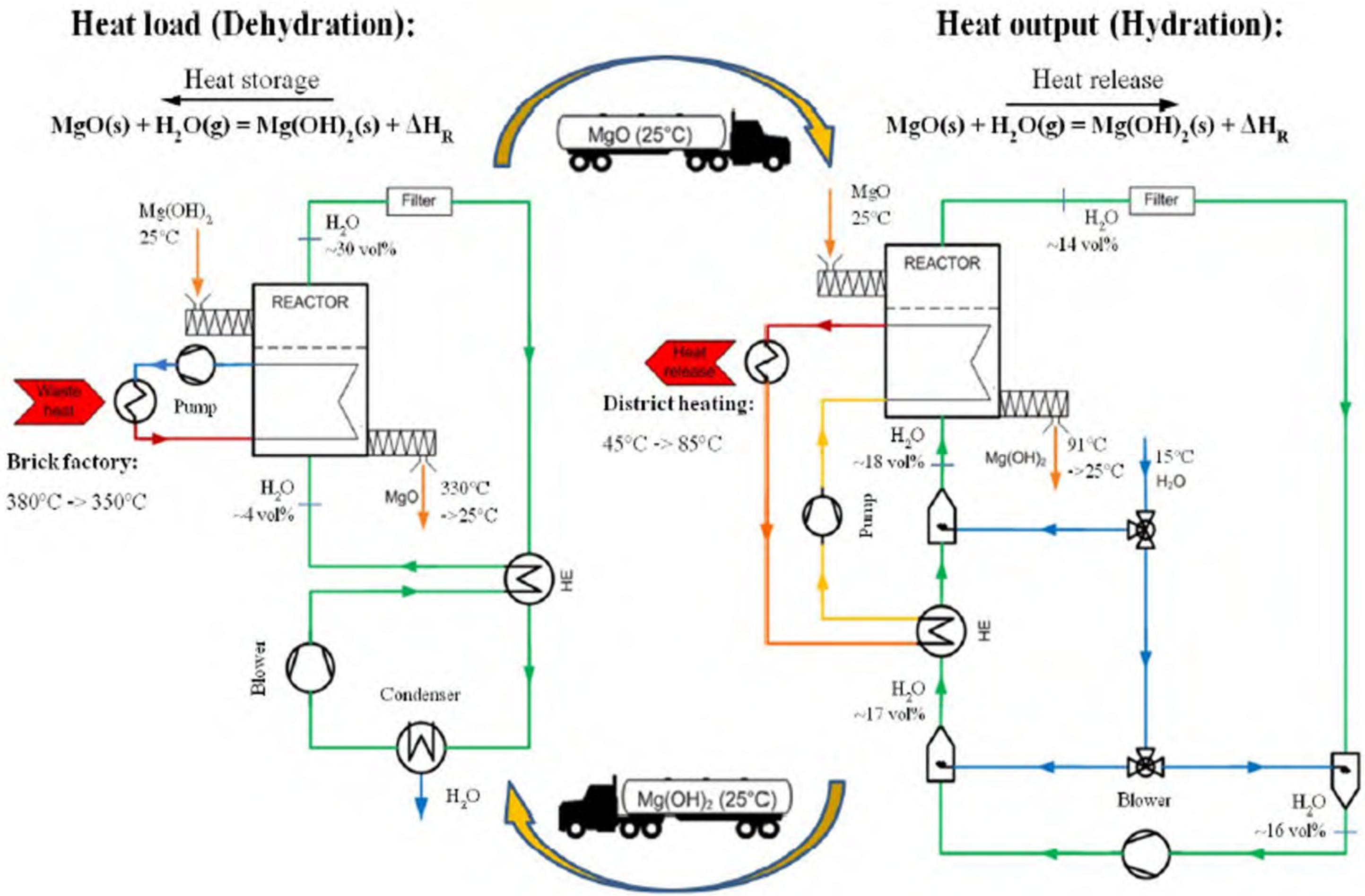
Height of the cylinder: 3m (height of the storage material; without freeboard)
Slope of then cone approx. 15°
Total height of the hopper: 3,5m
Total fluidized height over the sinter floor approx. 4 to 4,5 m
Diameter of the cylinder: 4 m

For a temperature difference of approx. ΔT = 500°C following capacities are possible:

Silica sand (c_p = 900 J/kgK): capacity: 6,2 MWh
Corundum ($\rho_{Schütt}$ = 1458 kg/m3; c_p = 1100 J/kgK): capacity: 8,9 MWh

Thermochemical energy storage

Thermochemical energy storage
What's this?



SolidHeat Basic

Algorithmic data base search

- Search to potential reactions in HSC
  - ✓ restricted to solid/gas – reaction
  - ✓ gas: H_2O, CO_2, O_2, SO_2, NH_3
  - ✓ ~ 3000 reactions detected

Li2SO4 --> SO2 + Li2O2
BaSO4 --> SO2 + BaO2
2 LiCl*H2O --> 2 H2O + Li2Cl2
Rb2SO4 --> SO2 + Rb2O2
K2SO4 --> SO2 + K2O2
Al4C3*6H2O --> 6 H2O + Al4C3
Cs2SO4 --> SO2 + Cs2O2
Na2SO3 --> SO2 + Na2O
[illegible]
[illegible]
[illegible]
AlCl3*6H2O --> 6 H2O + AlCl3
EuCl3*6H2O --> 6 H2O + EuCl3
PbO*PbSO4 --> SO2 + Pb2O3
2 Al(OH)3 --> 3 H2O + Al2O3
CaMg(CO3)2 --> 2 CO2 + CaO*MgO
2 CaHPO4*2H2O --> 5 H2O + Ca2P2O7
[illegible]
[illegible]
MgCO3 --> CO2 + MgO
2 FeSO4 --> 2 SO2 + Zn0.3Fe2.7O4
[illegible]
[illegible]
Mg(OH)2 --> H2O + MgO
[illegible]
[illegible]
NH4NO3 --> NH3 + HNO3
Ba(ClO4)2*3H2O --> 3 H2O + Ba(ClO4)2
[illegible]
[illegible]
NiSO4*7H2O --> 7 H2O + NiSO4

MnSO4*7H2O --> 7 H2O + MnSO4
YbCl3*6H2O --> 6 H2O + YbCl3
CoCO3 --> CO2 + CoO
MgSeO3*6H2O --> 6 H2O + MgSeO3
2 FeSO4 --> 2 SO2 + Zn0.7Fe2.3O4
ZnSO4*7H2O --> 7 H2O + ZnSO4
Na2HPO4*12H2O --> 12 H2O + Na2HPO4
CuSO4*5H2O --> 5 H2O + CuSO4
CoSO4*7H2O --> 7 H2O + CoSO4
FeCO3 --> CO2 + FeO
FeSO4*7H2O --> 7 H2O + FeSO4
SnSO4 --> SO2 + SnO2
KOH*H2O --> H2O + KOH
MgTeO3*6H2O --> 6 H2O + MgTeO3
NaClO2*3H2O --> 3 H2O + NaClO2
CsAl(SO4)2*12H2O --> 12 H2O + CsAl(SO4)2
LiClO4*3H2O --> 3 H2O + LiClO4
CeCl3*7H2O --> 7 H2O + CeCl3
Al2O3*2SiO2*2H2O --> 2 H2O + Al2O3*2SiO2
2 Yb(OH)3 --> 3 H2O + Yb2O3
PrCl3*7H2O --> 7 H2O + PrCl3
NaOH*H2O --> H2O + NaOH
ErCl3*6H2O --> 6 H2O + ErCl3
TbCl3*6H2O --> 6 H2O + TbCl3
DyCl3*6H2O --> 6 H2O + DyCl3
LaCl3*7H2O --> 7 H2O + LaCl3
HoCl3*6H2O --> 6 H2O + HoCl3
AgF*4H2O --> 4 H2O + AgF
RbOH*2H2O --> 2 H2O + RbOH
2 Tm(OH)3 --> 3 H2O + Tm2O3
Al2Si2O5(OH)4 --> 2 H2O + Al2O3*2SiO2

KF*2H2O --> 2 H2O + KF
Na2CO3*10H2O --> 10 H2O + Na2CO3
Na2B4O7*10H2O --> 10 H2O + Na2B4O7
2 Na2HPO4*12H2O --> 25 H2O + Na4P2O7
CoCl2*6H2O --> 6 H2O + CoCl2
CoBr2*6H2O --> 6 H2O + CoBr2
KAl(SO4)2*12H2O --> 12 H2O + KAl(SO4)2
Cu(NO3)2*6H2O --> 6 H2O + Cu(NO3)2
[illegible]
[illegible]
[illegible]
Zn(NO3)2*6H2O --> 6 H2O + Zn(NO3)2
SrBr2*6H2O --> 6 H2O + SrBr2
CaBr2*6H2O --> 6 H2O + CaBr2
CuF2*2H2O --> 2 H2O + CuF2
SmCl3*6H2O --> 6 H2O + SmCl3
CaC2O4*H2O --> H2O + CaC2O4
[illegible]
[illegible]
MgCl2*6H2O --> 6 H2O + MgCl2
LiI*3H2O --> 3 H2O + LiI
[illegible]
2 LiOH*H2O --> 3 H2O + Li2O
3 PbCO3 --> 2 CO2 + *2PbO*PbCO3
[illegible]
[illegible]
CaCO3 --> CO2 + CaO
Ba(OH)2 --> H2O + BaO
[illegible]
[illegible]
SrCO3 --> CO2 + SrO

BaCO3 --> CO2 + BaO
Li2CO3 --> CO2 + Li2O
Na2CO3 --> CO2 + Na2O
SrSO4 --> SO2 + SrO2
CsOH --> H2O + Cs2O
2 NaOH --> H2O + Na2O
K2CO3 --> CO2 + K2O
2 RbOH --> H2O + Rb2O
Na2SO4 --> SO2 + Na2O2
Cs2CO3 --> CO2 + Cs2O
2 KOH --> H2O + K2O
2 AlCl3*6H2O --> 12 H2O + Al2Cl6
Pd(OH)2 --> H2O + PdO
Np(OH)4 --> 2 H2O + NpO2
Th(OH)4 --> 2 H2O + ThO2
CuHPO4*H2O --> H2O + CuHPO4
Ba(N3)2*H2O --> H2O + Ba(N3)2
UOF2*H2O --> H2O + UOF2
Pt(OH)2 --> H2O + PtO
Hg2CO3 --> CO2 + Hg2O
Tc2O7*H2O --> H2O + Tc2O7
Cu(IO3)2*H2O --> H2O + Cu(IO3)2
NH4(UO2)2F5*4H2O --> 4 H2O + NH4(UO2)2F5
Ra(BrO3)2*H2O --> H2O + Ra(BrO3)2
Co(NH3)5*H2O*Cl3 --> H2O + (Co(NH3)5Cl)Cl2
Ba(IO3)2*H2O --> H2O + Ba(IO3)2
PuO2(OH)2*H2O --> H2O + PuO2(OH)2
Ra(IO3)2*H2O --> H2O + Ra(IO3)2
Eu(IO3)3*2H2O --> 2 H2O + Eu(IO3)3
Ir(OH)4 --> 2 H2O + IrO2
2 Th(OH)3 --> 3 H2O + Th2O3

2 FeO*OH --> H2O + Fe2O3
NH4HSO4 --> NH3 + H2SO4
Mn(OH)2 --> H2O + MnO
BeSO4*4H2O --> 4 H2O + BeSO4
Ni(NO3)2*6H2O --> 6 H2O + Ni(NO3)2
Fe(OH)2 --> H2O + FeO
CdCO3 --> CO2 + CdO
SrCl2*6H2O --> 6 H2O + SrCl2
[illegible]
[illegible]
[illegible]
Mg(NO3)2*6H2O --> 6 H2O + Mg(NO3)2
Na2SO4*10H2O --> 10 H2O + Na2SO4
FeCl2*4H2O --> 4 H2O + FeCl2
NdCl3*6H2O --> 6 H2O + NdCl3
NiCO3 --> CO2 + NiO
[illegible]
[illegible]
[illegible]
FeCO3 --> CO2 + FeO1.056
2 TlOH --> H2O + Tl2O
2 Bi(OH)3 --> 3 H2O + Bi2O3
PbCO3 --> CO2 + PbO
Co(NO3)2*6H2O --> 6 H2O + Co(NO3)2
2 NH4F --> NH3 + NH4HF2
Ni(OH)2 --> H2O + NiO
Tl2CO3 --> CO2 + Tl2O
2 PbCO3 --> CO2 + PbO*PbCO3
UO2(NO3)2*6H2O --> 6 H2O + UO2(NO3)2
NH4ReO4 --> NH3 + HReO4
Cd(OH)2 --> H2O + CdO

Fe(OH)2 --> H2O + FeO1.056
KCr(SO4)2*12H2O --> 12 H2O + KCr(SO4)2
NH4*H2PO4 --> NH3 + H3PO4
Ca(H2PO4)2*H2O --> 3 H2O + Ca(PO3)2
Ag2CO3 --> CO2 + Ag2O
LiCl*H2O --> H2O + LiCl
Na2S2O3*5H2O --> 5 H2O + Na2S2O3
Cd(NO3)2*4H2O --> 4 H2O + Cd(NO3)2
Cu(OH)2 --> H2O + CuO
Pb(OH)2 --> H2O + PbO
Ca(NO3)2*4H2O --> 4 H2O + Ca(NO3)2
CuCl2*2H2O --> 2 H2O + CuCl2
MoO3*H2O --> H2O + MoO3
NaClO4*H2O --> H2O + NaClO4
VOCO3 --> CO2 + VO2
ReO2*2H2O --> 2 H2O + ReO2
Na2WO4*2H2O --> 2 H2O + Na2WO4
AuCl3*2H2O --> 2 H2O + AuCl3
K2CuCl2(H2O)2*Cl2 --> 2 H2O + K2CuCl4
Cu3(PO4)2*3H2O --> 3 H2O + Cu3(PO4)2
AgCl*NH3 --> NH3 + AgCl
RaBr2*2H2O --> 2 H2O + RaBr2
CaTeO3*H2O --> H2O + CaTeO3
NiSeO3*2H2O --> 2 H2O + NiSeO3
MoO2Cl2*H2O --> H2O + MoCl2O2
RaCl2*2H2O --> 2 H2O + RaCl2
CoSeO3*2H2O --> 2 H2O + CoSeO3
Rb2CO3*H2O --> H2O + Rb2CO3
CdCl2*H2O --> H2O + CdCl2
HgCO3 --> CO2 + HgO
V2O5*H2O --> H2O + V2O5

CaHPO4*2H2O --> 2 H2O + CaHPO4
BaI2*2H2O --> 2 H2O + BaI2
Sr(NO3)2*4H2O --> 4 H2O + Sr(NO3)2
CaSeO4*2H2O --> 2 H2O + CaSeO4
BaCl2*2H2O --> 2 H2O + BaCl2
Zn(OH)2 --> H2O + ZnO
CuCO3 --> CO2 + CuO
(NH4)2SO4 --> NH3 + NH4HSO4

NaI*2H2O --> 2 H2O + NaI
Sr(BrO3)2*H2O --> H2O + Sr(BrO3)2
UO2SO4*3H2O --> 3 H2O + UO2SO4
CaSO4*2H2O --> 2 H2O + CaSO4
BaBr2*2H2O --> 2 H2O + BaBr2
CuSeO3*2H2O --> 2 H2O + CuSeO3
PbC2O4 --> 2 CO2 + Pb
CdSO4*H2O --> H2O + CdSO4
Li2SO4*H2O --> H2O + Li2SO4
AlF3*3H2O --> 3 H2O + AlF3
K4Fe(CN)6*3H2O --> 3 H2O + K4Fe(CN)6
Ba(BrO3)2*H2O --> H2O + Ba(BrO3)2
2 KOH*2H2O --> 5 H2O + K2O
2 KOH*H2O --> 3 H2O + K2O
2 NaOH*H2O --> 3 H2O + Na2O
Ce(SO4)2*5H2O --> 5 H2O + Ce(SO4)2
2 RbOH*2H2O --> 5 H2O + Rb2O
2 H3PO4*0.5H2O --> 4 H2O + P2O5
2 RbOH*H2O --> 3 H2O + Rb2O
2 Na3PO4*12H2O --> 24 H2O + Na6P2O8
2 B(OH)3 --> 3 H2O + B2O3
Li2SO3 --> SO2 + Li2O
K2SO3 --> SO2 + K2O

2 CaB3O3(OH)5*4H2O --> 13 H2O + *2CaO*3B2O3
2 Nd(OH)3 --> 3 H2O + Nd2O3
2 BaC2O4*0.5H2O --> 4 CO2 + Ba(OH)2
(NH4)2SO4*3NH3 --> 5 NH3 + H2SO4
2 Gd(OH)3 --> 3 H2O + Gd2O3
2 NaAl(OH)4 --> 4 H2O + Na2O*Al2O3
CaSO3 --> SO2 + CaO
NaNH3 --> NH3 + Na
2 Dy(OH)3 --> 3 H2O + Dy2O3
RaSO4 --> SO2 + RaO2
2 Na2HPO4*2H2O --> 5 H2O + Na4P2O7
Na3PO4*12H2O --> 12 H2O + Na3PO4
MnI2*4H2O --> 4 H2O + MnI2
Pt(NH3)2Br2 --> 2 NH3 + PtBr2
Sr(IO3)2*6H2O --> 6 H2O + Sr(IO3)2
Pt(NH3)4I2 --> 4 NH3 + PtI2
2 Ac(OH)3 --> 3 H2O + Ac2O3
Ag2SO3 --> SO2 + Ag2O
RbF*H2O --> H2O + RbF
LuPO4*2H2O --> 2 H2O + LuPO4
Am2(CO3)3 --> 3 CO2 + Am2O3
U(SO3)2 --> 2 SO2 + UO2
*2PbO*PbSO4 --> SO2 + Pb3O4
ZrO(OH)2 --> H2O + ZrO2
UO2Cl2*3H2O --> 3 H2O + UO2Cl2
2 Au(OH)3 --> 3 H2O + Au2O3
CaAl2Si2O7(OH)2*H2O --> 2 H2O + CaO*Al2O3*2S
YPO4*2H2O --> 2 H2O + YPO4
NH4I*2NH3 --> 2 NH3 + NH4I
UO2F2*3H2O --> 3 H2O + UO2F2
ZnBr2*2H2O --> 2 H2O + ZnBr2

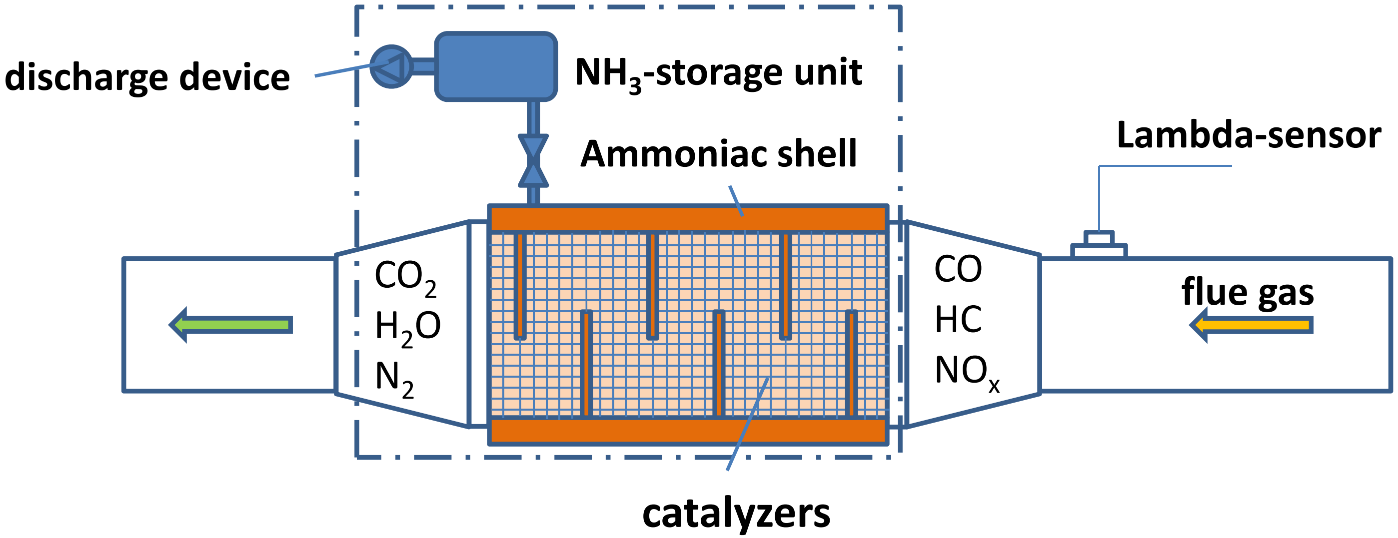
SolidHeat Kinetics

From SolidHeat Basic → SolidHeat Kinetics, to investigate the reaction kinetics of storage material combinations of interest:

- $CaC_2O_4.H_2O <> CaC_2O_4$
- $H_3BO_3 <> B_2O_3$
- $Ca(OH)_2 <> CaO$
- $Mg(OH)_2 <> MgO$
- $MgSO_4.7H_2O <> MgSO_4$
- $Co_3O_4 <> CoO$
- $Cu_2O <> CuO$
- $FeSO_4.7H_2O <> FeSO_4$
- $PbO_2 <> PbO$

Compact heat storage
transition metal ammoniac compounds

Problem: operation temperature of catalyzers after a cold start will be reached slowly

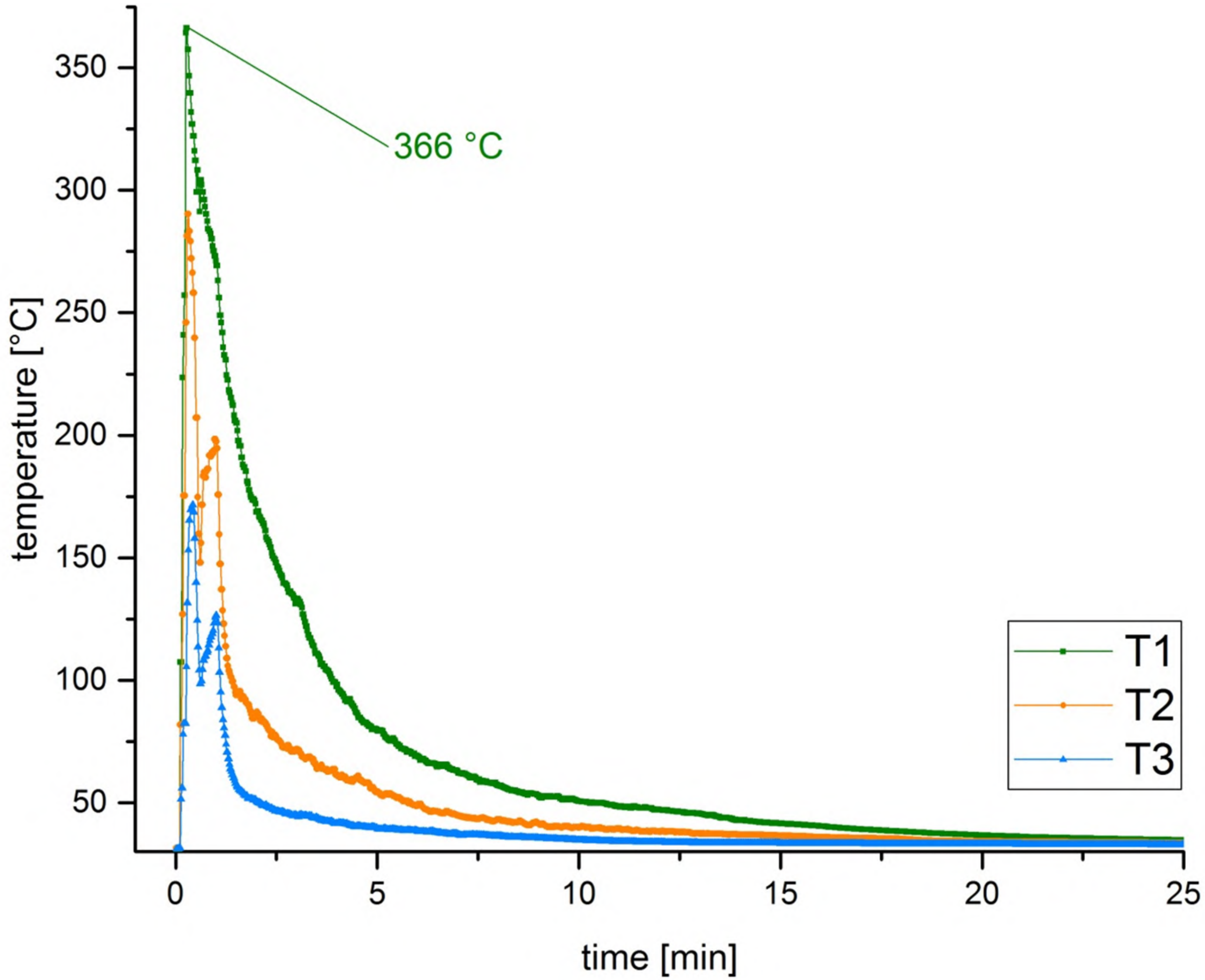


Solution: fast preheating of the catalyzers: with the help of transition metal ammoniakate

Austrian Patent, 2016, Verfahren zur thermochemischen Energiespeicherung

SolidHeat Kinetics: transition metal ammoniac compounds

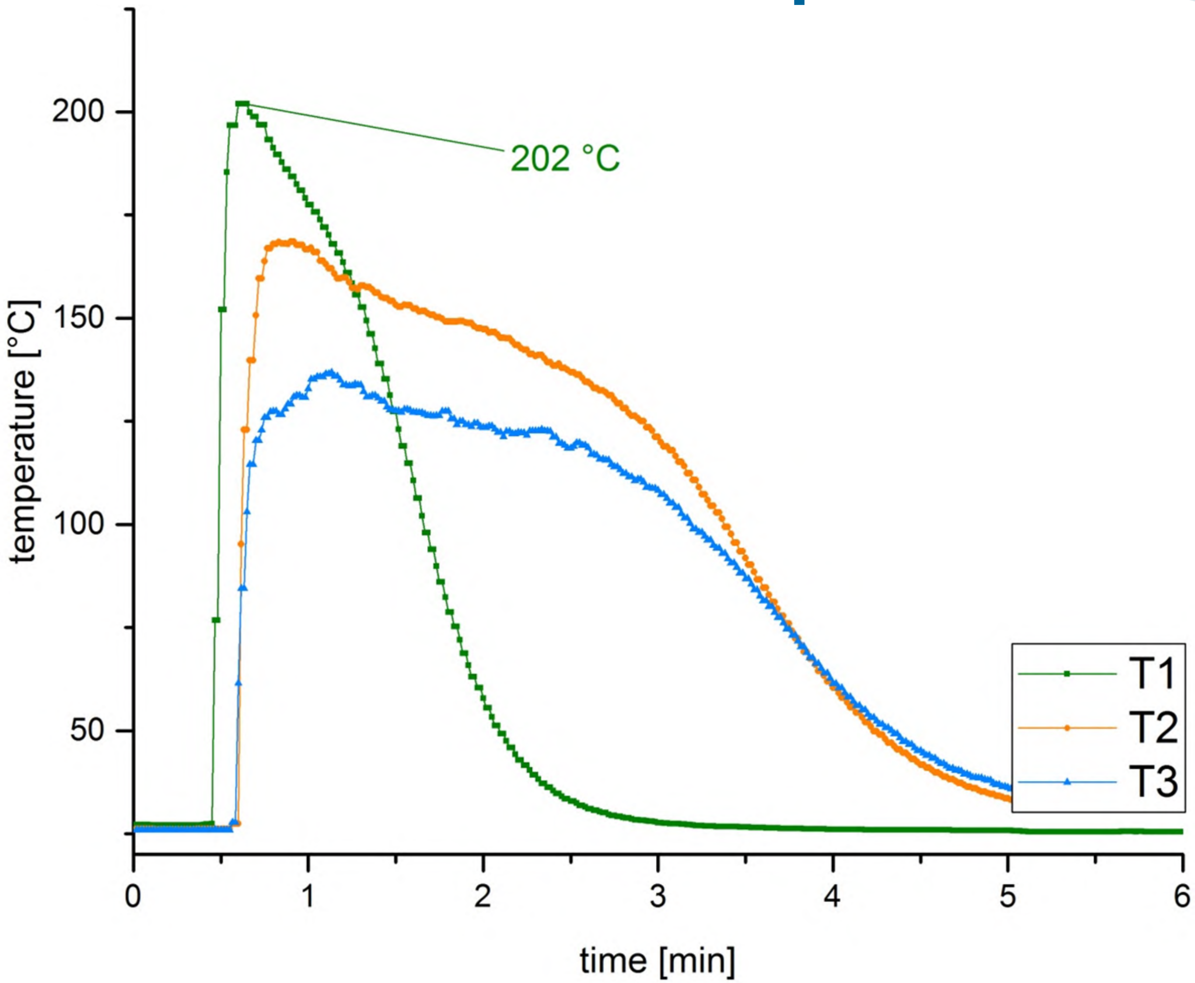
$CuCl_2$, NH_3 undiluted as reactive gas



Austrian Patent, 2016, Verfahren zur thermochemischen Energiespeicherung

Compact heat storage
transition metal ammoniac compounds

$CuSO_4$ on Zeolith, NH_3 undiluted as reactive gas



Austrian Patent, 2016, Verfahren zur thermochemischen Energiespeicherung

Aims, chance, problems of TC-TES

- **Aims:** supply of energy storage materials with high storage density and power and related systems
- **Chance:** based on the basic research knowledge is given also for other scientific areas: reaction technology, improvement of measurement methods
- **Problems & risks:** TRL-level so, that an intensive industrial research can start with experimental reactors in semi-industrial size – therefore interested industrial partners with relevant financial resources are looked for!

Acknowledgement

Funded in FFG-project „Advanced Regenerator: particle-High temperature heat exchanger without rotating components with counter-current flow characteristic" (FFG-project number 858916) and prototype funding of the Austrian Wirtschaftsservice „Fluidized bed heat storage with micro encapsulated phase change material (PCM)" (project number P1621702).

The K-Project GSG-GreenStorageGrid is funded in the framework of COMET - Competence Centers for Excellent Technologies by the Federal Ministry of Transport, Innovation and Technology, the Federal Ministry of Science, Research and Economy, the Vienna Business Agency, the Federal Province of Lower Austria and by the Federal Province of Upper Austria. The program line COMET is administered by the Austrian Research Promotion Agency (FFG)

Thank you for your attention

Ao. Prof. Dr. Heimo Walter
heimo.walter@tuwien.ac.at
TU-Wien
Institute for Energy Systems and Thermodynamics
Tel.: ++43 1 58801 302318

Ao. Prof. Dr. Andreas WERNER
andreas.werner@tuwien.ac.at
TU-Wien
Institute for Energy Systems and Thermodynamics
Tel.: ++43 1 58801 302314