Molten salt chemistry in nitrate salt storage systems:

Linking experiments and modeling

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Motivation

- Improve cost efficiency of thermal energy storage (TES) in Solar Salt (Na,KNO_3)

- Approaches:
  - Substitution of Solar Salt by low price filler materials, e.g. rock in TESIS_store (see poster 234, C. Odenthal)

  - Enhance storage capacity
  - Enhance energy conversion efficiency
  - Faster heat transfer (charging)

  } $T_{max} \uparrow$

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Motivation

$T_{max} \uparrow$

- Formation of gases, pressure increase
- Mass losses
- Corrosion due to formation of oxides

based on chemical reactions

Literature

- $NO_3^- \rightleftarrows NO_2^- + 0.5\ O_2$ [Freeman 1956, Bartholomew 1966, Tracey 1978, Nissen 1983]
  - Thermodynamics ✓
  - Kinetics ~
  - Mass transport limitations ✗
- Reactions that form e.g. O^{2-}, NO_x [Protsenko 1965, Lee 1972, Hoshino 1981, Wei 2014]
  - Thermodynamics ✗
  - Kinetics ✗
  - Mass transport limitations ✗
- Vapor pressures [Glazov 2003] ~

Objective

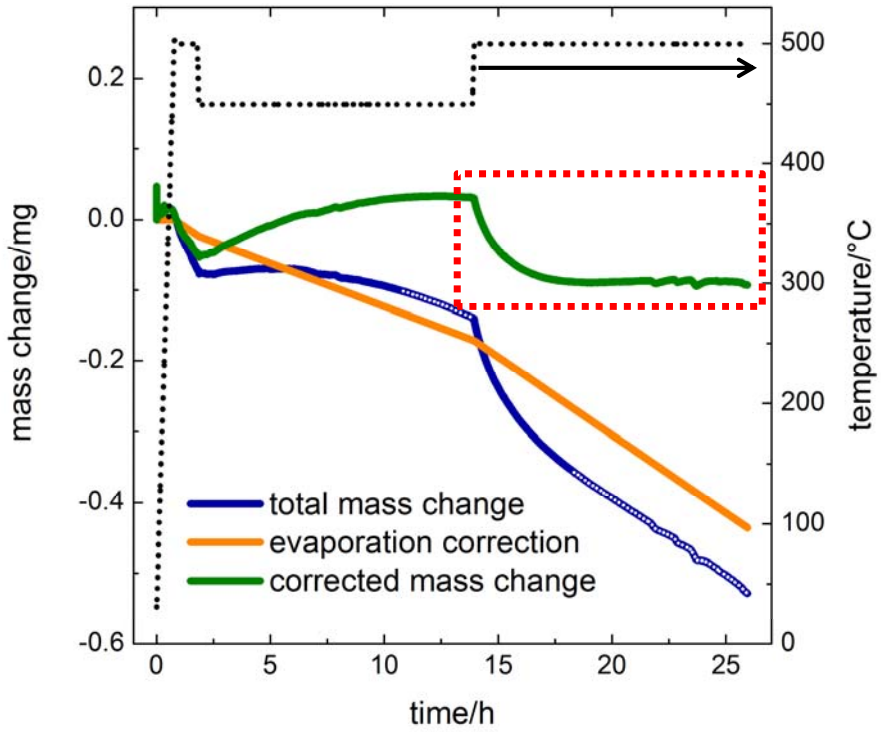
1) Prove applicability of thermogravimetric analysis for investigation of reaction kinetics

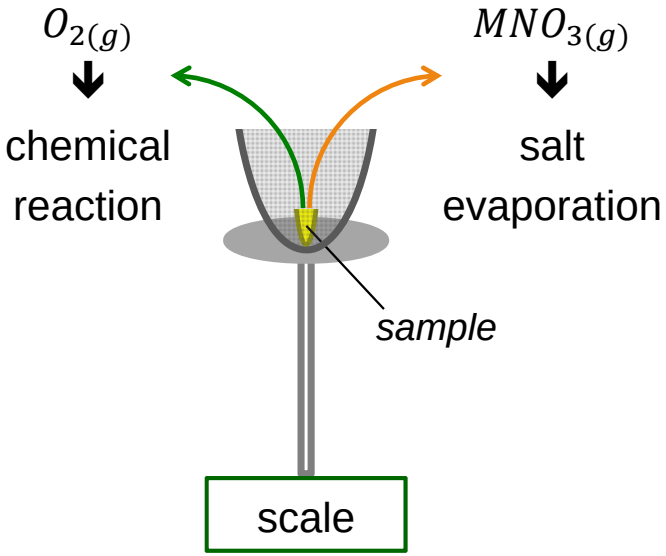
2) Improve understanding of the first crucial chemical reaction $NO_3^- \rightleftarrows NO_2^- + 0.5\ O_2$

   → Identify experimental sizes and geometries with and without mass transport limitations

3) Compare experimental results and simulation curves

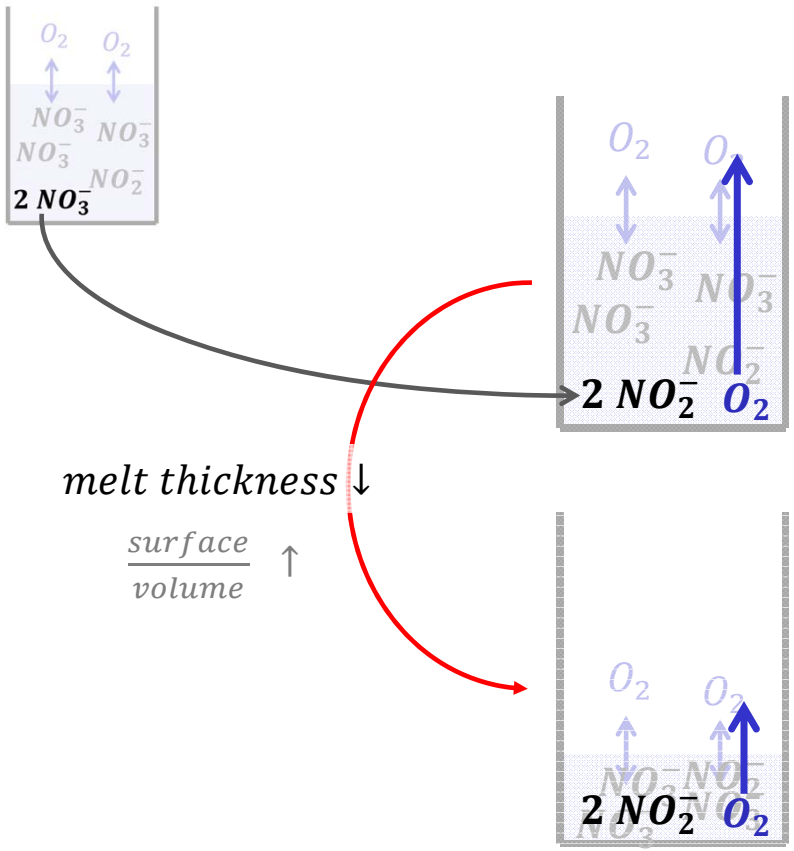
Thermogravimetric Analysis





[Carling Sandia 1981, Duncan 2001, Glazov 2003]

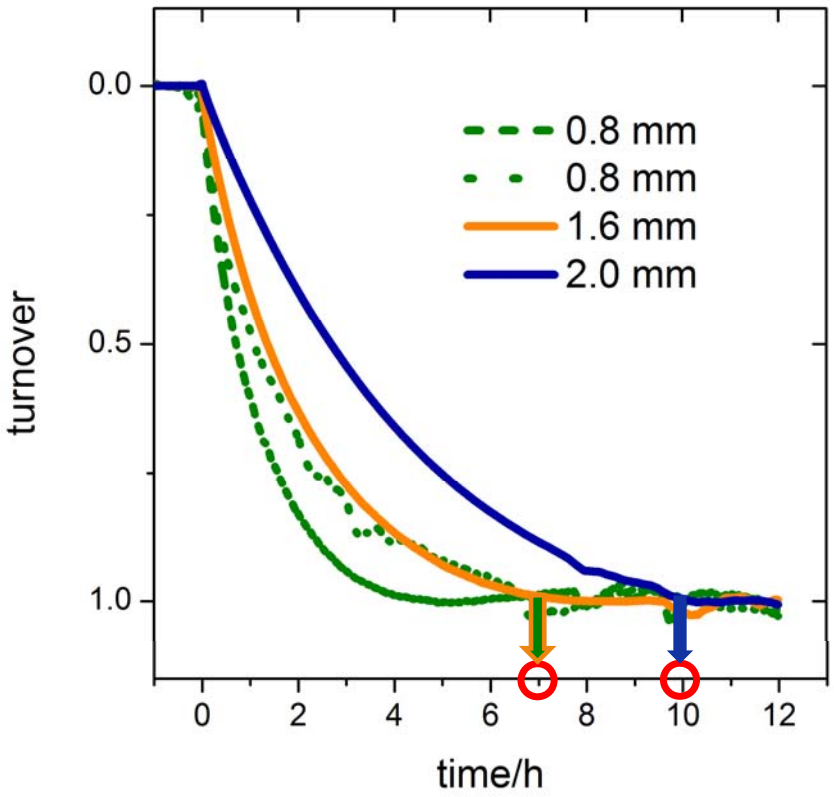
Reaction kinetics and mass transport limitations



Reaction velocity = Reaction kinetics **plus** Mass transport limitations

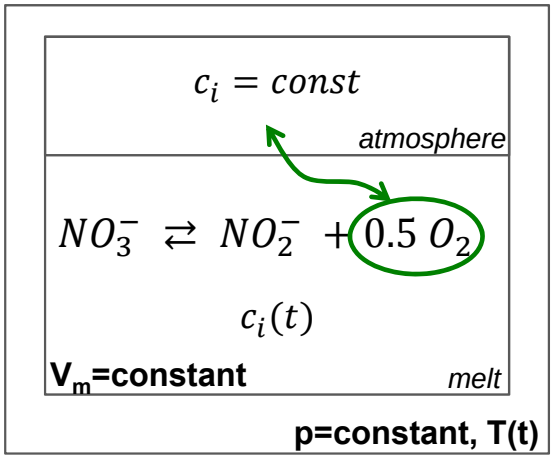
Reaction velocity ≈ Reaction kinetics

Reaction kinetics and mass transport limitations



Measurement uncertainty and mass transport effects are in the same order of magnitude for the 0.8 and 1.6 mm experiments.

Model description



Amount of substance-balance of nitrite ions NO_2^-:

$$\frac{dn_{NO_2^-}}{dt} = \nu_{NO_2^-} r(c_{NO_3^-}, c_{NO_2^-}, c_{O_2}, E^f, A^f,\ E^r,\ A^r, T) V_m$$

$\nu_{NO_2^-}$: Stoichiometric coefficient of NO_2^-, -1

r: Reaction rate $[\frac{mol}{m^3 s}]$

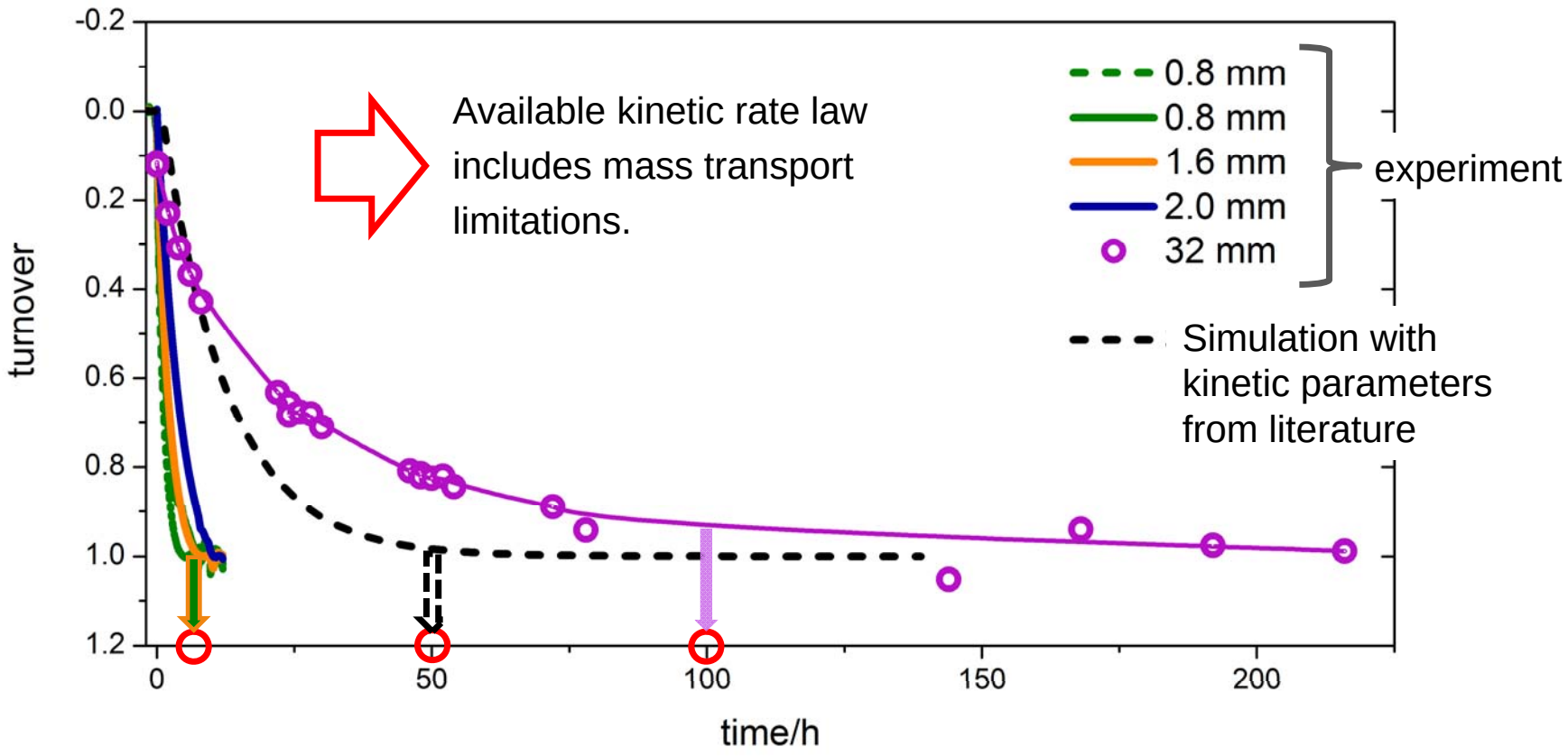
V_m: Volume of the melt, constant

$$r = \frac{n_{NO_3^-}}{V_m} \cdot A^f \exp(-\frac{E^f}{RT}) - \frac{n_{NO_2^-}}{V_m} p_{O_2} \cdot A^r \exp(-\frac{E^r}{RT})$$

forward reaction kinetics – reverse reaction kinetics

[Nissen 1983]

Experimental and simulation results



Summary and conclusion

1) Thermogravimetric analysis data was corrected with regard to salt evaporation
   → appropriate method for reaction velocity investigations

2) The velocity of the reaction

$$NO_3^- \rightarrow NO_2^- + 0.5\, O_2$$

   is significantly influenced by experiment geometries,
   Thermogravimetric analysis allows experiments, where mass transport limitations can be neglected

3) Kinetic rate law from the literature includes mass transport limitations

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Thank you for listening!

Contact
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DLR

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