# Kinetics of the calcium evaporation from active $CaF_2$-slags during pressure electro slag remelting

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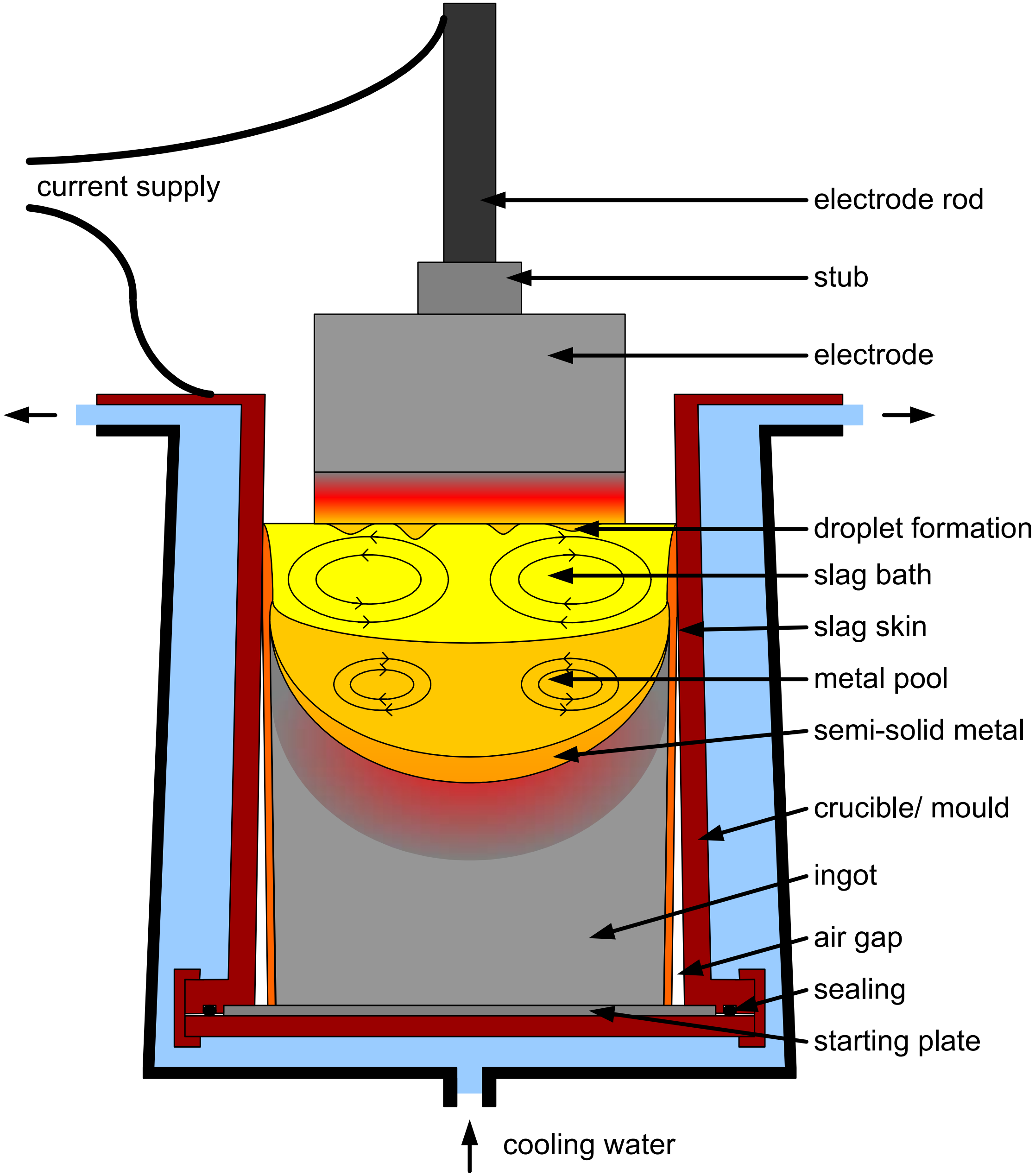
# Application of PESR with active slags at IME Aachen




active slag:

- $CaF_2$ + Ca-metal (+ CaO)
- no $Al_2O_3$, $SiO_2$, etc.

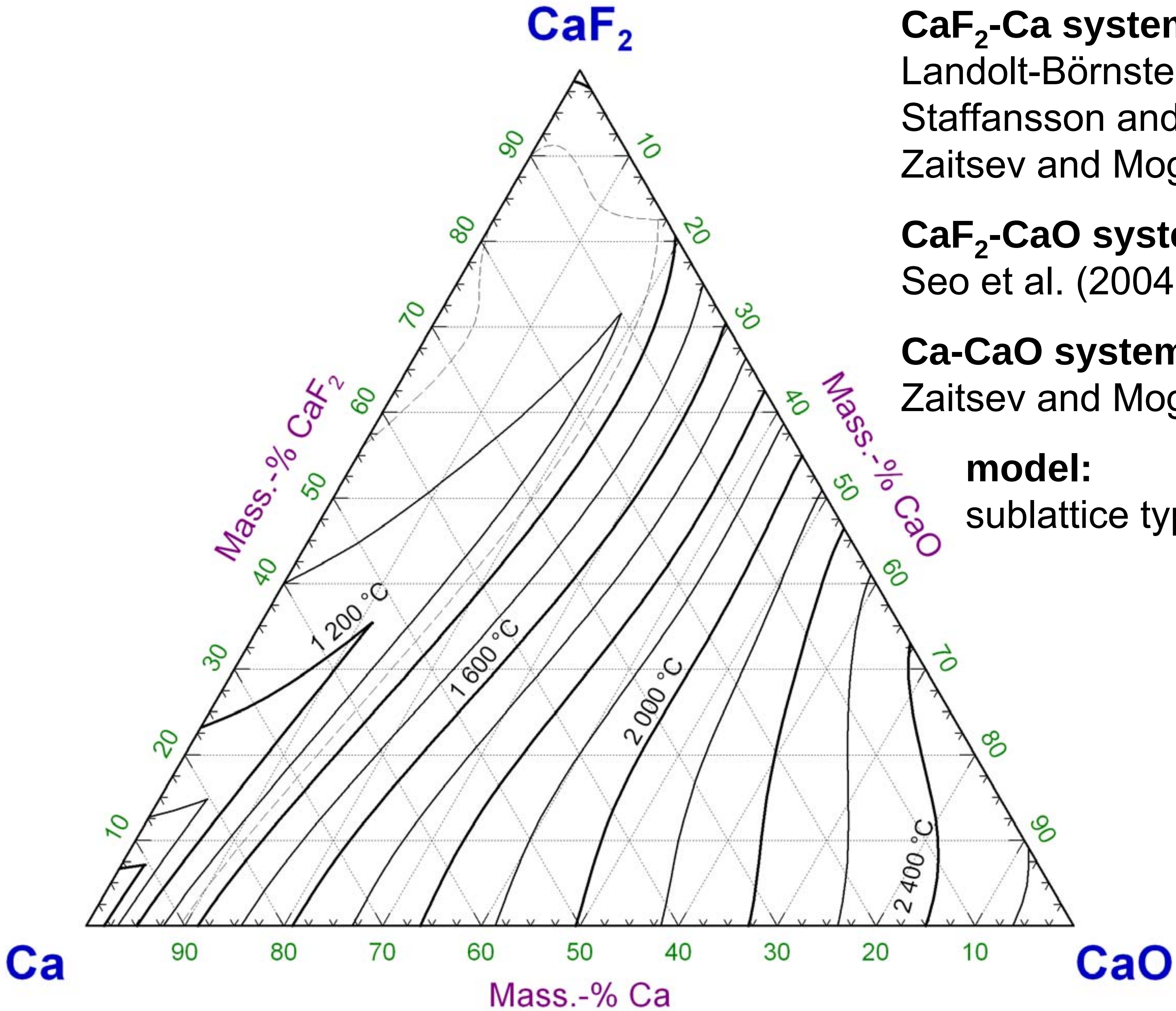
desoxidation of:

- Fe-Cr-alloys
- Ti-(Al)-alloys

preventing oxidation of:

- Ni-Fe-Be-alloy

# Ternary $CaF_2$-Ca-CaO system modelled with OptiSage



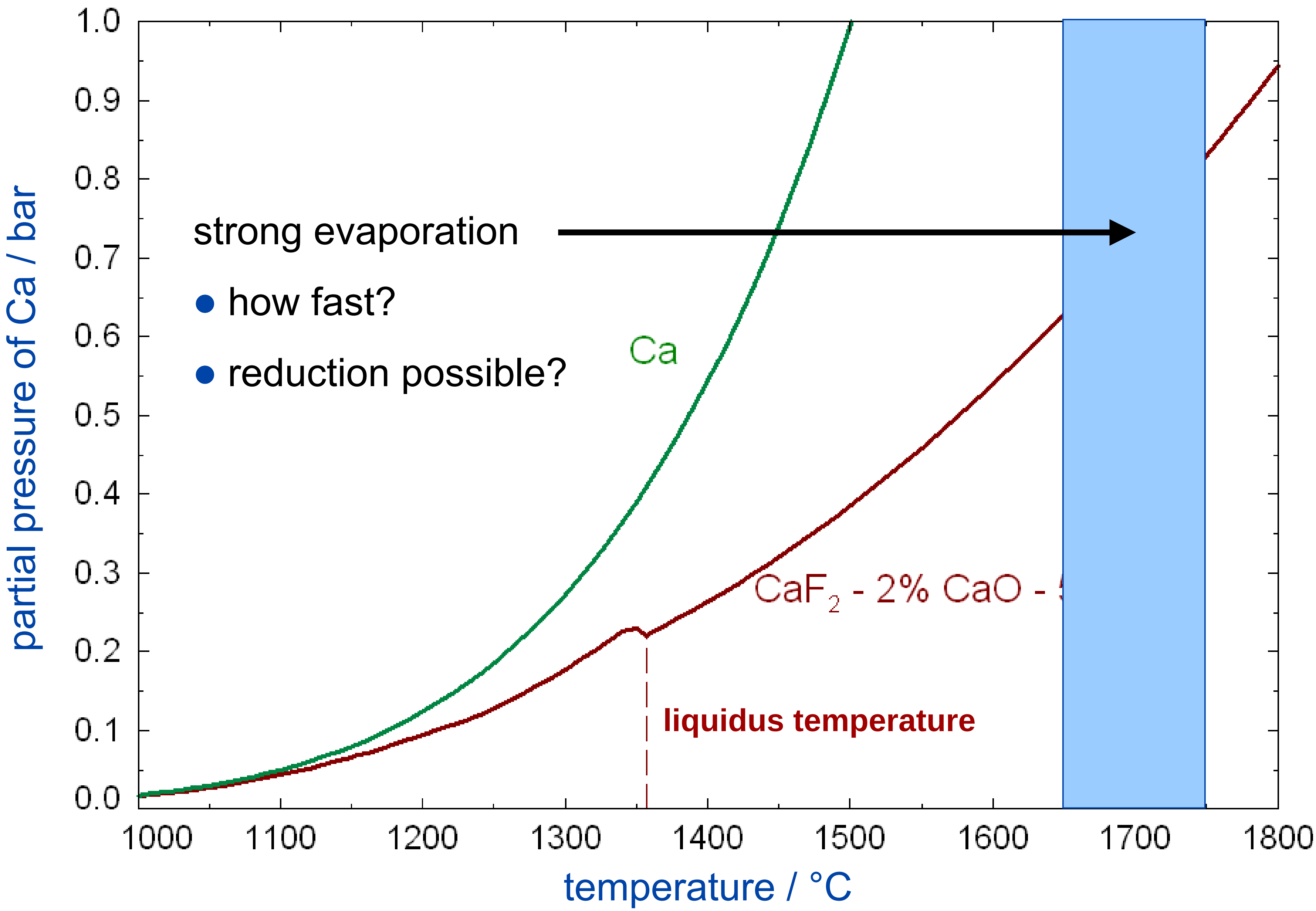

**$CaF_2$-Ca system:**
Landolt-Börnstein (1993),
Staffansson and Sichem (1992),
Zaitsev and Mogutnov (2001)

**$CaF_2$-CaO system:**
Seo et al. (2004)

**Ca-CaO system:**
Zaitsev and Mogutnov (2001)

**model:**
sublattice type, Kohler/Toop

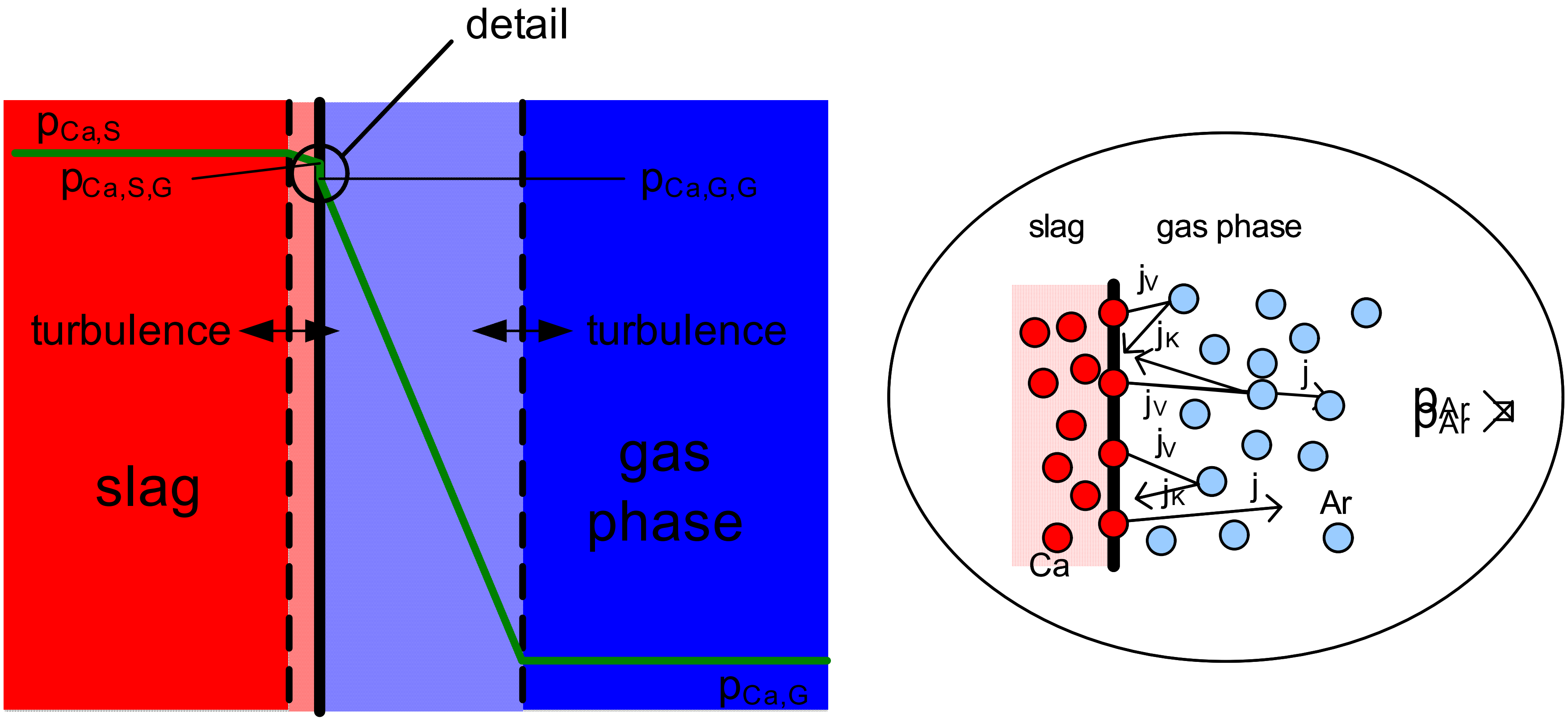
# Partial pressure of Ca in equilibrium



# Fundamentals of the Ca evaporation

$$[Ca]_{slag} \Leftrightarrow \{Ca\}_{gas} \quad \rightarrow \quad k = \frac{p_{Ca} / p^*}{x_{Ca,slag} \cdot f_{Ca,slag}}$$

→ thermochemical view: no system pressure dependency, if $f_{Ca}$ = const.




→ kinetical view: dependency from system pressure and gas turbulence!

# Kinetic of the evaporation step

Hertz-Knudsen:

$$j = j_V - j_K = \alpha_V \cdot \frac{1}{\sqrt{2\pi M_{Ca} R T}} \cdot p_{Ca,S,G} - \alpha_K \cdot \frac{1}{\sqrt{2\pi M_{Ca} R T}} \cdot p_{Ca,G,G}$$

Example:

- $\alpha_V = \alpha_K \approx 1$
- $p_{Ca,G,G} = 0$ (Ca-transport in the gas phase is indefinitely fast)
- T = 1973 K

→ j = 1130 mol/m²s and 16,8 mol/s in IME-PESR-furnace, respectively

→ The evaporation step would be nearly indefinitely fast.

→ The mass transport in the gas phase must be the limiting step.

# Kinetic of the mass transport in the gas phase I

diffusion layer model (Fick's 1st Law):

$$j = -D \cdot \frac{\Delta c}{\Delta x} = -\frac{D}{\Delta x} \cdot \frac{p_{Ca,G,G}}{R\,T} \approx -\frac{D}{\Delta x} \cdot \frac{p_{Ca,S}}{R\,T}$$

calc. of the diffusion coefficient (kin. gas theory + med. free length of path) :

$$D = \frac{3}{16}\,\bar{v}\,\lambda = \frac{3}{16}\sqrt{\frac{8\,R\,T_S}{\pi\,\mu_{Ca-Ar}}} \cdot \frac{k\,T_S}{\sqrt{2}\,\sigma\,p} = \frac{3}{8}\sqrt{\frac{k^2\,R\,T_S^3}{\pi\,\mu_{Ca-Ar}\,\sigma^2\,p^2}} \sim \frac{1}{p}$$

$$j \sim \frac{1}{\sqrt[3]{p}}$$

calc. of the diffusion layer thickness:

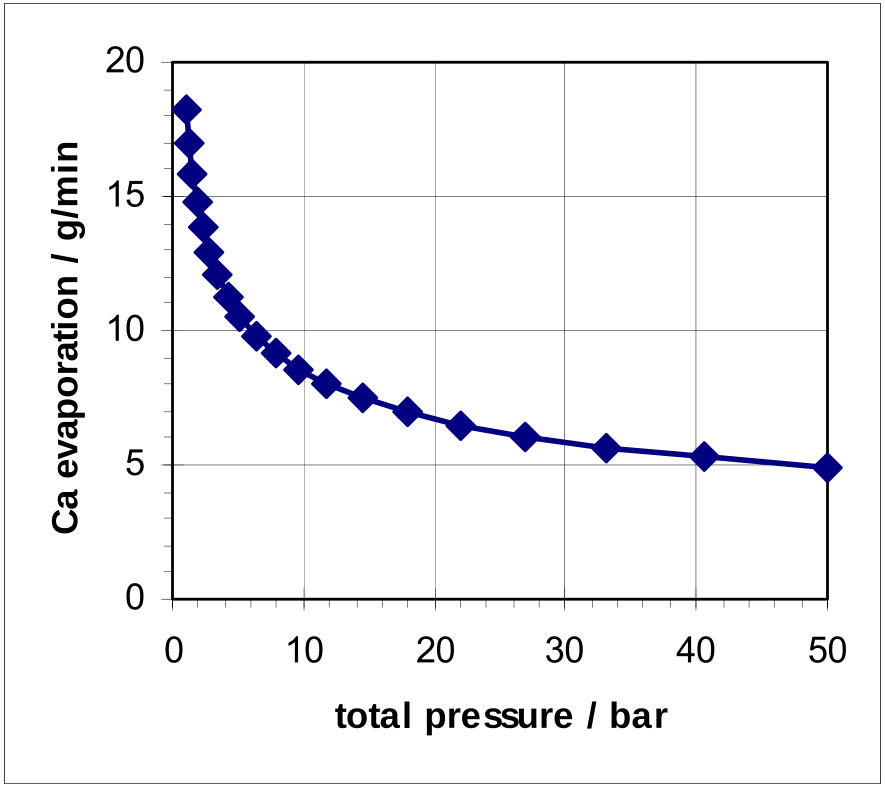
$$\Delta x = \frac{L}{0{,}15 \cdot \sqrt[3]{Gr \cdot Sc \cdot f_2(Sc)}} = \frac{1}{0{,}15 \cdot \sqrt[3]{\frac{T_S - T_m}{T_m} \cdot \frac{g}{\nu \cdot D_m} \cdot f_2(Sc)}} \sim \frac{1}{p^{2/3}}$$

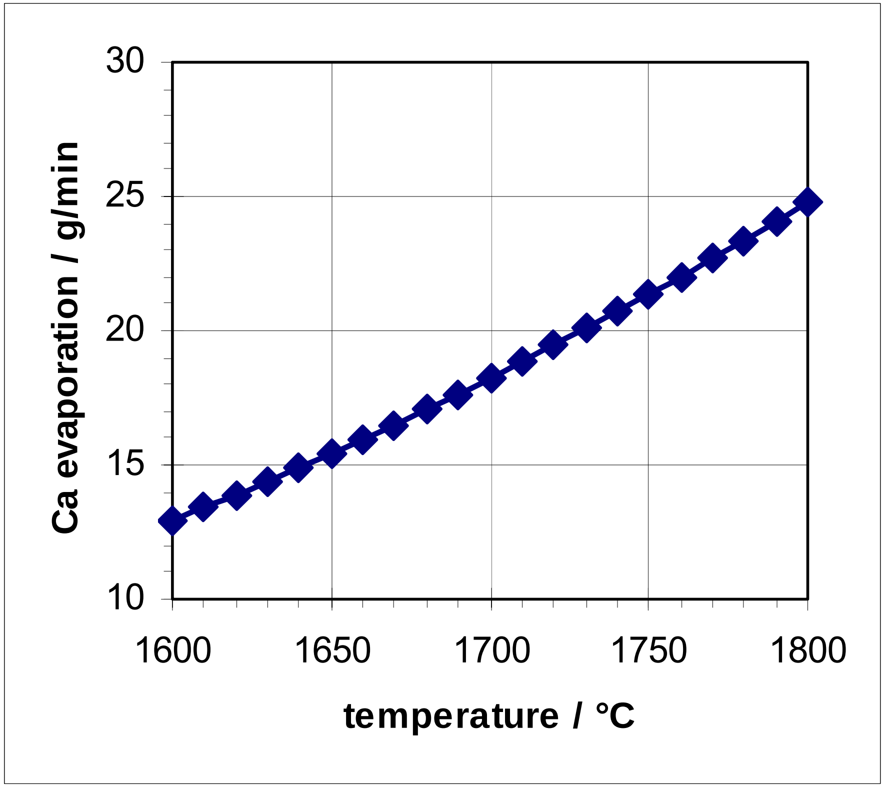
Sherwood's No. (Sh)

# Kinetic of the mass transport in the gas phase II

Example:

- $T_m$ = 100 °C
- → $\mu_{Argon}$ = 2,7x$10^{-5}$ ... 2,8x$10^{-5}$ Pa s (1 ... 50 bar)
- → $\nu_{Argon}$ = 2x$10^{-5}$ ... 4,3x$10^{-7}$ m²/s (1 ... 50 bar)



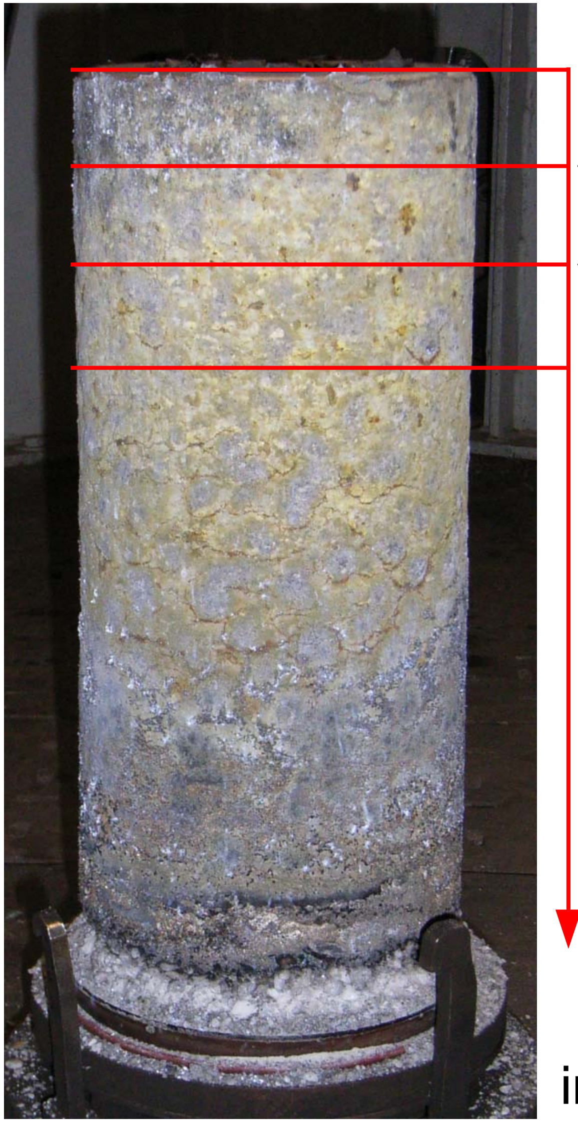



# Experimental examination

- 5 electrodes:
  - material: St 37
  - diameter: 100 mm
  - length: 1000 mm
- slag system:
  - 95 % $CaF_2$-slag (Wacker 2052, > 97% $CaF_2$, 1,2 % CaO)
  - 5 % Ca-metal
- shielding gas: Argon
- pressure: +1, +3, +7, +15 and +40 bar (over pressure).
- pressure increase during melting due to furnace temperature, blow off all 5 minutes
- side experiment:
  - temperature measurement with fibre optics and IR-pyrometer

# Experimental examination - results

# Experimental examination – evaluation I



0

5cm

34cm

rate

51cm

0

melting rate

70 min

0 min

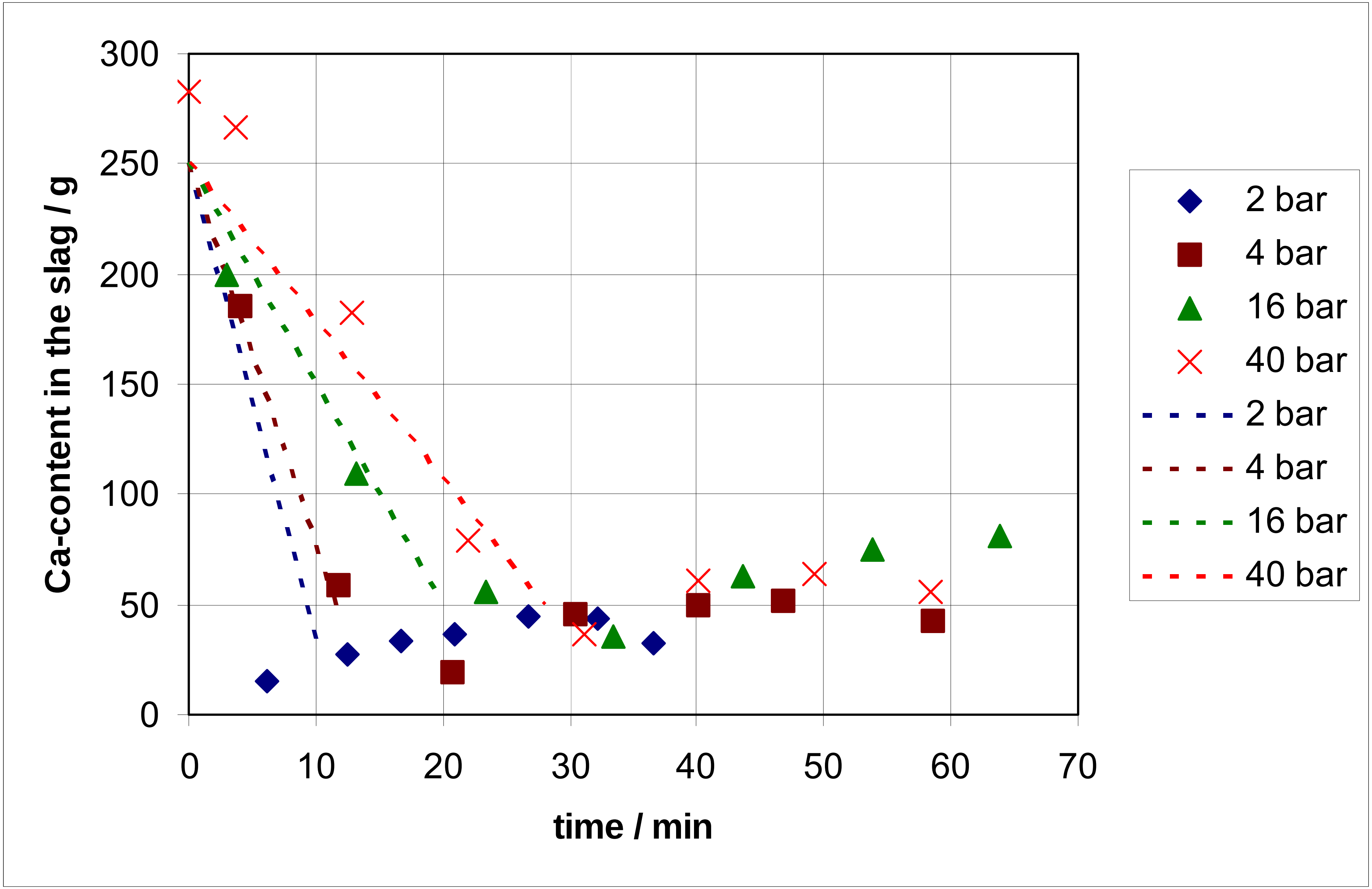
sample V03

t=25min

c(Ca)=3,3%

ingot ⇨ electrode ⇨ melting time

# Experimental examination – evaluation II



# Summary and outlook

## Summary

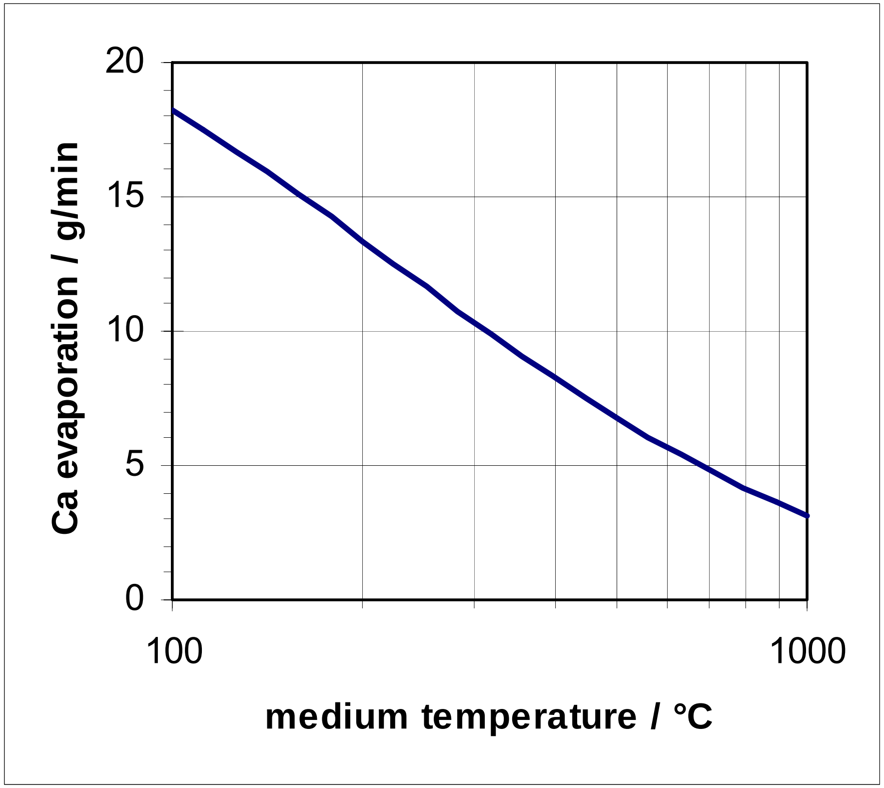
- Instead of the evaporation step (Hertz-Knudsen), the mass transport in the gas phase is relevant for the Ca losses.
- A kinetic model for calculation of the Ca losses was found using the similarity of heat and mass transfer:
  $Nu = f(Gr, Pr) \rightarrow Sh = f(Gr', Sc)$.
- Increased pressure has low influence on the Ca losses (3$^{rd}$ root).

## Outlook

- Isolation of the mould top increases the medium gas temperature and decreases convection and Ca losses,

# Summary and outlook

$$\Delta x = \frac{1}{0{,}15 \cdot \sqrt[3]{\frac{T_S - T_m}{T_m} \cdot \frac{g}{\nu \cdot D_m} \cdot f_2(Sc)}}$$

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## Outlook

- Isolation of the mould top increases the medium gas temperature and decreases convection and Ca losses,
- Transfer of the model into other systems (Al-Mg, Al-Li, Ti-Al, ...).

RWTH AACHEN UNIVERSITY

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DIE METALLURGEN

# Thank you for your attention

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