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The importance of computational thermodynamics in process modeling and control: dephosphorisation as an example

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Content

❖ Dephosphorisation in the converter process: What is known?

❖ why considering a comp. thermodynamics approach?

❖ Simulation results: P distribution in heterogeous slags

❖ Dynamic modeling approach in the BOF DePhos Project

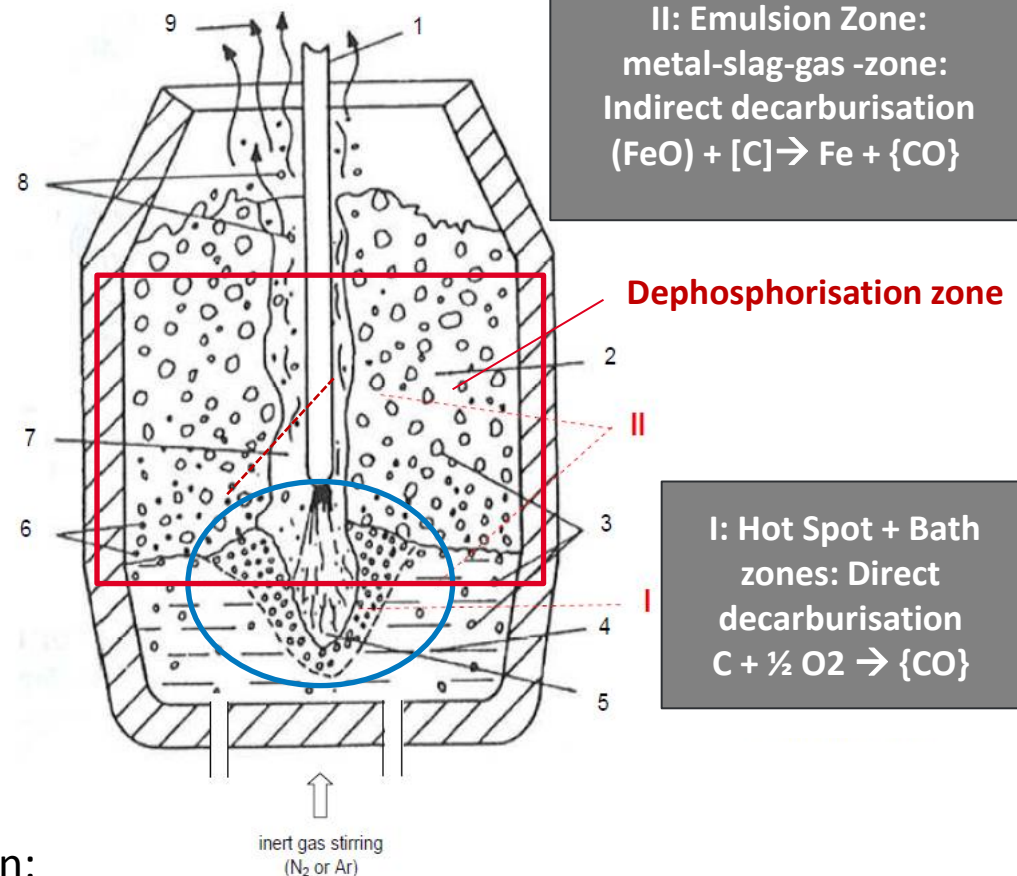❖ Conclusion and future work

Dephosphorisation in the converter process

Introduction

- P in steel should be removed up to a certain ultra low values < 0.01 wt.

❖ Dephosphorisation reaction : metal-slag-reaction

$[P]_{droplet} + (O)\ slag + [O]\ droplet \leftrightarrow (PO_4^{3+})$
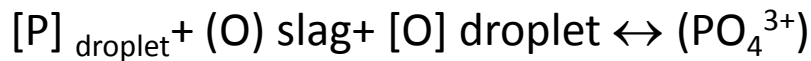
- The converter process is an excellent aggregate for P removal

  ➢ enhanced deP thermodynamics
    - oxidizing conditions
    - basic slag formation
  ➢ enhanced deP reaction kinetics
    - high mixing in bath: oxygen jet impingement + decarburisation reaction
    - droplets generation to the emulsion: ↑ metal-slag interface

II: Emulsion Zone: metal-slag-gas -zone: Indirect decarburisation (FeO) + [C]→ Fe + {CO}

Dephosphorisation zone

I: Hot Spot + Bath zones: Direct decarburisation C + ½ O2 → {CO}

1) Top lance; 2) Foamy slag; 3) CO-bubbles; 4) Bath; 5) Fire spot; 6) Iron droplets; 7) Lance channel; 8) iron droplets; 9) Brown fume

P-Distribution relation (Equilibrium)

➢ **Dephosphorisation reaction**

$$[P] + (O) + [O] \leftrightarrow (PO_4^{3+})$$

➢ **Phosphorus capacity**

$$K_{PO} = \frac{(\%P)}{[\%P]}(\%FeO)^{-2.5}$$ or $$K_{PO} = \frac{(\%P)}{[\%P]}[O]^{-2.5}$$

▪ Example of a P-distribution equations for CaO-FeO-SiO2-MgO-P2O5 (< 5 wt.% P2O5)

❖ Turkdogan 1999

$$\underbrace{\log(\frac{(\%P)}{[\%P]})}_{L_P} = \underbrace{\frac{21740}{T} - 9.87 + 0.071 \cdot \underbrace{((\%CaO) + 0.15 \cdot (\%MgO))}_{BO} + 2.5 \cdot \log(Fe)}_{\log(K_{PO})}$$

➢ Various Lp and KPO relations (Equilibrium) are available in the literature

• Turkdogan 1999	• Suito	• Fruehan 1999	• Healy
• Turkdogan 2004	• Zhang	• Lachmund 2001	• Balajiva
• Fischer	• Ide & Fruehan	• Schürmann 1991	• Basu & Lahiri

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Why computational thermodynamics for P-equilib. study?

Why considering a comp. thermodynamic based approach?
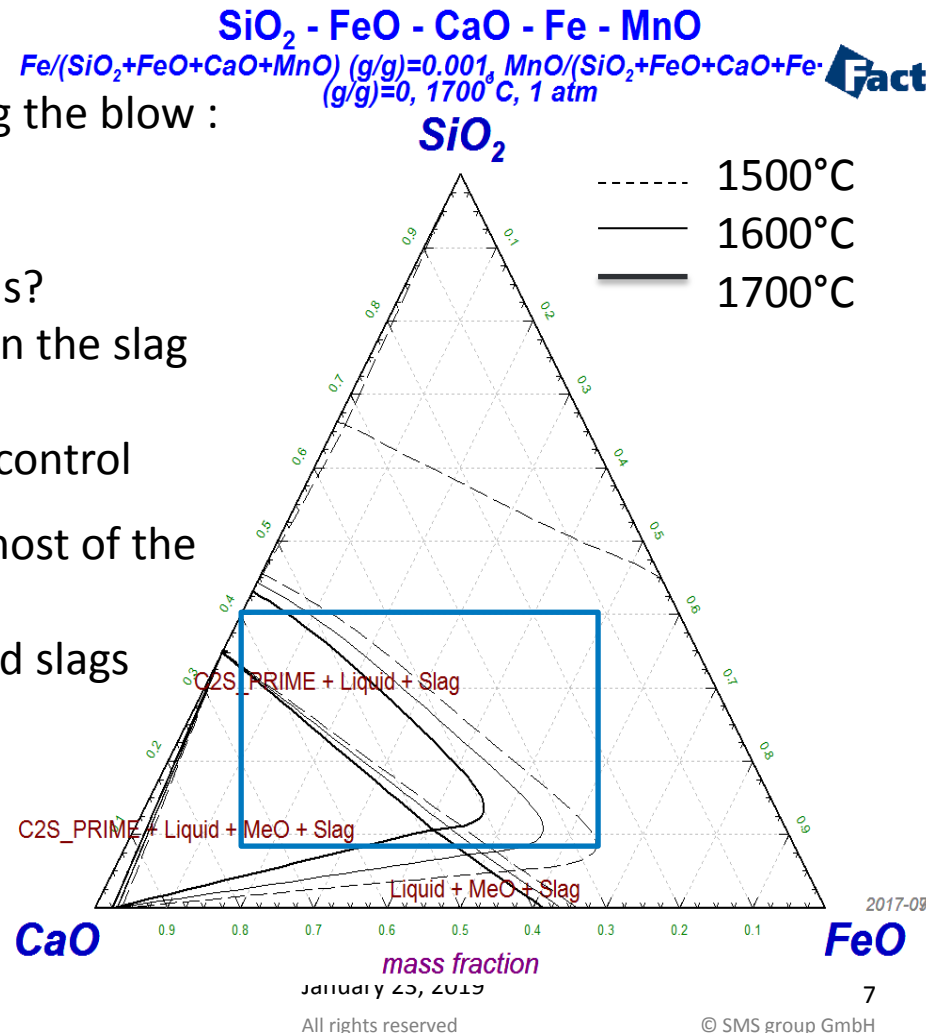
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- P distribution relations were developed at certain experimental conditions
  - slag composition: around lime saturation (considered as target zone)
  - Temperature ranges : 1550°-1600 C°
  → conditions at end of blow

- However:

  - do not cover the tot. variation ranges during the blow :
    – Temp: 1250-1750°C
    – FeO varies between 10-60 wt.%
    → Applicability beyond the exp. conditions?
  - Strong evidence that P end values depend on the slag path CaO-FeO-SiO$_2$ (main system)
  → dynamic modeling required for P end point control

- Converter slags are saturated on C2S during most of the blow, also C3S, monoxide can be present
  – previous relations developed for liquid slags
  – effect of solid phases on Lp?

➡ Modeling P equilibrium (Lp) based on computational thermodynamics approach

SiO$_2$ - FeO - CaO - Fe - MnO
Fe/(SiO$_2$+FeO+CaO+MnO) (g/g)=0.001, MnO/(SiO$_2$+FeO+CaO+Fe· (g/g)=0, 1700°C, 1 atm

------- 1500°C
——— 1600°C
━━━ 1700°C

SiO$_2$

C2S_PRIME + Liquid + Slag

C2S_PRIME + Liquid + MeO + Slag

Liquid + MeO + Slag

CaO 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 *FeO*

mass fraction

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7

Simulation results

Effect of C2S phase on Lp equilibrium

- ➢ illimited solubility of P in C2S
    - C2S →C2S_C3P in the presence of (P2O5) in the slag
    - complete replacement of SiO4- anion by the P3O4+ possible

- ❖ Conclusion:

- ▪ thermodynamically, the C2S phase has a high potential of dissolving P in oxygen steelmaking pocesses!
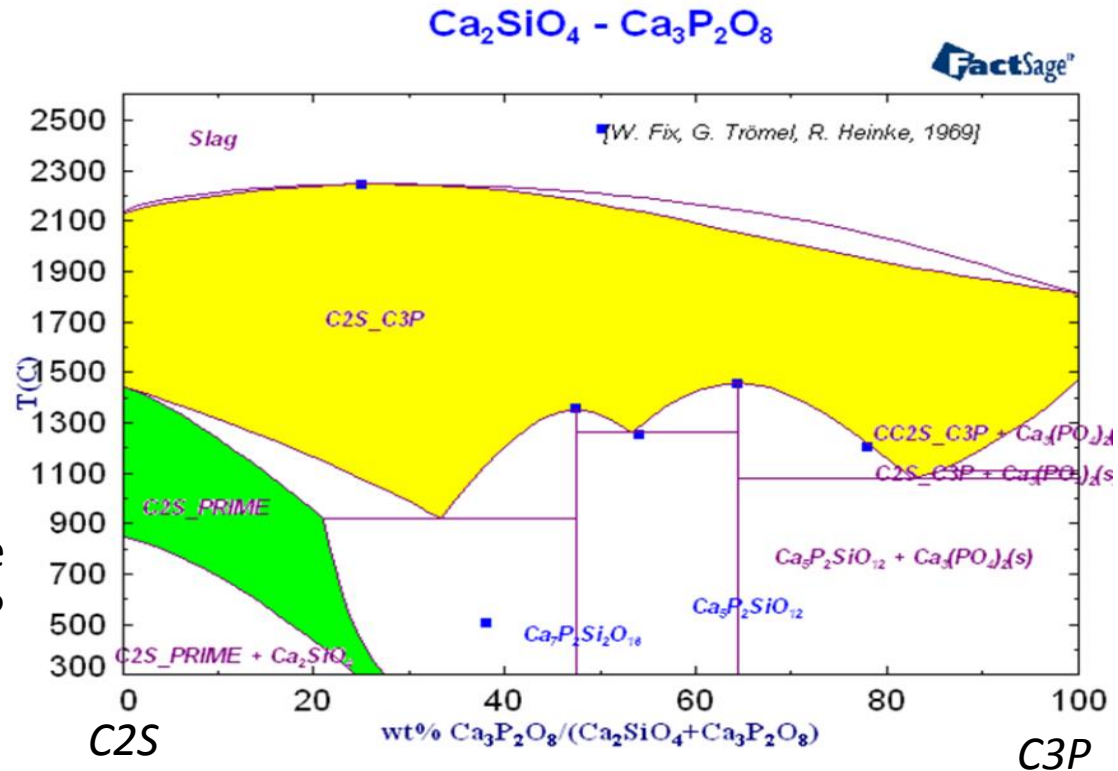
C2S: Ca2SiO4
C3P: Ca3P2O8
C2S_C3P: phases
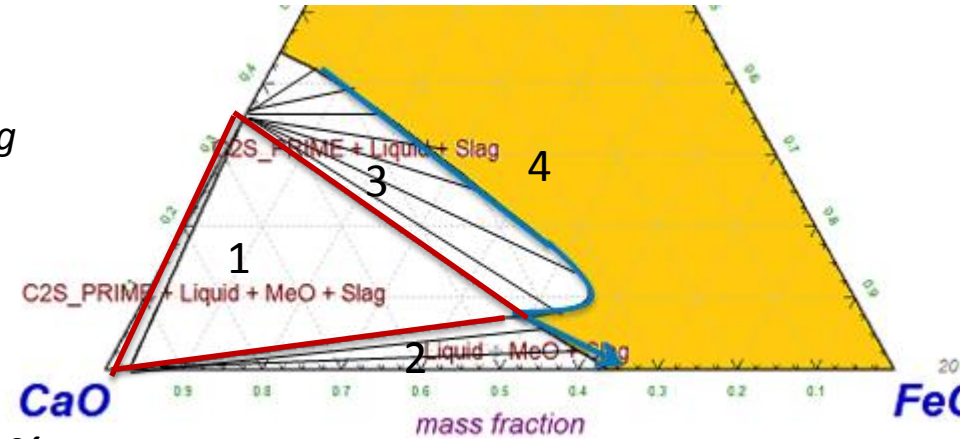
Phosphorus distribution modeling for Converter slags (1)

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➢ P-distribution in **multi-phase-slag**

Lp_tot= (%P) mps/[%P]   *mps: multi-phase-slag*

➢ Simulation results: BOF DePhos database:

▪ P-distribution in **Zone 1** and **Zone 3**
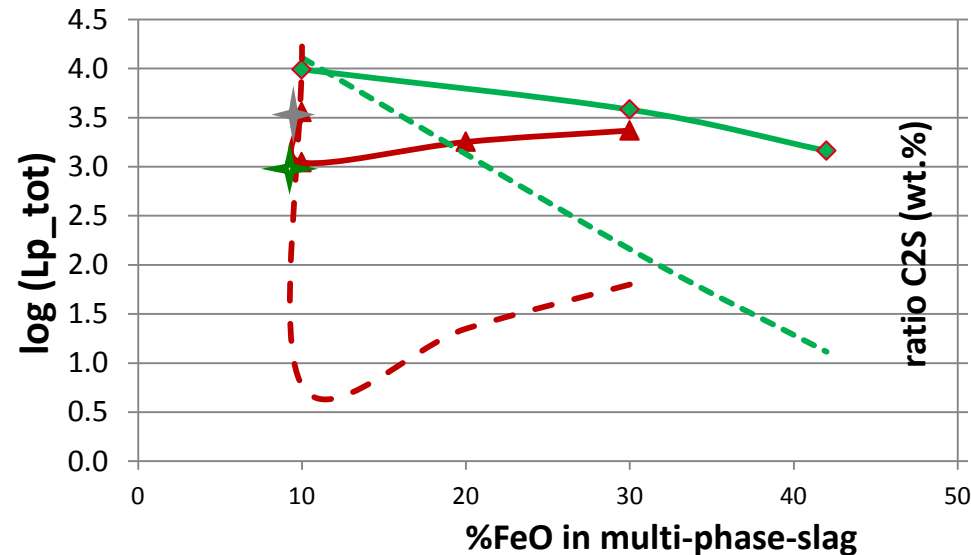
Lp_tot Vs. FeO at Temp. : 1600°C, P2O5: 2 wt.%

➢ Lp_tot in C_2S-saturated slags:

- mainly a function of the C_2S wt.%
- very high : > 1000
- Lp (Zone 3) > Lp (Zone1)

→ reconsider target zone for end of blow?

- cannot be expressed in terms of multi-phase-slag composition (FeO, basicity…)

  ○ applicability of exp. relations for liq. slags?

Phosphorus distribution modeling for Converter slags (2)

➢ **Experimental observations of Suito et al. [ISIJ 2006]**

- P-distribution between C2S (meso-phase) and liquid slag phase (1560°C)

  - strong function of C2S/liquid phase ratios
  - experimental max ≈ 1000, at 30 wt.% C2S
    → much lower than theoretical values (> 5000)

  - Lp increased by 80% in case of stirring

- Exp. values are much higher than the exp. values given in the previous Lp-relations (Turkdogan, …)
    - relations are not applicable for C2S-saturated slags
    - can only be applied for liquid slags and/or liquid slag part

- investigated P distribution between C2S and liquid slag: Lp_slag
  - depends mainly on (%SiO2)

➢ What is the industrial limit for Lp_tot and at which C2S ratio?

Effect of Stirring

Lp = 1260
Lp= 680

ratio C2S/liquid
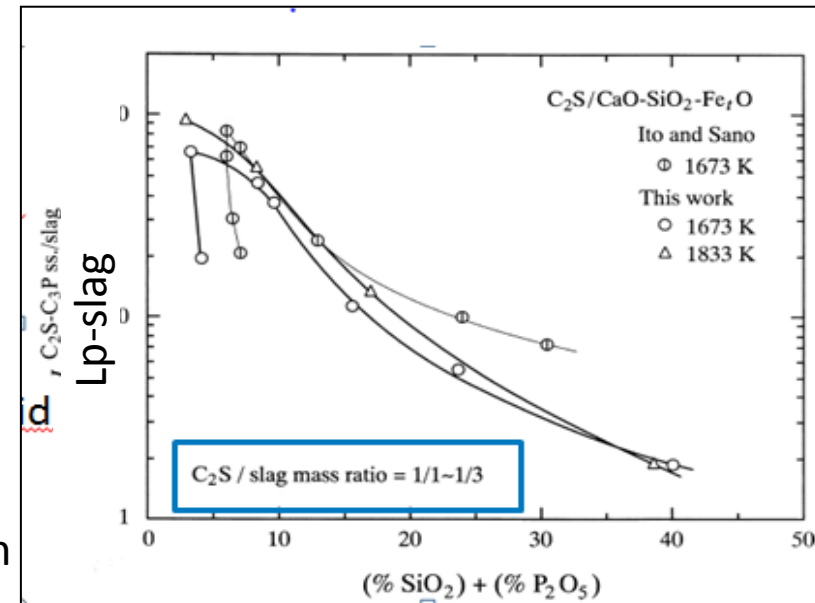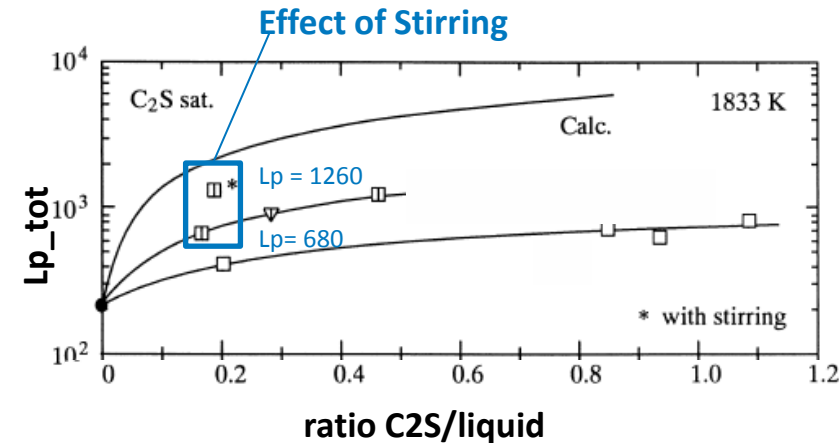
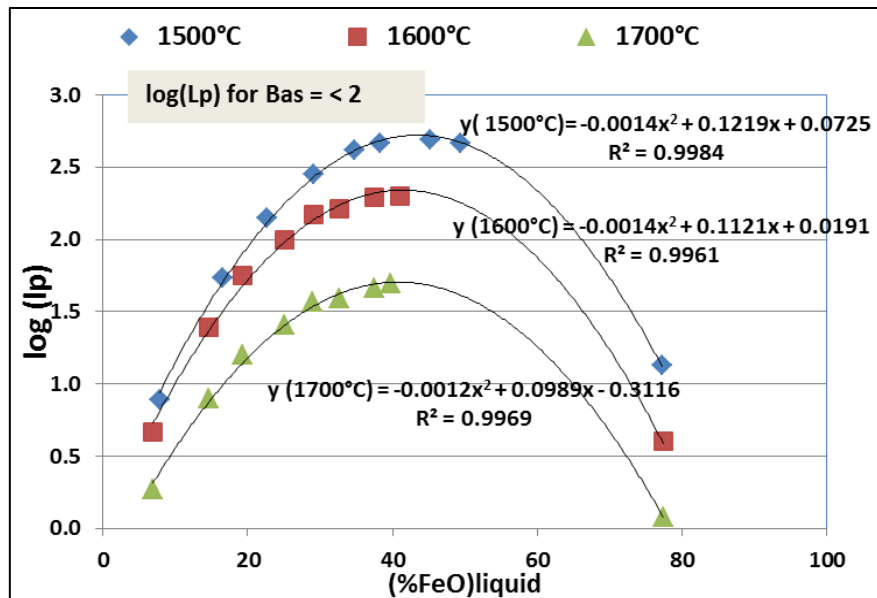# Phosphorus distribution modeling for Converter slags (3)

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❖ Adapted Lp approach

➢ P-distribution in between metal and a **multi-phase-slag**

Lp_tot = Lp_liquid (1 + Lp_slag*W)/(1 + W))

- Lp_slag: P distribution between C2S and liquid slag part: (Experimental findings [Ito,Suito])
- W: ratio C2S /liq_slag; Lp_liquid = (%P) slag/[%P]metal (thermodynamic simulations)

■ Results of Lp modeling in <u>liquid slag</u> for a wide range of compositions and temperature

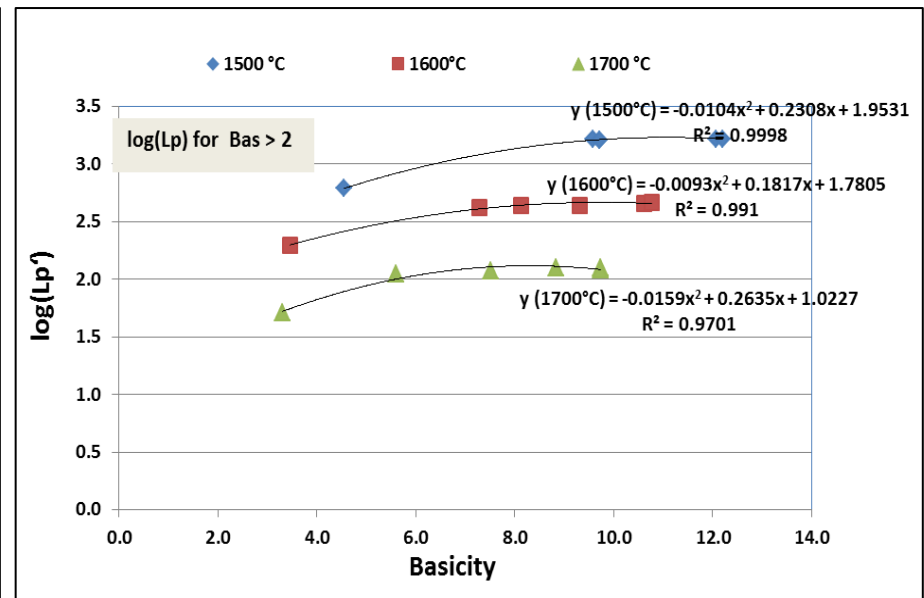I) liquid slags with basicity < 2

Lp_liquid = f(Fe$_t$O,Temp)

II) liquid slags with basicity > 2

Lp_liquid = f(Bas,Temp)

Left chart:
◆ 1500°C   ■ 1600°C   ▲ 1700°C

log(Lp) for Bas = < 2

$y(1500°C) = -0.0014x^2 + 0.1219x + 0.0725$
$R^2 = 0.9984$

$y(1600°C) = -0.0014x^2 + 0.1121x + 0.0191$
$R^2 = 0.9961$

$y(1700°C) = -0.0012x^2 + 0.0989x - 0.3116$
$R^2 = 0.9969$

y-axis: log (lp); x-axis: (%FeO)liquid

Right chart:
◆ 1500 °C   ■ 1600°C   ▲ 1700 °C

log(Lp) for Bas > 2

$y(1500°C) = -0.0104x^2 + 0.2308x + 1.9531$
$R^2 = 0.9998$

$y(1600°C) = -0.0093x^2 + 0.1817x + 1.7805$
$R^2 = 0.991$

$y(1700°C) = -0.0159x^2 + 0.2635x + 1.0227$
$R^2 = 0.9701$

y-axis: log(Lp'); x-axis: Basicity

**Is the C2S_C3P phase behind unexplained discrepancies?**

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- Early laboratory studies of P-distribution in the CaO-FeO-P2O5-SiO$_2$ slags (high P system) :

  ➢ [%P] Equilibrium values > = 0.02 over the total comp. range

  ≠ LD-AC process: [%P] values as low as 0.004 wt.% were found in droplets!

  → absence of mixing in equilib studies (majority) : no P-enrichement of C$_2$S

  ➢ for (%FeO) contents > 15-20% no longer contribute to lowering [%P]

  ≠ real plant observations!

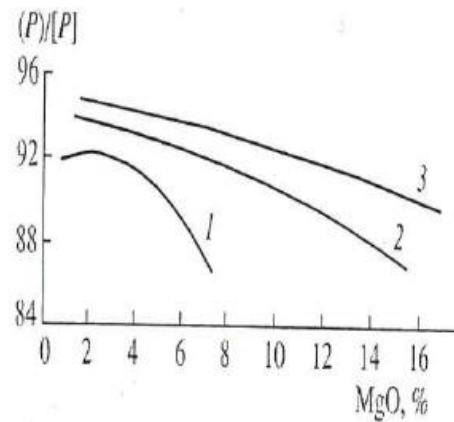 → high (%FeO)-content in the slag increases LP_slag (between liquid slag and C$_2$S_C3P ss.)

[%P] > 0.015 wt

[%P] equilib
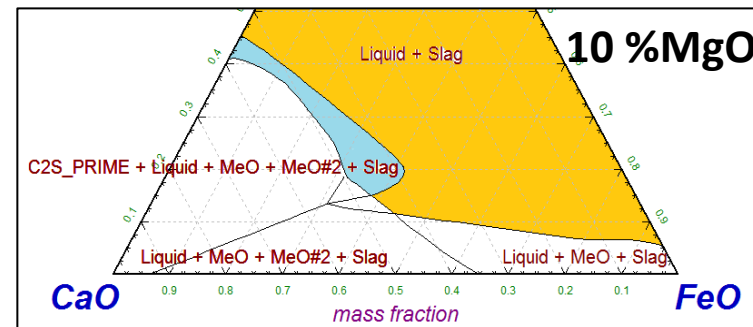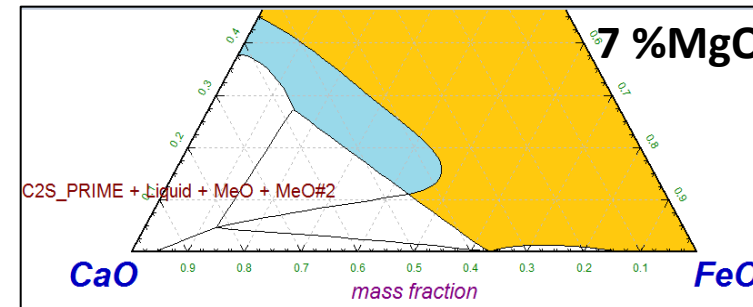
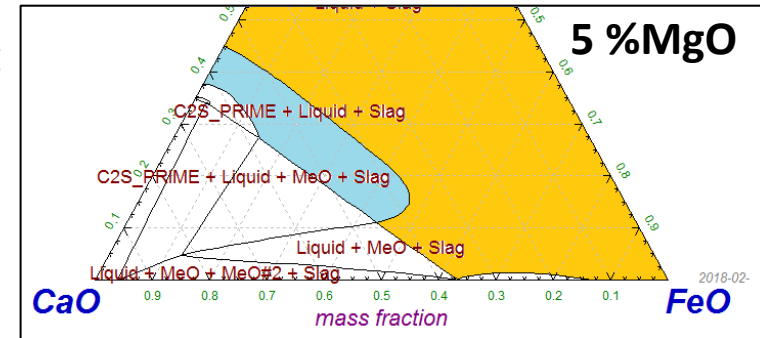**(%P2O5)**
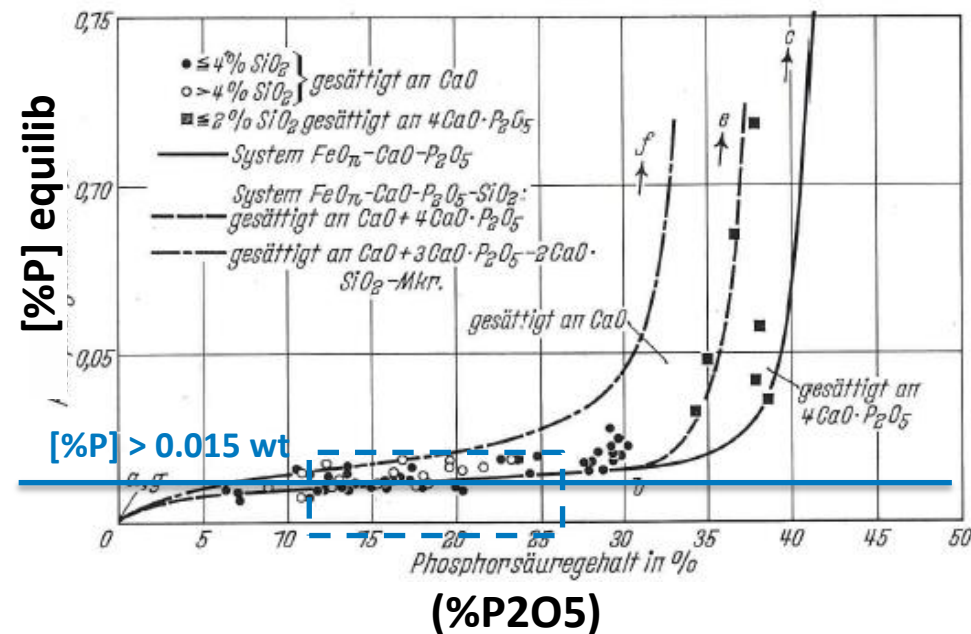
Low P system

- Equilib studies in the CaO-FeO-SiO$_2$ (Low-P-System)
  - ➤ (%MgO) has a positive effect
  - ≠ some Plant observations: MgO has negative effect
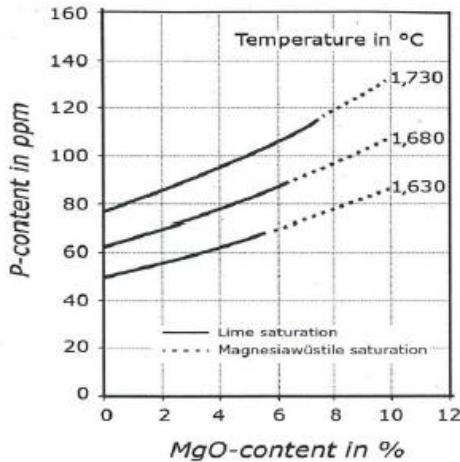
Lachmund, et al, 2007

Mittal USA/Kazakhstan 2007

- Results of thermochemical simulations:
  - MgO addition leads to
    - ○ ↓ C2S-amount ⟹ ↓ Lp_tot
    - ○ ↑ monoxide phase

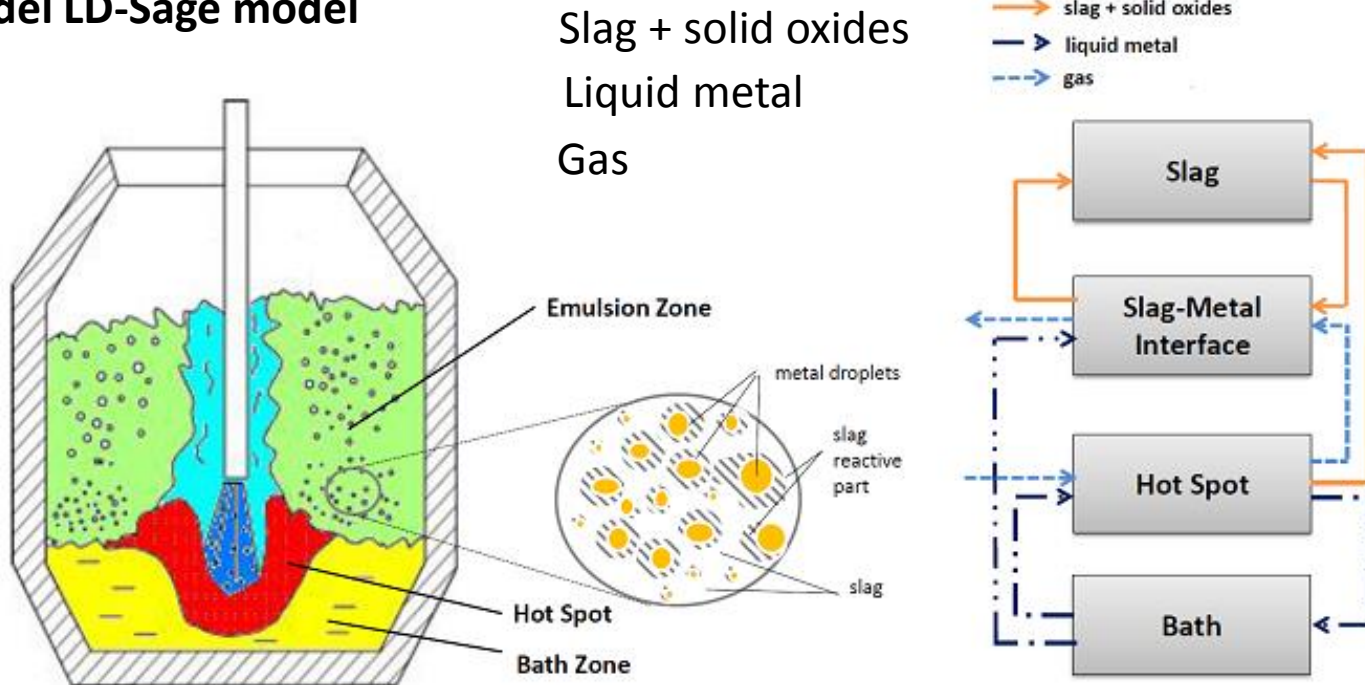# Considered dynamic modeling approach

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- **1. dynamic converter model: LD-Sage (GTT/SMS)**

➤ **Principal of interlinked local-equilibria**

- local equilibria in the reaction zone : integration of BOF DePhos thermochemical database
- using SimuSage-Software

➤ **4 Zone model LD-Sage model**

Slag + solid oxides
Liquid metal
Gas

➤ **Consideration of kinetic aspects (independently developed)**

- circulation rate : based on CFD approach = f (dynamic practice data, lance height, flow rate, stirring rate…)
- Lime dissolution rate: Experimental investigations (KTH)
- residence time of droplets in the emulsion

- **2. dynamic model: SMS Kinetic model (internal)**

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- Simplified sequence of kinetic dephosphorisation calculation in the BOF Design Model for a time step Δt

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Conclusion

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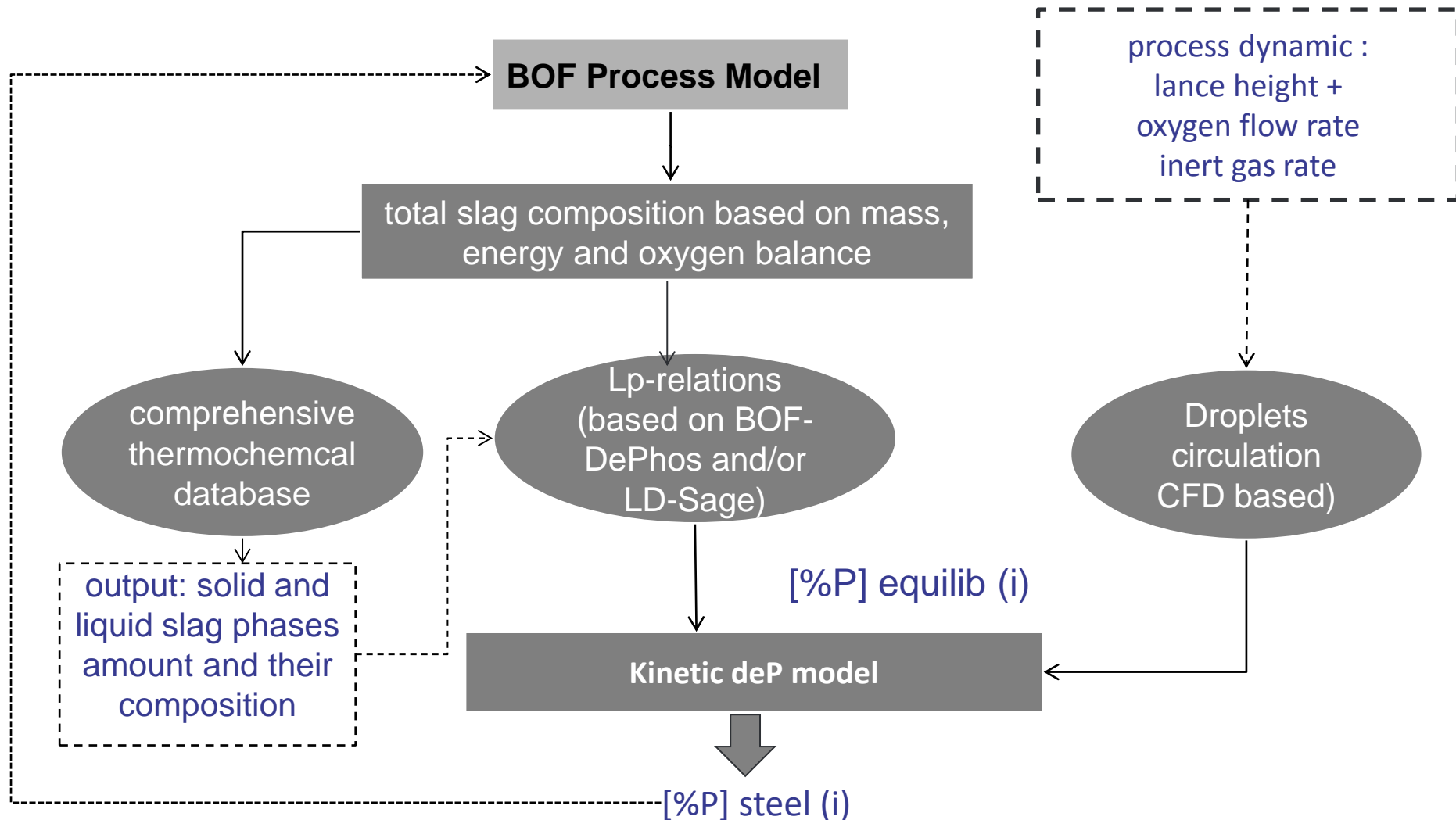
Conclusion/Outlook

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- Converter slags are heterogenous during the blow and , under certain conditions, also at the end of blow
  - saturated on C_2S, or
  - double saturated on C_2S and CaO-ss
- a general relation relating Lp and heterogenous slag composition could not be established:
  - determination of solid and liquid slag phases + their composition essential
  - developement of P distribution relations seperately for :
    - between metal and liquid slag ✓
    - between liquid slag and solid phases : industrial trials required
    - → Lp between multi-phase-slag and liquid metal
- The C_2S-phase plays an important role in dephosphorisation
  - for both high + low P systems
  - P distribution values > 1000 are achievable
  - confirmed by several industrial findings
  - Study of enrichement process of this phase required
    - laboratory scale: effect of stirring, foaming…
    - industrial plant trials
    - → subject of future investigations