Looking for future solutions by digging into the past:

How computational thermochemistry helps us solve old industrial mysteries

Sabrine Khadhraoui [1], Klaus Hack [2], Tatjana Jantzen [2]

[1] SMS group GmbH, Germany

[2] GTT Technologies, Germany

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1. The past, present and future situation for phosphorus (1)

➢ Phosphorus is a harmful element for steel

- reduces ist ductility and thoughness
- must be removed from the liquid iron by oxidation, up to a value of [0.007-0.01] wt%

➢ Past: back in the 1960s and 1970s, German (and also French) steelworks used local iron ores

- were caracterized by a high P-content in the range 1-1.6%
- target P in steel can only be achieved with a double slag strategy: 2 step refining with an intermediate deslagging

➢ Present: In Germany, the iron ores used for producing steel are imported, mainly from Brasil

- which were caracterised by a low P-content 0.07-0.1 wt%
- considered low compared to other regions, such as Japanese and Indian steel works, where the initial [%P] content of the ores is in the range of 0.15 wt%

1. The past, present and future situation for phosphorus (2)

➢ Future: An increasing trend for (initial) P-content in hot metal

- ▪ due to tendency to mine low-grade iron ores (high P-content) instead of high-grade (low P) iron ores.

- ▪ an increase in initial P in hot metal up to 0.15-0.25 wt% may be possible in the future.

- ▪ will European steelworks have to adapt the double slag practice similar to Japanese and Indien steelworks?

- ▪ "Green steel": A transition from C-based to an H_2-based reduction processes will not improve the situation with respect to P-removal

  - o may drive the tendency to use low-grade iron ores further

  - o The double slag practice (in its current version) can no longer be implemented in such a case

    - • The high P removal rates are achieved by setting a low process temperature:1250°C-1450°C .

    - • The temperature of hot metal produced from C-based reduction is in the range 1200-1350 °C

    - • However, hot metal from a C-free reduction must be processed at T>1536°C

  ⇨ We need to develop new solutions for an effective P removal in the future

2. Computational thermochemistry

➢ Development of a thermodynamic database

- ▪ based on the CALPHAD-approach
- ▪ using the thermodynamic computing software FactSage™

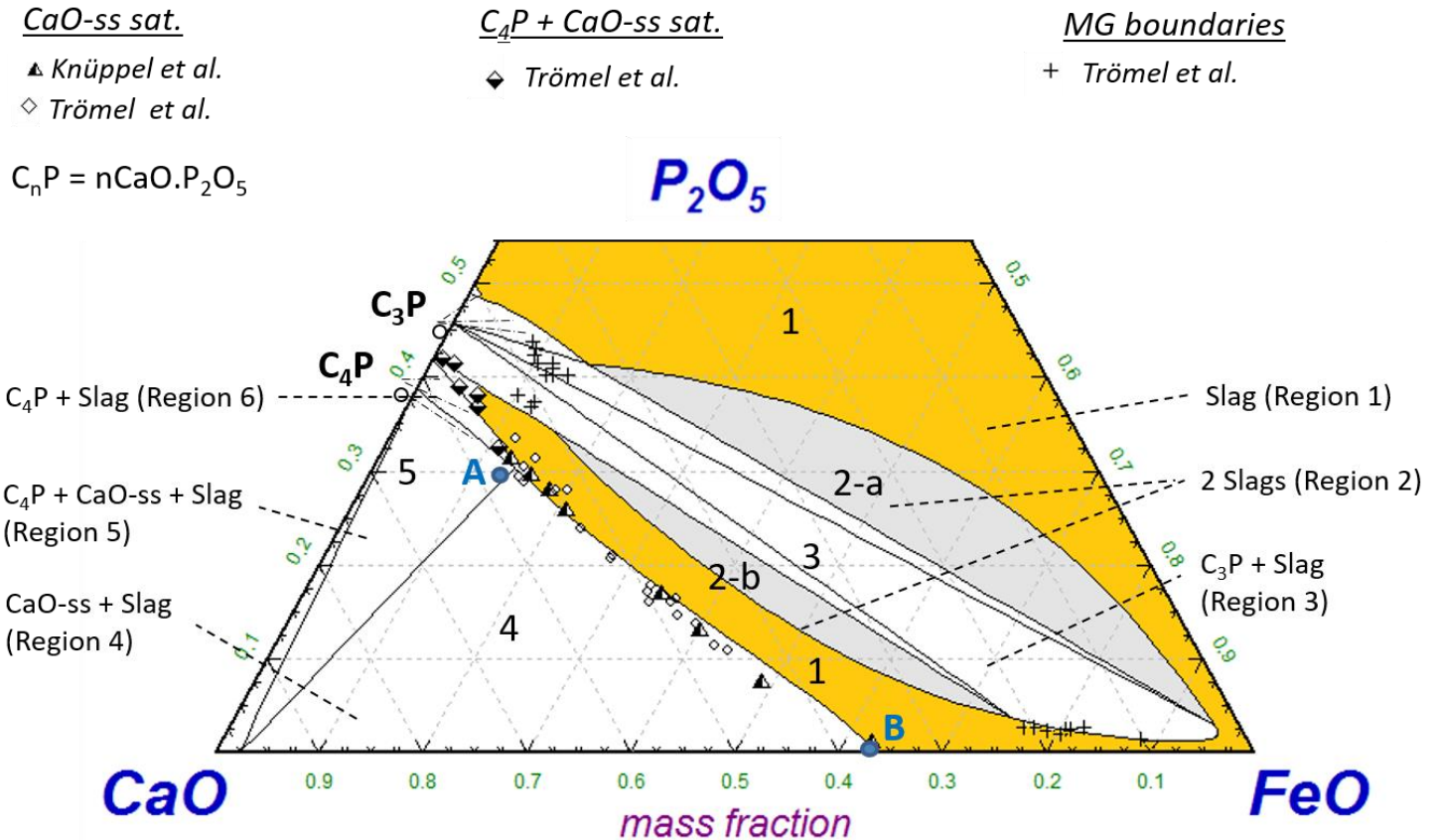| Phases	Gibbs energy model
Liquid oxide	non-ideal associate solution model
Solid solutions	Compound Energy Formalism
Stoichiometric compounds	a temperature dependent equation

➢ Why CALPHAD ?

- ▪ due to its capability of extrapolating from:
  - • known systems: for which experimental data are available (past)
  - • to model the thermochemical behavior of new systems, for which complete sets of data are missing (present + future)

➢ We can use this approach to evaluate and reflect back on past industrial practices

- • there is a (relatively) large amount of experimental and industrial data for high phosphorus slags .
- • May be we can gain valuable information to improve the present and future practices?

➢ Calculated system's boundaries at reduced $p(O_2)$ (in equilibrium with liquid Fe) and 1873 K (1600°C)

- a large number of experimental data, describing the lime saturation line available → considered as the „target region" in the industrial process.

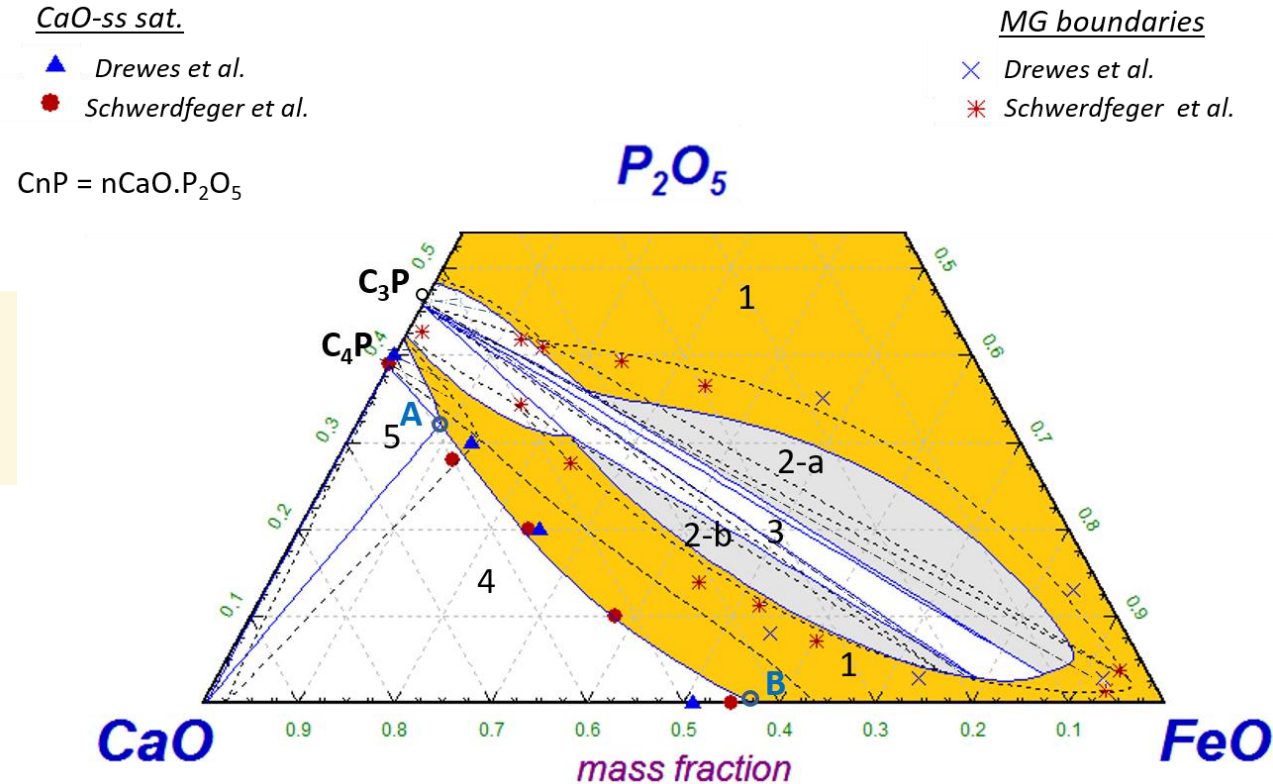→ the agreement between calculated lime saturation line and the experimental data is very good.

CaO-ss sat.
▲ Knüppel et al.
◇ Trömel et al.

$C_nP = nCaO.P_2O_5$

_C_4P + CaO-ss sat._
◆ Trömel et al.

MG boundaries
+ Trömel et al.

C_3P
C_4P
C_4P + Slag (Region 6)
C_4P + CaO-ss + Slag (Region 5)
CaO-ss + Slag (Region 4)

Slag (Region 1)
2 Slags (Region 2)
C_3P + Slag (Region 3)

P_2O_5

CaO — mass fraction — FeO

➢ Calculated system's boundaries at elevated $p(O_2)$ and 1873 K (1600°C)

▪ an increase in the Fe_2O_3/FeO ratio is found to have a tremendous effect on the system !

- • ↑ CaO-saturation of the slag by about 3-8 wt%
- • expansion of the liquid slag region
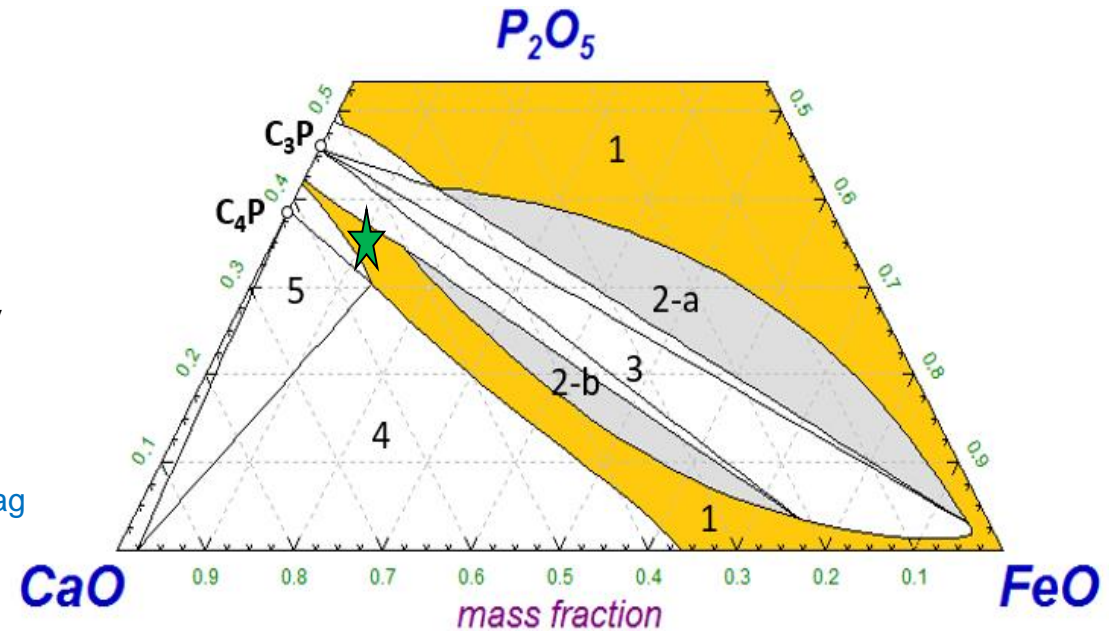- → more flexibility in achieving a fully liquid slag.
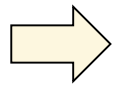
The importance of using CALPHAD-based approaches: New information about the behavior of (well-established) ternary systems gained.

CaO-ss sat.
- ▲ *Drewes et al.*
- ● *Schwerdfeger et al.*

MG boundaries
- × *Drewes et al.*
- ✳ *Schwerdfeger et al.*

$CnP = nCaO.P_2O_5$

S. Khadhraoui, K. Hack, T. Jantzen, H.-J. Odenthal: Study of the State of Industrial P_2O_5-Containing Slags Relevant to Steelmaking slags (…), Steel research international (2019) 1900085.

3. Re-examining an industrial mystery with respect to P-equilibrium (1)

- In a series of <u>independent</u> plant trials:
  - inexplicably low [%P] ~ 0.007 wt% were measured in metallic droplets (granules embedded in slag samples)
  - the samples had a low $(\%FeO)_x$ content ~ 10 wt%.
- Why were those observations considered controversial:
  1. the fundamentals of deP: a high $[O]_{metal}$ is a necessary condition:

      - $[P]_{metal} + 5/2\ [O]_{metal} + 3/2\ (O^{2-})_{slag} \leftrightarrow (PO_4^{3-})_{slag}$

      $[O]_{metal} = f((\%FeO), Temperature)$

  2. laboratory P-equilibrium studies reported that the minimum of [%P] equilibrium ~ 0.02 wt%!

- Let us re-investigate this <u>old</u> case using our <u>new</u> thermodynamic database!

1. Why was P-oxidation possible at low FeO_x?

- The studies reported that the samples contained 7-10 wt% SiO_2

- Consider the quaternary phase diagram at 10 % SiO_2

  - the samples were saturated with C2S_C3P $(2CaO.SiO_2\_3.CaO.P_2O_5)$
  - the liquid slag part has a high $FeO_x > 50\%$ independently of the total FeO_x-content of the „heterogeneous" slag!

    → high $[O]_i$ established between metal droplets and the liquid slag part !
    → progress of the P-oxidation reaction

- 10% SiO_2, 1873 K

4': liquid + C2S_C3P + CaO-ss   4': liquid + C2S_C3P
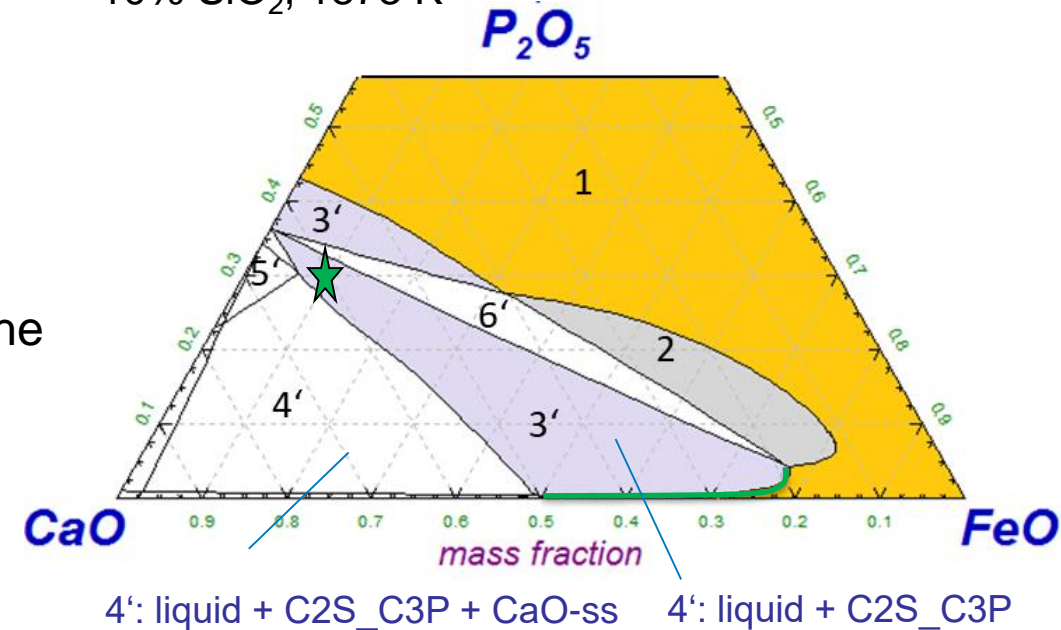
2. How can [P] < [%P] equilibrium?

- The laboratory studies were carried out in fully liquid slags (zone 1 in ternary system)

  → Transferribility of those studies for describing the equilibrium state in C2S_C3P saturated slags?

- Our calculations indicated that this solid phase has a great potential for removing phosphorus:

  → C2S_C3P sat. shifts the [%P]-equilibrium to much lower values (as low was 0.004 wt%).

  → this industrial „mystery" can be considered as an evidence for the P-removal potential of this phase

4. Conclusion

➢ Computational Thermochemistry helps us learn from the past in a way that:

▪ we use old experimental data in the developement and optimization of thermodynamic databases

▪ it provides a reliable method for extrapolating from those optimized systems to new systems relevant for the present and the future situation

→ significant reduction of the experimental and industrial effort.

▪ we can be use it to re-evaluate and reflect back on previous industrial practices, explain past controversies and learn something for the future.