

BOFdePhos II

Slag formation in the BOF converter process: Thermochemical and experimental Findings

GTT User Meeting– 28.06.2017, Herzogenrath

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Objective of the BOF Dephos project

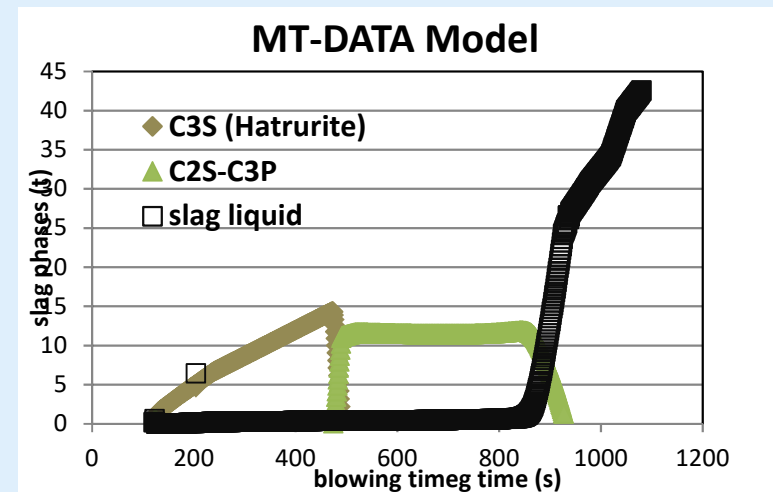
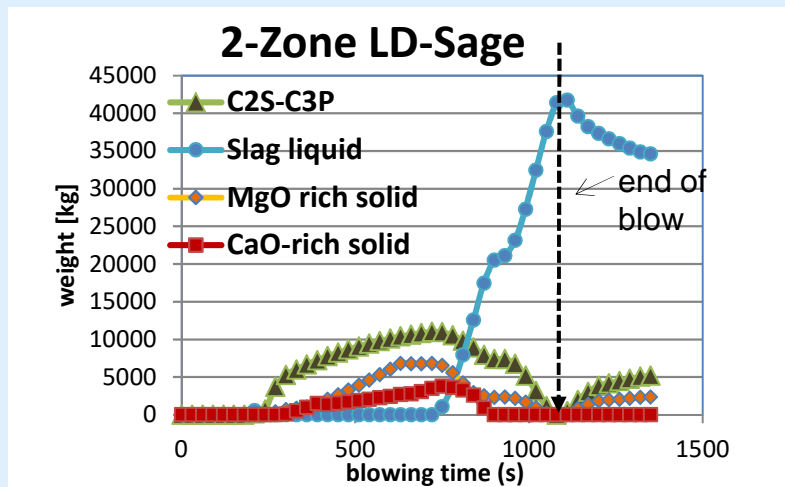
- Enhancement of dynamic on-line models for an optimized BOF end-point control
 - with focus on dephosphorisation
 - by means of
 - comprehensive thermochemical data base
 - detailed multi-zone reaction models
 - laboratory experiments relevant to dephosphorisation reaction
 - CFD Model investigation of flow fields
 - Validation of the results based on BOF process data from
 - Port Talbot plant
 - IJmuiden plant

Multi-Zone-Models

- 2 Models based on interlinked local equilibria

| Multi-Zone-Models | LD-Sage | MT-Data |
|-------------------------------|--|---------------------------------|
| Developer | GTT/SMS | Tata Steel |
| Therm. data base | FactSage (GTT) | MT-DATA (NPL) |
| Number of zones (Status 2016) | 2-3: bath + slag-metal + (optional) hot spot | 3: bath + slag-metal + hot spot |

- Slag formation according to Models : absence of liquid slag until middle of the blow



The liquid slag issue: slag-metal equilibrium

- (FeO) formation begins only when [%C] drops to a certain level
 - 1 % in case of LD-Sage
 - 0.2% in case of MT-Data
- intensive BOF DePHOS data base review (master thesis) → consistency of data base

Investigation of (%FeO)-[%C] equilibrium

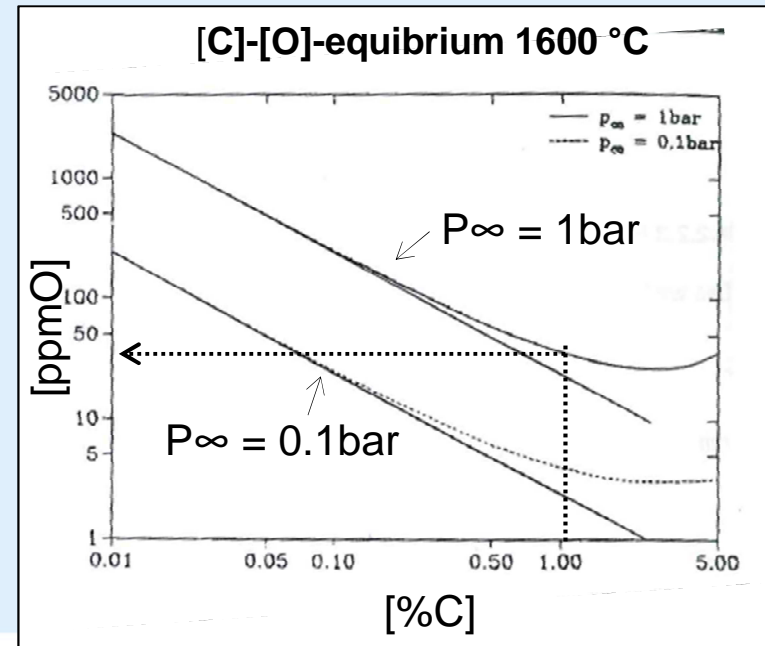
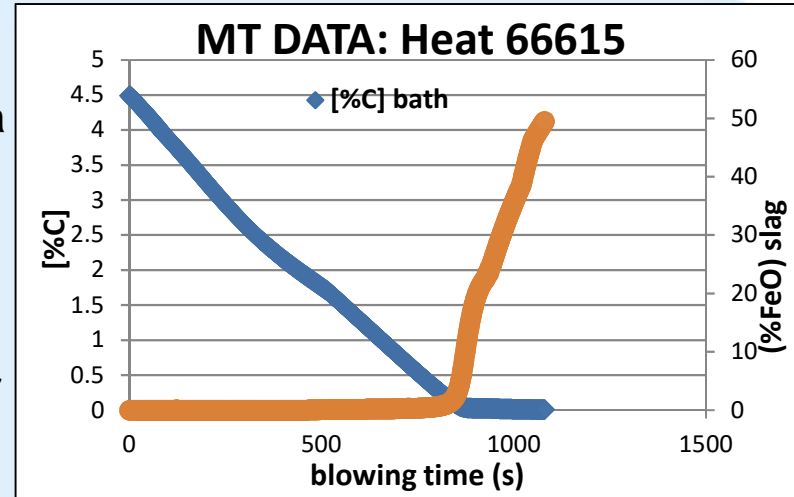
(%FeO)-[O] equilib:

$$a_{(FeO)} = \frac{[O]_{actual}}{[O]_{max}}$$

[C]-[O] equilib:

$$K_{CO} = \frac{P_{CO}}{[%C]_{eob} [%O]_{eob}}$$

- no to little dissolution of [%O] in bath possible in equilibrium with high [%C]
 - for [%C]=1% ↔ [ppmO]< 50 ppm!
 - no (%FeO) in slag → no liquid slag

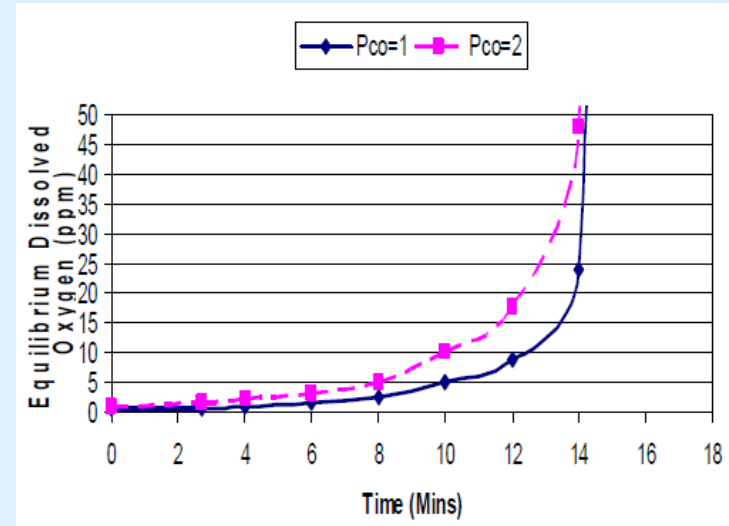


The liquid slag issue: literature overview

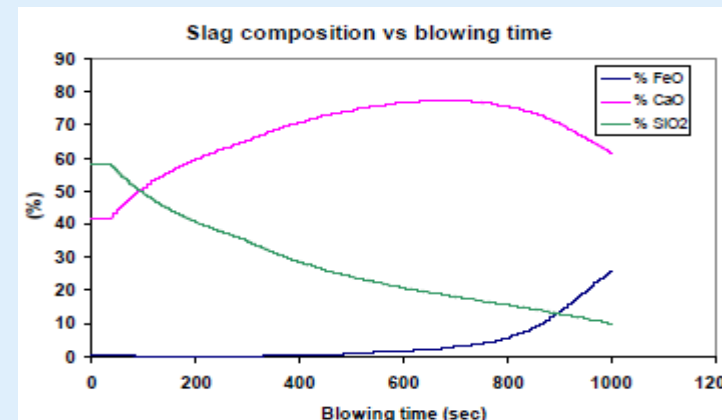
- IMPHOS⁽¹⁾ project: calculation with FactSage
 - no dissolution of oxygen possible in the bath until middle of the blow
 - no relevant improvement through $\uparrow P_{CO}$
 - slag equil. calculated without reference to liquid metal phase

„although the slag has a direct association with hot metal/liquid steel, thermodynamic analysis will not allow a slag phase with such high proportions of FeO to be in equil. with hot metal chemistry “

- DeO⁽²⁾: calculation with FactSage
 - slag phases during the blow for BOF converter
 - no (%FeO) in slag until middle of blow



IMPHOS⁽¹⁾ : [O] equil. calc. by FACTSAGE



DeO⁽²⁾ : slag phases calc.by FACTSAGE

(1) RFSR-CT-2006-00006; Improving Phosphorus Refining (IMPHOS); 12/2009

(2) DeO,B.; 5th International Congress on the Science and Technology of Steelmaking ; Dresden, 1. – 3. Oct. 2012

The liquid slag issue : literature overview

➤ calculated (%FeO) early in the blow lower than practice values

• Shukla ⁽³⁾ : deviation from equilibrium at the beginning ➔ due to increased loss of iron to dust

– (FeO) increase from 20% (equilib) to 50% (dynamic)

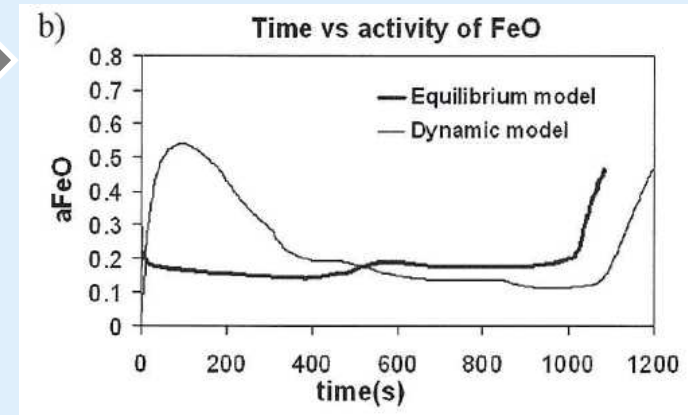
• Brooks ⁽⁴⁾: rapid FeO formation early in the blow hard to explain, possibilities:

– FeO-SiO₂ slag supresses gas removal ➔ provides a kinetic barrier

– *“In the view of the authors, a rigorous experimental study is required to assess this issue”*

➤ Summary: FeO formation early in the blow

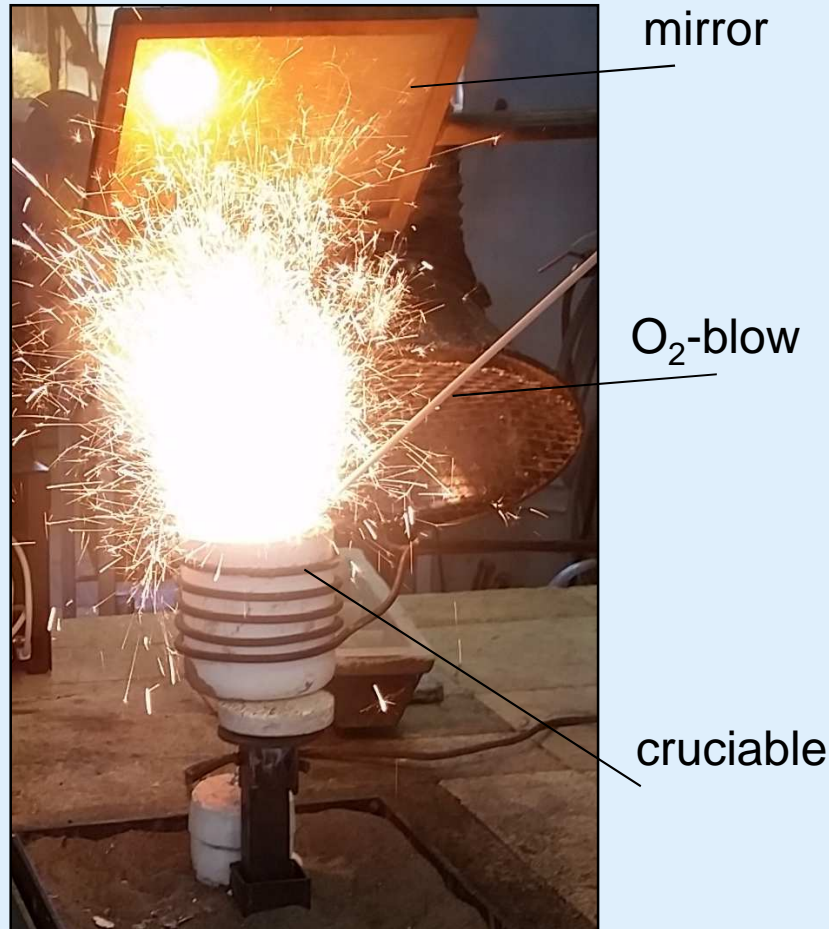
- Significant deviations between thermodynamical and industrial findings
- Laboratory experiments vs. Industrial findings?



(3) Shukla: Steel Research int.10 (2010) ,N°11, p 940-948

(4) Brooks, J; CAMP-ISIJ Vol.28 (2015)-509

Experimental set up



Initiation

- Master thesis at the University of Duisburg-Essen, Department of Metals Technology
- Idea to experimentally investigate the slag formation during O₂-blow

Procedure

O₂-blow of a high and a low C melt

- Fe-C-Si-Mn melt
- initial composition (similar to Heat 66615)
- 1 kg melt at temp 1550 °C
- O₂-blowing rate 2.4 l/min + Blowing time 2 mins (lime input time)
- sampling: bath+ slag
- record experiments by a camera

Videos of the experiments

Low Carbon



V2_2016-11-03_SMS_Low Carbon.mp4 - Verknüpfung.Ink

High Carbon



V1_2016-11-03_SMS_High Carbon.mp4 - Verknüpfung.Ink

■ Observations

- „Dimpling“ blow was observed
- liquid + solid slag formation observed
- braun gas/ dust generation in case of high C melt
- no emulsion or foamy slag formation

Results of the experiments

1. Experiment: Low C melt

- Crucible: Graphite

Sample Analysis (1)

| Bath analysis (wt.-%) | C | Si | Mn |
|-----------------------------------|----------------------|---------------------|-------------|
| initial | 0,13 | 0,76 | 0,63 |
| after 2 mins of blow | 0,22 | 0,18 | 0,17 |
| $\Delta\%$ [element] after 2 mins | -0.09 | 0.58 | 0.46 |
| Slag comp. (wt.-%) | (FeO) _{tot} | (SiO ₂) | (MnO) |
| | 24 | 59 | 17 |

- O₂ mass balance
 - Blown: 6.24 l (blowing time 2.6 mins)
 - consumed: 5.6 l → 90% efficiency
- ~ 0.1% C dissolved from crucible
- ↑ Si- and ↑ Mn- oxidation (fast) at ↓C melt
- formed slag is SiO₂-saturated

2. Experiment: High C melt

- Crucible: Alumina

Sample Analysis (2)

| Bath Analysis (wt.-%) | C | Si | Mn |
|--|----------------------|---------------------|-------------|
| initial | 4,17 | 0,71 | 0,71 |
| after 2 mins of blow | 4,11 | 0,51 | 0,56 |
| $\Delta\%$ [element] after 2 mins | 0.05 | 0.16 | 0.12 |
| Slag comp. (wt.-%) | (FeO) _{tot} | (SiO ₂) | (MnO) |
| Not available: too little to be analysed | | | |

- no slag analysis
 - no mass balance verification possible
- no to little C-oxidation when ↑ Si present
- ↓ Si and ↓ Mn oxidation in high C melts
 - ~ 26% slower than 1.exp
- ↓ formed slag amount compared to 1.exp

Findings

1. Experiment: Low C melt


- very fast Si- and Mn- oxidation although
 - dimpling blow (low mixing energy through top lance) + no inert gas stirring :
→ high diffusion potential of those elements to the reaction site
 - absence of an emulsion: Mn and Si oxidation not necessarily occurring in the emulsion
 - Gibbs energy at 1550°C $\frac{\Delta G_{MnO}^o}{\Delta G_{SiO_2}^o} = 0.82$ in accordance with $\frac{\Delta[\%Mn]}{\Delta[\%Si]} = 0.79$
- Conclusions for last blowing phase (after C critical point)
 - $\uparrow \Delta [\%Mn]$ as high as 0.5% possible during the last 2 mins of blow
→ Mn-reversion during the middle of blow can be fully recovered
 - a high amount of reactive FeO-rich slag can be formed quickly

Findings

2. Experiment: High C melt

■ Effect of \uparrow [%C] in bath

- blocking Fe-oxidation and liquid slag formation
- \downarrow Si- and \downarrow Mn-oxidation rate: $\sim 72\%$ lower as in the 1.experiment
- no to very little C-oxidation \rightarrow what was the braun gas/dust?

 \uparrow [%C] blocks [%O] dissolution in the bath

- in accordance with multi-zone models results (LD-Sage + MT-DATA)
 - no to little slag formation
 - no Mn-removal
 - Si-removal only due C_2S phase formation
- disagrees with the formation \uparrow amounts of liquid slag in industrial process!!!
 - explanation?

- rapid FeO-formation early in the blow in converter process, possibilities:
 - forced [%O] dissolution due to high O₂-jet impact velocity ?
 - O₂-lance in converter: O₂-exit velocity supersonic → expands at ambient furnace temperature
 - ↑ Flow rate 1000 Nm³/min → ↑ Impact velocity in the range of 250-400 m/s ⁽⁵⁾
 - experiment carried out at ↓ flow rate of 2.4 l/min (scaled for 1 kg of melt)
- Next: Further experiments for a high C melt
 - O₂ blow at increased oxygen flow rate: 4 * higher than in previous exp.
 - sampling at different blowing times, for example at 30 s

we will let you know about the results next year!

(5) internal calculations, SMS group