TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG

Die Ressourcenuniversität. Seit 1765.

ZIK Virtuhcon

Thermodynamic modelling of the behaviour of mineral matter in the BGL-gasification process

Stefan Guhl

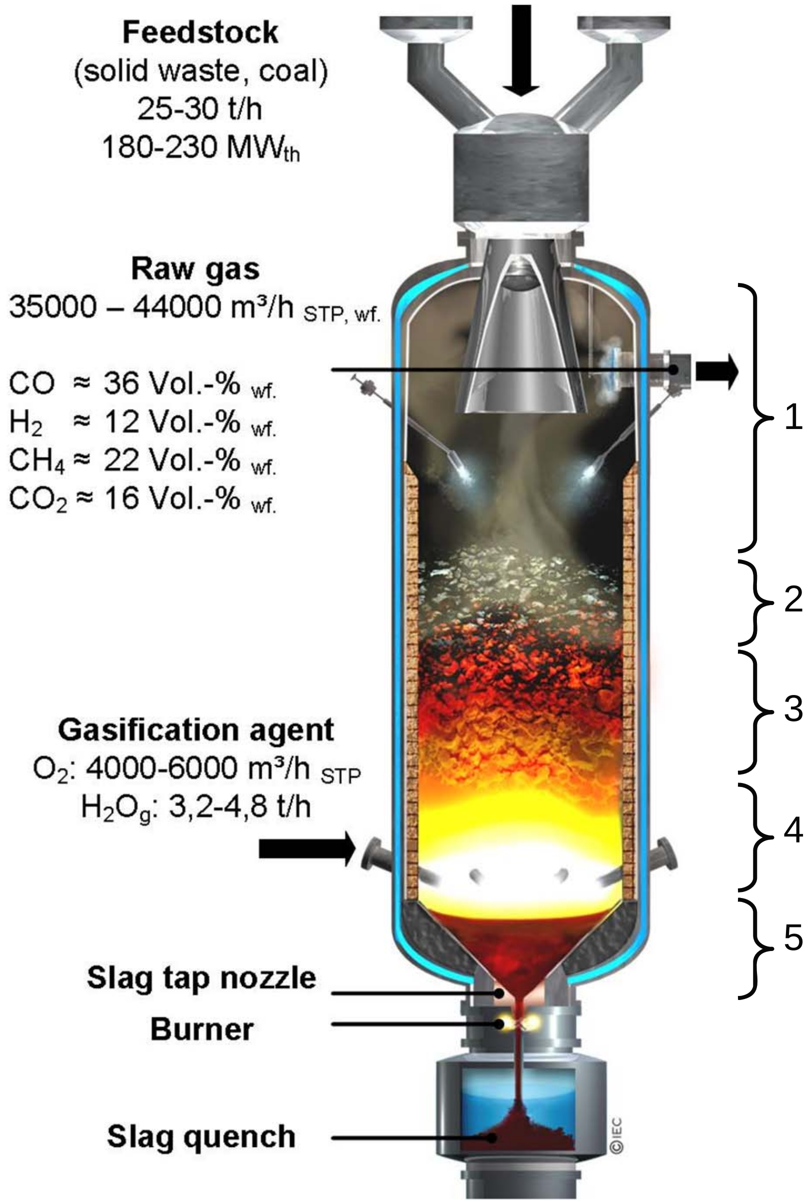
GTT-Workshop 2012 - 12.07.2012 Herzogenrath

TU Bergakademie Freiberg I Zentrum für Innovationskompetenz Virtuhcon
Reiche Zeche I 09596 Freiberg I Tel. +49(0)3731/39 4511 I Fax +49(0)3731/39 4555
E-Mail info@virtuhcon.de I Web www.virtuhcon.de

Content

- British Gas – Lurgi Gasifier was operated from 2001-2007 at the SVZ-Schwarze Pumpe GmbH near Dresden/Germany
- Syngas production out of industrial and municipal solid waste and coal for methanol synthesis
- 2004-2007 cooperation of IEC (Department of Energy Process Engineering and Chemical Engineering) and SVZ-Schwarze Pumpe GmbH within the frame of a R&E Project

The BGL-gasification process



Reaction zones in gasifier:

1. Gas free space, 550°C

2. Drying and pyrolysis, 550-900°C
   Feedstock → coke, H_2O, CO, CO_2, CH_4, hydrocarbons

3. Gasification zone, 900-1250°C
   $C + CO_2 \leftrightarrows 2CO$
   $C + H_2O \leftrightarrows CO + H_2$

4. Oxidation zone, >1250°C
   $C + O_2 \leftrightarrows CO_2$

5. Slag bath, 1250-1400°C

Technical issues related to mineral matter

Investigation of 23 runs 2004-2007, reasons for outages of gasifier:

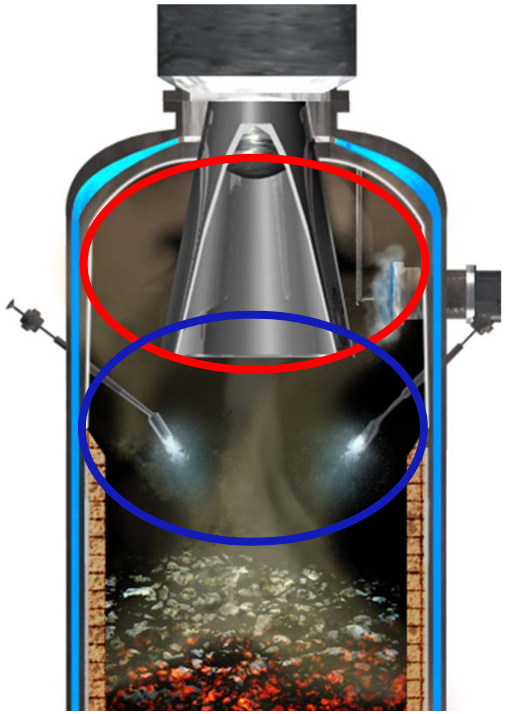
- 5 times blockage of gas exit by deposit
- 13 times disorders at lower section (oxidation zone, slag bath and discharge)
  - T-damage at refractory and tuyers
  - blockage of slag tap nozzle

Damage at refractory

Damage at Tuyere

Investigation of deposit formation around raw gas exit:

- analysis of 5 samples from different runs by SEM/EDX, thermo gravimetric analysis coupled with MS, leaching test
- volatile mineral components (Zn, Pb, S, KCl and NaCl) form matrix for dust and coke particles
- reduction of gas temperature over fixed bed by water quench, shift of condensation of volatile mineral components from cooled refractory to free gas area
    - without quench 600-900°C, condensation at refractory, partial melting
    - partial quench ≈ 550°C, condensation at particles, no partial melting



Investigation of disorders at lower section:

- 30 samples of bed material after shut down
- axial and radial concentration profiles for Zn, Pb, S, **K**, **Na**, accumulation in upper fixed bed and near refractory
- ash-slag agglomerates above tuyers, formation due to low melting phases
  - disturbance of downward fixed bed movement
  - deflection of oxygen jet → temperature damages
  - lower heat release to slag bath → blockage of discharge

➔ **internal alkali cycle as reported for blast furnace [1], [2]?**
➔ **thermochemical modeling of mineral behavior**

[1] J. Davies et al.: Alkalis in the blast furnace. In Ironmaking and Steelmaking 4 (1978)
[2] W. Altperer et al.: Auswirkungen von Alkalien im Hochofen. In Stahl und Eisen 108 (1988), Nr. 17

Model preparation and adjustment

Material balance over three days of stable operation:

- 10 feedstock and 10 slag samples (inhomogeneous feedstock mix!)
- process data (T, p, syngas composition, amount of feedstock, oxygen and steam)

➔ slag amount, water content raw gas, amount and composition of dust and tar fraction within raw gas

➔ element distribution on output streams raw gas and slag

Element	Element in slag related to input in %
S	**9**
Pb	**10**
Cl	**14**
Zn	**32**
K	**46**
Na	71
Fe	76
Mg	88
P	89
Si	91
Al	95
Ca	95

Model preparation and adjustment

Preparation of data file in FactSage™ for calculations in SimuSage™ :

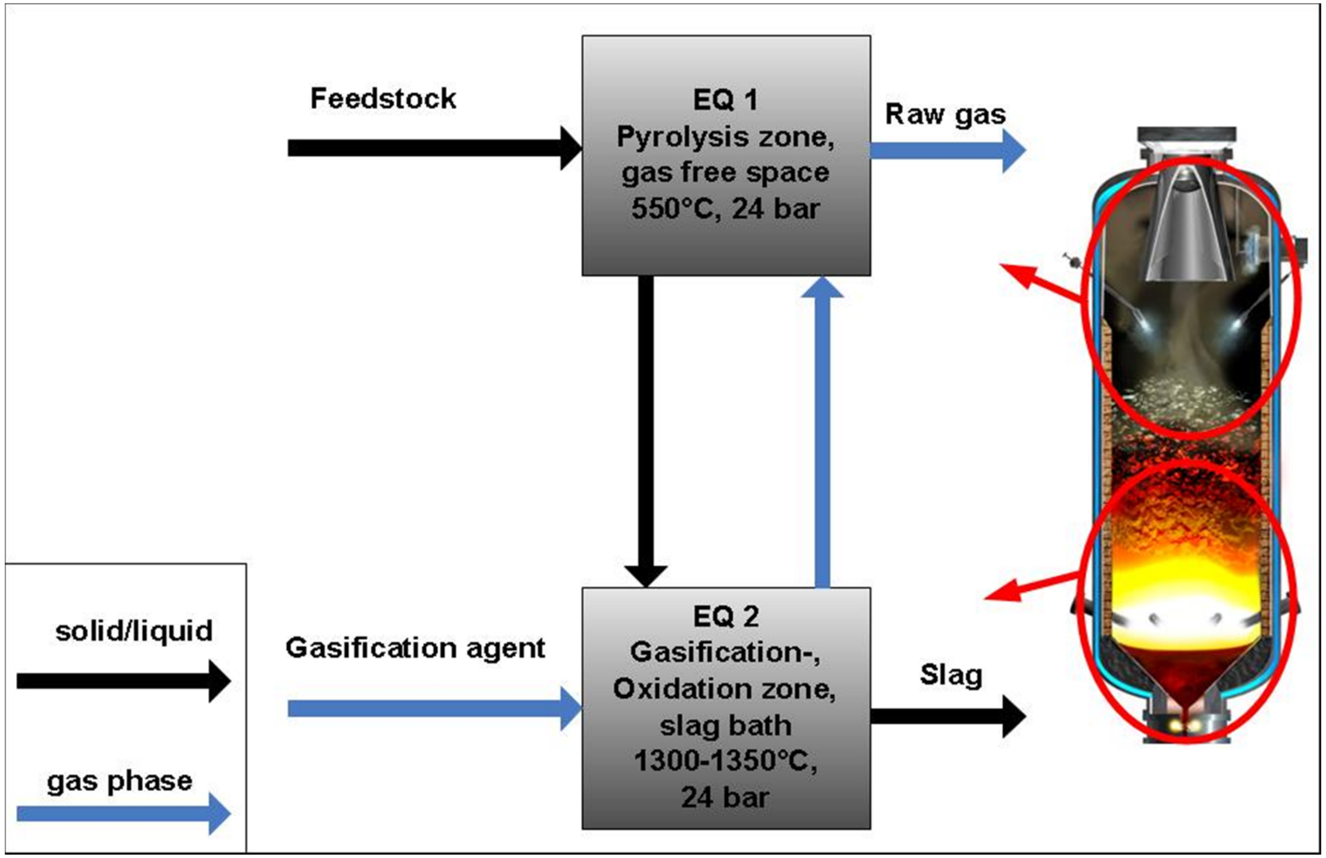
- considered elements:
  - feedstock, gasification agent, syngas: C, H, N, O
  - mineral matter: Si, Ca, Al, Fe, Mg, Ti, P, Cu, K, Na, Zn, Pb, S, Cl
- beside pure components out of FACT 5.3 choice of solution phases out of FToxide, FTmisc and FTsalt (ASlag-liq, Fe-liq, BAlkCl-ss_rocksalt, …)
- Quality of thermodynamic data for interaction alkali metal oxides – slag?
  - interactions of main slag components (SiO_2, CaO, Al_2O_3, MgO) well reproduced
  - interactions of K_2O und Na_2O with main slag components only approximately [3],[4], database documentation

➔ only qualitative description of alkali behavior by model

[3] J.-W. Seok: Thermodynamische Modellrechnungen zur Entwicklung korrosionsbeständiger keramischer Werkstoffe für Flüssigascheabscheider in kohlenstaubbefeuerten Energieanlagen. Aachen, Fakultät für Bergbau, Hüttenwesen und Geowissenschaften, Rheinisch-Westfälische Technische Hochschule Aachen. Diss., 2002
[4] T. Bause: Thermodynamik der Alkalimetall- und Schwermetallabscheidung für die Bedingungen der Druckkohlenstaubfeuerung. Freiberg, TU-Bergakademie Freiberg, Fakultät für Maschinenbau, Verfahrens- und Energietechnik. Diss., 2004

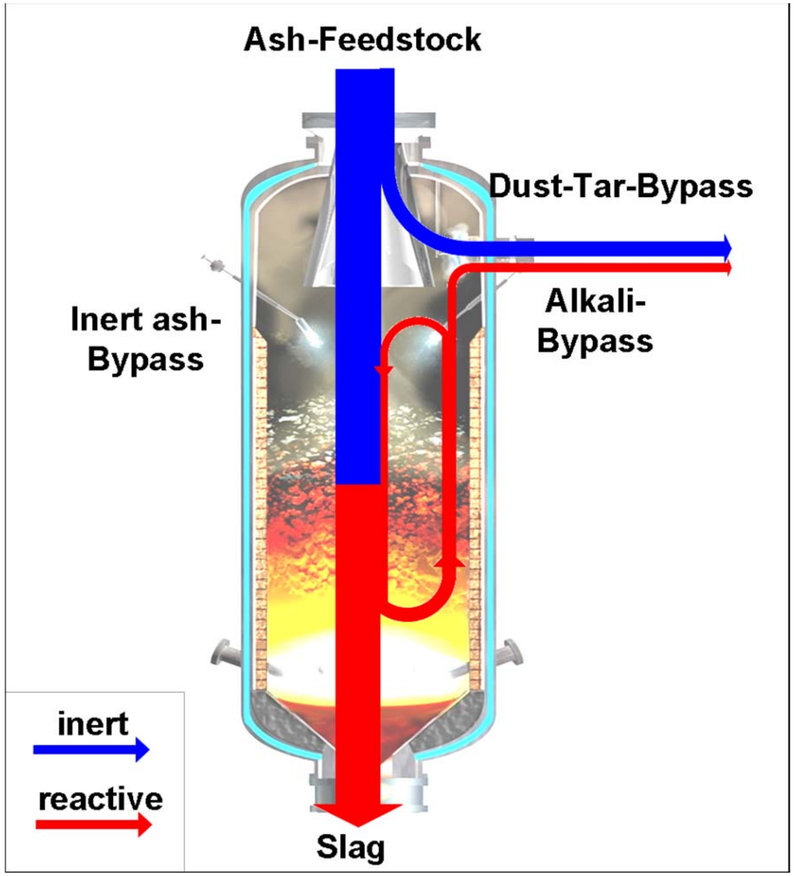
Model preparation and adjustment

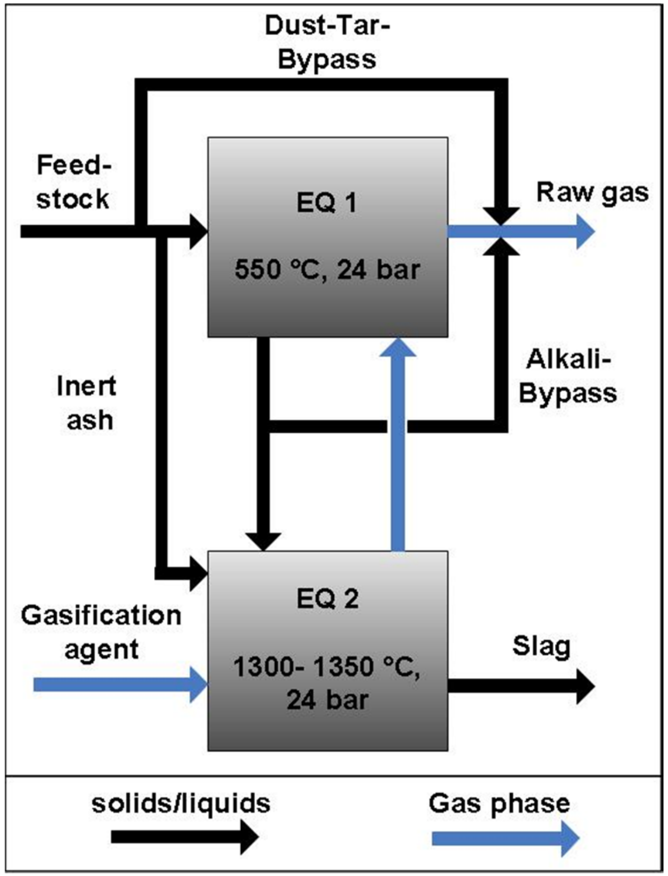
- base model consist of 2 equilibrium stages (isothermal, isobaric)
- counter flow of solids and gas and therefore interaction of stages considered by splitters and material streams
- **assumption of chemical equilibrium for all components?**
- **consideration of separation and transport effects?**



Model preparation and adjustment

- no reactions for mineral components at 550 °C → Inert ash bypass
- exit of particles (feedstock, coke) with raw gas → Dust-Tar-Bypass
- exit of condensed cycle components with raw gas particles → Alkali-Bypass





Model preparation and adjustment

- further non equilibrium states considered by bypasses:
  - pyrolysis tars and oils within raw gas
  - residual coke in slag
  - partial reactivity of Chlorine and Sulfur in 550°C-stage

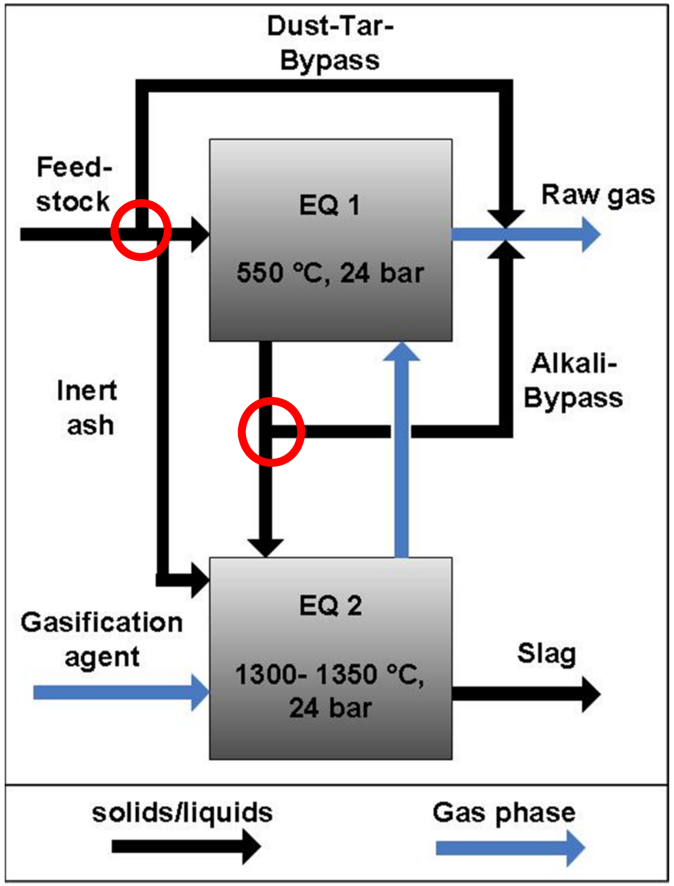
- insufficient consideration of Zn and Pb by the model:
  - high accumulation without reaching the Pb- and Zn- concentrations in slag according to material balance
  - overall cycle-species are sulfides ($ZnS_{(g)}$, $ZnS_{(s)}$,…), hence insufficient consideration of Sulfur

- Phosphor not included within ASlag-liq, formal consideration by Ca_3P_2

→ adjustment of all bypasses according to the element distribution of the material balance

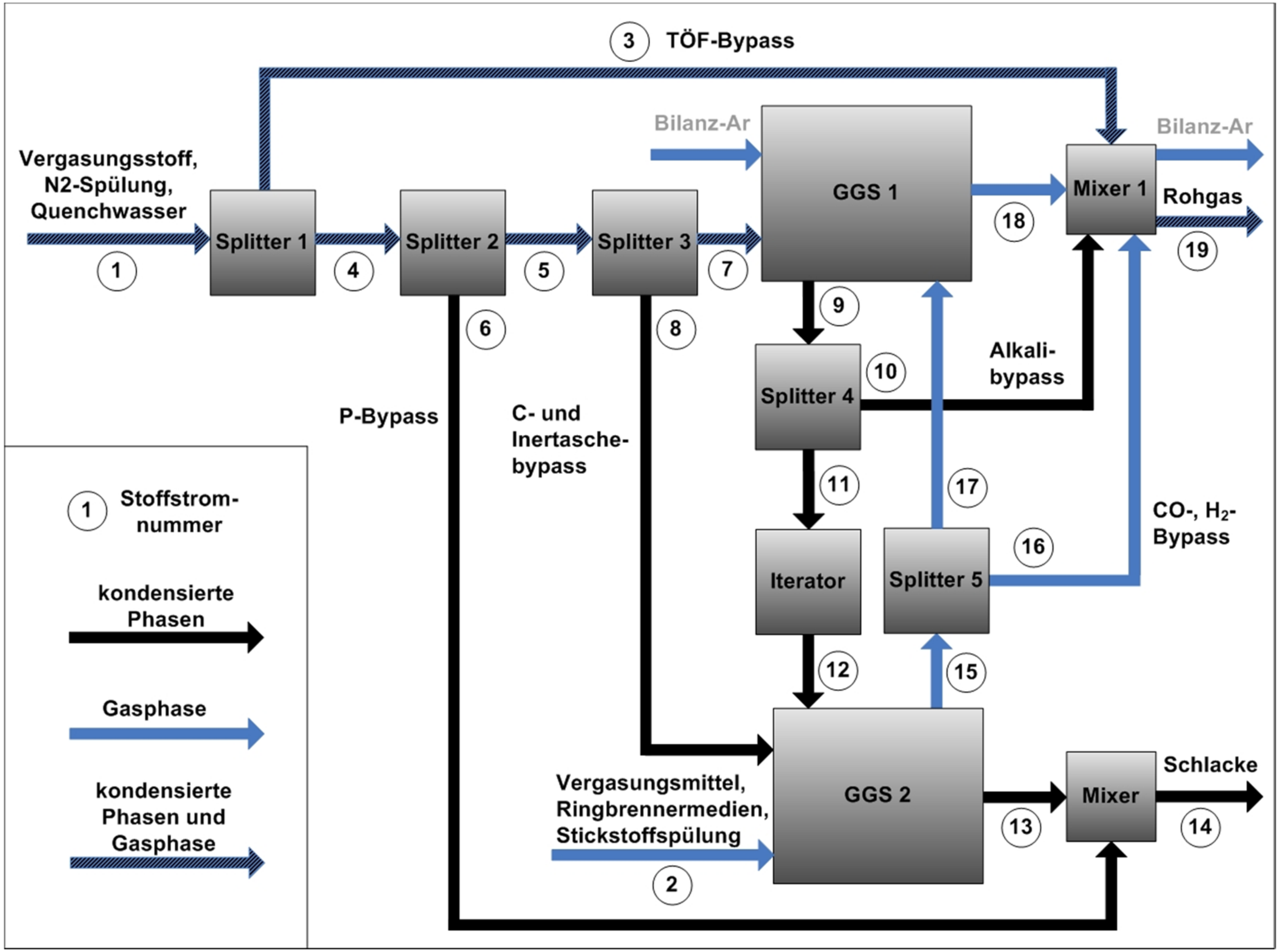
Model preparation and adjustment

- adjustment of split factors for bypasses:
  - global split factor for Alkali-Bypass on base of element distribution of Potassium according to material balance
  - element specific split factors for Dust-Tar-Bypass for remaining ash components



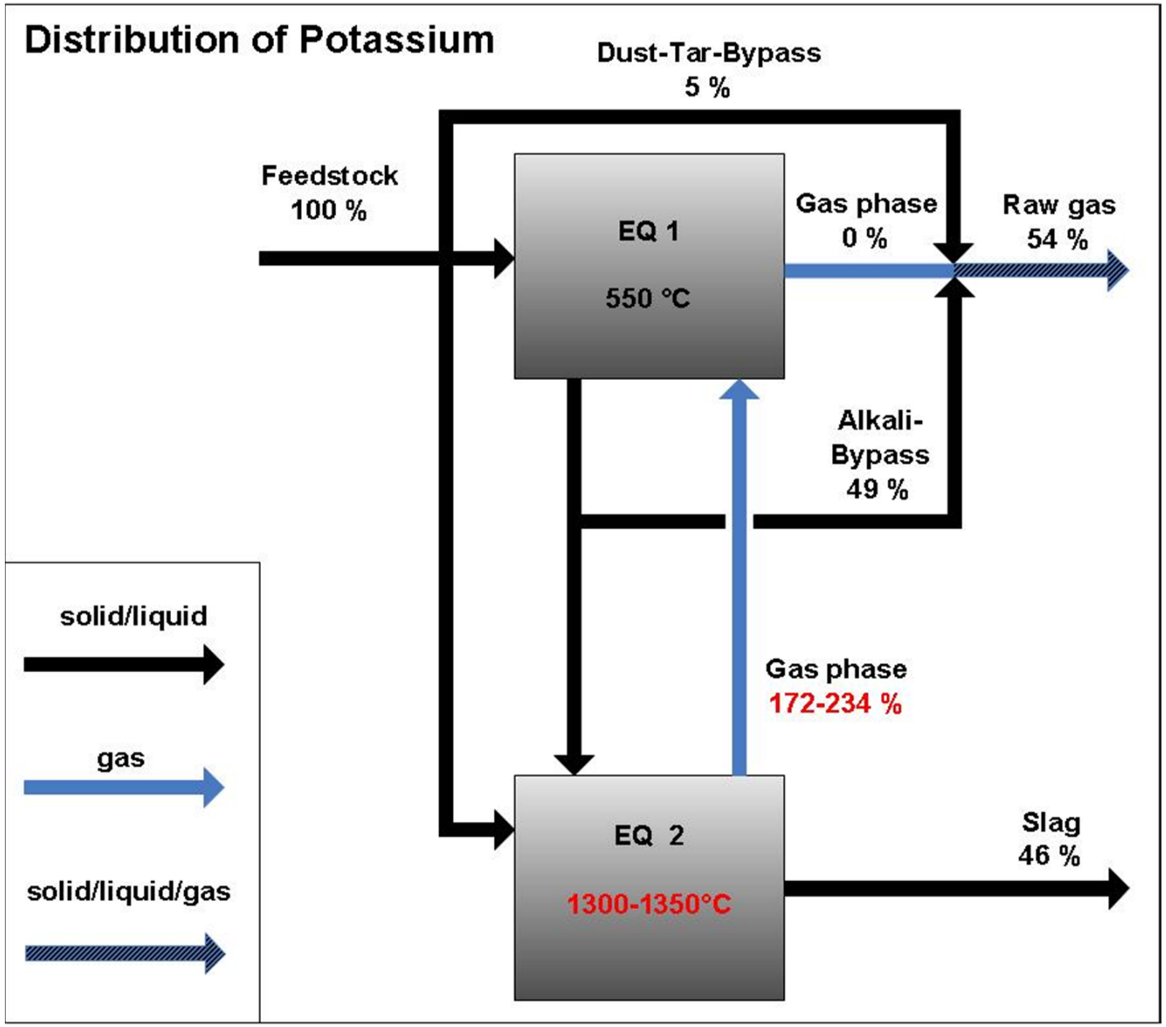
- adjusting split factors on the base of the material balance, variation of T EQ 2 (no measurement, uncertain assumption on base of AFT)
- split factors represent adjustments on mass transport and are therefore valid for changed chemistry
- use of adjusted split factors for calculation of unknown operation cases (without material balance)

Model preparation and adjustment



Model results

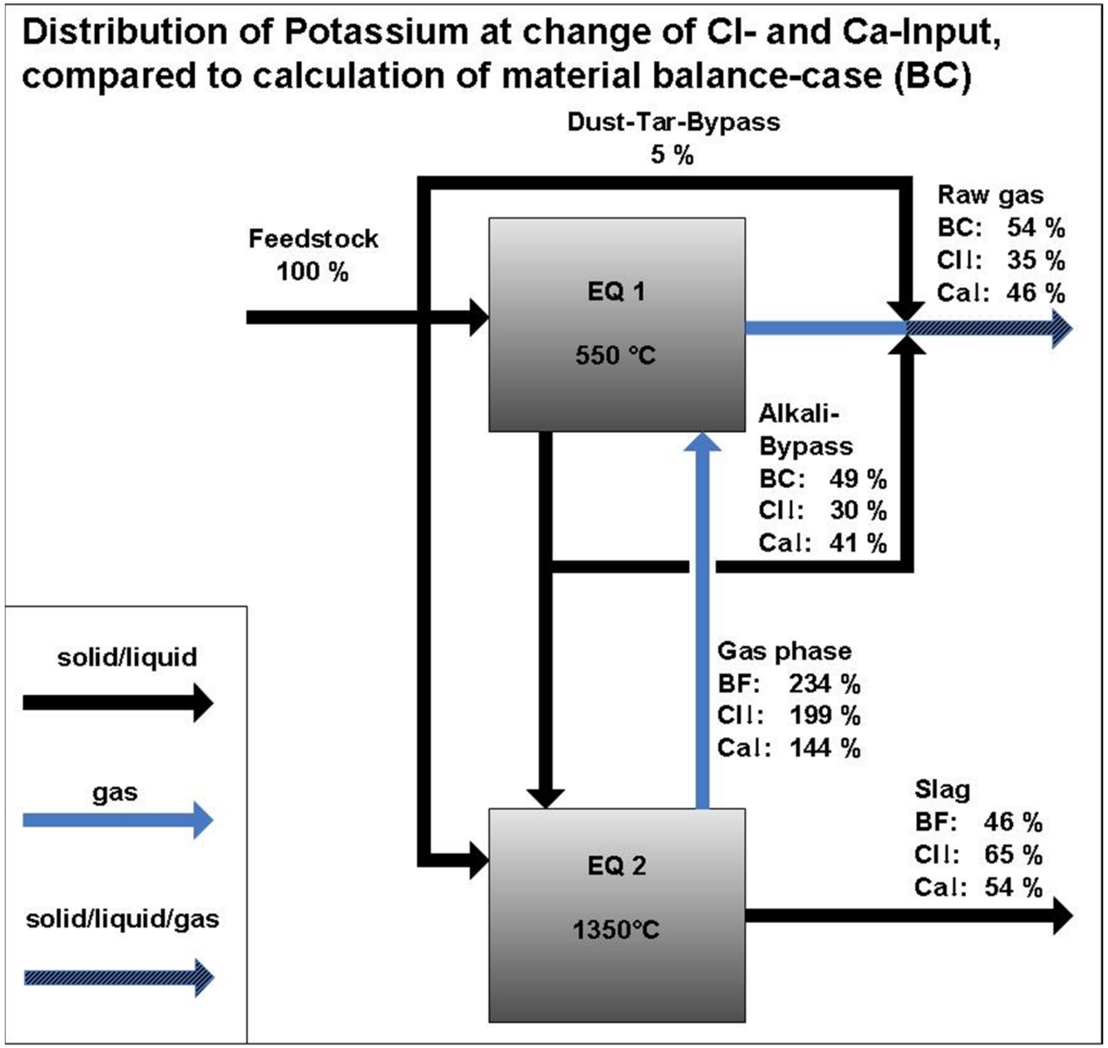
- Results of model calculation:



- complete melting of mineral matter, formation of slag- and iron phase in EQ 2
- degree of accumulation of cycle components
- cycle dominated by KCl(g) and KCl(s), KCl : NaCl ≈ 10 : 1
- almost complete condensation of cycle components at 550°C

Model results

- results for parameter calculations to prove countermeasures according alkali accumulation:



- reducing Cl-content of feedstock by 50%
- decreasing Ca-content of feedstock by 20% (decreased slag basicity by decreased flux addition, $CaCO_3$)

→ increased solubility of alkalis in slag

→ decrease of material amount in cycle

Model results

Parameter:	1300 °C	1350 °C	1350 °C, Cl↓	1350 °C, Ca↓
amount of salt phases in EQ 1 (550°C) in kg/h	360	493	290	413
amount of salt phases in fixed bed in kg/h	259	390	230	328
partial pressures of alkali chlorides above slag bath (EQ 2) in bar				
$KCl_{(g)}$	0,10	0,14	0,09	0,12
$NaCl_{(g)}$	0,012	0,018	0,009	0,013

- amount of salt phases in EQ 1 correlates with deposit formation
- amount of salt phases in fixed bed correlates with ash/slag-agglomerate formation in fixed bed
- partial pressures of alkali species as input for detailed investigations on refractory corrosion
- measures for decreasing alkali accumulation:
  - decrease of temperature (steam/oxygen ratio)
  - decrease of slag basicity
  - feedstock with low chlorine content

} η_{25}, optimized flux dosing

Conclusions

- qualitative (and quantitative) description of commercial operated BGL-gasifier by thermodynamic model, deficiencies according to available thermodynamic data and process information (samples!)

- 10 MW_{th}, 40 bar pilot scale BGL-gasifier under installation at IEC, TU-Freiberg
  - detailed experimental investigations
  - improved sampling, in-situ investigation
  - commissioning Q1 2013

  → more detailed process information for model adjustment and validation

- new developments in field of thermodynamic databases (HotVeGas, ZIK Virtuhcon)

  → increased confidence on equilibrium calculations

Source: ENVIROTHERM

Thanks for your attention!

Acknowledgements:

Results of the presentation was obtained in the frame of the R&D project „Neue BGL-Vergasung/COORETEC“, funded by Saxon Ministry of Science and the Fine Art and European Regional Development Fund, 4212/04-08.

Contact:

Dr.-Ing. Stefan Guhl

Technische Universität Bergakademie Freiberg
Department of Energy Process Engineering and Chemical Engineering - ZIK VIRTUHCON

Fuchsmühlenweg 9, Haus 2
09596 Freiberg / GERMANY

+49 (0) 3731 39 4485
Stefan.Guhl@iec.tu-freiberg.de