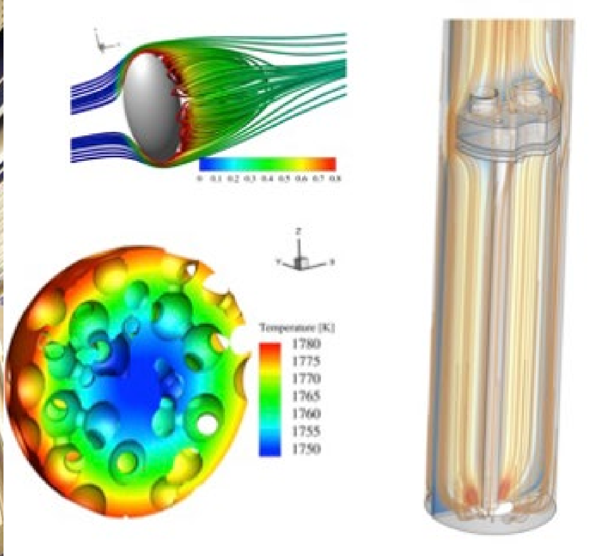
Asche, Schlacke und Mauerwerkskorrosionsproblematik in Hochtemperatur-Reaktoren



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5. Freiberger FEUERFEST Symposium

Freiberg, 24.04.2024

VISION + MISSION for our Future Developments

e-lectrifiction of	Use of renewable electric energy for
Circular **C**arbon and	provision of anthropogenic, biogenic and atmospheric carbon for circular chemistry and energy storage, and
H_2-	provision of H_2 from hydrogen carriers for primary industry and energy storage
Technologies	via technology development and engineering based on thermochemical conversion processes supported by LCA and TEA.

Introduction IEC - Research Groups

DBI Virtuhcon

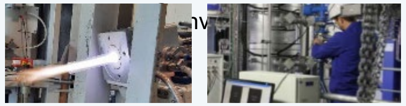
Subject Matter Expert
Prof. B. Meyer

Energy Process Engineering
Prof. Martin Gräbner

Scientific Divisions

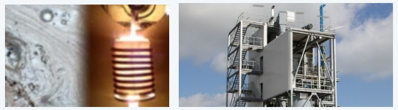
e^- | C | H_2 | T

eTC
electro- & Thermo-chemical



Dr. Steffen Krzack
(S. Thiel)

GS
Gasification Systems



Dr. Stefan Guhl
(Dr. R. Schimpke)

CCT
Circular Carbon Technologies

Dr. Jörg Kleeberg
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ST
Syngas Technologies

Dr. Peter Seifert
(M. Scheithauer)

TA
Technology Assessment

Antonia Helf
(Dr. F. Keller)

Cross-Functions

Laboratory

Dr. M. Schreiner
(Dr. A. Guhl)

Plant Operation

Olaf Schulze
(T. Peissig)

Controlling

K. Wieczorek
(S. Opitz)

72 Employees (February 2024)

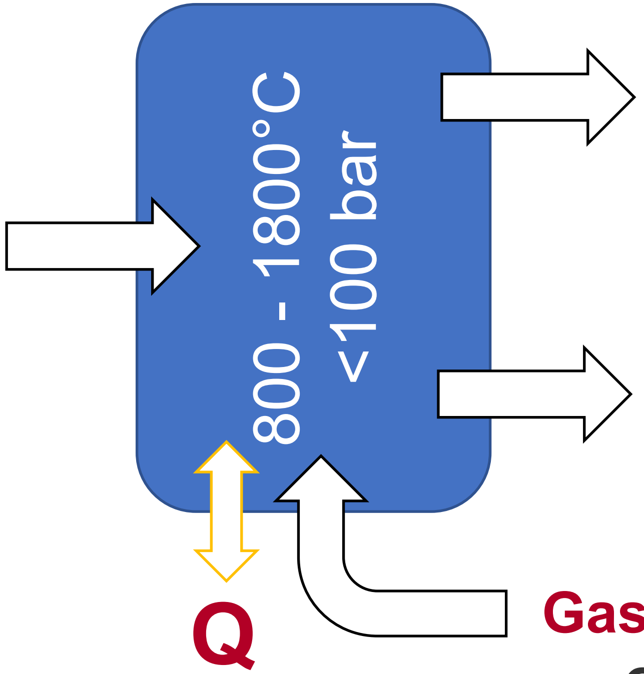
Engineers, Chemists, Physicists, Mineralogists, Economists, Lab and Technical Staff

Basics Gasification Technologies - Definition

Gasification = Thermo-chemical conversion of carbonaceous fuels <u>with</u> a reactant to a combustible gas

Feedstock

Coal
Peat
Wood
Coke
Domestic wastes
Sludge
Liquid hydrocarbons
Refinery residues
Chemical wastes
Natural gas
Stranded gas
…



Raw gas

$CO + H_2$
(CH_4, CO_2)

Residue

ash/slag

Gasification agent

O_2, H_2O, CO_2

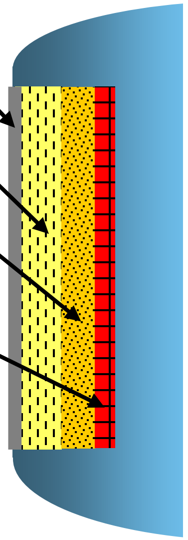
Formal Reactions	$\Delta H_{R,25}$ kJ/mol
$C + O_2 \rightarrow CO_2$	-406
$C + CO_2 \leftrightarrow 2CO$	+160
$C + H_2O \leftrightarrow CO + H_2$	+119
$CO + H_2O \leftrightarrow CO_2 + H_2$	-41

Autothermal processes: heat supply internal by O_2

Allothermal processes: heat supply by external heating or plasma

Basics Gasification Technologies - Classification by wall type

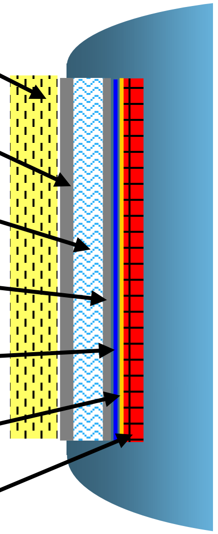
Refractory lining



e.g. slurry and fluidized bed gasifiers

- Low heat loss
- Slow startup/shutdown
- Dissolution and spalling problems → replacements

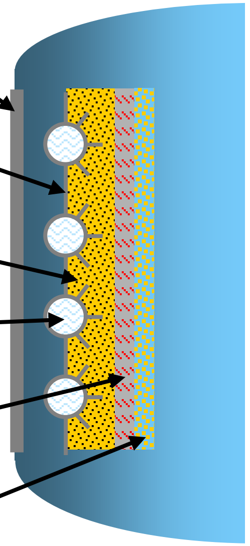
Water jacket



e.g. fixed-bed gasifiers

- Moderate heat loss
- Inherent safety
- Low thermal stress

Cooling screen



e.g. dry-feed gasifiers

- High heat loss
- Quick startup/shutdown
- Stable slag layer formation required

Pilot plants at IEC

FlexiPox – High pressure partial oxidation

- <100 bar, 5 MW_{th}, natural gas or liquid feeds, <1500 °C
- Classical refractory concept

FlexiEntrained – GSP gasifier

- 26 bar, 5 MW_{th}, up to 450 kg/h coal, biomass or pet coke feed, <1800°C
- Cooling screen and slag quench

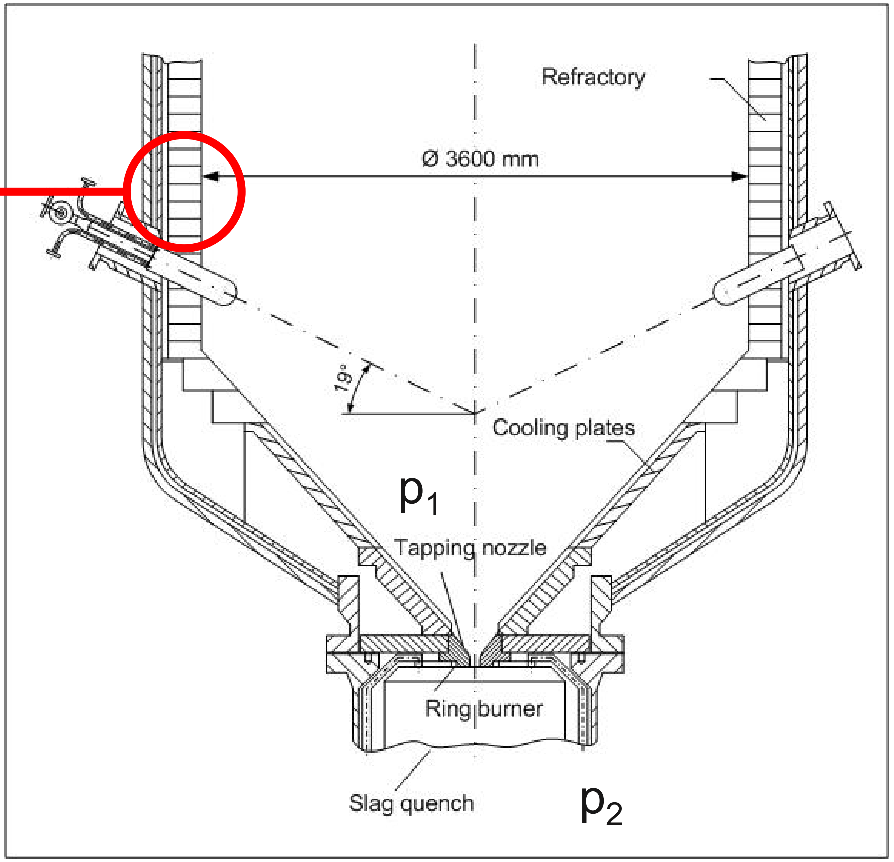
Pilot plants at IEC

FlexiSlag according BGL principle

- 40 bar, 10 MW_{th}, up to 1000 kg/h pet coke, coal, MSW, wood, sewage sludge
- Water jacket + cooling screen

Practical Example: BGL – SVZ Schwarze Pumpe

Refractory malfunction in BGL gasifier of SVZ Schwarze Pumpe (2001-2007)

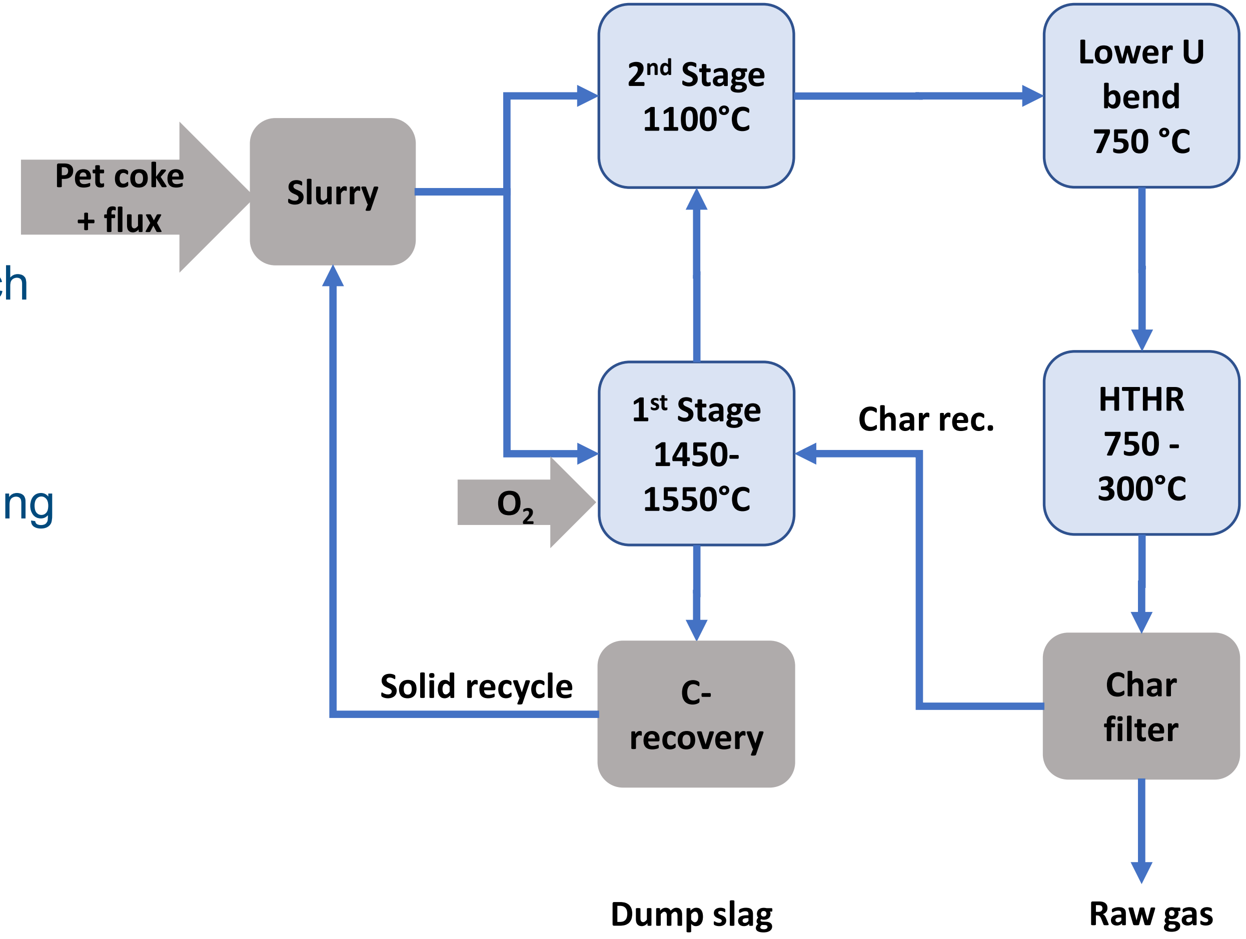


- Local refractory malfunction caused by instable operation (ash/slag-agglomeration and bridging cause instable raceway and O_2 channeling)
- Alternatives for early hot spot detection (local thermocouples not sensitive)?

Practical Example: Pet coke gasification system

Reactor configuration

- 1 GW_{th}, 60 bar, E-gas design
- Pet coke slurry feed
- 50 t/h slurry + O_2 in 1st stage, < 1600°C
- 15 t/h slurry in 2nd stage, chemical quench
- 2 recycle streams (recycling of dust from raw gas and residual char from slag)
- Classical refractory concept without cooling

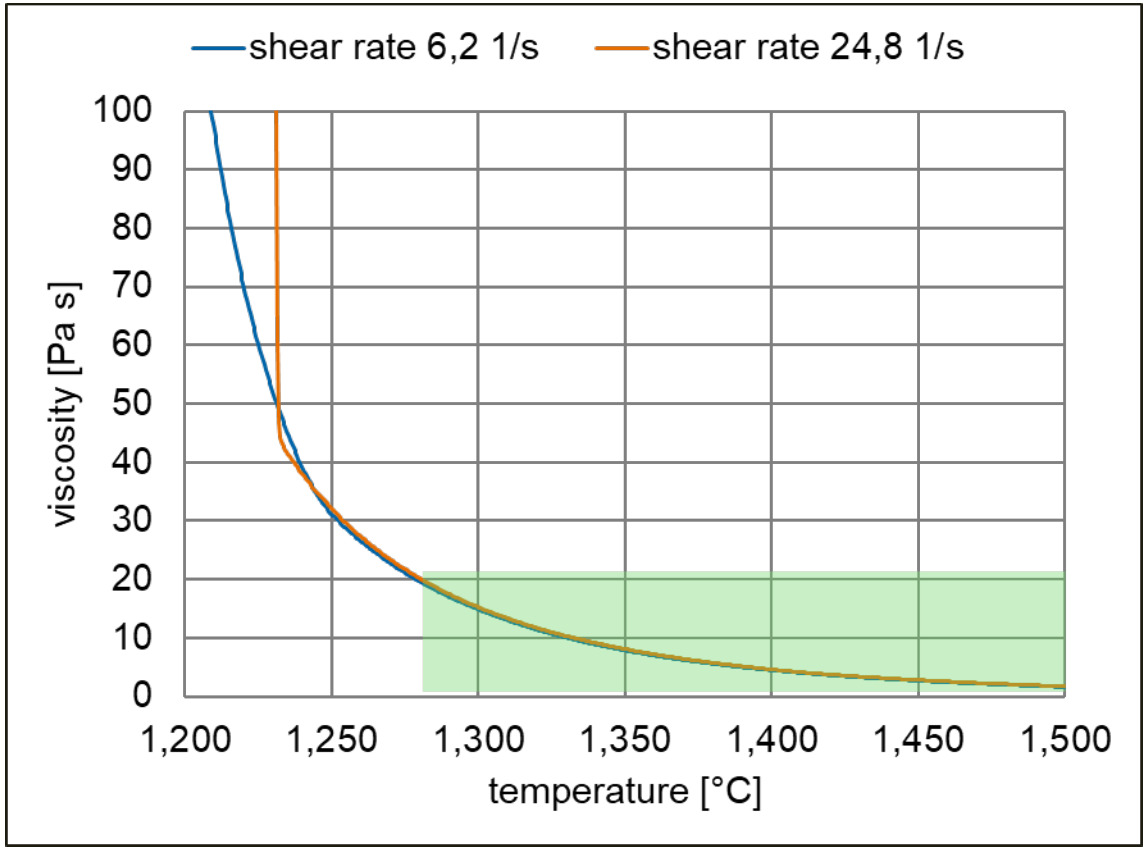


Practical Example: Pet coke gasification system

Systemic approach

- Reference Run and sampling campaigns, shipment of 10 sample sets
  - > 100 representative samples of feed, slag, recycle streams
  - > 50 samples of deposits, refractory, HTHR- tubes)
  - Large set of process data

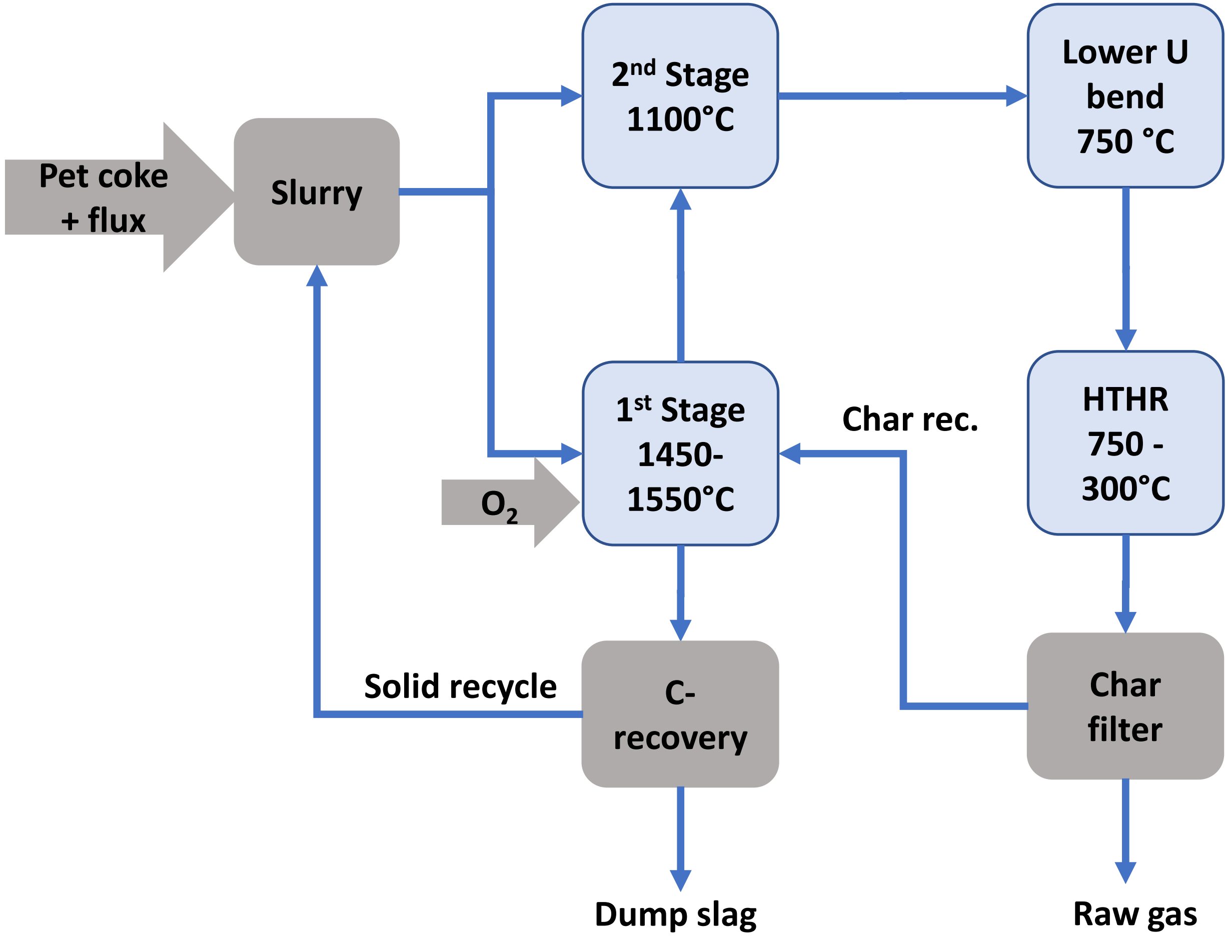
- Sample analysis:
  - Fuel analysis (ultimate analysis, heating value, ash content)
  - Ash/slag analysis (elemental composition by XRF and ETV-ICP OES, phase analysis by XRD, structure by SEM-EDX)
  - Slag viscosity and ash fusion test in CO/CO_2
  - Grain size distribution
  - Petrography



Practical Example: Pet coke gasification system

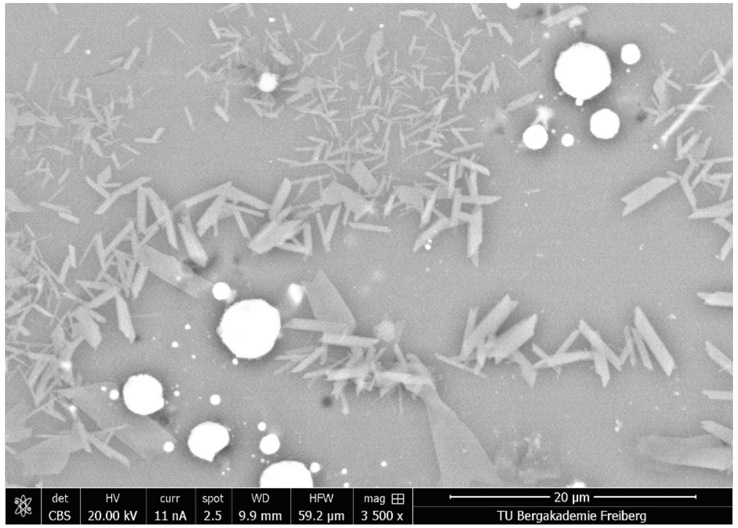
Systemic approach

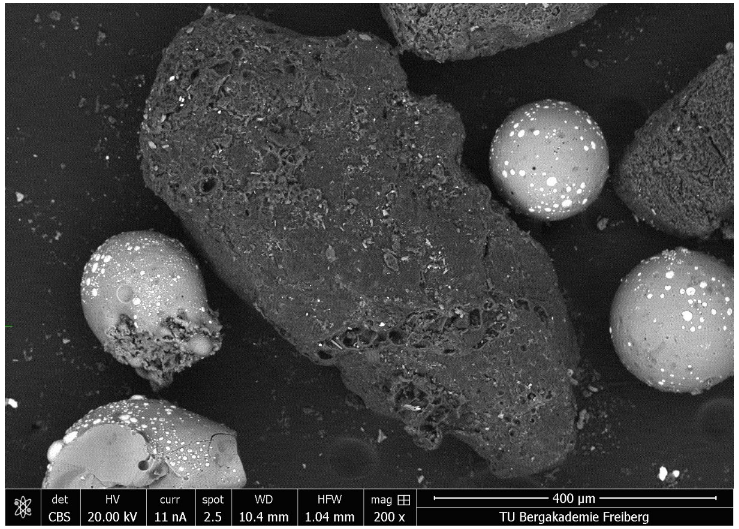
- **Flowsheet Modelling (ASPEN Plus)**: General M&E-balance of main components (C, H, O, S, ash) of whole system as well as stages/process units
  → general material composition and temperature of all process units
- **Detailed mass balance** for ash components and traces (22 elements)
- **Thermochemical Modelling (FactSage)** for all ash components and traces→ distribution of gas/liquid/solid
- **CFD-Modelling** → local T- and species distribution
- Joint interpretation of results with operator

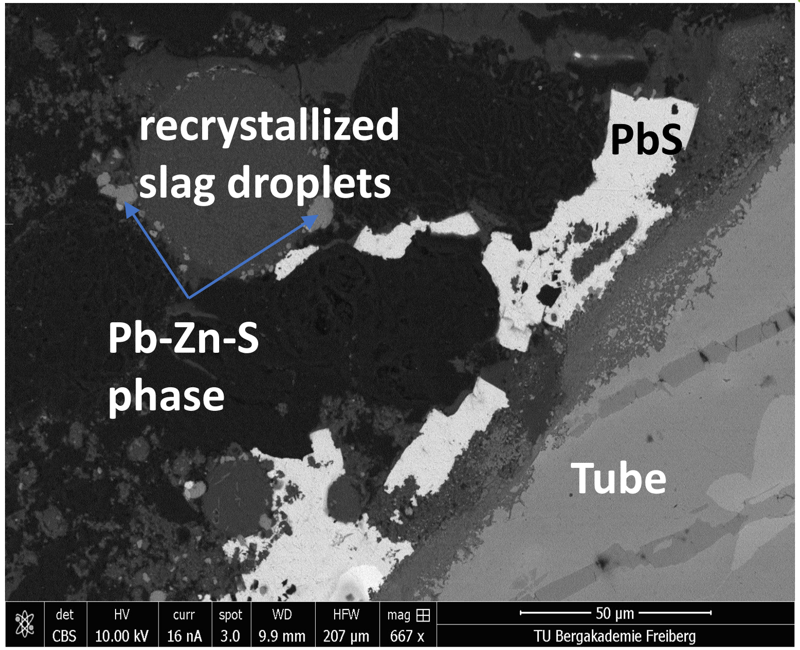


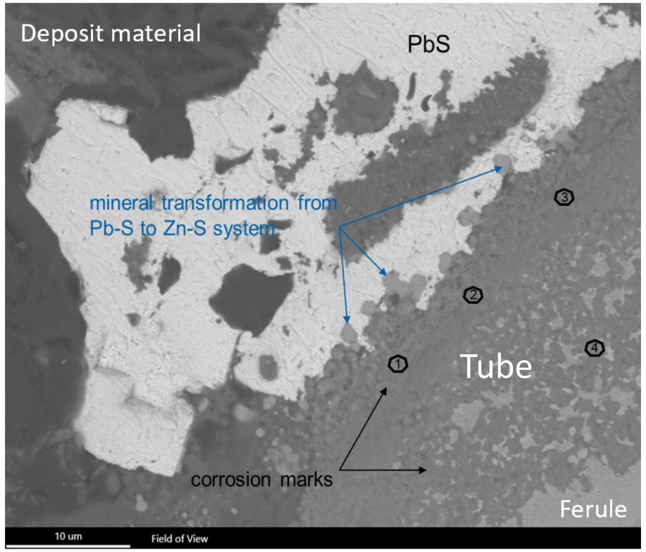
Practical Example: Pet coke gasification system

Detailed investigation of process samples



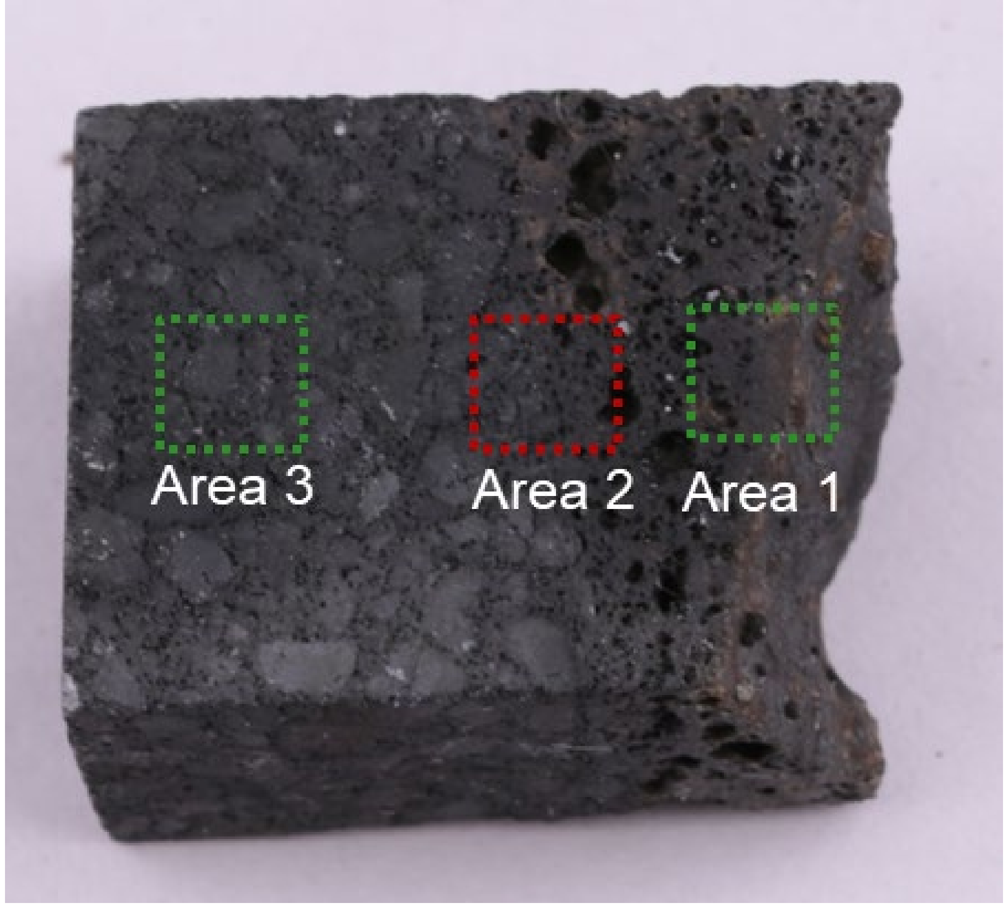


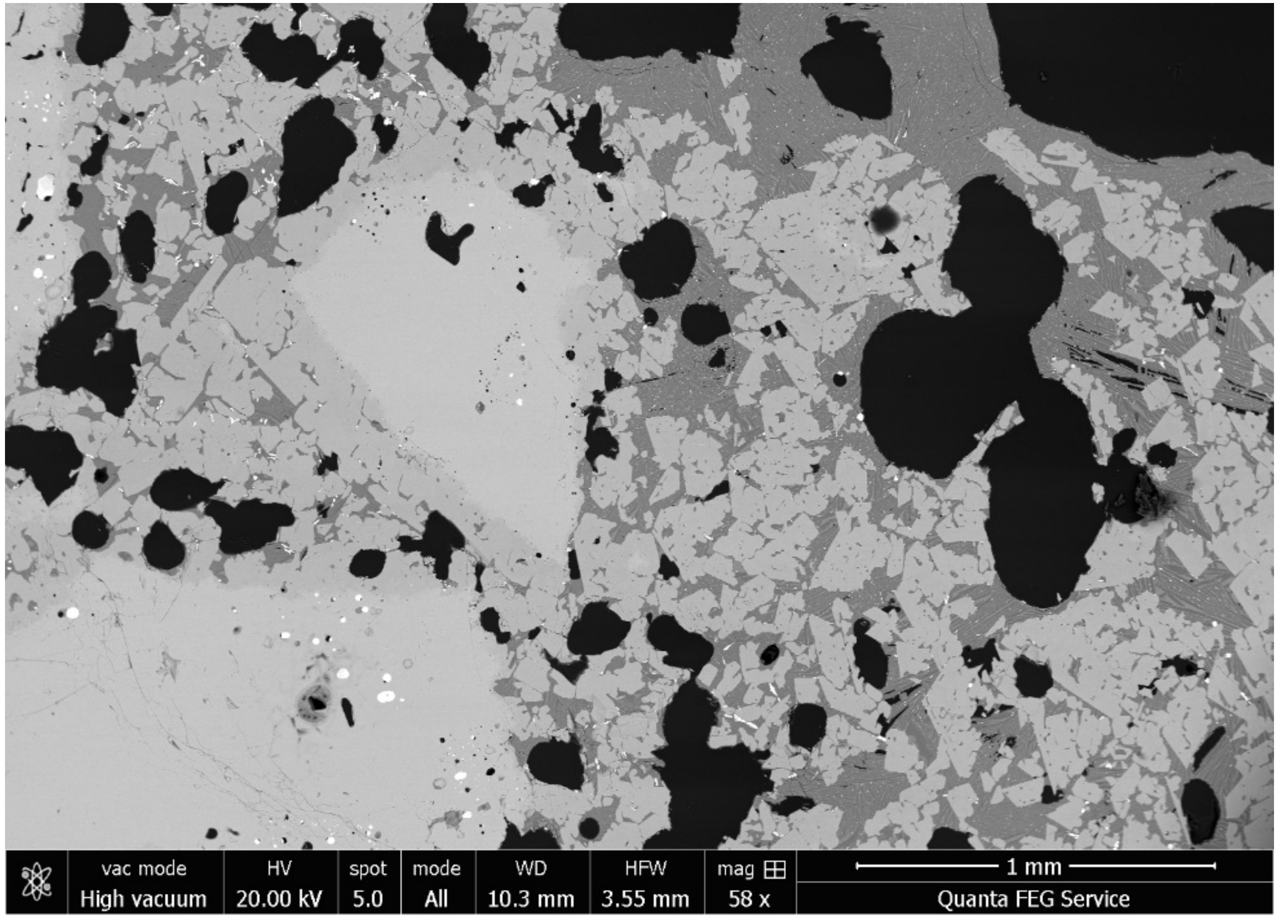




Practical Example: Pet coke gasification system

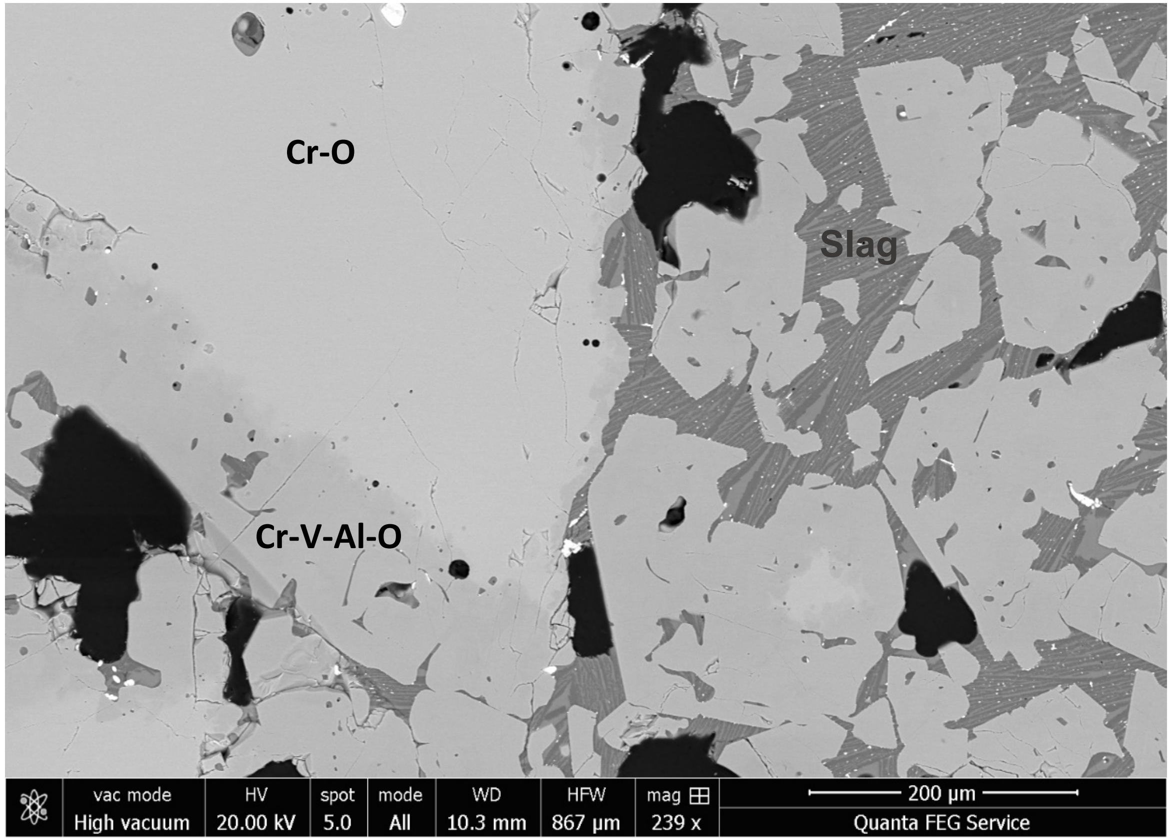
Detailed investigation of process samples

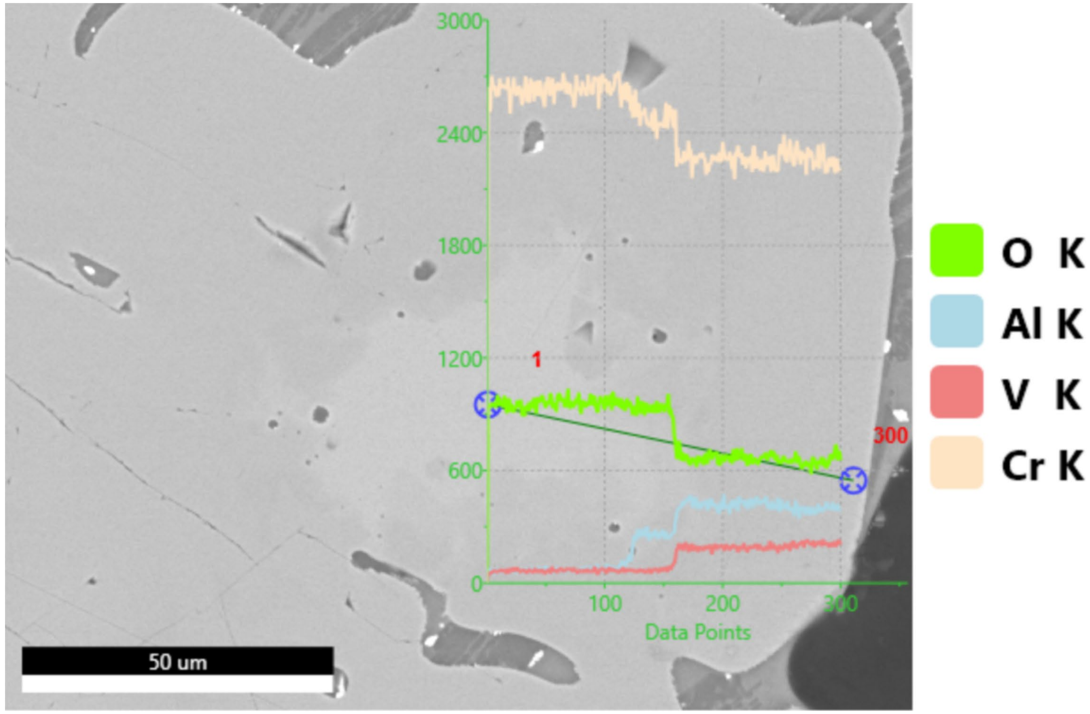




Practical Example: Pet coke gasification system

Detailed investigation of process samples

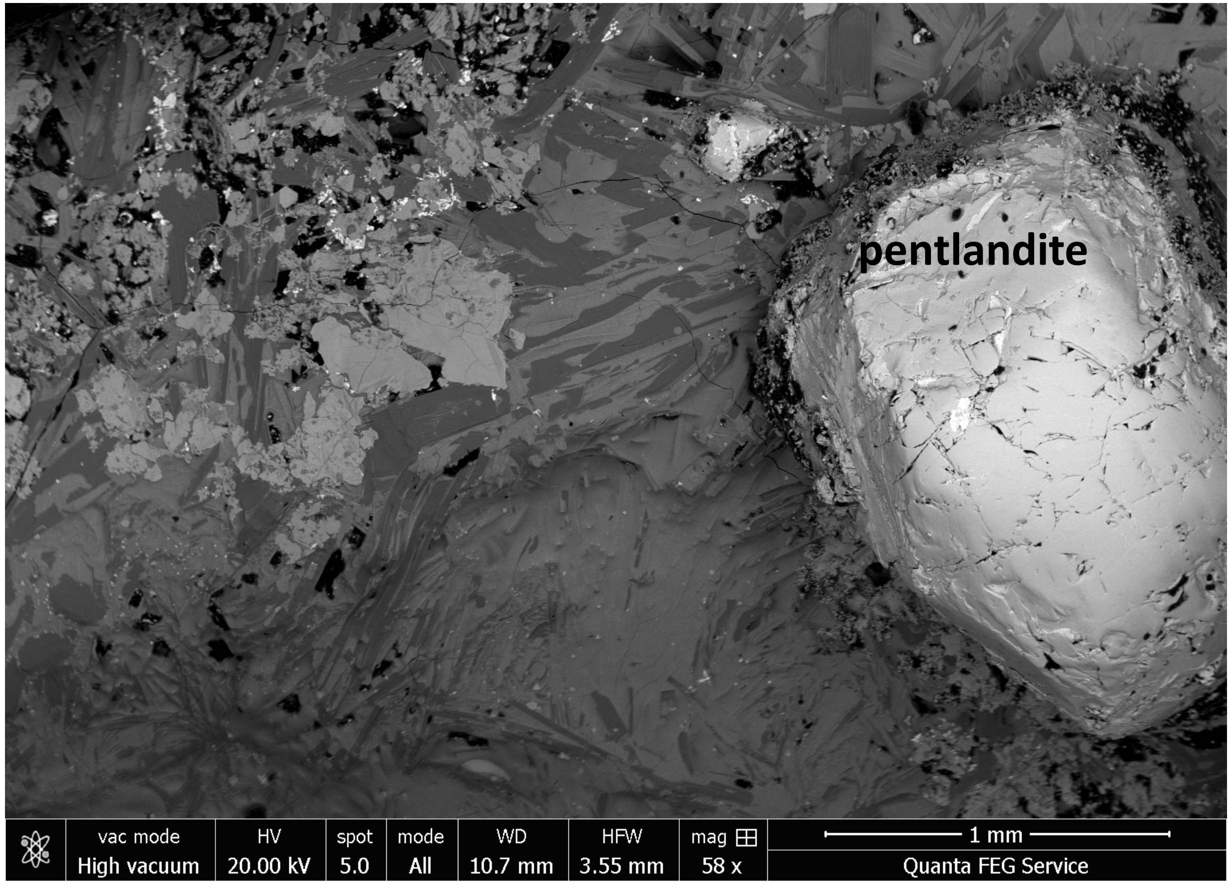




- Infiltration of Vanadium into Cr_2O_3-grains with Cr-depletion
- Grouping of Cr with Fe and V-oxides in boundary slag layer (dissolved matrix)
- single Zr-oxide-grains in boundary slag layer (i.e. Zr not dissolved)

Practical Example: Pet coke gasification system

Detailed investigation of process samples



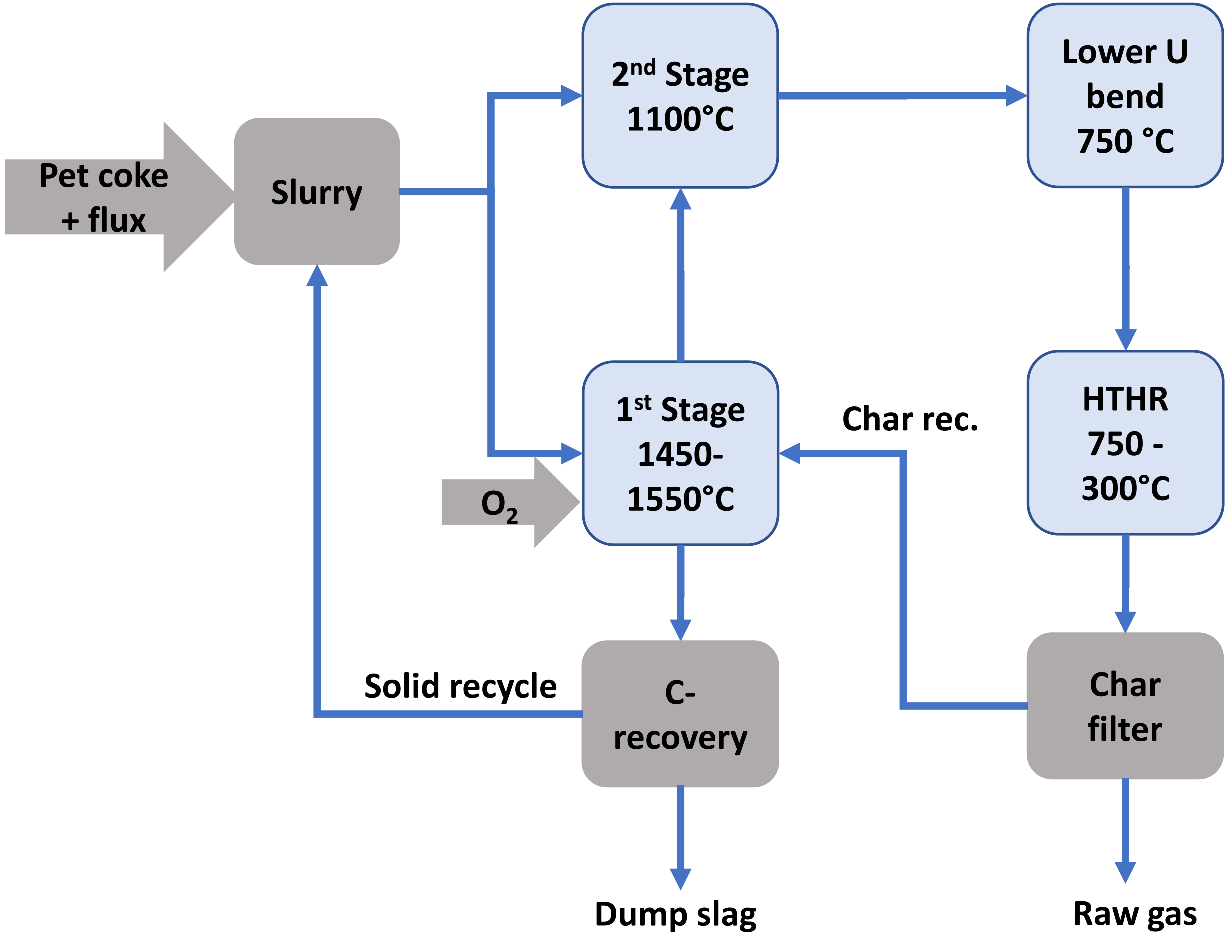
Practical Example: Pet coke gasification system

Conclusions for process optimization

- Improved temperature control in 1st stage based on validated ASPEN-model
  → Minimized slag deposition in 2nd stage
  → Minimized refractory corrosion due to over-temperature (Vanadium accumulation detected)

- HTHR deposition caused by binder phases:
  - liq. Matte, accumulation by solid recycle
  - PbS-ZnS, accumulation by char recycle

  → Partial opening of recycle and adjusted flux
  → Changed design and adjusted temperature control in HTHR



Conclusions and outlook

- Process optimization by combination and joint evaluation of:
  - Process samples and data
  - Detailed chemical-mineralogical analysis
  - Modelling and M&E-balance (ASPEN, FactSage, CFD)

  → detailed description of local and global reaction systems (T, n_i, p_i), understanding of corrosion mechanism

- Future requirements and challenges with respect to refractory lining for gasification processes
  - Change from well known feedstocks to MSW and biomasses → new corrosive components (phosphorus, alkali metals, chlorine, high ash feedstocks)
  - Change from autothermal to allothermal systems by plasma integration → local hotspots, reduced p_{O2}
  - Safety aspects (early warning system for refractory malfunction?)

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