Modelling and Experiments for Stainless Steel Slag Valorisation

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http://www.mtm.kuleuven.be/Research/THERMO/

World steel production: ~ $1.25 \cdot 10^9$ tons

Slag/steel ratio: 1/3 ~ 1/4

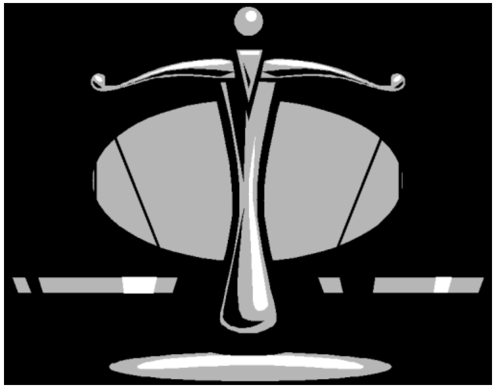
World steel slag production: ~ $350 \cdot 10^6$ tons

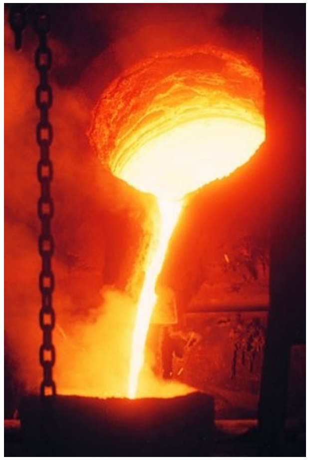
- 50 pyramids of Gizeh every year
- WASTE?
  - Large dumping fees
  - Ecological implications
- Or… VALORISATION
  - Small revenue for the "secondary resource"
  - Sustainability & Zero waste

Secondary resource	↔	Primary resources
slag	↔	sand, gravel, natural rocks

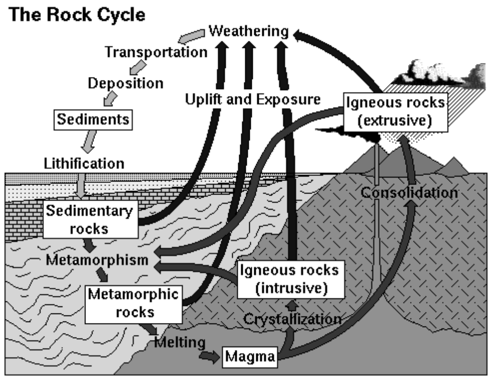
When balancing the choice of resource:

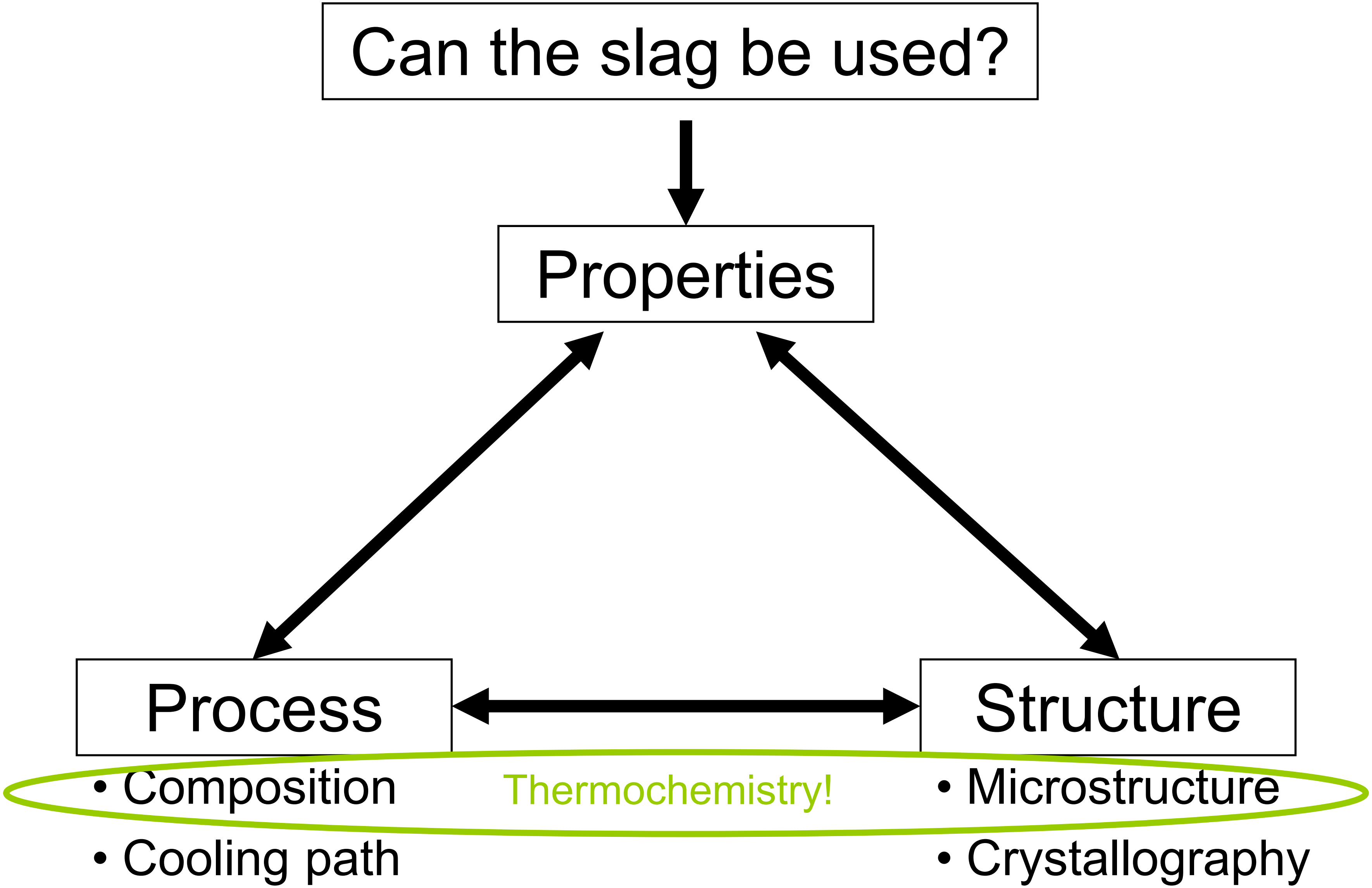
Cost, availability, grain size distribution, strength, abrasion resistance, polishing resistance, volume stability, hydraulic properties, heavy metal leaching, porosity…





Human time-scale vs. Geological time-scale




Can the slag be used?
Properties
Process
Structure
• Composition
• Cooling path
Thermochemistry!
• Microstructure
• Crystallography

Industrial project

- Research group: Thermodynamics in metallurgy
  - High-T centre
  - IWT-project on stainless steel slag valorisation
- Use FactSage data for
  - Process modelling
    - Previous project: VOD, EAF
    - Current project: de-sulphurisation, slag additions
  - Solidification modelling
- Also a need for data valorisation

LEUVEN centre
for high temperature processes, metallurgy and refractory materials

UGINE & ALZ
Arcelor Group

Content

- Experimental verification of liquidus
- Slag solidification modelling
- Process model for additions

Experimental liquidus verification

- Goal:
  - Verify the applicability of FactSage for multicomponent slags at high temperature
  - Simplify stainless steel slag system to:

    $CaO\text{-}SiO_2\text{-}MgO\text{-}Al_2O_3\text{-}Cr_2O_3$ (CSMAK)

Literature data on liquidus

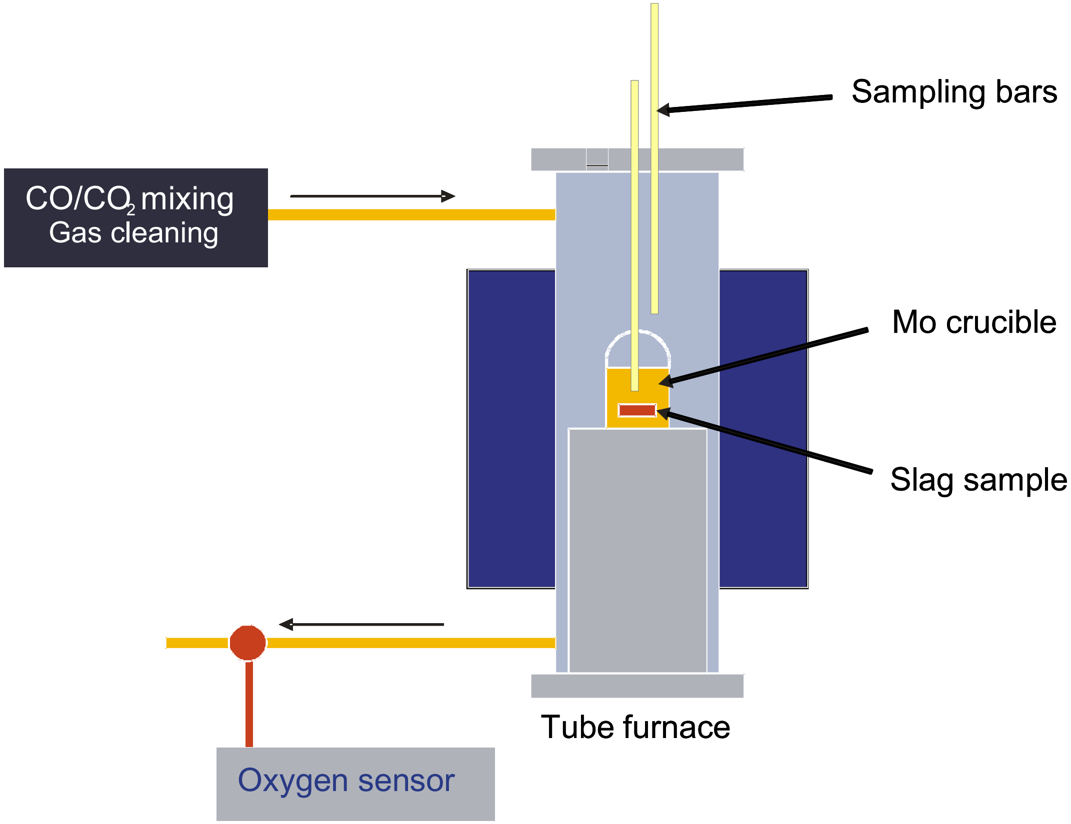
- Experimental
  - Mostly ternary
  - Up to ternary already used in optimizations
  - Some quaternary (CSAK…)
- Optimizations
  - 7 out of 10 ternaries
  - Other 3 have high liquidus temperatures (CMK, CAK, MSK)

Optimized data

- FactSage 5.4: database info
  - Slag
    - In the absence of SiO_2: extensively optimized for oxides of Al, Ca, Co, Cr^{II}, Cr^{III}, Fe^{II}, Fe^{III}, Mg, Ni, Zn, some regions.
    - In the absence of Cr: fully evaluated and optimized for oxides of Al, Ca, Fe^{II}, Fe^{III}, Mg, Si, all regions.
    - Fully optimized for **Al_2O_3-CaO-CrO-Cr_2O_3-SiO_2** solutions
    - Roughly optimized for **CrO-Cr_2O_3-MgO-SiO_2** solutions.
  - Spinel-solution
    - Evaluated and optimized over all compositions (but… pure MK is formed in calculations)
- CRCT: Completely optimized

Experimental method

- Mixing powders
- Equilibration
- Sampling
- EPMA-WDS

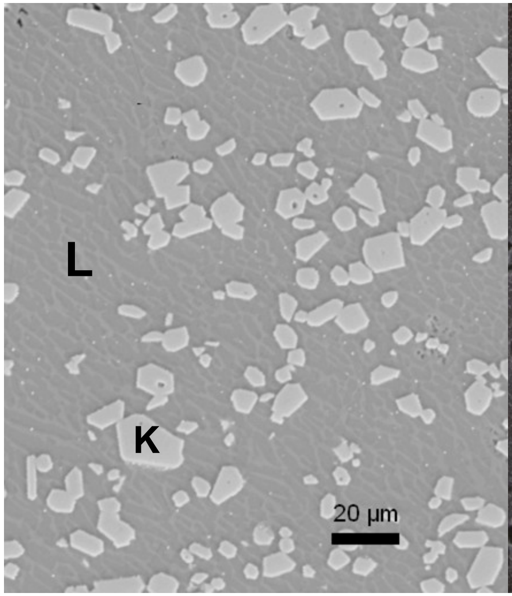


Parameters

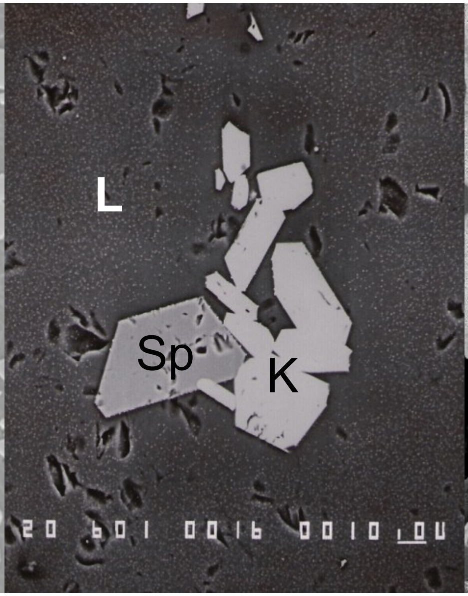
Temperature	1500°C and 1600°C
CO/CO_2 ⇒ p_{O2}	20 and 50 $10^{-10.16}$ and $10^{-9.36}$ atm
Basicity C/S	0.5 and 1.2
Al_2O_3	0, 10, 20, 30 wt%
MgO Cr_2O_3	chosen in 2 or 3-phase area

Results: microstructures

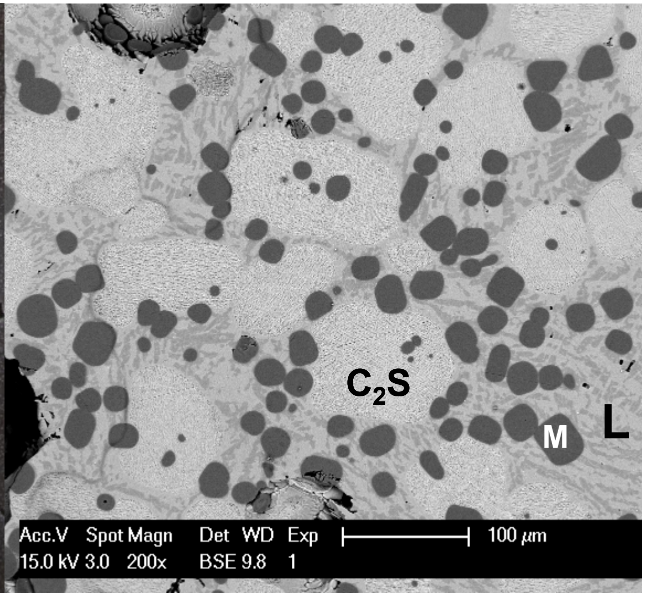
- Phases correspond with the expected
- Amount of precipitates mostly higher than calculated



Slag + Cr_2O_3



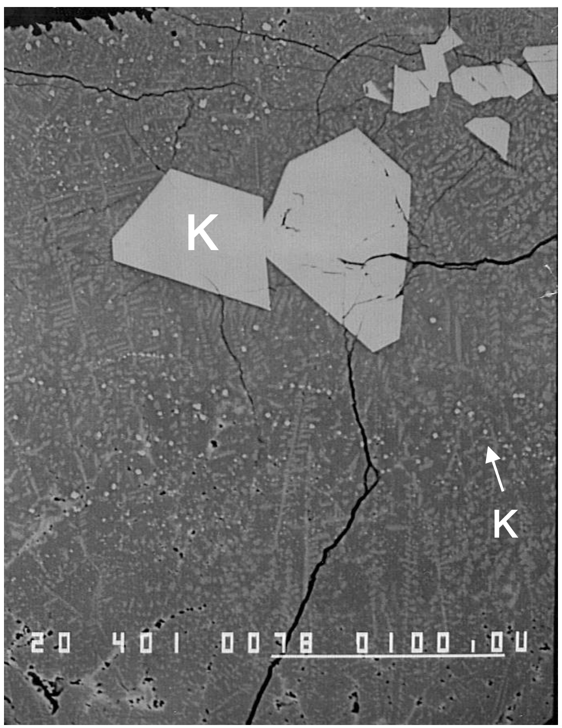
Slag + Cr_2O_3 + spinel

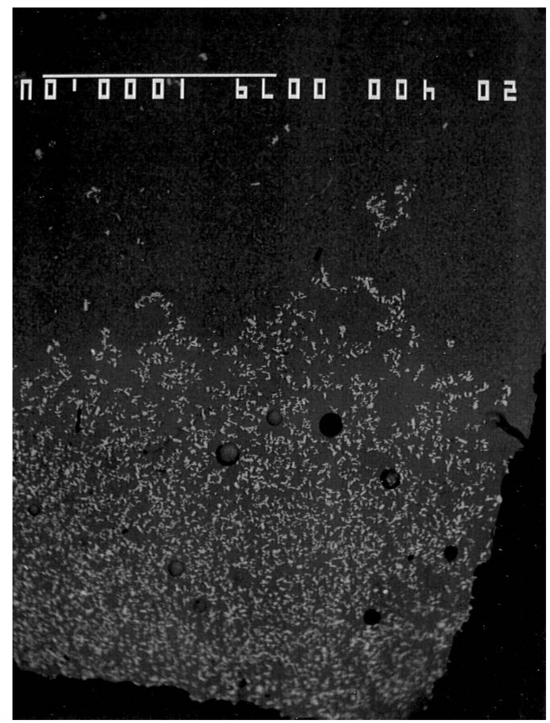


Slag + C_2S + MgO

Results: microstructures

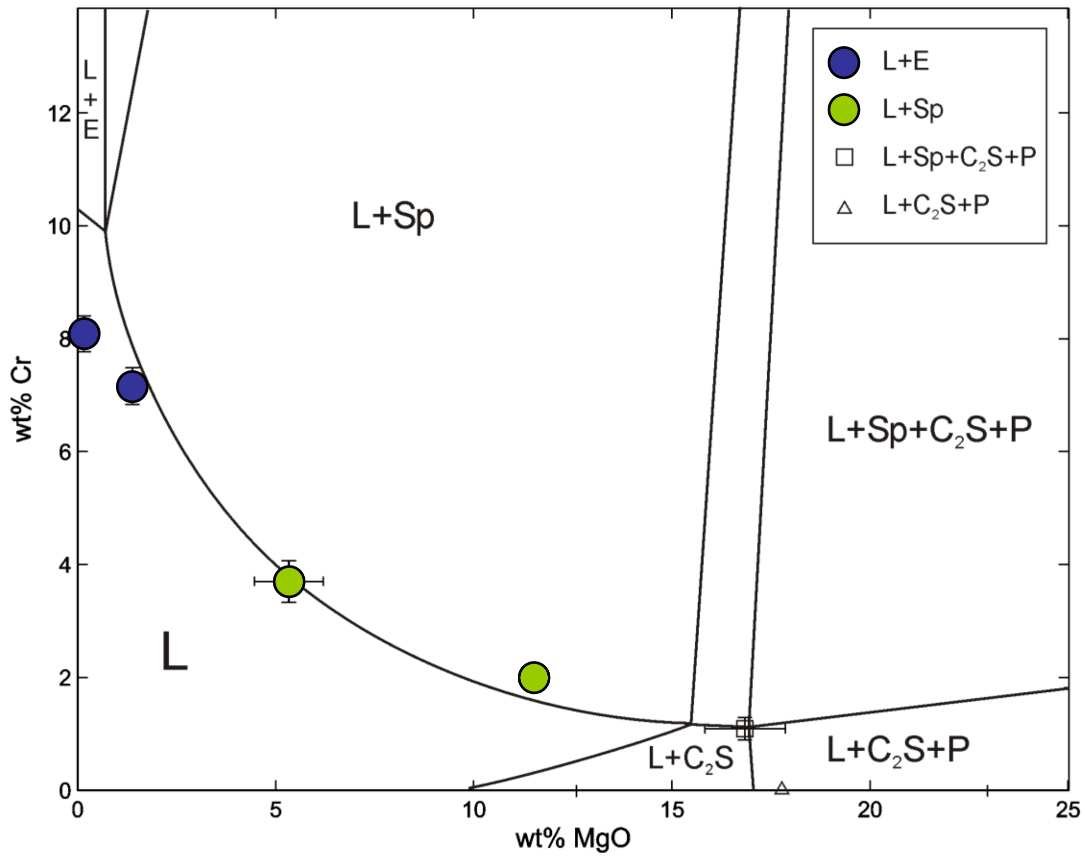
- Cooling speed is finite
- Matrix crystallisation occurs
- Interaction with precipitates
- Sedimentation ⇒ zones
- Wetting ⇒ loss of liquid





Results: liquidus

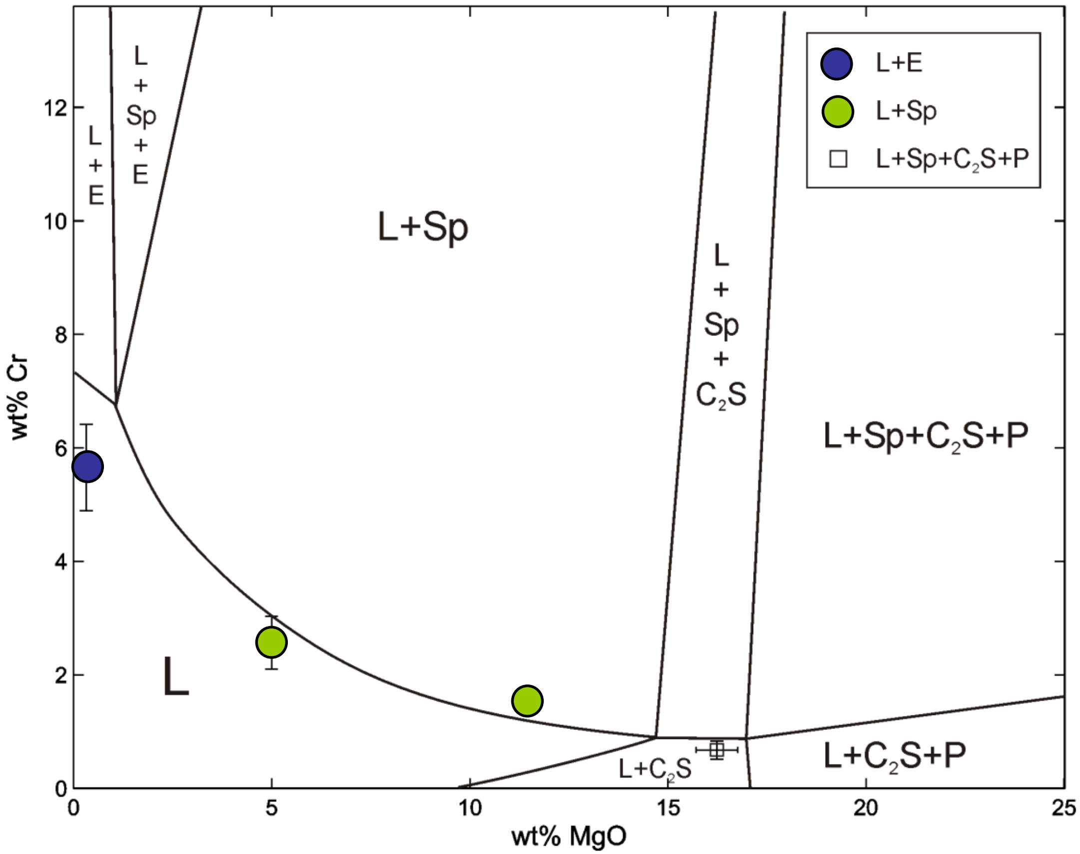
- Tests in different p_{O2}, no Al_2O_3



T=1600°C
$p_{O2}=10^{-10.16}$ atm
B=1.2

Results: liquidus

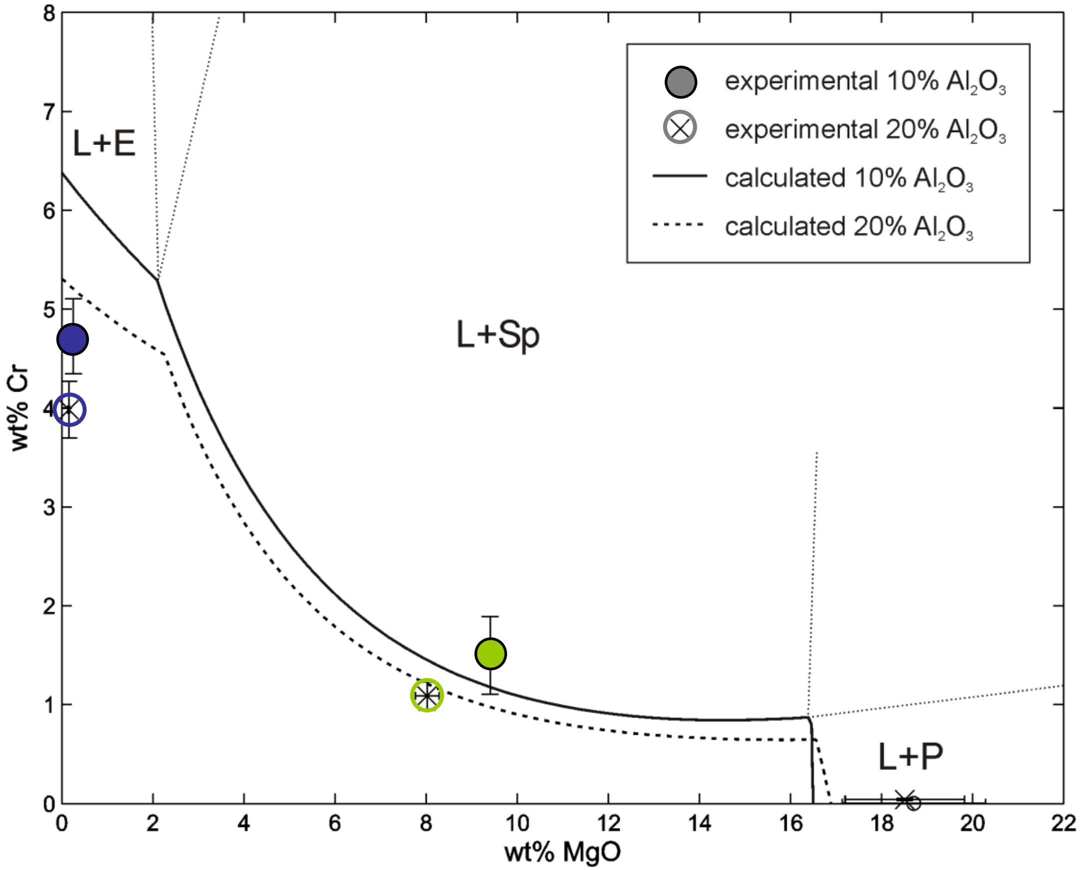
- Tests in different p_{O2}, no Al_2O_3



T=1600°C
$p_{O2}=10^{-9.36}$ atm
B=1.2

Results: liquidus

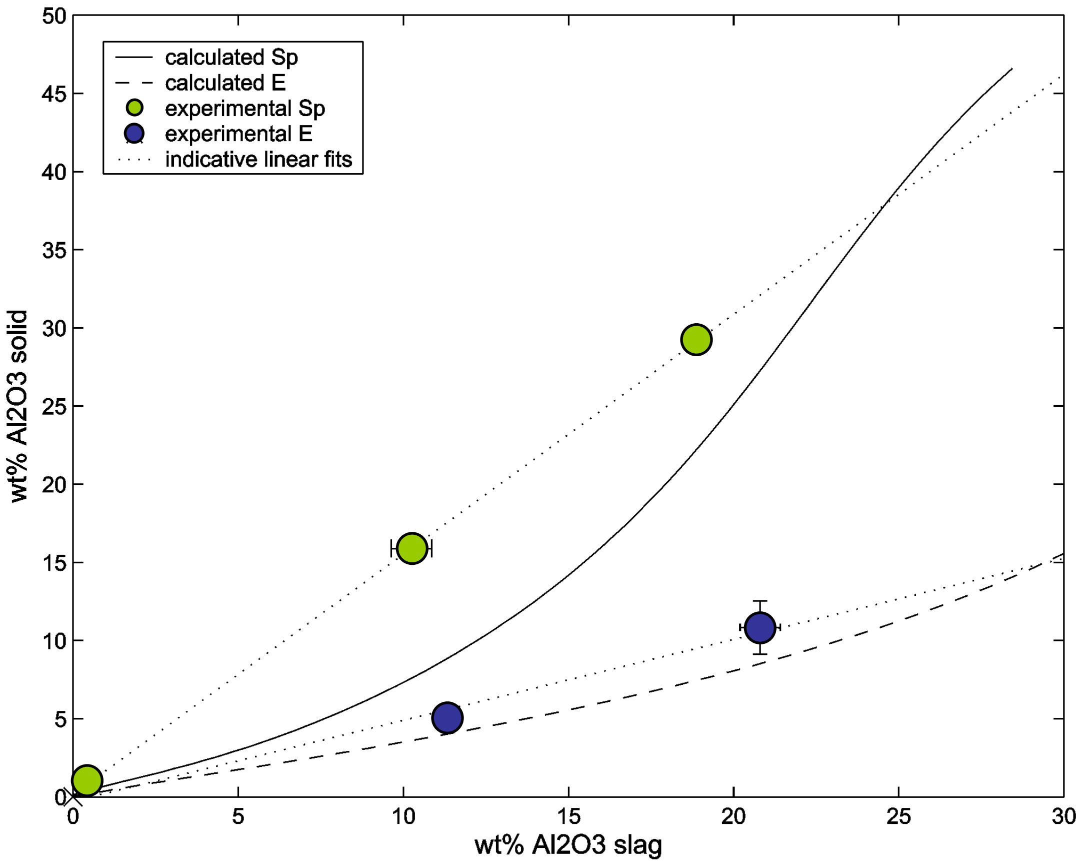
- Tests in known p_{O2}, changing Al_2O_3



T=1600°C
$p_{O2}=10^{-9.36}$ atm
B=1.2

Results: solidus

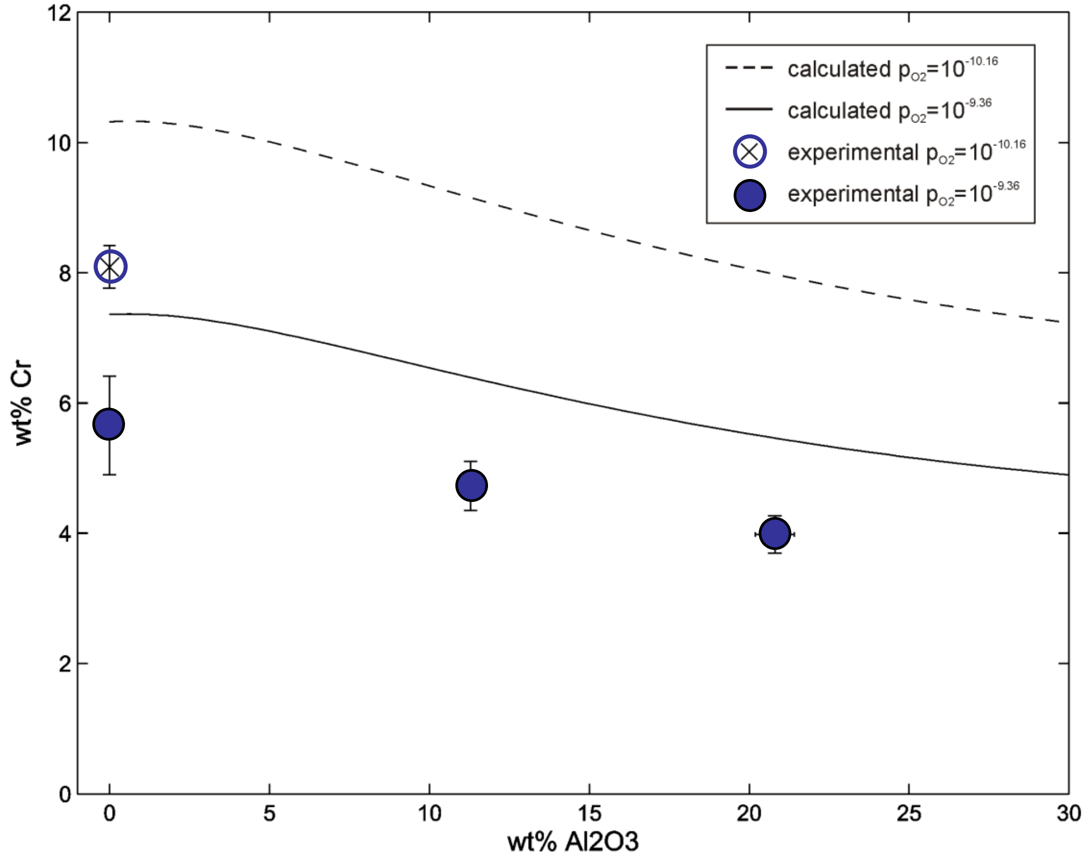
- Relation between Al_2O_3 in slag and in solid



T=1600°C
$p_{O2}=10^{-9.36}$ atm
B=1.2
(E: 0% MgO)
(Sp: 9% MgO)

Results: eskolaite liquidus

- Relation between Al_2O_3 and Cr_2O_3 in slag

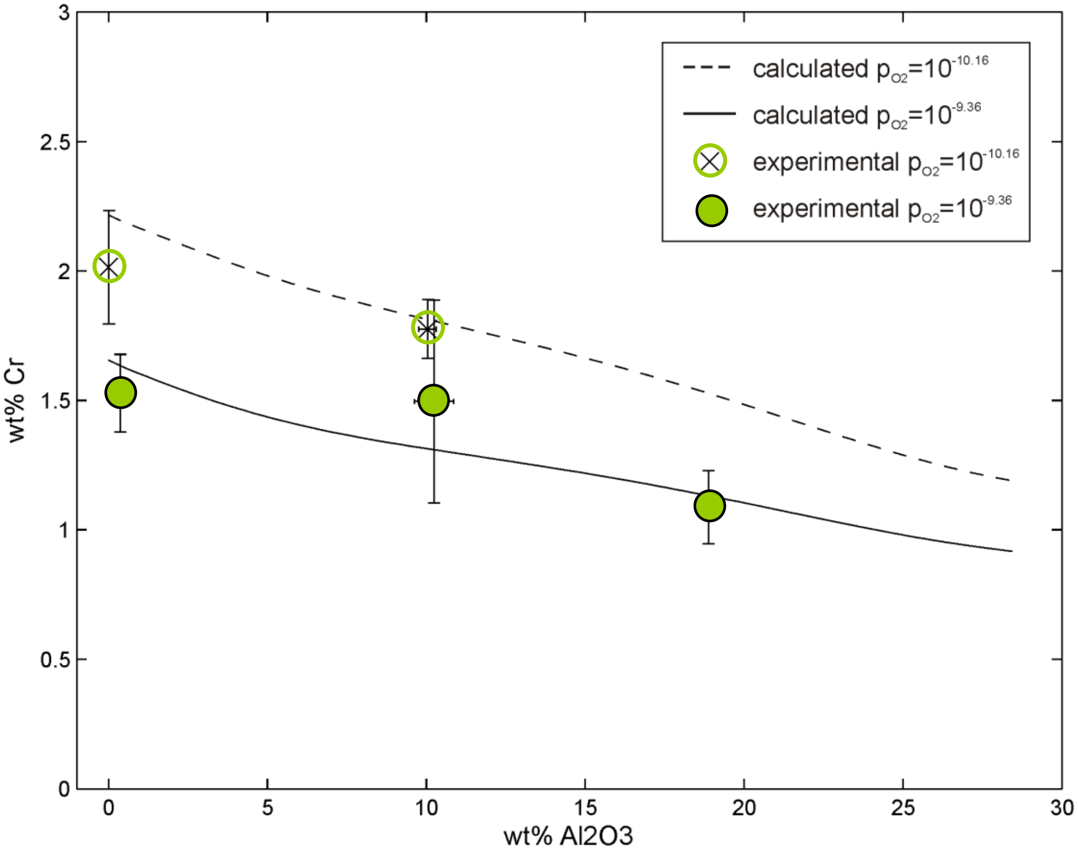


T=1600°C
$p_{O2}=10^{-9.36}$ atm
B=1.2

E: 0% MgO

Results: spinel liquidus

- Relation between Al_2O_3 and Cr_2O_3 in slag



T=1600°C
$p_{O2}=10^{-9.36}$ atm
B=1.2

Sp: 9% MgO

Discussion

- Sampling technique with nice results
- Good match with FactSage
- Improvement possible for
  - Eskolaite liquidus
    - Difference originates in ternary system
  - Solid compositions

Content

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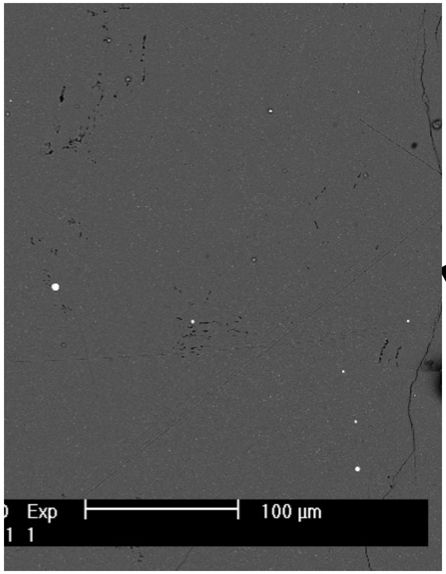
- Slag solidification modelling
- Process model for additions

Industrial slag solidification




24 h



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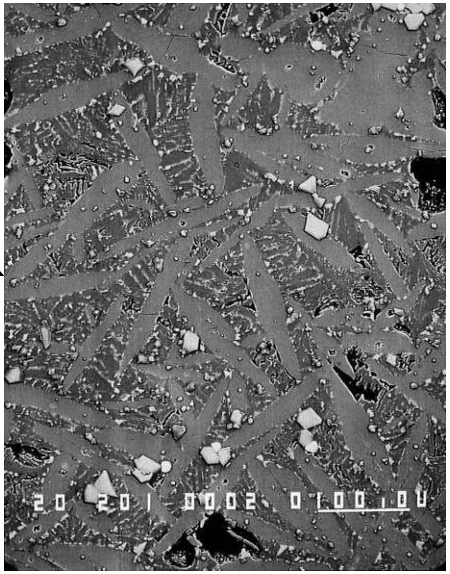
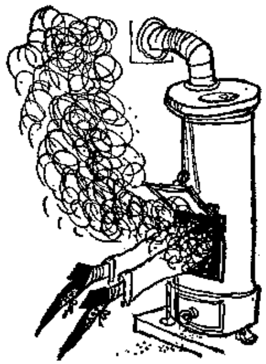
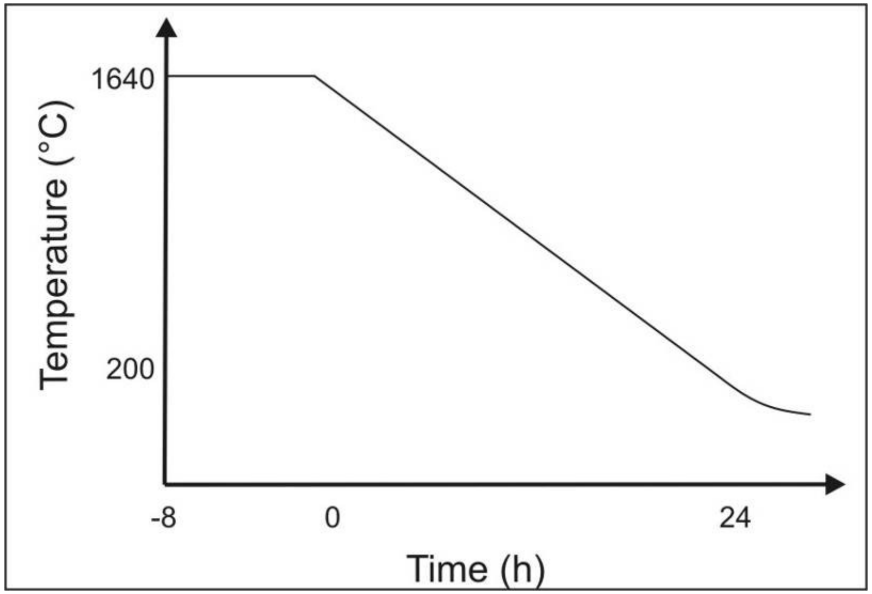


Research methodology

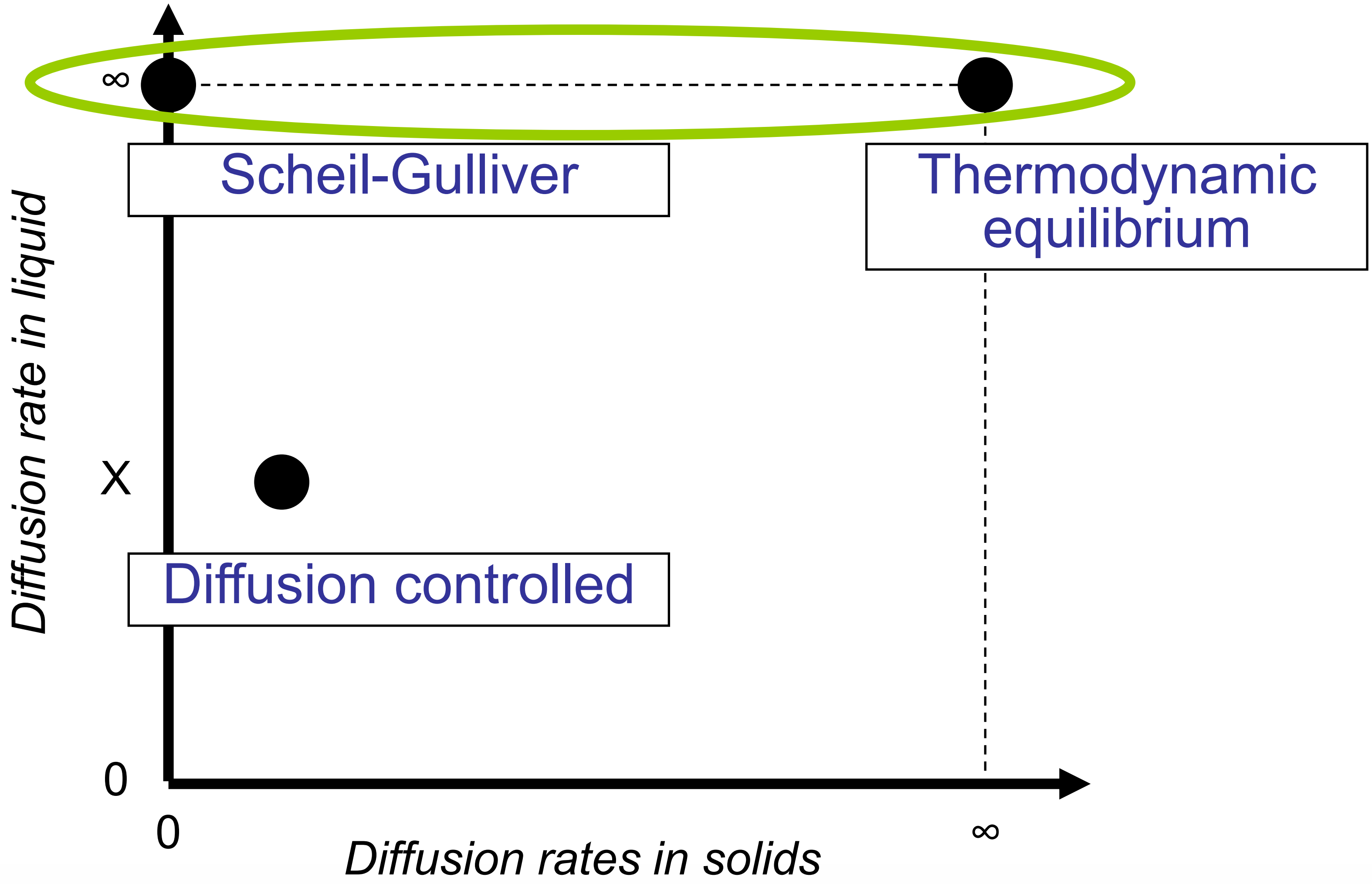
Industrial observation	Laboratory experiment	Simulation
		
Complex system & cooling path	*Simple system & cooling path*	*Known kinetic restrictions*
Relevant data: • Microstructure after complete cooling	Relevant data: • Microstructure after complete cooling • Microstructure during cooling	Relevant data: • Microstructure after complete cooling • Microstructure during cooling

Laboratory experiment

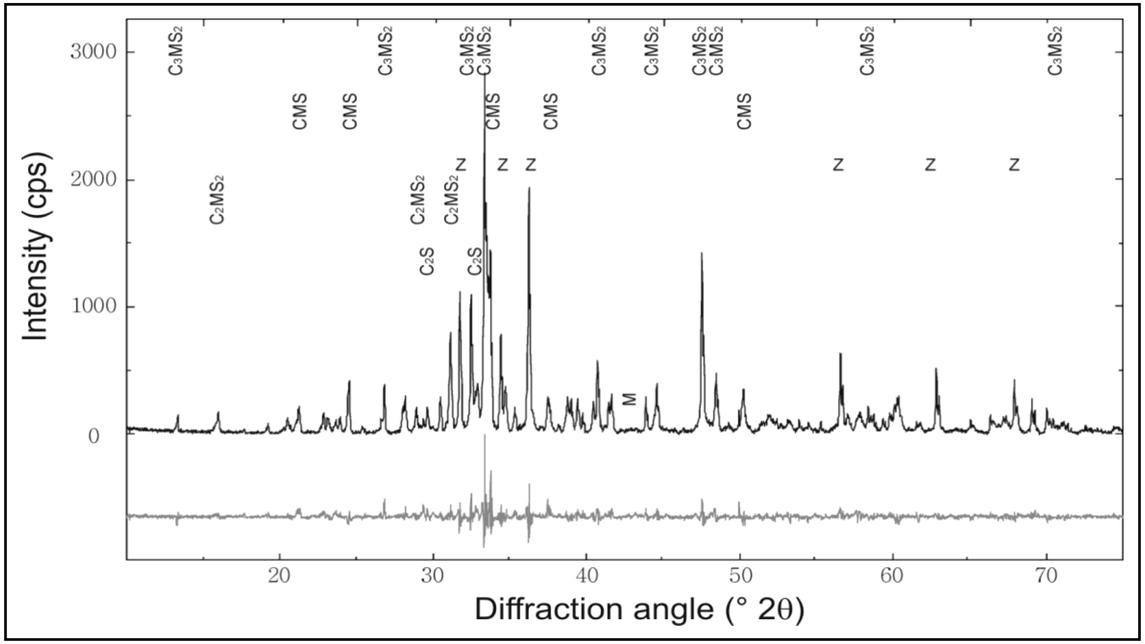
- Synthetic CaO-MgO-SiO_2 slag
- Thermal path
- Analysis techniques
  - Quantitative XRD (Rietveld analysis)
  - EPMA-EDS

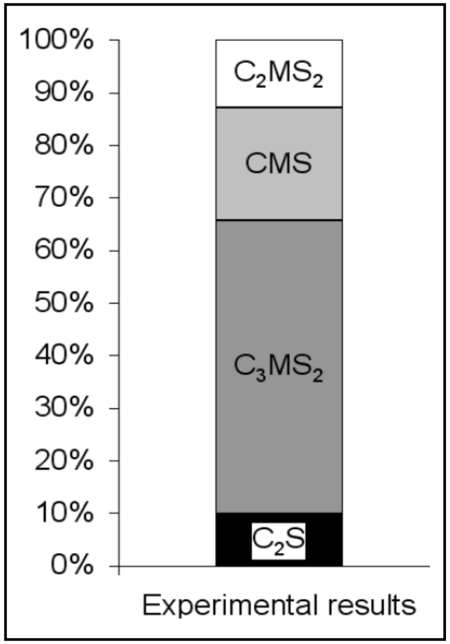


Common approaches to solidification modelling

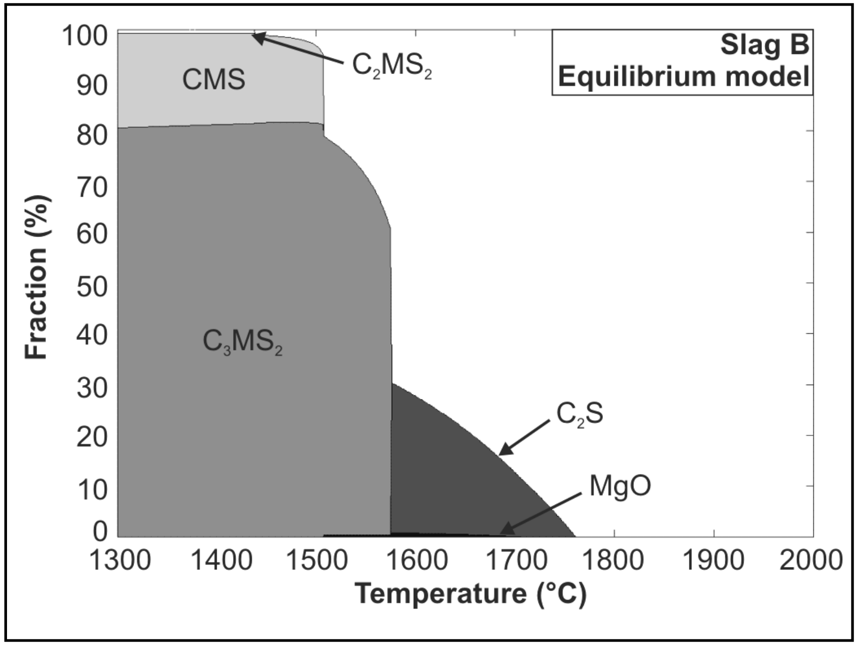


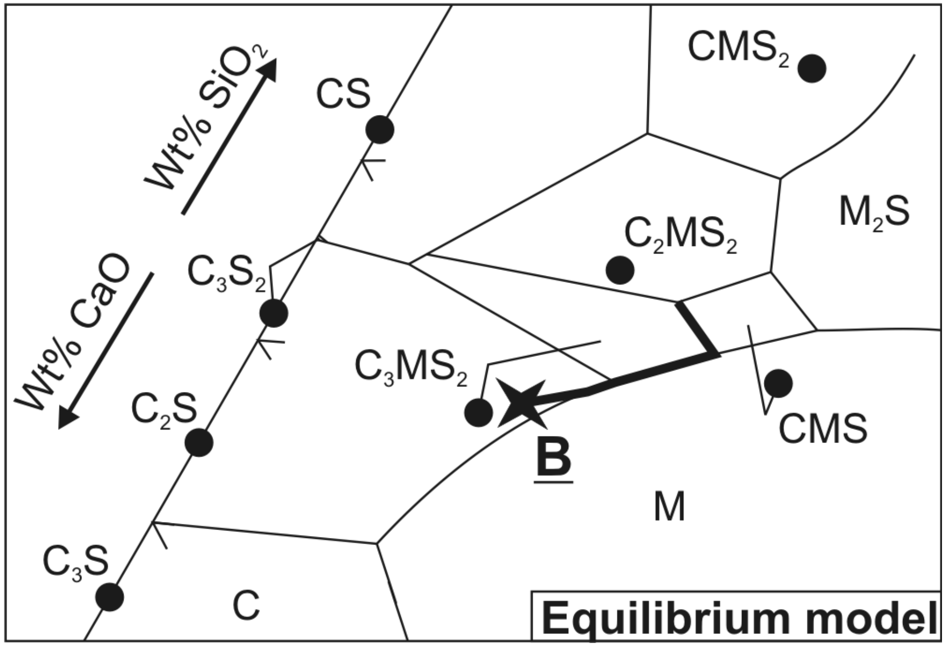
Mineralogy: Experiment



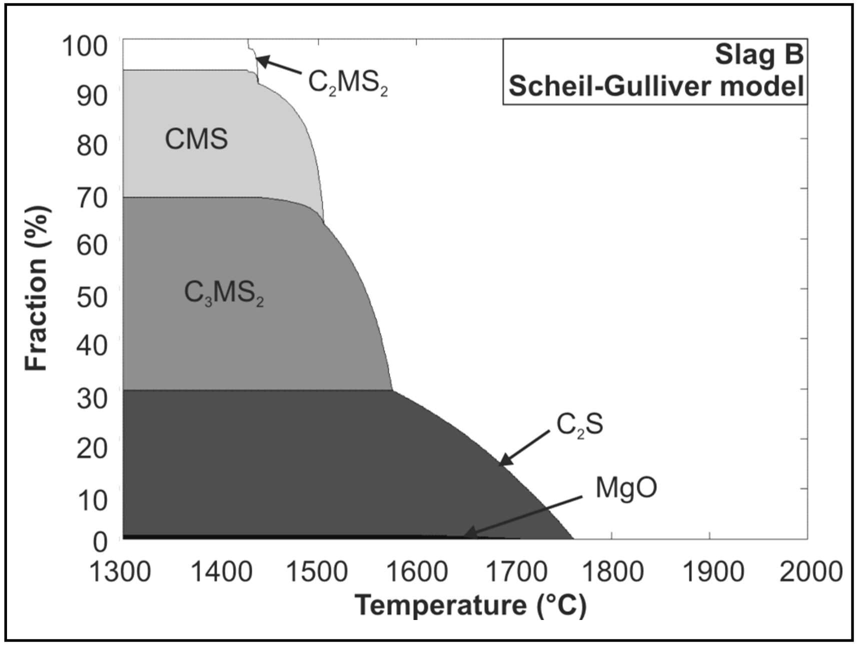


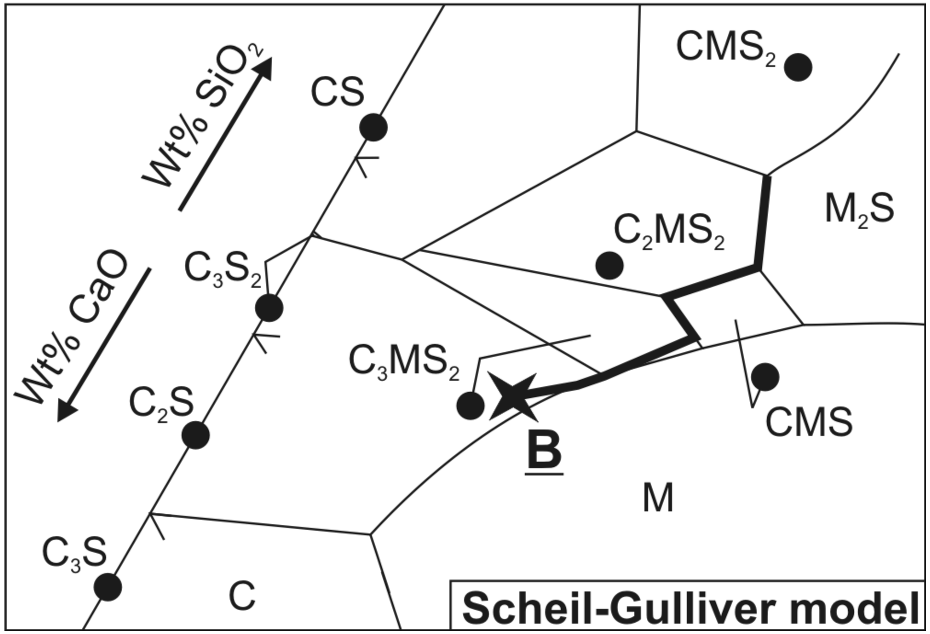
Mineralogy: **Equilibrium**





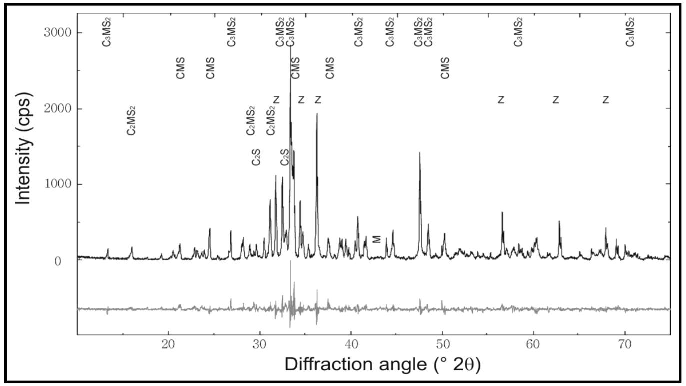
Mineralogy: **Scheil-Gulliver**



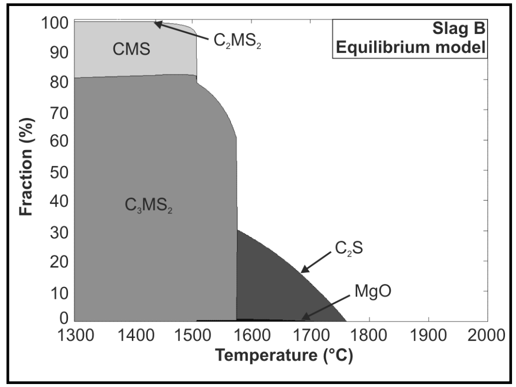


Mineralogy

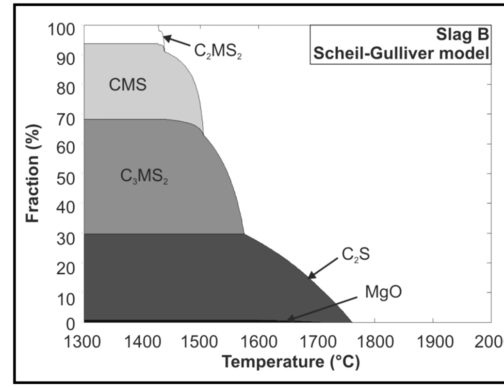
Experiment

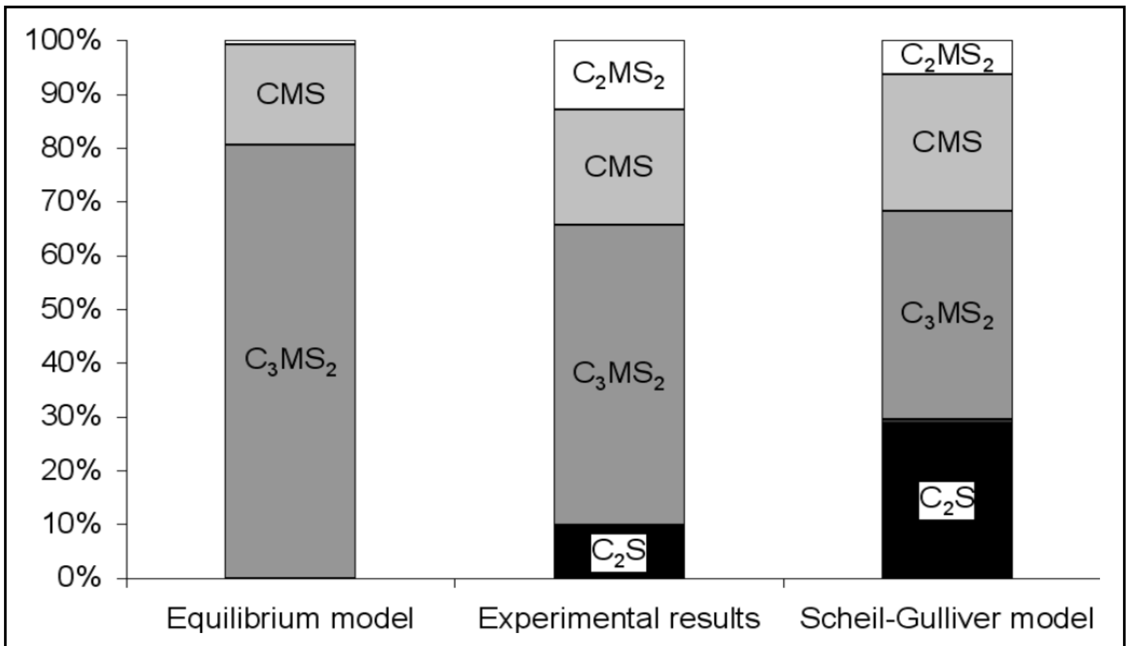


Equilibrium



Scheil-Gulliver



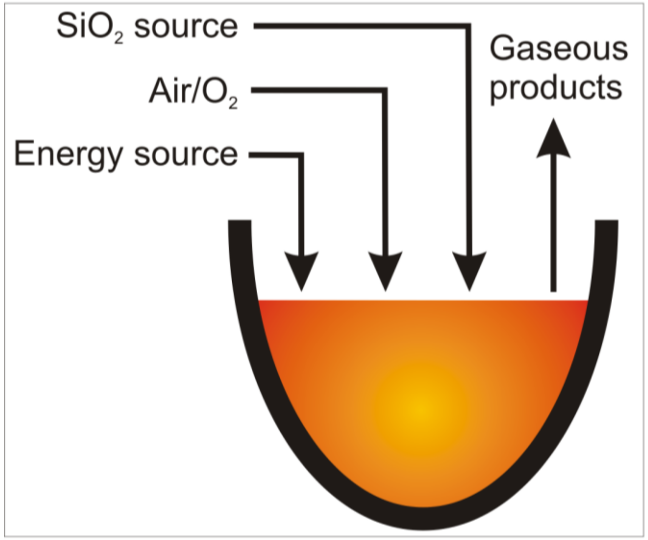


Content

- Experimental verification of liquidus
- Slag solidification modelling
- Process model for additions

Slag post-treatment

- Idea:
  - Lower slag basicity
  - Avoid C_2S formation
  - Avoid subsequent slag dusting
- Main problem:
  - Limited heat capacity and conductivity
  - Limited potential to dissolve SiO_2.
- Possible solution:
  - Co-inject energy source (metal + O_2)



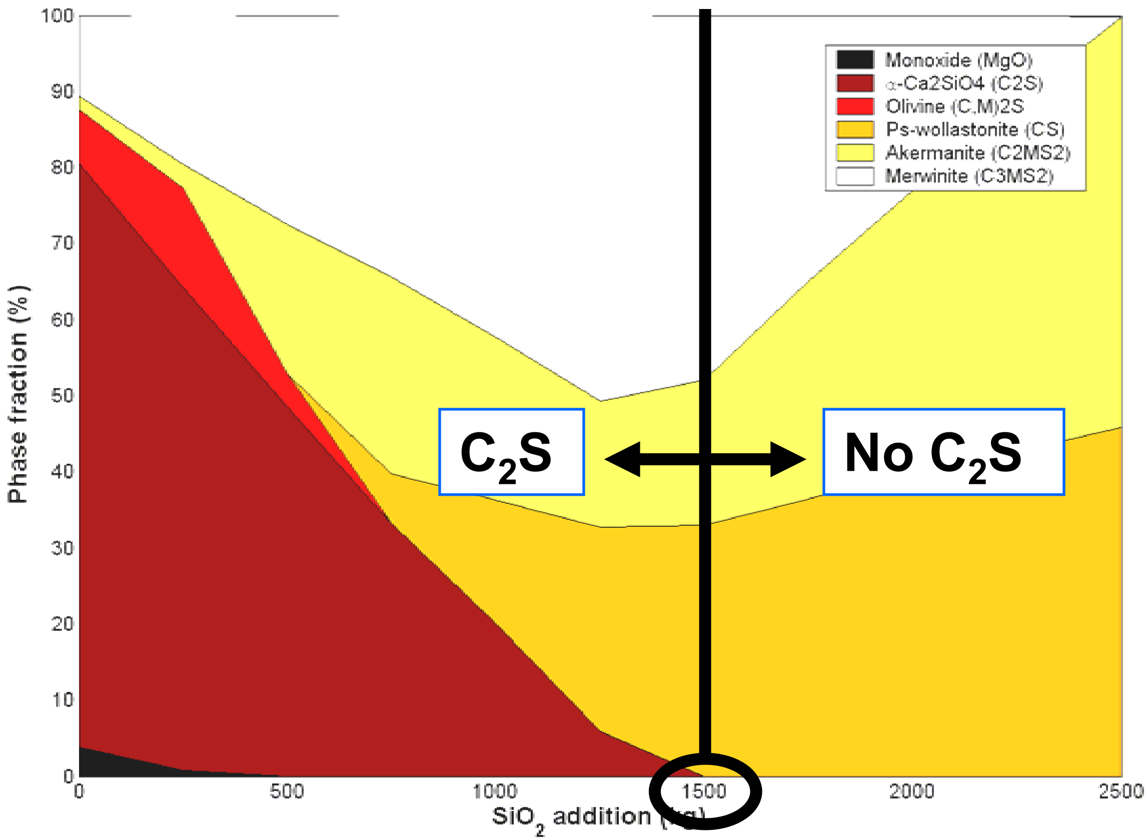
Slag post-treatment model

- Developed based on:
  - Solidification model (composition → microstructure)
  - Process model (additions → composition & temperature)

- Guidelines concerning:
  - Required SiO_2 addition
  - Al or FeSi as energy source
  - Air or oxygen as gas (stirring + oxidation)

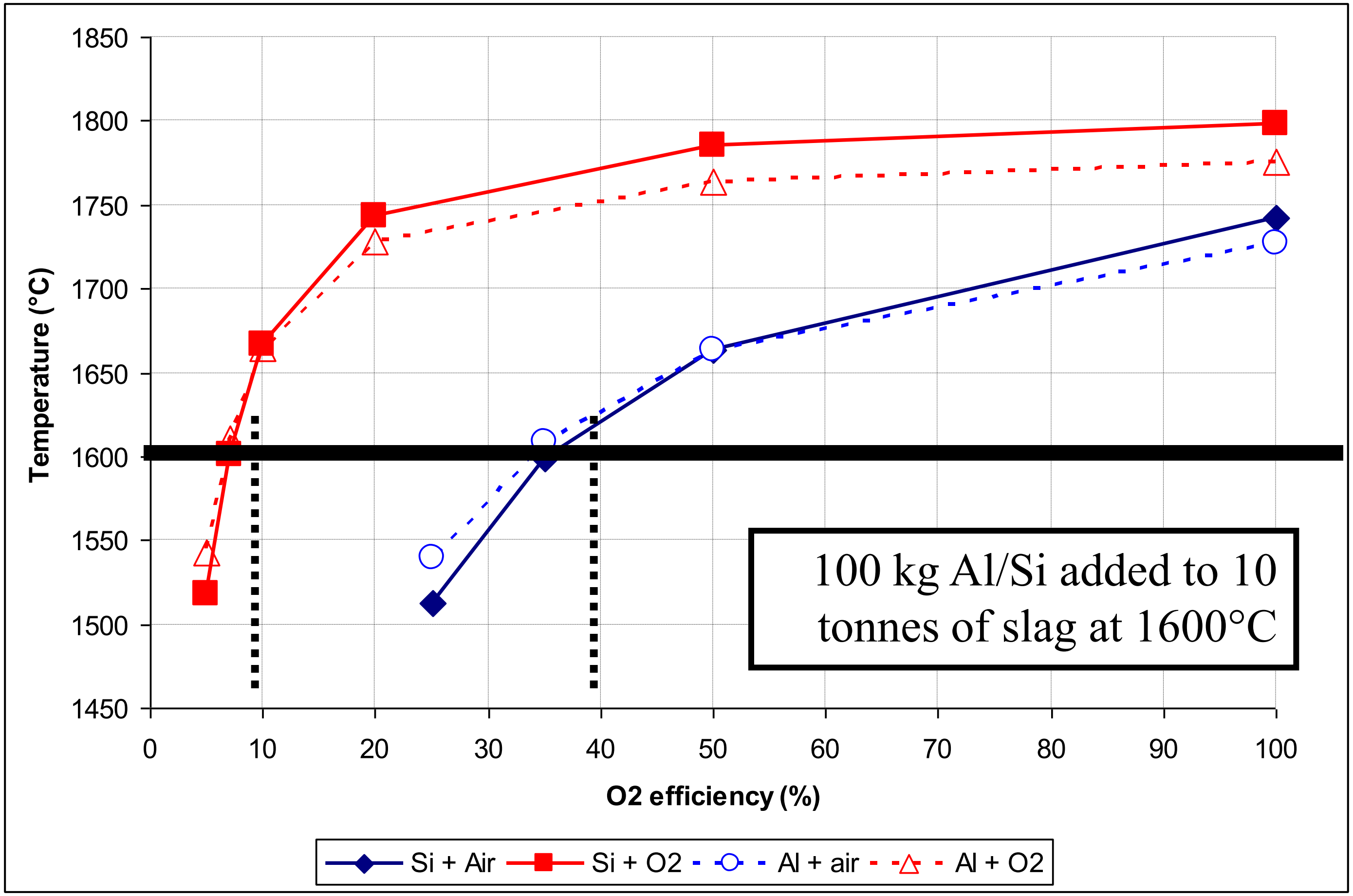
Slag post-treatment model

- Required SiO2 addition?



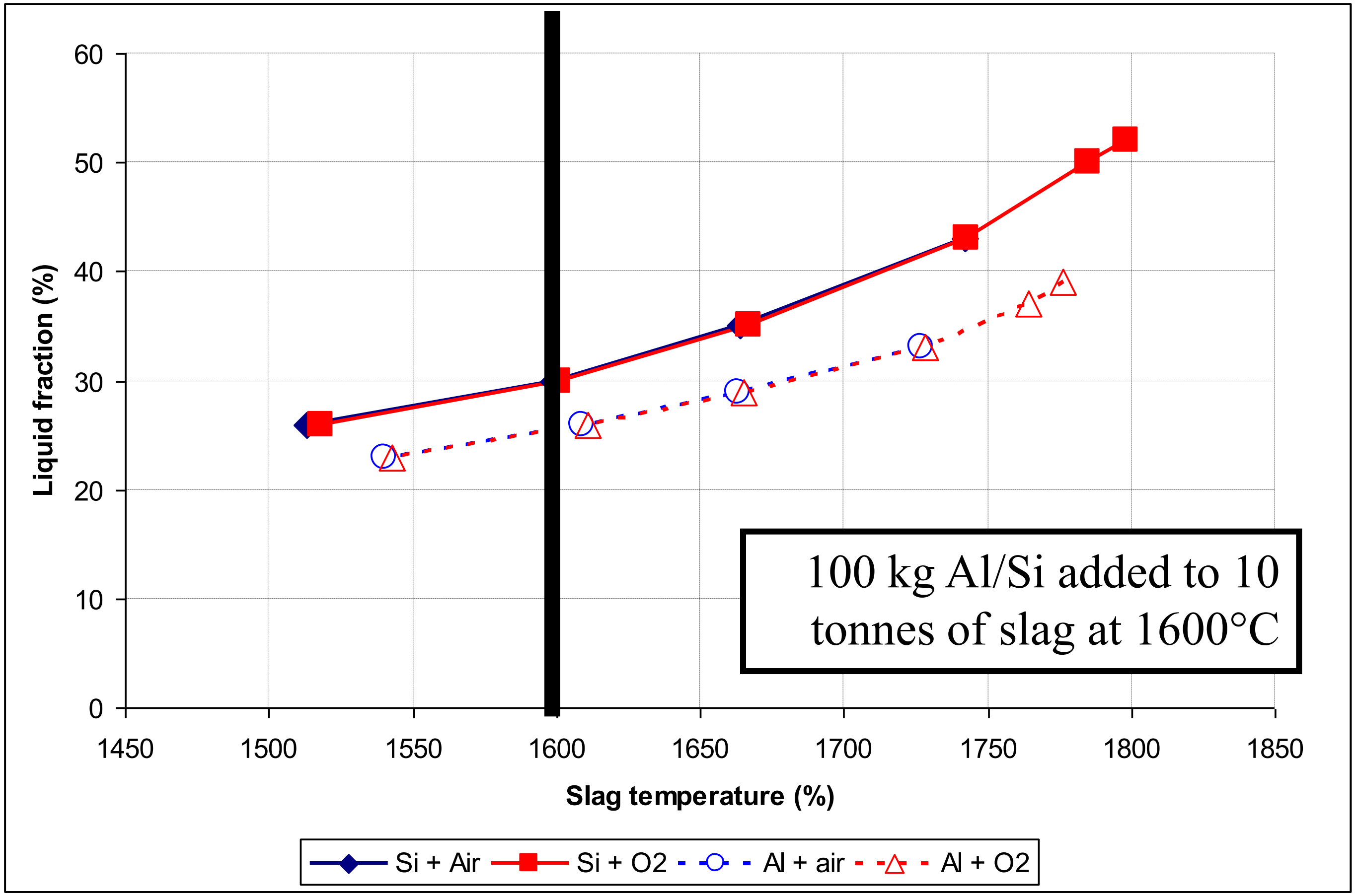
Enthalpy source

- Al or FeSi? → Heating effect



Enthalpy source

- Al or FeSi? → Slag liquidity



Guidelines from process model

- Guidelines

Oxygen injection
- 100 kg of Si or 130kg of FeSi
- 340 kg or 250 Nm³ of O_2
- 1300 kg of SiO_2

- Practical implementation ongoing
- Macroscopic properties should not deteriorate

Conclusions

- Liquidus measurements:
  - Data at high temperature match well
- Cooling microstructure:
  - Easy assumptions give good approximation
- Process model:
  - Fast guidelines