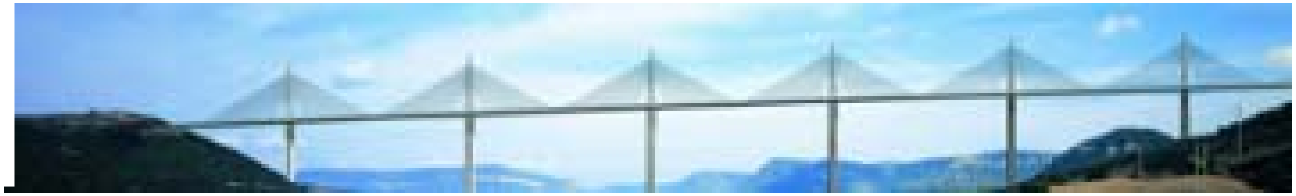


Stainless steel slags and the use of ChemApp

Bart Blanpain

Dirk Durinck, Sander Arnout, P. Tom Jones, Muxing Guo, Frederik Verhaeghe, Patrick Wollants

Thermodynamics in Materials Engineering

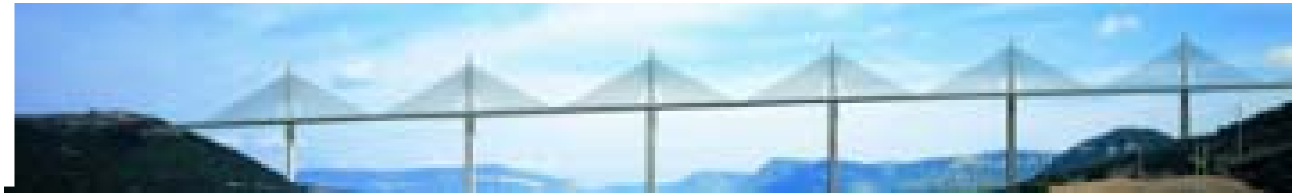
Dept. Metaalkunde en Toegepaste Materiaalkunde

Katholieke Universiteit Leuven, Belgium

GTT – 5 June 2008

Outline

- Introduction
- EAF process in stainless steel production
- Slag stabilisation and microstructure calculation

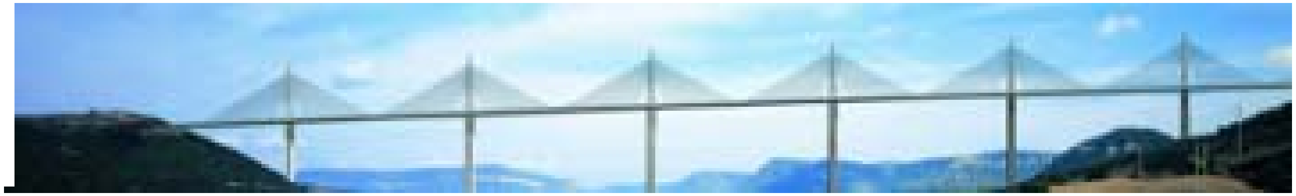


Katholieke Universiteit Leuven


DE RECTOR
Pizza-Hut


Quick

thermo
research group



GTT - TECHNOLOGIES

Thermodynamics in Materials Engineering Research Group

Department

of

Metallurgy and Materials Engineering


thermo
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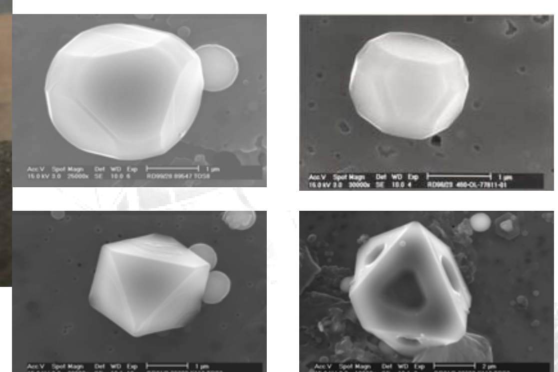
I. Pyrometallurgical processing

- Vessel integrity
- Slag practice and properties
- Steel cleanliness
- Modelling



Centre for high temperature processes, metallurgy and refractory materials

LEUVEN
HT centre
for high temperature processes, metallurgy and refractory materials

- Cooperation with industrial partners active in high temperature metals processing: ArcelorMittal, Heraeus Electro-Nite and Umicore
- Fly wheel function for intense collaboration through substantial research projects and doctoral research programs

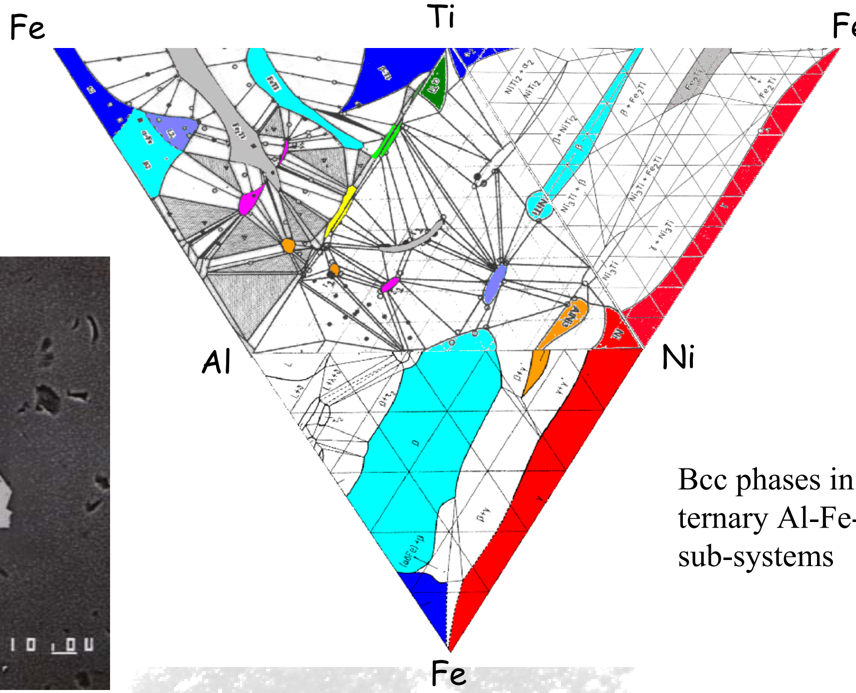
umicore
materials for a better life

Heraeus
Electro-Nite

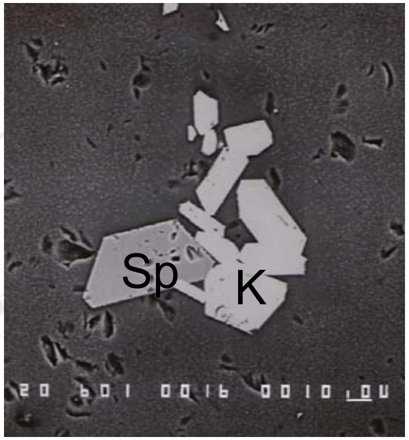
ArcelorMittal

II. Phase relations in materials systems

- Determination and optimisation of phase diagrams in metallic systems
- Phase relations in slag systems
- Thermodynamics of nanomaterials systems

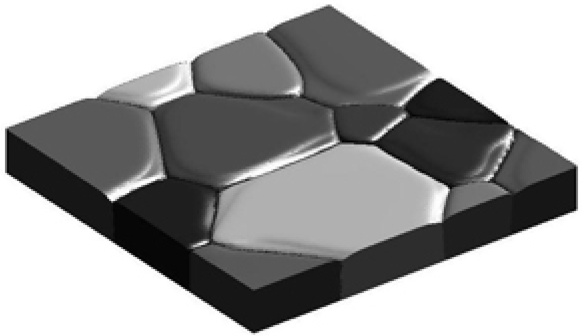


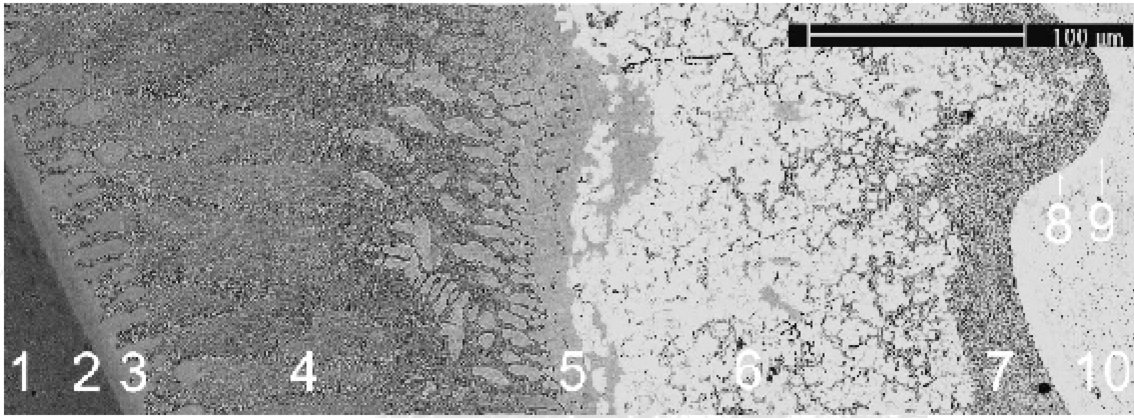
Bcc phases in th
ternary Al-Fe-N
sub-systems

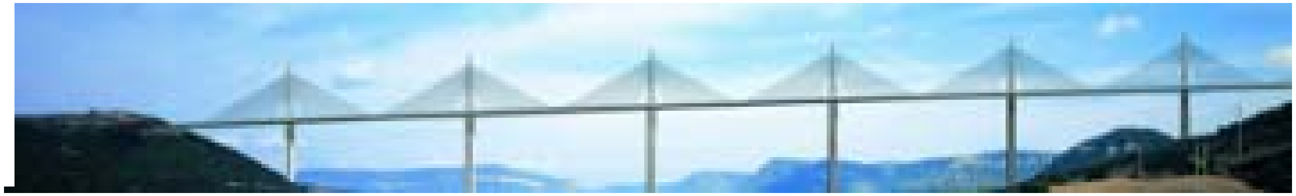


III. Microstructure evolution modelling

- Grain growth
- Lead-free solder systems
- Dissolution of ferro-alloys in liquid steel
- Solidification of slags







Stainless steel slags

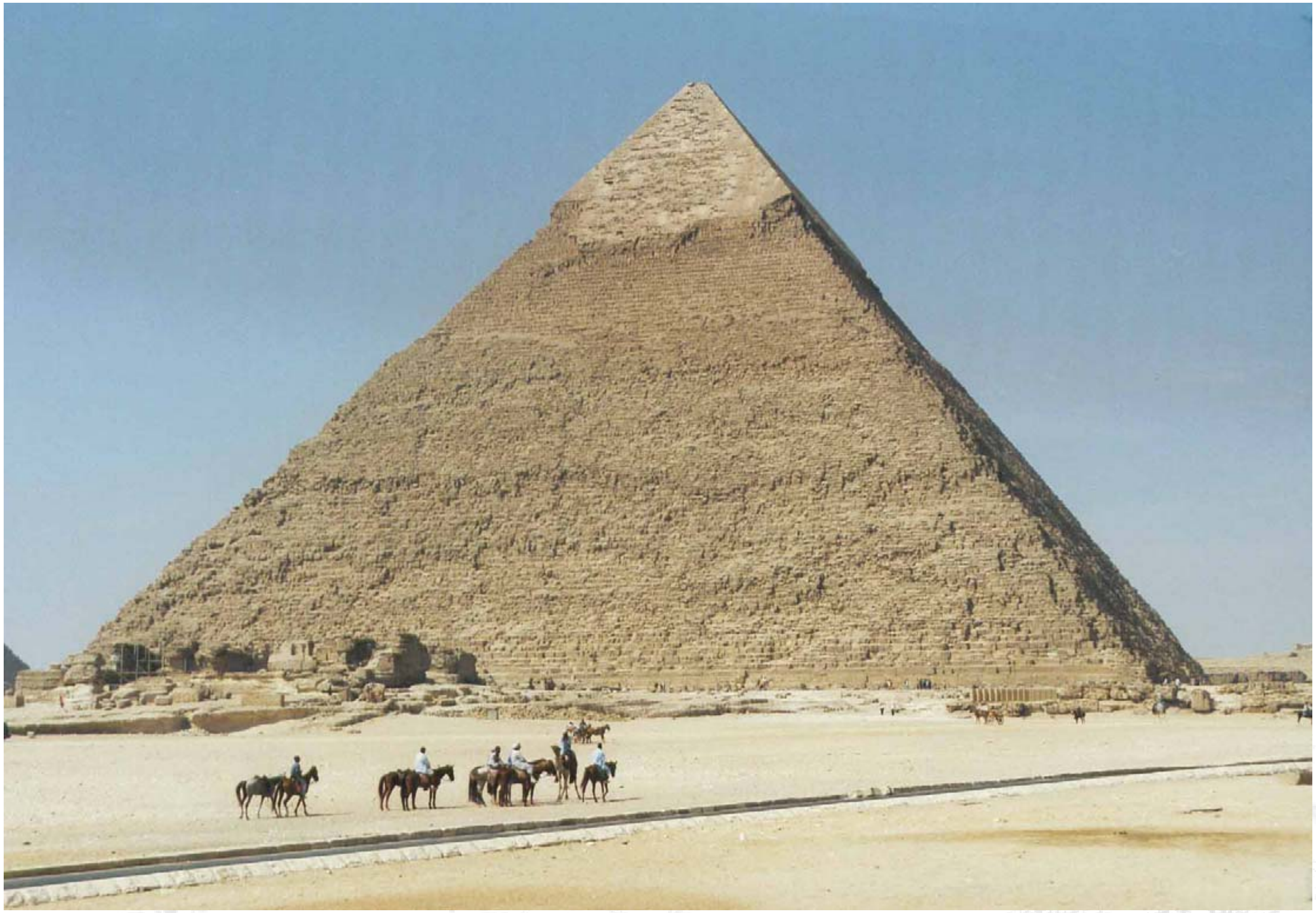
Steel production sites in Belgium

Steel production sites in Belgium

Stainless steel slags

- General
  - By-product/waste of stainless steel production
  - Metallurgical functions:
    * Oxidation shielding
    * Impurity removal
    * Thermal insulation
- Amounts
  - Slag-to-steel ratio: 275 kg slag / 1000 kg steel
  - Global stainless steel production: 25 Mt steel
    (source: ISSF,IISI)

→ **~ 7 Mt stainless steel slag / year**

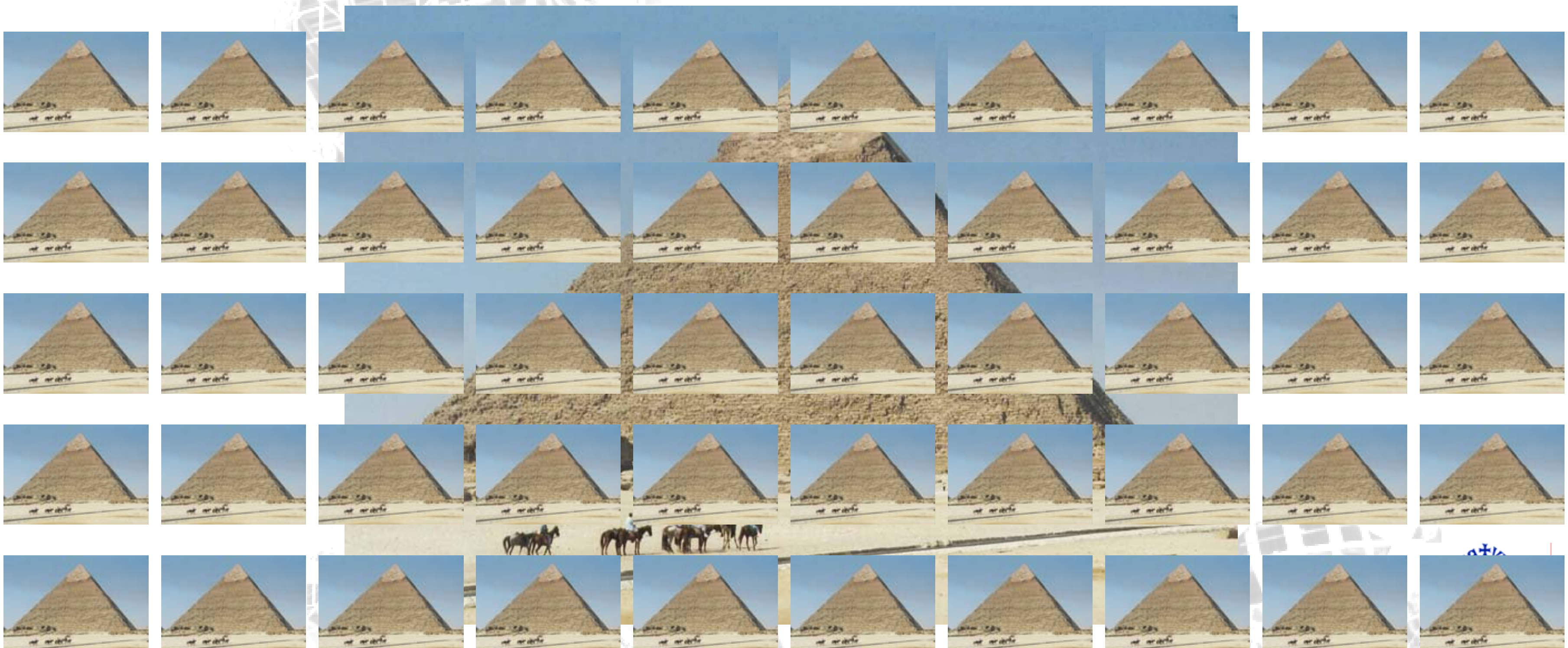


Assumptions: density = 2.5 ton/m³, Gizeh pyramid dimensions = 230m.230m.137m

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

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

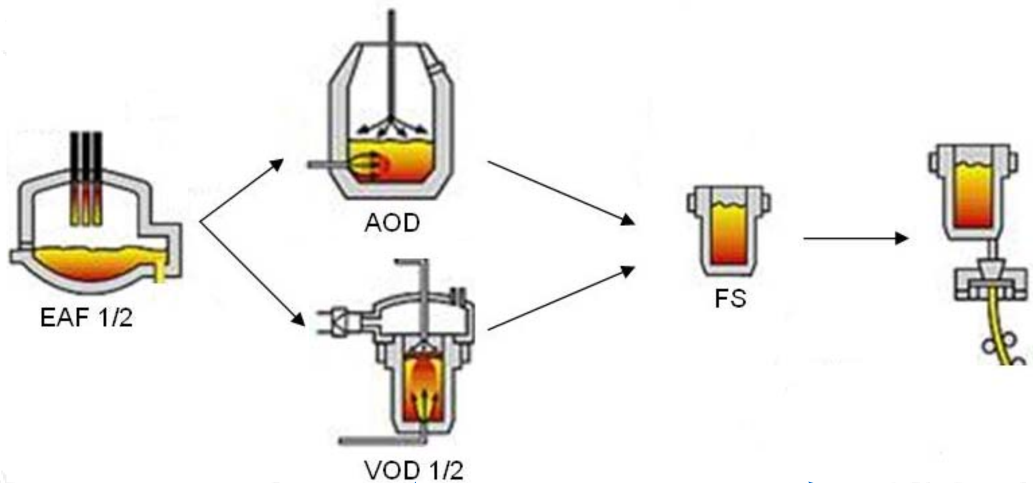
World iron and steel slag production: ~ $350 \cdot 10^6$ tons



Assumptions: density = 2.5 ton/m³, Gizeh pyramid dimensions = 230m.230m.137m

Stainless steel production

- 3-step process (before casting)
  - EAF: scrap melting
  - AOD/VOD: de-C and de-S
  - Ladle refining: de-S

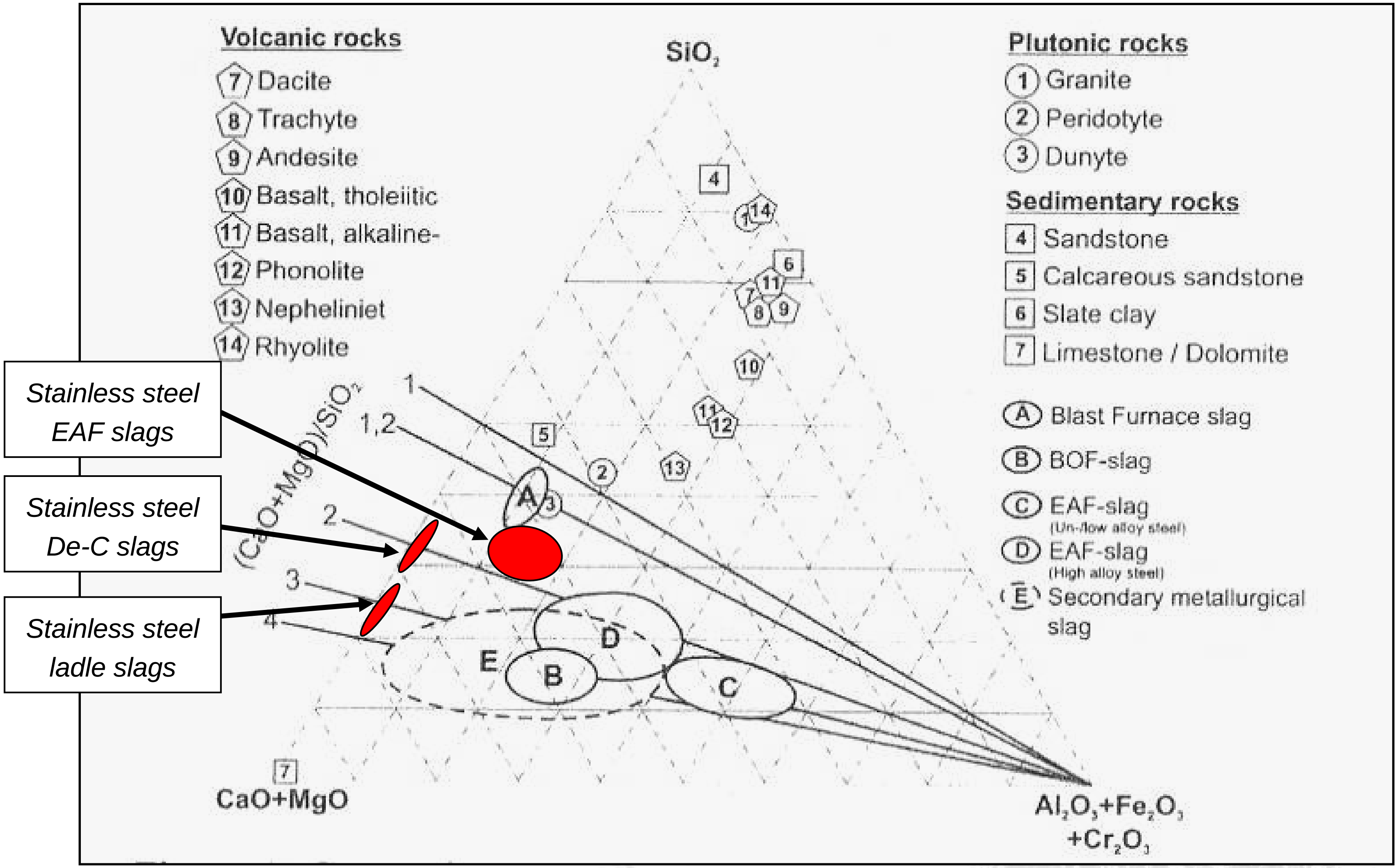


EAF slag
125 kg/ton steel

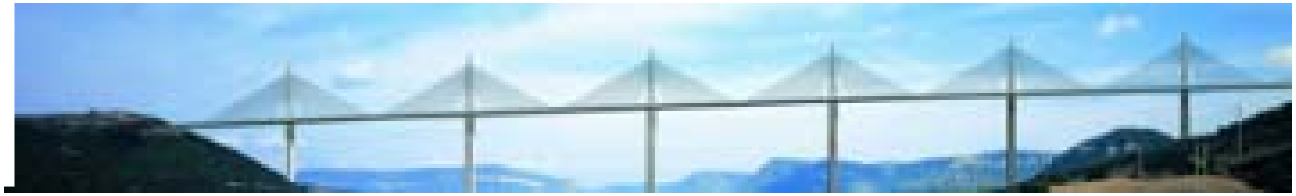
De-C slag
180 kg/ton steel

Ladle slag
20 kg/ton steel

Overview slag compositions



Motz and Kuhn., Scanmet II, 2004



Process Modelling: Chromium recovery and foaming in the EAF

S. Arnout, F. Verhaeghe, B. Blanpain, P. Wollants, R. Hendrickx, G. Heylen,, Steel Research International, 77 (5) (2006), 317 - 323

S. Arnout, D. Durinck, M. Guo. B. Blanpain, P. Wollants, J. American Ceramic Society, 91 (2008) 1237-1243

M.X. Guo, D. Durinck, P.T. Jones, G. Heylen, R. Hendrickx, R. Baeten, B. Blanpain, P. Wollants, Steel Research International, 78 (2) (2007), 117 - 124

D. Durinck, P.T. Jones, M.X. Guo, F. Verhaeghe, G. Heylen, R. Hendrickx, R. Baeten, B. Blanpain, P. Wollants, Steel Research International, 78 (2) (2007), 125 – 135

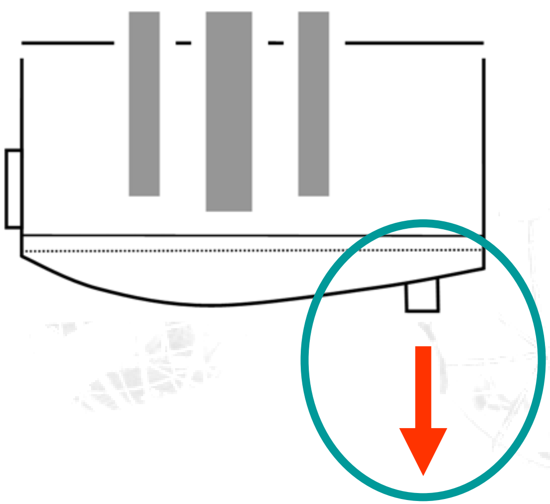
Slag in the EAF

The EAF process

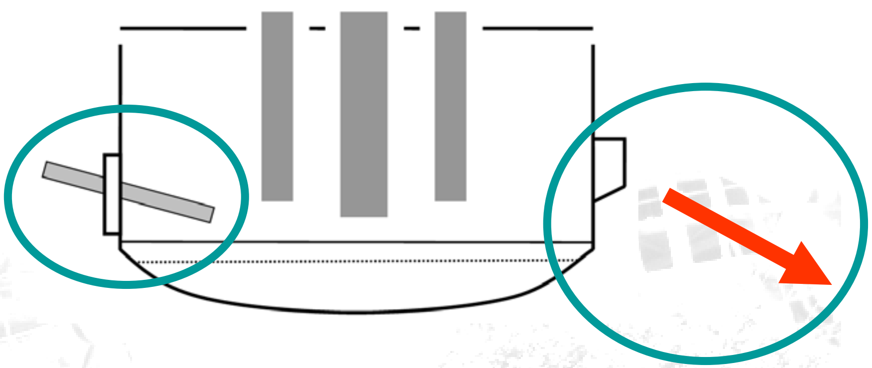
- Slag issues during EAF refining
  - Early liquid slag formation → prevent over-oxidation of Cr
  - Slag foaming → increase furnace productivity, refractory lifetime, energy and material efficiency
  - Chromium recovery → economical & environmental reasons
  - Immobilisation of CrO_x → enhance slag valorisation potential
- All affected by high-T slag microstructure

Furnace types

- Two distinct 120t EAFs
  - EAF1 = Eccentric Bottom Tapping Furnace
    No C/O_2 lance → no foaming
  - EAF2 = Spout Tapping Furnace
    C/O_2 lance → slag foaming



EAF1 (EBTF)

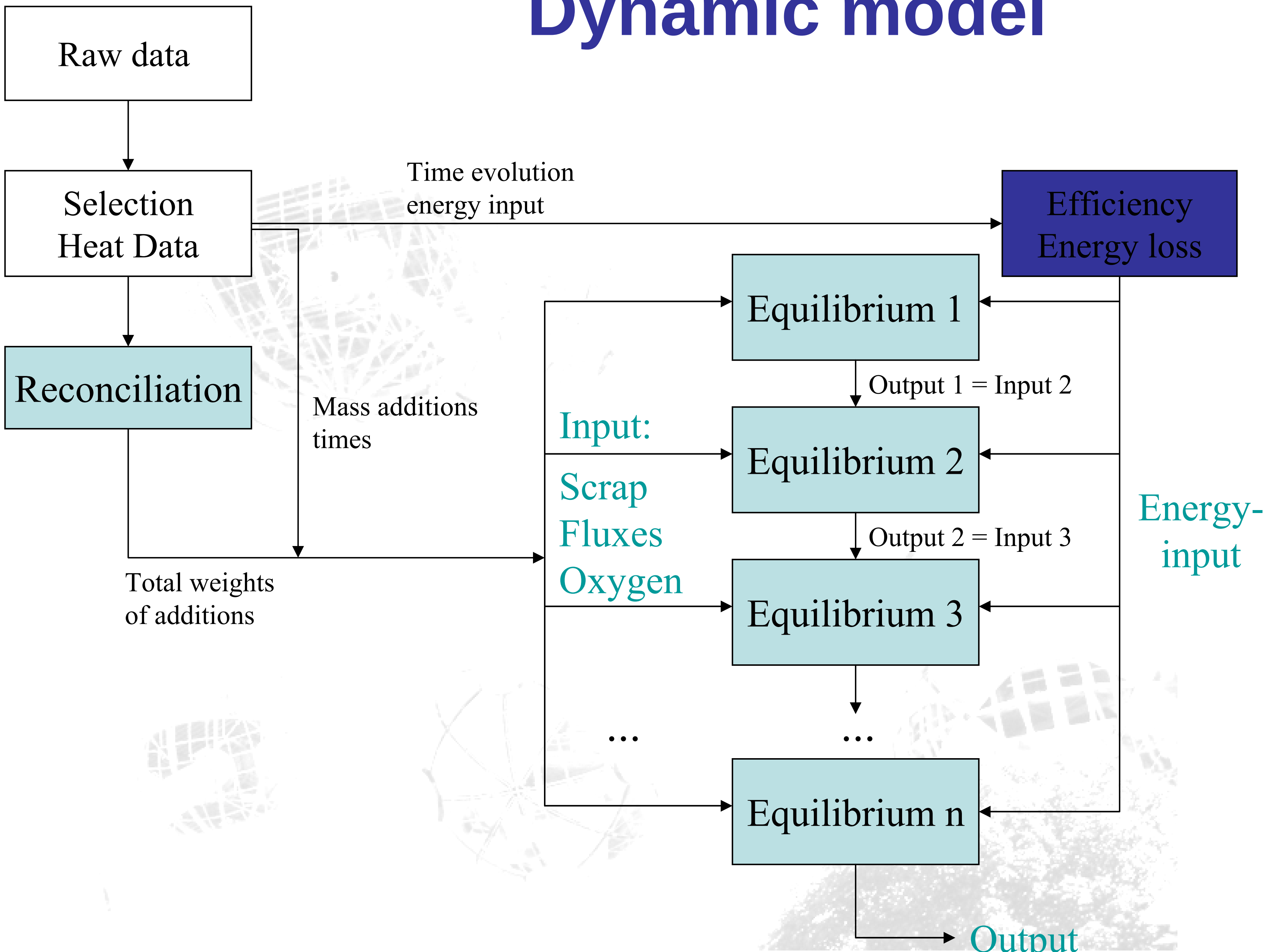


EAF2 (STF)

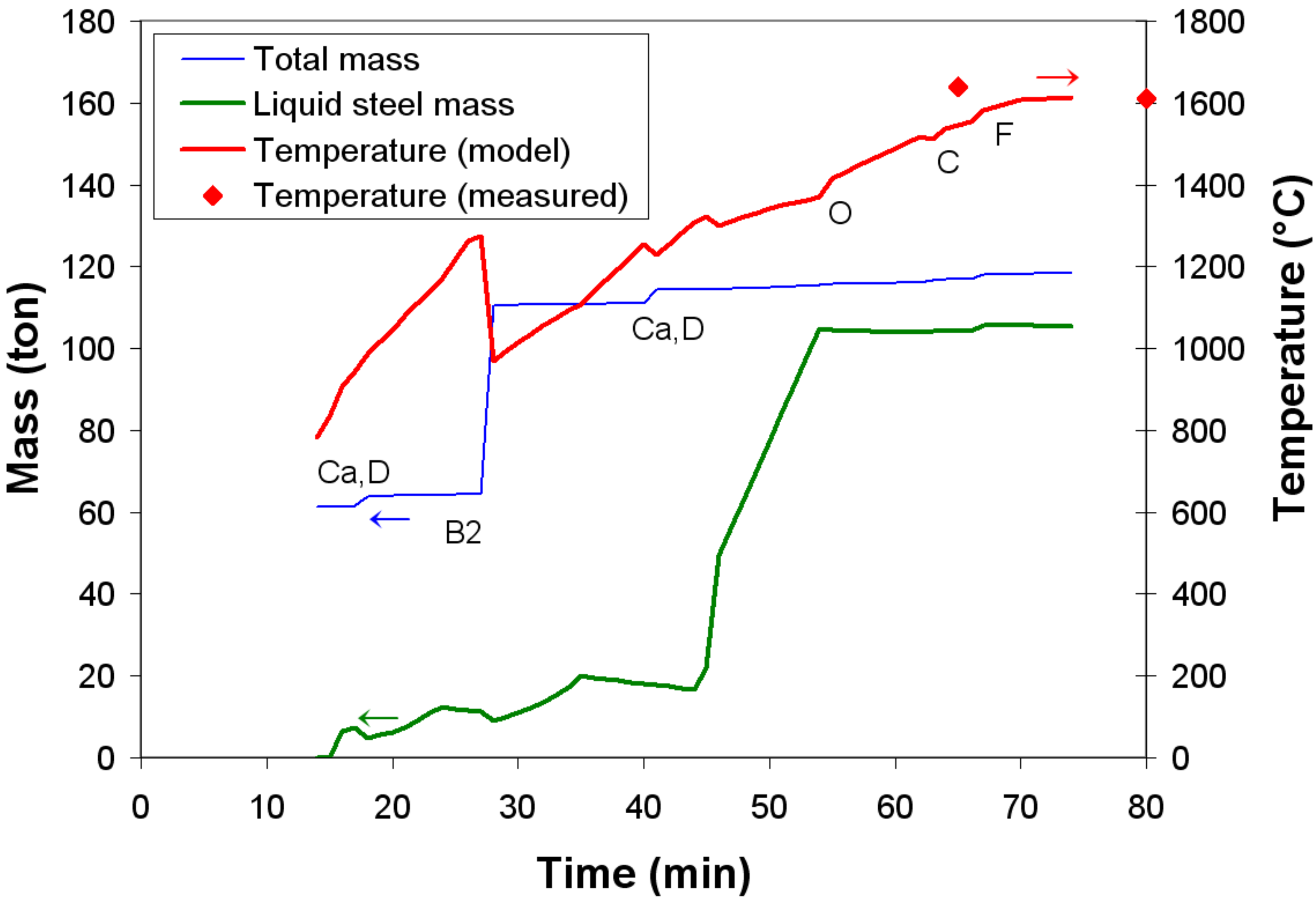
EAF operations

Min.	Operation	Min.	Operation	Abbr.
1-6	Charging 1st bucket			B1
7-26	Arc on	12	Start of calculations	S
		17-20	Calcia additions	Ca
		18	Dolomite and chamotte add.	D
28	Charging 2nd bucket			B2
29-70	Arc on	41	Dolomite and calcia addition	Ca,D
		49-63	Calcia additions	Ca
		55	O_2 injection	O
		63	C/O_2 injection	C
		67	Fe-Si and fluorspar addition	F
74			Tapping	T

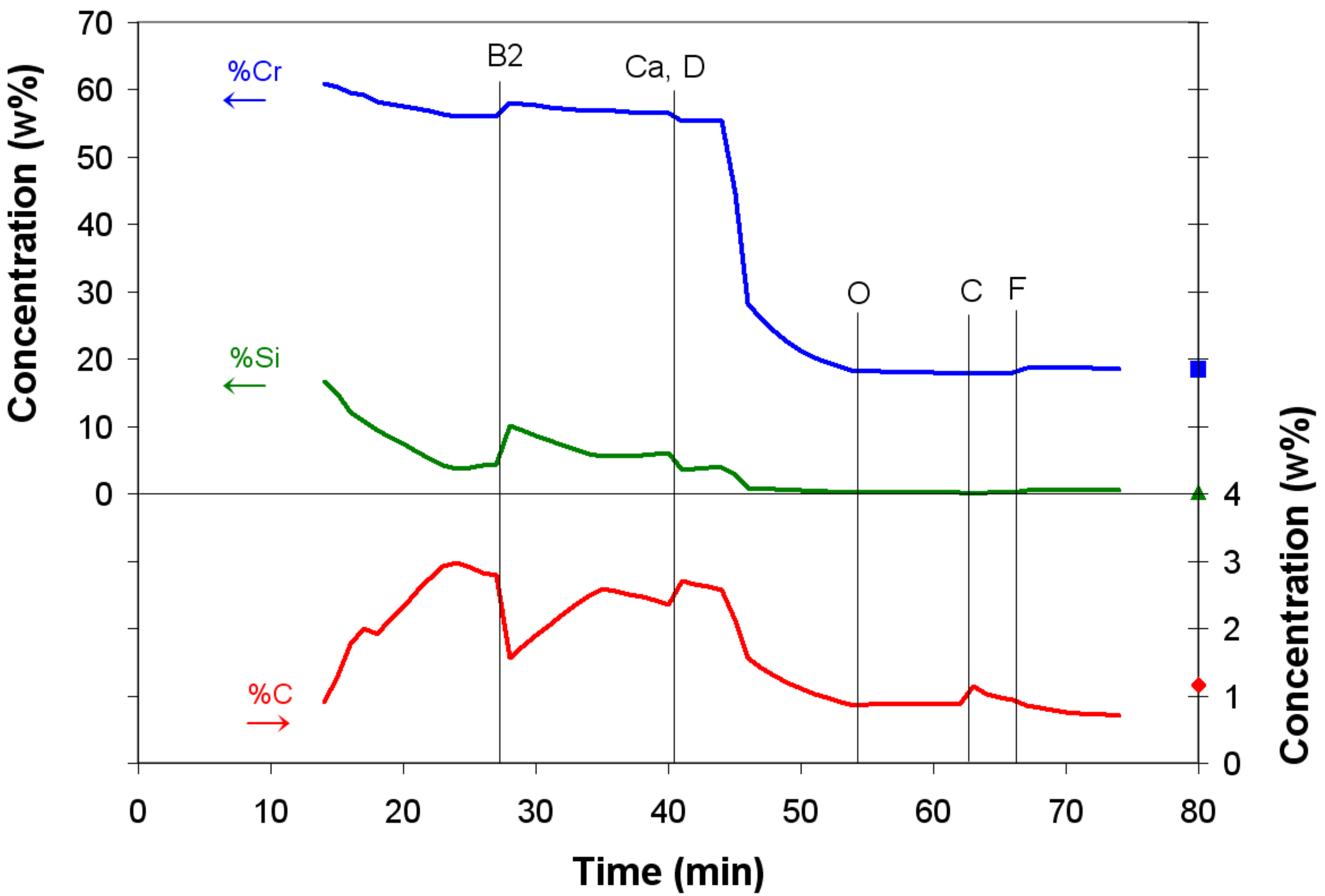
Dynamic model



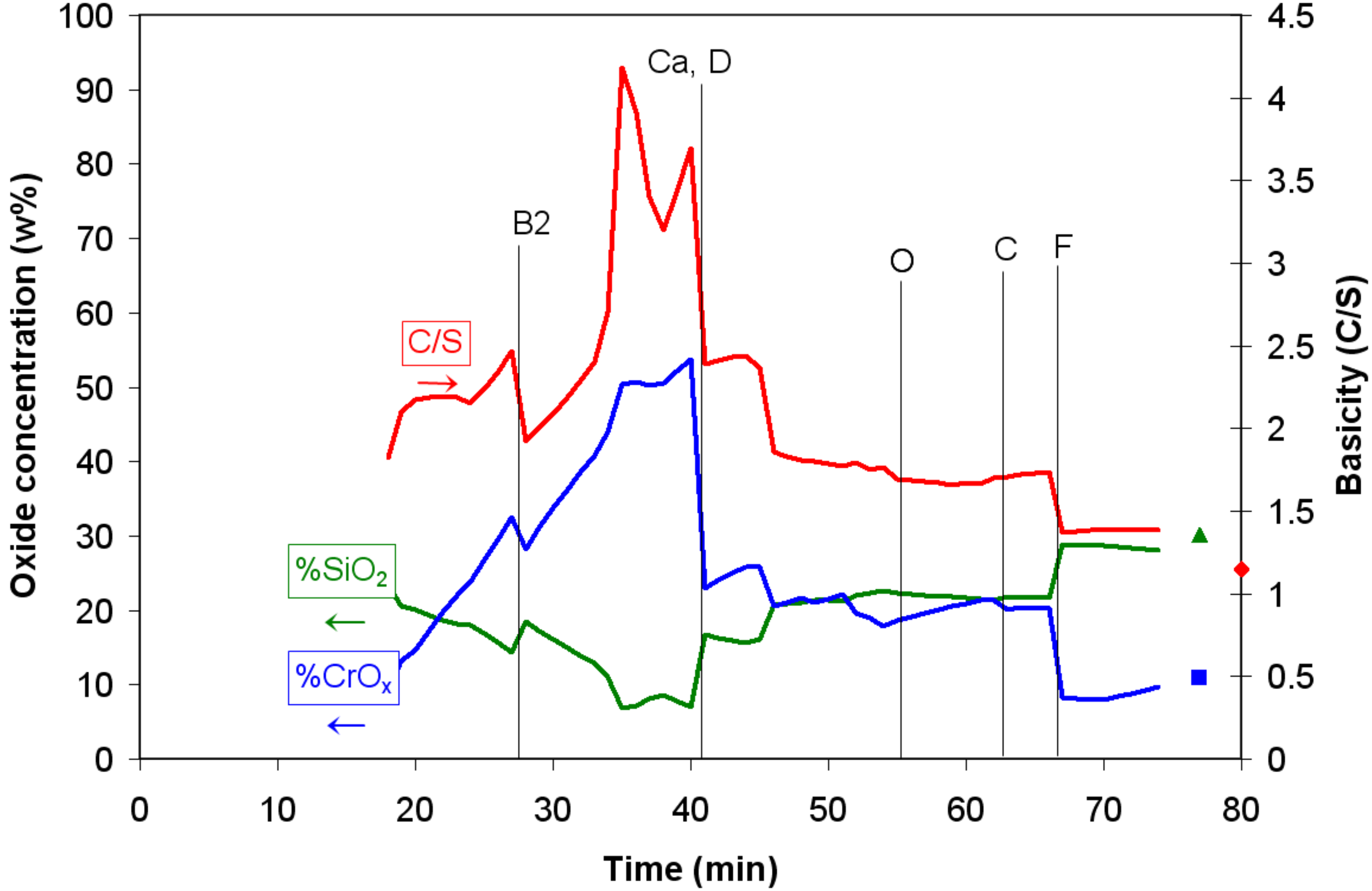
Temperature evolution



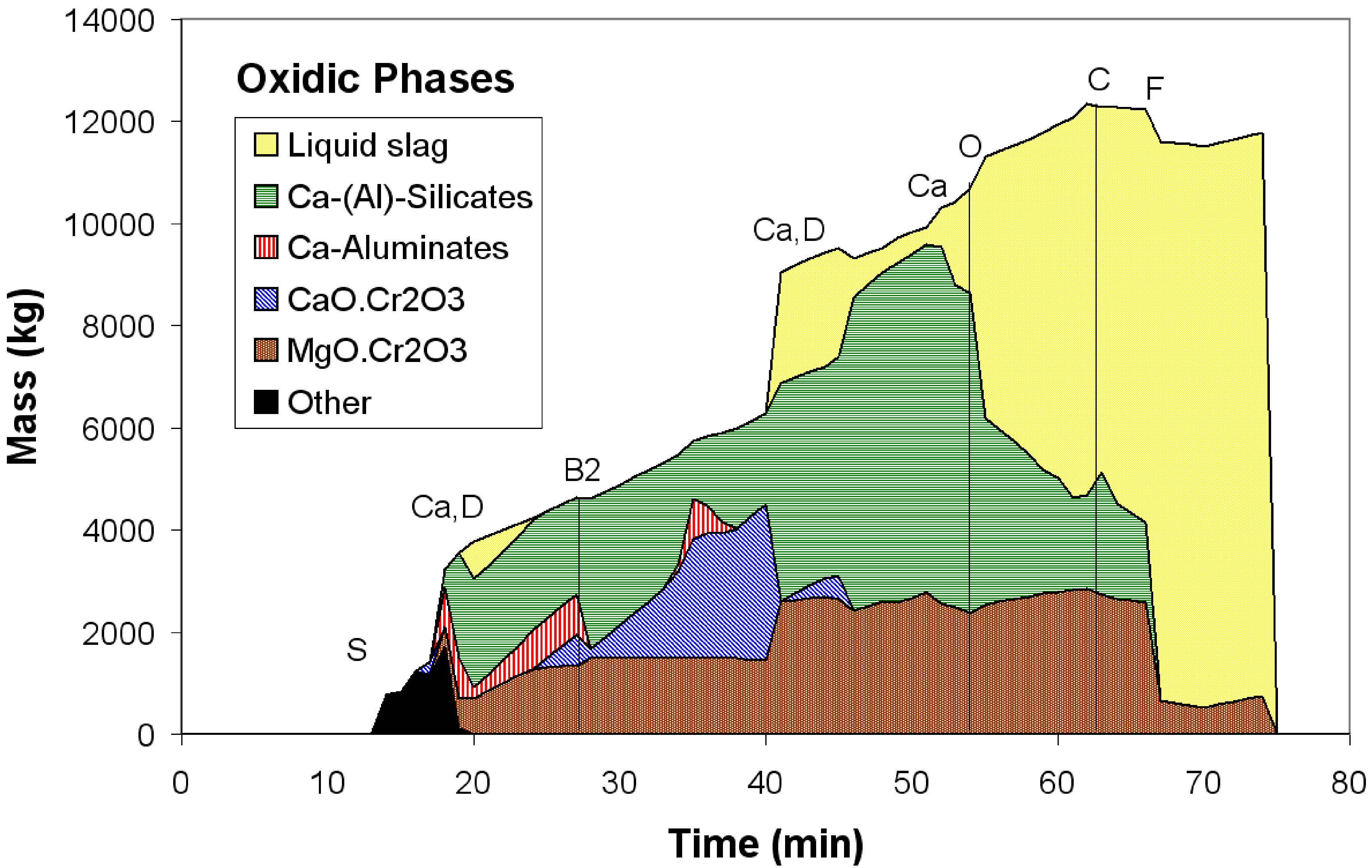
Steel composition



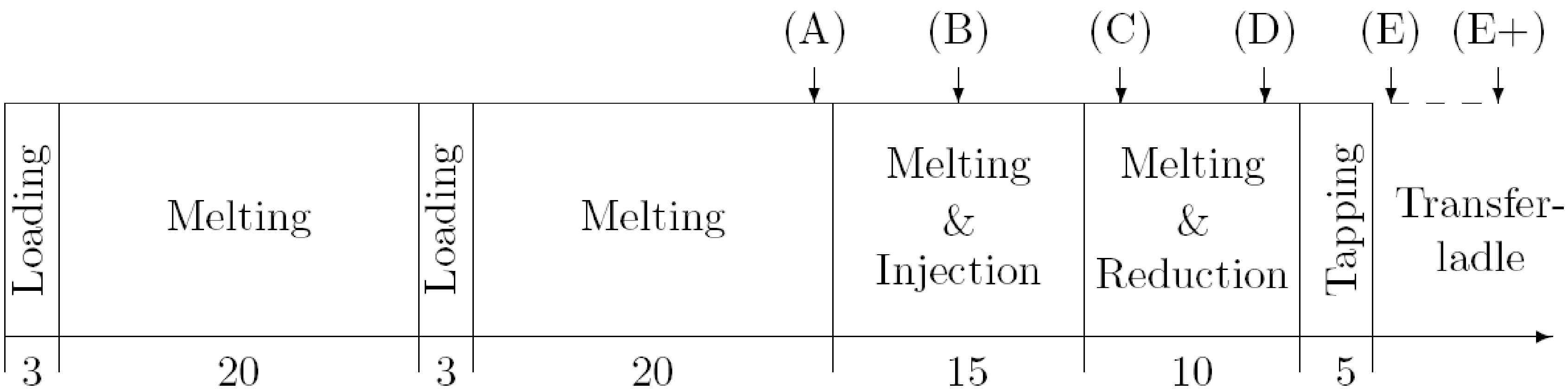
Slag composition



Phases in the slag



Slag Sampling



Schematic diagram of EAF process (STF) and sampling moments

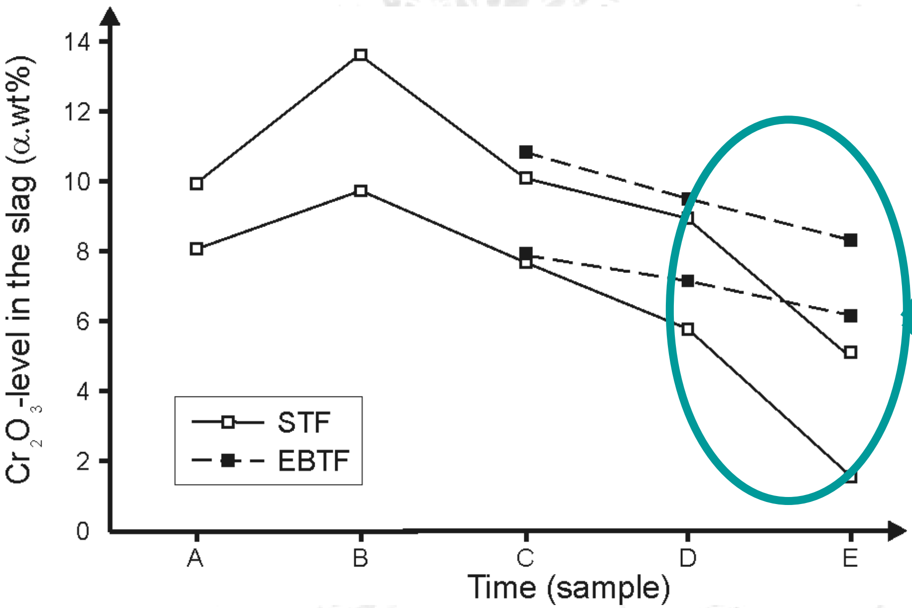
Results – Evolution slag composition

- Evolution in STF-slag composition:
  - (C+M)/S (basicity) decreases during process (FeSi additions for Cr-recovery)
  - FeO drops significantly
  - CrO_x mainly drops during tapping
- Evolution in EBTF-slag composition:
  - Higher final CrO_x levels due to tapping procedure

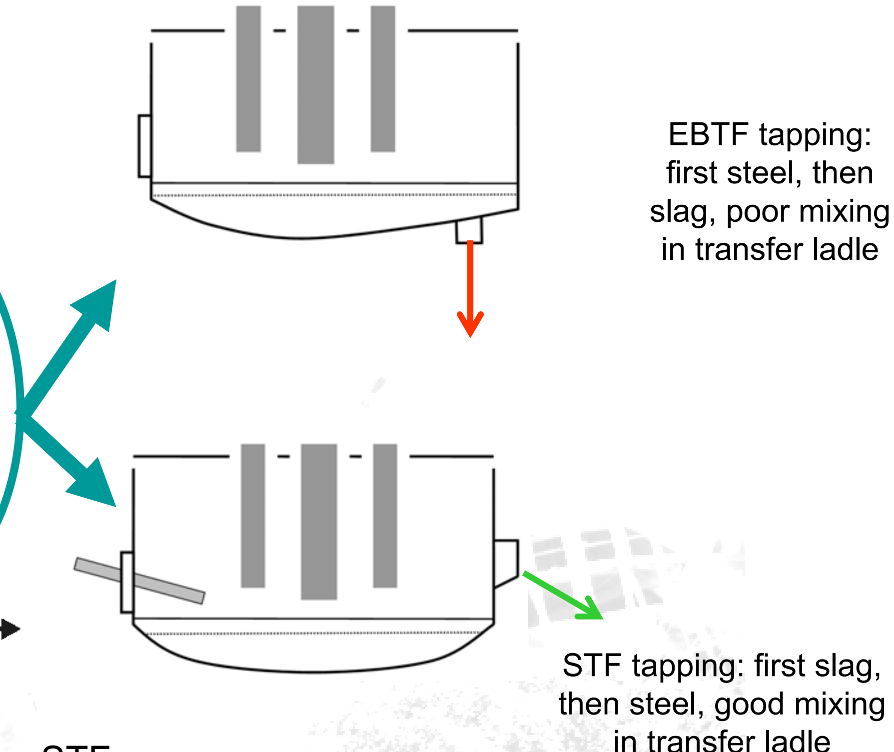
Observed range of global slag composition during STF-process

Results – Final CrO_x values (tapping)

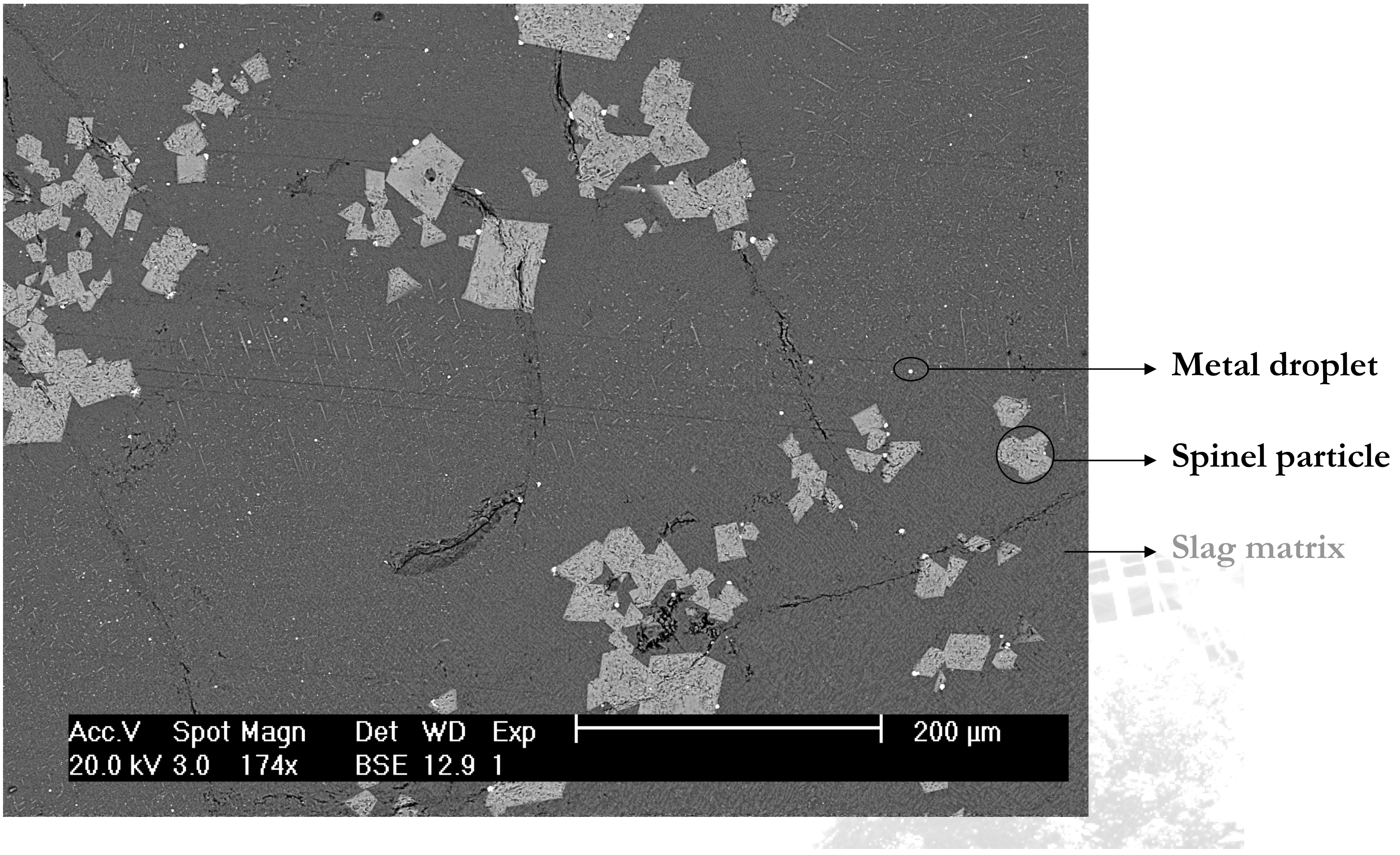
- Difference in Cr recovery due to tapping procedure
  - EBTF: poor mixing
  - STF: excellent mixing



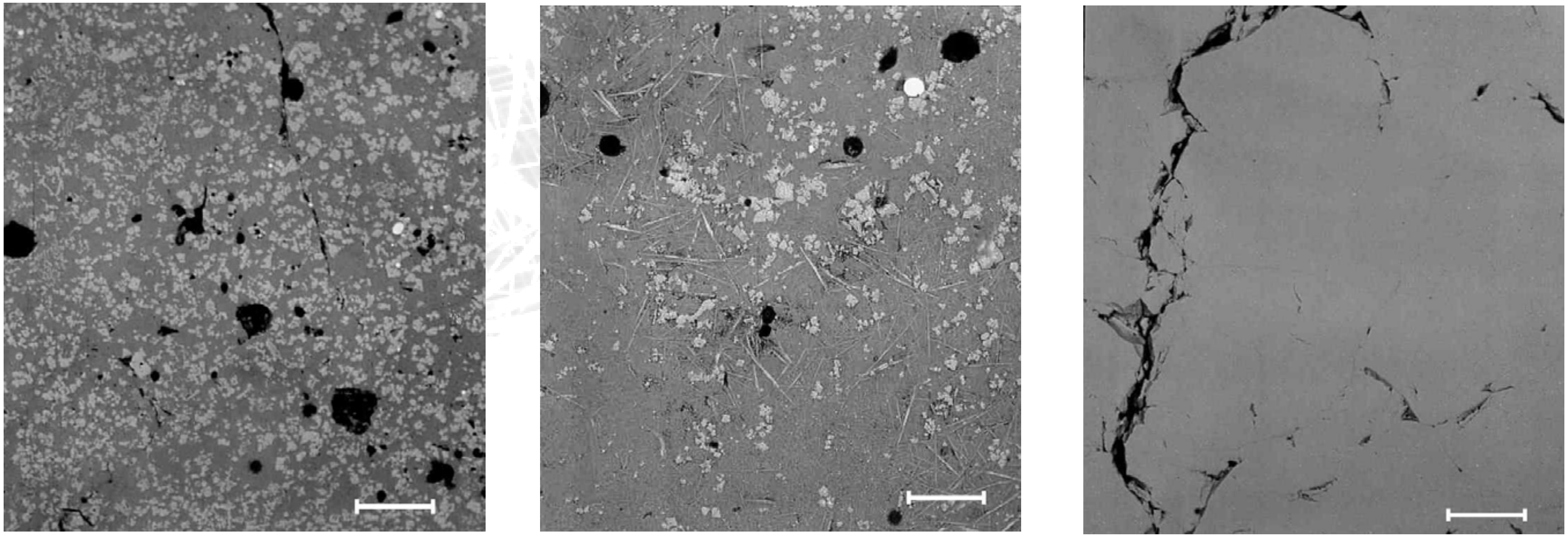
Evolution ‘Cr_2O_3’ level (global slag composition) during STF-process



Slag microstructure



Results – Evolution slag microstructure



STF – Before blowing
(bar = 250 μm)

STF – After blowing
(bar = 250 μm)

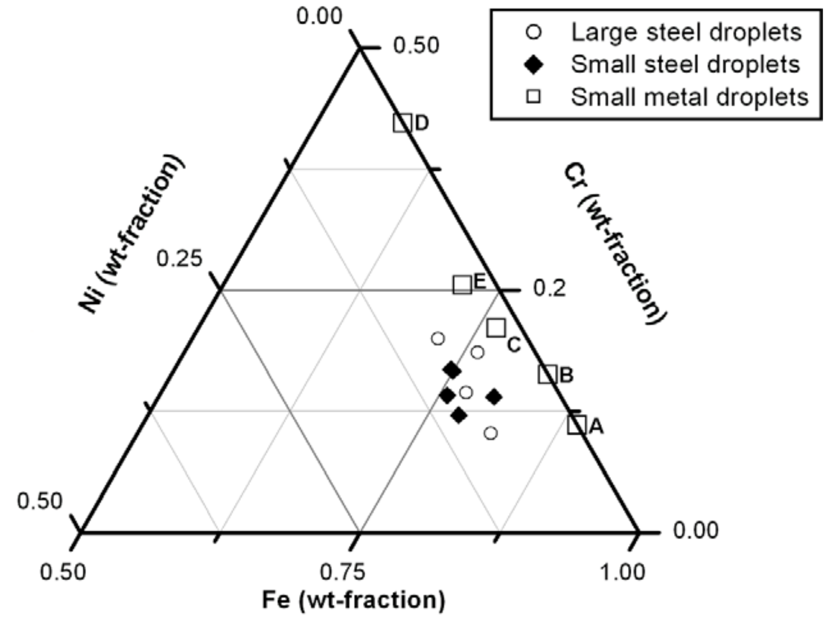
STF – After tapping
(bar = 250 μm)

Slag microstructure – metal droplets

- Type 1: large (>50 μm): stainless steel particles (originating from steel bath)
- Type 2: small (< 5 μm)
  - Type 2a (25%): stainless steel composition
  - Type 2b (75%): Fe/Cr (no Ni) from two reactions:

$$FeO_{slag}(l) + CO(g) = Fe(l) + CO_2(g)$$

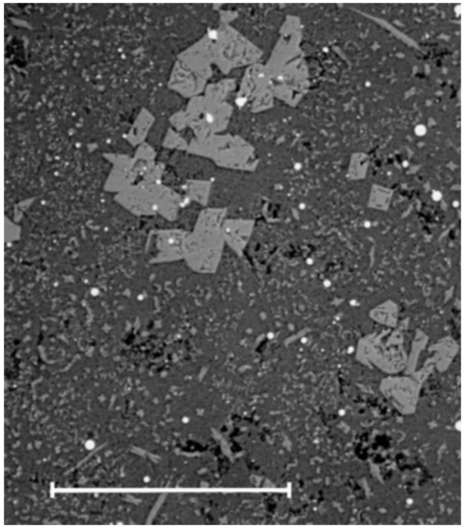
$$CrO_{x,slag}(l) + x.CO(g) = Cr_{\underline{Fe}}(l) + x.CO_2(g)$$



Composition metallic droplets in the slag

Slag microstructure – spinel particles

- Size: ~20 µm, shape: angular
- Present at high temperature
- Composition: (Mg,Fe,Mn)O.$(Cr,Al)_2O_3$
- Evolution in composition (see table)
- Amount of particles decreases with process time (~ FeSi addition & Cr-recovery)
- STF-samples after tapping: almost no particles left



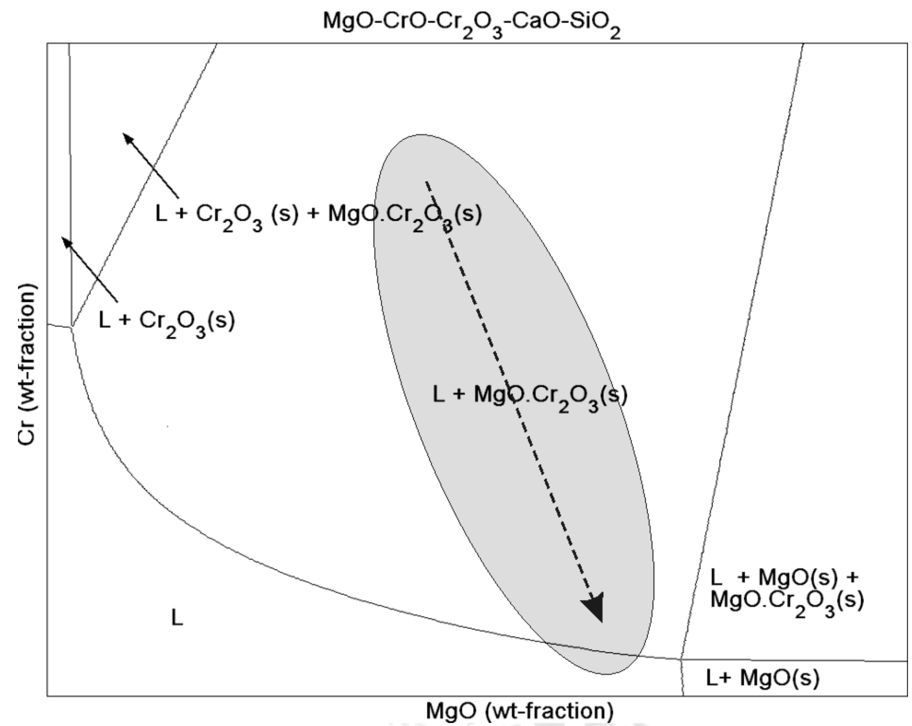
Spinel particles in slag
(bar = 100 μm)

Compositional evolution spinel particles during STF-process

Sample	Cr^{3+}	Al^{3+}	Mg^{2+}	Fe^{2+}	Mn^{2+}	Ca^{2+}	M^{3+}/M^{2+}
448032 A	25.0	2.6	6.4	5.9	1.8	0.9	**1.8**
448032 B	25.0	2.7	7.4	2.2	2.9	1.4	**2.0**
448032 C	24.9	3.6	8.3	0.8	3.4	0.9	**2.1**
448032 D	24.9	3.5	9.2	1.1	2.5	0.9	**2.1**
448032 E	19.5	6.3	12.3	0.3	1.6	0.7	**1.8**

Slag microstructure – spinel particles

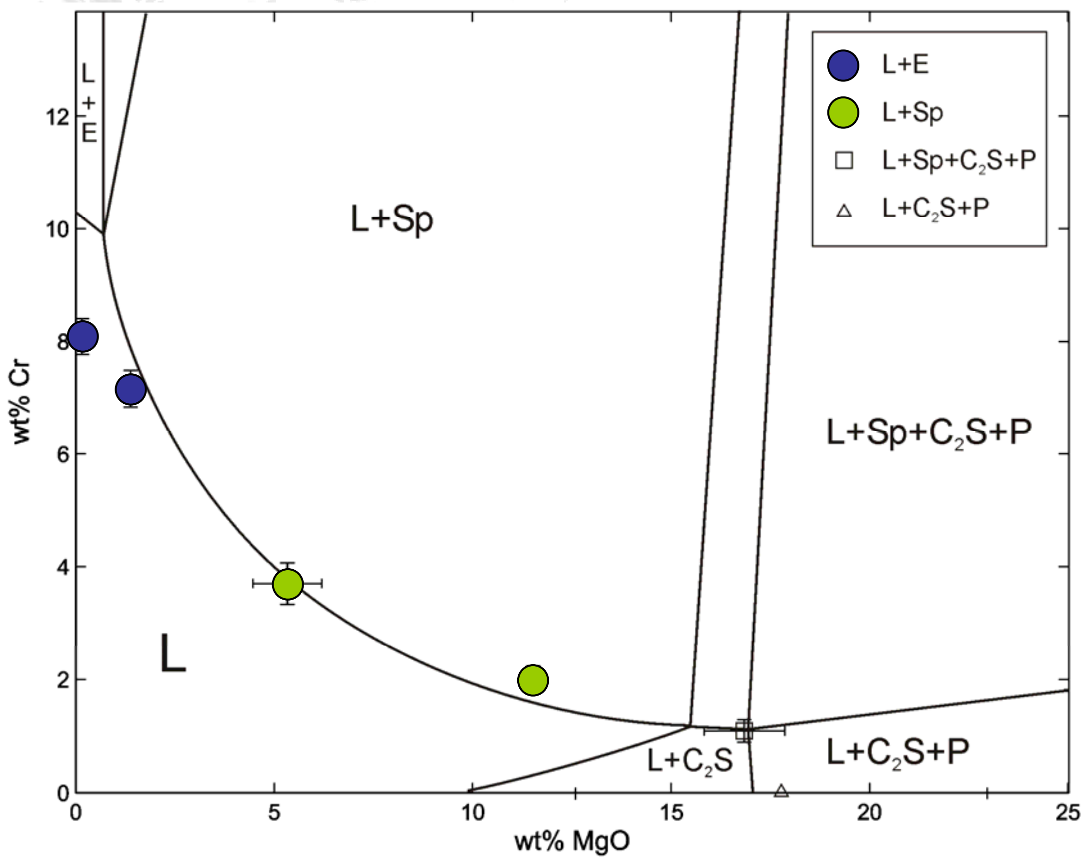
- Formation and dissolution of spinel particles controlled by: Cr_2O_3/Al_2O_3 (l) + MgO (l) ←→ $MgO.(Cr,Al)_2O_3$ (s)
- Equilibrium influenced by T, pO_2 (influences CrO/Cr_2O_3 level) , C+M/S, CrO_x and MgO level
- FactSage 5.2 + Chemapp V5.1.6 → qualitative phase diagram
- Process evolution shown by arrow: from L/spinel → L region without spinel



Qualitative phase diagram: C/S, p, p_{O2} and T are kept constant

Results: liquidus

- Tests in different known p_{O2}, no Al_2O_3



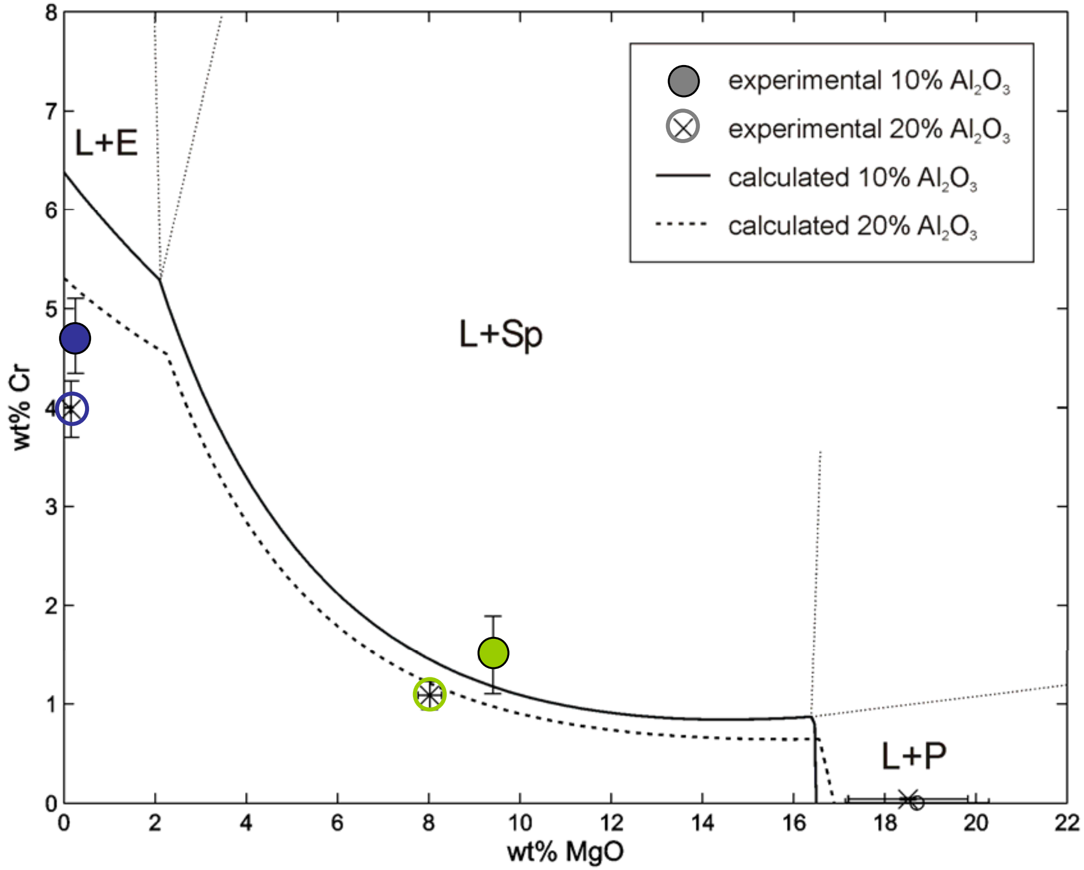
T=1600°C

$p_{O2}=10^{-10.16}$ 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

Other examples of process modelling

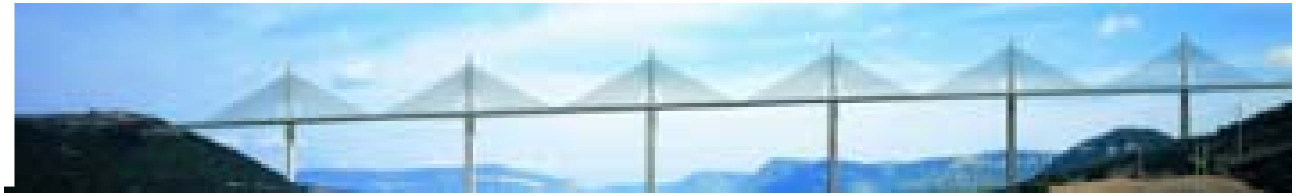
- VOD stainless steel refining
  - S. Smets et al., unpublished.

- Zinc fuming (including freeze lining formation)
  - Cooperation with E. Jak and P. Hayes
  - K. Verscheure et al., Met. Trans. B, **38B** (2007), 13 – 33

- Lead Blast Furnace
  - Cooperation with E. Jak and P. Hayes
  - F. Verhaeghe et al., Proc. CSIRO, 4th Australian Melt Chemistry Symposium , 10-11 December 2002

- Exergy analysis of pyrometallurgical processes
  - B. Klaasen et al, master thesis K.U.Leuven, 2008 (in dutch)

thermo research group



GTT - TECHNOLOGIES

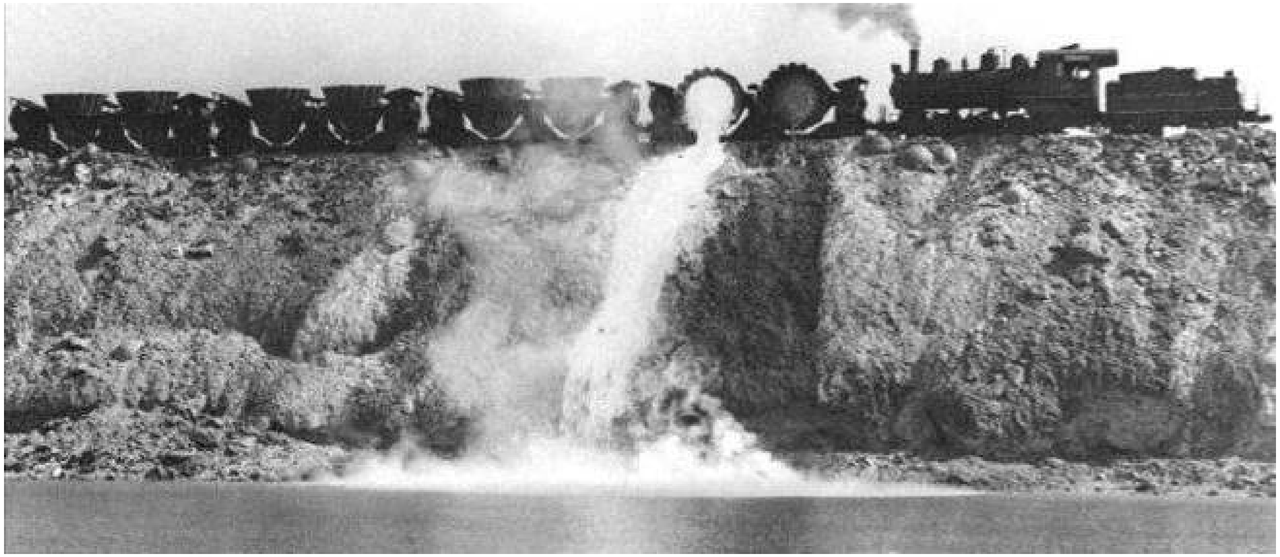
Slag Valorisation: the importance of microstructure

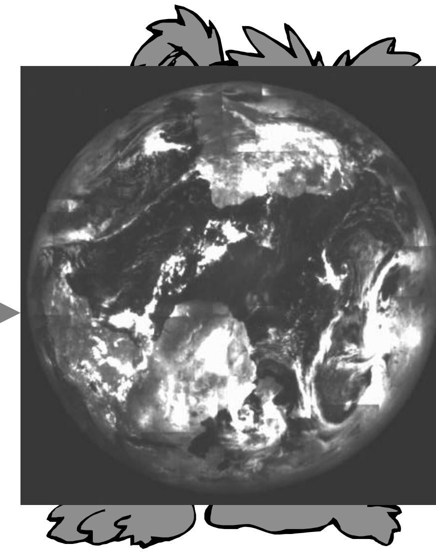
Roadways to a stable slag product

D. Durinck, S. Arnout, G. Mertens, E. Boydens, P.T. Jones, J. Elsen, B. Blanpain, P. Wollants, JOURNAL OF THE AMERICAN CERAMIC SOCIETY 91(2008) 548-554

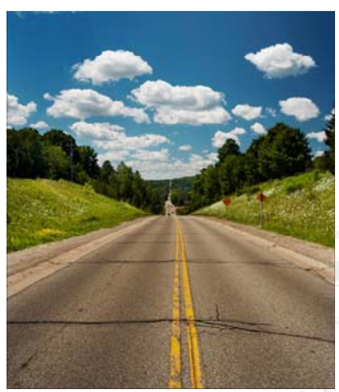
D. Durinck, P.T. Jones, B. Blanpain, P. Wollants, G. Mertens, J. Elsen, Journal of The American Ceramic Society, 90 (4) (2007), 1177 - 1185

Dumping





Valorisation

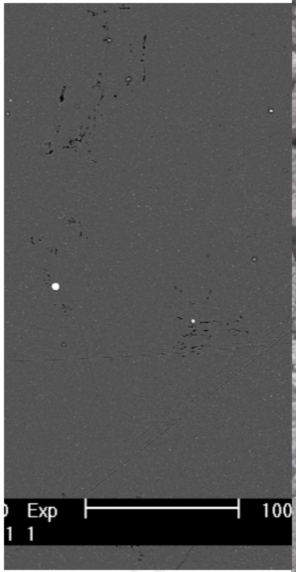


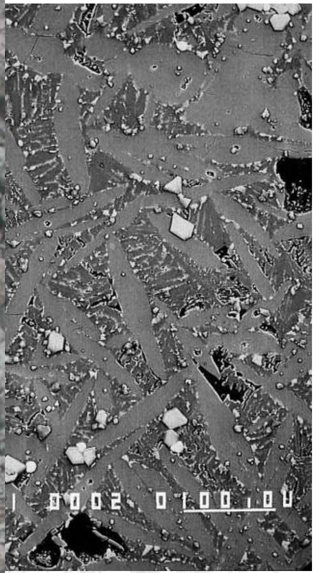
Slag valorisation chain

Slow slag solidification







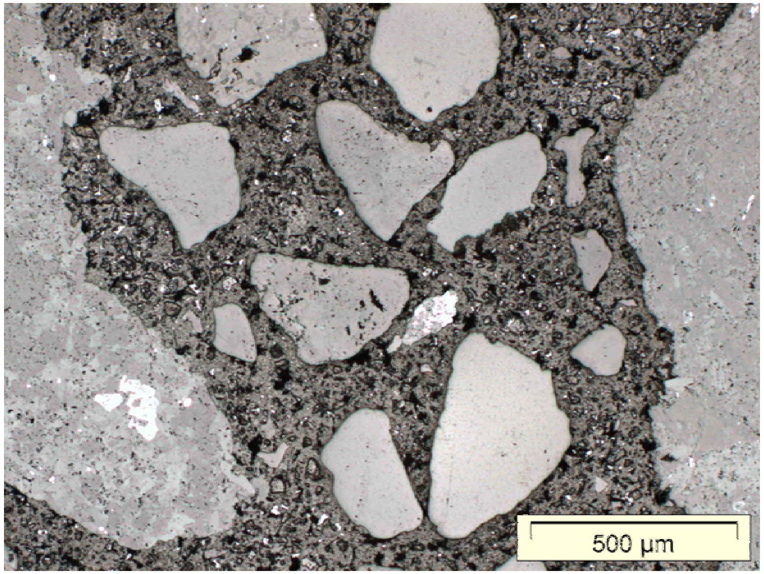
Slag valorisation chain

Main applications:

- Flemish environmental law: "*aggregates within other products*"

→ **Concretes**

- Cementitious concrete
- Asphalt concrete



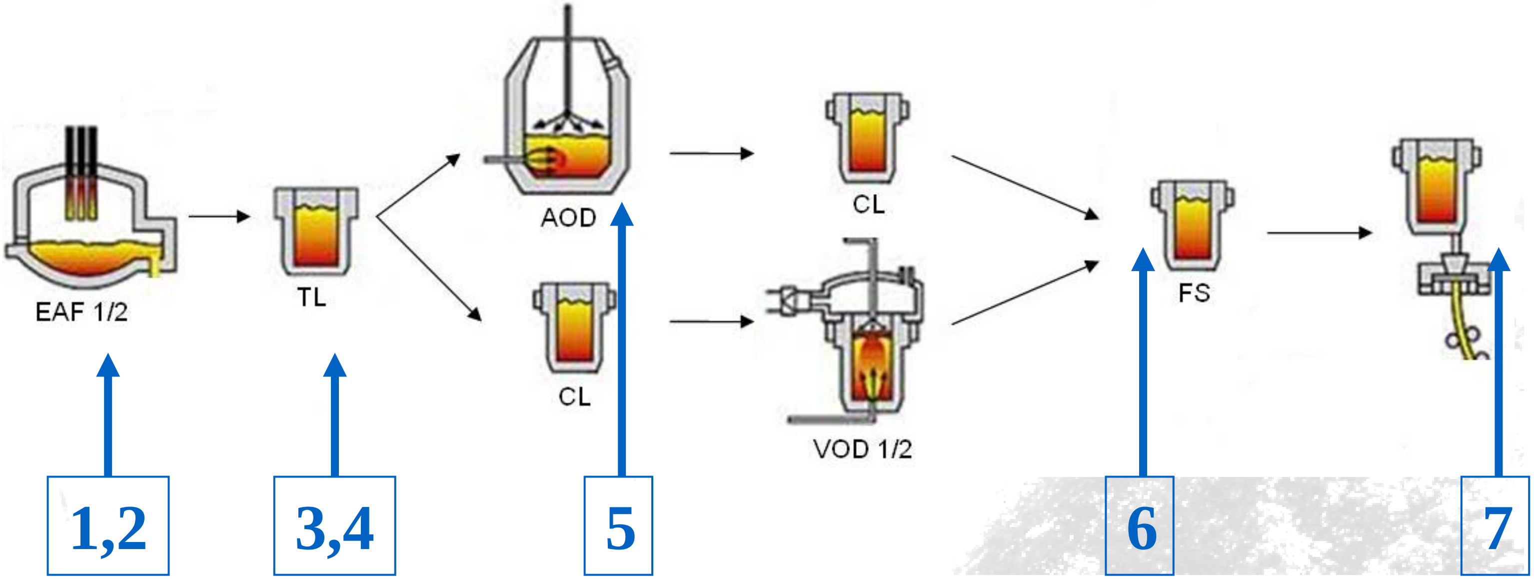
Slag valorisation chain

Required slag properties for aggregate for asphalt concrete:

- Particle size > 2 mm
- Resistance against polishing
- Abrasion resistance
- Strength
- Cr leaching
- Volume stability

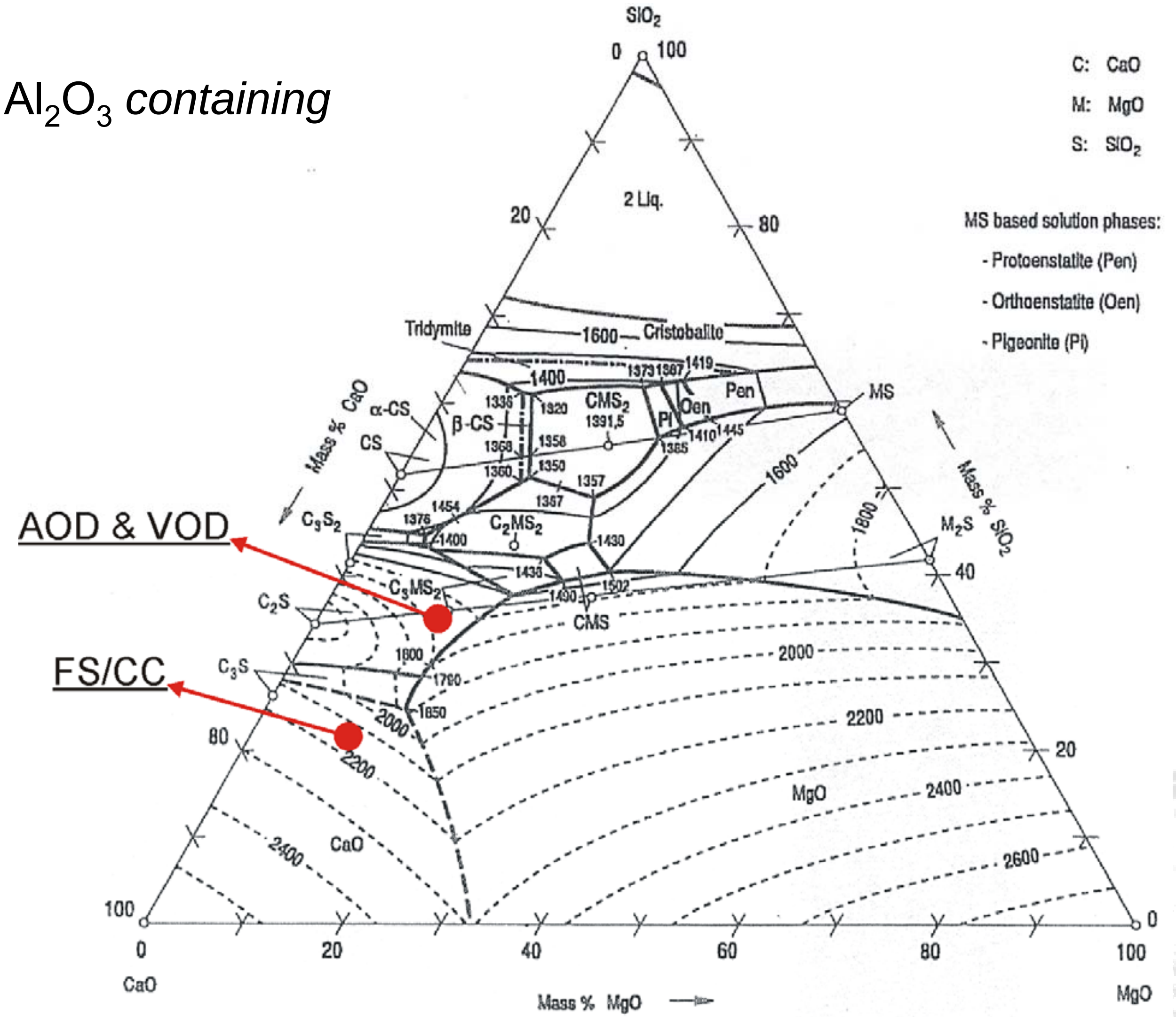
Slag composition

	'CaO'	SiO_2	MgO	Al_2O_3	Amount
		wt%			*Ton slag/100 ton steel*
DS1	40	26	7	9	6
DS2	40	30	11	9	7
AOD	51	34	11	1	8
VOD	51	34	11	1	5
FS/CC	64	21	9	1	2



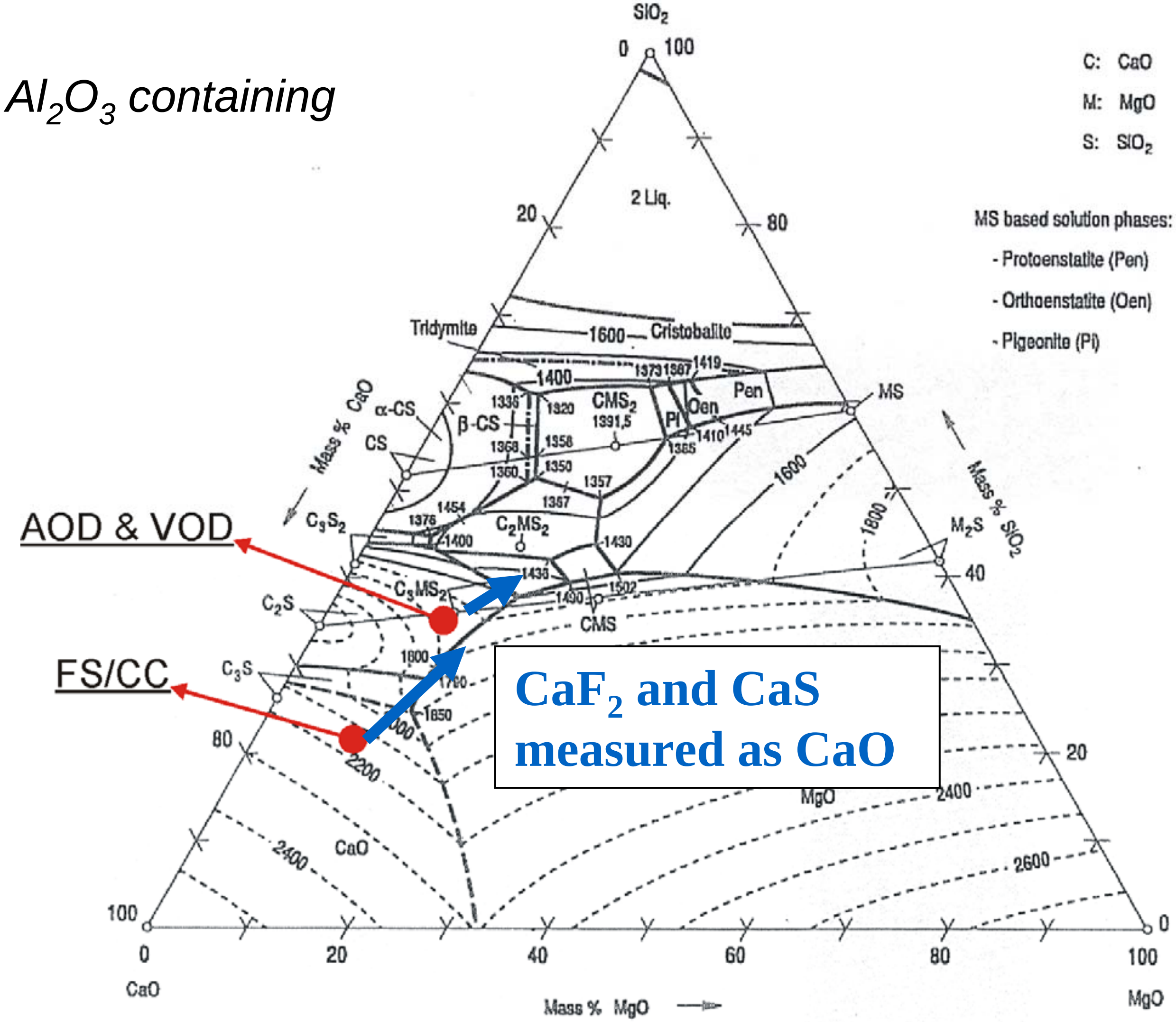
Slag composition

EAF = Al_2O_3 *containing*



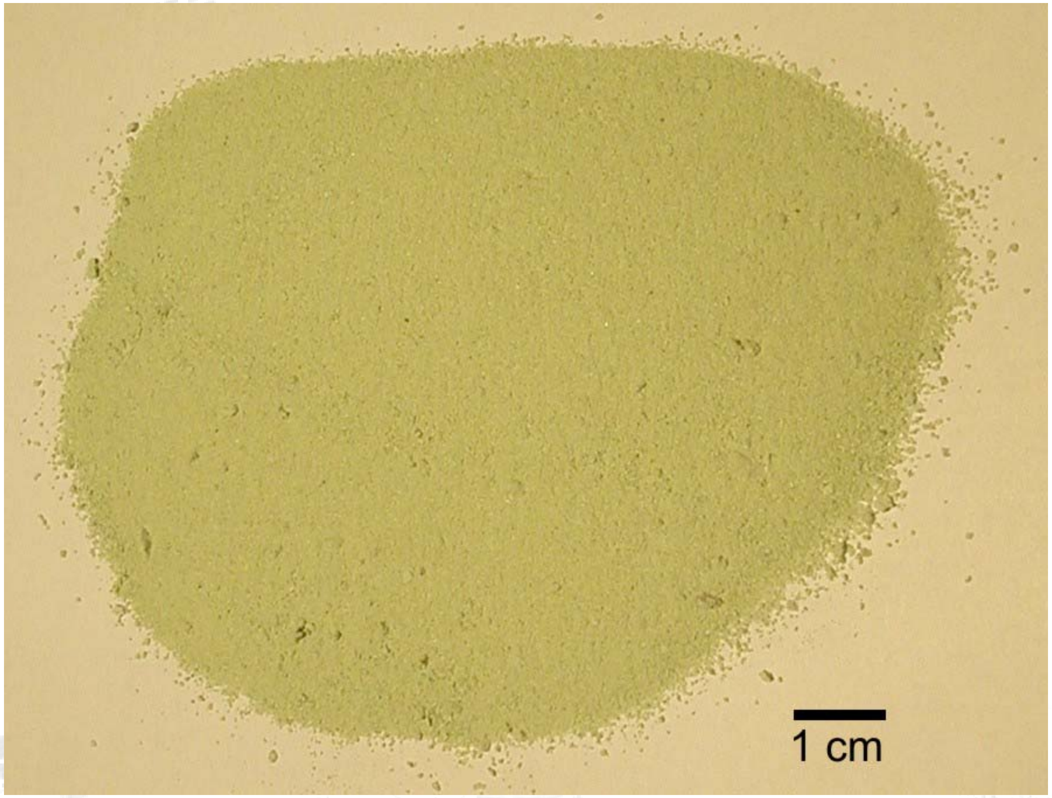
Slag composition

EAF = Al_2O_3 containing



Slag disintegration

- FS/CC slag after cooling: Too fine to valorise



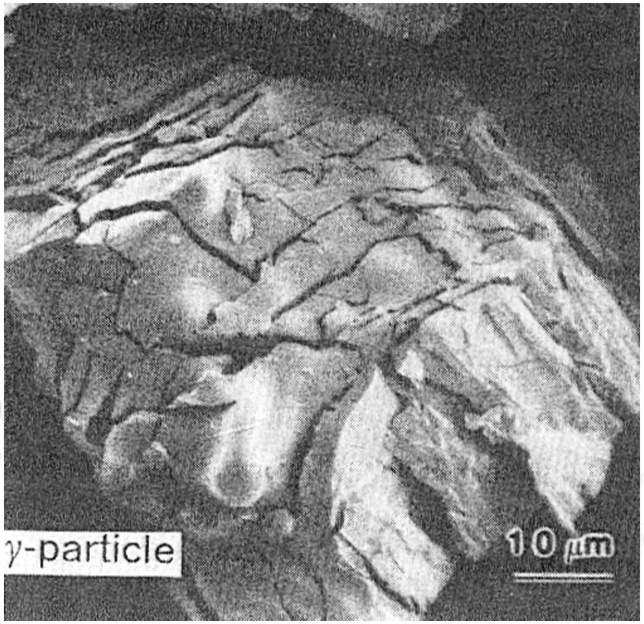
Lab simulation

Slag disintegration

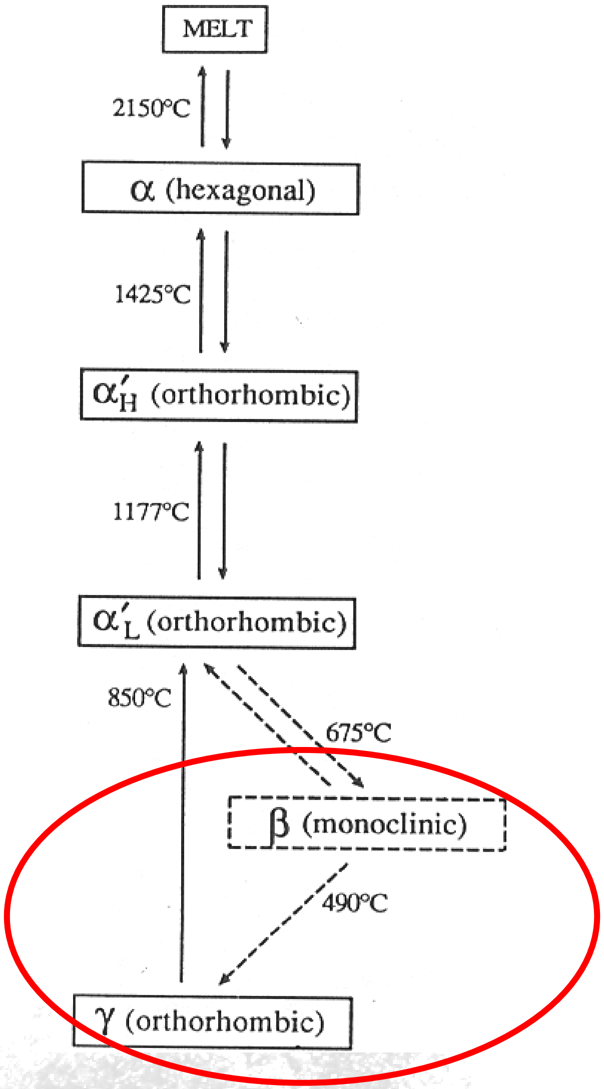
- Visual observation at the slag yard

Cause of slag disintegration

- Presence of $2CaO.SiO_2$ (C_2S)
  - several phase transformations during cooling
  - β to γ transformation causes a 12% volume expansion



Chan et al., J. Am. Cer. Soc., 1992



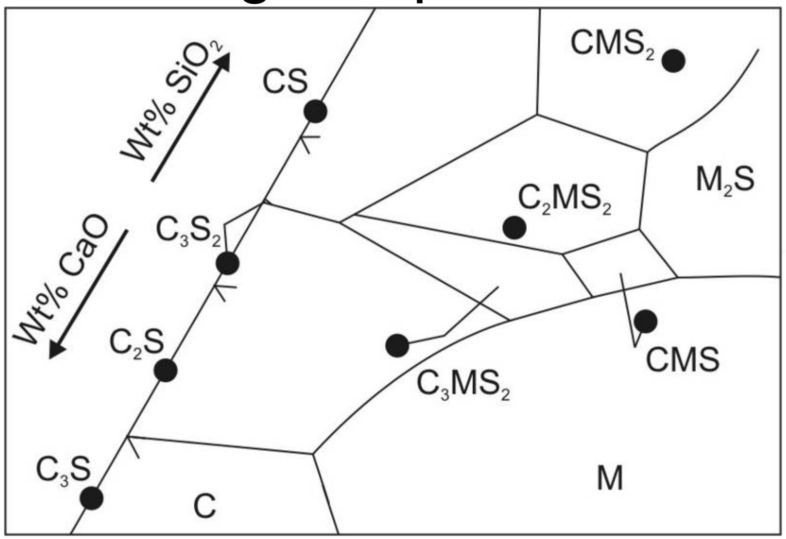
Kim et al., J. Am. Cer. Soc., 1992

What can be done?

- Internal slag recycling
  - Benefits: Ca resource, fluxing agent, possible heat source
  - Problems: Logistics (dry slag required / molten slag addition)
- Physical slag stabilisation
  - Grain size
  - Matrix constraint
  - Cooling rate
- Chemical slag stabilisation
  - Stabilise β-C_2S to room temperature by doping

Laboratory experiment

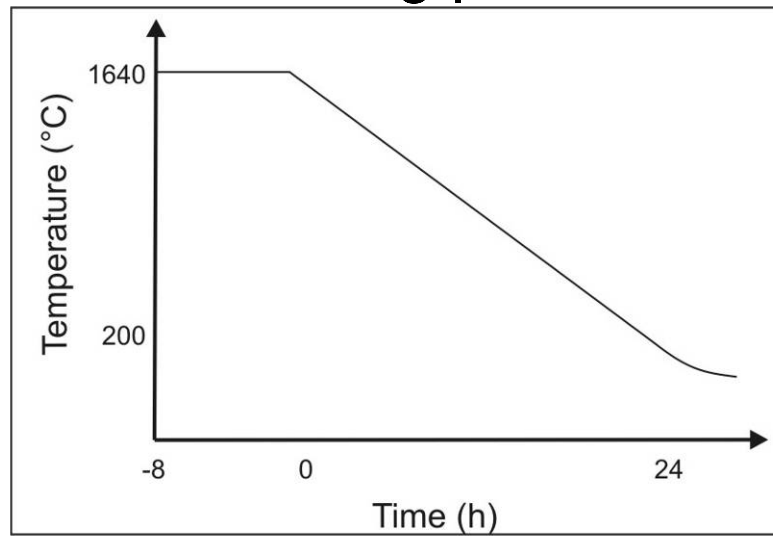
Slag composition



CaO-SiO_2-MgO

- Well known system
- p_{O2} independent
- Stainless steelmaking slag
- Peritectic reaction

Cooling path

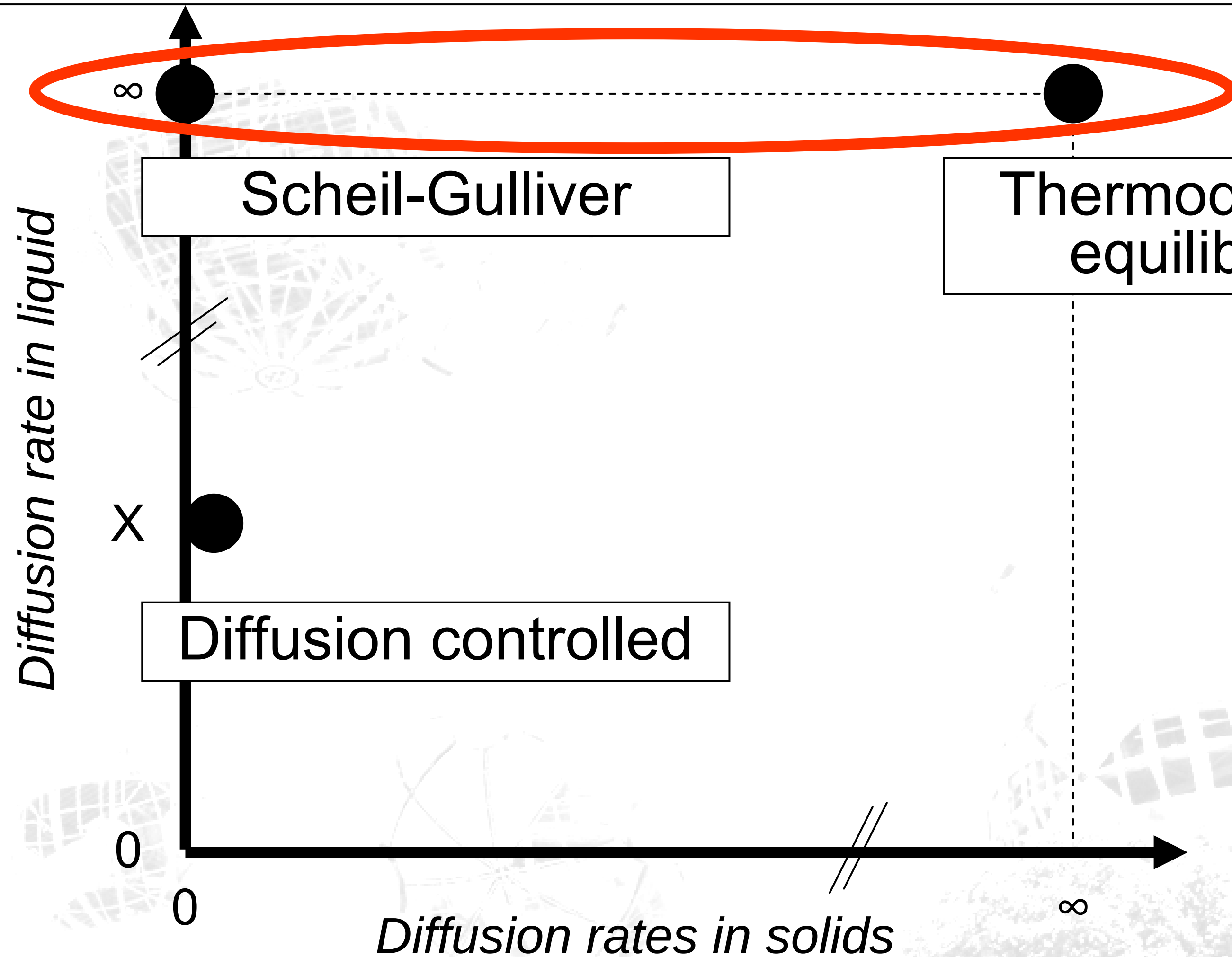


Cooling rate 1°C/min

- Simple cooling path
- Used in other references
- Comparable to industry

(not equal!)

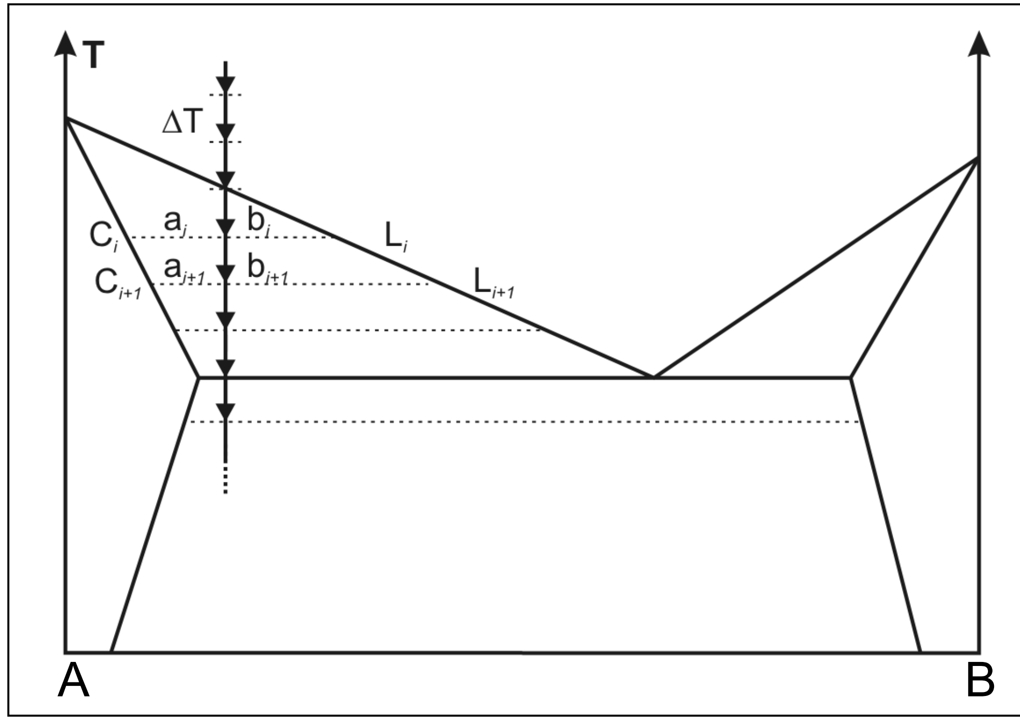
Common approaches to solidification modelling



Thermodynamic equilibrium model

<u>Assumptions</u>

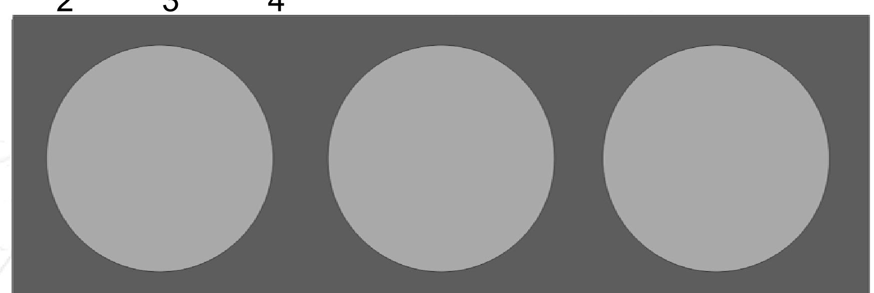
- Equilibrium @ L/S interface
- Infinitely rapid diffusion in L
- Infinitely rapid diffusion in S



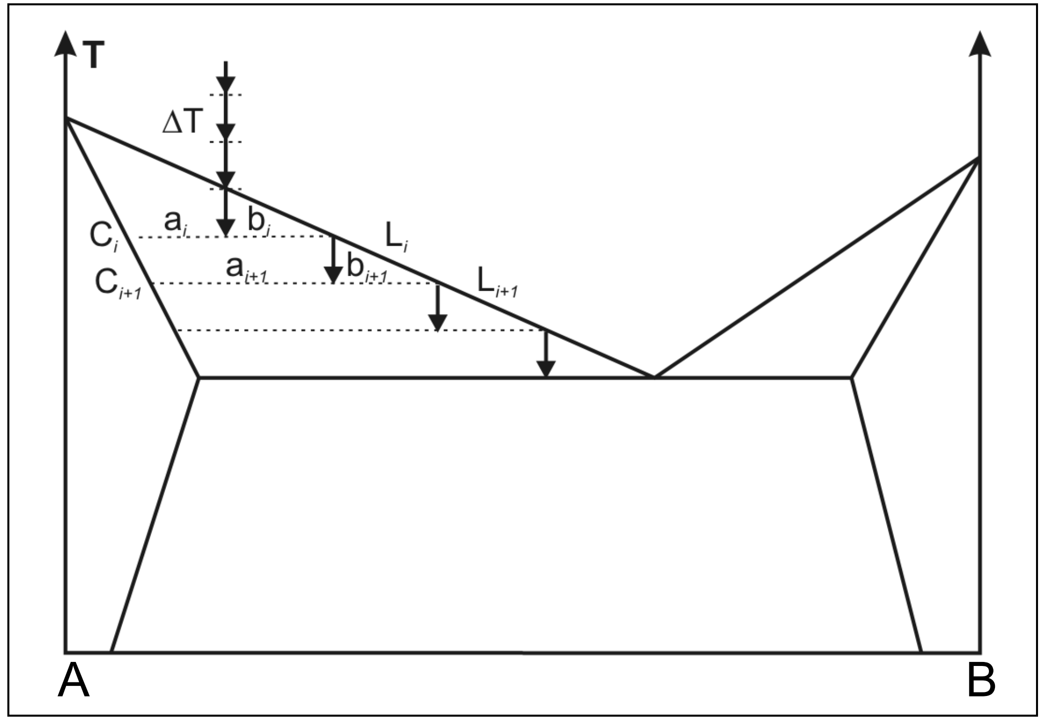
<u>Amount of A:</u>

$$f_{s,equil} = \frac{b_i}{a_i + b_i}$$

$T_1 > T_2 > T_3 > T_4$



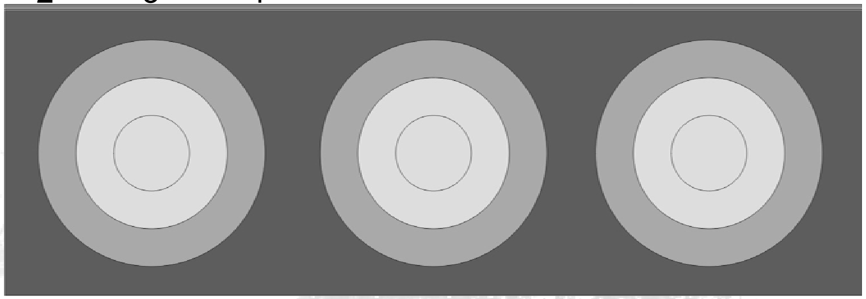
Scheil-Gulliver model



Assumptions

- Equilibrium @ L/S interface
- Infinitely rapid diffusion in L
- No diffusion in S

$T_1 > T_2 > T_3 > T_4$

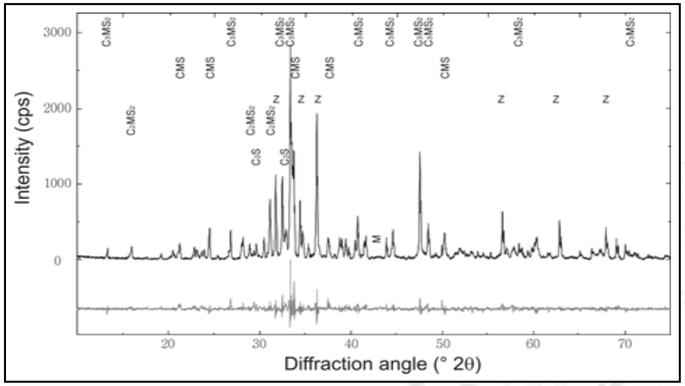


Amount of A:

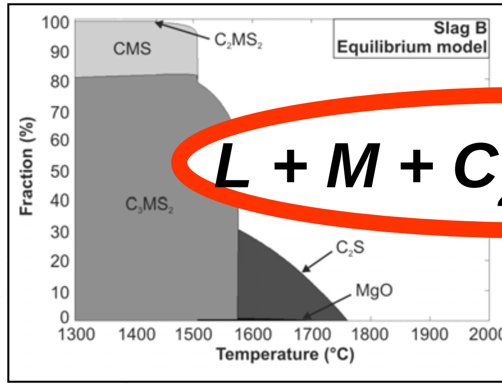
$$f_{s,SG} = \sum_{i=1 \to N} \frac{b_i}{a_i + b_i}$$

Mineralogy

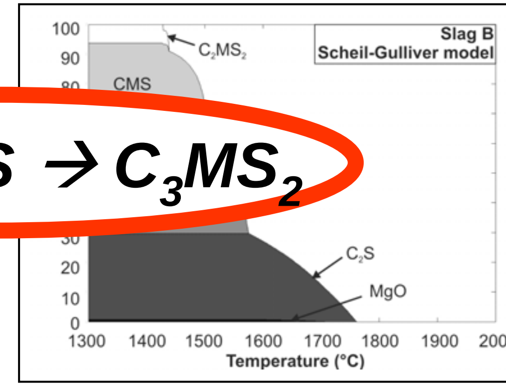
Experiment



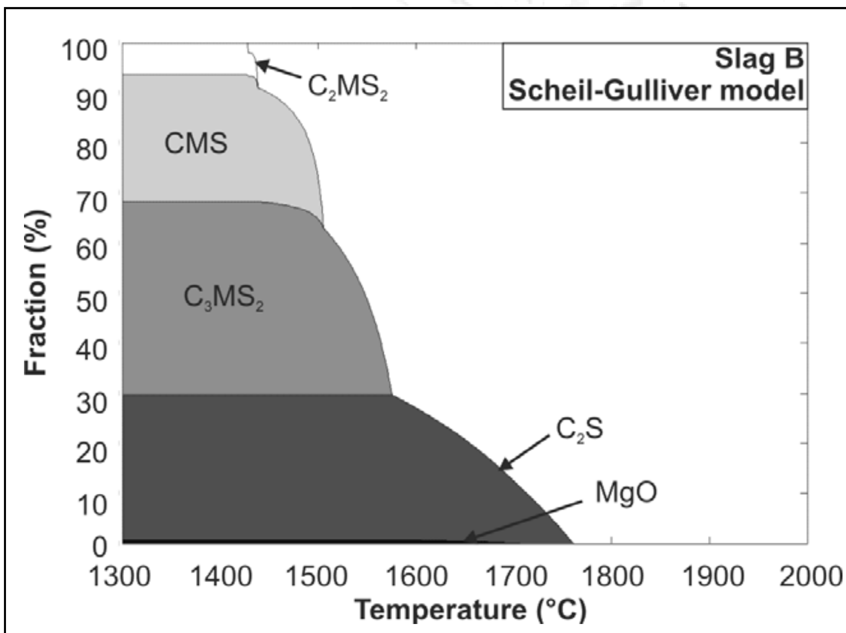
Equilibrium

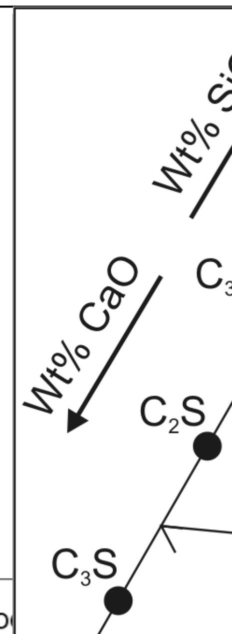


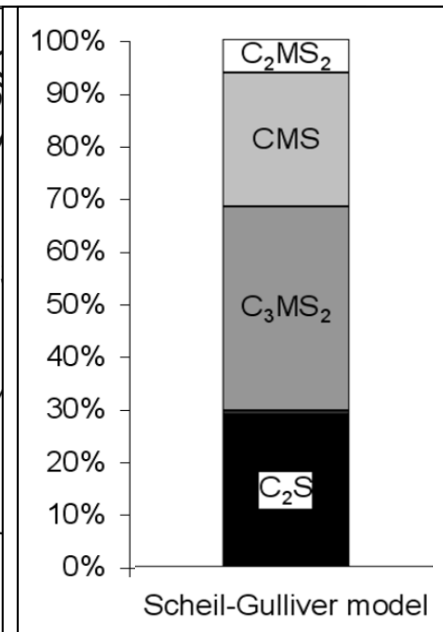
Scheil-Gulliver

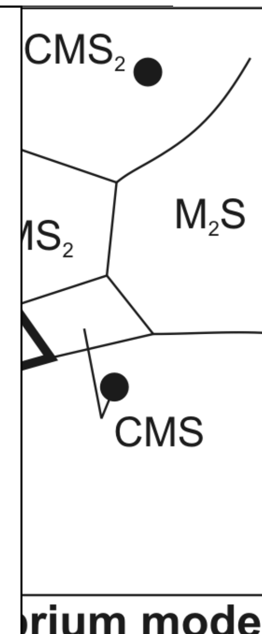


$$L + M + C_2S \rightarrow C_3MS_2$$

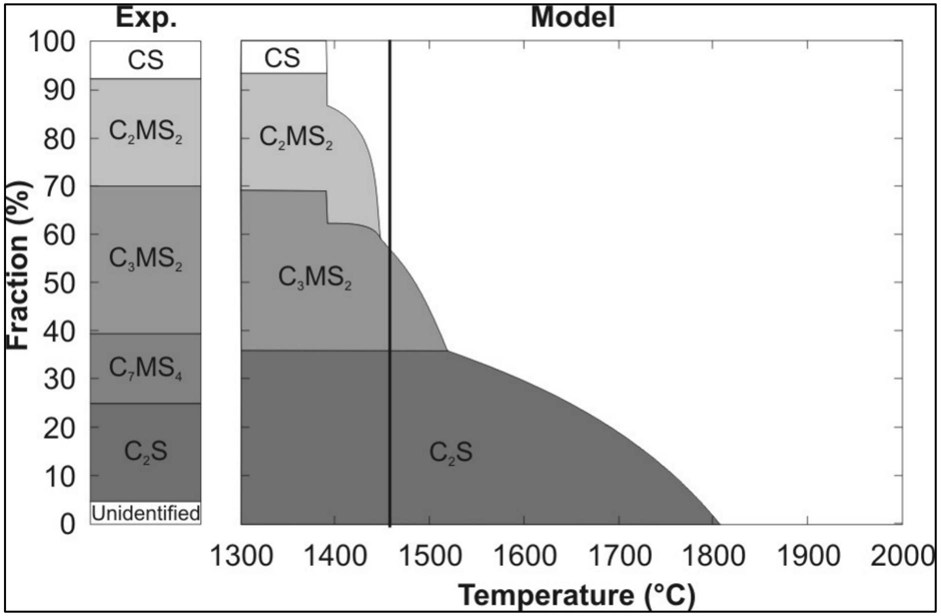


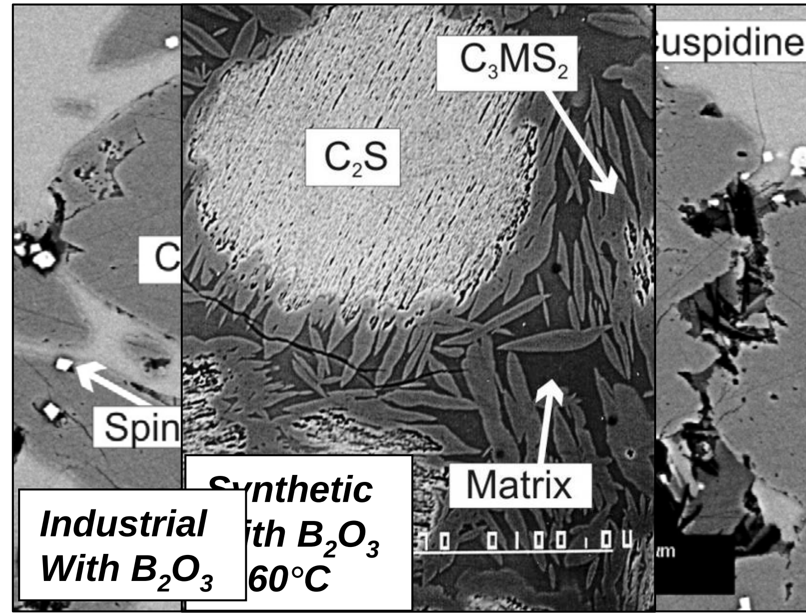






Microstructure



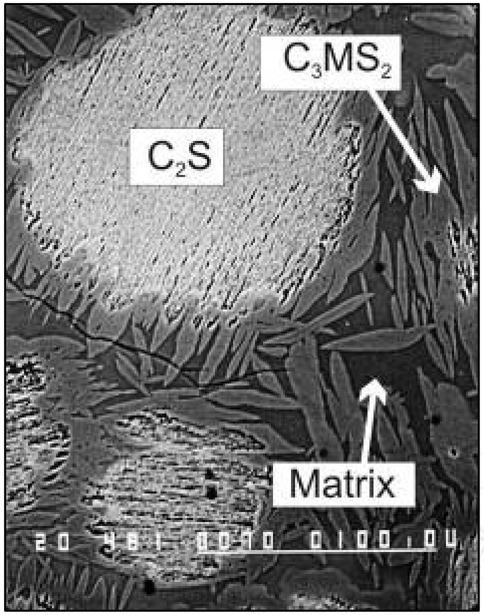


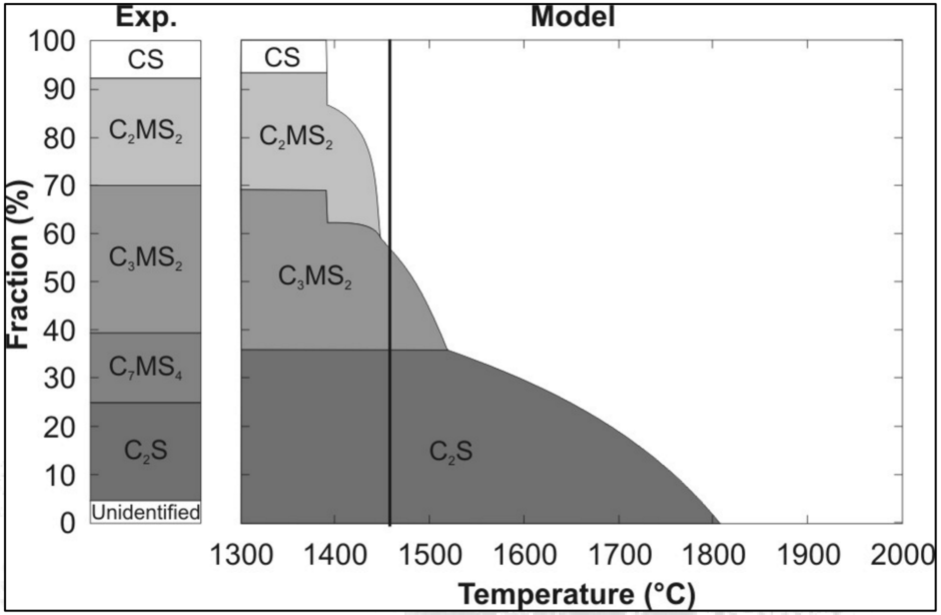
~~$L + M + C_2S \rightarrow C_3MS_2$~~

$$2.C_2S + C_3MS_2 \rightarrow C_7MS_4$$

Air-cooled solidification

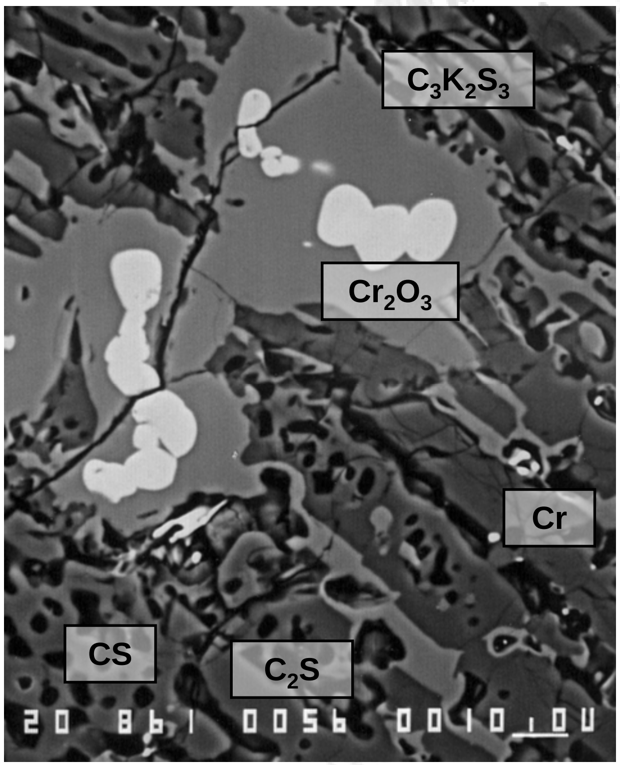
- pO_2 independent systems (*i.e.* $CaO\text{-}MgO\text{-}SiO_2$)
  - Scheil-solidification model
  - Lab experiments + QXRD
  - Validated with industrial samples

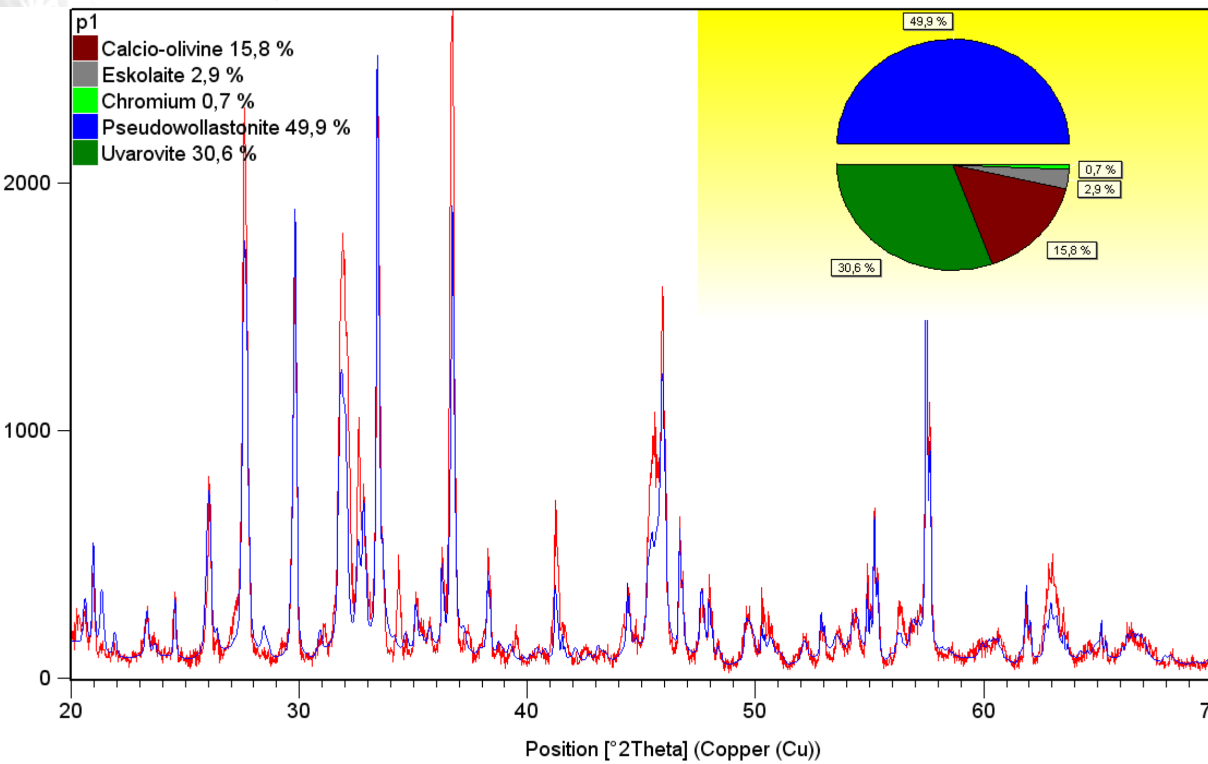




Air-cooled solidification

- Preliminary results





Microstructural calculations

- $CaO\text{-}SiO_2\text{-}MgO\text{-}CrO_x$ model system – pO_2 dependent
  - D. Durinck et al., J. Am. Cer. Soc., accepted
- Description of the formation of freeze lining systems
  - Cooperation with E. Jak and P. Hayes
  - M. Campforts et al., Met. Trans. B. , 38B(2007)6, p.841-851
- Phase field modelling for the solidification of oxide systems
  - Cooperation with GTT and Access
  - J. Heulens and N. Moelans

Conclusions

- Basic research tools in high temperature metallurgical research
  - Thermodynamic modeling (ChemApp and FactSage)
    - Process modelling
    - Microstructure calculations
  - Laboratory and industrial experiments
  - Microstructural and (micro-)analytical characterization