APPLICATIONS OF THERMODYNAMIC DATABASE FOR REFRACTORIES - STEELMAKING -

Steelmaking Chemistry

The important chemical systems of non-metallic phases for steelmaking processes can be summarized as follows. All of these are modeled in the FactSage databases.

1) Molten slag for refining process

a) $CaO-FeO-Fe_2O_3-SiO_2-MgO-MnO-P_2O_5$ system: BOF process

b) $CaO-MgO-Al_2O_3-SiO_2-FeO-Fe_2O_3$ system: ladle refining process

c) $CaO-MgO-SiO_2-CaF_2$ system: stainless steel refining

d) $CaO-CrO-Cr_2O_3-MgO-SiO_2$ system: AOD and VOD process for stainless steel

e) $CaO-MgO-SiO_2-MnO-CrO-Cr_2O_3$ system: high Mn stainless steel

2) Mould flux for casting process

a) $CaO-MgO-Al_2O_3-SiO_2-Na_2O-Li_2O-F$ system: conventional process

b) $CaO-MgO-Al_2O_3-SiO_2-Na_2O-Li_2O-B_2O_3$ system: new candidate.

3) Non-metallic inclusions

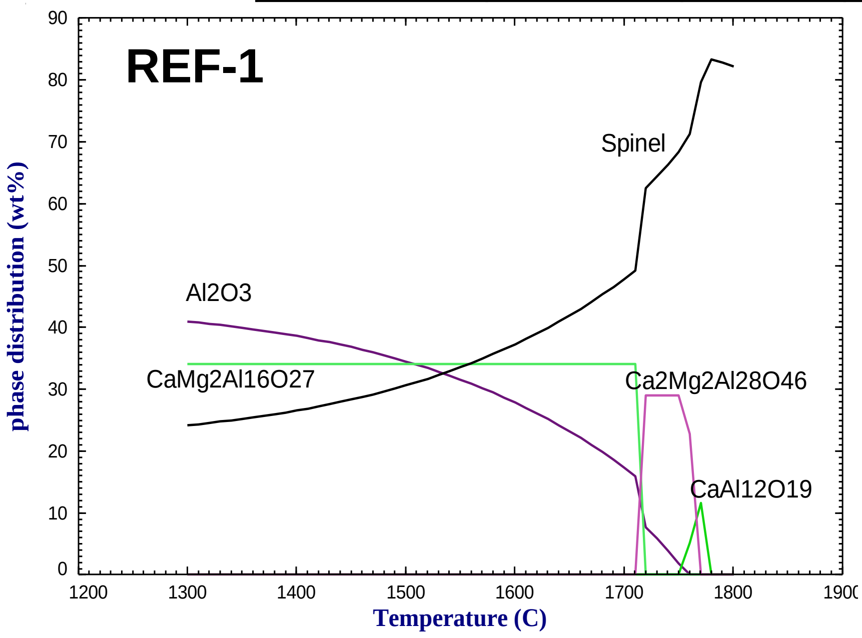
a) CaO-Al_2O_3-MgO-CaS: conventional low carbon steels
b) MnO-SiO_2-Al_2O_3-CaO-MnS: wire steels and free cutting steels
c) MnO-SiO_2-Ti_2O_3-TiO_2-Al_2O_3: high strength steels
d) Al_2O_3-Ti_2O_3-TiO_2: interstitial Free (IF) steels
e) Ti-Nb-C-N: high-strength low-alloy (HSLA) steels containing Ti and Nb

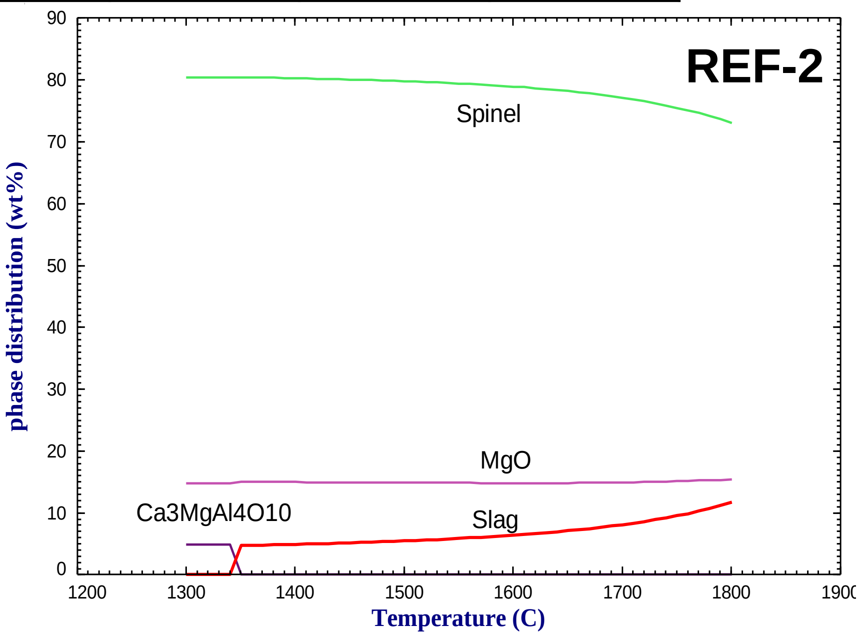
4) Refractories

a) MgO-C: BOF and RH vessel refractories, ladle slag line
b) MgO-Al_2O_3: ladle castable
c) MgO-Cr_2O_3-FeO-Fe_2O_3-Al_2O_3: VOD and AOD refractories
d) Al_2O_3-ZrO_2-SiO_2-C: nozzle refractories and tundish plugs

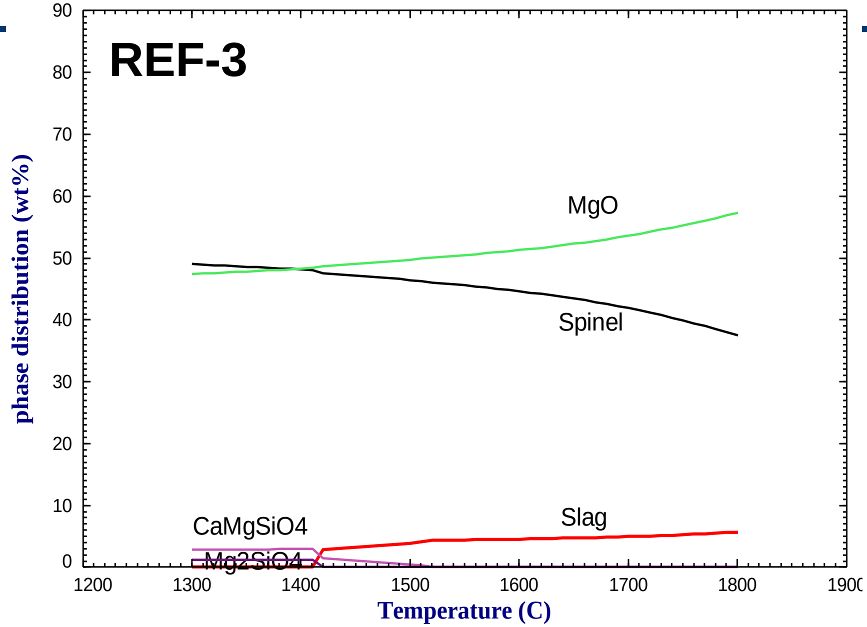
Thermal Stability test of RH refractories

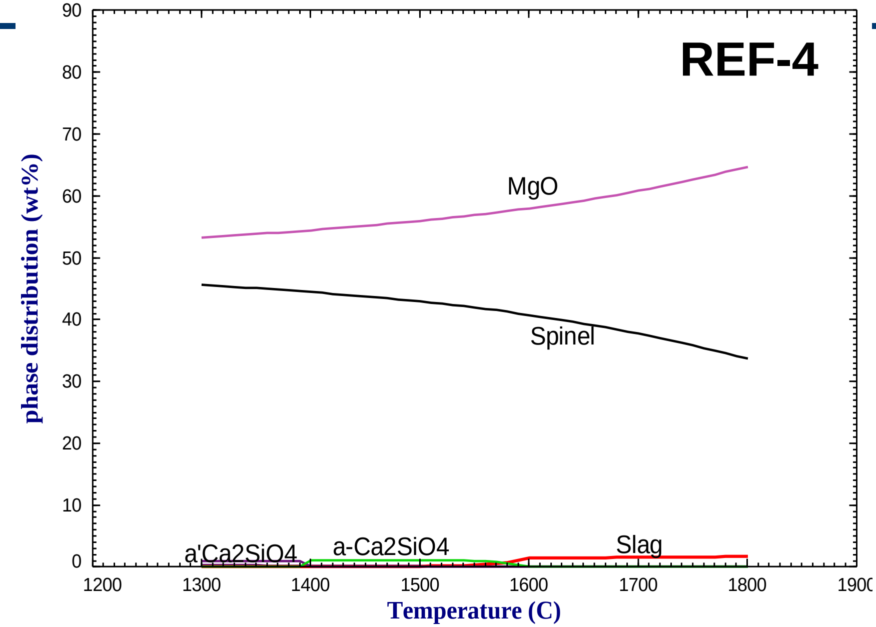
wt%	REF-1	2	3	4	5	6
Al_2O_3	88	60	11	4	0.5	0.5
MgO	9	38	58	61	89	75
CaO	2	2	0.9	0.7		
Cr_2O_3			20	29		
Fe_2O_3			8.8	4.8		
SiO_2			1.6	0.4	0.5	1.2
C					7	17
Al					2	4

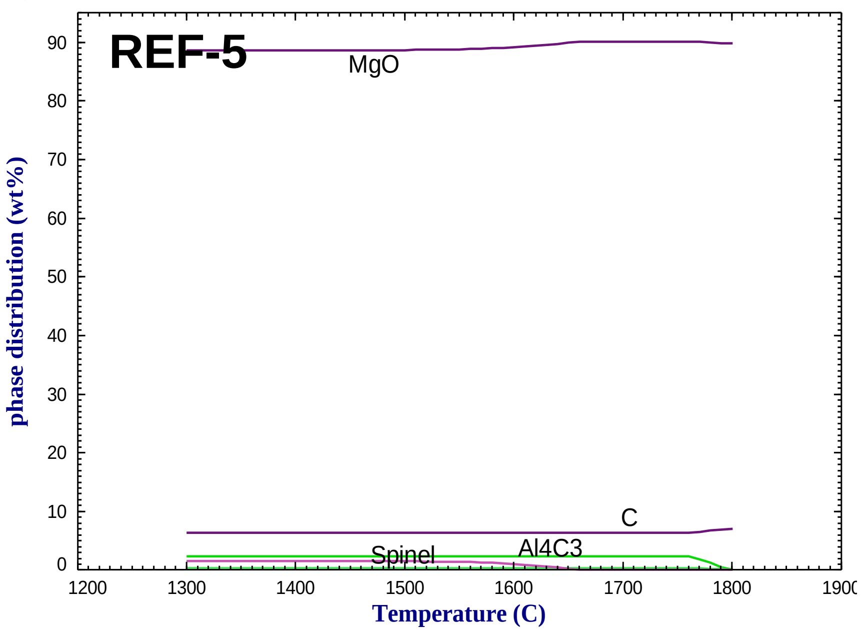




Stability test of RH refractories



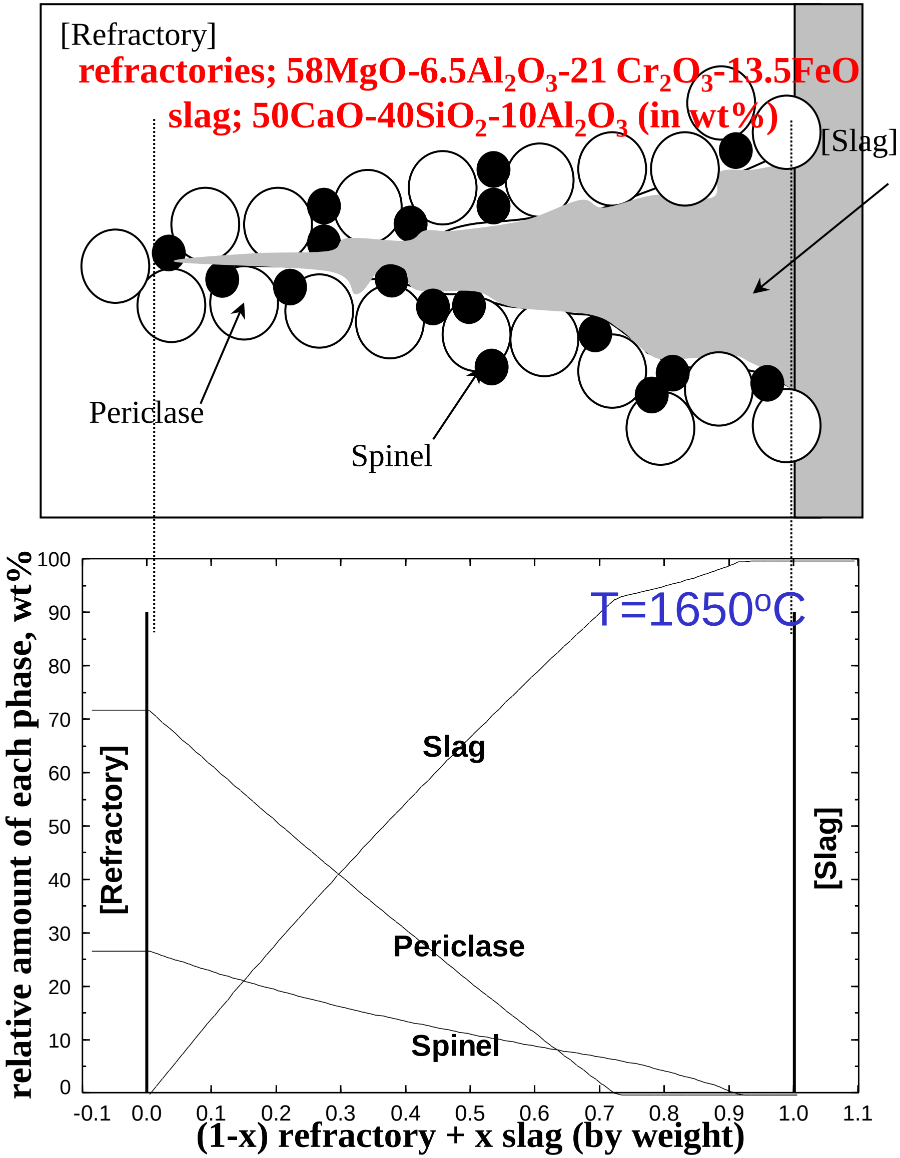


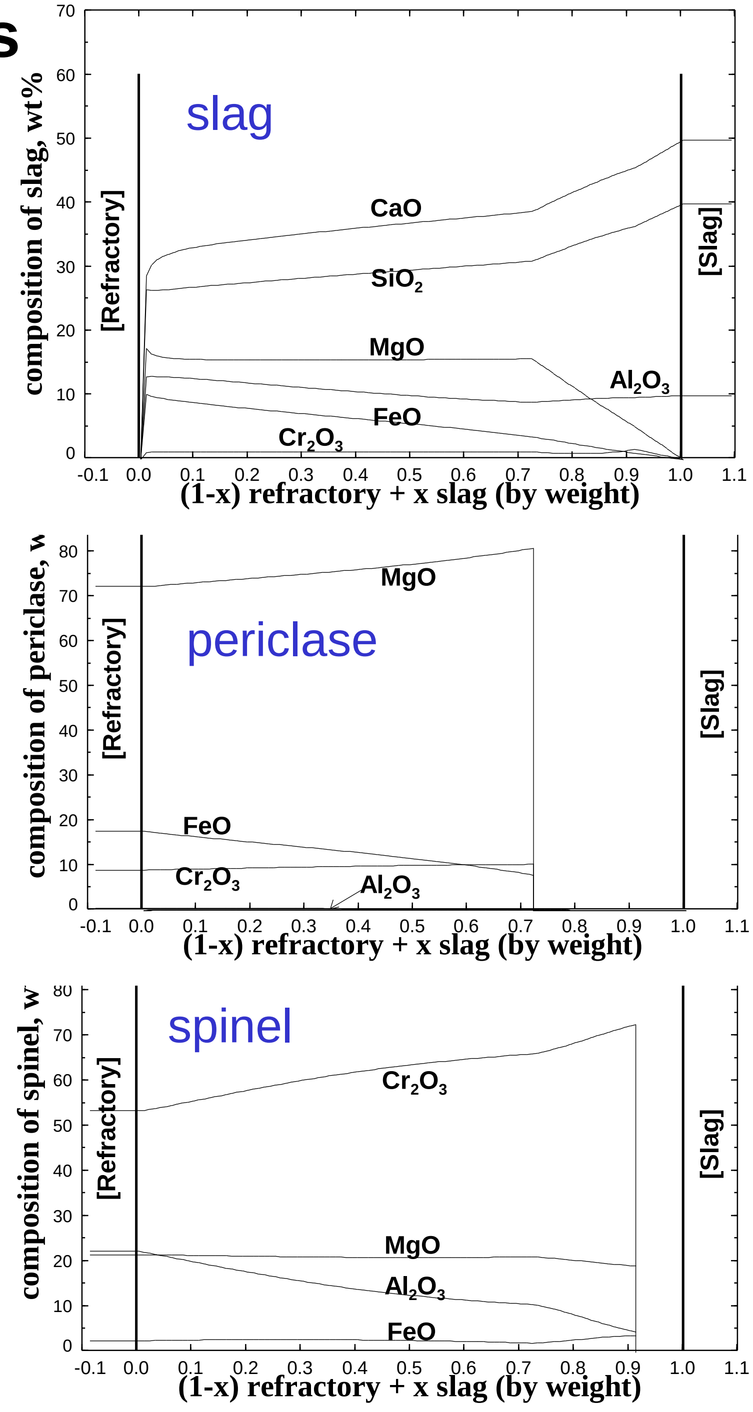


Depending on the refractory compositions, the refractory components can vary drastically.

- **Formation of liquid**
  - **Stability of refractory ↓**
- **Change in MgO/Spinel fraction**
  - **Mechanical wear resistance**
  - **Volume change**

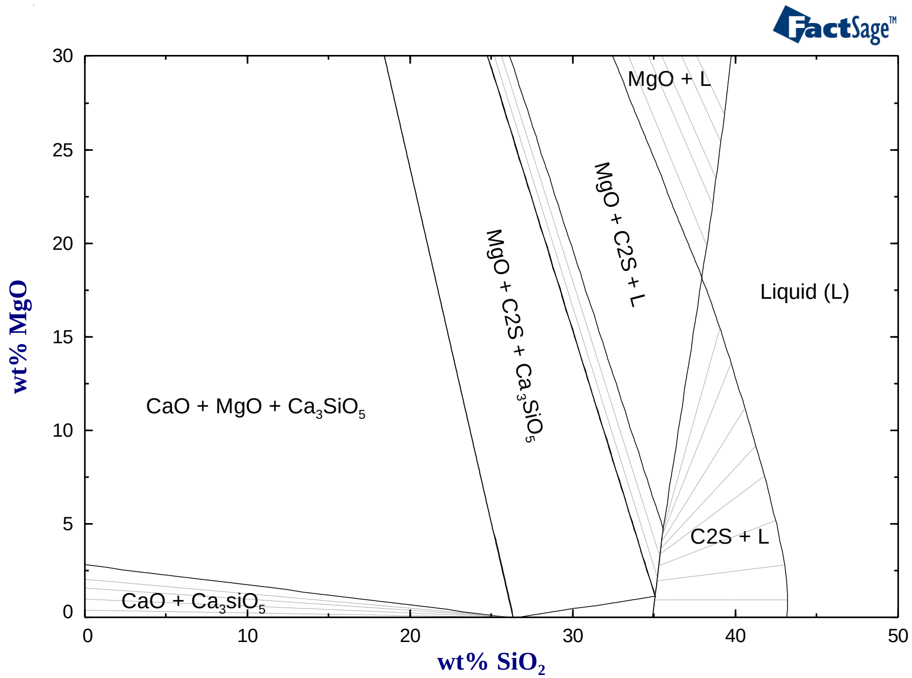
Refractory/Slag rxn in VOD process





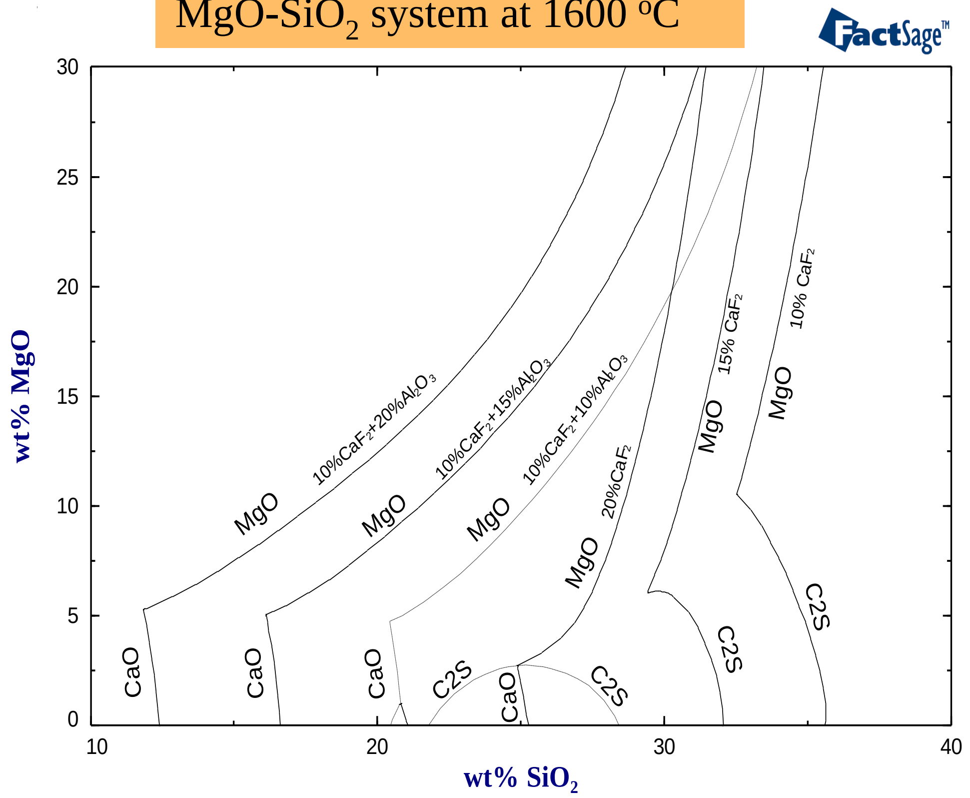
Jung et al., Taikabutsu, vol. 56, 2004, pp. 382-386.

Refractory reaction with F-containing slag/flux

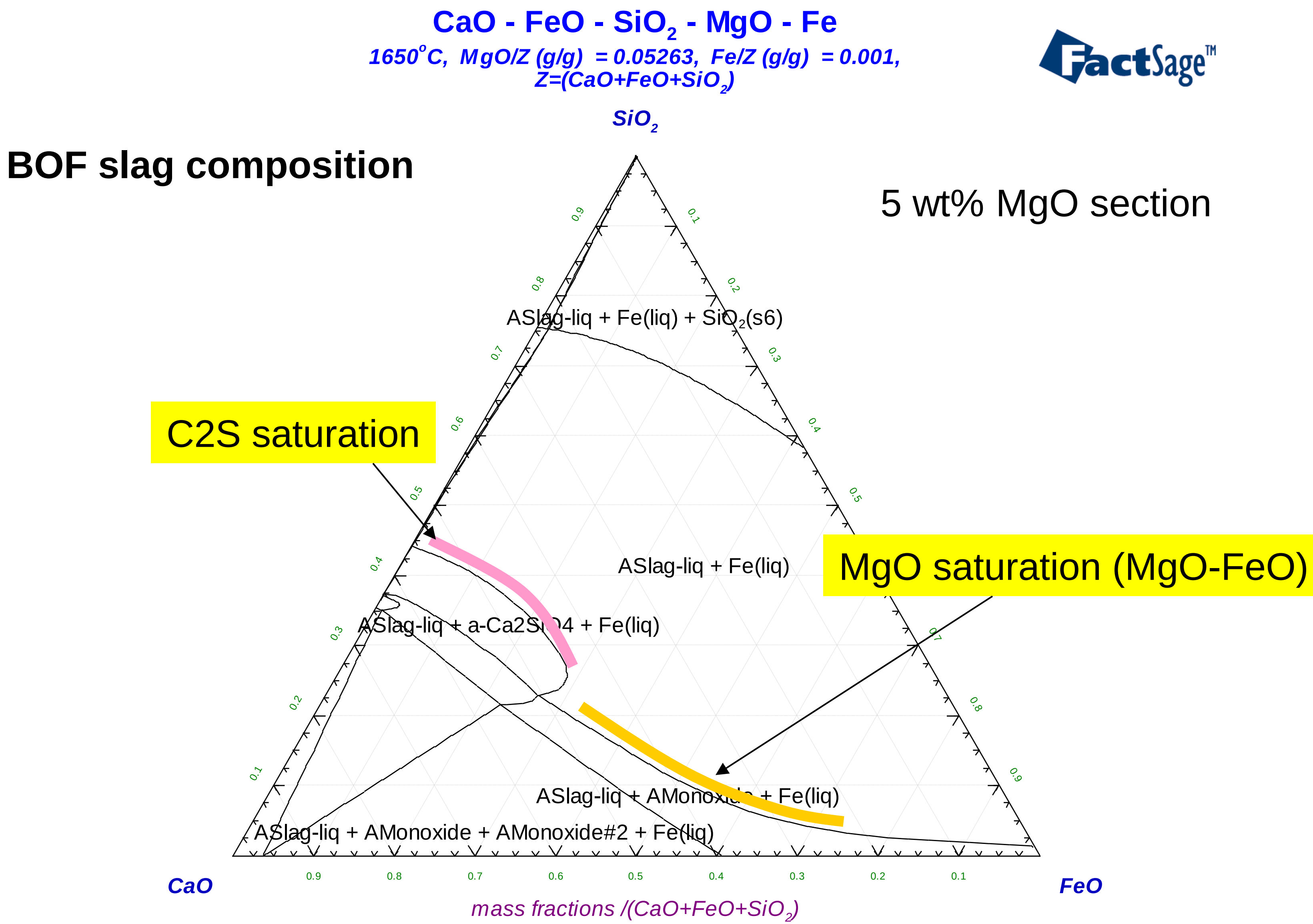


Phase diagram of the CaO-MgO-SiO$_2$ system at 1600 ^{o}C

Influences of CaF$_2$ and Al$_2$O$_3$ on the liquidus of the CaO-MgO-SiO$_2$ system at 1600 ^{o}C

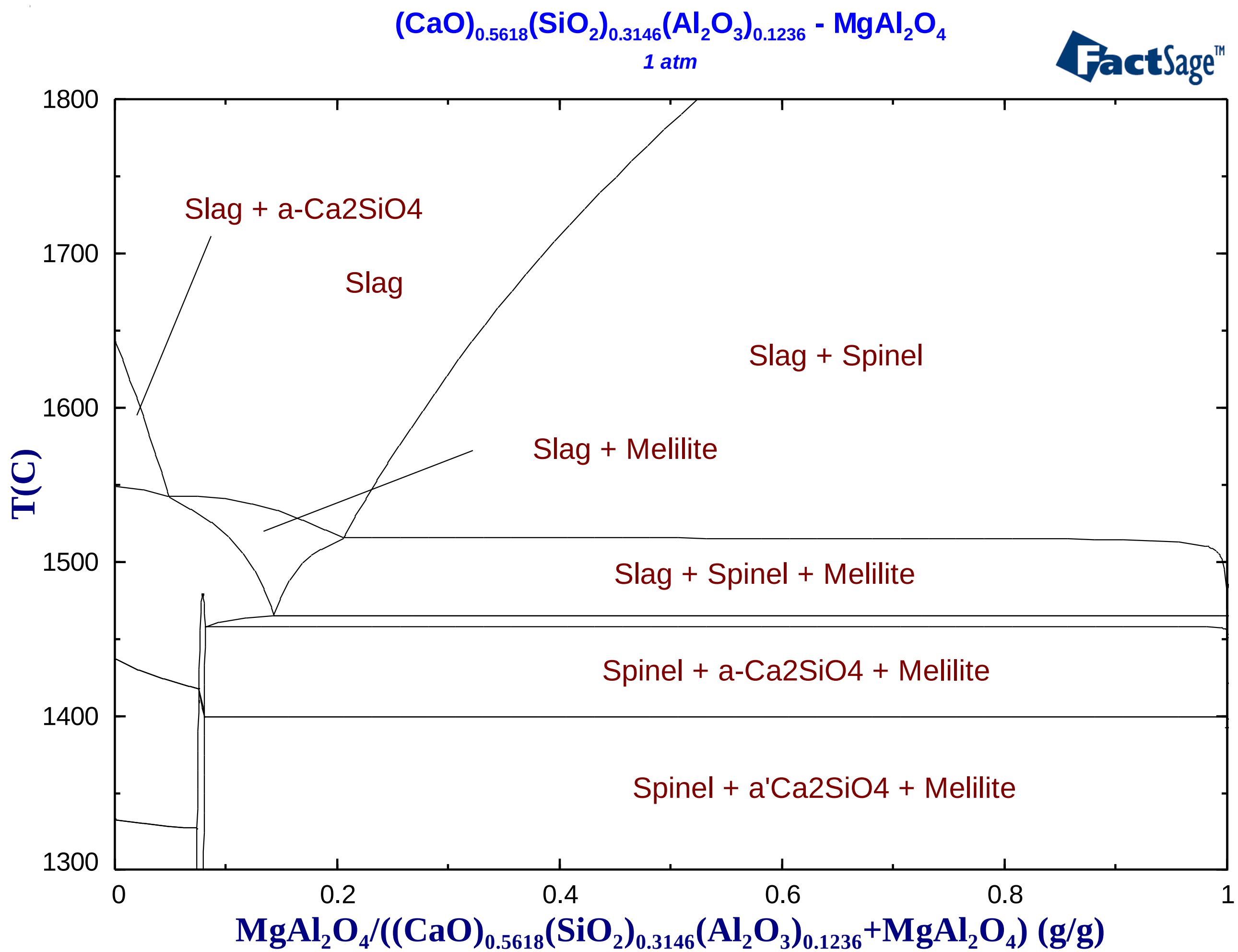


Refractory: $CaO-Fe_tO-SiO_2$-5wt%MgO system with Fe saturation



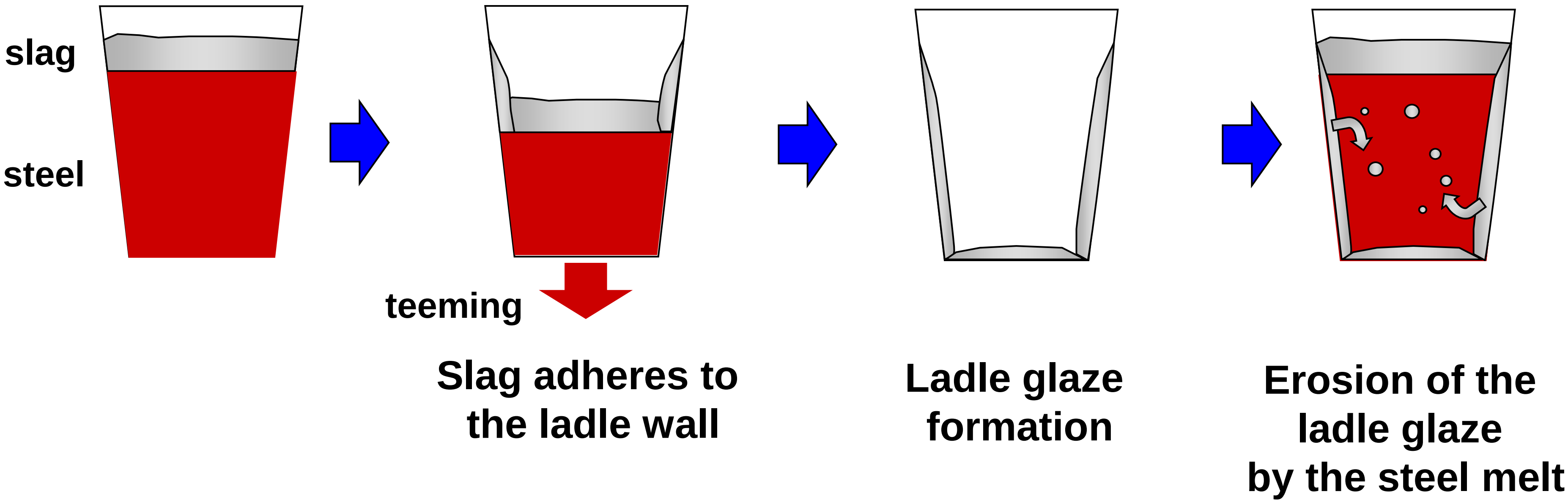
CaO-Al2O3-SiO2 slag – MgAl2O4 refractory

50%CaO-30%SiO2-20%Al2O3 slag → in mole: $(CaO)_{0.5618}(SiO2)_{0.3146}(Al2O3)_{0.1236}$
(Equilib or Phase Diagram's components are in molar base)



Ladle Glaze

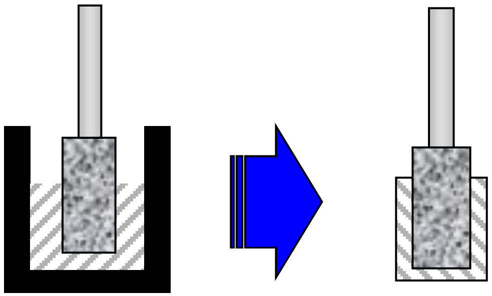
- Reactions with Ladle refractory lining
- Formation of non-metallic Inclusions



Purpose of the present study

- Glaze formation mechanism / Glazed refractory
- Influence on melt cleanliness (inclusion): Al, Al/Ca

Ladle Glaze formation



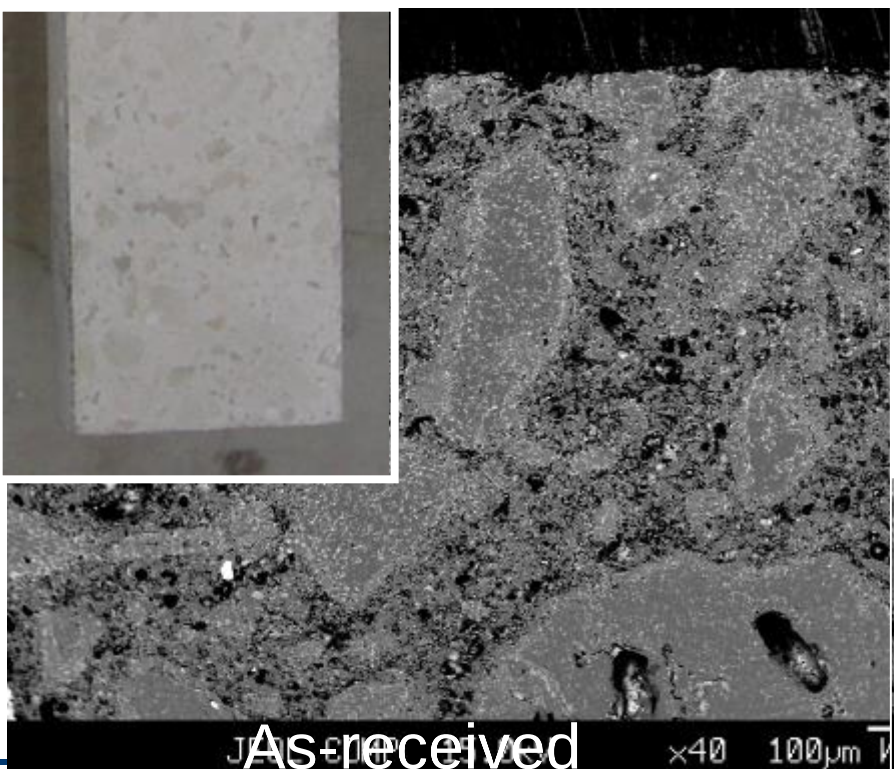
Dipping time: 120 sec

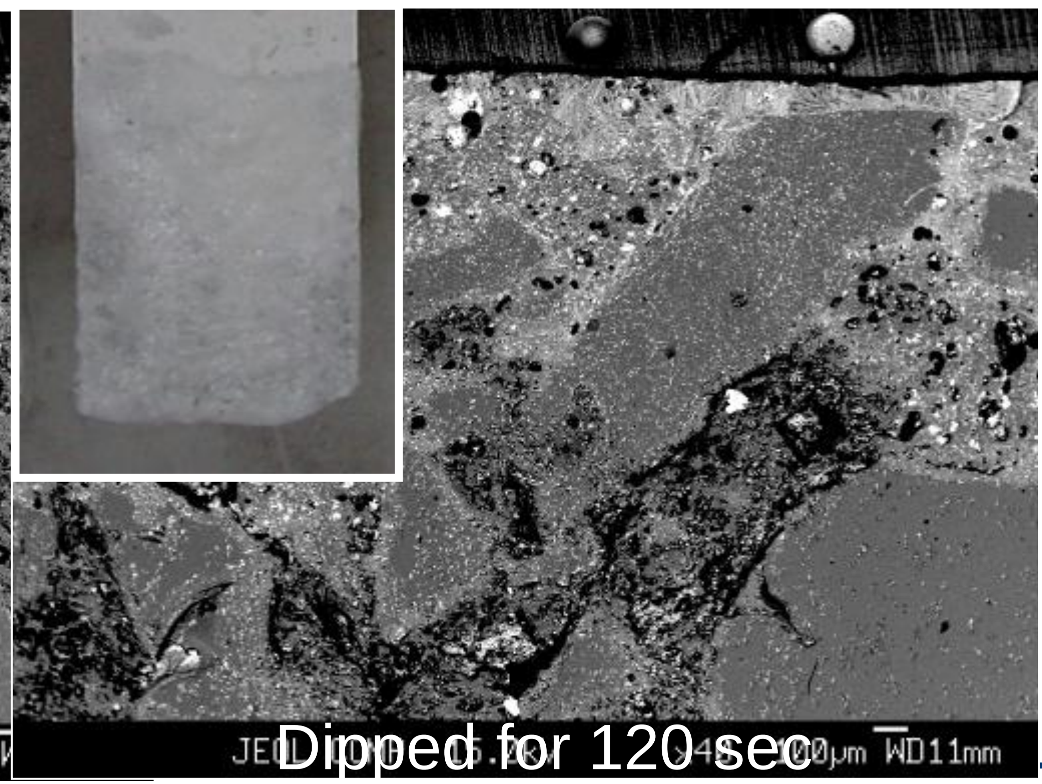
Refractory composition (wt.%)

CaO	SiO2	Al2O3	MgO
2.35	0.76	88.06	8.35

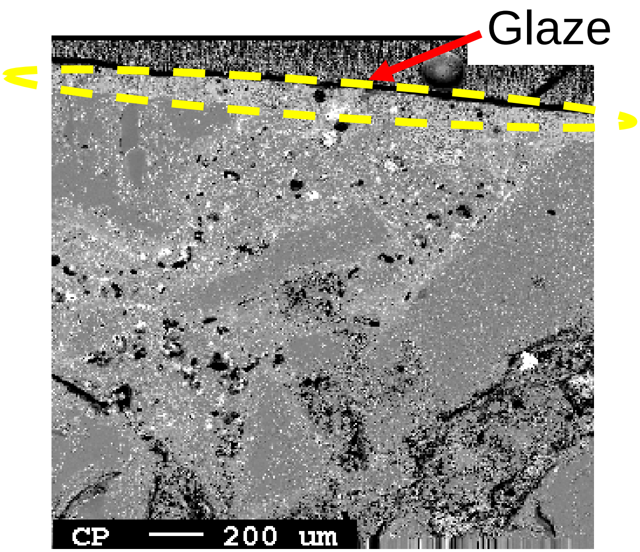
Slag composition (wt.%)

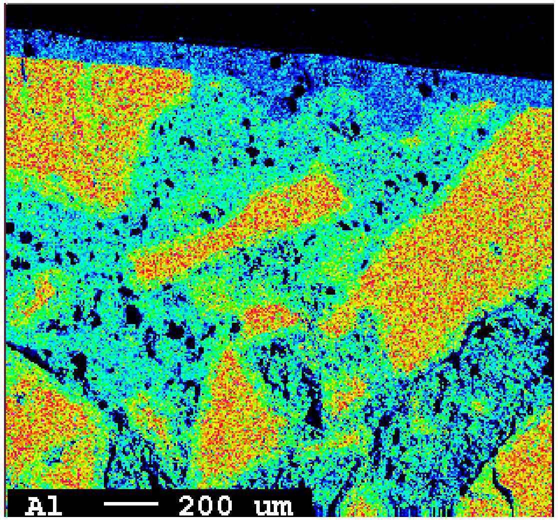
CaO	SiO2	Al2O3	MgO
54.06	10.47	26.24	9.23

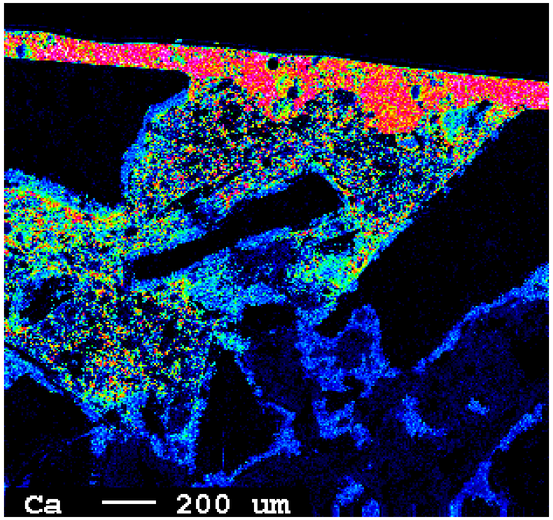


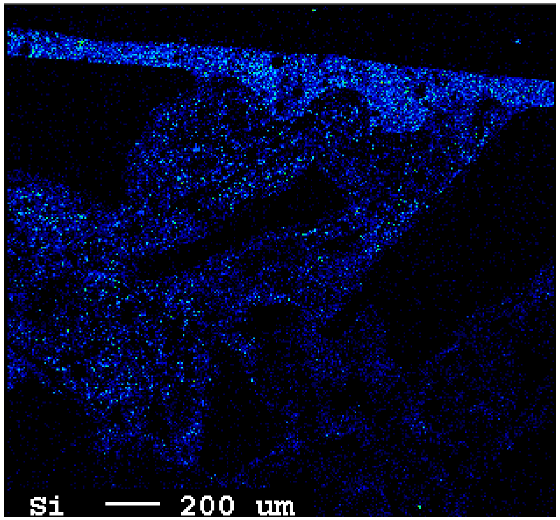


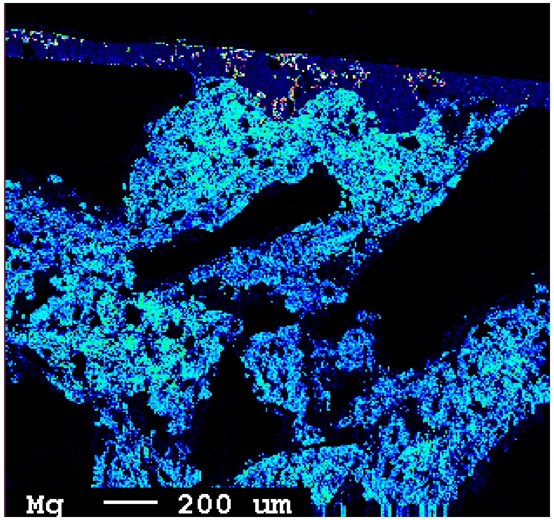
Glazed Refractory



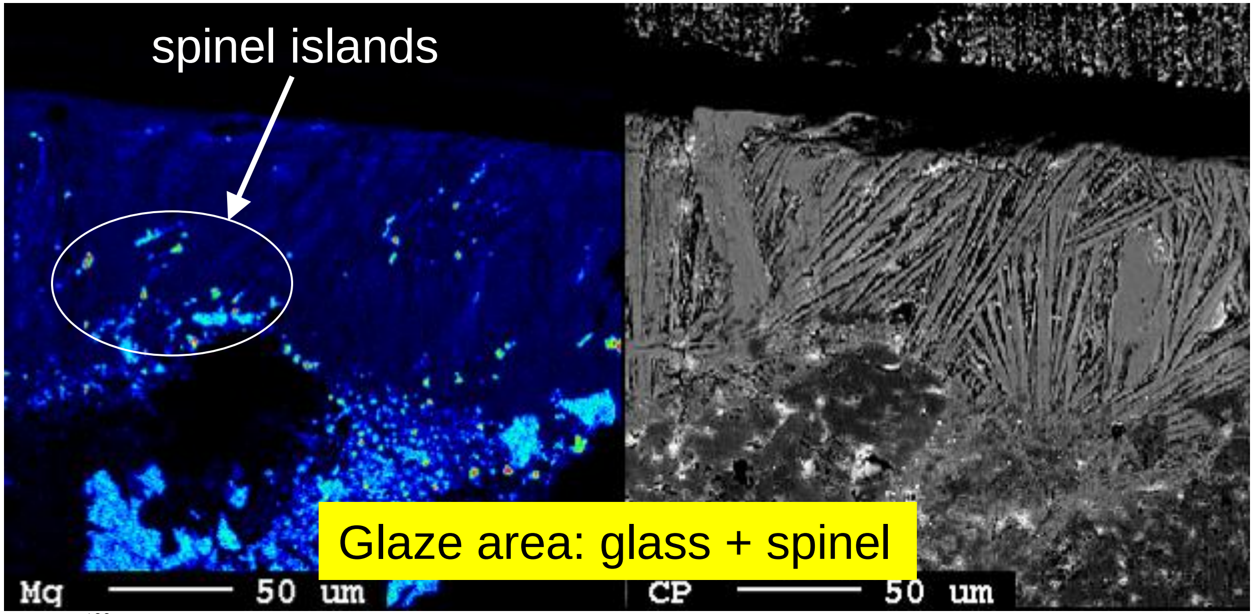






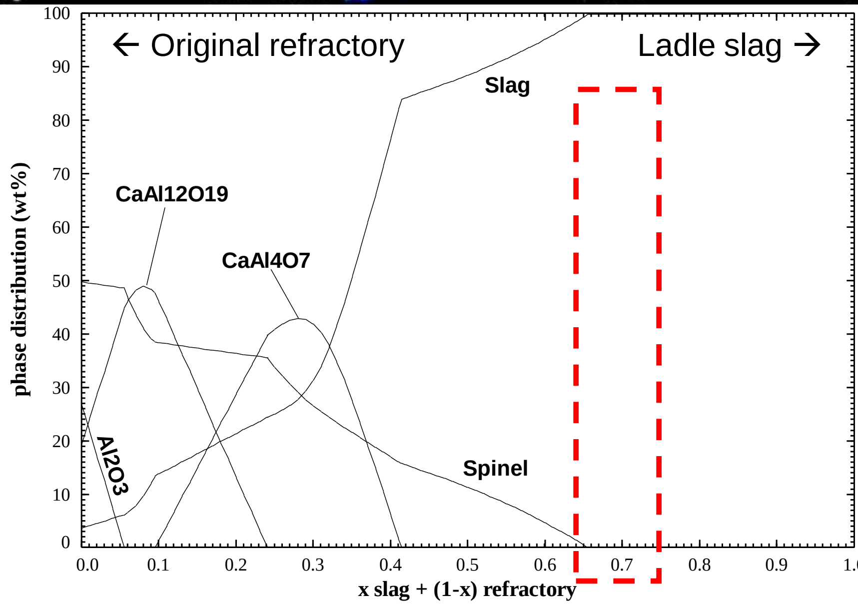


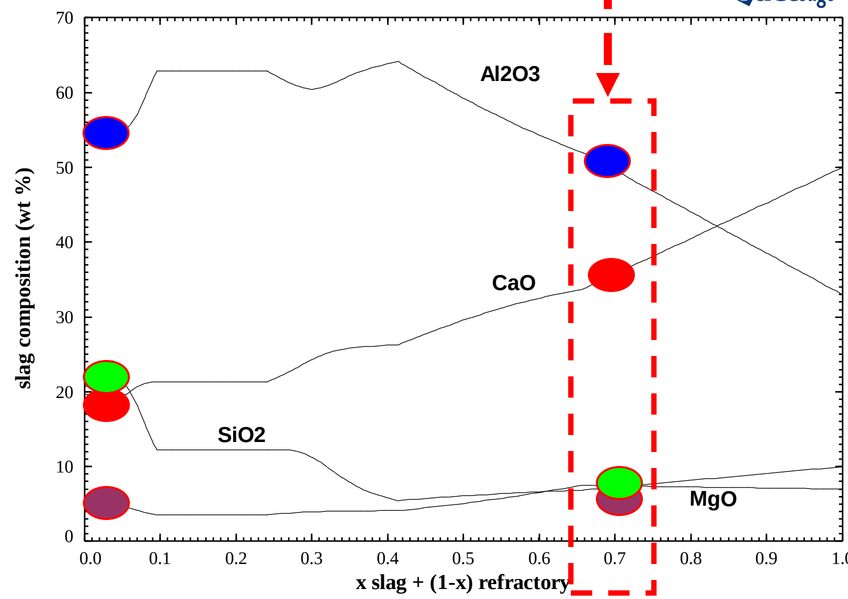
Glaze (Reaction product of slag and refractory)



Glaze composition (glass)

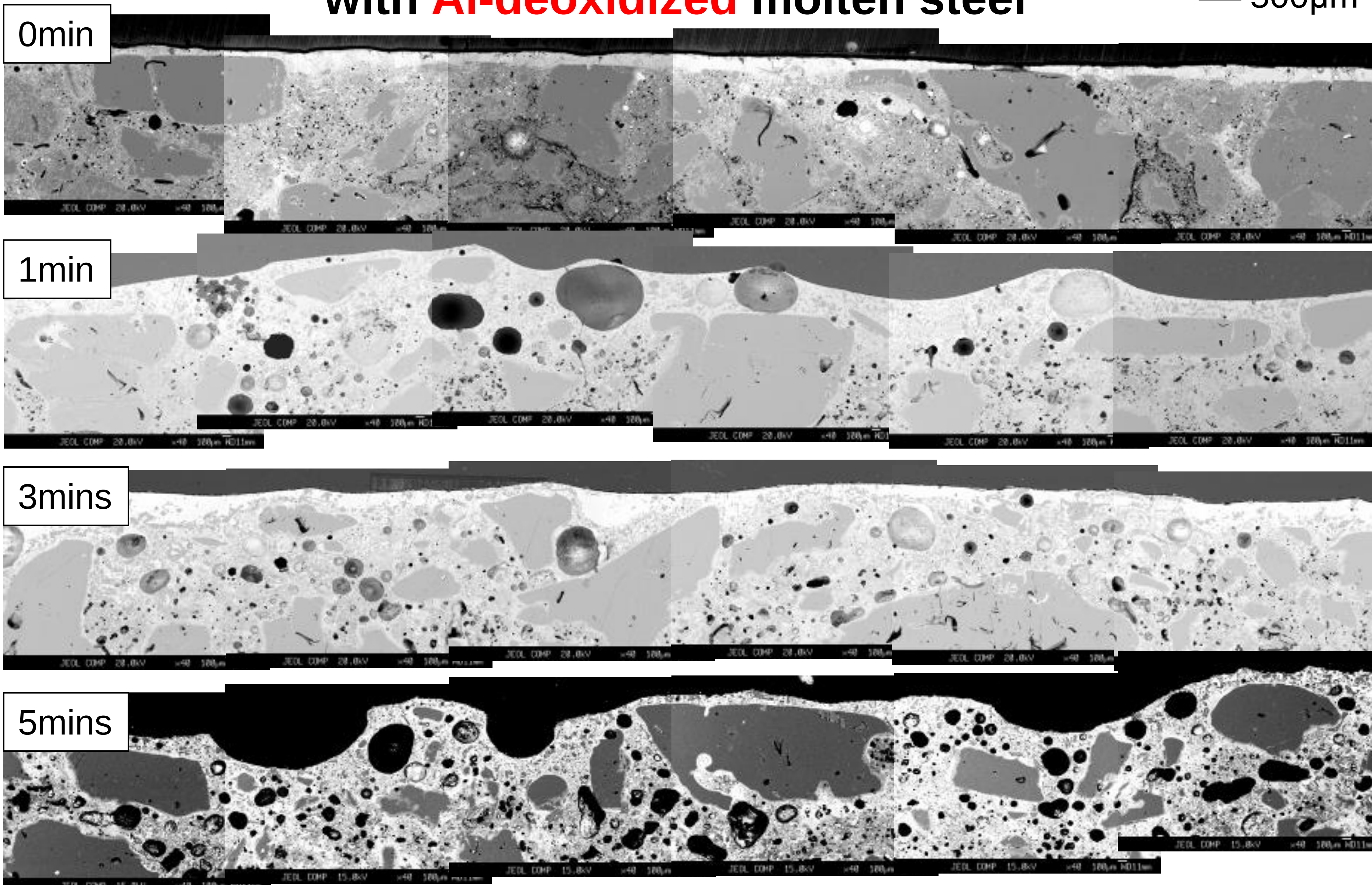
CaO	SiO2	Al2O3	MgO
35.8	6.6	51.1	6.5



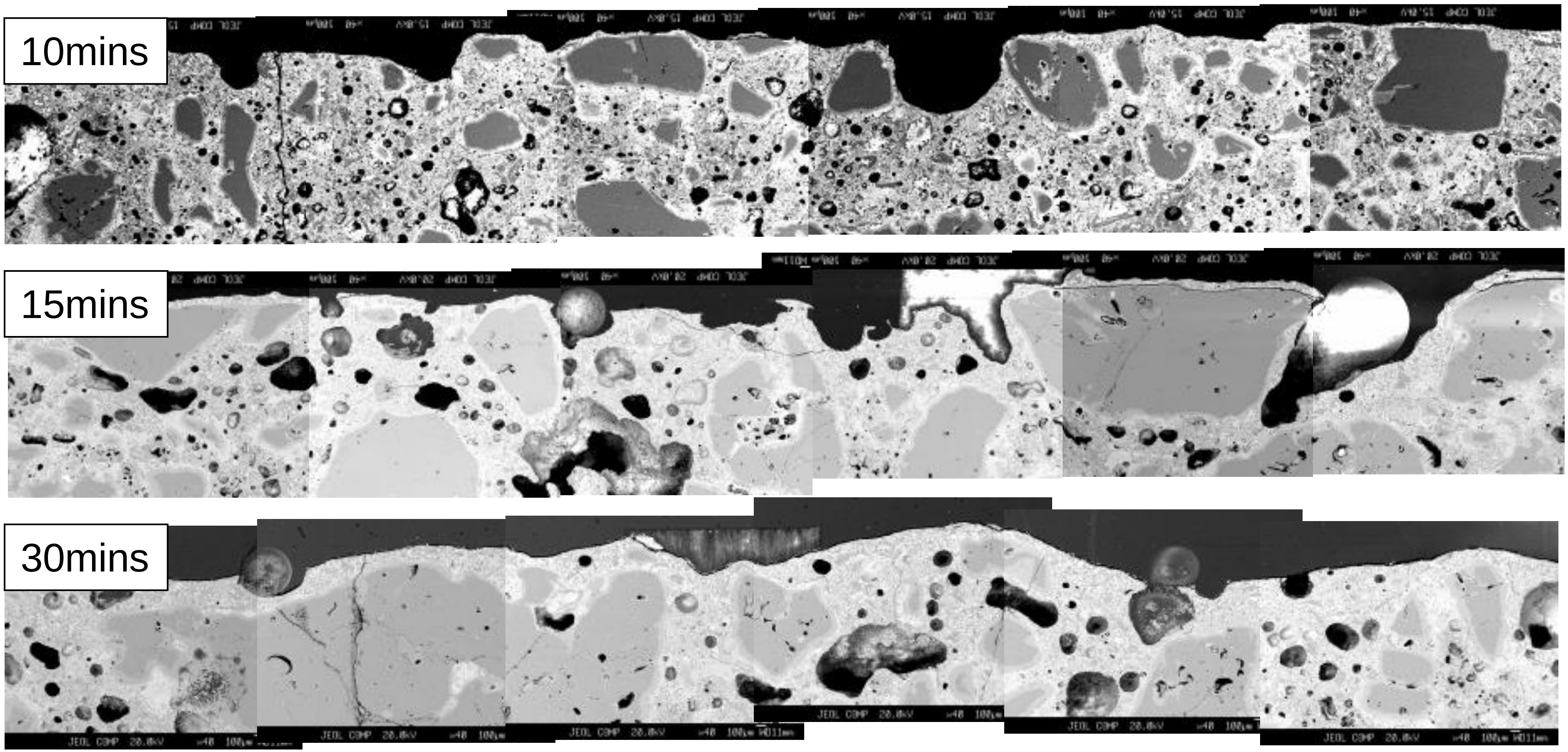


Change of Glazed refractory by chemical reaction with Al-deoxidized molten steel

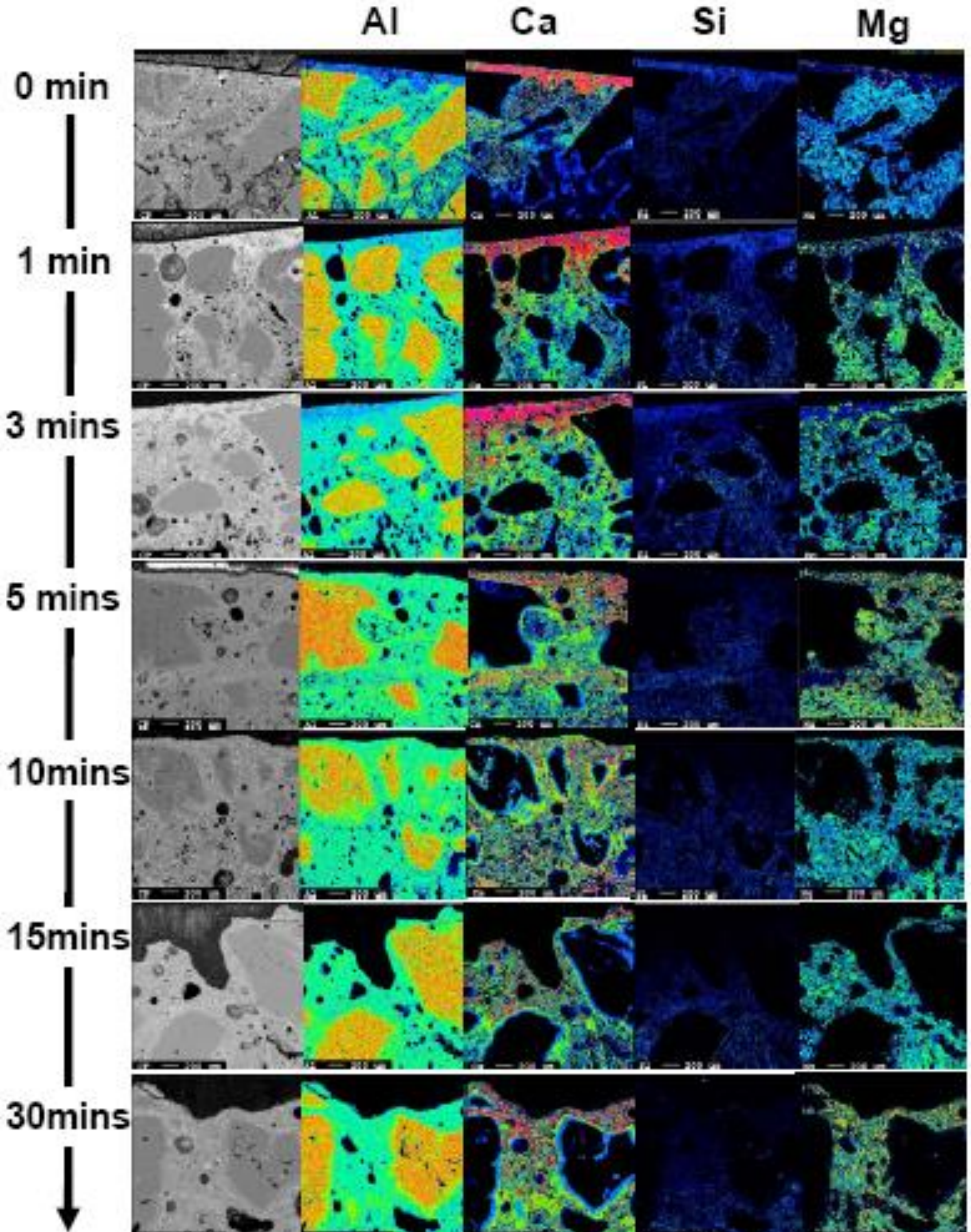
500μm



Change of Glazed refractory by chemical reaction with Al-deoxidized molten steel

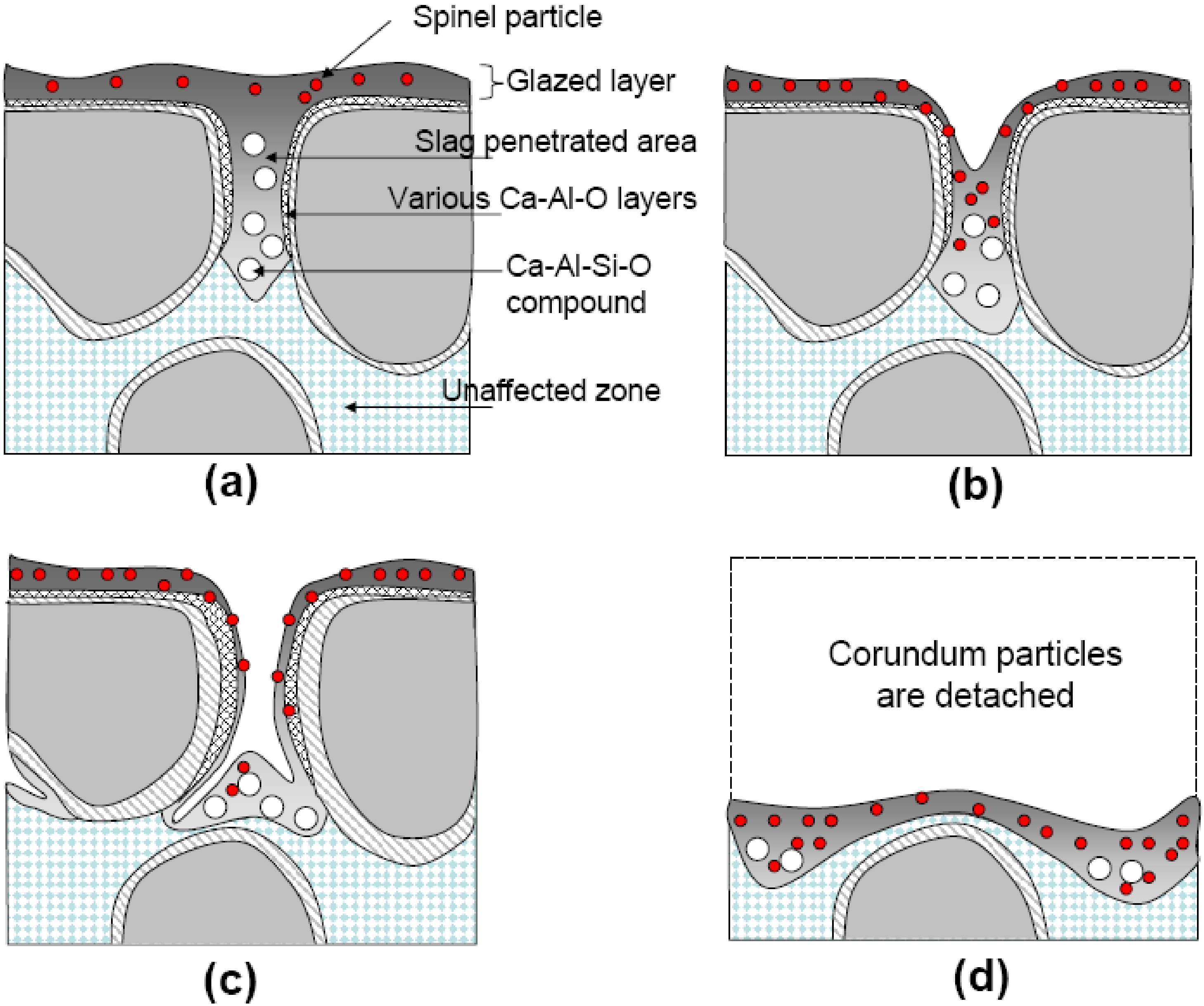


Morphology of Glazed refractory in molten steel (Al-deoxidized)

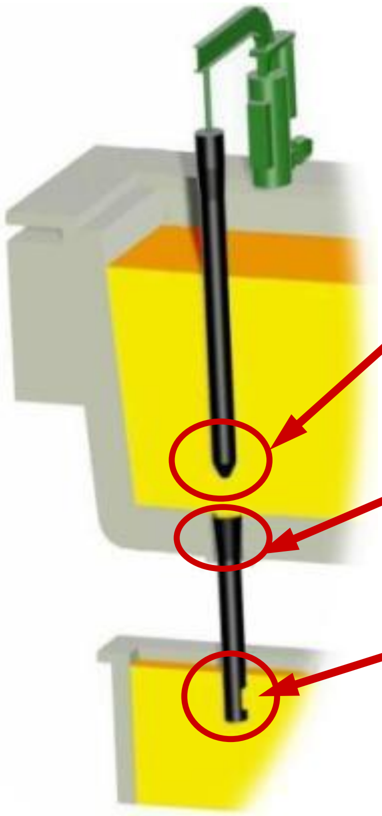


Penetration of Glaze into refractory (Ca and Si mapping images)

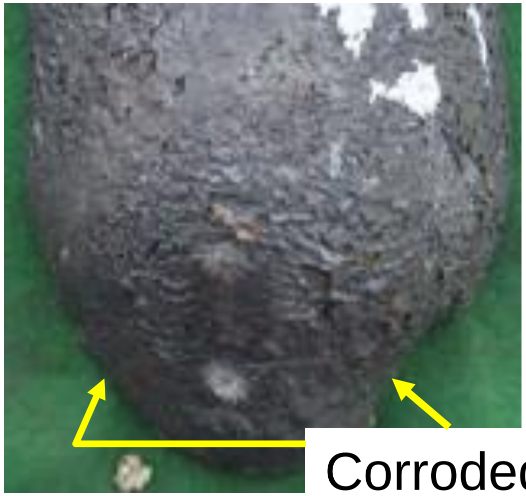
Change of Glazed refractory in Al (Al/Ca) steel

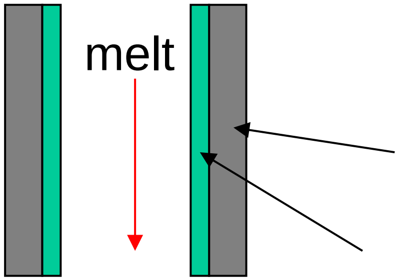


Refractory – Liquid Inclusion Interactions



Stopper (Al2O3-C)

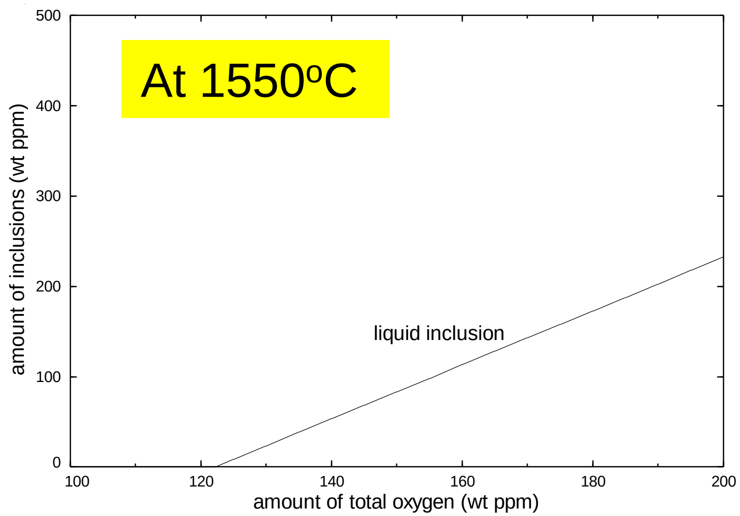




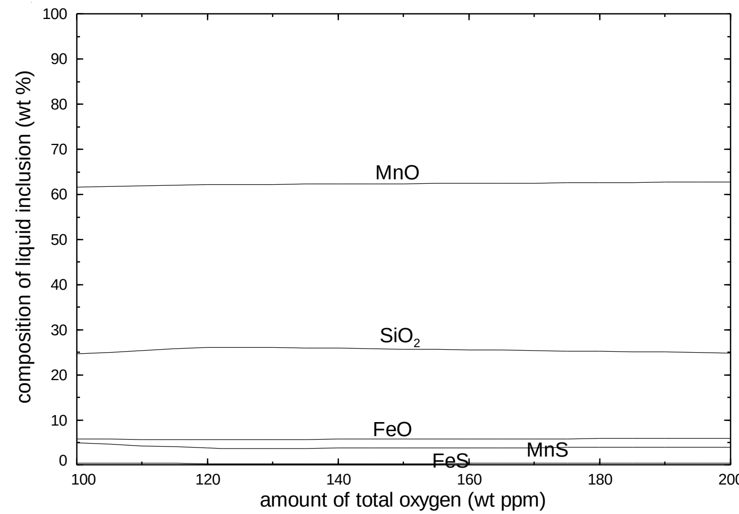
M.-K. Cho and I.-H. Jung, "Corrosion of nozzle refractories by liquid inclusion in high oxygen steels", ISIJ Inter. 2012, vol. 52, pp. 1289-1296.

Refractory – Liquid Inclusion Interactions

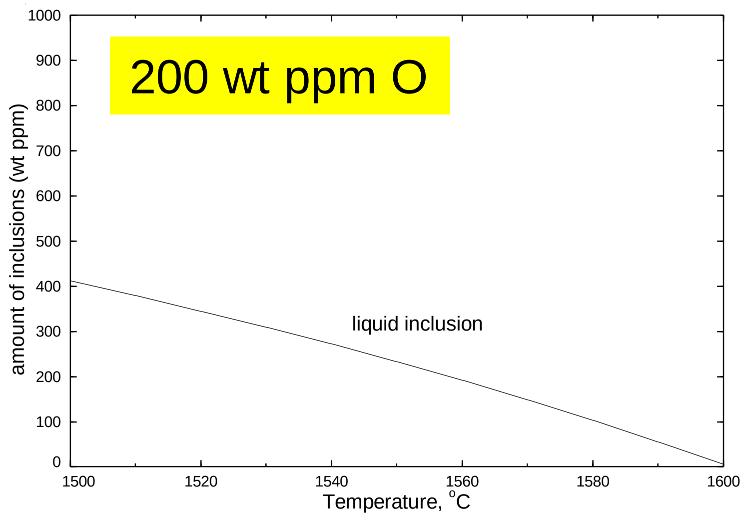
Fe-0.08C-1.2Mn-0.3S-0.01Si-O-minor P, Bi, etc. in wt %

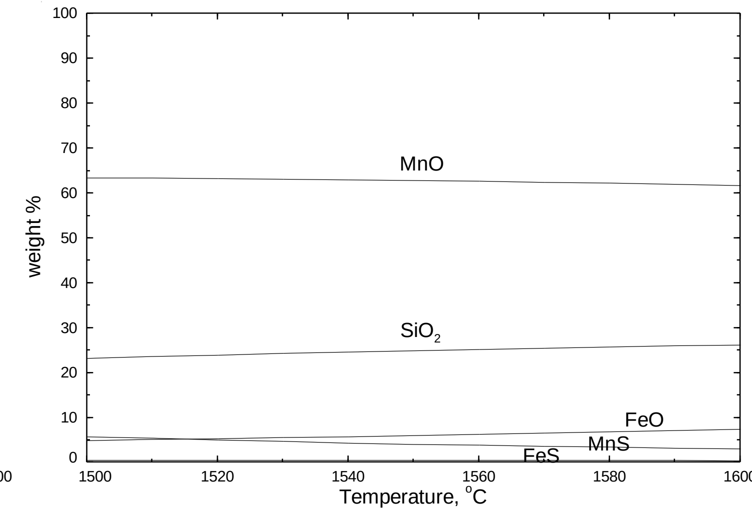


(a)



(b)



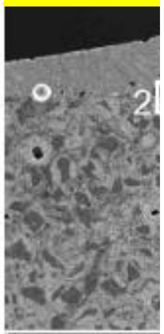


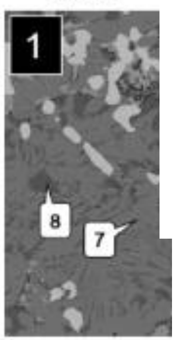
Refractory – Liquid Inclusion Interactions

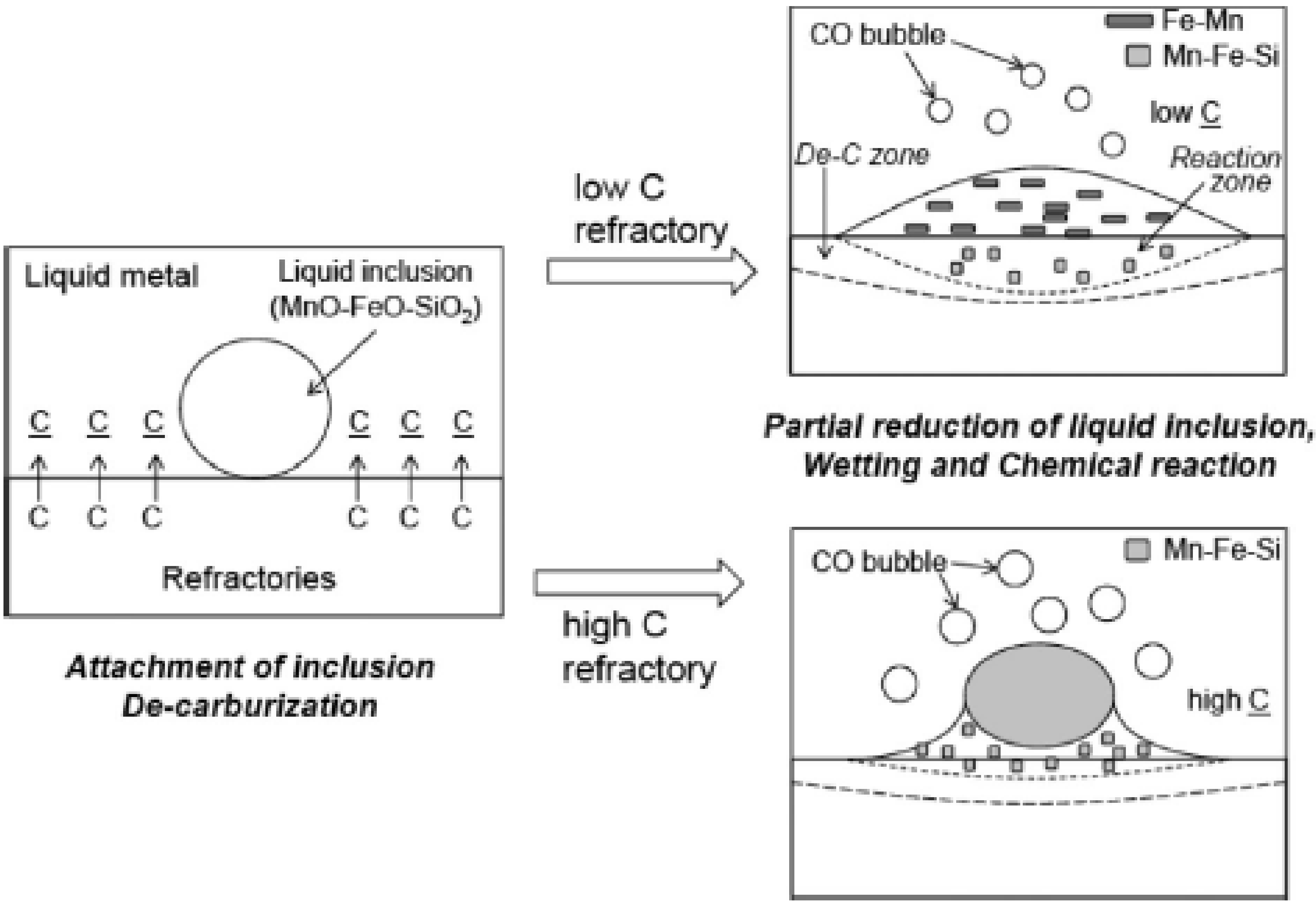
Table 1. Chemical compositions of the refractories investigated in

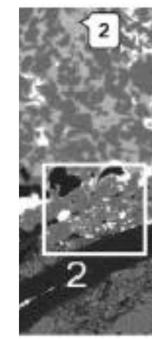
wt%
Al_2O_3
MgO
ZrO_2
C

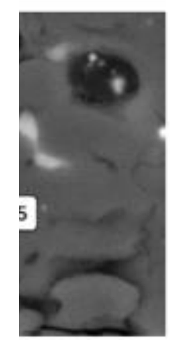
Al2O







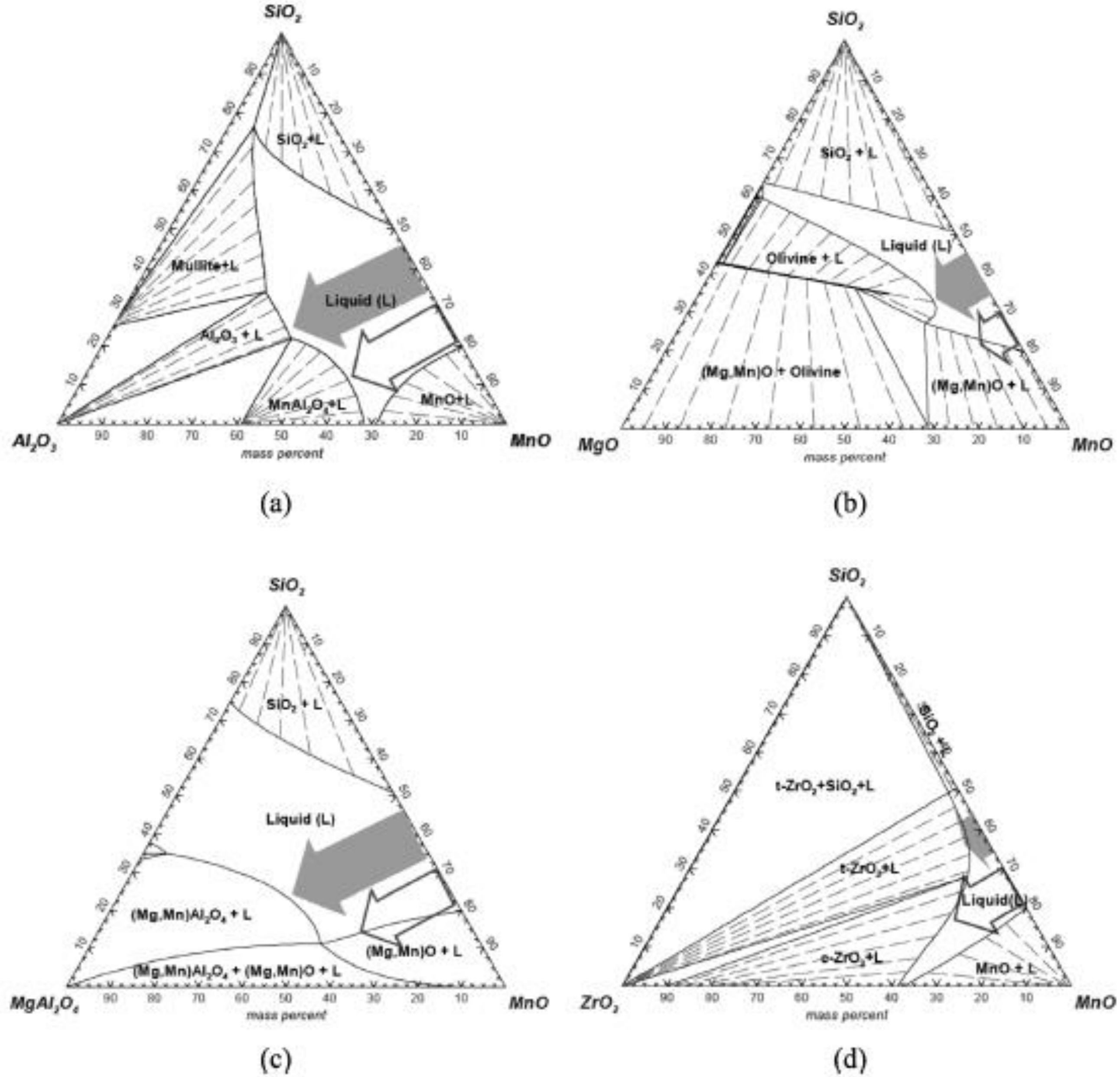




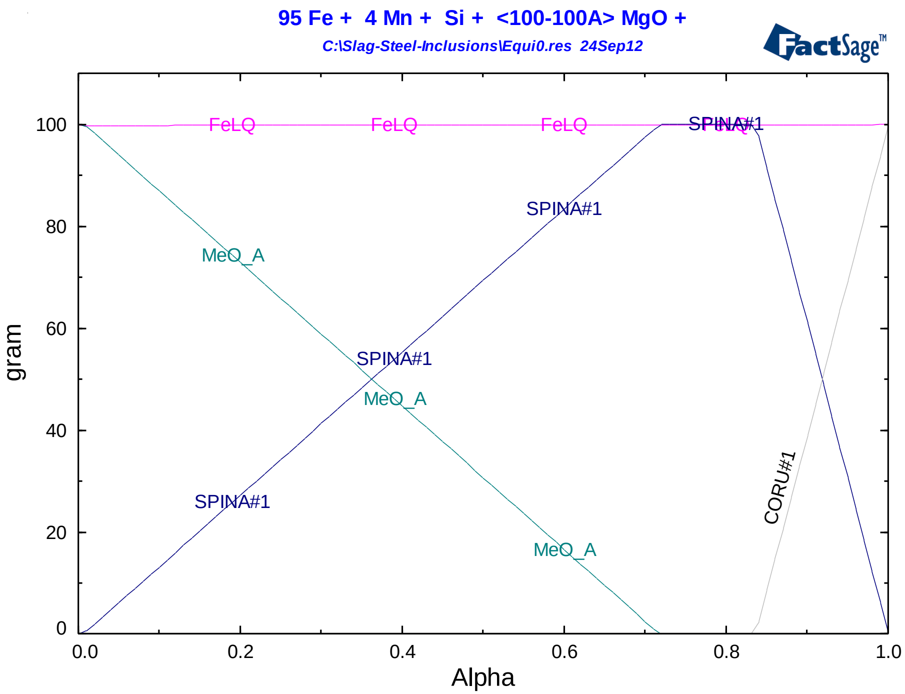
30µm 60µm 10µm

Refractory – Liquid Inclusion Interactions

Relative Stability of the refractories against liquid MnO-SiO2 type inclusion



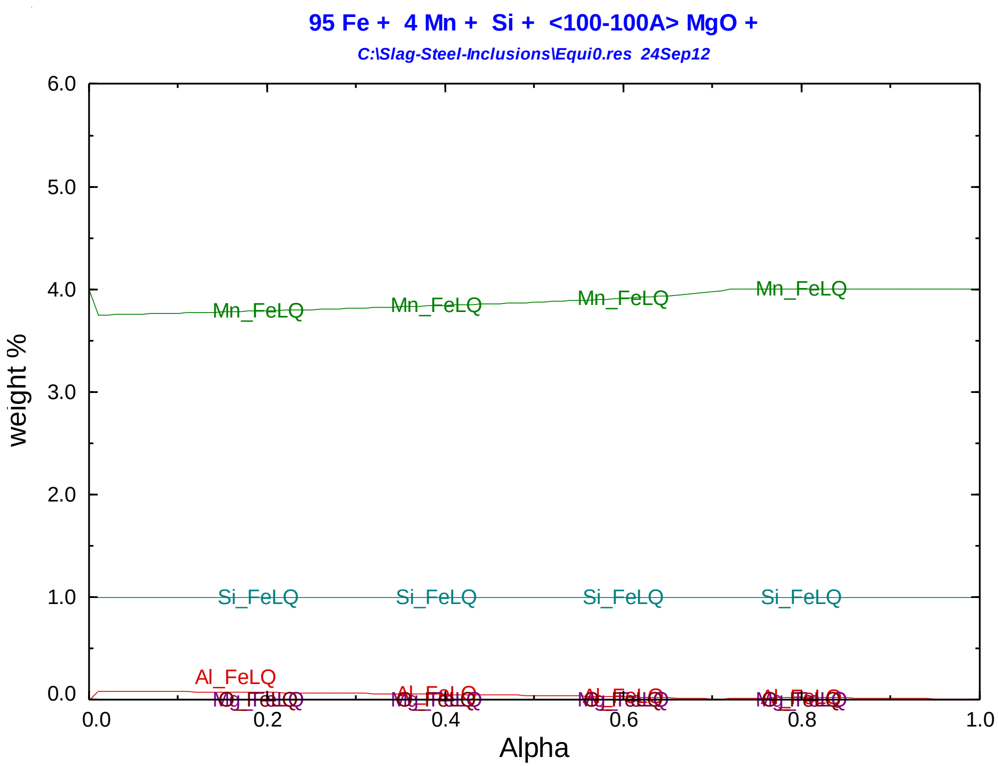
Refractory-Steel Interaction



← Change in the amount of phases

<100A> Al2O3 + <100-100A> MgO

Change in steel composition →



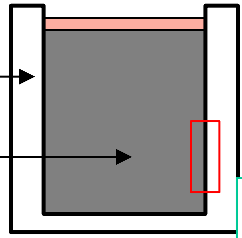
<100A> Al2O3 + <100-100A> MgO

High Mn-Fe melt storage for TWIP Steel production

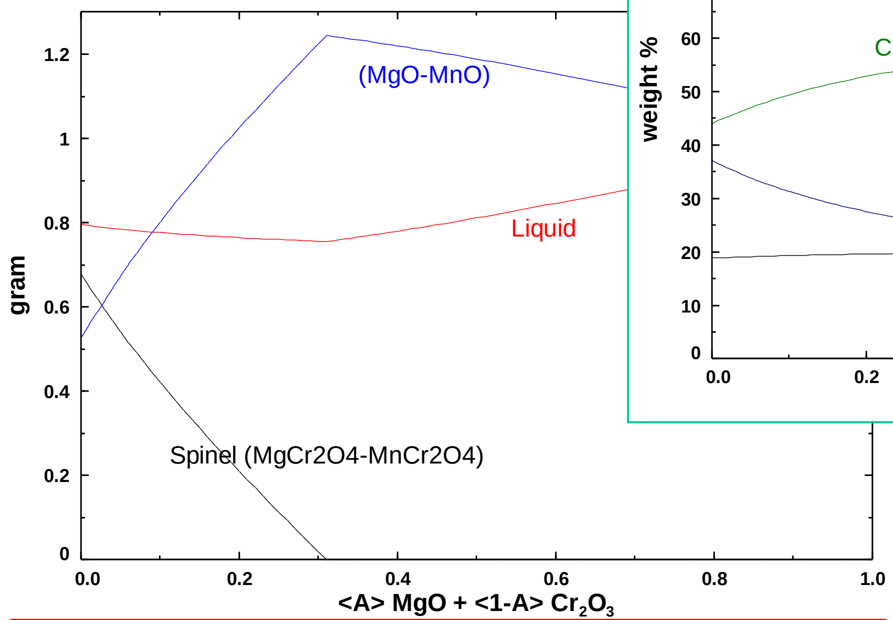
Melt / refractory reactions simulation

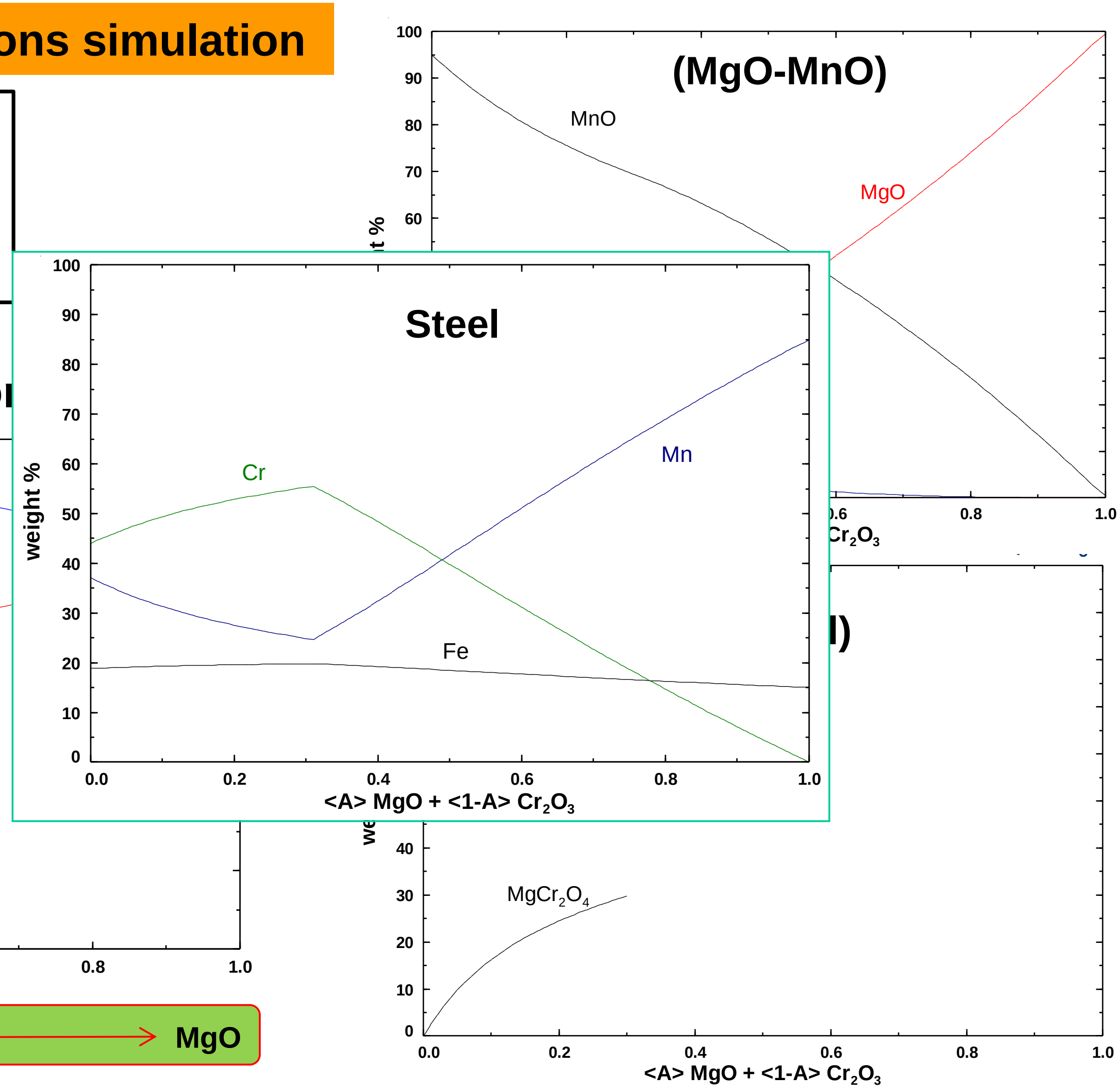
Refractories

85%Mn-15%Fe melt



1g Mn-Fe melt + 1g refractor

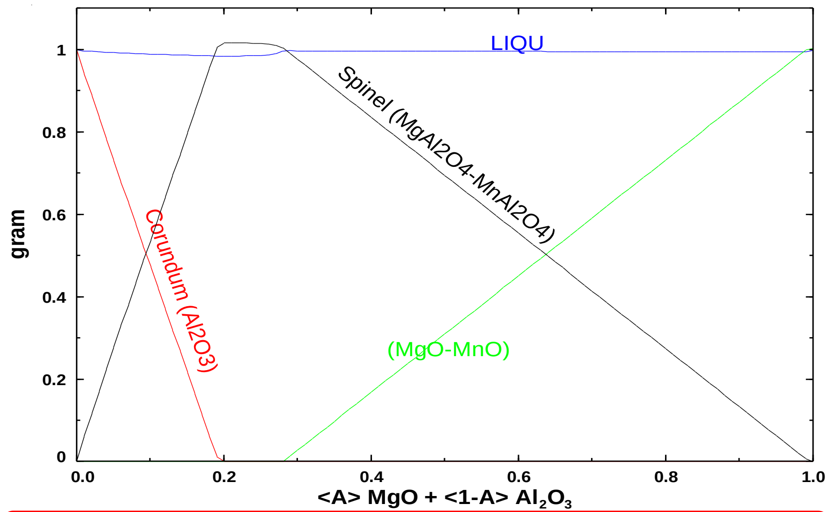




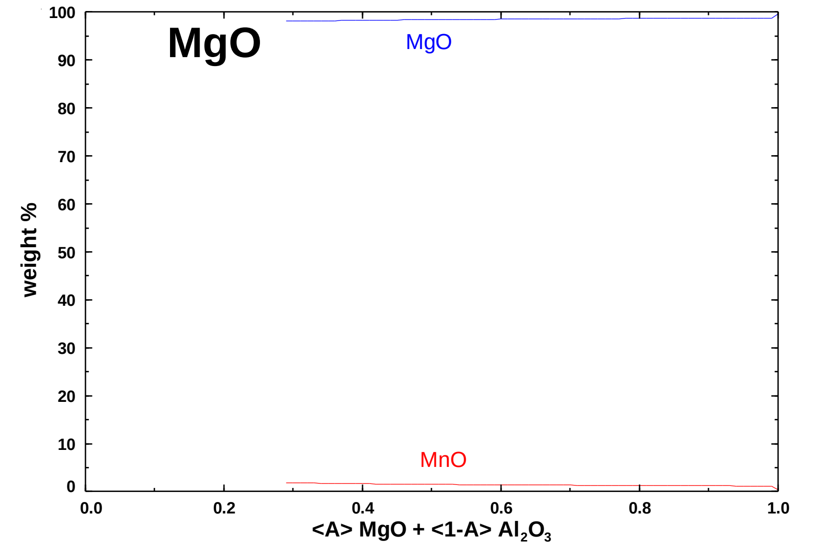
Cr_2O_3 <=> $MgCr_2O_4$ <——————> MgO

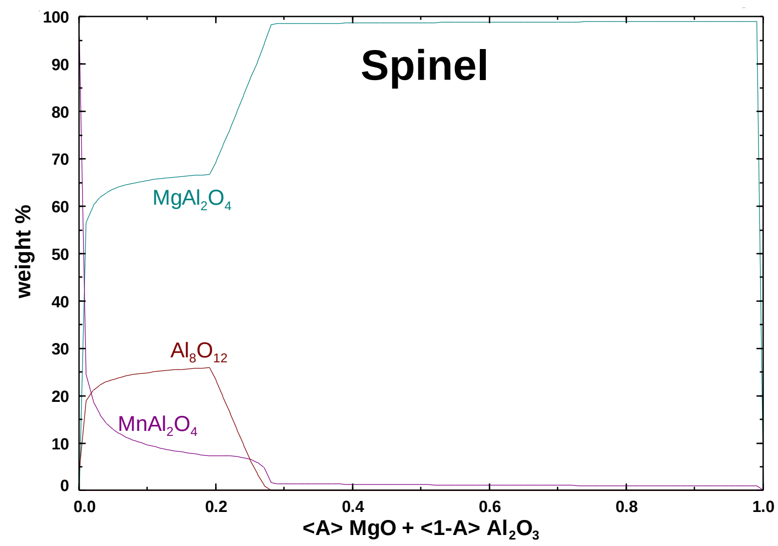
High Mn-Fe melt storage for TWIP Steel production

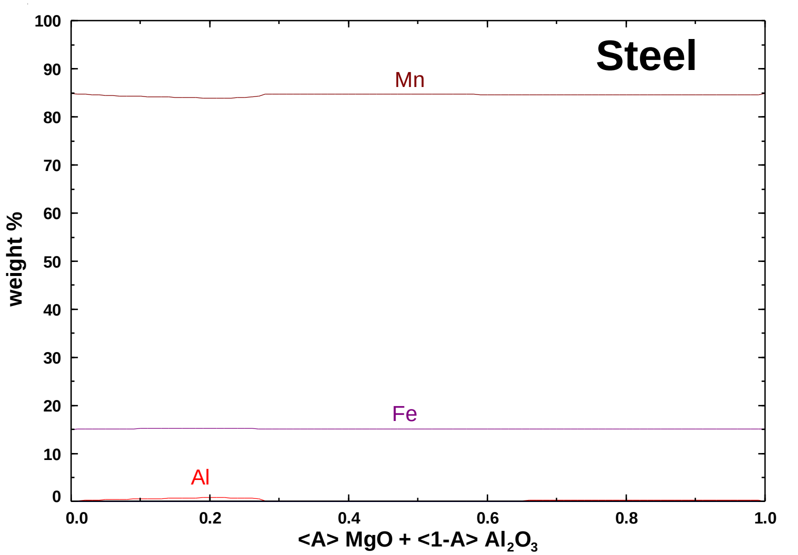
1g Mn-Fe melt + 1g refractory (MgO-Al_2O_3)



Al_2O_3 ↔ $MgAl_2O_4$ ↔ MgO

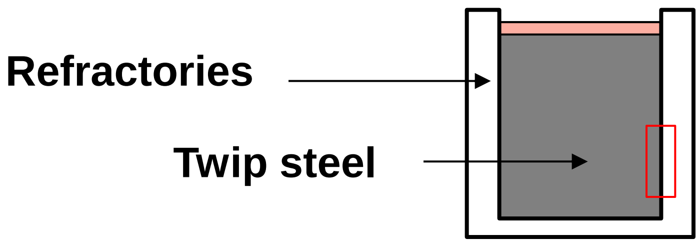


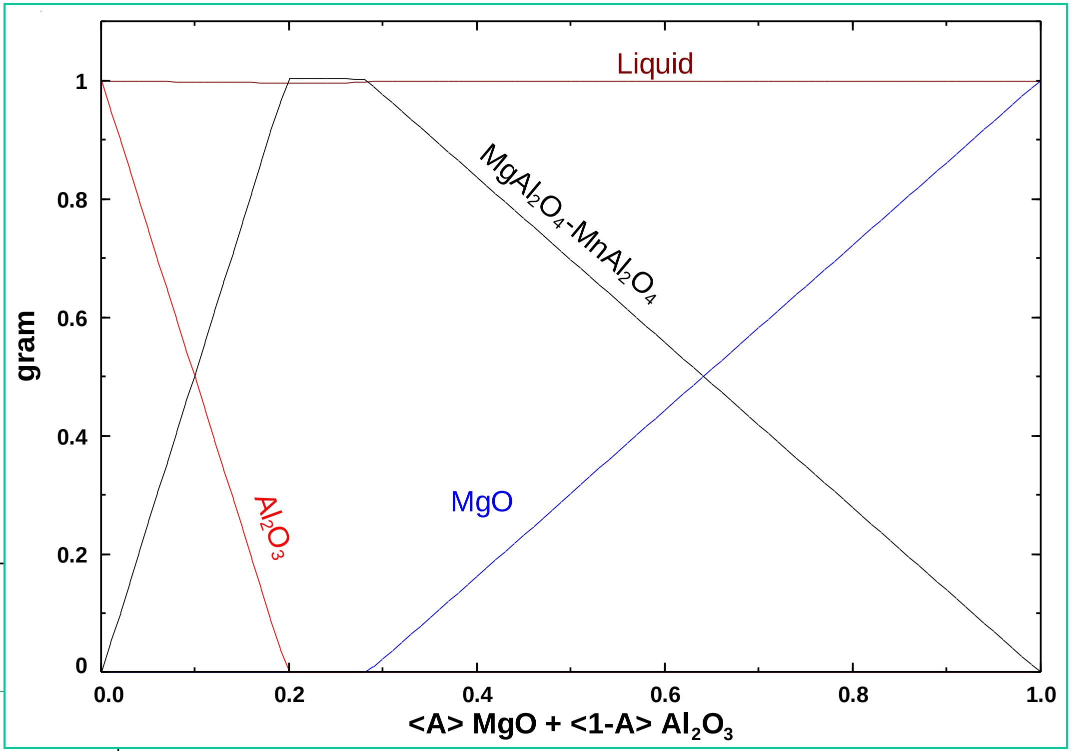


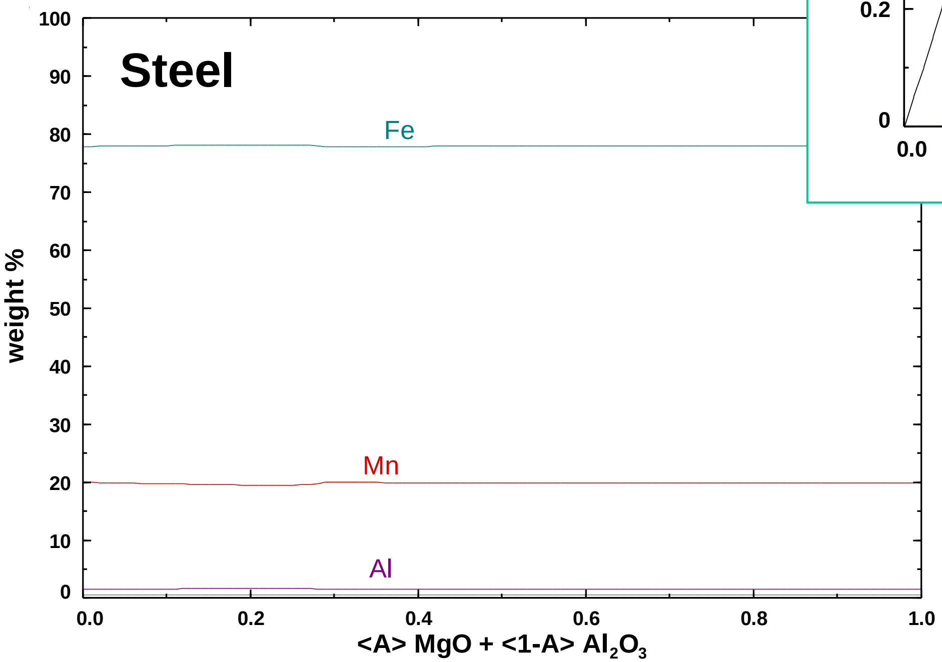


Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C



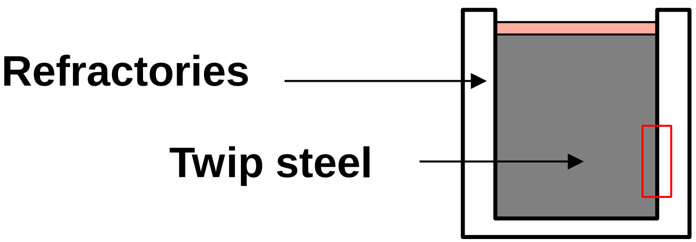


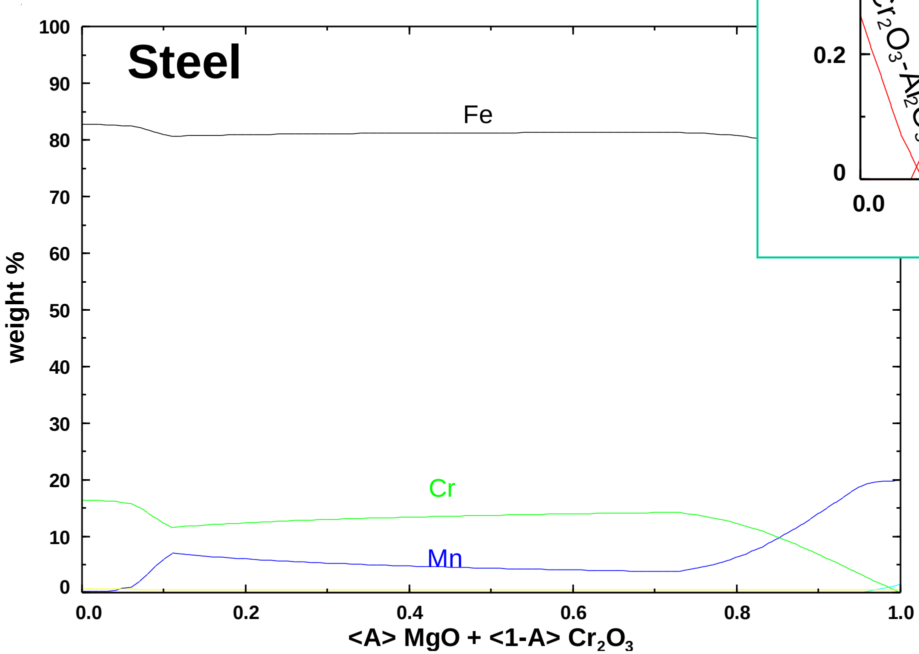


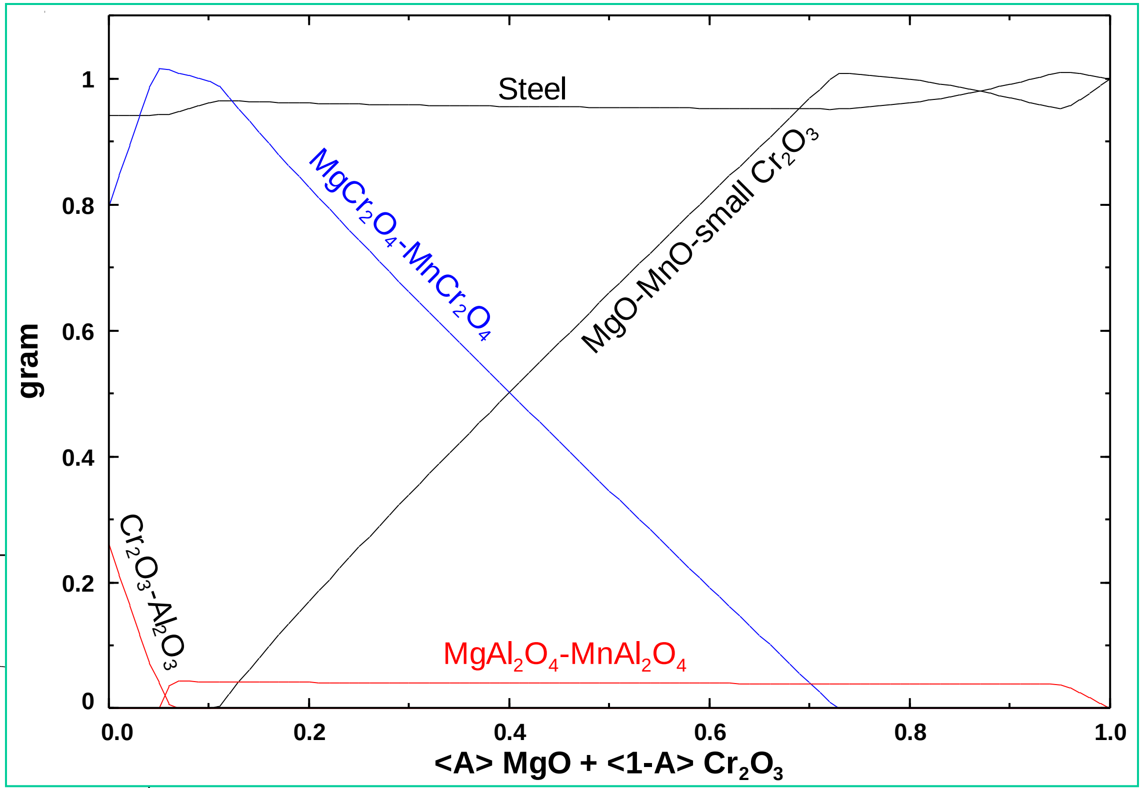
MgO-Al2O3 type: Very stable refractory

Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C







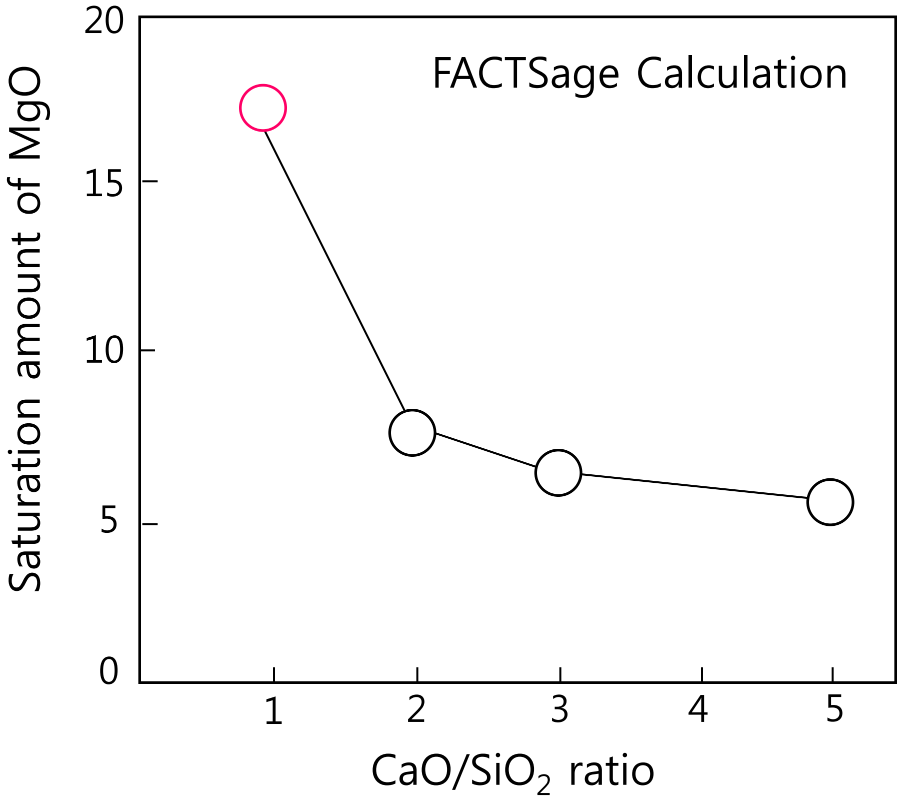
MgO-Cr2O3 type: less stable

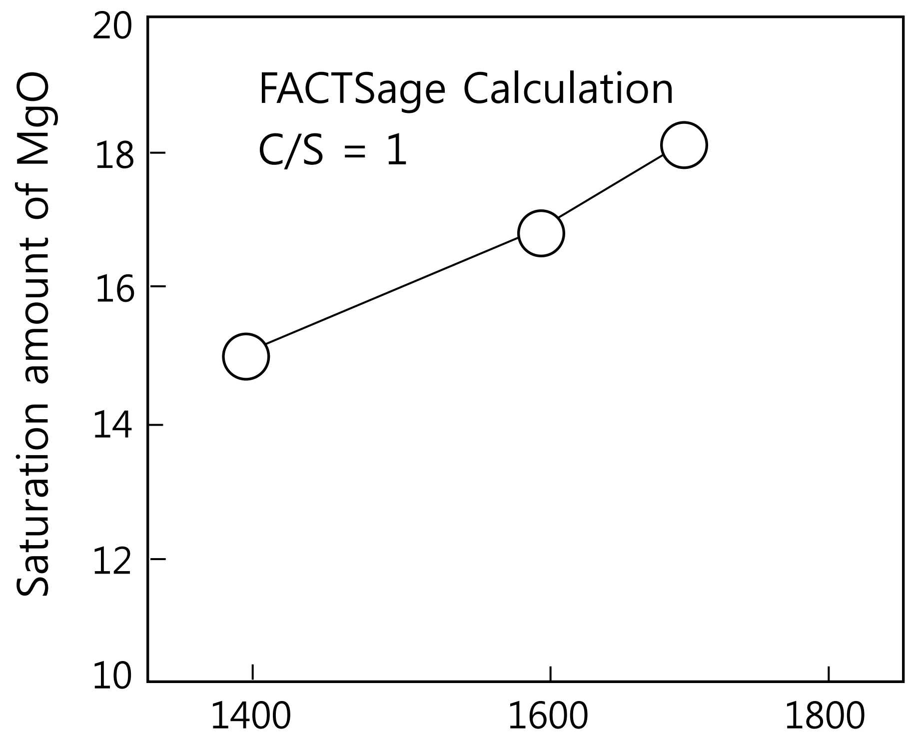
→ Cr pickup

→Al loss

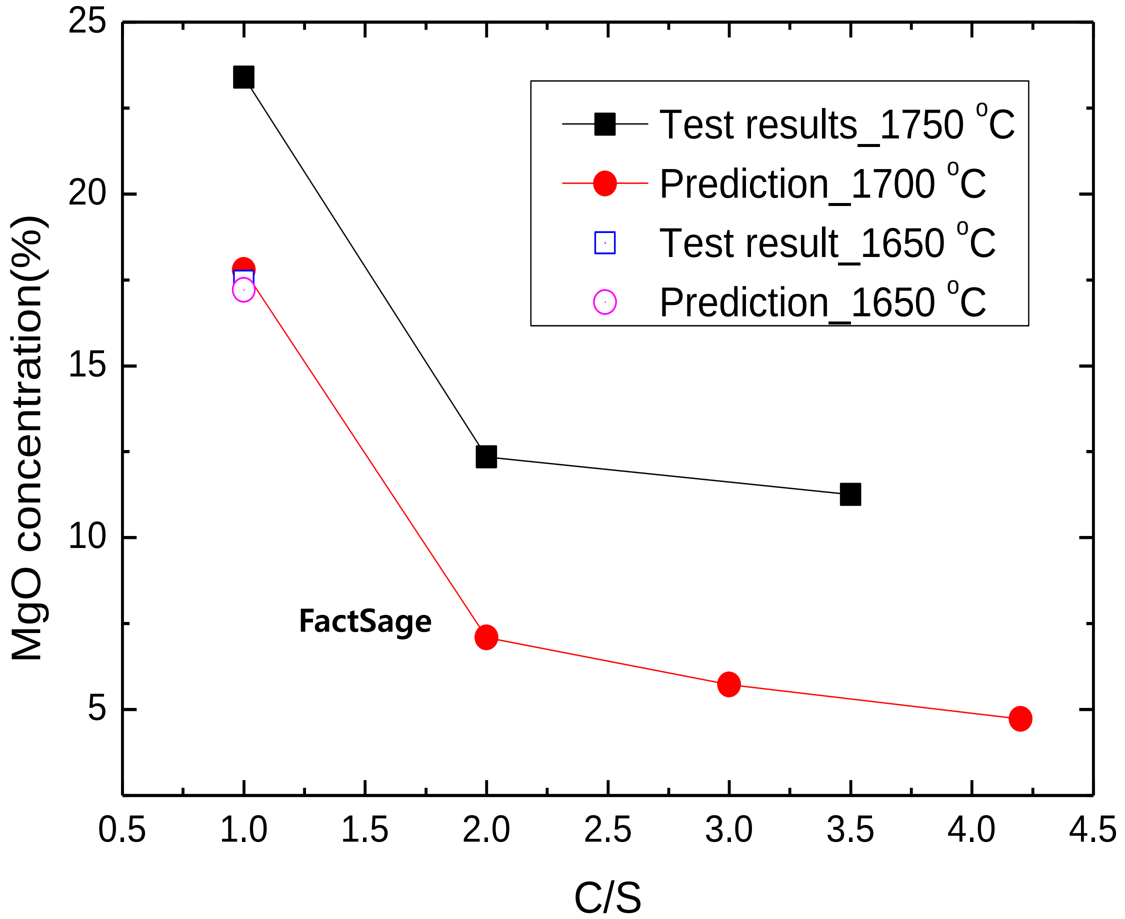
Refining slag for High Mn Steel

- Slag : MnO 20~50%, CaO-SiO2 system
- Refractory : MgO-C (C=18%)
- **Variants: Slag basicity, FeO/MnO content, and temperature**





Experimental MgO solubility vs. calculated results from FactSage



Development of a kinetic model for the RH process

Marie-Aline Van Ende and In-Ho Jung

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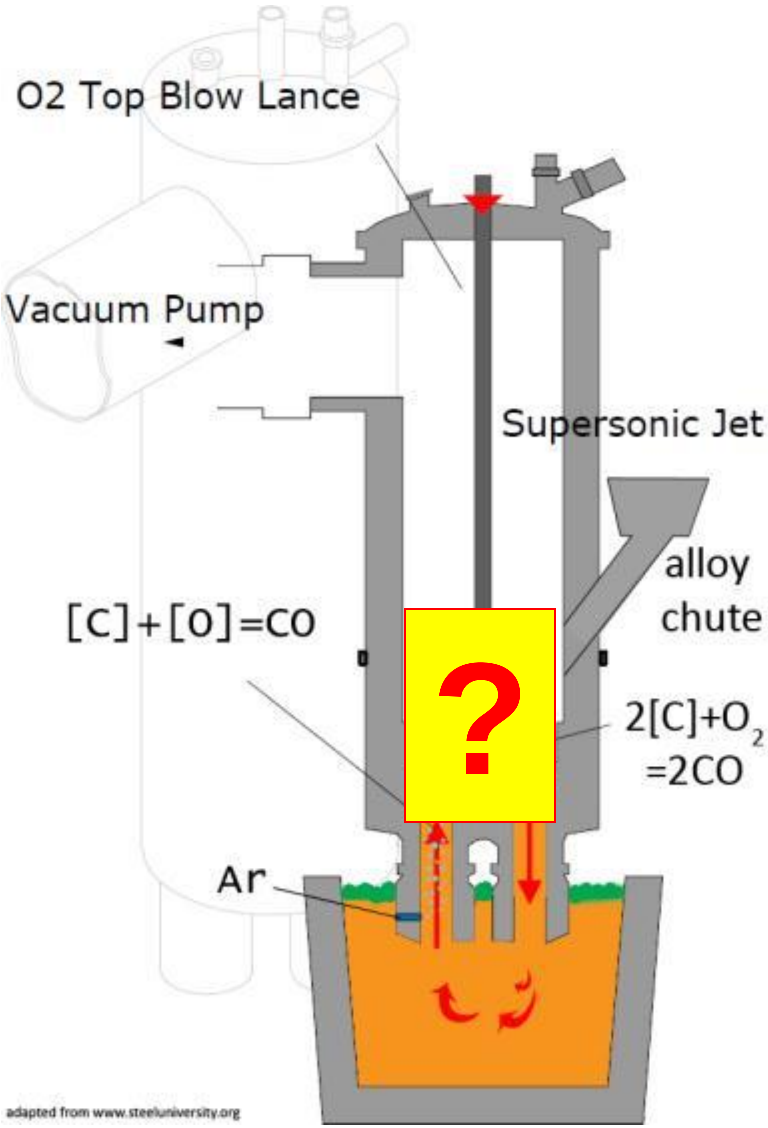
McGill University

Van Ende et al: ‘A Kinetic Model for the Ruhrstahl Heraeus (RH) Degassing Process’, Metall. Mater. Trans. B, 2011, p. 477

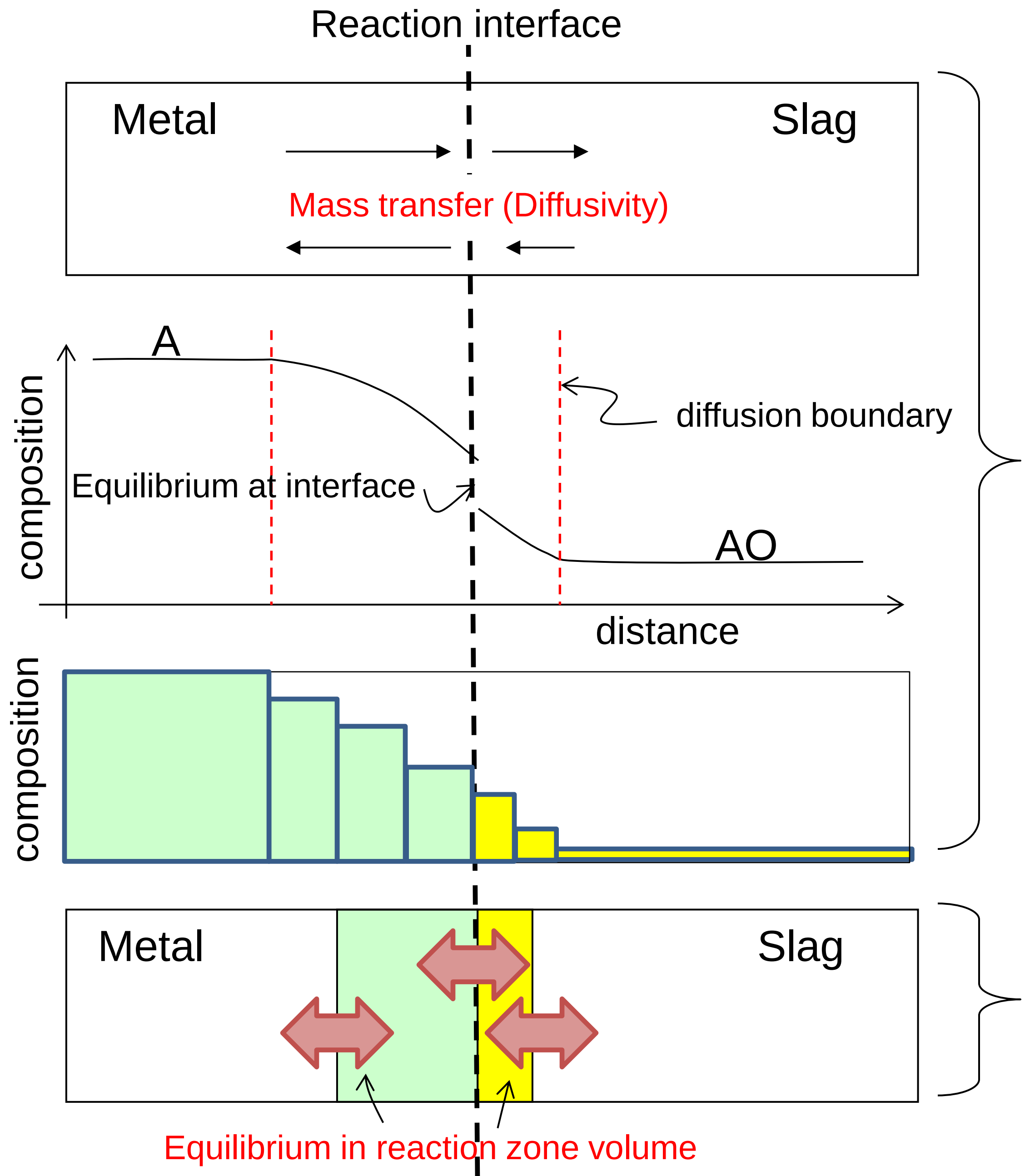
Operations in recirculation RH degasser

- Pair of snorkel lowered into liquid steel
- Vessel pressure lowered to ~1 torr
- Ar injected in one of the snorkel ⇒ steel up into the unit and out again through the other snorkel
- O_2 injected through a top lance
- Addition of alloys

http://www.aksteel.com/production_facilities/fac_pop_ash.html



Effective Equilibrium Reaction Zone model



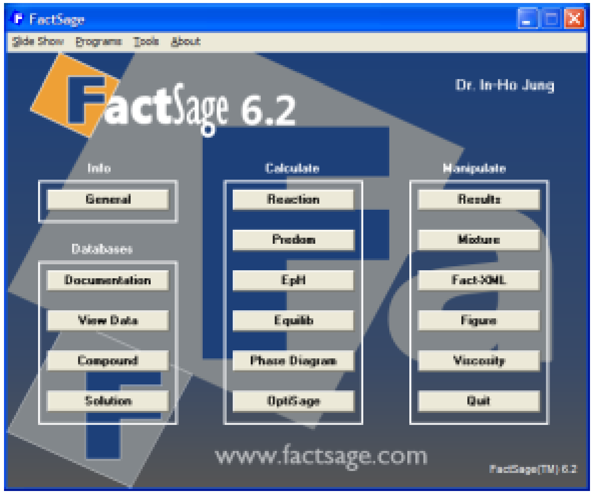
Real Process

- Very complex
- Difficult to find diffusivities
- Case by Case

Reaction Zone Model

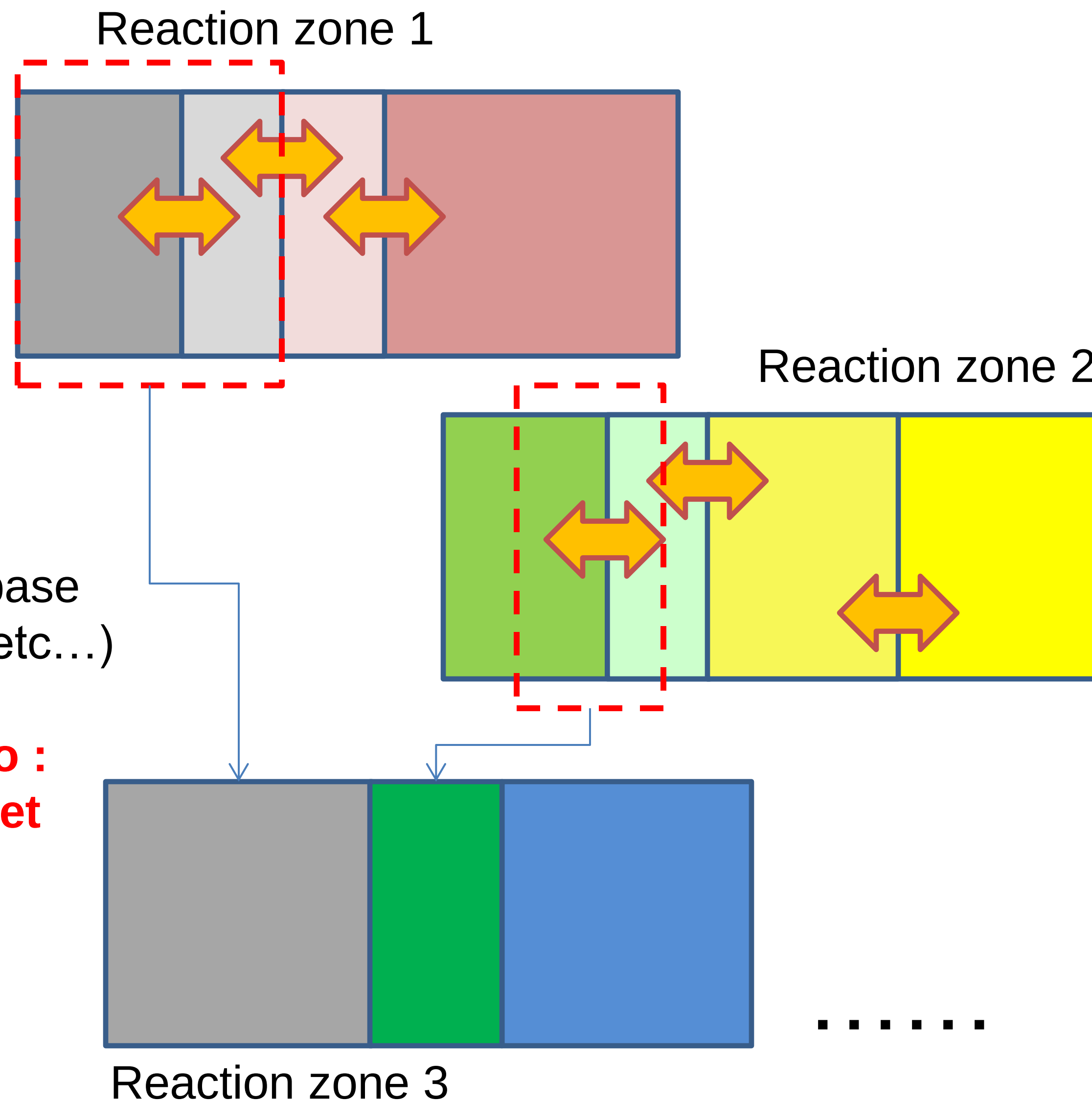
- Simple
- Easy to find by experiment

Concept for process simulation modeling



Quite enough thermodynamic database
(gas, molten steel, slag, refractory, etc…)

Write kinetic process using Macro :
input/output to Excel spread sheet



Heat & Mass balance !!

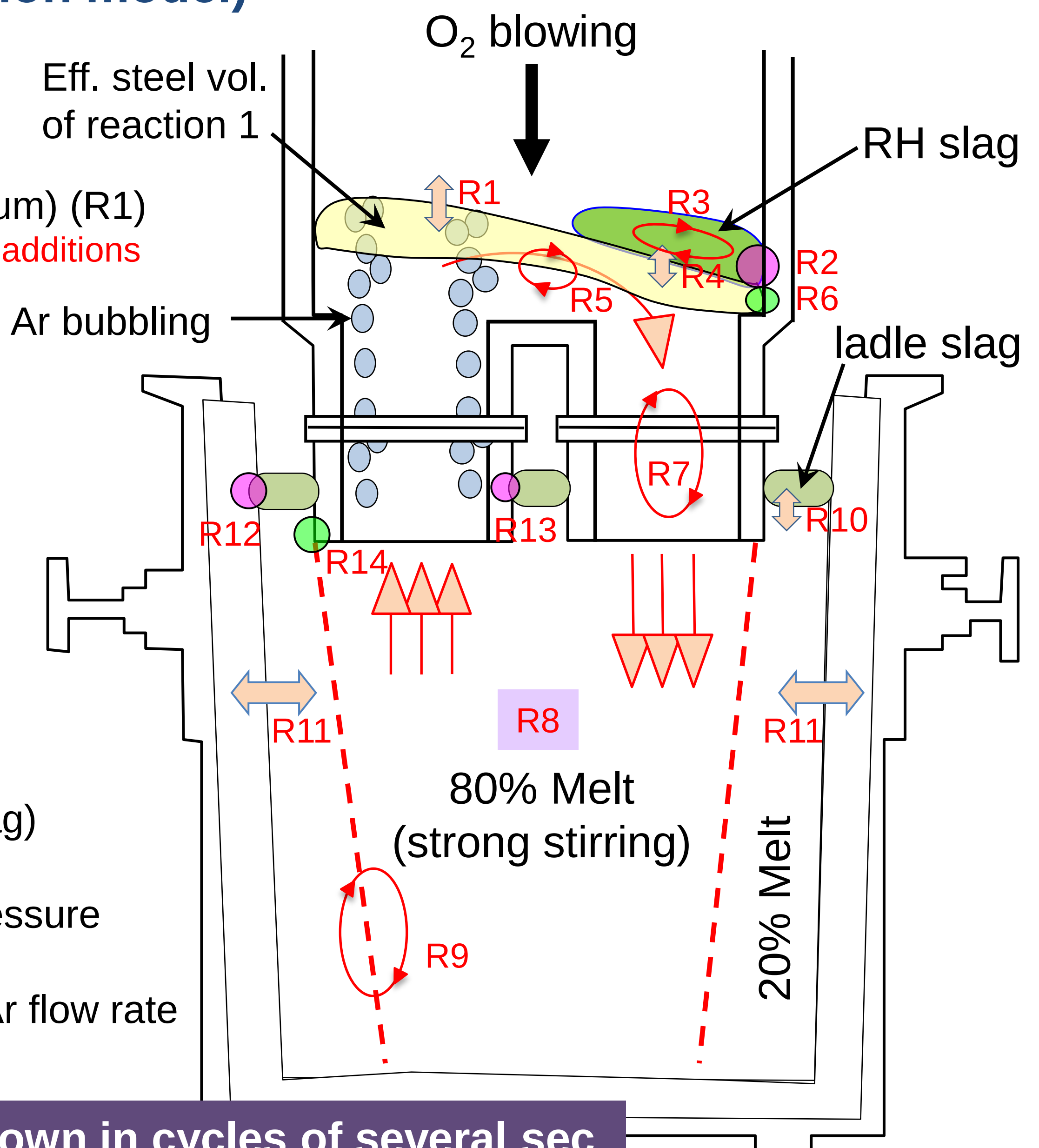
RH process model (3rd generation model)

9 reaction zones:

- RH steel + RH atmosphere (O_2 or vacuum) (R1)
  effective steel volume + X% O_2 + vacuum + additions
- RH slag + RH refractory (R2)
- RH slag mixing (R3)
- RH steel + RH slag (R4)
- First mixing in RH (R5)
- RH steel + RH refractory (R6)
- Second mixing in RH (R7)
- Mixing in ladle circulation zone (R8)
- Homogenization in ladle (R9)

Main assumptions:

- RH steel capacity: 21 ton
- Initial RH slag amount: 260 kg (ladle slag)
- Adiabatic heat condition (no heat loss)
- Limited steel exposure to RH vessel pressure
- RH refractory: pure $MgO.Cr_2O_3$
- RH circulation force dependent on the Ar flow rate and on the RH vessel pressure



⇒ The RH process is broken down in cycles of several sec

How to determine the reaction volumes?

Physical description of the reaction kinetics

↓

- Mathematical expressions (literature)
- Empirical relations (plant data, lab experiments, etc.)
- Fitting parameters

↓

Mathematical expressions of the effective reactions zone volumes as a function of the process conditions

FactSage Macro processing

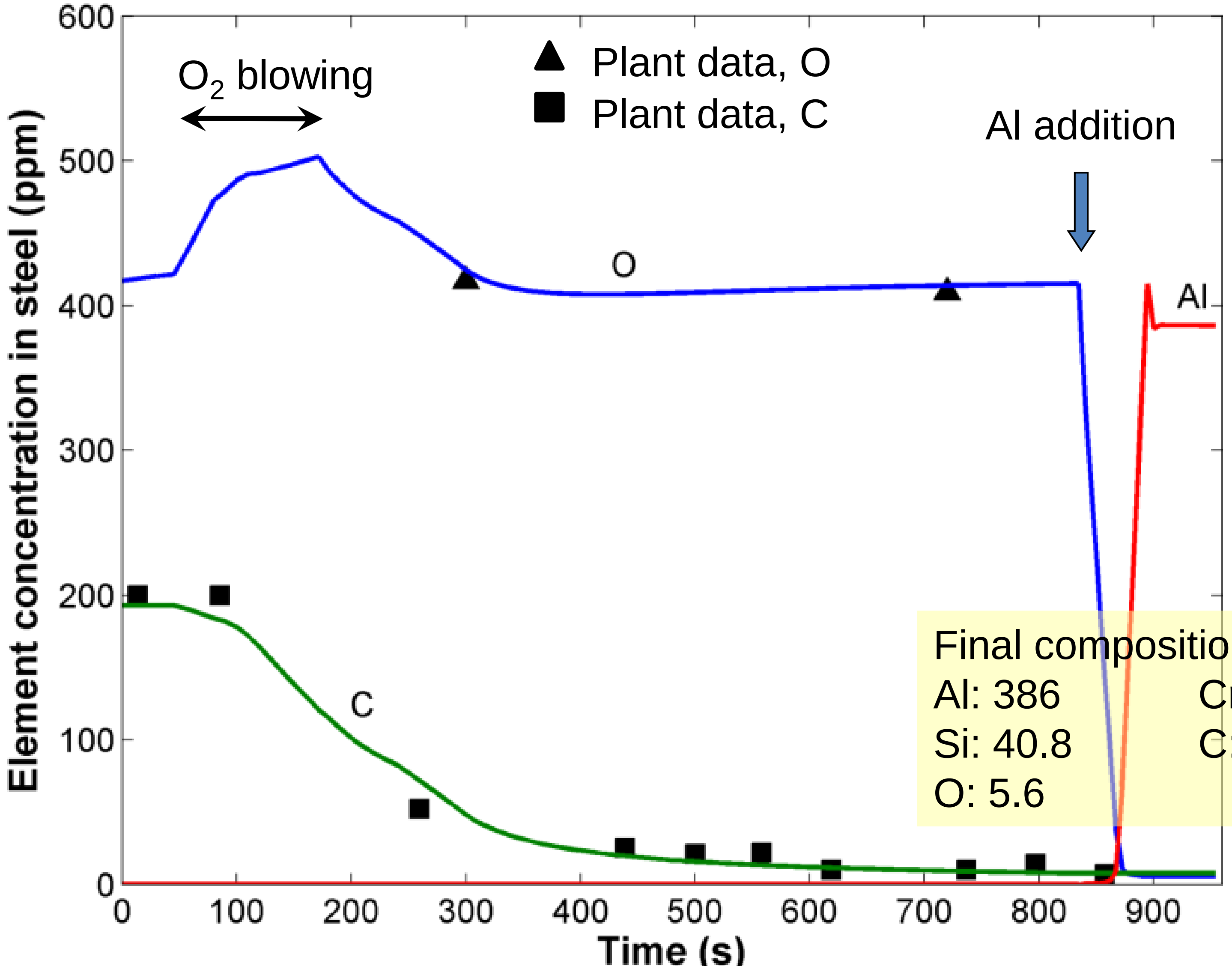
RH treatment duration: ~25 min ⇒ ~300 cycles * 9 reactions

~ **2700 Equilib runs!**

Macro processing is a powerful tool to deal with such complex process

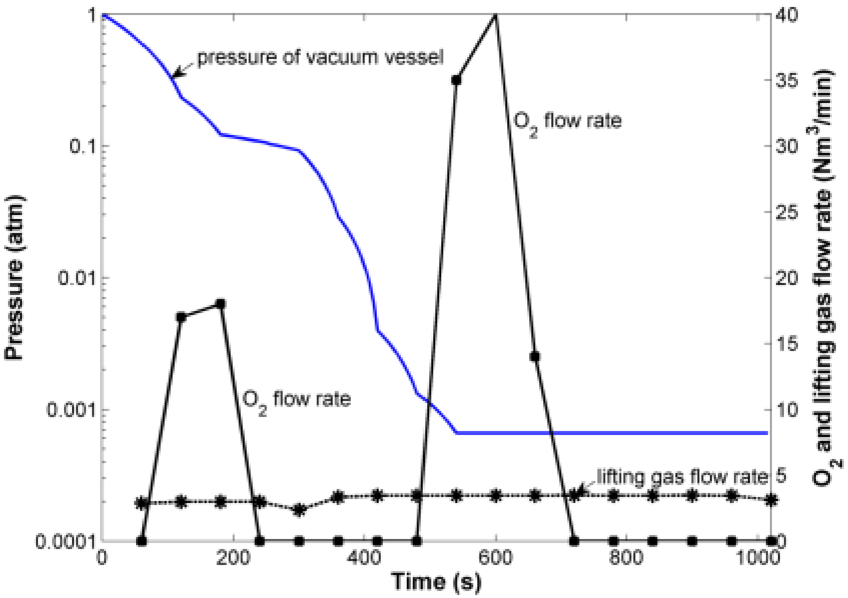
- Run Equilib files for each reaction automatically
- Handle all streams between each cycle
- Read the input and store the results in Excel spreadsheets

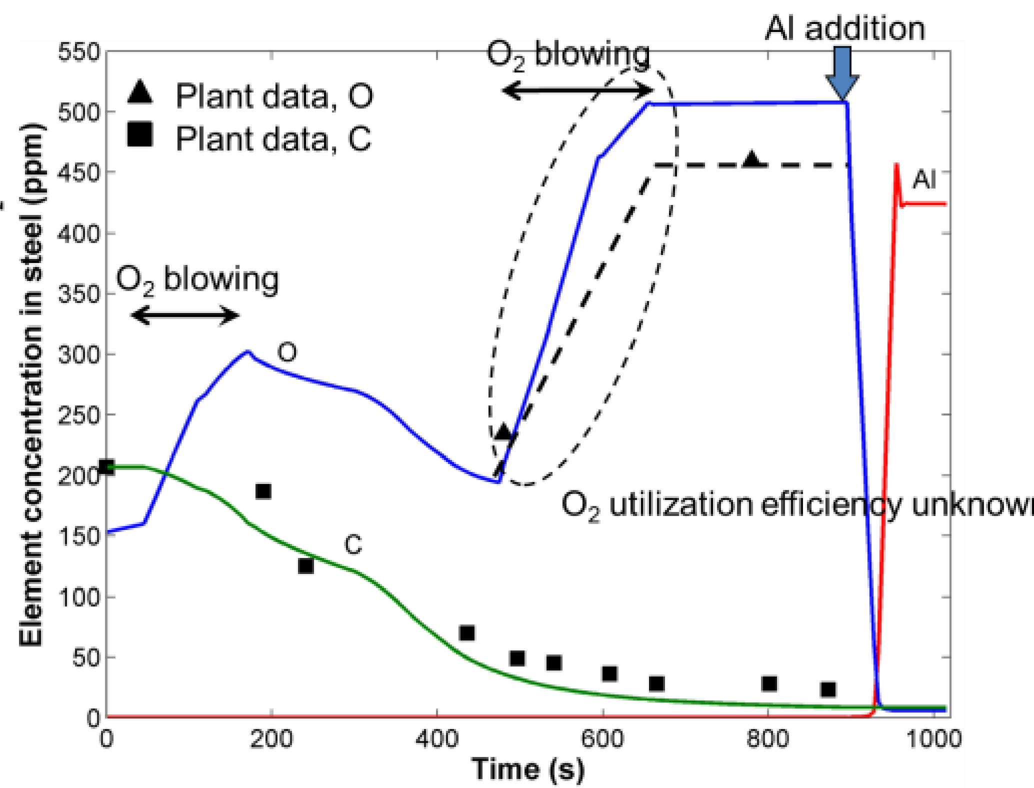
Evolution of ladle steel composition



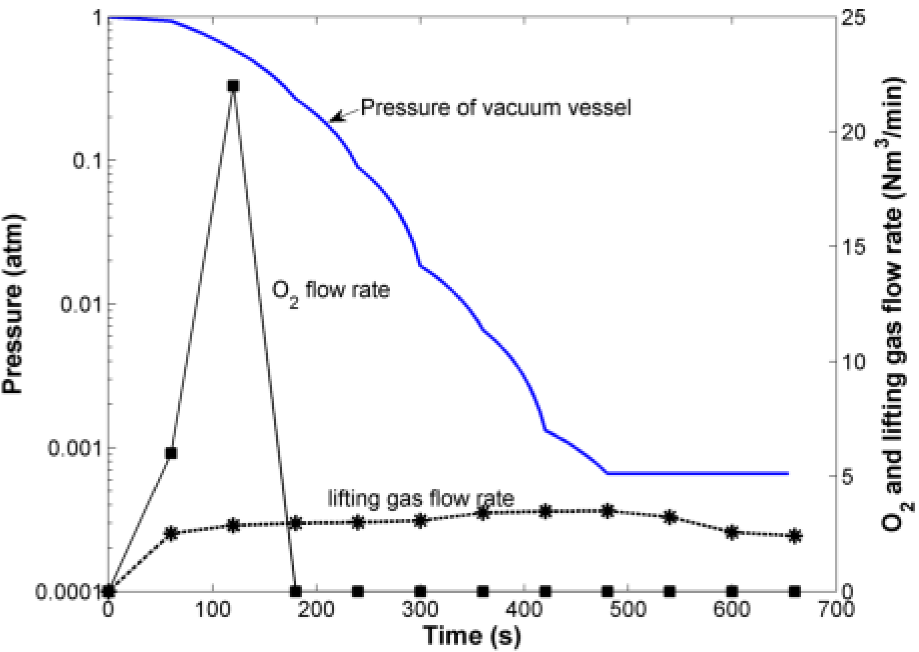
Final composition (ppm):
Al: 386
Cr: 98.9
Si: 40.8
C: 7.8
O: 5.6

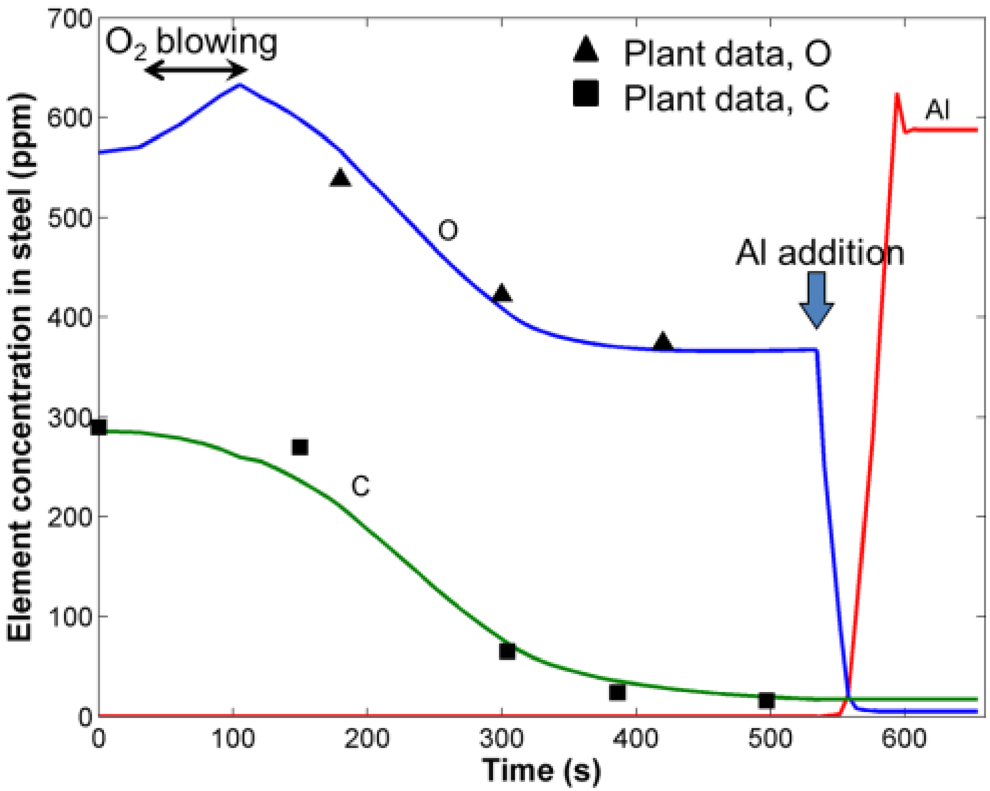
Application to extreme process conditions
Case 1: low O content



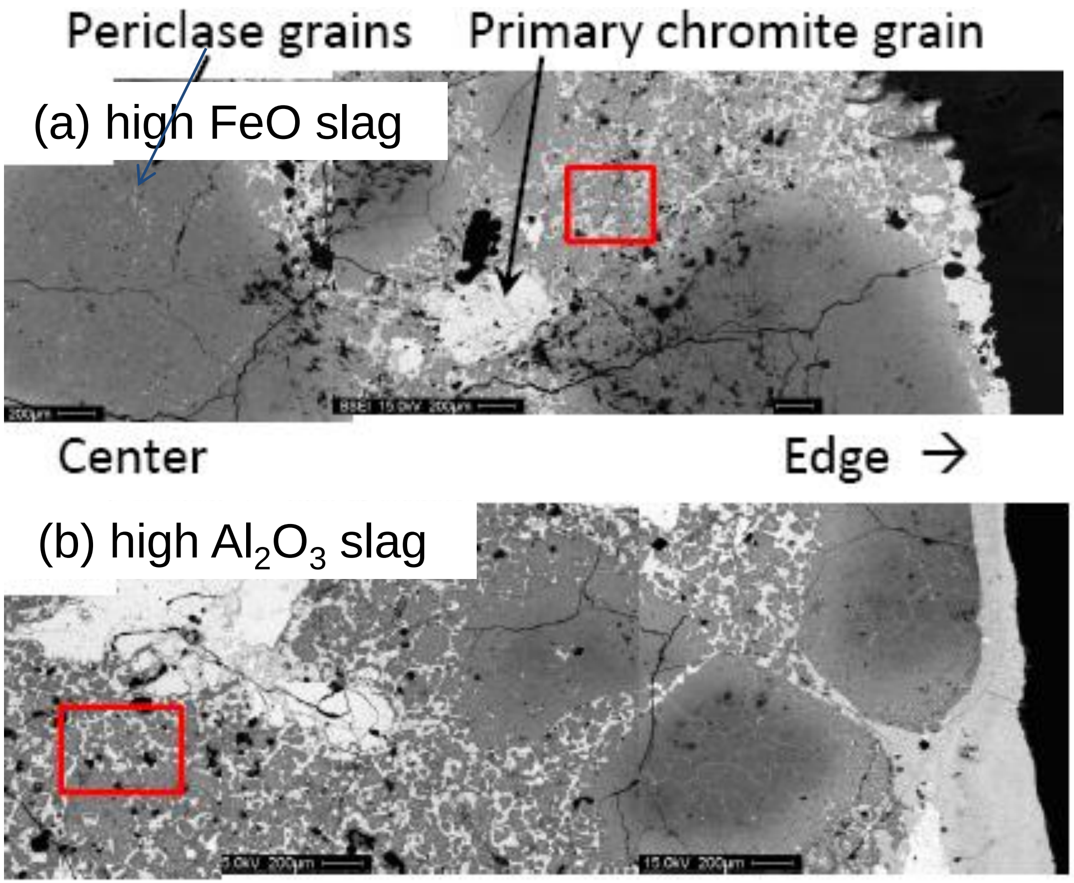


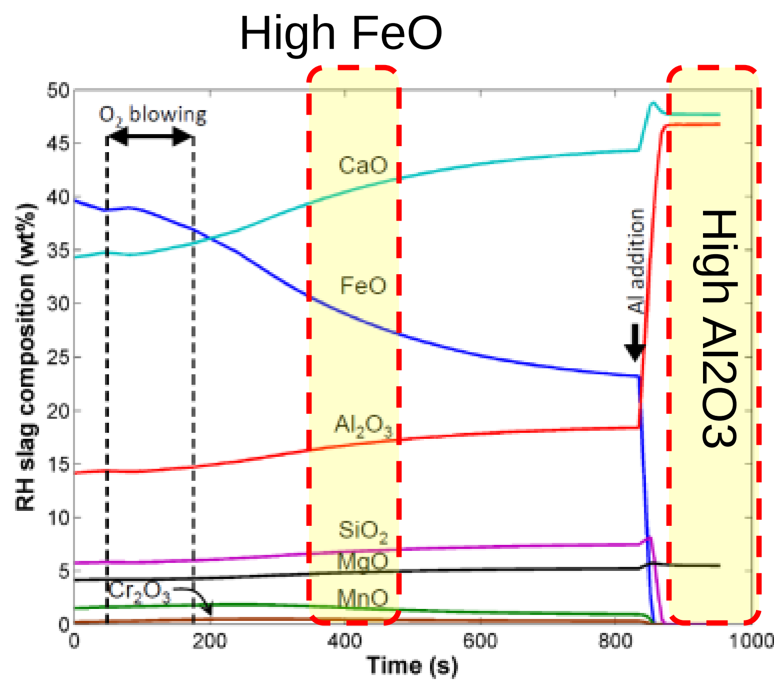
Application to extreme process conditions
Case 2: high O content





Corrosion of RH Vessel Refractory by RH slag



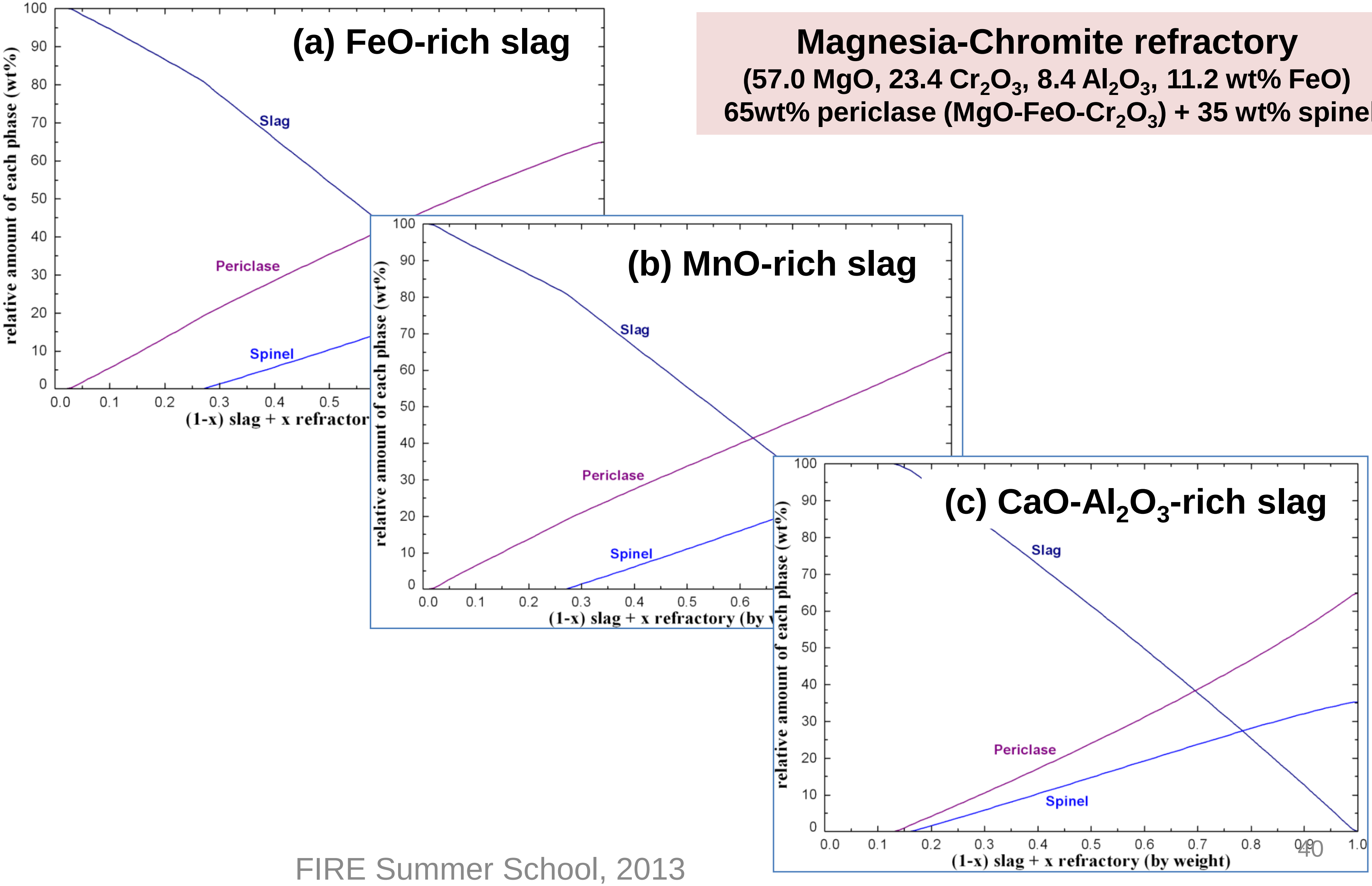


SEM-BSE images of magnesia-chromite refractories reacted with (a) high FeO slag and (b) high Al_2O_3 slag for 10 mins at 1600°C

→ Refractory with 1.5 cm is completely infiltrated by slag

→ Spinel grains were almost completely dissolved

Corrosion of RH Vessel Refractory by RH slags



Magnesia-Chromite refractory
(57.0 MgO, 23.4 Cr_2O_3, 8.4 Al_2O_3, 11.2 wt% FeO)
65wt% periclase (MgO-FeO-Cr_2O_3) + 35 wt% spinel