



# VOD Process Simulation

(**V**acuum **O**xxygen **D**ecarburization)

MIME 572

Computational Thermodynamics



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# 1. Basic concept of VOD

- 1) Main purpose
- 2) Process
- 3) Importance

## 1-1 Main Purpose

### Achieve

Extremely low carbon content in a molten steel  
(mostly less than 0.04 wt%, ultra low less than 0.005 wt%)

Lower amount of undesired elements (such as nitrogen,  
oxygen, etc)

Demanded composition of desired element (such as  
Chromium)

### Focus

Low Carbon and Nitrogen content at the same time (<80ppm)

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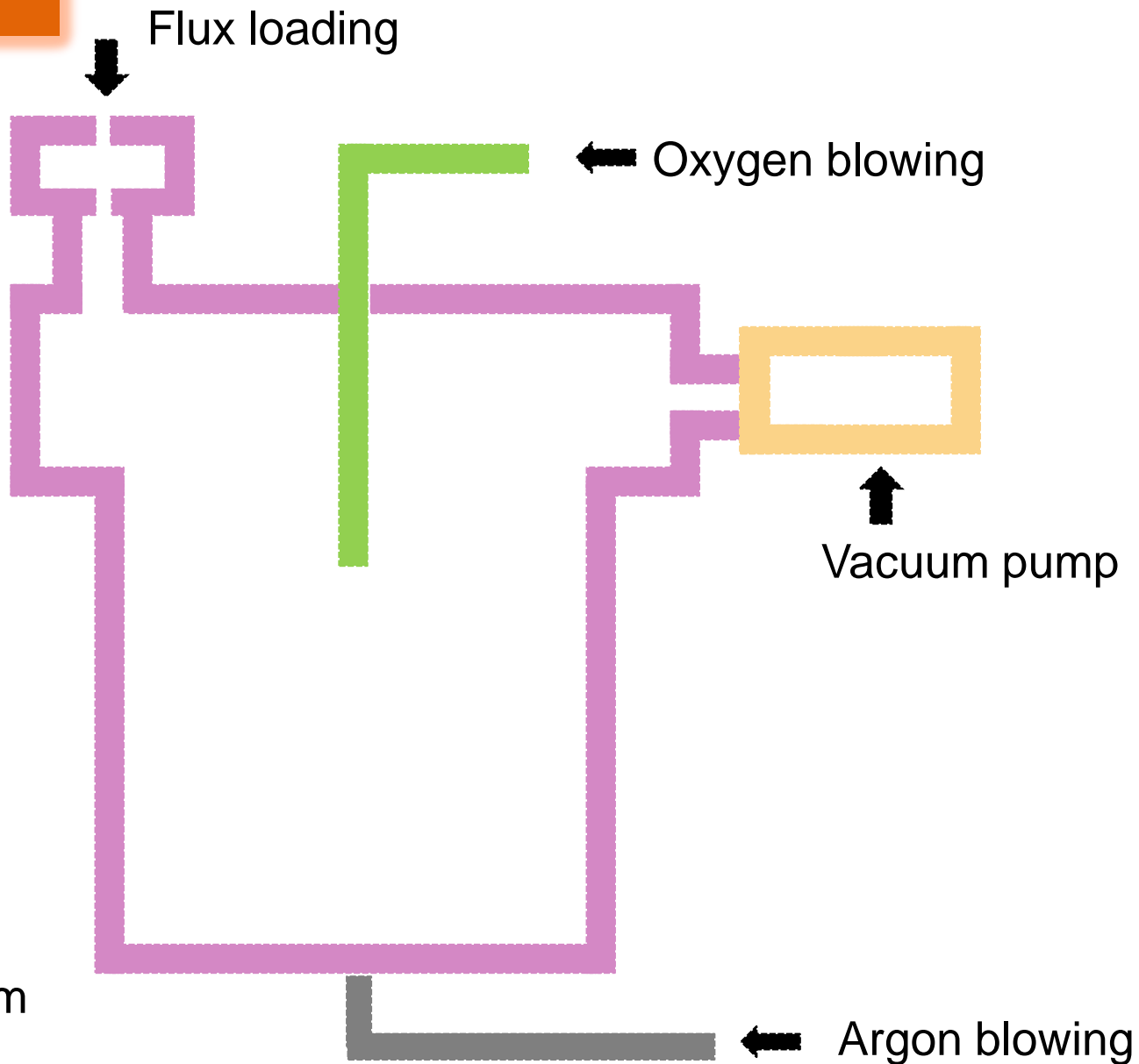
→ Improving Mechanical Property

Chromium content as 18 wt%

Three stages of VOD process

- 1) Oxygen blowing stage
- 2) Degassing stage
- 3) Reduction stage

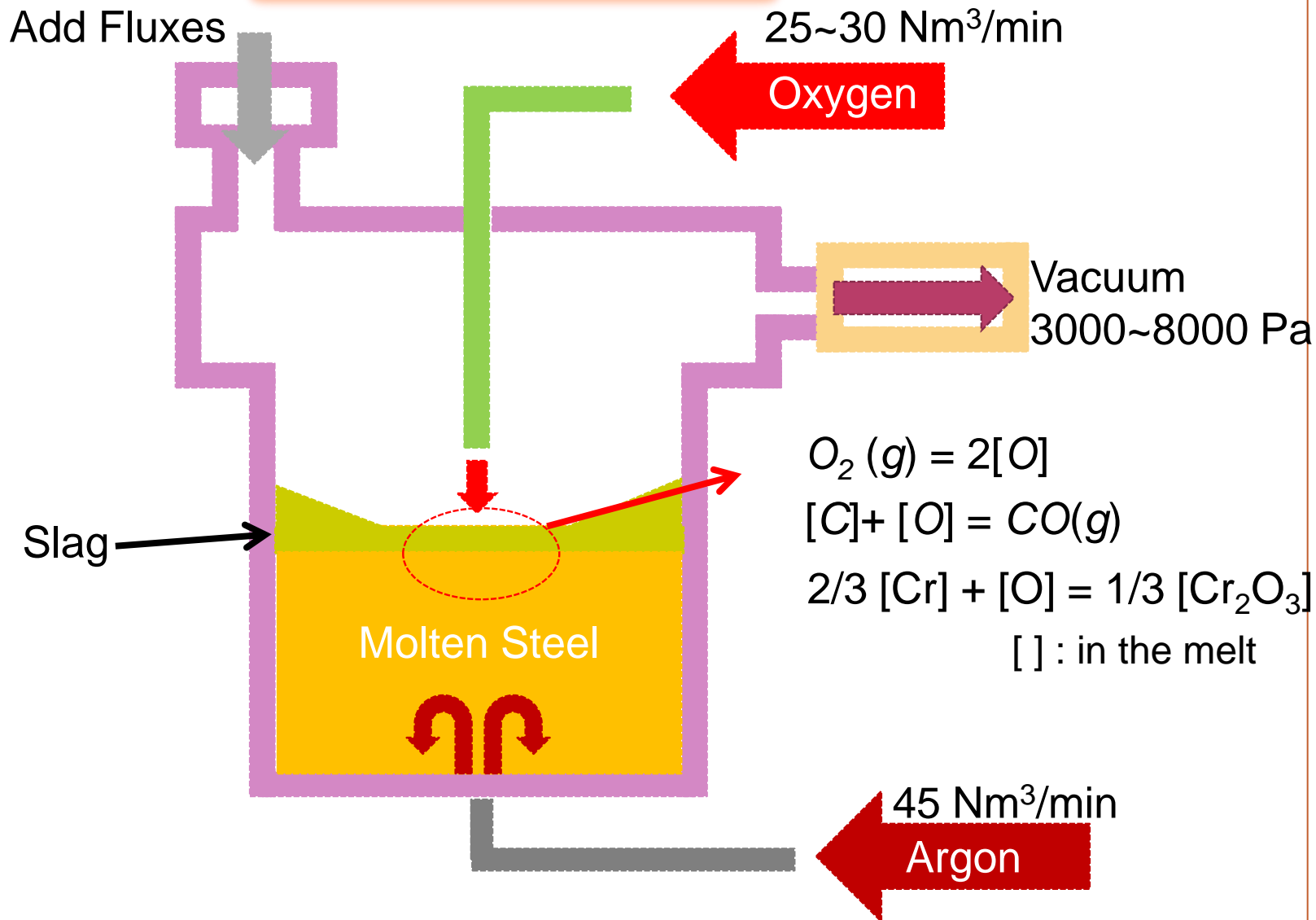
# 1-2 Process



Schematic diagram  
VOD vessel

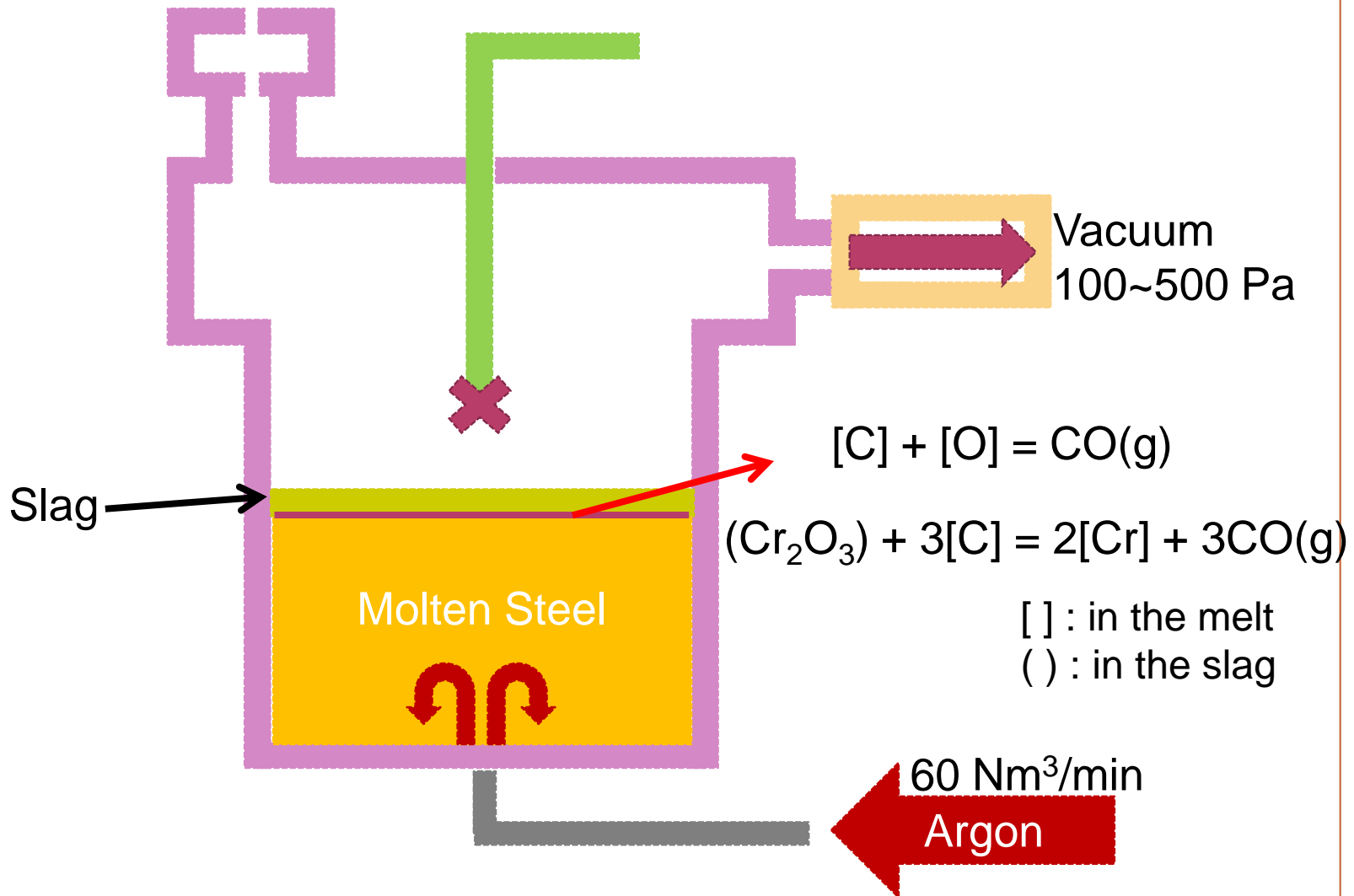
# 1-2 Process

## Oxygen Blowing stage



1-2 Process

Degassing stage



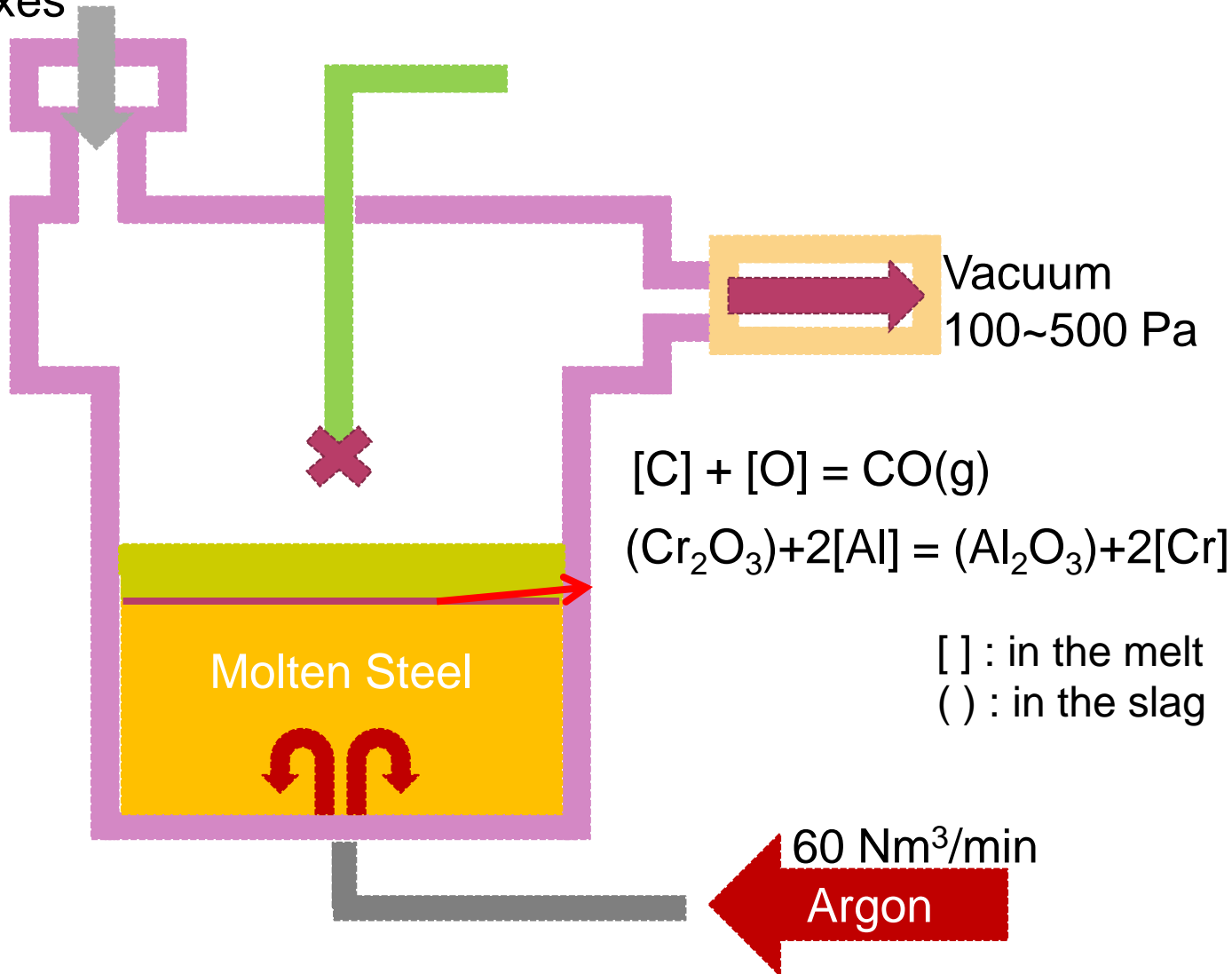
1. Basic concept of VOD



1-2 Process

Reduction stage

Add Fluxes



1. Basic concept of VOD

## 1-3 Importance

VOD process can achieve ultra low carbon and nitrogen content ([C]+[N] = 60~90 ppm)

Lower consumption for Argon and Silicon (60 to 90 ppm)

Stainless steel production grows steadily

High demand for ferritic stainless steel grades (e.g. AISI409, 439) which require lower carbon content

VOD process has not been understood well

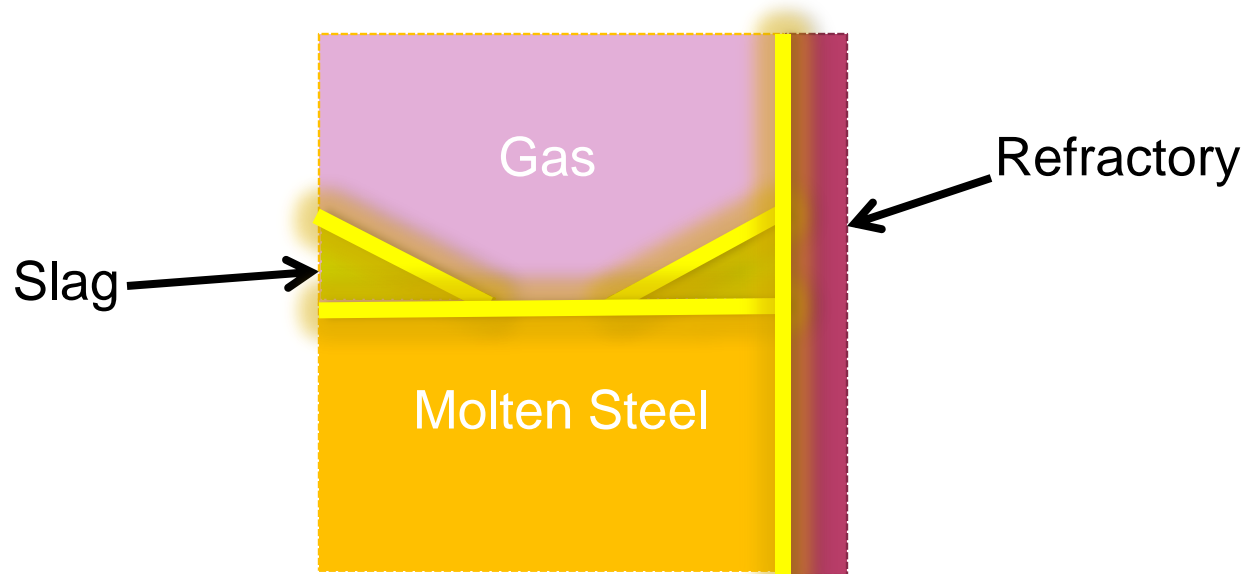
Because its complexity of reactions and harsh condition in vacuum

## 2. Simulation strategy

- 1) Parameters
- 2) Calculation plan
- 3) Understanding of relation  
Time, Temperature, Carbon content

## 2 – 1 Parameters

### Considering Reactions



Molten steel / Slag / Solid oxides / Gases / Refractories

## 2 – 2 Calculation Plan

Initial Composition (wt%) :

[C] 0.25 [Cr] 18 [N] 0.015 [O] 0.02 [Si] 0.21 [Mn] 0.6

Temperature (°C) : 1600

$\Delta T = 5$  min

Vessel = 120 ton of melt

Oxygen blowing = 30 Nm<sup>3</sup> / min

Data from **Bao Steel, ALZ** (Stainless steel making companies)

### Purpose

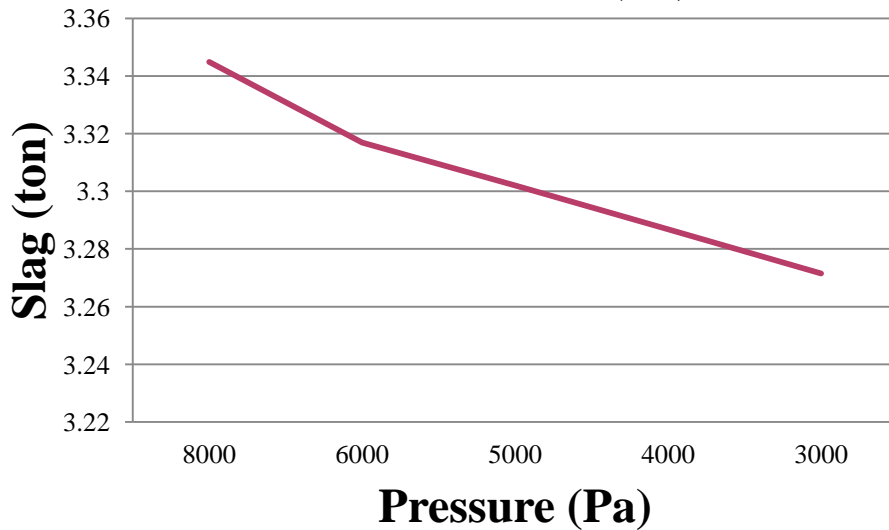
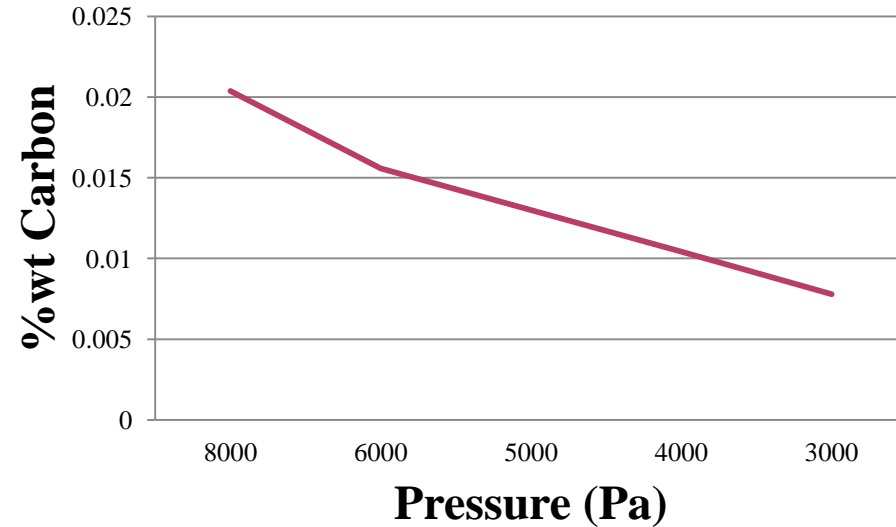
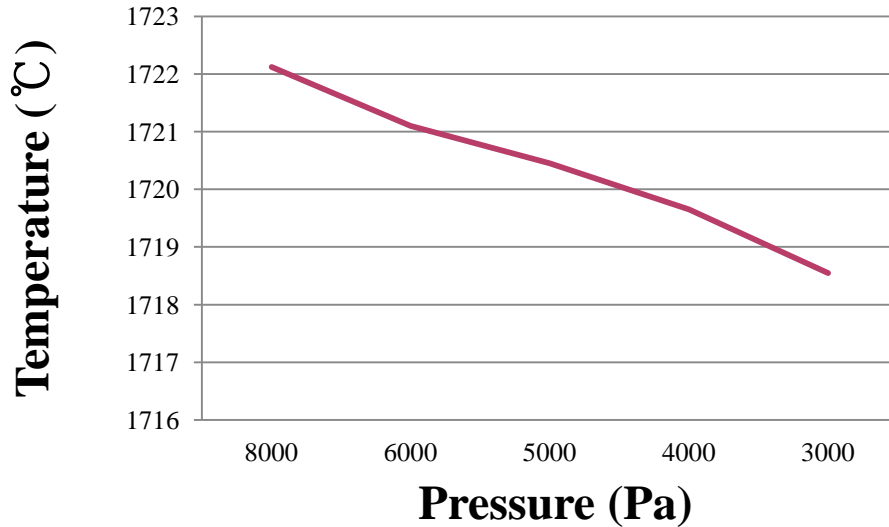
Find



1. Suitable Reacted oxygen amount with melt
2. Slag amount
3. Vacuum condition
4. Flux amount

## 2 – 3 Understanding of relation among Time, Temperature, Carbon content

### Fixed Reacted oxygen, Fluxes



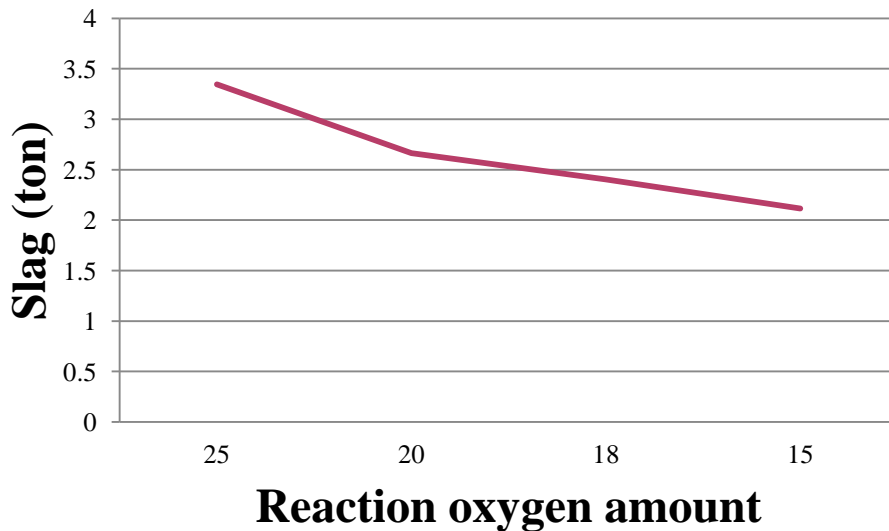
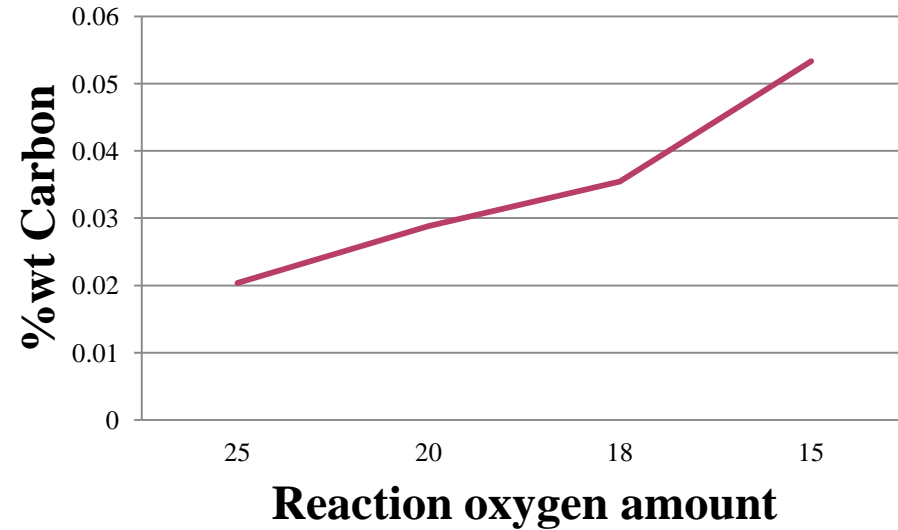
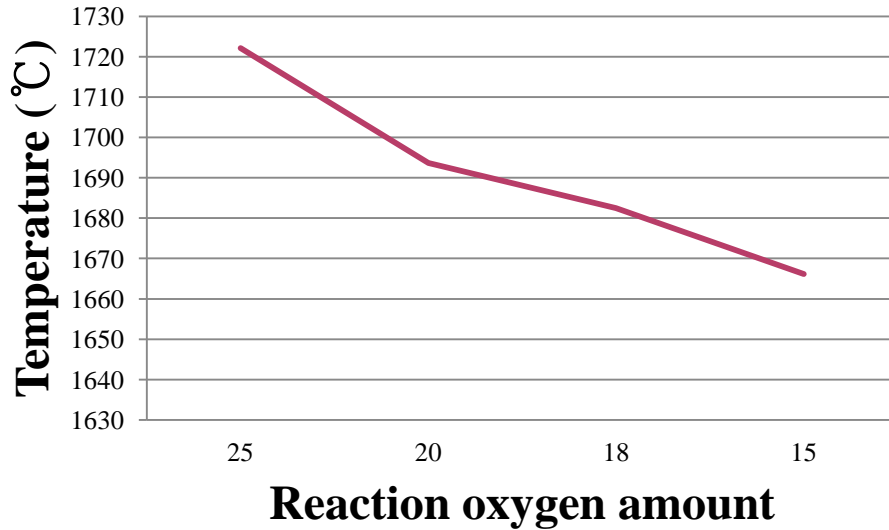
Pressure ↘ = Final Temperature ↘

Pressure ↘ = wt% Carbon ↘

Pressure ↘ = Slag amount ↘

## 2 – 3 Understanding of relation among Time, Temperature, Carbon content

### Fixed Vacuum, Fluxes



Oxygen ↓ = Final Temperature ↓

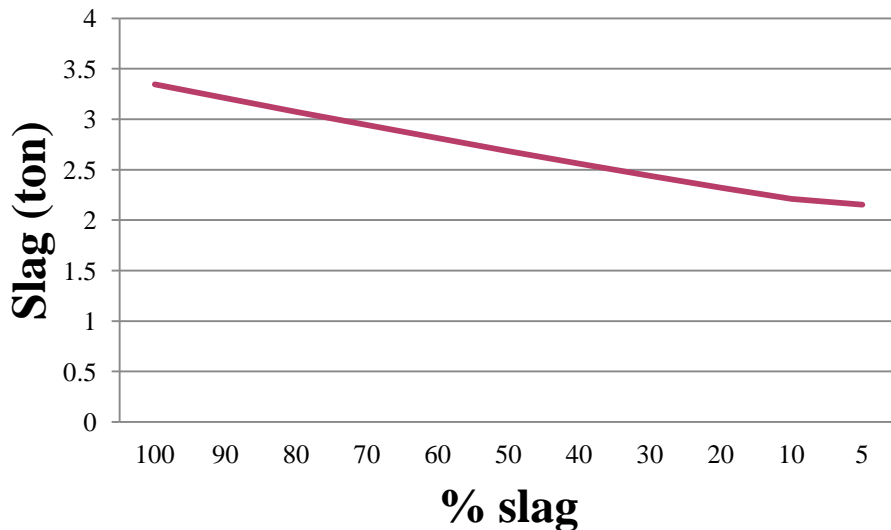
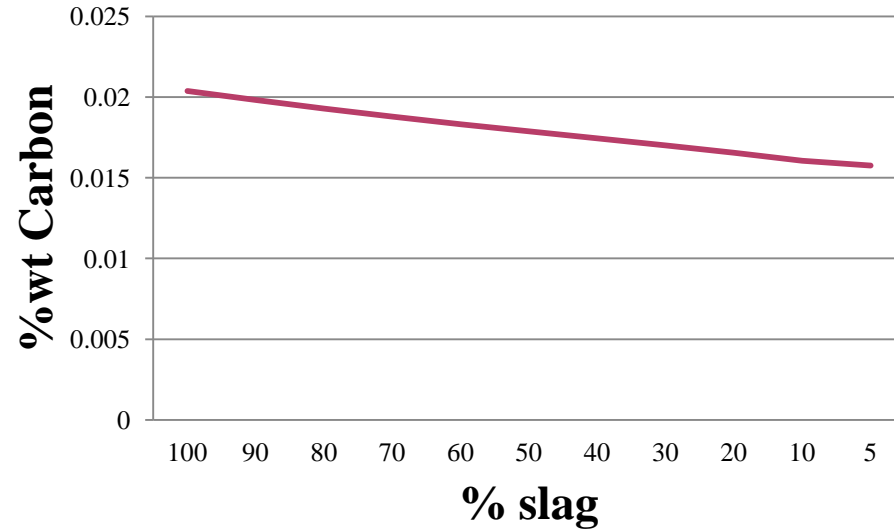
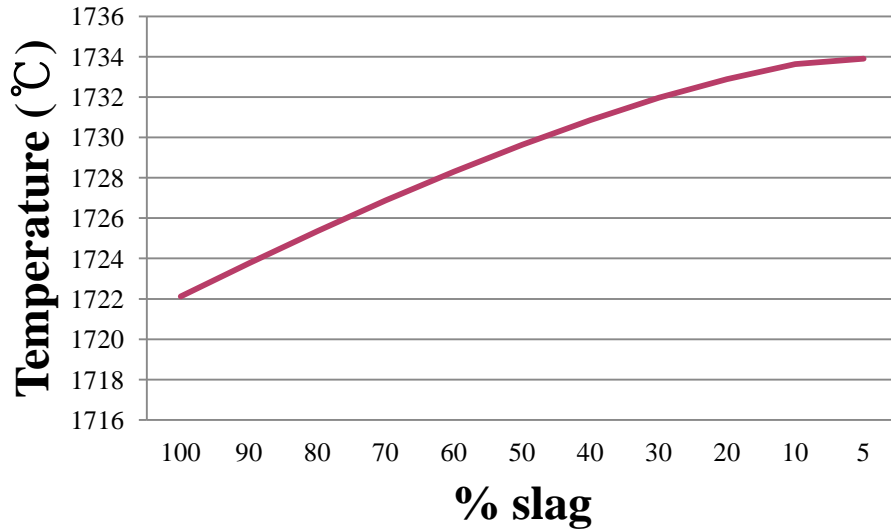
Oxygen ↓ = wt% Carbon ↑

Oxygen ↓ = Slag amount ↓



## 2 – 3 Understanding of relation among Time, Temperature, Carbon content

### Fixed Vacuum, Reacted oxygen



Slag ↓ = Final Temperature ↗

Slag ↓ = wt% Carbon ↓

Slag ↓ = Slag amount ↓

### 3. Preliminary calculation

- 1) Condition
- 2) Result & Modification

For Oxygen blowing stage

Reacted oxygen amount = 25 Nm<sup>3</sup>/min (83%)

Vacuum condition = 0.078 atm (8000Pa)

Fluxes = FeSi (76% Si)

Dolomitic lime (38%MgO, 58% CaO)

# 3 – 1 Condition

**F Reactants - Equilib**

File Edit Table Units Data S

1 - 6

**Mass(g)**

100%

+ 0.0984

+ 0.3116

+ 0.418

+ 0.638

+ <A>

**F Menu - Equilib: last system**

File Units Parameters Help

T(C) P(atm) Energy(J) Mass(g) Vol(litre)

**Reactants [6]**

(gram) 100% [O\_initial\_melt] + 0.0984 Fe + 0.3116 Si + 0.418 MgO +

(1600C,#1) (25C\_s1-FACT53 #2) (25C\_s-FACT53 #2) (25C\_s-FACT53,#2) [25

**Products**

Compound species

\*  gas  ideal  real

aqueous

pure liquids

\*  pure solids

suppress duplicates

\* - custom selection species:

Target

- none -

Estimate T(C): 1000

Mass(g): 0

	+	FTmisc-FeLQ	Fe-liq
		FToxid-SLAGA	ASlag-liq
	+	FToxid-SPINA	ASpinel
		FToxid-MeO_?	?Monoxide
	+	FToxid-bC2S	a'Ca2SiO4
	+	FToxid-aC2S	a-Ca2SiO4
	+	FToxid-OlivA	AOlivine
	+	FToxid-CORU	M2O3(Corundum)
	+	FToxid-CaSp	CaSpinel
	+	FToxid-Rhod	Rhodonite

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.0357129		1650	0.078	

30 steps

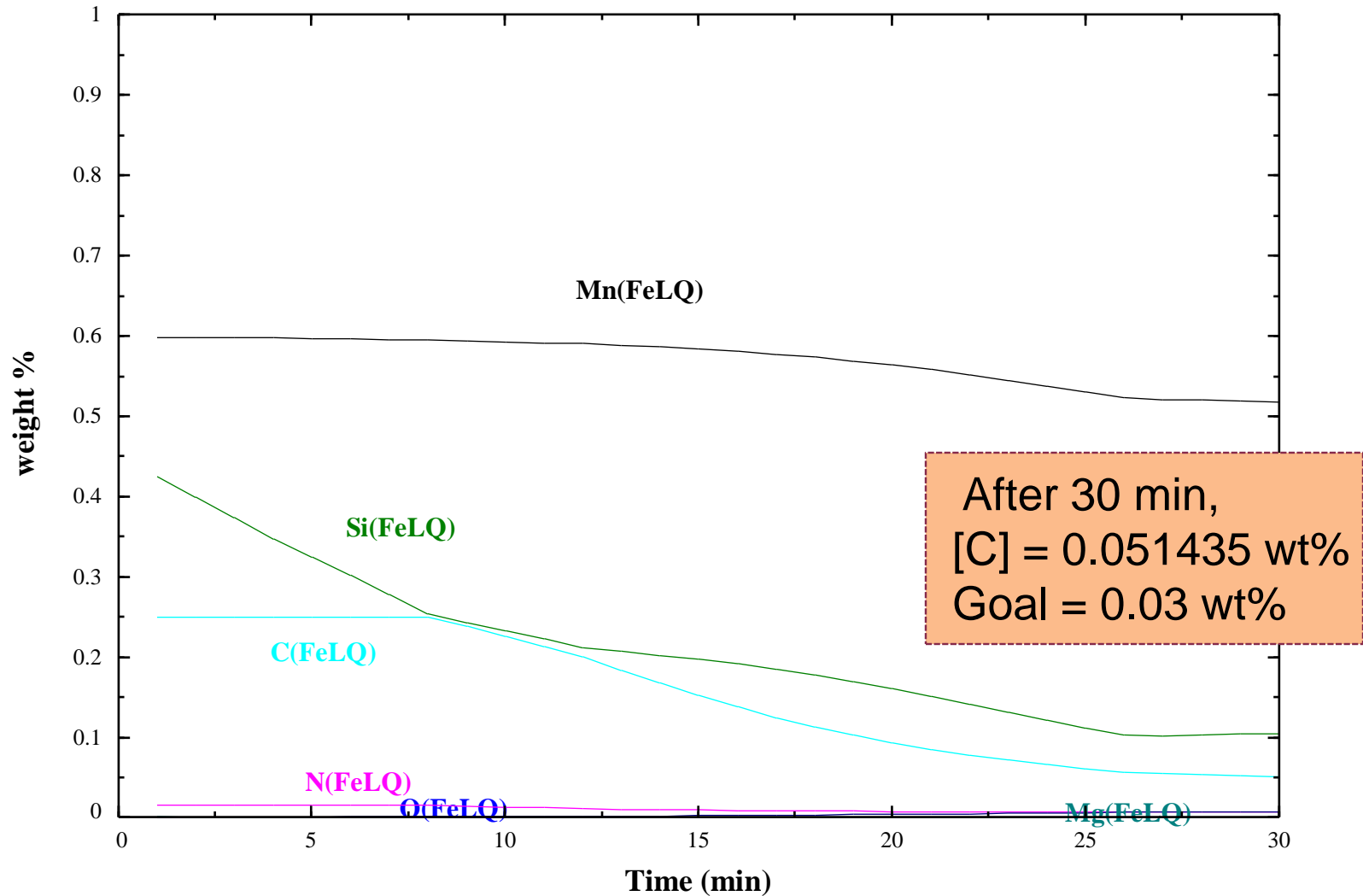
Table

30 calculation

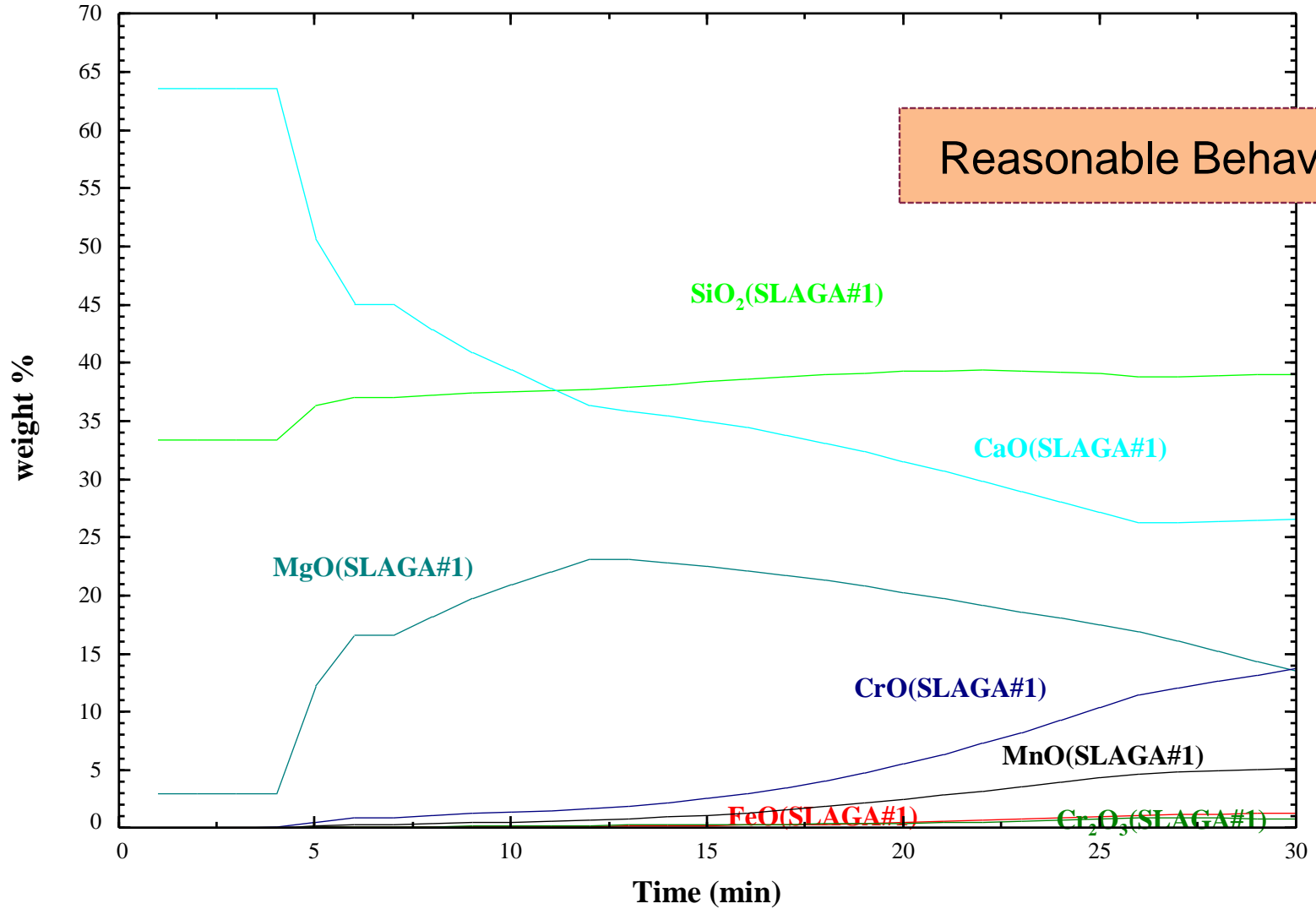
open  
 te >>

## 3 – 2 Result & Modification

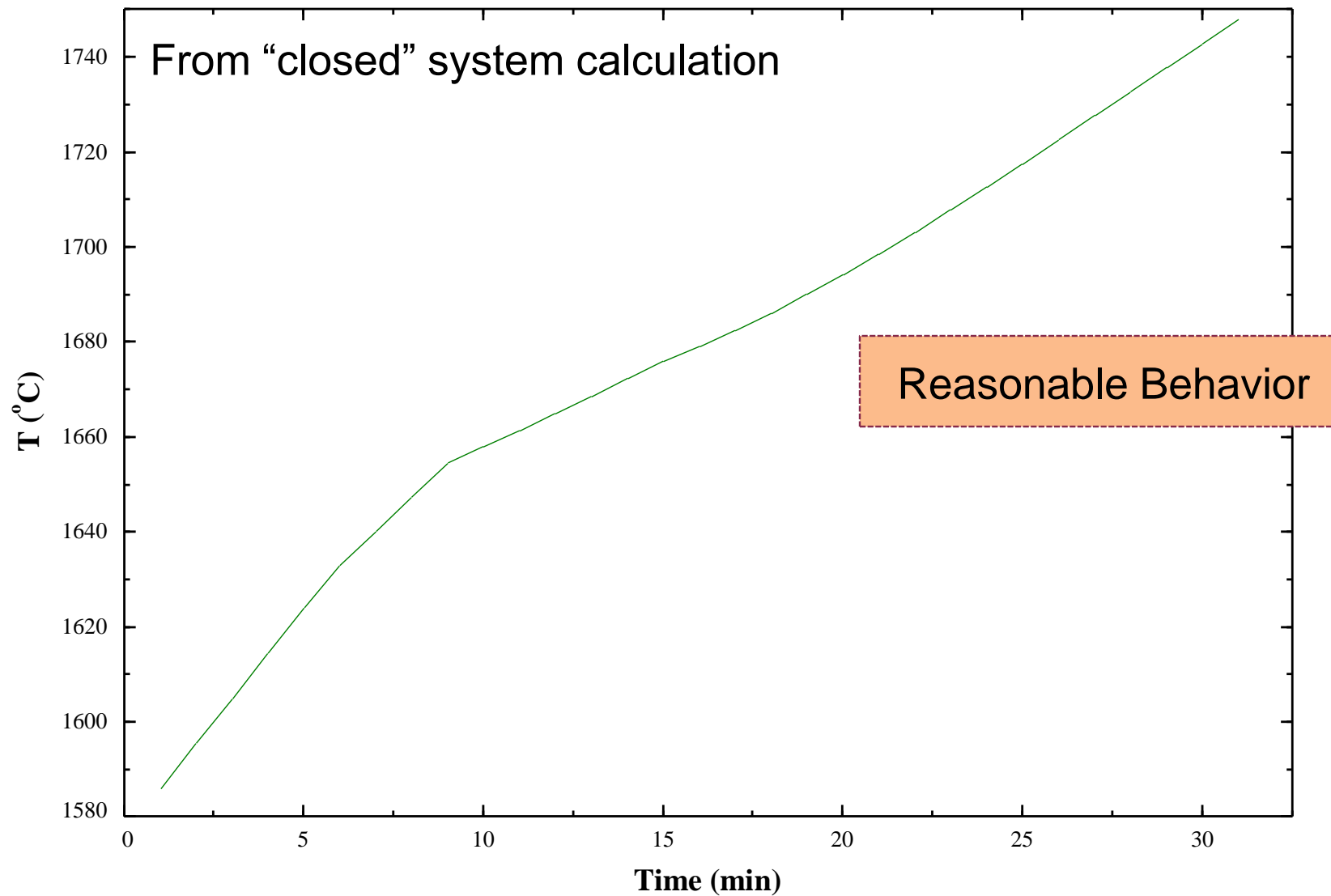
### [C], [N], [O], [Si], [Mn], [Mg] in the melt



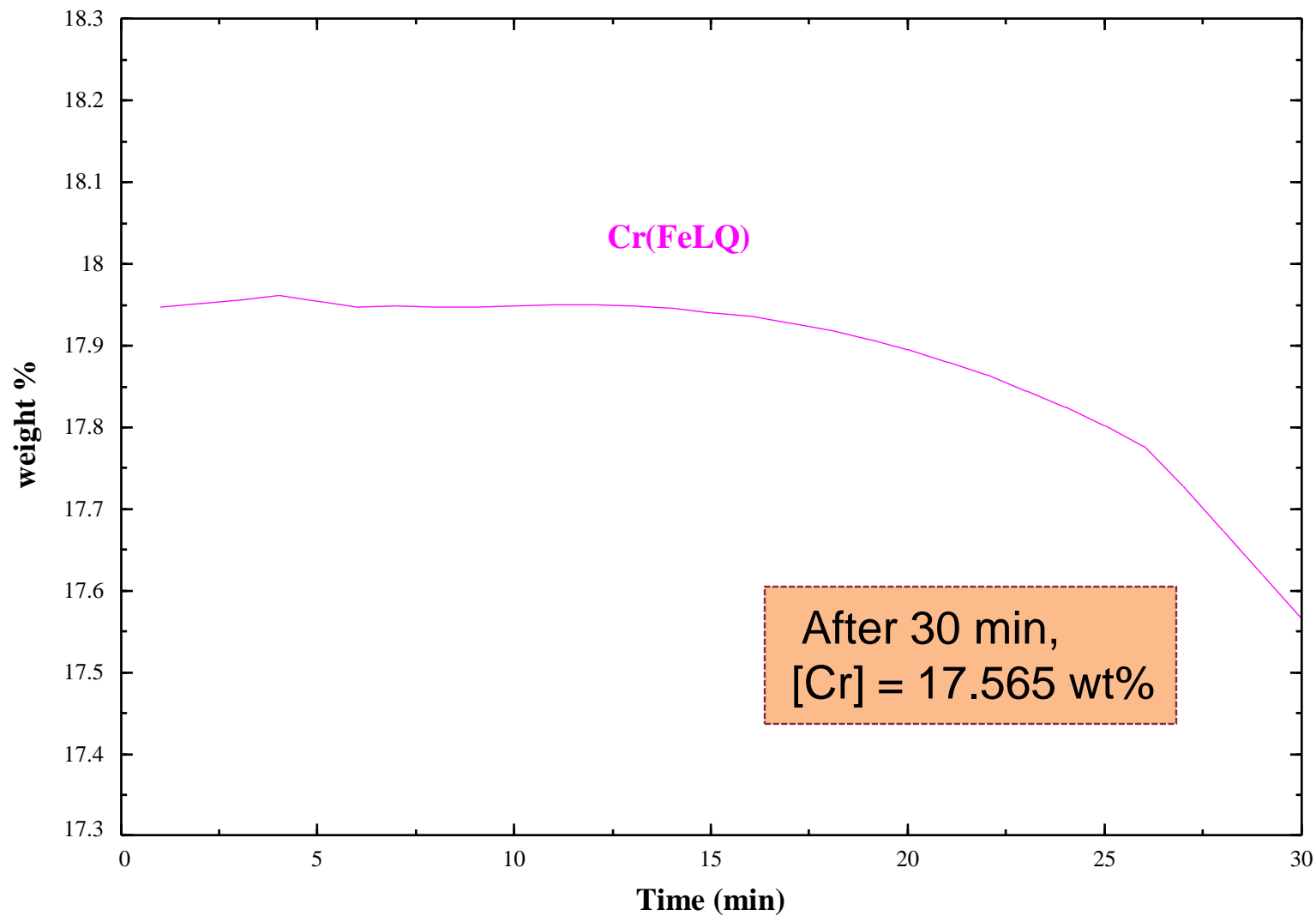
# Slag Composition



# Temperature

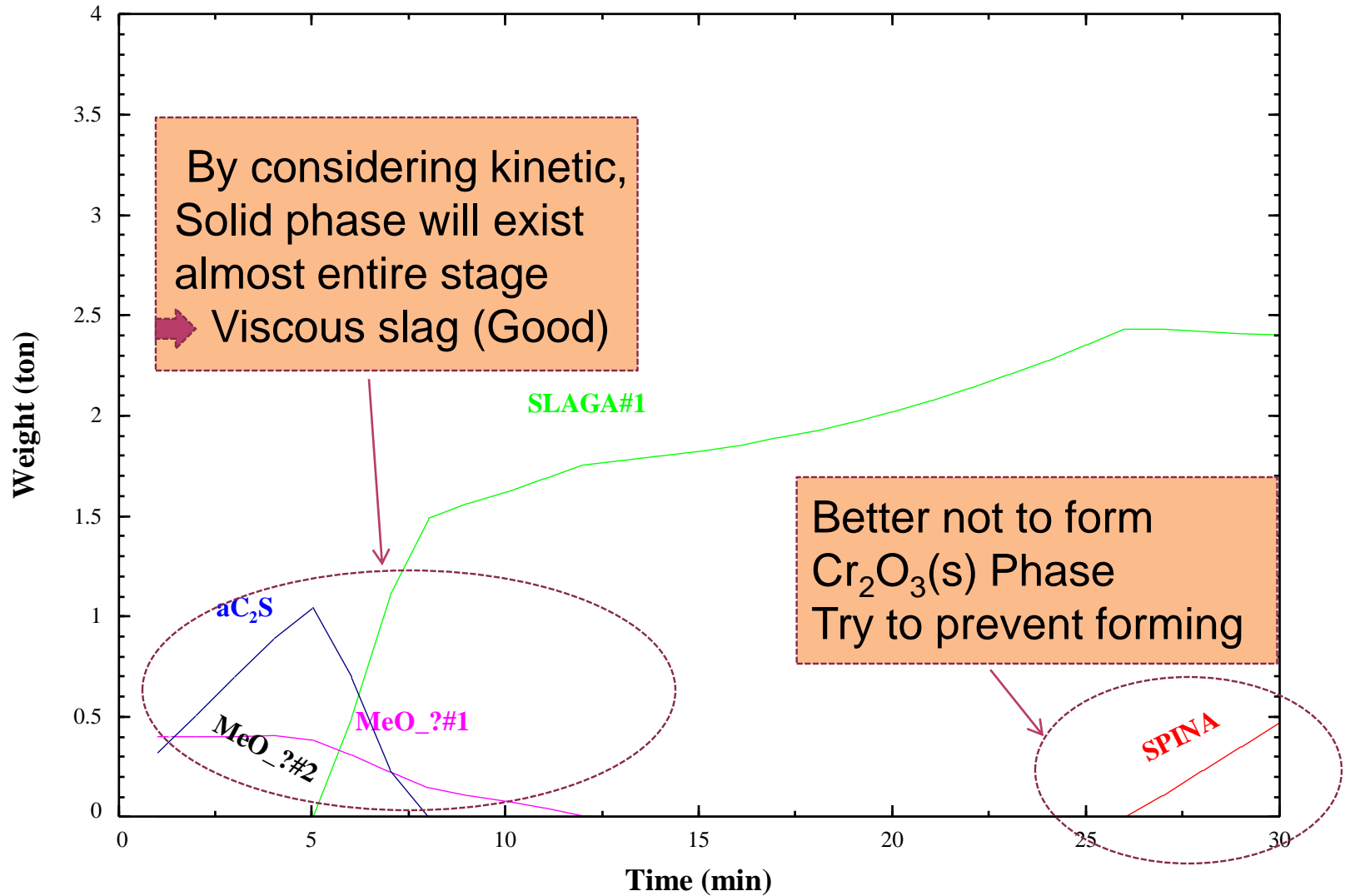


### Chromium content in the melt





# Solid phases



## 3 – 2 Result & Modification

From Previous calculations (section 2)  
and  
industrial data from Baosteel (09Xu)

More time for this stage (> 30min)

Reduce oxygen blowing to minimize  
 $\text{Cr}_2\text{O}_3(\text{s})$  phase (Between 26 – 27 min  
 $\text{Cr}_2\text{O}_3(\text{s})$  formed)

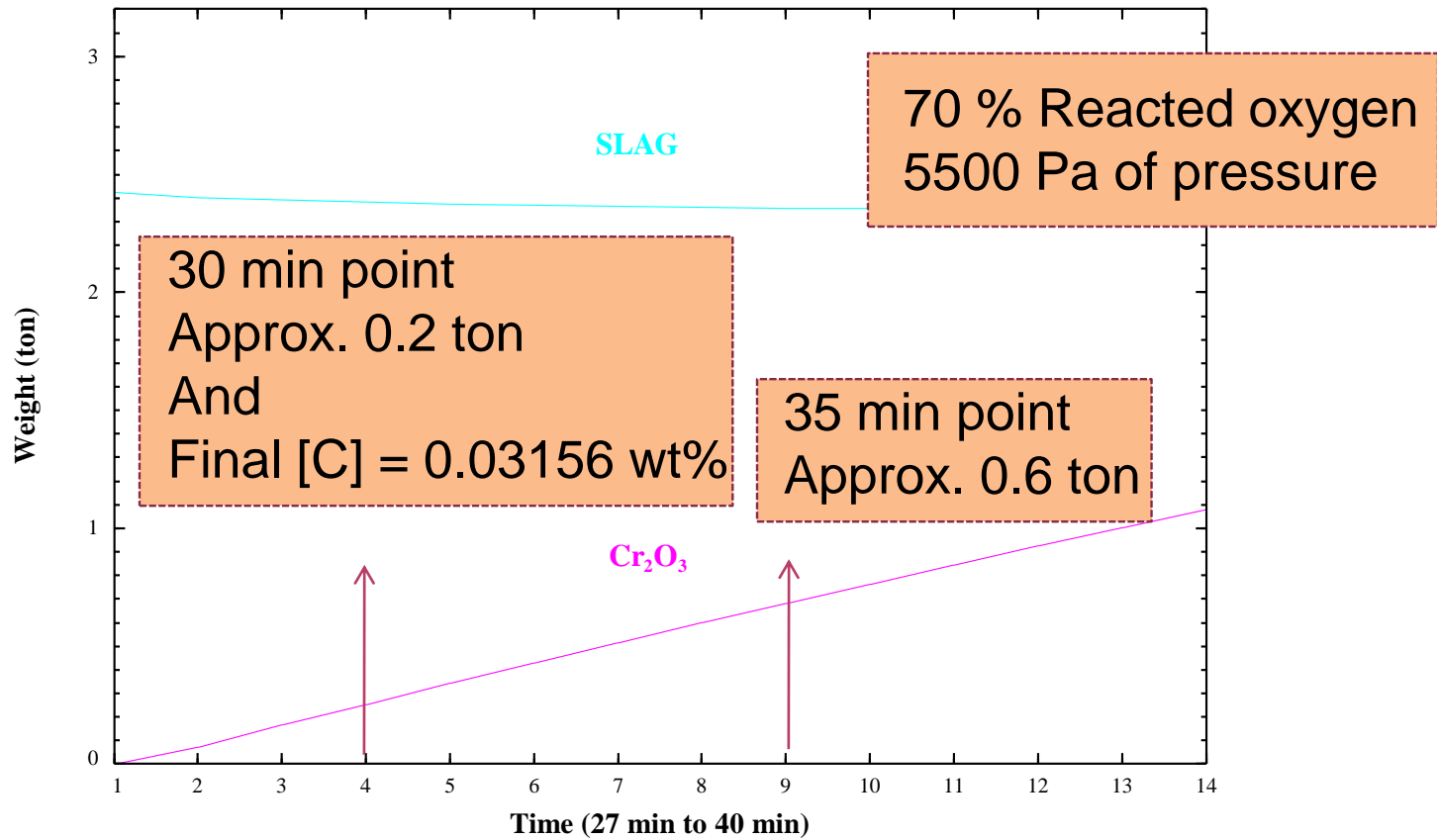
Reduce pressure to minimize slag  
amount

Keep flux amount (for reduction stage)

## 3 – 2 Result & Modification

Approximation for reducing  $\text{Cr}_2\text{O}_3(\text{s})$  phase

$\text{Cr}_2\text{O}_3$  (s) phase



For Reduction stage

By considering slow reaction between slag and melt, divide 8 small portion of reaction fluxes amounts

Vacuum condition = 0.0019 atm (200Pa)

Initial fluxes =

FeSiMn (28.8%Si, 63.7%Mn) : 900kg

Al (99.5% Al) : 160kg

Dolomitic Lime (38%MgO, 58%CaO) : 200kg

## 3 – 2 Result & Modification

### Result from approximate calculation

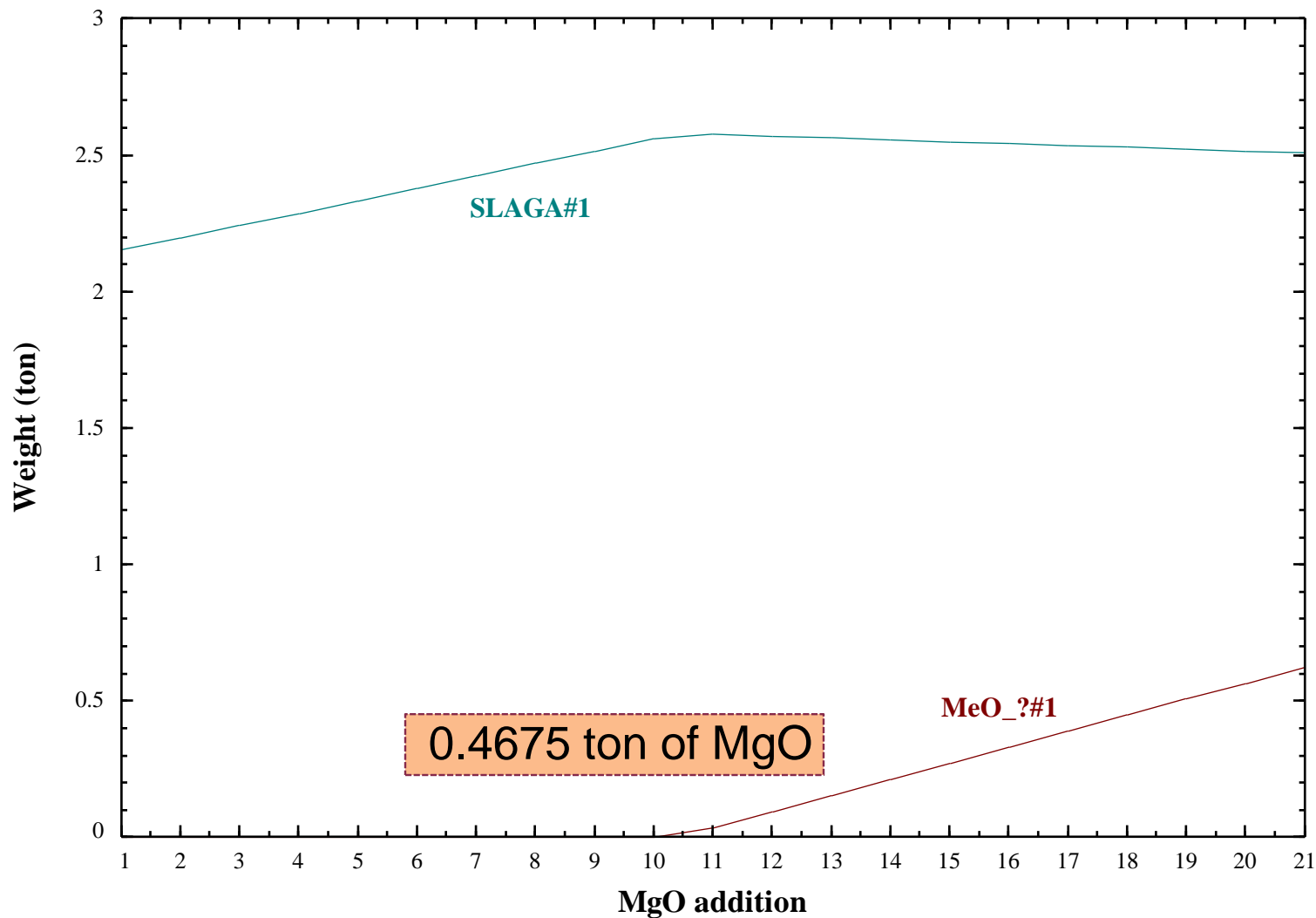
➔ + 9.4648E-06 wt.% C  
+ 17.868 wt.% Cr  
+ 7.1622E-04 wt.% N  
+ 0.11470 wt.% Si  
+ 1.0569 wt.% Mn

### Modification

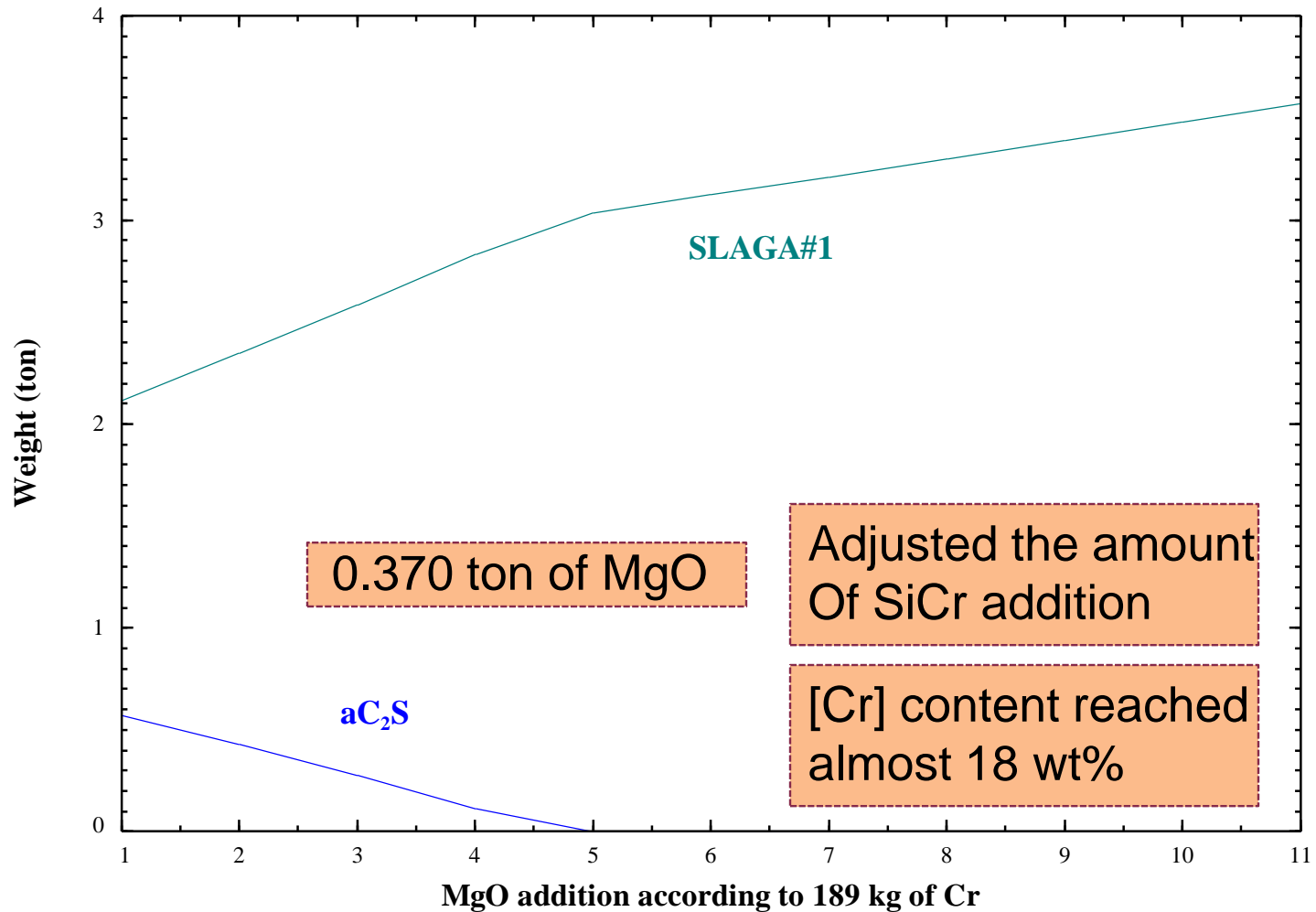
To achieve

- ➔ Fe, <0.12% C, 16-18% Cr, <0.75% Ni, <1.0% Mn, <1.0% Si,  
<STS grade 430 From Azon.com>
- ➔ Add SiCr to adjust final [Cr]  
Add more MgO to saturate MgO in the slag to prevent  
reaction between slag and refractories  
(assume refractories are mainly consist of MgO-rich phase)

## Find MgO saturation point



### Preventing solid phase forming (because of Si)



## 3 – 2 Result & Modification

### Estimation calculation for Reduction stage

**F Reactants - Equilib**

File Edit Table Units Data Search Help

T(C)

1 - 9

Mass(g)	Species
100%	[45_FeLQ]
+ 100%	[45_Slag]
+ 0.135	Fe
+ 1.1466	Mn
+ 0.1592	Al
+ 0.38	MgO
+ 0.7136	CaO
+ 0.189	Cr
+ 0.5604	Si

**F Menu - Equilib:**

File Units Parameters Help

T(C) P(atm) Energy(J) Mass(g) Vol(litre)

**Reactants [9]**

(gram) 100% [45\_FeLQ] + 100% [45\_Slag] + 0.135 Fe + 1.1466 Mn  
(1701.6C,1.900000E-03atm,#1) (1701.6C,1.900000E-03atm,#2) (25C,s1-FACT53,#3) (25C,s1-FACT53)

**Products**

Compound species

- gas  ideal  real 62
- aqueous 0
- pure liquids 0
- pure solids 84
- suppress duplicates apply
- \* - custom selection species: 146

Target

- none -

Estimate T(C): 1000

Mass(g): 0

**Solution species**

*	+	Base-Phase	Full Name
	+	FToxid-SPINA	ASpinel
		FToxid-MeO_?	?Monoxide
	+	FToxid-bC2S	a'Ca2SiO4
	+	FToxid-aC2S	a-Ca2SiO4
	+	FToxid-OlivA	AOlivine
	+	FToxid-CORU	M2O3(Corundum)
	+	FToxid-CaSp	CaSpinel

Legend

| - immiscible 2  Show  all  selected

+ - selected 8

species: 124 solutions: 12 Select

**Final Conditions**

P(atm) Delta H(J)

0.0019 0

**Equilib**

normal

Calculate

FactSage 6.1 Compound: 3/16 databases



## 3 – 2 Result & Modification

### Result - Melt

+ 120.81 gram Fe-liq	
(120.81 gram, 2.2034 mol)	
(1625.71 C, 1.9000E-03 atm, a=1.0000)	
( 80.467 wt.% Fe	FTmisc
+ 1.9321E-03 wt.% Al	FTmisc
+ 1.9204E-05 wt.% C	FTmisc
+ 4.2150E-08 wt.% Ca	FTmisc
+ 17.965 wt.% Cr	FTmisc
+ 1.0346 wt.% Mn	FTmisc
+ 6.3495E-04 wt.% N	FTmisc
+ 6.0079E-04 wt.% O	FTmisc
+ 0.51398 wt.% Si	FTmisc
+ 3.2650E-05 wt.% Mg	Ftmisc



Fe, <0.12% C, 16-18% Cr, <0.75% Ni, <1.0% Mn, <1.0% Si

## 3 – 2 Result & Modification

### Result - Slag

+ 3.0180 gram ASlag-liq#1  
(3.0180 gram, 5.2305E-02 mol)  
(1625.71 C, 1.9000E-03 atm, a=1.0000)  
( 9.8177 wt.% Al<sub>2</sub>O<sub>3</sub> FToxid  
+ 33.583 wt.% SiO<sub>2</sub> FToxid  
+ 44.746 wt.% CaO FToxid  
+ 5.9575E-02 wt.% FeO FToxid  
+ 2.1620E-04 wt.% Fe<sub>2</sub>O<sub>3</sub> FToxid  
+ 10.540 wt.% MgO FToxid  
+ 0.65223 wt.% MnO FToxid  
+ 0.55160 wt.% CrO FToxid  
+ 5.0136E-02 wt.% Cr<sub>2</sub>O<sub>3</sub> FToxid  
+ 7.7029E-05 wt.% Mn<sub>2</sub>O<sub>3</sub> FToxid)



Almost same result from paper (01Jon)

## 4. Main calculation (by using stream function)

- 1) Condition
- 2) Calculation
- 3) Result & Discussion

**Oxygen Blowing Stage**

<b>Time(min)</b>	0-5	6-10	11-15	16-20	21-25	26-30	31-35
<b>Oxygen(Nm<sup>3</sup>/min)</b>	20	20	20	20	20	15	10
<b>Vacuum(Pa)</b>	8000	8000	8000	8000	8000	6750	5500

Initial fluxes =

FeSi (76% Si) 410kg

Dolomitic lime (38%MgO, 58% CaO) 1100kg

**Degassing Stage**

<b>Time(min)</b>	36-40	41-45
<b>Oxygen(Nm<sup>3</sup>/min)</b>	0	0
<b>Vacuum(Pa)</b>	250	200

No fluxes added

## 4 – 1 Condition

### Reduction Stage

Time(min)	46-50	51-55	56-60	61-65	66-70	71-75	76-80
Oxygen(Nm <sup>3</sup> /min)	0	0	0	0	0	0	0
Vacuum(Pa)	200	200	200	200	200	200	200

Fluxes	Composition	Total amount
FeSiMn	28.8%Si, 63.7%Mn	787.5kg
SiCr	31.5%Cr, 50.2%Si	525kg
Al	99.5% Al	140kg
Dolomitic Lime	30.9%MgO, 58%CaO	1076.25kg

Assume that 1/7 of fluxes react with melt on each time interval

### Stream calculation

#### 1. Calculate first step

Save as stream files

Result – liquid steel, slag, solid, gas formed

Take all of formed phase except gas phases

#### 2. Calculate second step

Liquid steel  
Slag  
Solid phases



In condition of second step  
(e.g. different pressure)

Result – liquid steel, slag, solid, gas formed

Take all of formed phase except gas phases for next step calculation

#### 3. Calculate third step as done on second step

# 4 – 2 Calculation

## Initial steel

**Reactants - Equilib**

Mass(g)	Species
0.3	C
+ 21.6	Cr
+ 0.018	N
+ 0.024	O
+ 0.252	Si
+ 0.72	Mn
+ 97.086	Fe

**Menu - Equilib: last system**

Reactants (7): (gram) 0.3 C + 21.6 Cr + 0.018 N + 0.024 O + 0.252 Si + 0.72 Mn + 97.086 Fe

**Products**

Compound species:  gas  ideal  real 47  
 aqueous 0  
 pure liquids 0  
 pure solids 83  
 suppress duplicates apply  
\* - custom selection species: 130

Solution species:

*	+	Base-Phase	Full Name
		FTmisc-FeLQ	Fe-liq

Legend: +- selected 1  Show  all  selected  
species: 11  
solutions: 1

Final Conditions: T(C) 1600, P(atm) 1

Equilibrium:  normal  transitions  
 predominant  open

Calculate >>

# 4 – 2 Calculation

Start process

**Reactants - Equilib**

File Edit Table Units Data Search Help

T(C) P(atm) Energy(J) Mass(g) Vol(litre)

1 - 6

Mass(g)	Species
100%	[0_initial_melt]
+ 0.142851785	O2
+ 0.0984	Fe
+ 0.3116	Si
+ 0.418	MgO
+ 0.638	CaO

FactSage 6.1 Compound: 3/16 databases

**Data Search**

Databases - 3/16 compound databases, 2/18 solution databases

**Fact** **FactSage™** **SGTE**

<input type="checkbox"/> ELEM	<input type="checkbox"/> FSopp	<input type="checkbox"/> BINS
<input type="checkbox"/> FACT	<input type="checkbox"/> FSlead	<input type="checkbox"/> SGPS
<input checked="" type="checkbox"/> Fact53	<input type="checkbox"/> FSlite	<input type="checkbox"/> SGTE
<input checked="" type="checkbox"/> FToxid	<input type="checkbox"/> FSstel	<input type="checkbox"/> SGnobl
<input type="checkbox"/> FTsalt	<input type="checkbox"/> FSupsi	<input type="checkbox"/> SGsold

compounds only  
solutions only  
no data

Clear All

**Miscellaneous**

<input type="checkbox"/> ALGE	<input type="checkbox"/> CAF2	<input type="checkbox"/> CAF3
<input type="checkbox"/> CF21	<input type="checkbox"/> DG11	<input type="checkbox"/> DONG
<input type="checkbox"/> EXAM	<input type="checkbox"/> INHO	<input type="checkbox"/> TESS
<input type="checkbox"/> TEST		

**Results - Equilib 1624 C**

Output Edit Show Pages

T(C) P(atm) Energy(J) Mass(g) Vol(litre)

```
(gram) 100% [0_initial_melt] + <A> O2 + 0.3116 Si + 0.418 MgO +  
(1600,1,stream,#1) (25,1,g-FACT53,#2) (25,1,s-FACT53,#2) (25,1,s-FACT53,#2)  
(gram) 0.638 CaO + 0.0984 Fe =  
(25,1,s-FACT53,#2) (25,1,s1-FACT53,#2)
```

mol	gas_ideal	
0.00000	(1624.00 C, 7.8954E-02 atm, a=0.27921)	
( 0.17359	Mg	FACT53
+ 5.6259E-02	CO	FACT53
+ 4.0988E-02	N2	FACT53
+ 5.4640E-03	Mn	FACT53
+ 1.1326E-03	Fe	FACT53
+ 1.1006E-03	Ca	FACT53
+ 6.1889E-04	Cr	FACT53
+ 5.1957E-05	SiO	FACT53
+ 3.1178E-06	CO2	FACT53
+ 3.5569E-07	Mg2	FACT53
+ 1.4180E-07	CrO	FACT53
+ 1.1180E-07	MgN	FACT53
+ 3.0552E-08	MgO	FACT53
+ 3.8653E-09	FeO	FACT53
+ 3.7825E-09	CaO	FACT53
+ 2.5295E-09	Si	FACT53
+ 4.8419E-10	CN	FACT53
+ 3.2898E-10	CrN	FACT53
+ 3.0970E-10	NO	FACT53
+ 1.3498E-10	N	FACT53



# 4 – 2 Calculation

## End of calculation

The screenshot shows the FactSage 6.1 interface with three windows open: 'Reactants - Equilib', 'Menu - Equilib: last system', and 'Results - Equilib 1629.99 C'. The 'Results' window displays the following information:

Output Edit Show Pages

T(C) P(atm) Energy(J) Mass(g) Vol(litre)

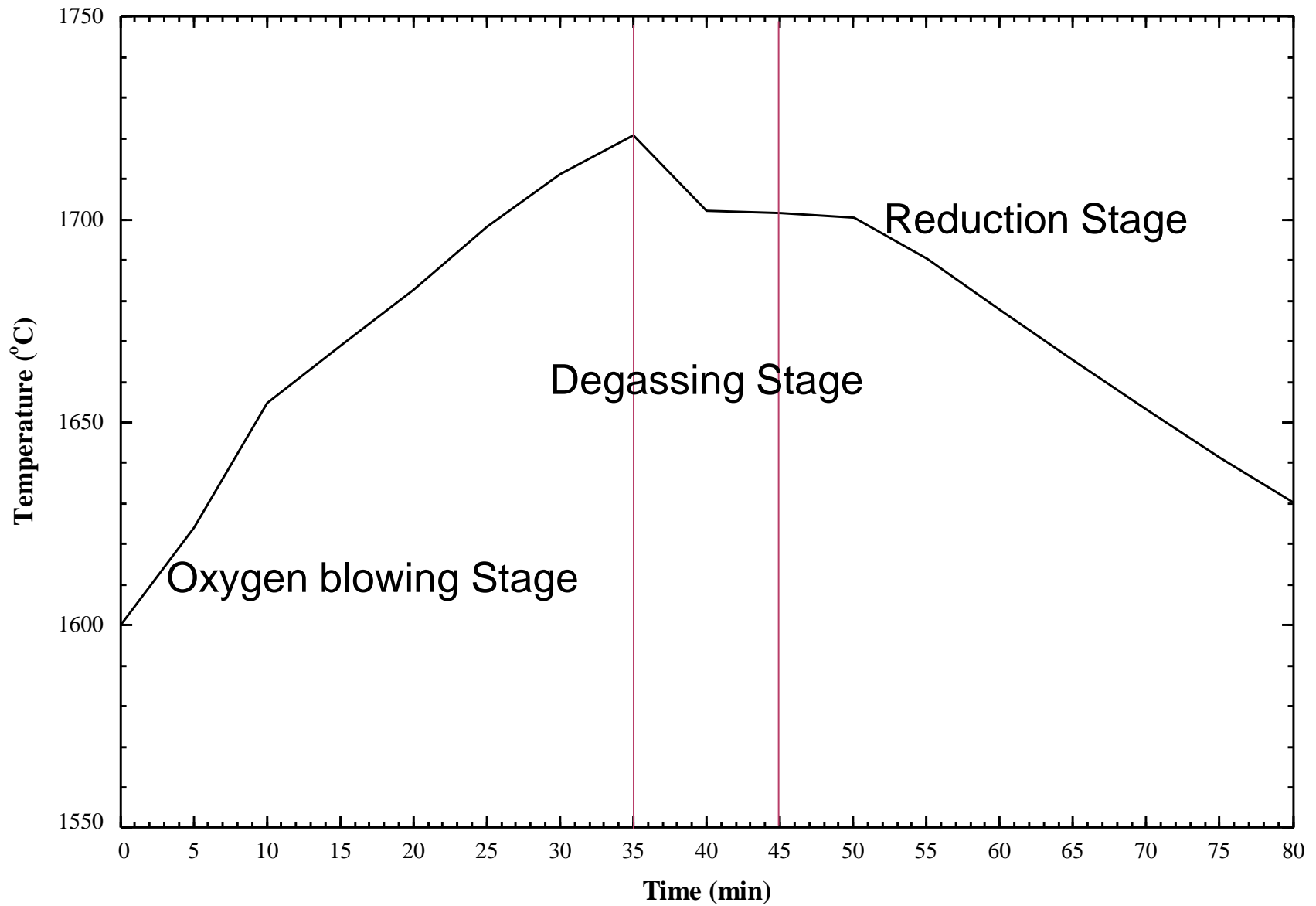
(gram) 0.016875 Fe + 0.143325 Mn + 0.0199 Al + 0.0475 MgO +  
(25,1,s1-FACT53,#3) (25,1,s1-FACT53,#3) (25,1,s-FACT53,#3) (25,1,s-FACT53,#3)  
(gram) 0.0892 CaO + 0.023625 Cr + 0.07005 Si + 100% [75\_FeLQ] +  
(25,1,s-FACT53,#3) (25,1,s-FACT53,#3) (25,1,s-FACT53,#3) (1641.19,1.900000E-  
(gram) 100% [75\_Slag] =  
(1641.19,1.900000E-03,stream,#5)

3.0511E-03 mol gas\_ideal  
(0.11828 gram, 3.0511E-03 mol, 250.78 litre, 4.7166E-07 g/ml)  
(1629.99 C, 1.9000E-03 atm, a=1.0000)

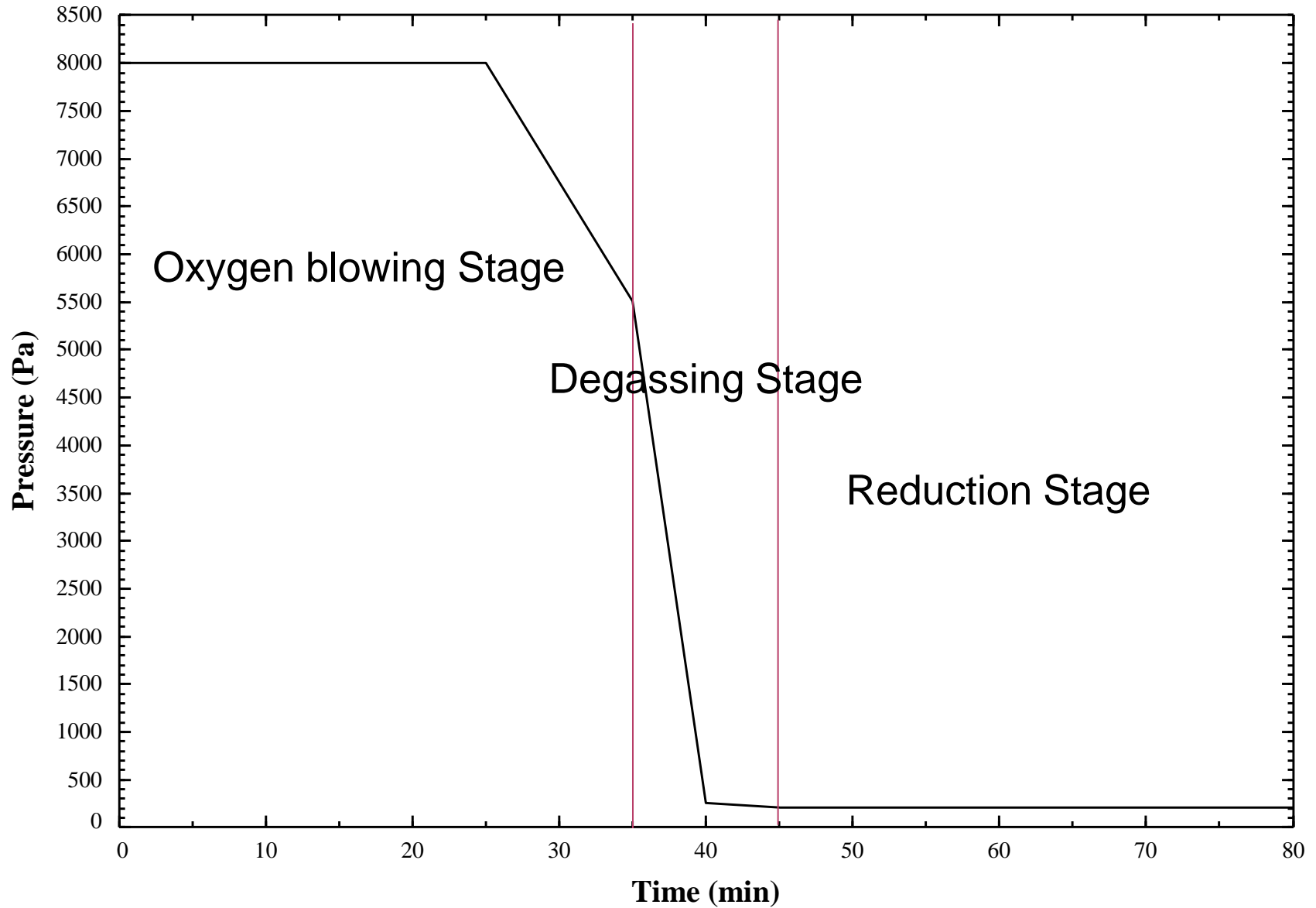
Amount	Species	Phase
0.51755	Mg	FACT53
0.37818	Mn	FACT53
5.0416E-02	Fe	FACT53
2.9581E-02	Cr	FACT53
2.2915E-02	SiO	FACT53
6.8797E-04	N2	FACT53
6.1300E-04	Ca	FACT53
5.7738E-05	CrO	FACT53
2.4293E-06	Al	FACT53
1.4850E-06	FeO	FACT53
8.0122E-07	MgO	FACT53
1.3964E-07	Si	FACT53
9.7625E-08	CO	FACT53
8.8547E-08	CrO2	FACT53
7.5497E-08	Mg2	FACT53
4.1279E-08	O	FACT53
2.1871E-08	AlO	FACT53

Result

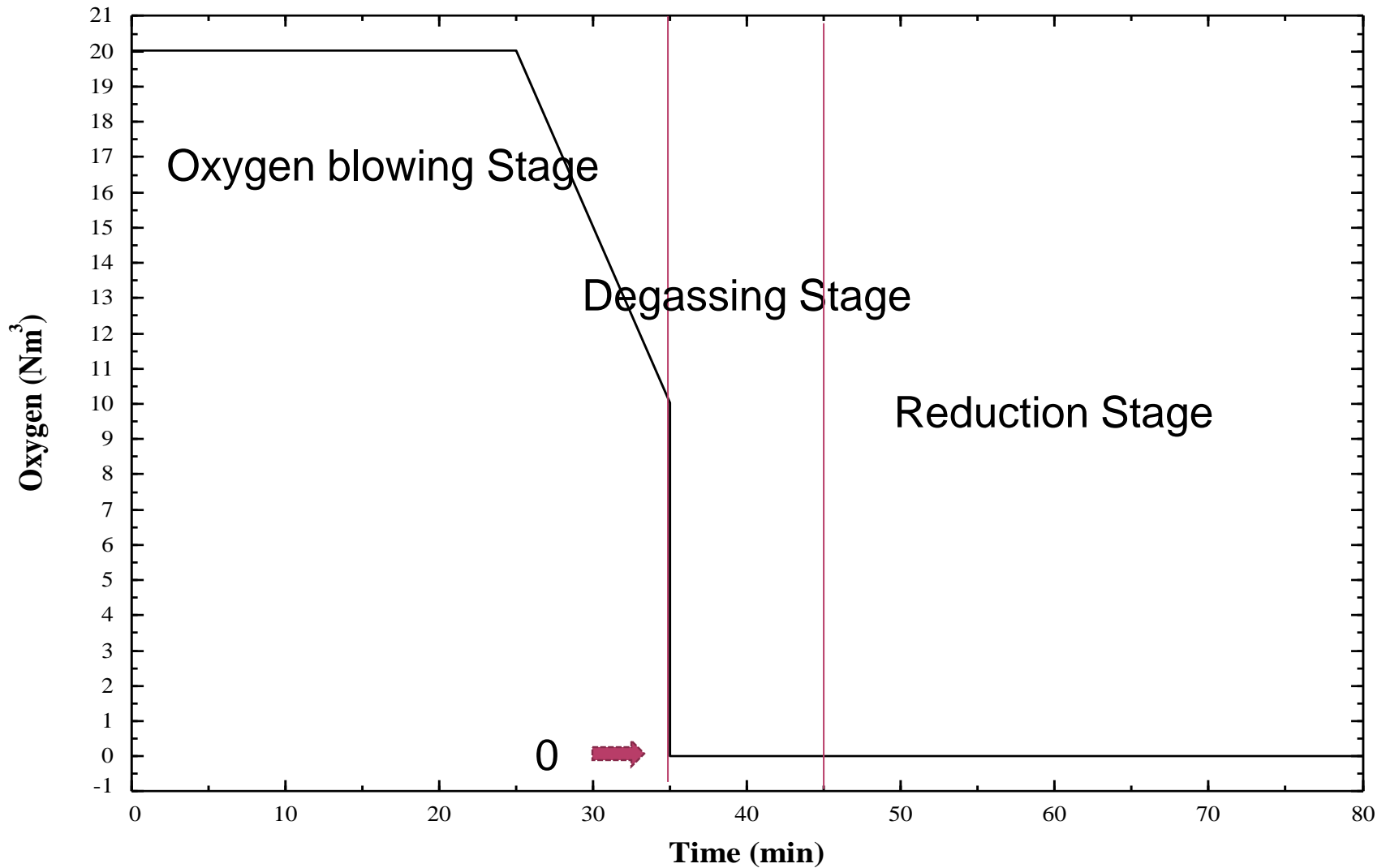
Vacuum, Temperature, Reacted oxygen



## Pressure (Pa)

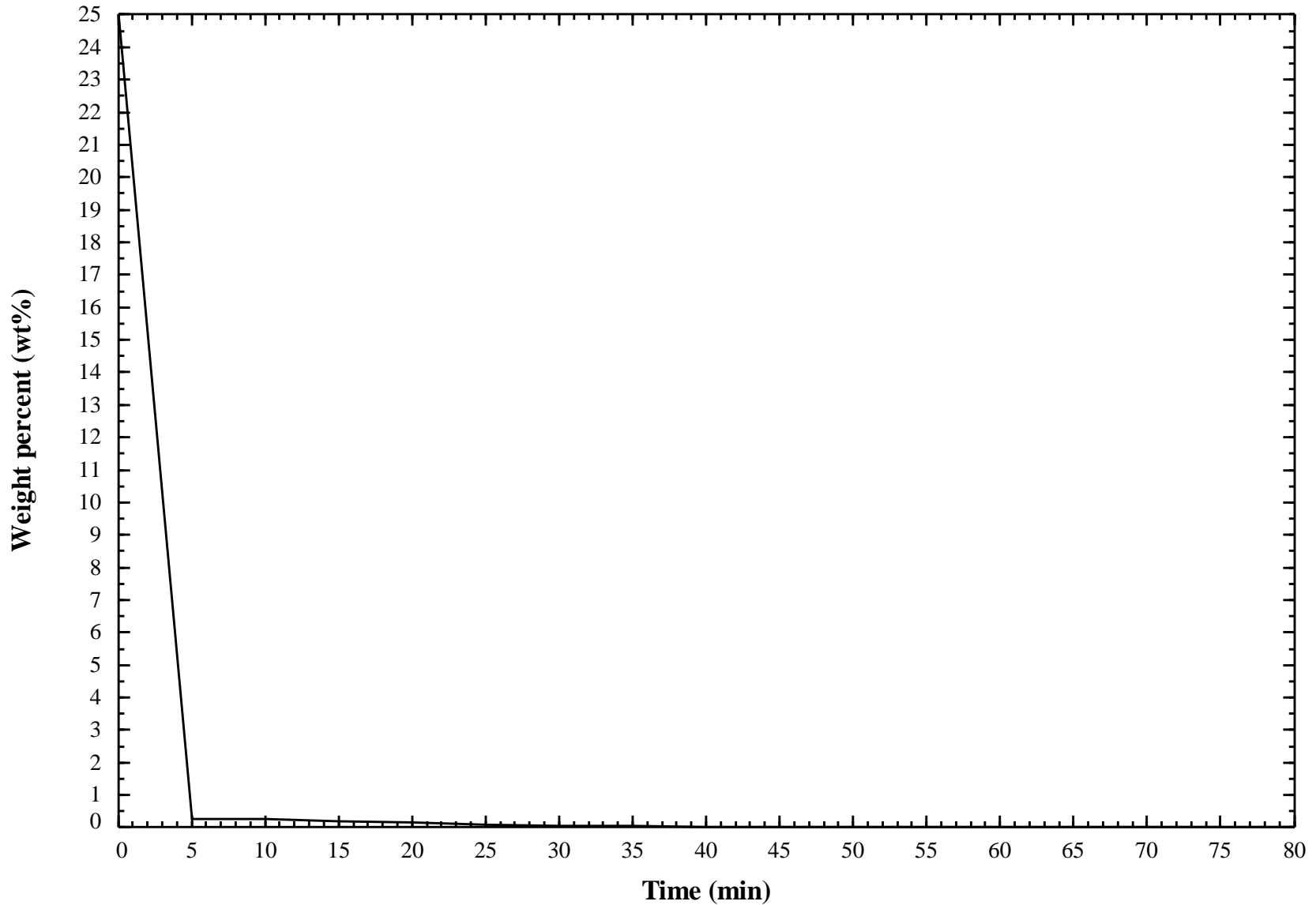


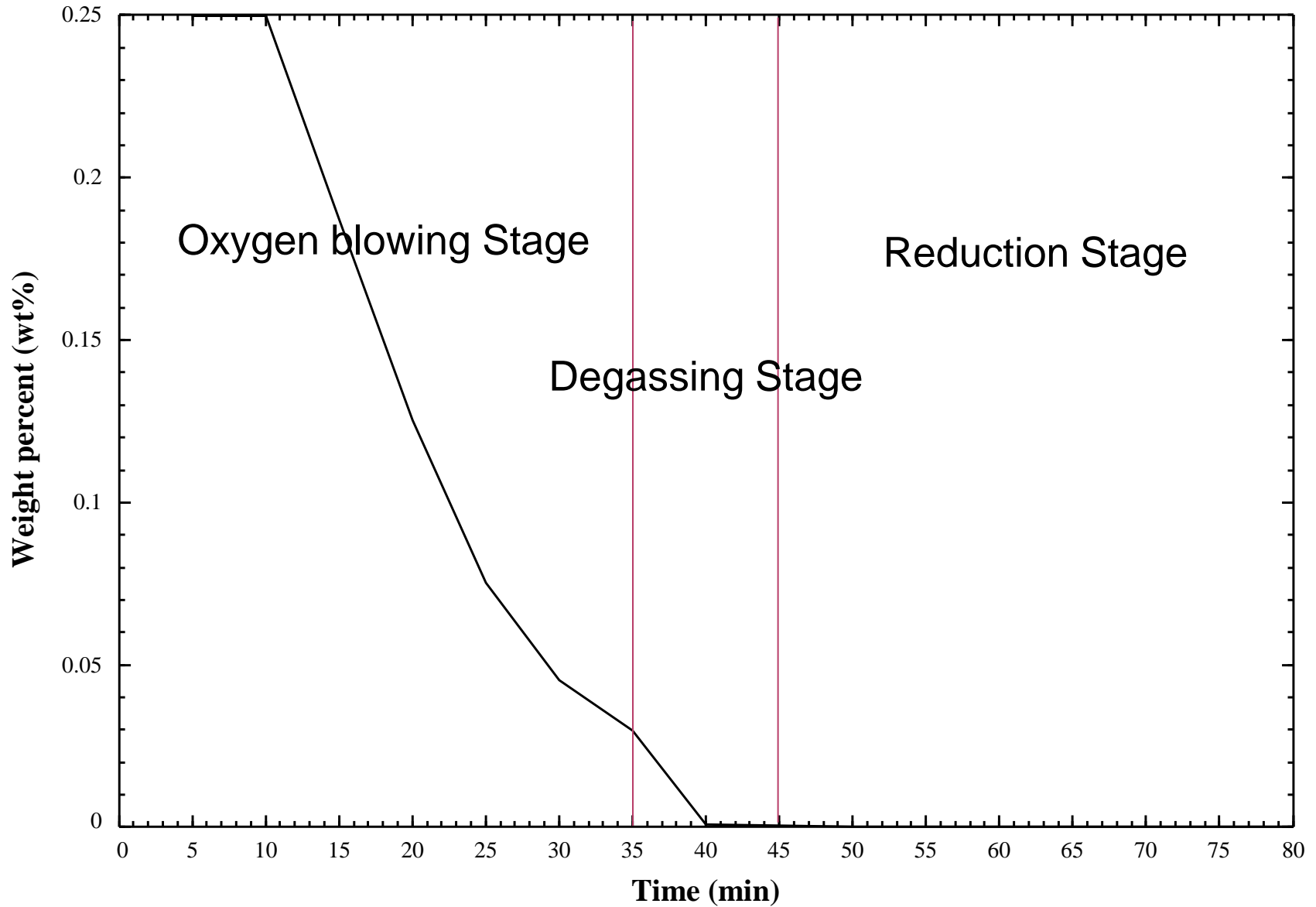
## Reacted Oxygen (shows blowing oxygen ratio)



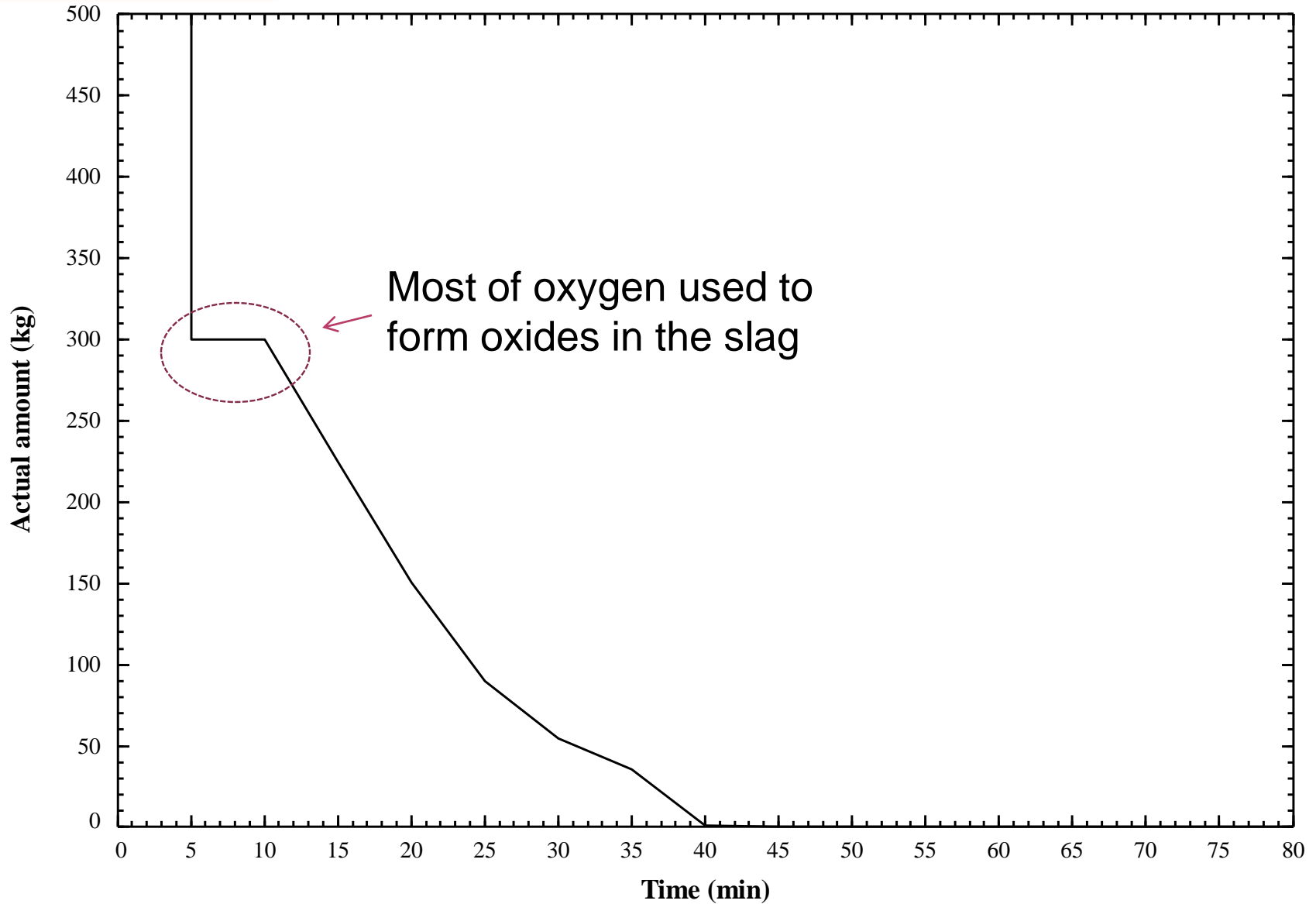
Result

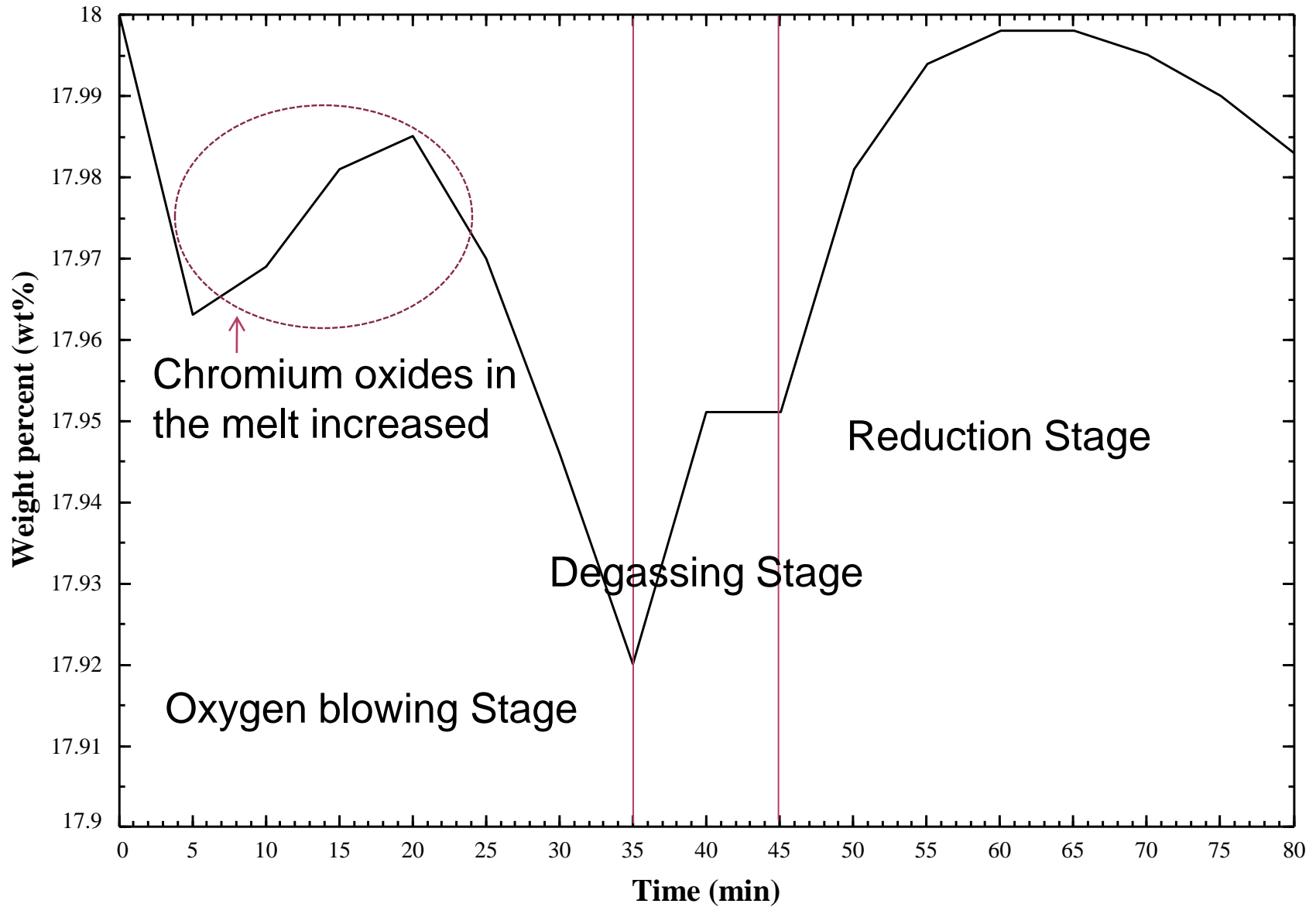
Liquid steel composition

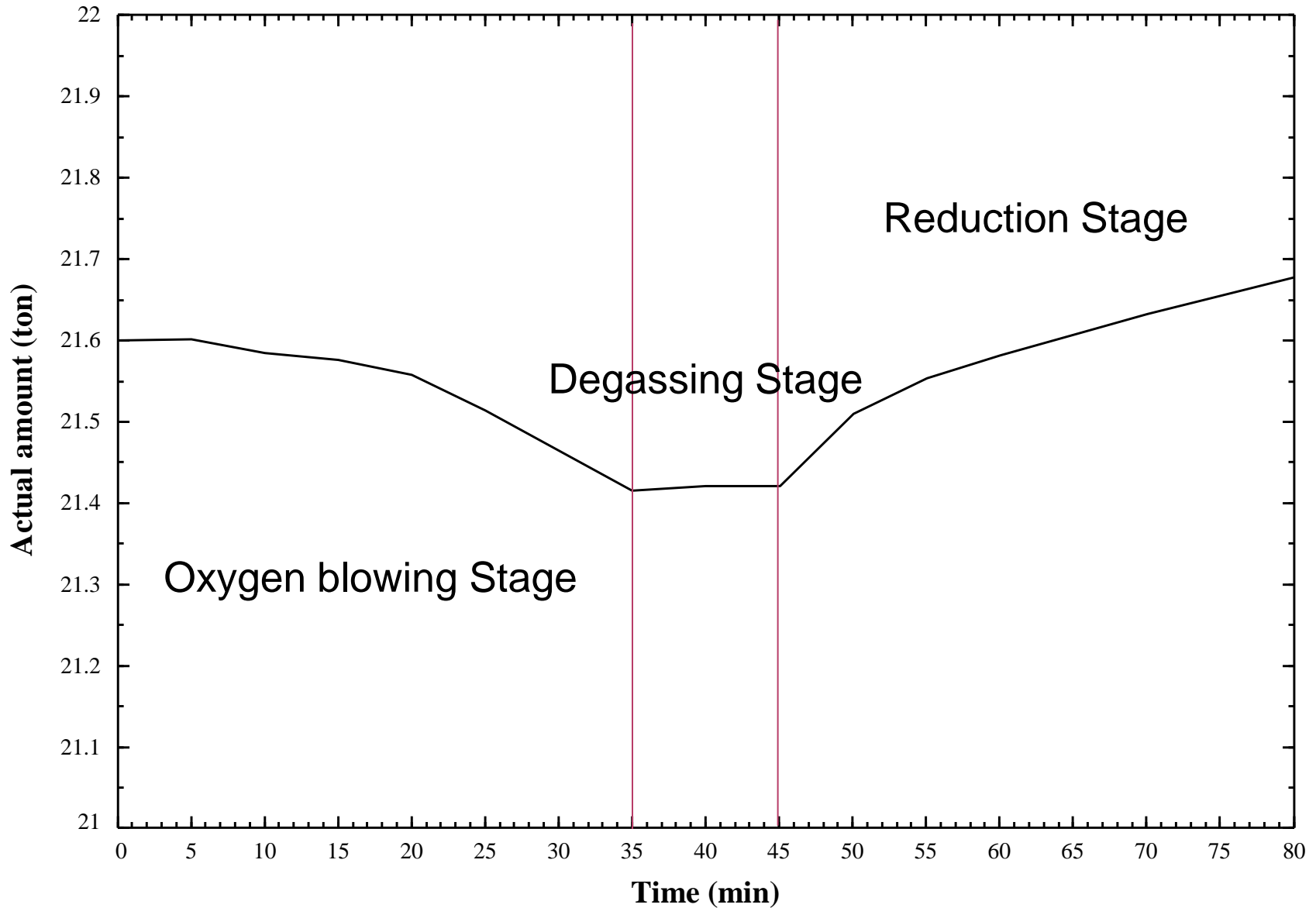


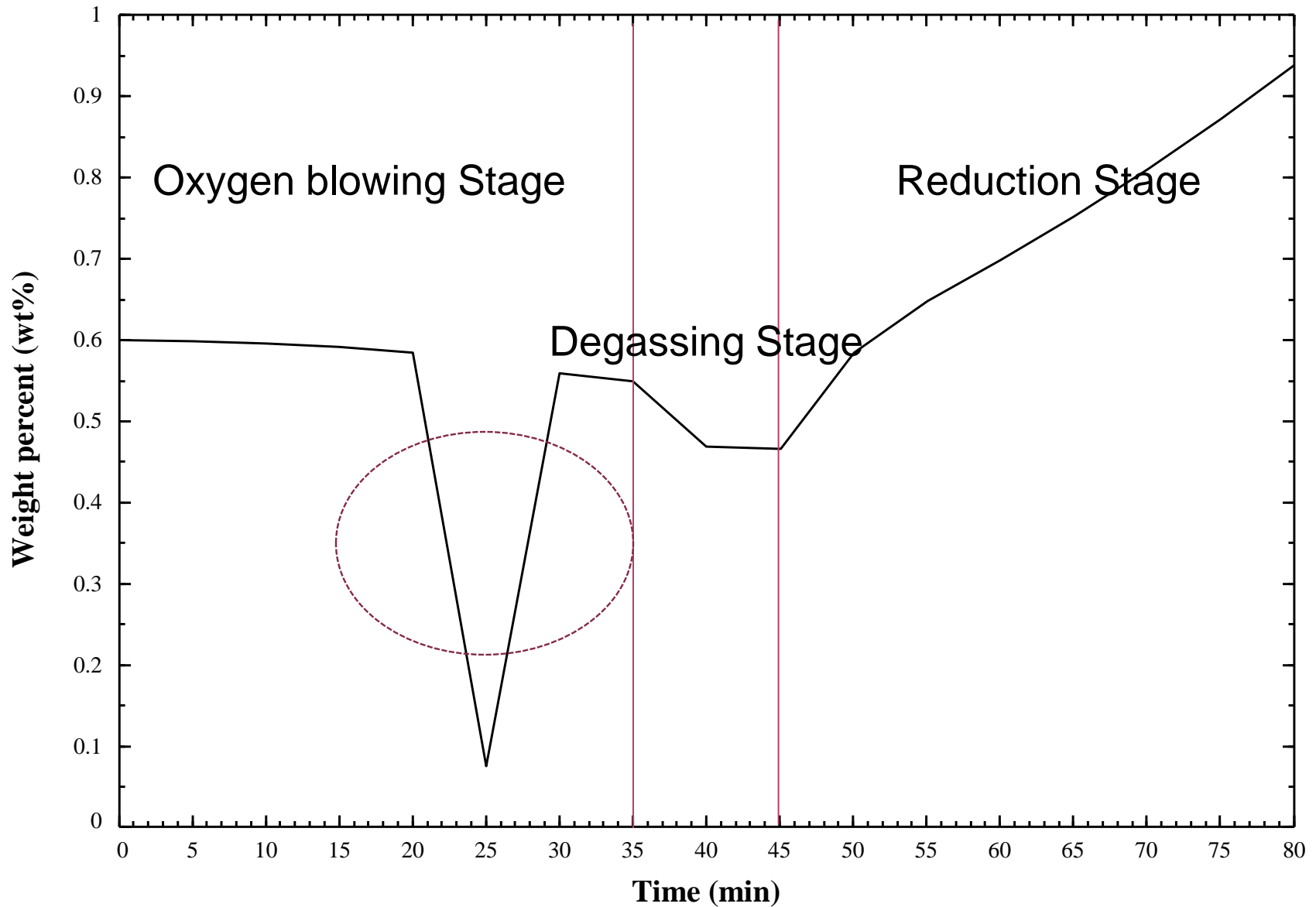


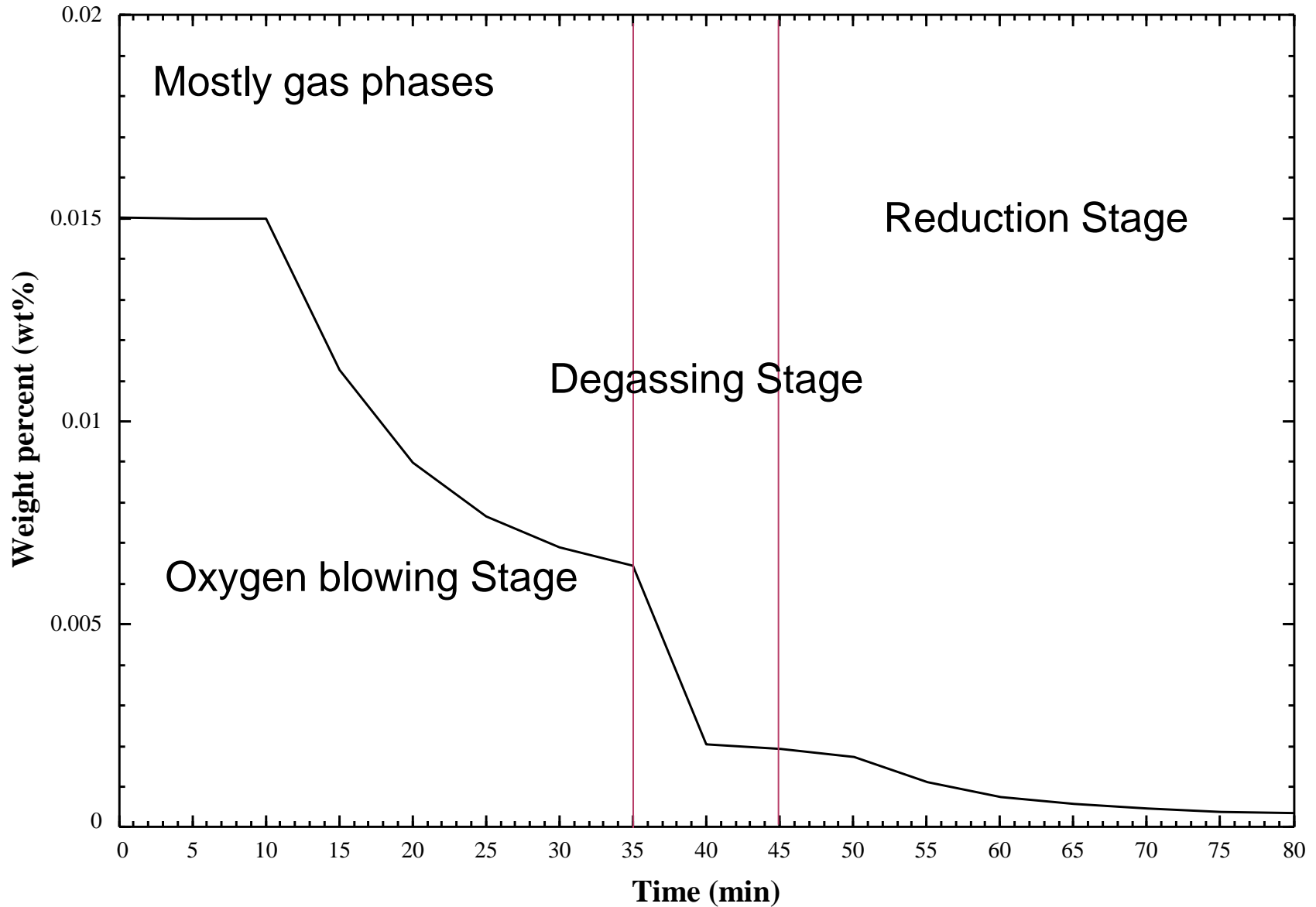


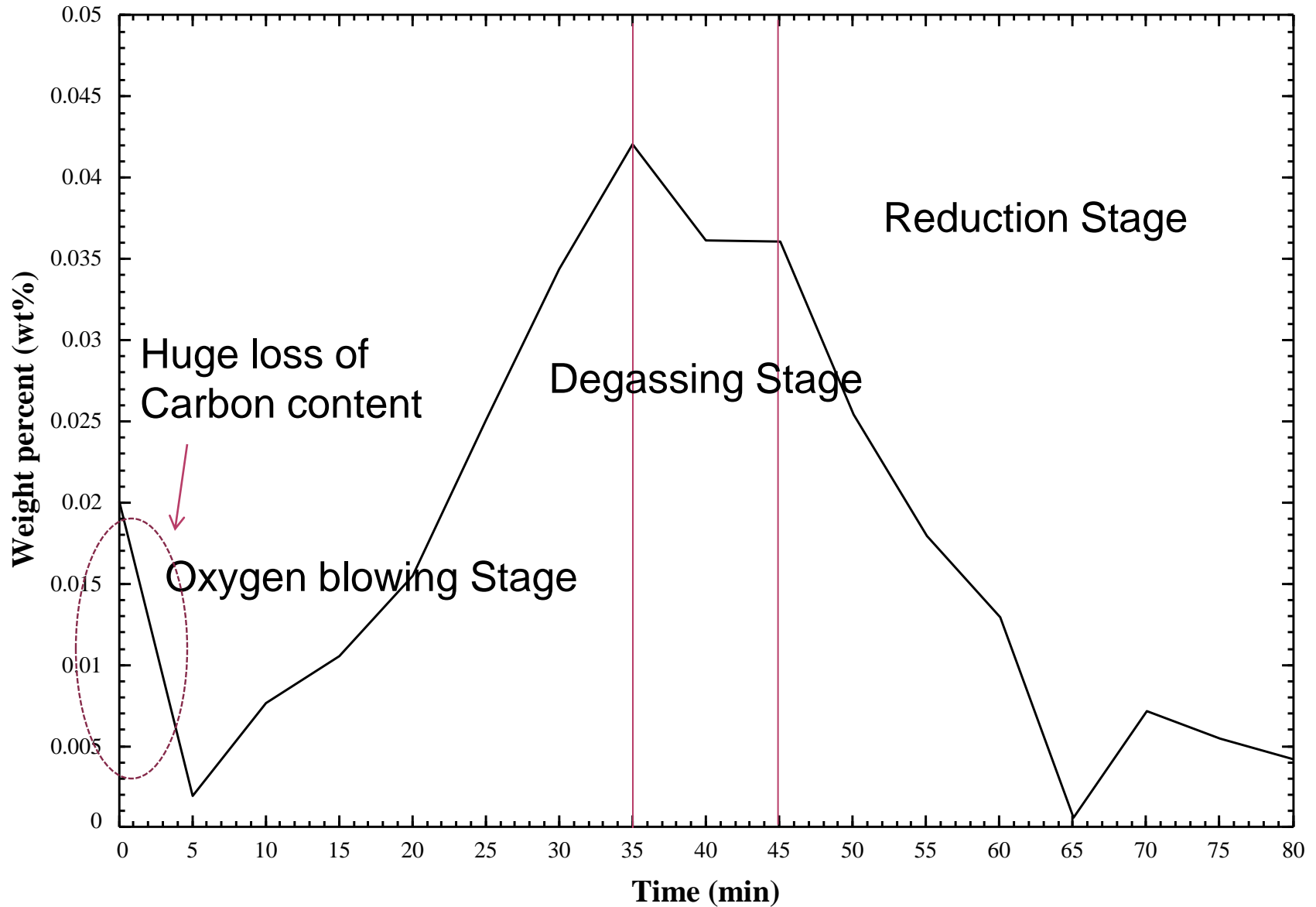


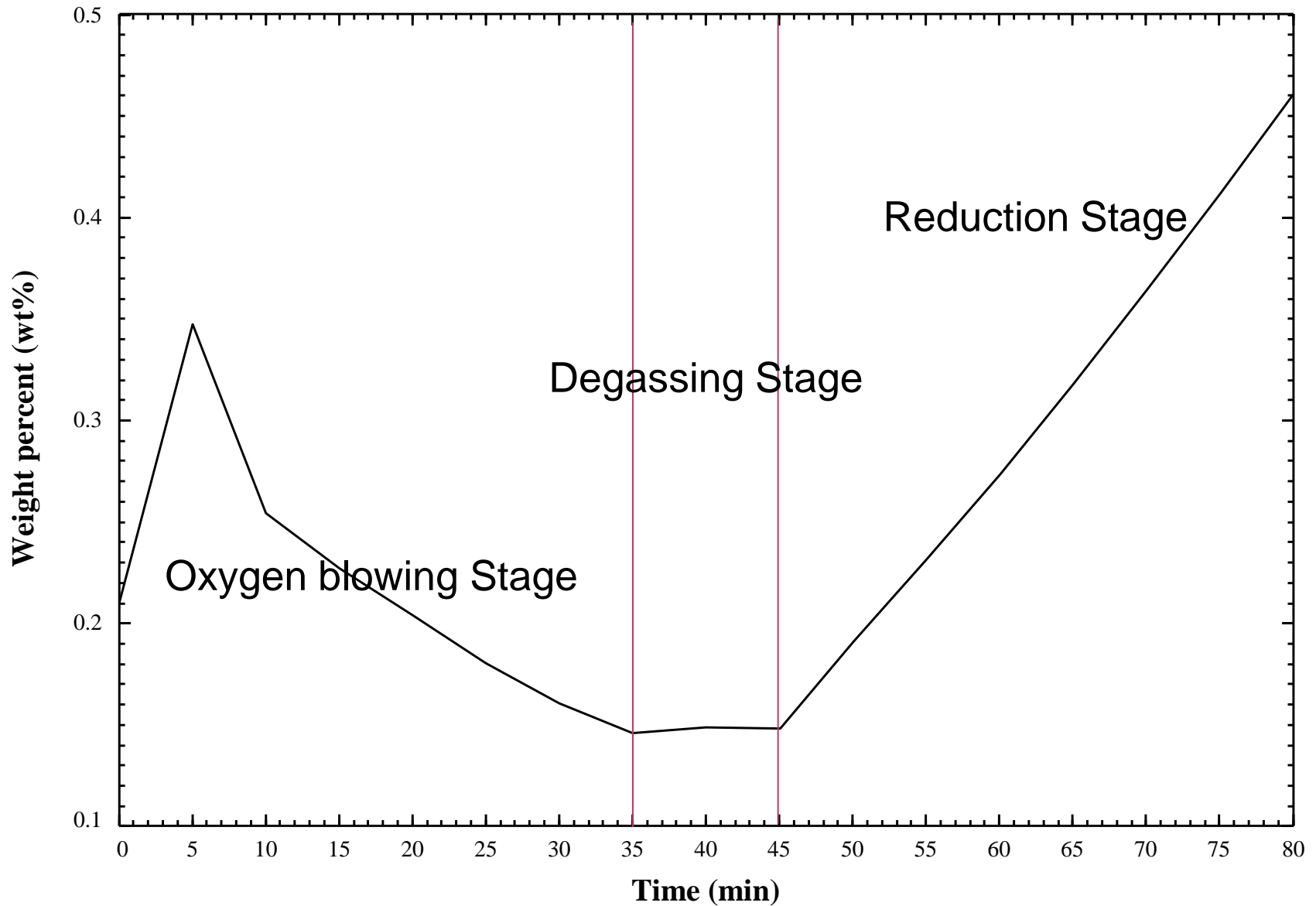


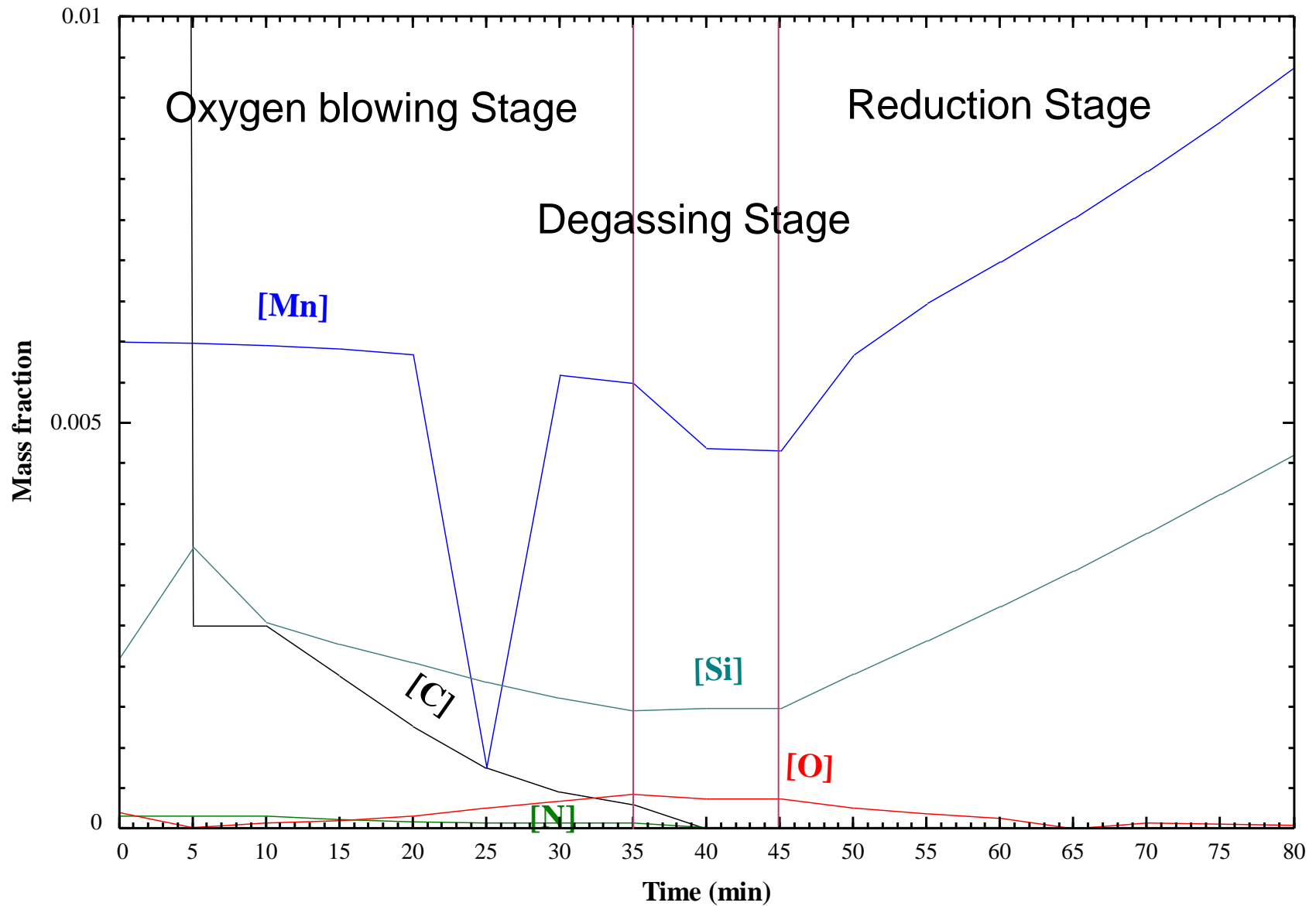








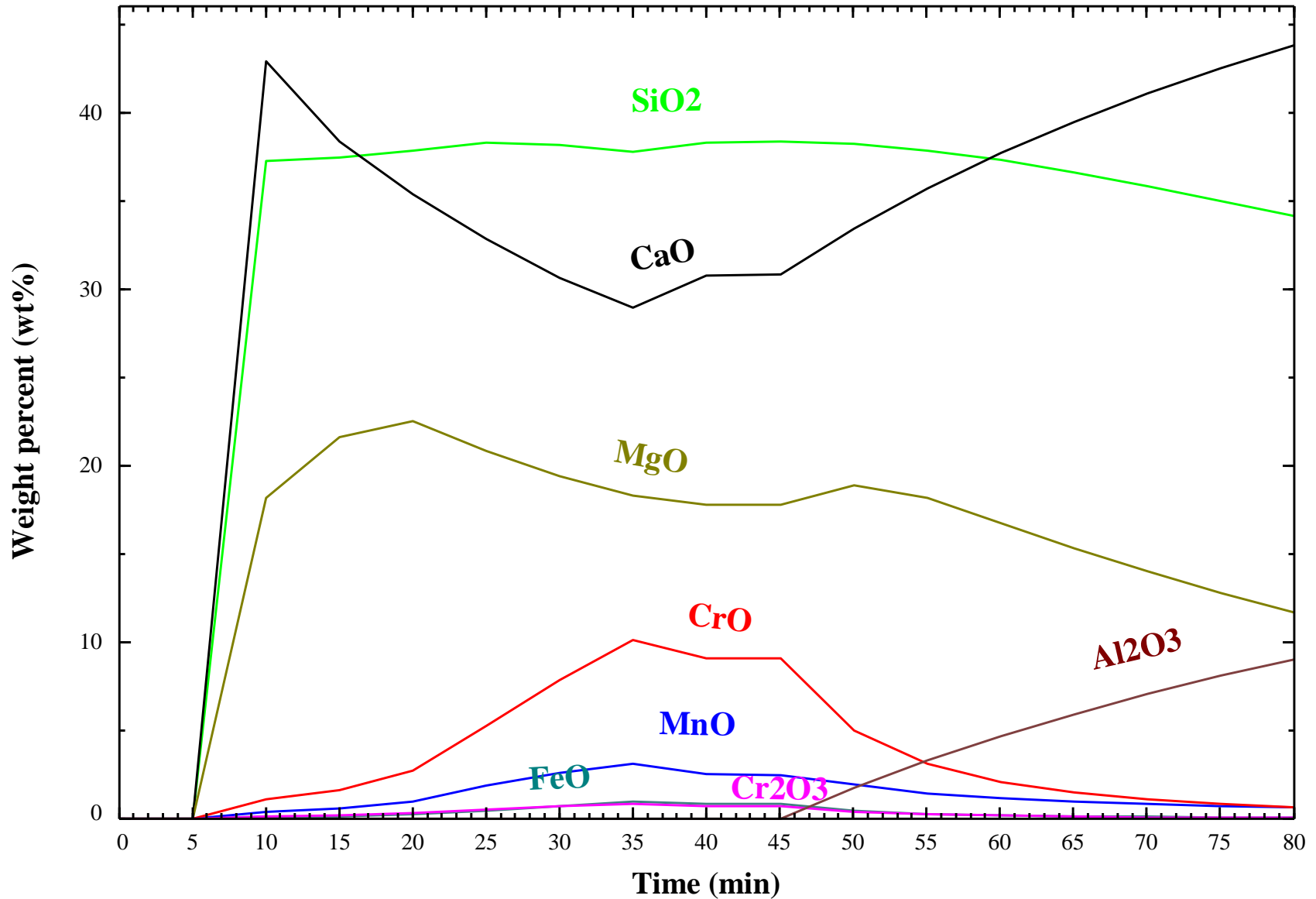


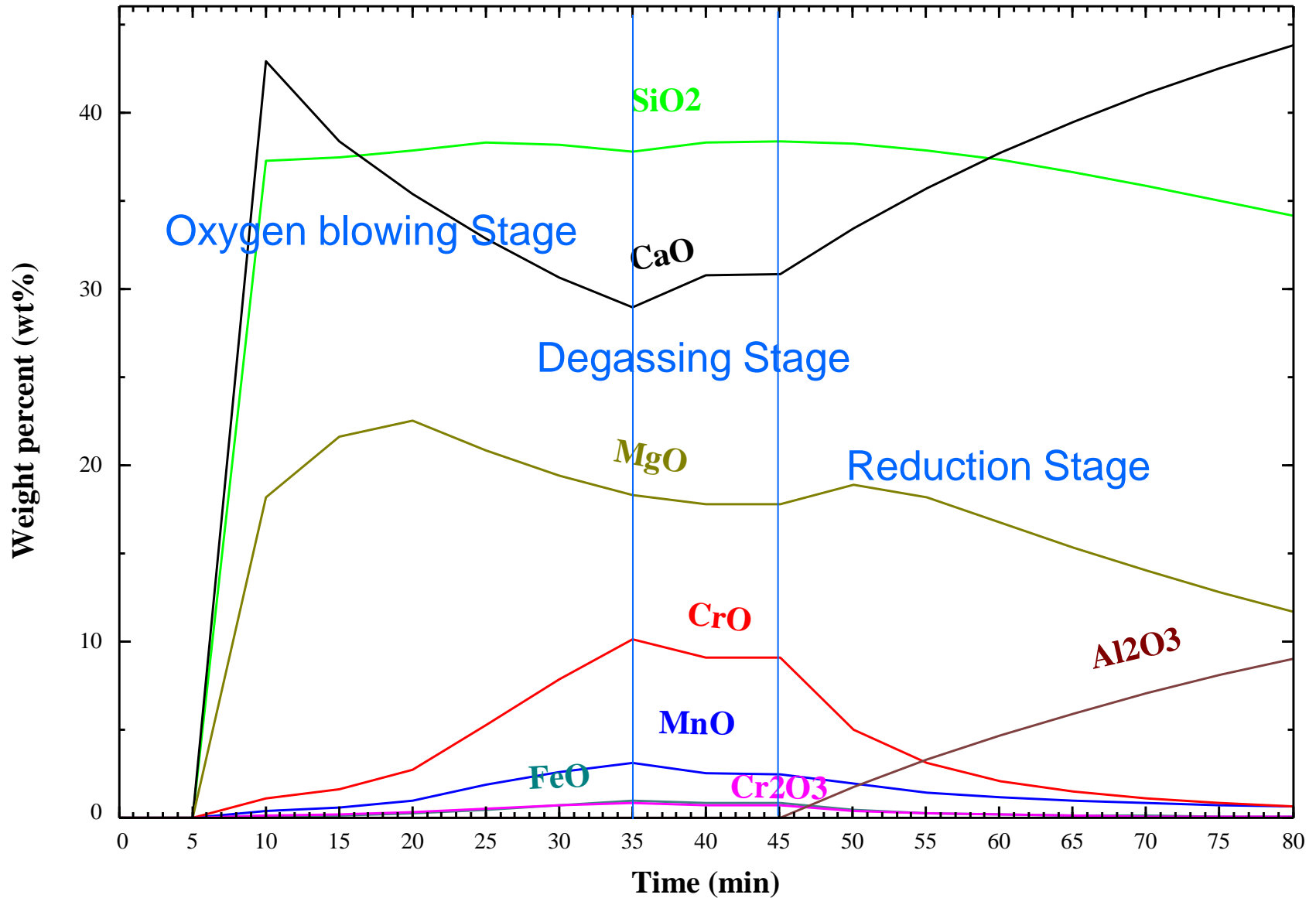


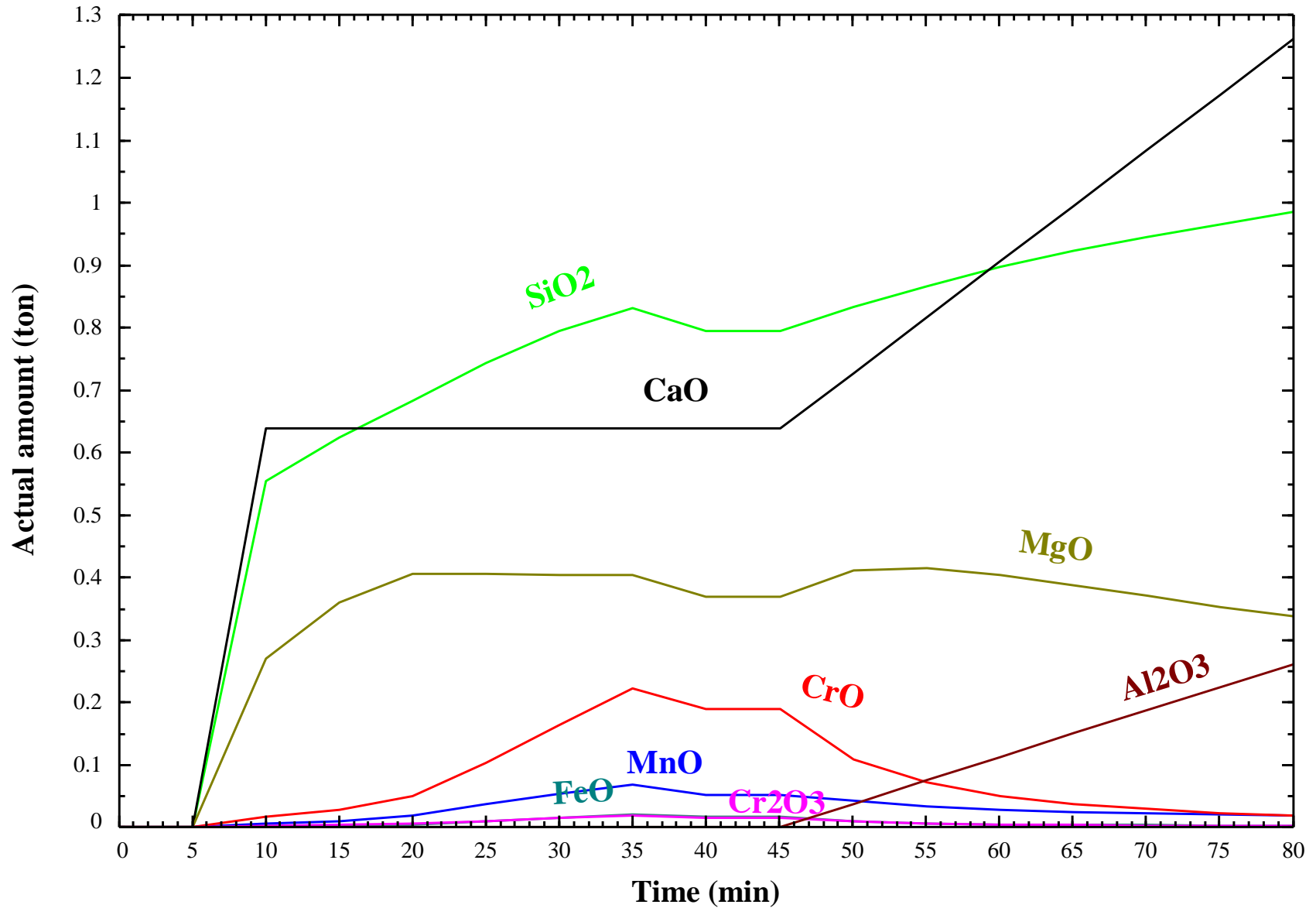


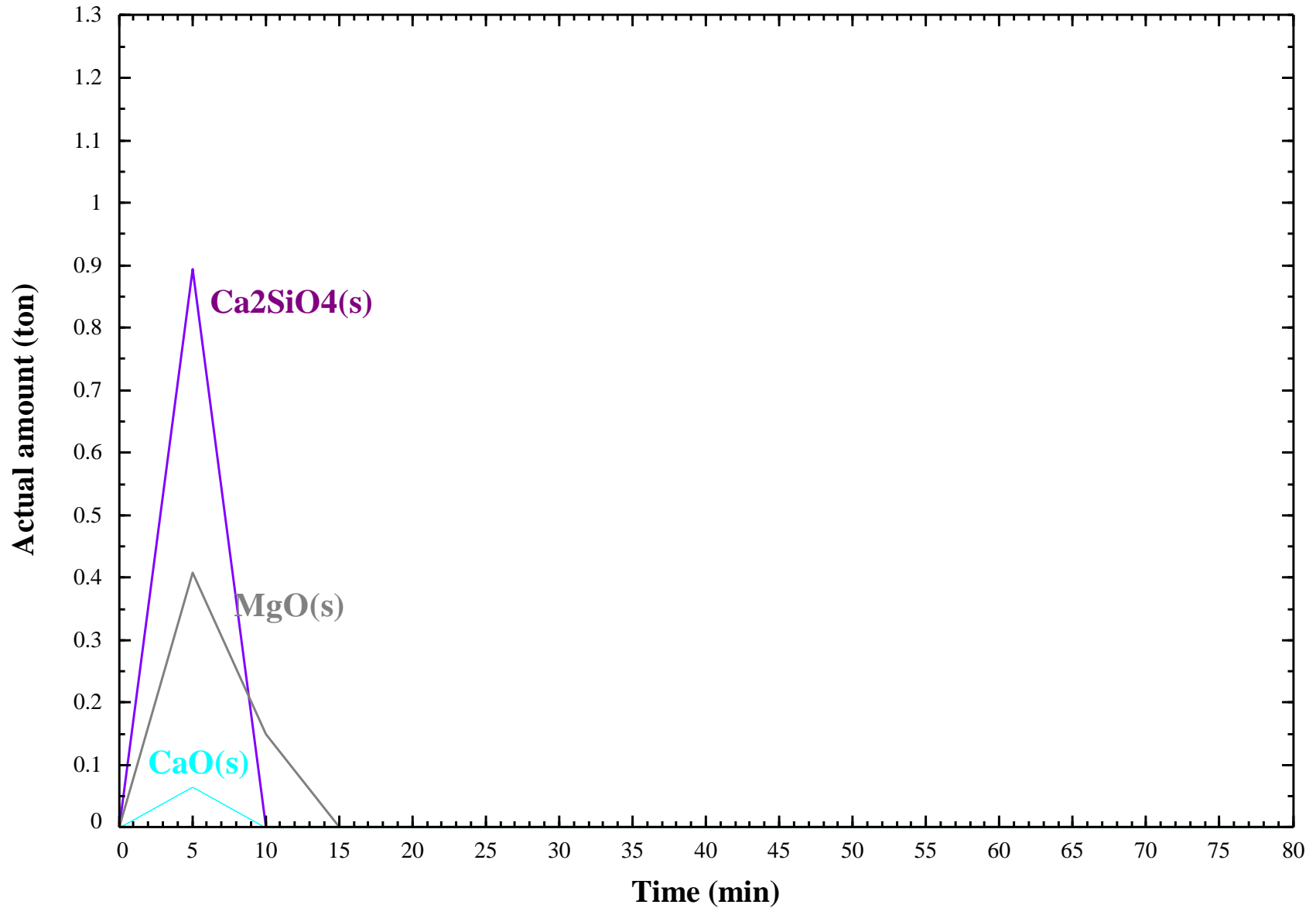
Result

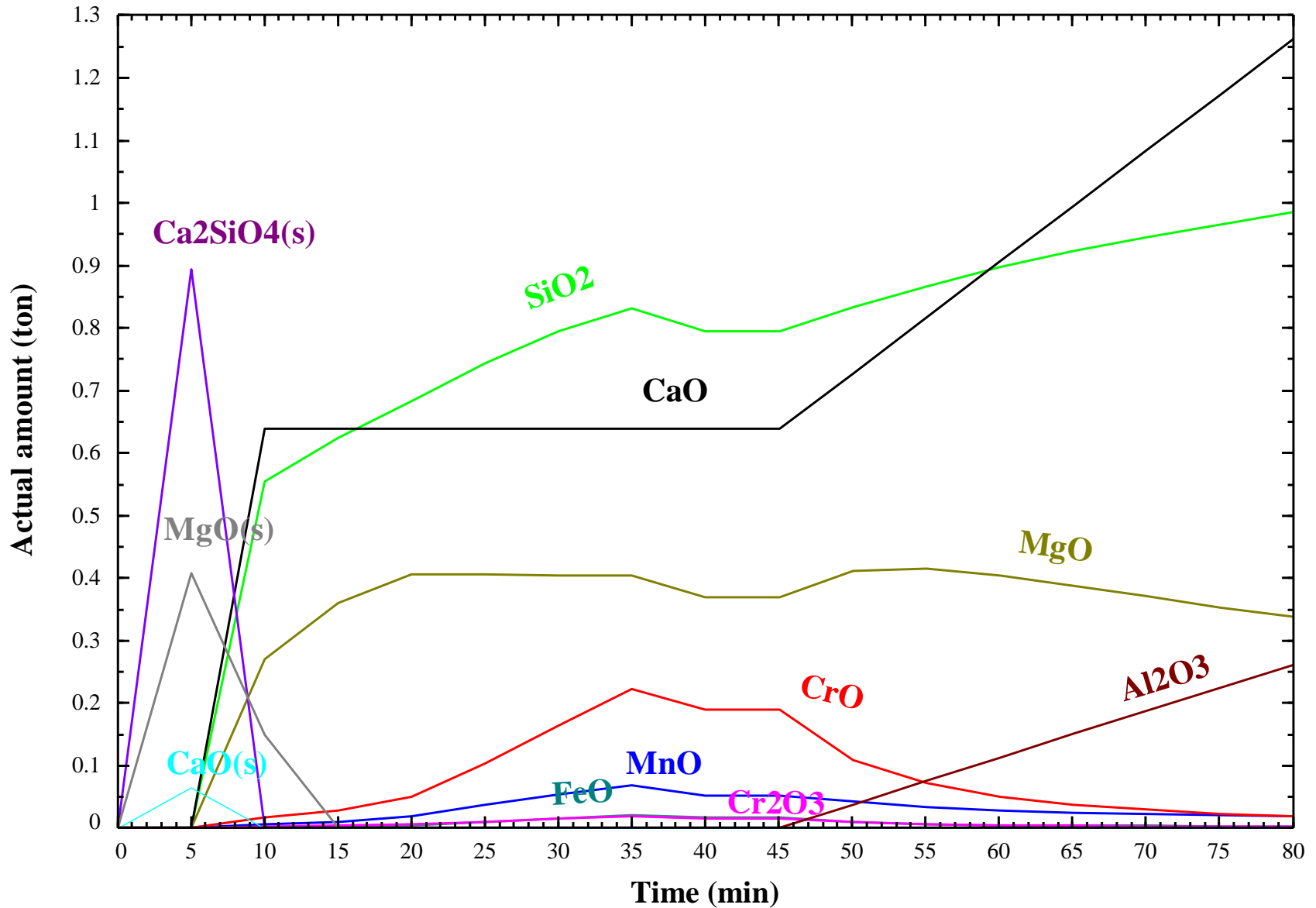
Slag composition











## 4 – 3 Result

### Slag composition from ALZ

11.6 ±1.1	MgO
43.5 ±2.9	CaO
6.1 ±0.4	Al <sub>2</sub> O <sub>3</sub>
1.8 ±0.6	Cr <sub>2</sub> O <sub>3</sub>
1.4 ±0.5	MnO
0.6 ±0.4	FeO
35.0 ±1.6	SiO <sub>2</sub>

### Slag composition from calculation

+ 11.694	wt.% MgO
+ 43.770	wt.% CaO
+ 9.0111	wt.% Al <sub>2</sub> O <sub>3</sub>
+ 5.8075E-02	wt.% Cr <sub>2</sub> O <sub>3</sub>
+ 0.64123	wt.% MnO
+ 6.6040E-02	wt.% FeO
+ 34.133	wt.% SiO <sub>2</sub>



Almost same for Slag basicity, MgO saturation

Less Cr<sub>2</sub>O<sub>3</sub>, FeO amount

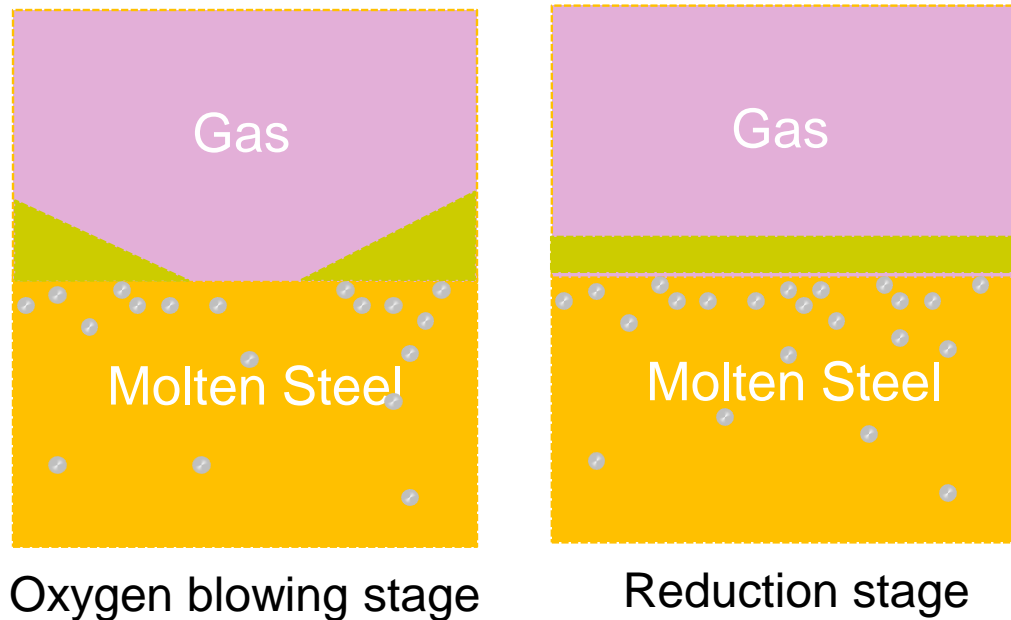
## 5. Optimization for the gas reaction

### Consider about gas equilibrium with melt

- Comparison for the whole 'oxygen blowing stage'
- Comparison for the whole 'reduction stage'

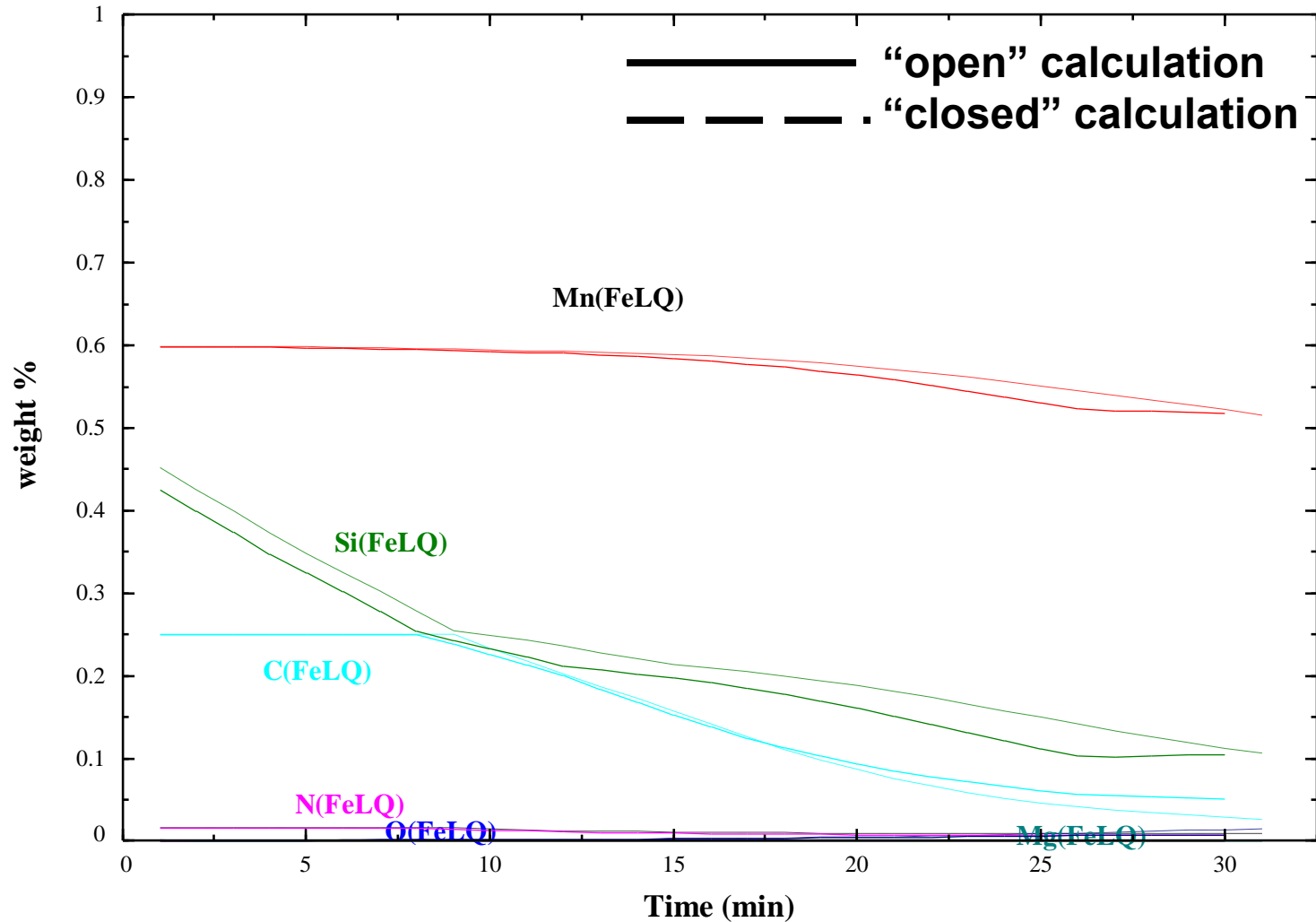
#### Purpose

Because in reality, there are a lot of gas bubbles in the melt so some of the portions of gas phase should be taken into account for the calculation



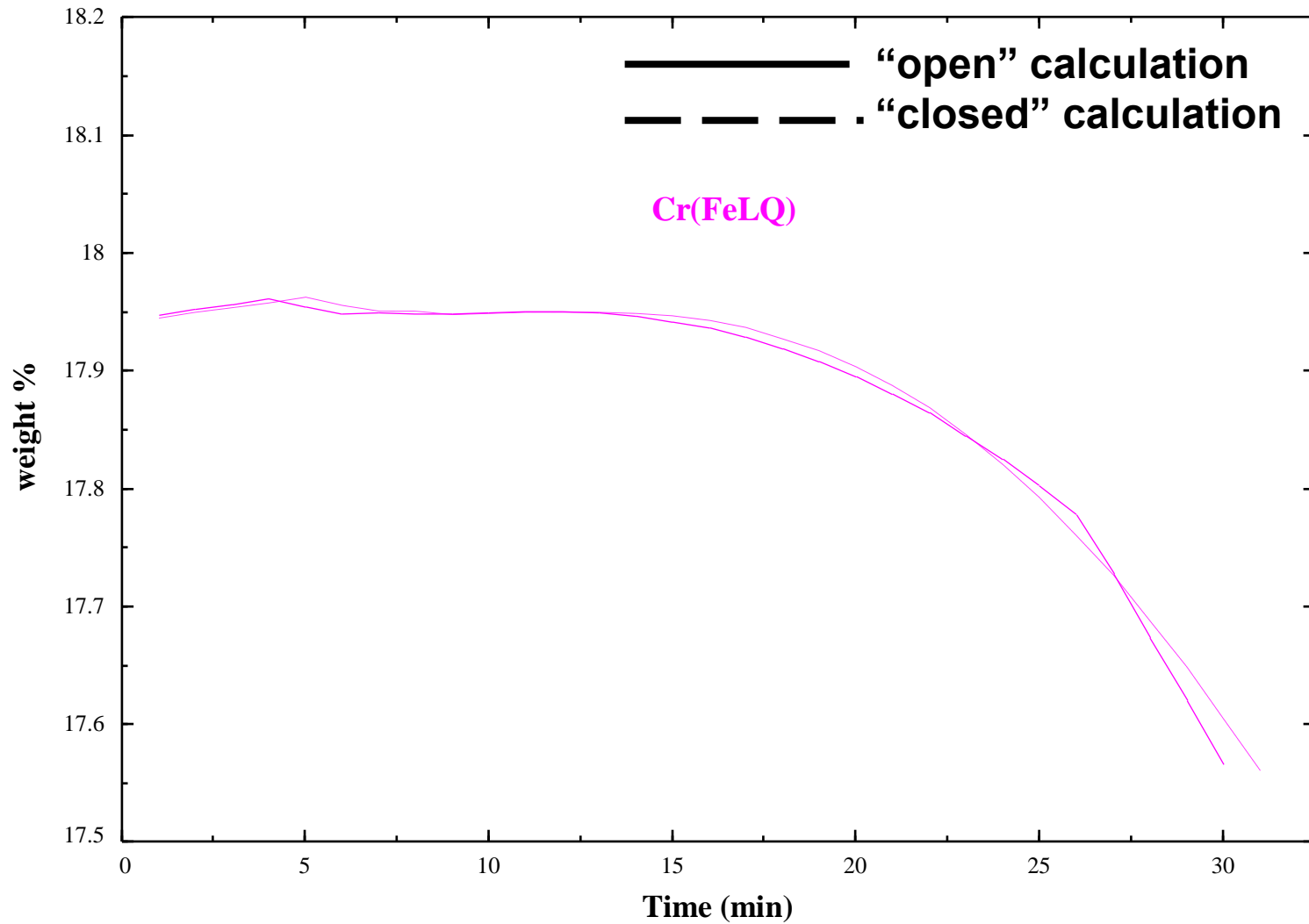


## Gas reaction comparison

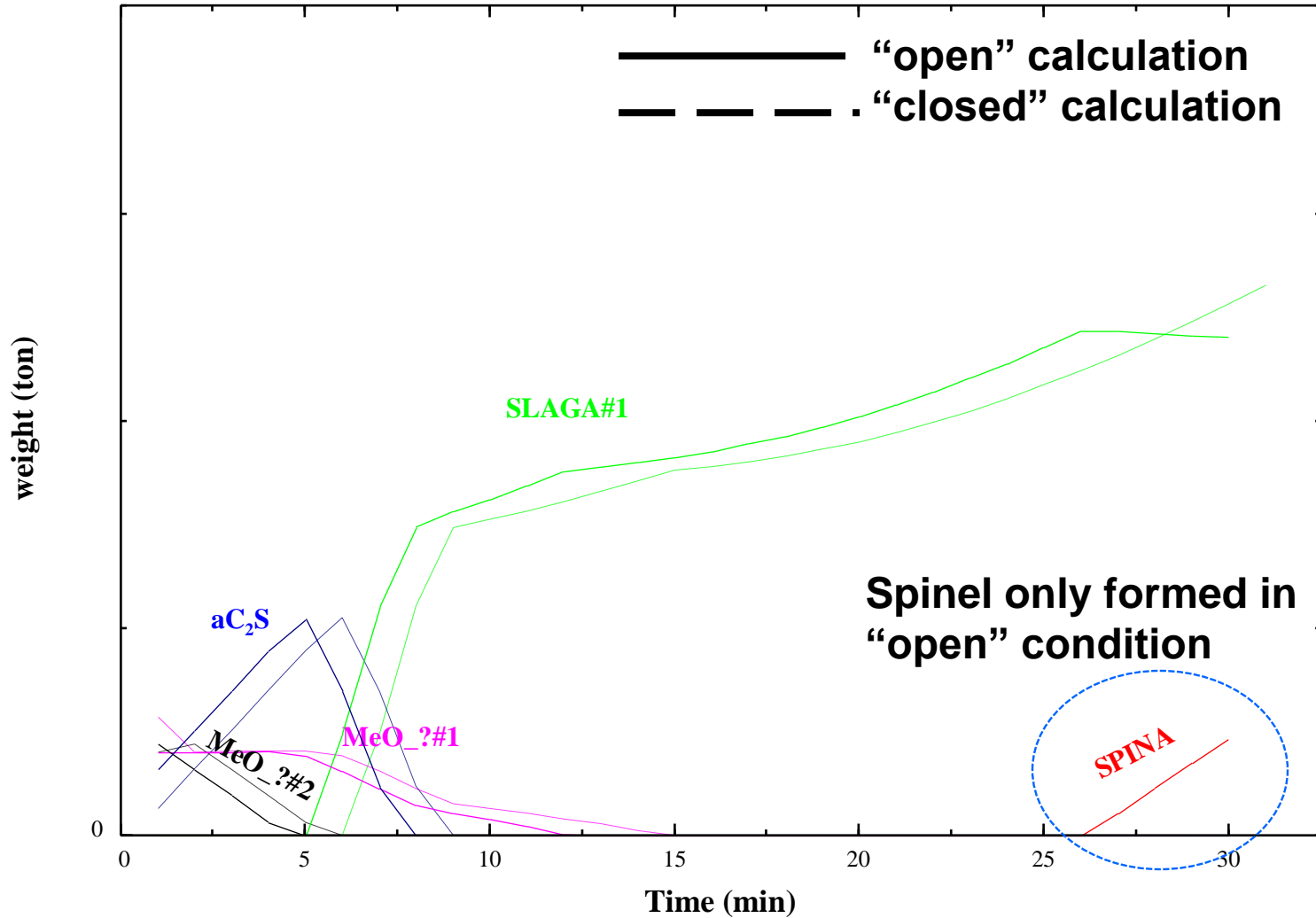




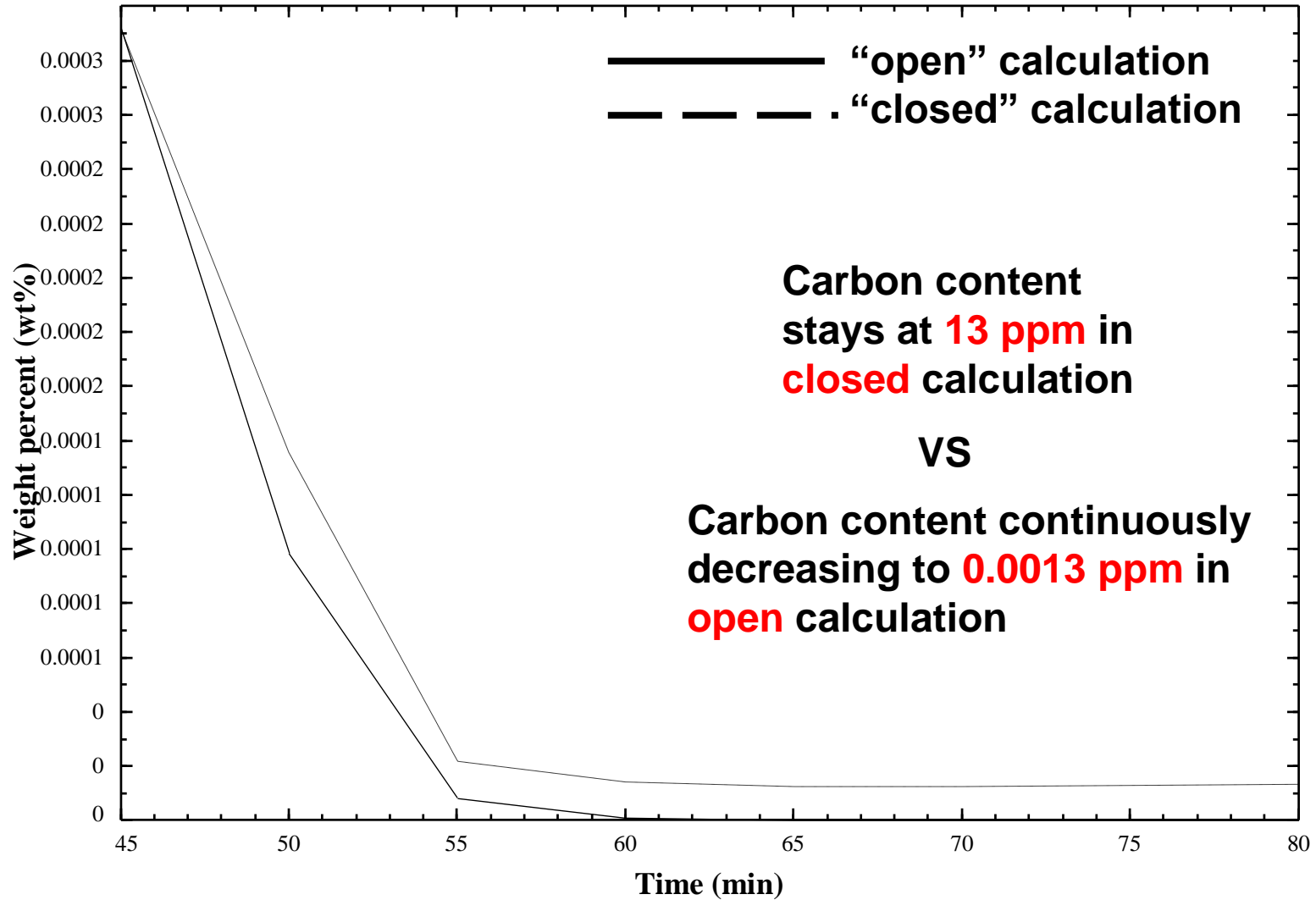
## Gas reaction comparison



# Gas reaction comparison



## [C] in the melt



### **From these two calculations,**

We can see significant difference in final carbon content in the melt.

Also, we found that even it is very small amount, it still has noticeable effect on phase equilibrium according to spinel phase



**For more accurate calculation, we need to consider gas phase equilibrium and it should be well defined by kinetic point of view and the activation energy for CO bubble forming is one of the important factor in estimation .**

## 6. Summary and Conclusion

## Summary

- VOD (Vacuum Oxygen Decarburization) is mainly for reducing Carbon, Nitrogen content and keep Cr content in the Liquid steel.
- Product quality from VOD is highly dependent on its vacuum condition, oxygen blowing rate, argon blowing rate(to reach equilibrium), fluxes, processing time.
- Melt, Slag compositions are well predicted by FactSage stream calculation.



## Conclusion

- Final composition estimations displayed quite reasonable result so that we can predict the final grade of molten steel from VOD process by using FactSage.
- From the result, we can track each compositions of slag by time. This help us to understand reactions in the VOD process and to develop better synthetic slag composition for reducing.
- Futher calculations with other elements such as phosphorous, sulfur and fluorides are possible.
- By understanding of slag composition changes, we can minimize dissolution amount from refractories.
- In terms of processing time, it could not show us good result, more work should be done for the kinetic part if we want get better result.

- Developing database which include sulfur, phosphorus,  $\text{CaF}_2$  in the slag and melt
- Calculation by using kinetic modeling program and FactSage at the same time
- Study economic aspects of VOD and process modification

## **Sincere thanks to**

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- Marie-Aline Van Ende
- Manas Paliwal
- Gabriel Garicia Curiel

and all of our group members

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Thank you for your attention!

Questions?