Distribution of Impurities in Magnesium via Silicothermic Reduction

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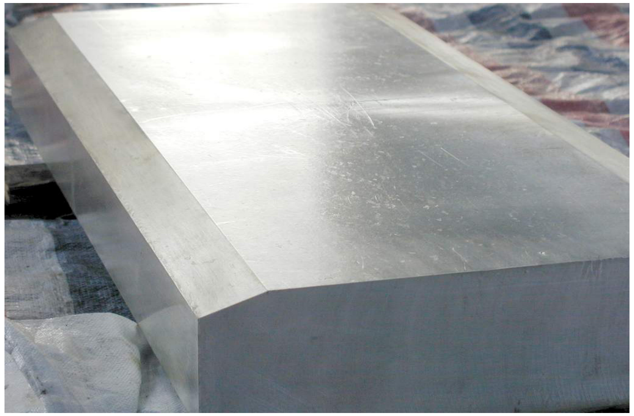
Introduction

- Magnesium has excellent properties
  - ☐ Lowest density of metal as constructional material (ρ_{Mg} = 1.74 g/cm^3; ρ_{Al} = 2.7 g/cm^3; ρ_{Fe} = 7.86 g/cm^3)
  - ☐ High specific strength: 158 kNm/kg
- Major usage of magnesium: Alloying element with Aluminium
- Purity requirement for 9980A Mg (ASTM B92):
  - ☐ Ca, Al, Si, and Fe: 0.05 wt% max
- Dominant processes:

Silicothermic:

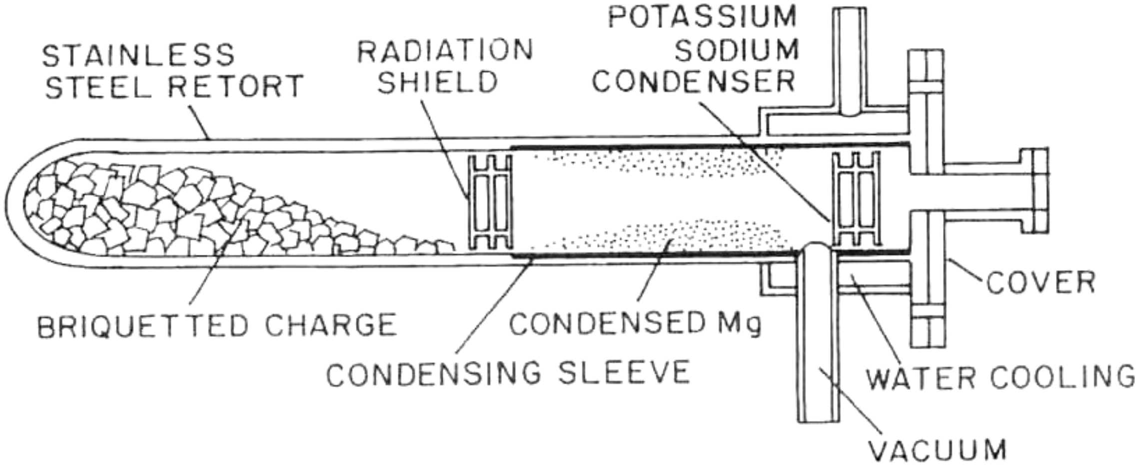
$$MgO + Si = Mg_{(g)} + SiO_2$$



Magnesium Ingot (Luoyang, China)

Pidgeon Process

Temperature = 1100-1200°C
Pressure = 10 – 67 Pa
Time = 8 hours



Kipouros & Sadoway (1987)

- Solid state reaction
- Low productivity
- Small batches

$$2CaO.MgO_{(s)} + Si.xFe_{(s)} = 2Mg_{(g)} + (CaO)_2SiO_{2(s)} + x.Fe_{(s)}$$

Bolzano Process: T ~ 1200°C, P < 400 Pa, vertical setup, internally heated

Magnetherm Process

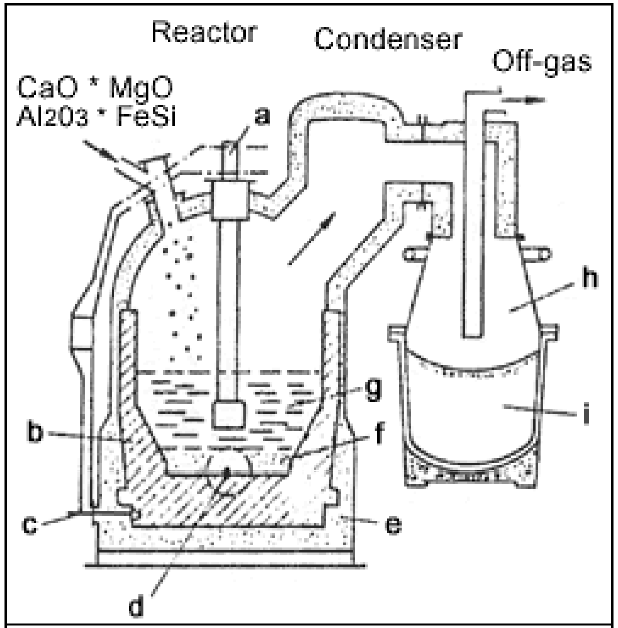
Temperature : 1550 - 1600°C
Pressure : 5 – 10 kPa

Liquid state reaction
(dicalcium silicate slag phase)

$$2\ (MgO) + Si = (SiO_2) + 2\ Mg_{(g)}$$

- Higher productivity than Pidgeon Process
- Disadvantage: air ingress during slag tapping

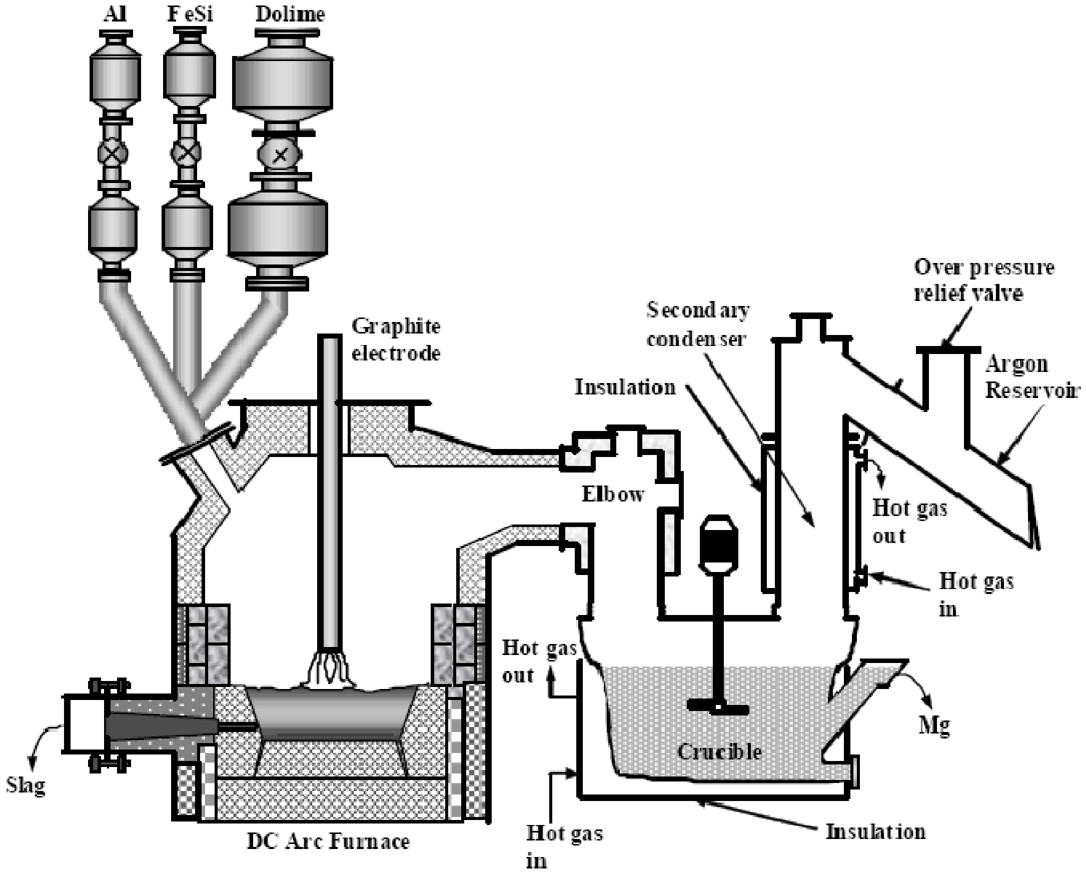
- Followed by Refining process



Magnetherm reactor
a) Copper electrode; b) Graphite lining;
c) Bottom electrode; d) Taphole;
e) Refractory; f) Low-grade FeSi; g) Slag
h) Condenser; i) Condenser crucible

Habashi (1997)

Mintek Process



Abdel-Latief, 2006

T = 1700-1750°C

P = atmospheric

- Calcium aluminate slag

- Continuous operation
- Liquid state reaction
- High productivity
- High impurities

Followed by refining process

Refining Stage

- Magnesium metal is remelted and stirred into flux containing $MgCl_2$ and KCl
- $MgCl_2 + Ca = Mg + CaCl_2$
- Mg loss during refining: 5-8%

Refining after Magnetherm process

Impurities	Initial	After Refining
Ca	0.77 – 1.05	0.005
Si	0.11 – 0.16	0.063
Al	0.037-0.088	< 0.05

Bowman (1986)

- In Mintek process, further refining process is carried out by the addition of $FeCl_3$ to remove silicon impurities.

Refining means higher production cost and less metal yield

Impurities of Commercial Magnesium

Operating Condition	Pidgeon	Magnetherm	Mintek
Pressure (atm)	$(0.66–0.6) \times 10^{-3}$	0.05-0.1 atm	~ 1 atm
Temperature (°C)	1100-1200	1550-1600	1700-1750
Productivity per furnace per day	50 kg	20 ton	100 ton
Indicated Impurities in Crude Magnesium (wt%)			
Al	0.004	0.01	0.066
Si	0.010	0.05	0.281
Ca	0.005	0.005	0.385
Fe	0.007	0.005	0.250

ASTM B92 Grade 9980A: 0.05% max each

Cradle to Gate of Mg Production Processes

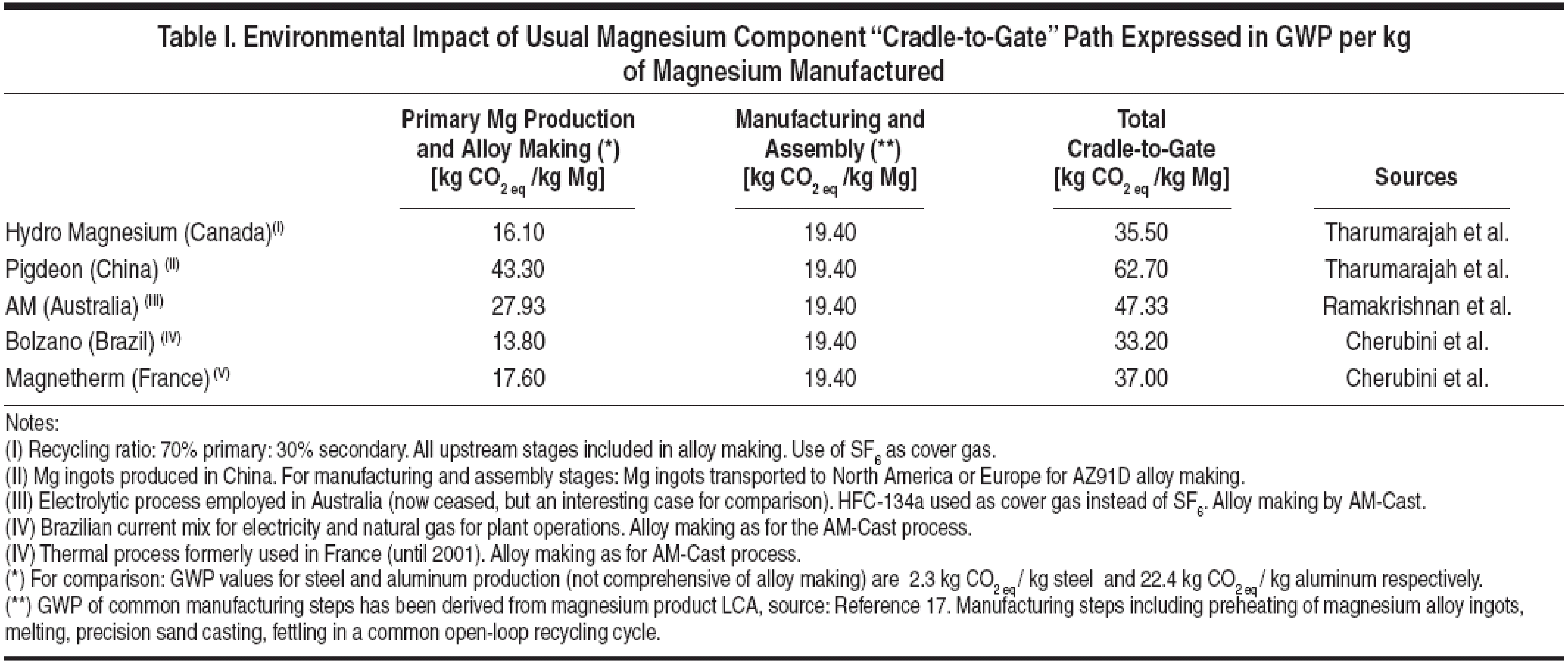


Table I. Environmental Impact of Usual Magnesium Component "Cradle-to-Gate" Path Expressed in GWP per kg of Magnesium Manufactured

	Primary Mg Production and Alloy Making (*) [kg $CO_{2\,eq}$ /kg Mg]	Manufacturing and Assembly (**) [kg $CO_{2\,eq}$ /kg Mg]	Total Cradle-to-Gate [kg $CO_{2\,eq}$ /kg Mg]	Sources
Hydro Magnesium (Canada)$^{(I)}$	16.10	19.40	35.50	Tharumarajah et al.
Pigdeon (China) $^{(II)}$	43.30	19.40	62.70	Tharumarajah et al.
AM (Australia) $^{(III)}$	27.93	19.40	47.33	Ramakrishnan et al.
Bolzano (Brazil) $^{(IV)}$	13.80	19.40	33.20	Cherubini et al.
Magnetherm (France) $^{(V)}$	17.60	19.40	37.00	Cherubini et al.

Notes:

(I) Recycling ratio: 70% primary: 30% secondary. All upstream stages included in alloy making. Use of SF_6 as cover gas.

(II) Mg ingots produced in China. For manufacturing and assembly stages: Mg ingots transported to North America or Europe for AZ91D alloy making.

(III) Electrolytic process employed in Australia (now ceased, but an interesting case for comparison). HFC-134a used as cover gas instead of SF_6. Alloy making by AM-Cast.

(IV) Brazilian current mix for electricity and natural gas for plant operations. Alloy making as for the AM-Cast process.

(IV) Thermal process formerly used in France (until 2001). Alloy making as for AM-Cast process.

(*) For comparison: GWP values for steel and aluminum production (not comprehensive of alloy making) are 2.3 kg $CO_{2\,eq}$ / kg steel and 22.4 kg $CO_{2\,eq}$ / kg aluminum respectively.

(**) GWP of common manufacturing steps has been derived from magnesium product LCA, source: Reference 17. Manufacturing steps including preheating of magnesium alloy ingots, melting, precision sand casting, fettling in a common open-loop recycling cycle.

Errico et al. (2009)

Present Study

Production of Mg with high purity and productivity?

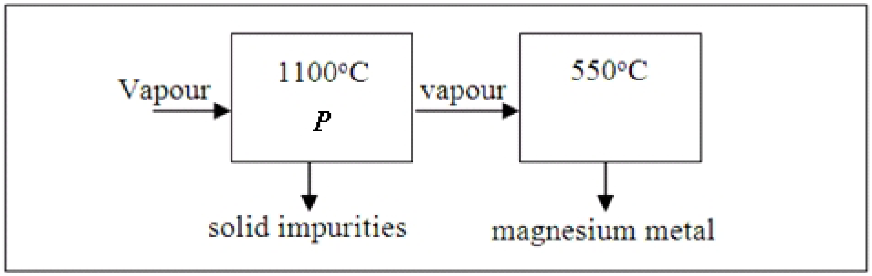
Approach of the present study:

- ☐ Thermodynamic modelling of silicothermic processes
  - ☐ Gibbs Energy Minimisation
  - ☐ Focusing on the behaviour of impurities and their distributions
- ☐ Experimental studies
- ☐ Development of thermodynamic database

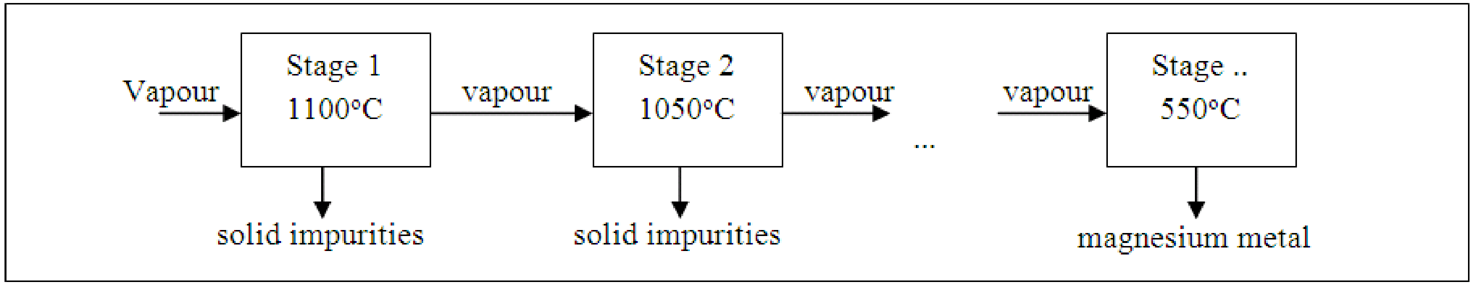
Present Study

Thermodynamic models

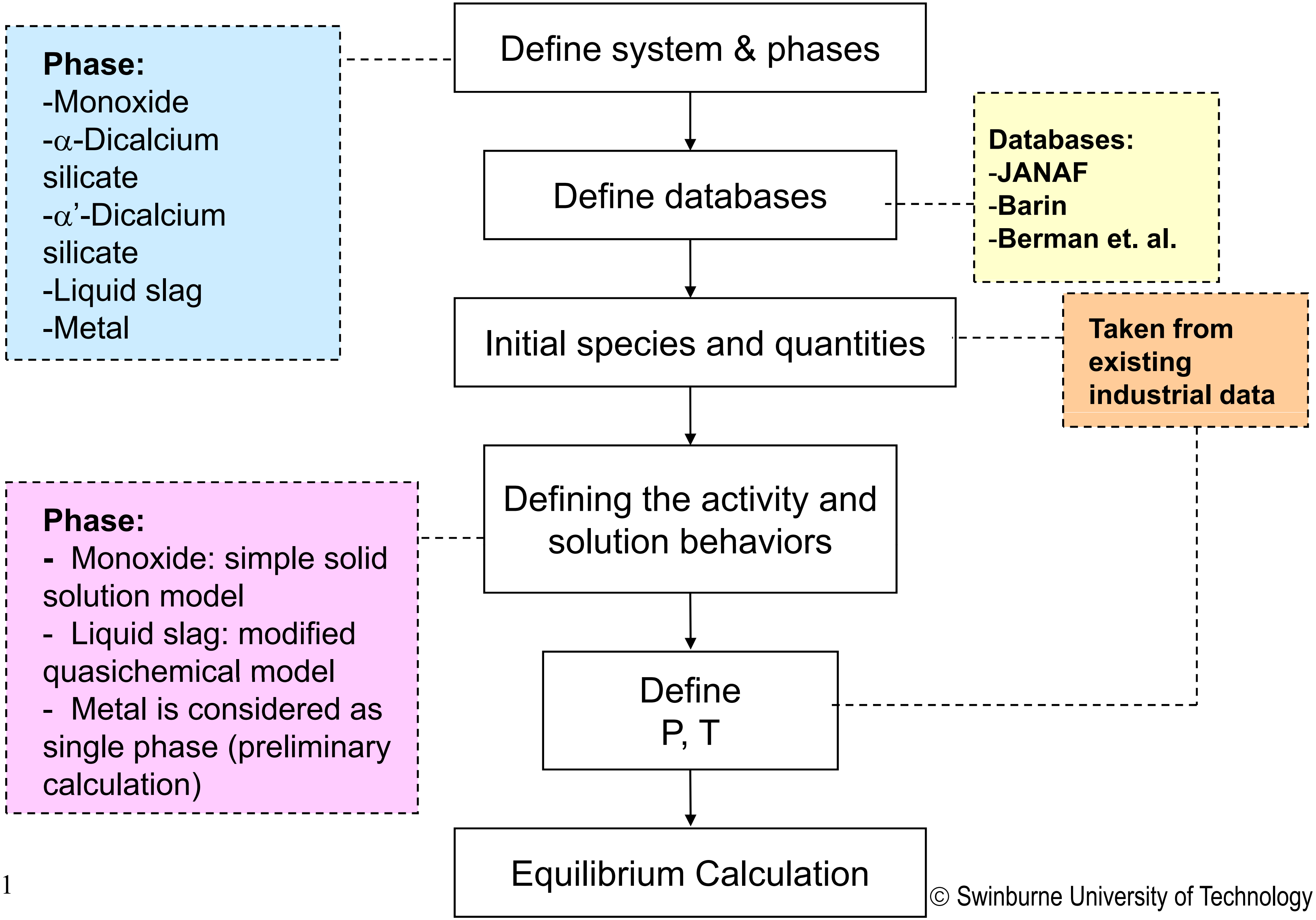
- Single-stage equilibrium model (MODEL I) to calculate the process in equilibrium at reaction stage and condensation stage.



- Multi-stage equilibrium model (MODEL 2) to investigate magnesium condensation process



Development of Equilibrium Model



Phase:
-Monoxide
-α-Dicalcium silicate
-α’-Dicalcium silicate
-Liquid slag
-Metal

Define system & phases

Define databases

Databases:
-JANAF
-Barin
-Berman et. al.

Initial species and quantities

Taken from existing industrial data

Defining the activity and solution behaviors

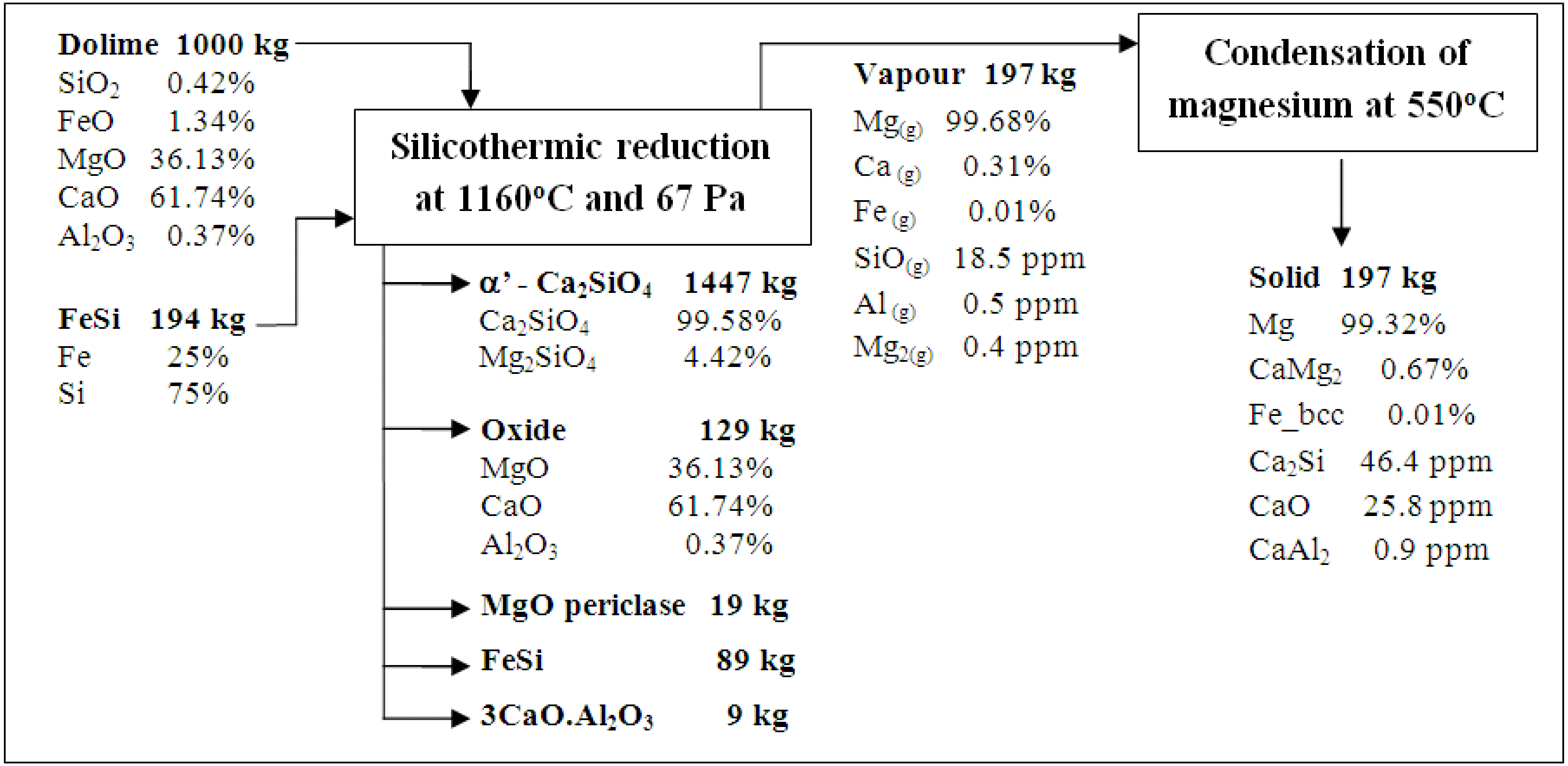
Phase:
- Monoxide: simple solid solution model
- Liquid slag: modified quasichemical model
- Metal is considered as single phase (preliminary calculation)

Define P, T

Equilibrium Calculation

Single-Stage Equilibrium Model – Pidgeon Process

Equilibrium calculation for the Pidgeon Process at 1160°C and 67 Pa



Dolime	**1000 kg**
SiO_2	0.42%
FeO	1.34%
MgO	36.13%
CaO	61.74%
Al_2O_3	0.37%

FeSi	**194 kg**
Fe	25%
Si	75%

Silicothermic reduction at 1160°C and 67 Pa

α' - Ca_2SiO_4	**1447 kg**
Ca_2SiO_4	99.58%
Mg_2SiO_4	4.42%

Oxide	**129 kg**
MgO	36.13%
CaO	61.74%
Al_2O_3	0.37%

MgO periclase	**19 kg**
FeSi	**89 kg**
$3CaO.Al_2O_3$	**9 kg**

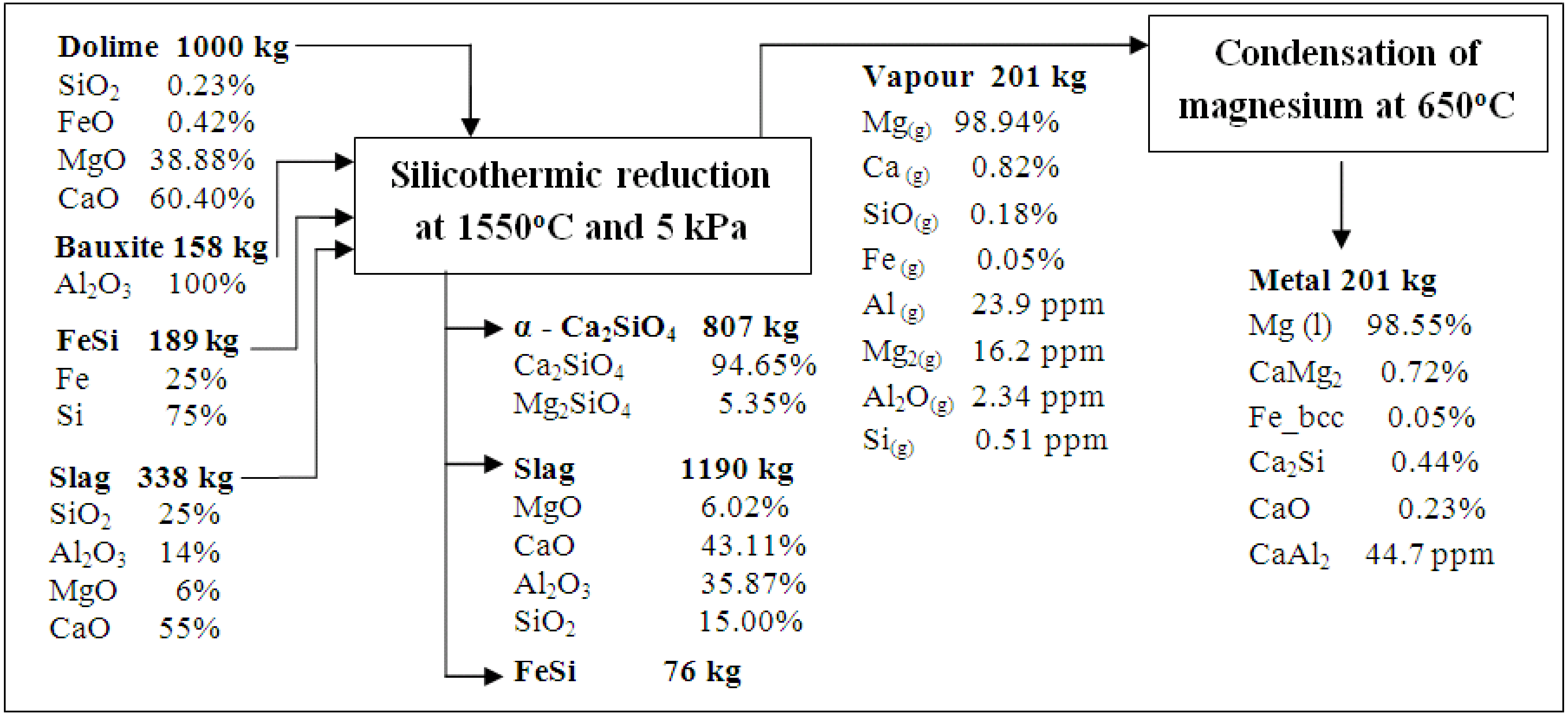
Vapour	**197 kg**
$Mg_{(g)}$	99.68%
$Ca_{(g)}$	0.31%
$Fe_{(g)}$	0.01%
$SiO_{(g)}$	18.5 ppm
$Al_{(g)}$	0.5 ppm
$Mg_{2(g)}$	0.4 ppm

Condensation of magnesium at 550°C

Solid	**197 kg**
Mg	99.32%
$CaMg_2$	0.67%
Fe_bcc	0.01%
Ca_2Si	46.4 ppm
CaO	25.8 ppm
$CaAl_2$	0.9 ppm

Single-Stage Equilibrium Model – Magnetherm

Equilibrium calculation for the Magnetherm Process at 1550°C and 5 kPa



Dolime 1000 kg

SiO_2	0.23%
FeO	0.42%
MgO	38.88%
CaO	60.40%

Bauxite 158 kg

Al_2O_3	100%

FeSi 189 kg

Fe	25%
Si	75%

Slag 338 kg

SiO_2	25%
Al_2O_3	14%
MgO	6%
CaO	55%

Silicothermic reduction at 1550°C and 5 kPa

α - Ca_2SiO_4 807 kg

Ca_2SiO_4	94.65%
Mg_2SiO_4	5.35%

Slag 1190 kg

MgO	6.02%
CaO	43.11%
Al_2O_3	35.87%
SiO_2	15.00%

FeSi 76 kg

Vapour 201 kg

$Mg_{(g)}$	98.94%
$Ca_{(g)}$	0.82%
$SiO_{(g)}$	0.18%
$Fe_{(g)}$	0.05%
$Al_{(g)}$	23.9 ppm
$Mg_{2(g)}$	16.2 ppm
$Al_2O_{(g)}$	2.34 ppm
$Si_{(g)}$	0.51 ppm

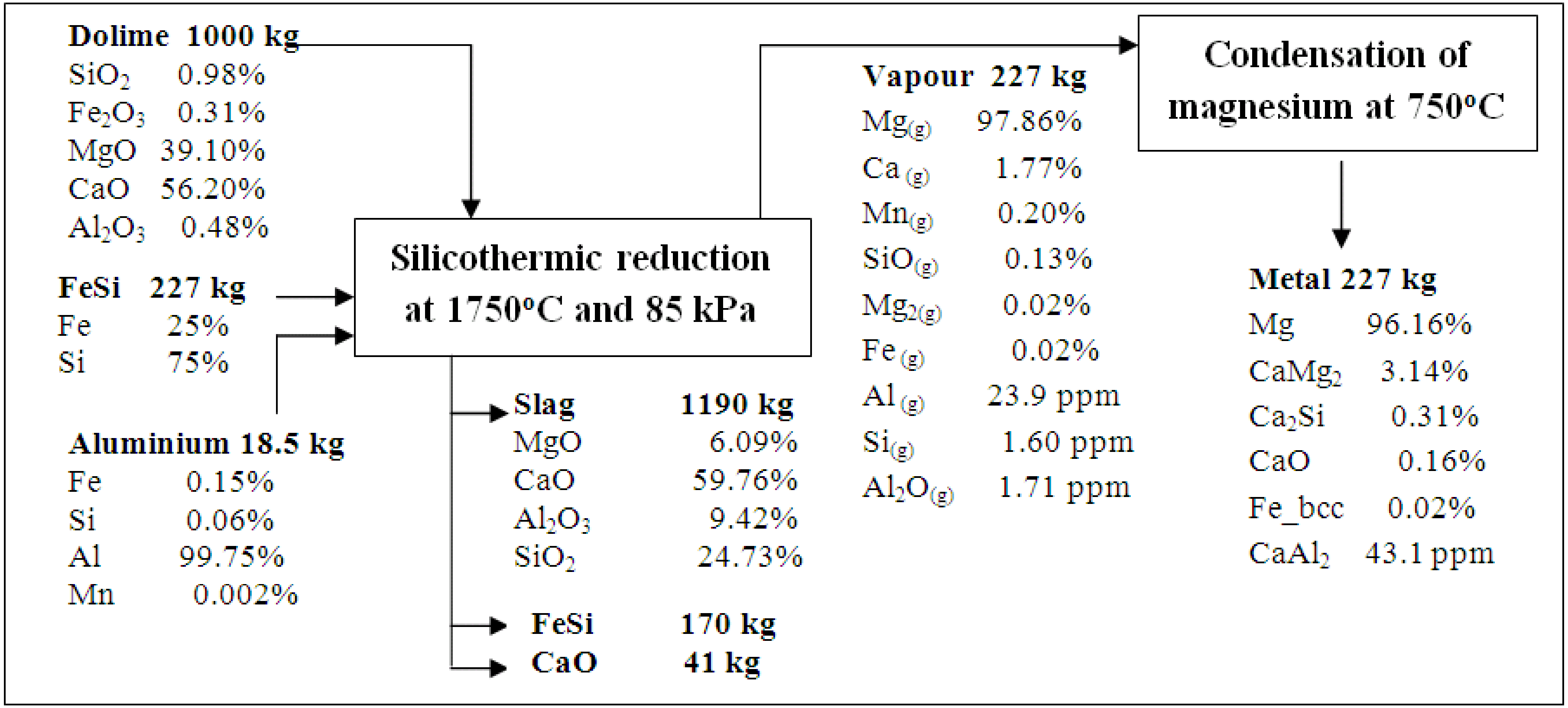
Condensation of magnesium at 650°C

Metal 201 kg

Mg (l)	98.55%
$CaMg_2$	0.72%
Fe_bcc	0.05%
Ca_2Si	0.44%
CaO	0.23%
$CaAl_2$	44.7 ppm

Single-Stage Equilibrium Model – Mintek Process

Equilibrium Calculation for the Mintek Process at 1750°C and 85 kPa



Dolime	**1000 kg**
SiO_2	0.98%
Fe_2O_3	0.31%
MgO	39.10%
CaO	56.20%
Al_2O_3	0.48%

FeSi	**227 kg**
Fe	25%
Si	75%

Aluminium	**18.5 kg**
Fe	0.15%
Si	0.06%
Al	99.75%
Mn	0.002%

Silicothermic reduction at 1750°C and 85 kPa

Slag	**1190 kg**
MgO	6.09%
CaO	59.76%
Al_2O_3	9.42%
SiO_2	24.73%

FeSi	**170 kg**
CaO	**41 kg**

Vapour	**227 kg**
$Mg_{(g)}$	97.86%
$Ca_{(g)}$	1.77%
$Mn_{(g)}$	0.20%
$SiO_{(g)}$	0.13%
$Mg_{2(g)}$	0.02%
$Fe_{(g)}$	0.02%
$Al_{(g)}$	23.9 ppm
$Si_{(g)}$	1.60 ppm
$Al_2O_{(g)}$	1.71 ppm

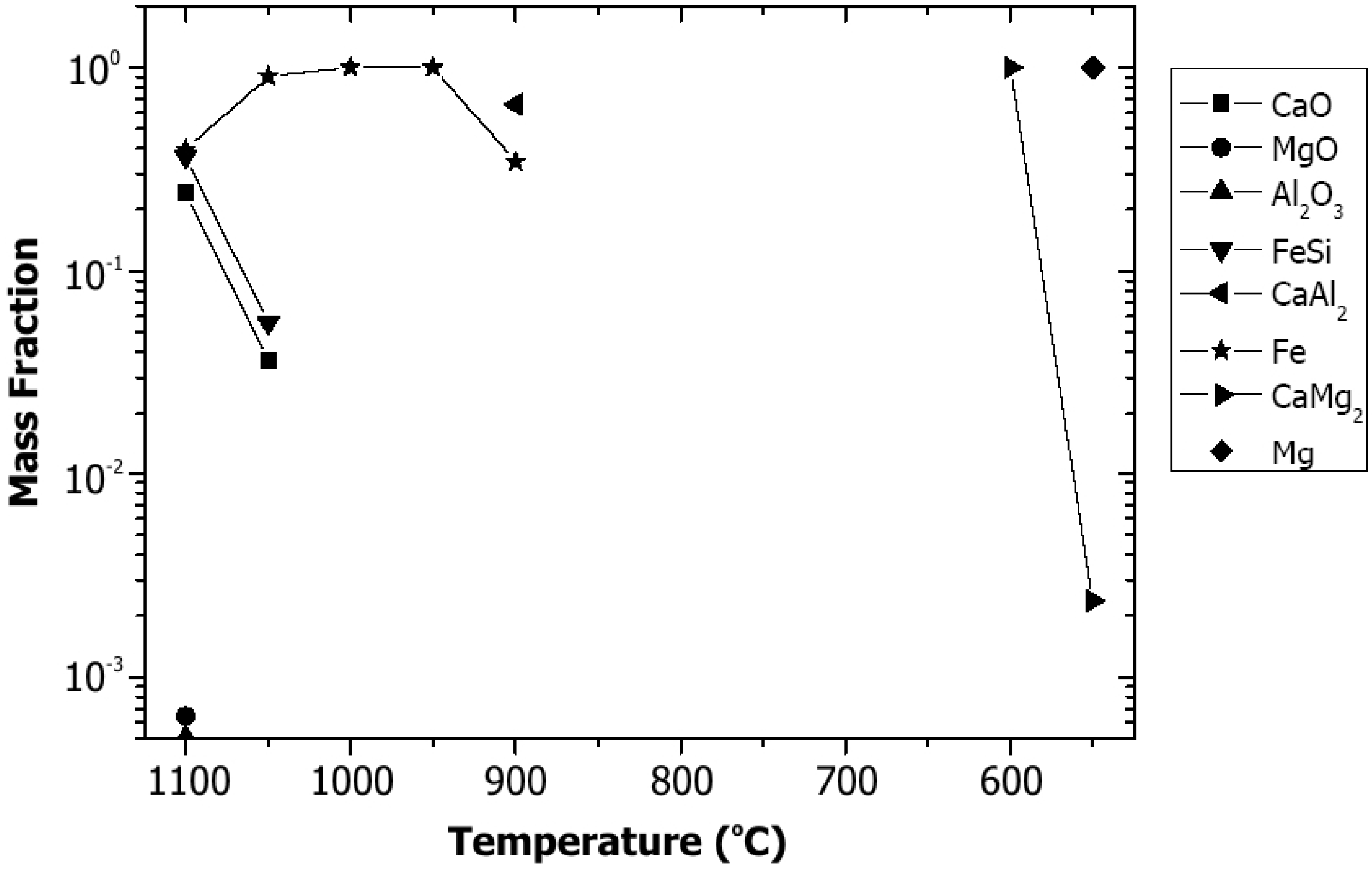
Condensation of magnesium at 750°C

Metal	**227 kg**
Mg	96.16%
$CaMg_2$	3.14%
Ca_2Si	0.31%
CaO	0.16%
Fe_bcc	0.02%
$CaAl_2$	43.1 ppm

- Formation of impurities from the main process:
  - ☐ $4\ CaO + Si = Ca_{(g)} + Ca_2SiO_4$
  - ☐ $Mg + SiO_2 = MgO + SiO_{(g)}$
  - ☐ Vaporization of volatilized materials: Mn, Pb, Zn (not included in the present thermodynamic modelling)

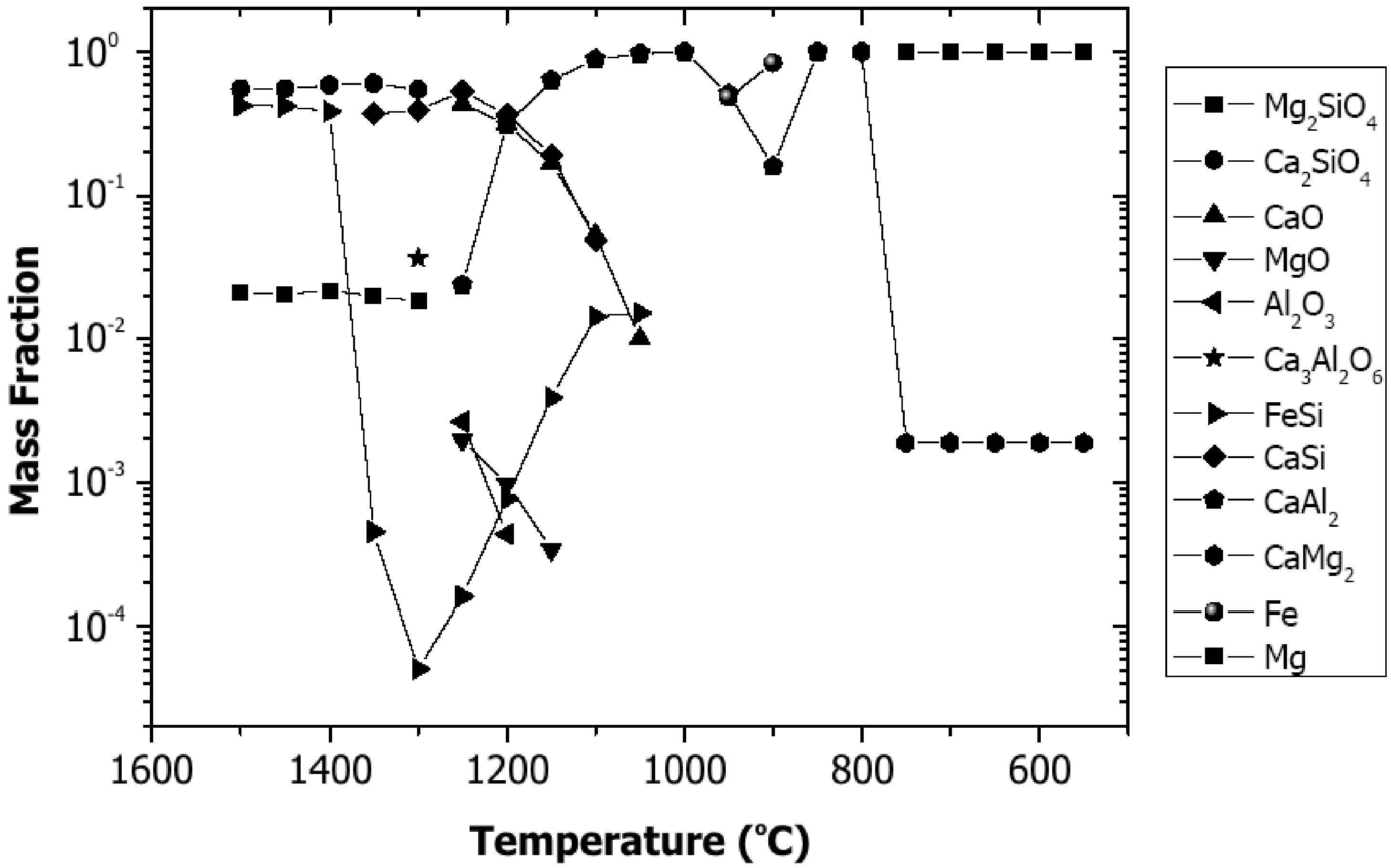
- Main impurities forming upon Mg condensation → Ca
  - ☐ Intermetallics: $CaMg_2$, Ca_2Si, $CaAl_2$
  - ☐ Oxides: CaO

Multi-Stage Equilibrium Model – Pidgeon Process



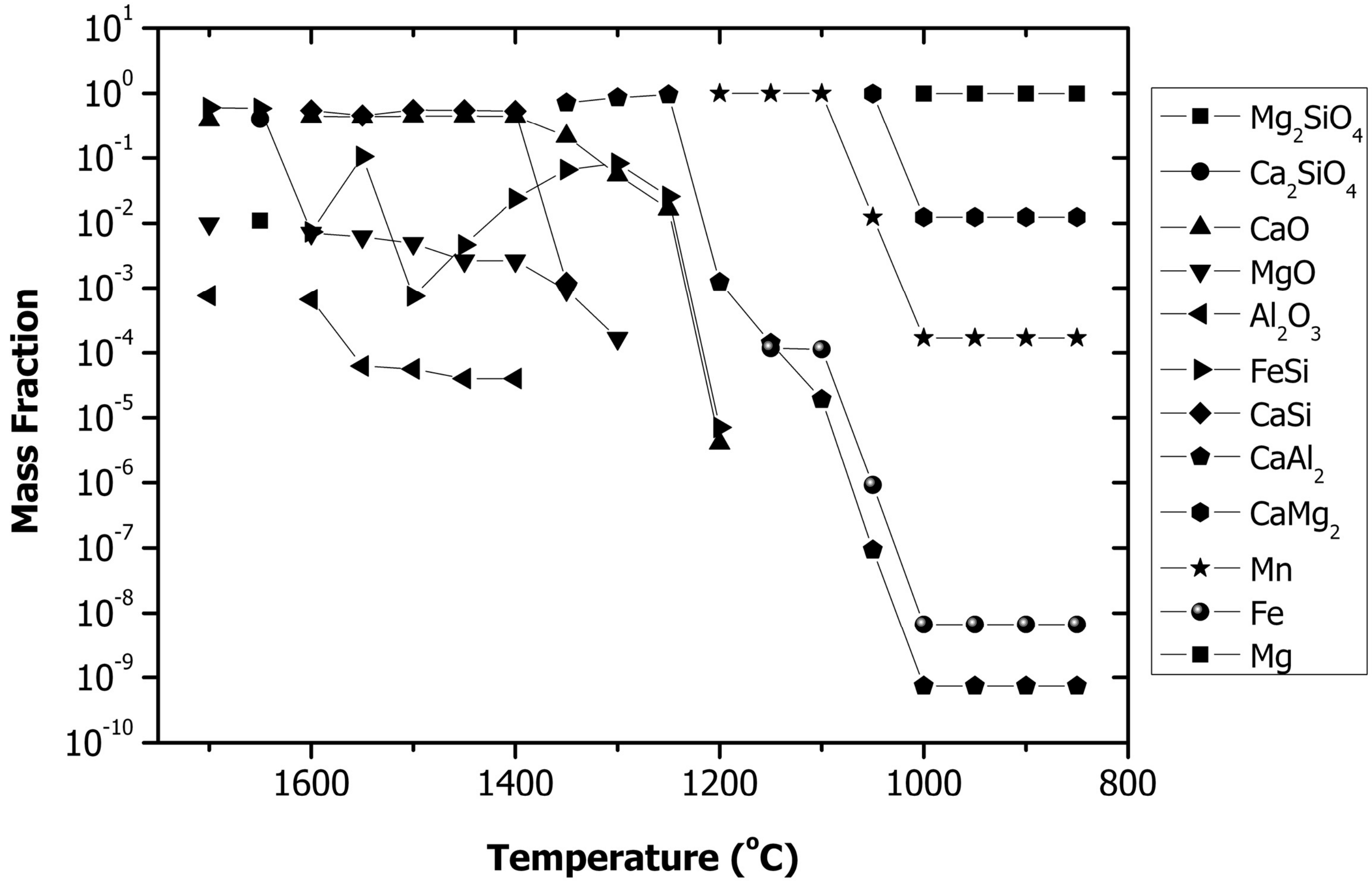
Mass fraction of solids precipitated from mixture of vapours produced from the Pidgeon Process

Multi-Stage Equilibrium Model – Magnetherm



Mass fraction of solids precipitated from mixture of vapours produced from the Magnetherm Process

Multi-Stage Equilibrium Model – Mintek Process



Mass fraction of solids precipitated from mixture of vapours produced from the Mintek Process

Magnesium and Impurities Content

	Pidgeon	**Magnetherm**	**Mintek**
Magnesium (wt%)			
Model 1	99.68	99.07	97.86
Model 2	99.89	99.92	99.42
Calcium (wt%)			
Model 1	0.31	0.82	1.77
Model 2	0.11	0.08	0.58
Model by [1]	-	0.44 – 1.11	-
Actual	0.002 – 0.06	0.77 – 1.05	0.03 – 0.385
Silicon (wt%)			
Model 1	0.002	0.11	0.08
Model 2	N.A	N.A.	N.A.
Model by [1]	-	0.44 – 1.19	-
Actual	0.03 – 0.07	0.11 – 0.16	0.1 – 1.1

Model 1: Single-stage Condensation

Model 2: Multi-stage Condensation

[1] Ritter & Sadoway, Light Metals 1988, pp. 799 - 805

Summary

The present thermodynamic modelling suggested that:

- Impurities in magnesium are in the form of metal oxides and intermetallics.
- By controlling the temperature, the major impurities can be precipitated before Mg condenses
    - Potentially, higher purity of Mg can be produced by designing suitable condenser

The present models do not give information on kinetics but provide the limits of the processes.

Further work: Refinement of thermodynamic modelling, experimental studies, development of thermodynamic database.