Production of High Purity Magnesium from Silicothermic Processes

Proposal Review

Winny Wulandari
Ph.D Student Commenced in May 2007
(Leave of Absence from 15/03/2008 to 16/06/2008)

Faculty of Engineering and Industrial Sciences
Supervisors: Prof. Geoff Brooks (SUT)
Dr. M. Akbar Rhamdhani (SUT)
Dr. Brian Monaghan (UW)

August 2008

SWINBURNE UNIVERSITY OF TECHNOLOGY

Outline

1. Background
2. Progress
   - Literature review (submitted June 25, 2008)
   - Research Issues
   - Thermodynamic Modelling of Pidgeon Process
   - Experimental Plan
3. Plan for the next stage

Background

- 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 Al
- Purity requirement for 9980A Mg (ASTM B92):
  - Ca, Al, Si, and Fe: 0.05 wt% max
- Dominant processes:

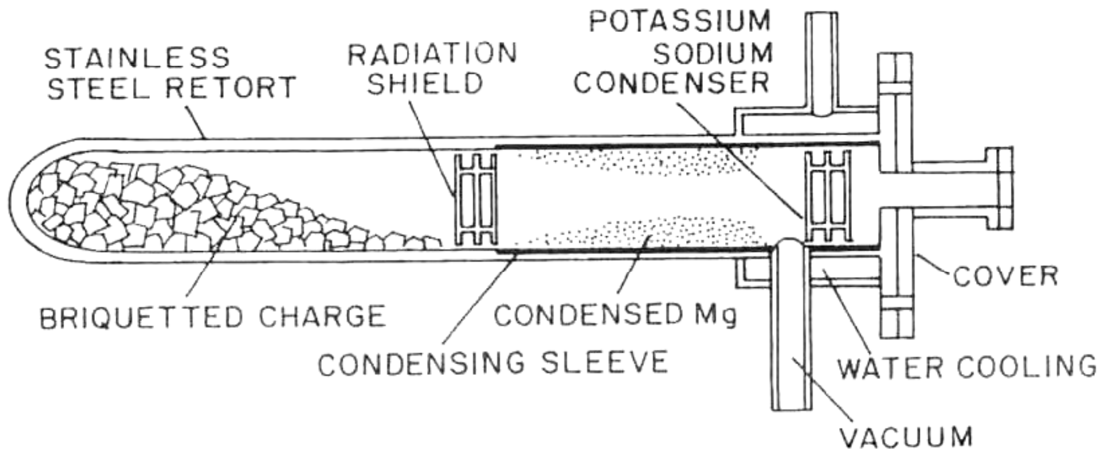
Silicothermic

Magnesium Ingot (Luoyang, China)

Pidgeon Process

T : 1100-1200^{o}C
P : 67-670 Pa
t : 8 hours

- Solid state reaction
- Low productivity
- Small batches

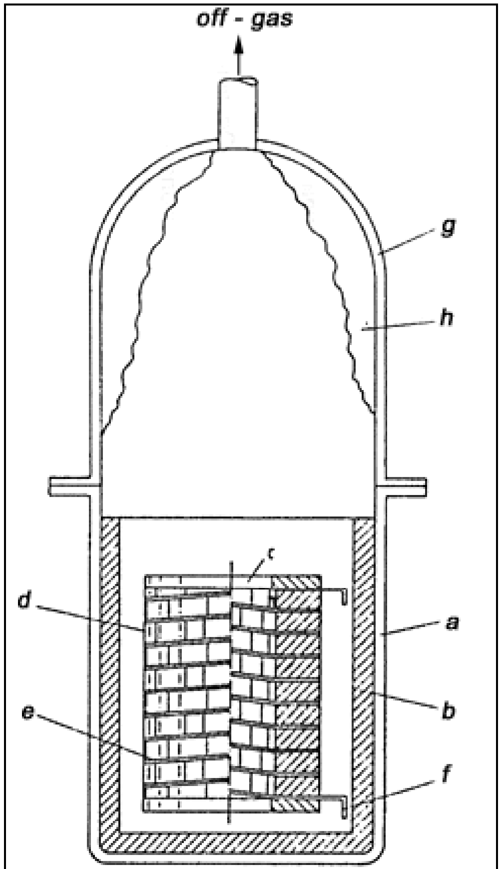


G.J. Kipouros, D.R. Sadoway., Advances in Molten Salt Chemistry., 1987

Reaction:

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

Bolzano Process



a) Steel mantel; b) Refractory;
c) Removable charge pack; d) Charge briquettes;
e) Charge support; f) Electric heating connection
g) Removable condenser; h) Condensed magnesium

F. Habashi: Handbook of Extractive Metallurgy, 1997, vol. 2

Temperature	: 1200°C
Pressure	: 400 Pa
time	: 20-24 hours

- Solid state reaction

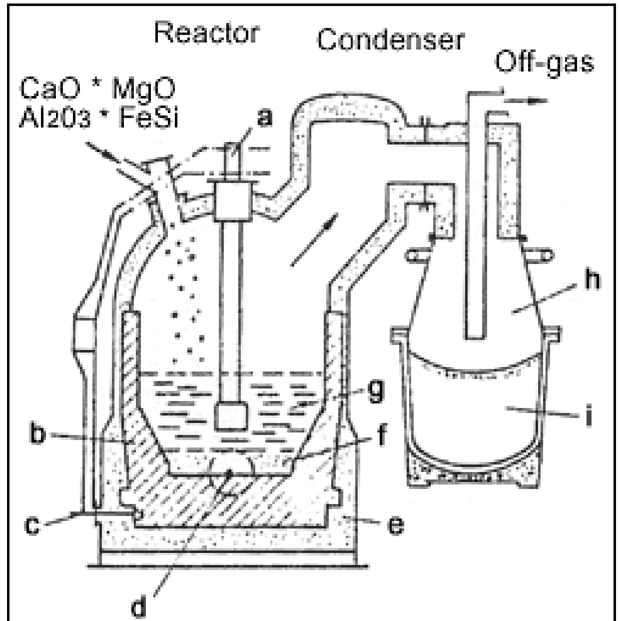
Magnetherm Process

Temperature : 1550 - 1600^{o}C
Pressure : 5 – 10 kPa

Liquid state reaction (dicalcium silicate slag phase, which consists of 58% CaO, 26.5% SiO_2, 11% Al_2O_3, and 4.5% MgO)

$$2MgO_{(l)} + Si_{(s)} = 2Mg_{(g)} + SiO_{2(s)}$$

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

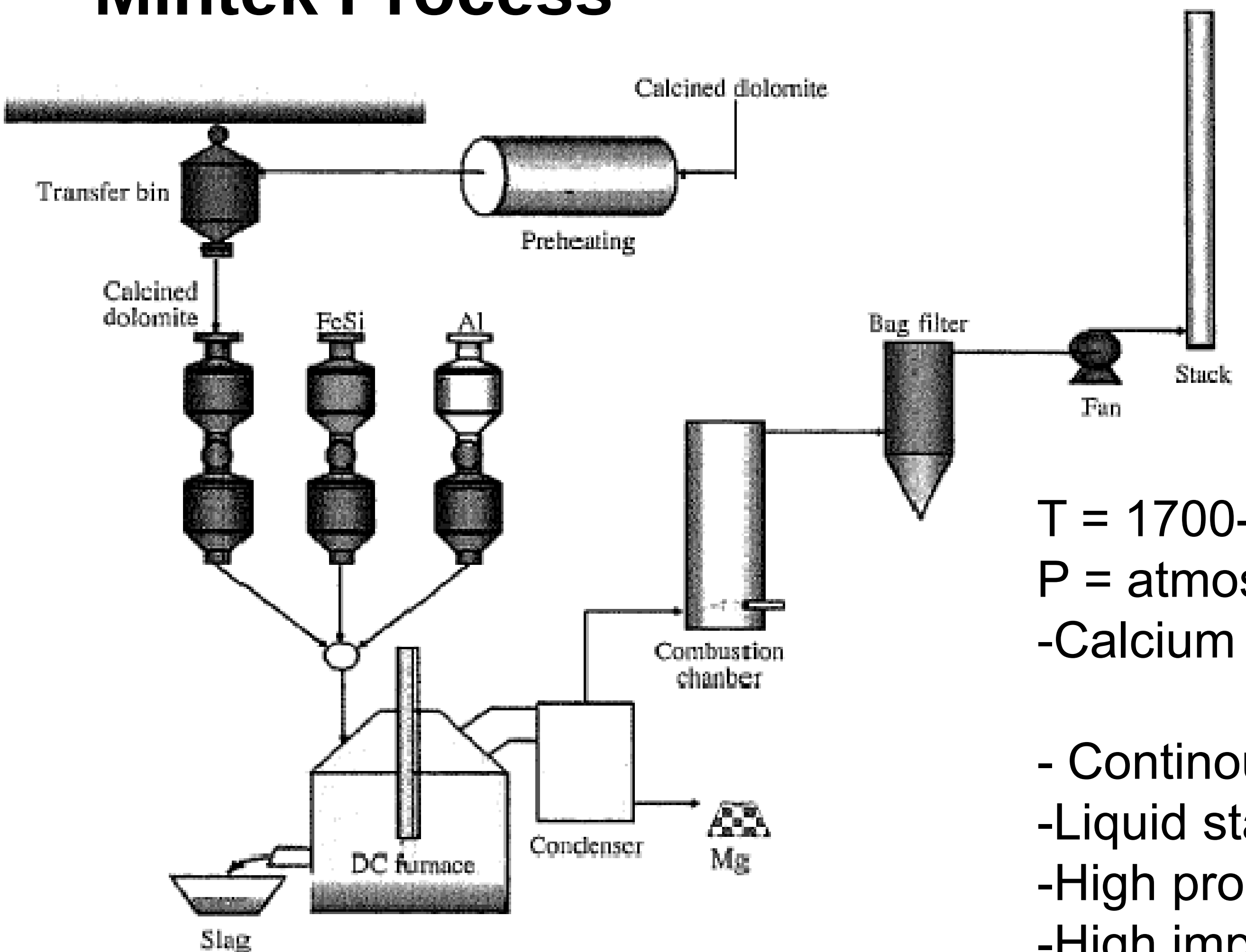


Magnetherm reactor

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

F. Habashi: Handbook of Extractive Metallurgy, 1997, vol. 2

Mintek Process



T = 1700-1750^{o}C
P = atmospheric
-Calcium aluminate slag

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

A.F.S Schoukens, M. Abdellatif, M.J Freeman,
Journal of The South African Institute of Mining and Metallurgy 2006

Impurities of Commercial Magnesium

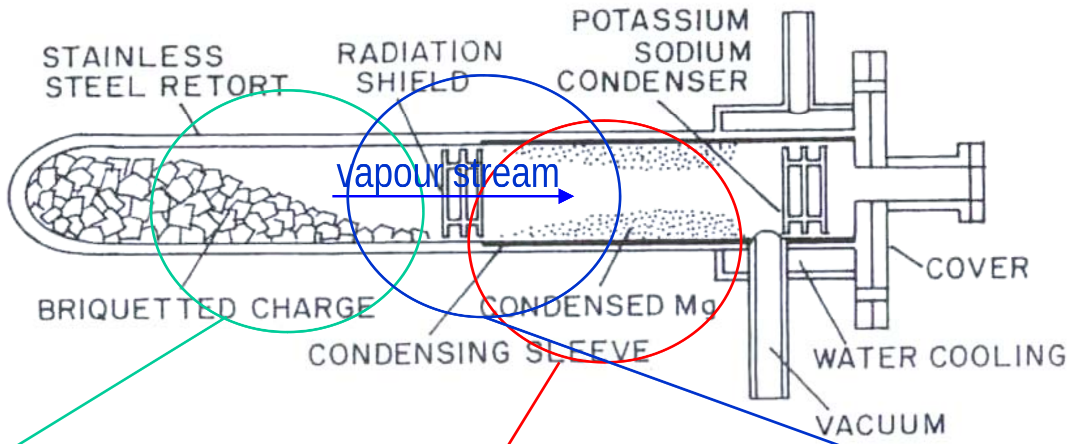
Operating Condition	Pidgeon	Magnetherm	Mintek	
Pressure (atm)	(0.66–0.6) x 10^{-3}	0.05-0.1 atm	~ 1 atm	
Temperature (^oC)	1100-1200	1550-1600	1700-1750	
Productivity per retort per day	50 kg	20 ton	100 ton	
Impurities	**Pidgeon**	**Magnetherm**	**Mintek**	
			Crude	**Clean**
Al	0.004	0.01	0.066	0.04
Si	0.010	0.05	0.281	0.095
Ca	0.005		0.385	0.023
Fe	0.007	0.005	0.25	0.047

ASTM B92 Grade 9980A: 0.05% max each

Objectives

- This project has aims to:
  - analyse the thermodynamic of silicothermic processes to determine the purity inside magnesium produced,
  - develop mathematical model to predict distribution of elements in these processes over a range of condition,
  - propose new operating condition for silicothermic route to obtain high purity magnesium, and
  - perform high temperature experiments to validate these predictions

Thermodynamic Modelling of Pidgeon Process



Model 1:
Equilibrium at
Reaction Temperature

Model 2:
Equilibrium at condensation
temperature by cooling
vapour stream

Model 3:
Multi-stage equilibrium model
during slow cooling
and remove solid impurities

Gibbs Energy Minimization

ΔG min $\rightarrow$ indicates a thermo-favoured process

$$G = \sum n_i G_i$$

$$G = \sum_{\substack{\text{ideal}\\\text{gas}}} n_i \left(G_i^o + RT \ln \frac{f_i}{P} \right) + \sum_{\substack{\text{pure}\\\text{condensed}\\\text{phases}}} n_i G_i^o$$

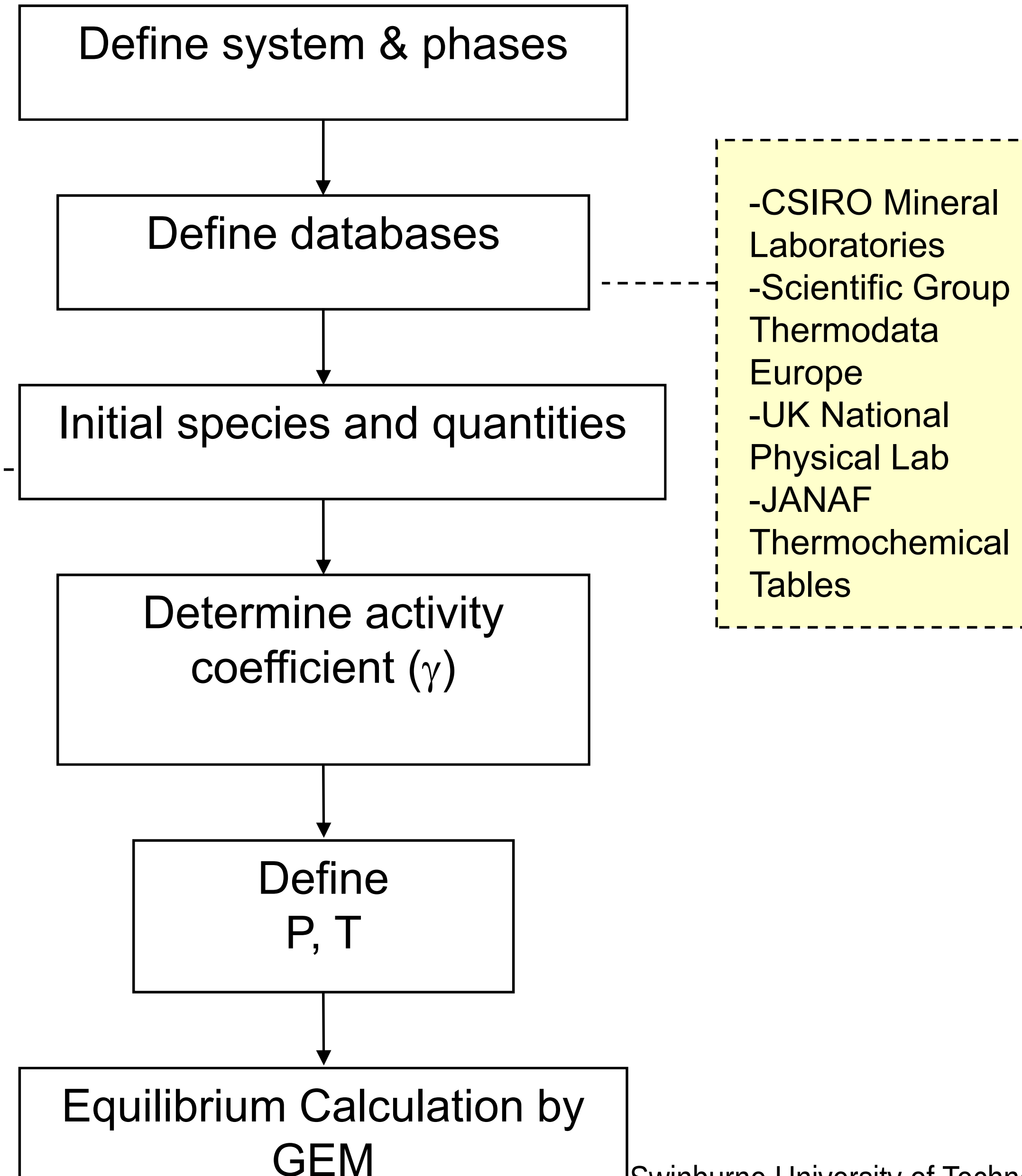
$$+ \sum_{\text{solution 1}} n_i \left(G_i^o + RT \ln X_i + RT \ln \gamma_i \right) +$$

$$\sum_{\text{solution 2}} n_i \left(G_i^o + RT \ln X_i + RT \ln \gamma_i \right) + \ldots + \ldots$$

Development of Equilibrium Model

Input (Toguri's data):

Calcined Dolomite		Ferrosilicon	
Constituent	%wt	Constituent	%wt
L.O.I	1.38	Fe	75
Insoluble	0.48	Si	25
R_2O_3	0.4		
CaO	57.5		
MgO	38.8		
Minor	1.44		
Calcined dolomite: 80.6%		Ferrosilicon: 16.8%	

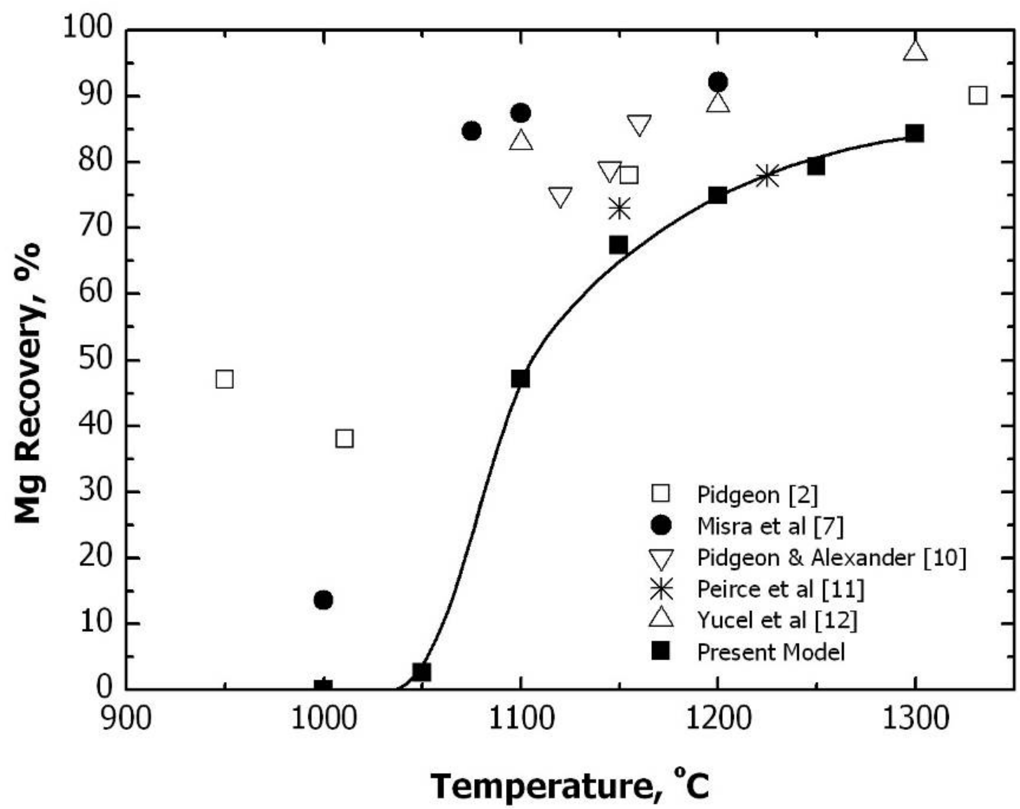


Result

Input:
$CaO.MgO_{(s)}$
$FeSi_{(s)}$

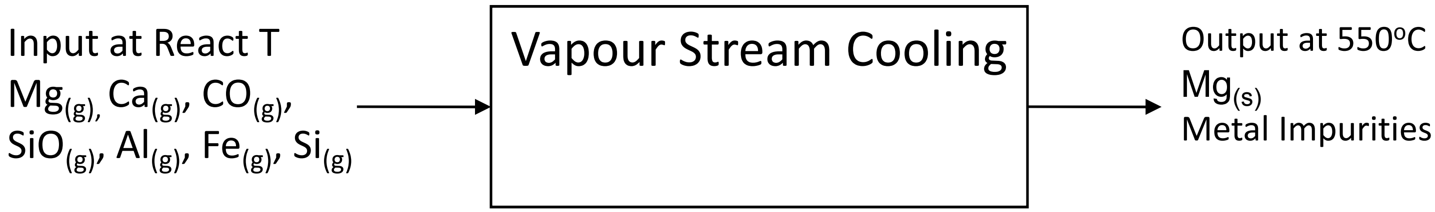
→ Equilibrium at Reaction Temperature →

T: Reaction Temp. (°C)
P: 0.66 mbar
Output: $Mg_{(g)}$, $MgO_{(s)}$, $CaO_{(s)}$, $FeSi_{(s)}$, $Ca_2SiO_{4(s)}$



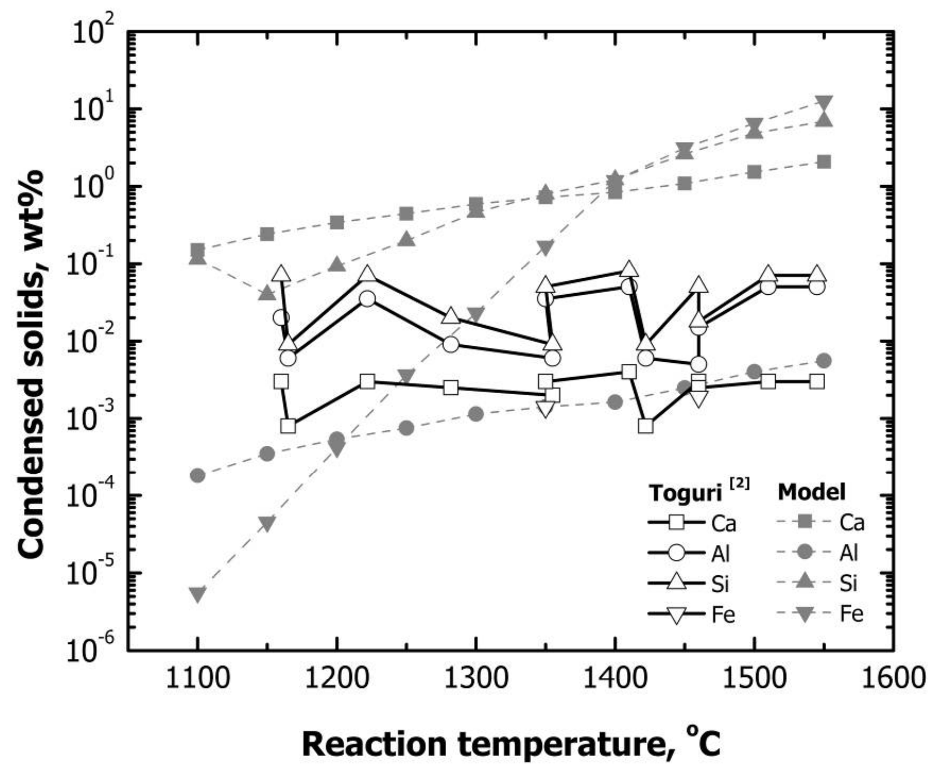
Variation of magnesium recovery with temperature;

the closed squares are the results from the present thermodynamic modeling

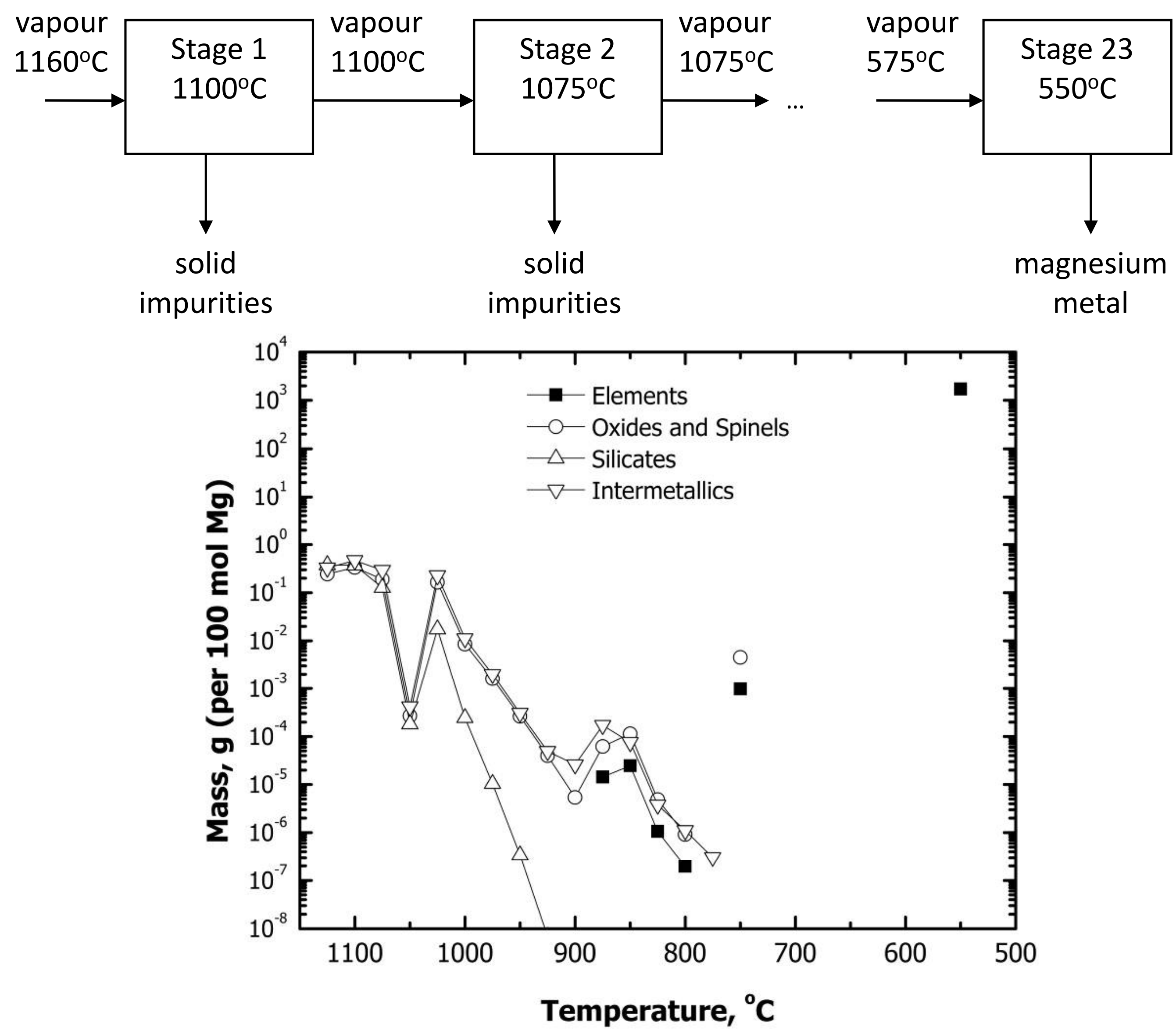


Mg vapour at 1160°C contains 99.64% Mg, 0.26% Ca, 0.02% CO, and 0.08% SiO

Metal impurities are formed in mixtures of metal oxides (CaO & MgO) and intermetallic ($CaAl_2$, Mg_2Si, and CaSi)



Comparison between the impurities in magnesium vapour (from current modeling) and the impurities in the magnesium solid (data by Toguri: Toguri, J.M and L.M.Pidgeon; Can. J. Chem, 1962, vol.42, pp. 1769-1776)



The precipitated solids from mixture of magnesium vapour produced from reaction at 1160°C at step cooling of 25°C determined from the current thermodynamic modelling.

Summary

- Equilibrium model predicts the minimum limit of magnesium produced over a range of temperature
- Metal impurities in magnesium are formed in metal oxide and intermetallic. This should be validated when experiment is conducted.
- The significant solid impurities are condensed in at 950^{o}C (before condensation temperature of magnesium).
- If there a way to separate solid impurities from magnesium vapour before it condenses, high purity magnesium can be obtained

Presentations, Papers

- “Modelling of Thermal Magnesium Processes”, University of Wollongong (July 19, 2007)
- “Equilibria among Metals, Slag, and Gas Phases in the Magnetherm Process”, High Temperature Processing Group Meeting (Feb 12, 2008)

- Paper titled “Thermodynamic Modelling of Magnesium Production through Pidgeon Process” is being prepared to be submitted to Metallurgical and Materials Transaction B.
- Abstract titled “Distribution of Impurities in Magnesium Production via Silicothermic Method” is submitted to European Metallurgical Conference 2009.

Plan for the next stage

- Second year:
  - Preparing experiment plan and experiment design and learning material characterization (currently underway, July – August 2008),
  - Conducting preliminary experiment as well as learning experimental and material characterization techniques (August – December 2008),
  - Starting experiment, with aim to perform reduction of CaO.MgO with ferrosilicon (November 2008 – April 2009), and
  - Develop thermodynamic modelling of the Magnetherm and Mintek Process (September-December 2008).
  - Designing condensation system (January-June 2009),
- Third year:
  - Writing papers about thermodynamic modeling and experimental results
  - Completing thesis writing

Thank You