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# Distribution of impurities in magnesium via silicothermic reduction

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## Abstract

The desire for light weight materials, particularly in the automotive field, is fuelling greater magnesium production. The Pidgeon process is currently the most widely used process for the production of magnesium. This batch process involves reduction of dolomite by ferro-silicon, carried out at temperature between 1100-1200°C under vacuum in a retort, producing magnesium vapour which is then cooled and collected as a condensate. The major attractions of the process are its simplicity and low capital cost; however, the process is also labour and energy intensive. The Magnetherm process is also a vacuum batch process based on similar chemistry but operates at higher temperatures with magnesia dissolved in a slag. Various operational issues relating to the batch and vacuum nature of the process have limited its development. Higher temperatures will improve the kinetics of the silicothermic reduction but will also promote greater impurities into the vapour. Thermodynamic analysis of the distribution of impurities during condensation of magnesium vapour has been carried using FactSage thermodynamic package. The results from the multi-stage equilibrium model show that at equilibrium it should be possible to condense solid impurities before the majority of the magnesium vapour is condensed below 750°C, depending on the operating pressure of the system and the particular chemistry of the process. The model predicts that purities above 99.8wt% can be achieved for the Pidgeon process and 99.4wt% for the Mintek process. Without multi-stage condensation, the impurities in the metal are predicted to be significantly higher for the Mintek process (2.14wt% compared to 0.6 wt%). These results are broadly consistent with existing industrial data.

## 1 Introduction

Magnesium has a density of 1700 kg/m<sup>3</sup>, which is two-thirds and one-sixth of the density of aluminium and steel, respectively. Its wide application in automotive and construction purposes has promoted an increase in magnesium consumption in recent years [1]. The dominant process to extract magnesium from its ores is the Pidgeon process where the magnesium is reduced from dolomite



through silicothermic reaction at moderate temperature. The process has dominated the production of magnesium in the world the last ten years with the proportion of almost 70% of the total magnesium produced [2]. The main advantage of this process is the simplicity of the process and the high purity of the magnesium produced. Other silicothermic processes include the Magnetherm and the Mintek process. Table 1 shows the differences between the three different silicothermic processes, in terms of operating conditions and the level of impurities produced. The higher temperature and atmospheric pressure as in the Mintek process operating condition lead to higher productivity of magnesium, but also leads to lower purity magnesium metal.

Table 1: Silicothermic process operating condition and impurities

	Pidgeon [3, 4]	Magnetherm [5-7]	Mintek [8, 9]
Operating Conditions			
Pressure	10 – 67 Pa	5 kPa	0.1 MPa
Temperature (°C)	1100 – 1200	1550 – 1600	1700 – 1750
Productivity per furnace per day	50 kg	20 ton	100 ton
Indicated impurities in crude magnesium, (in 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

In this paper, the process production of magnesium metal through silicothermic processes and the associated impurities in magnesium metal will be reviewed. There is only limited work published on the thermodynamics of magnesium condensation [10-12]. The work of Cameron *et al.* [11] and Brooks *et al.* [12] focused on the carbothermic route and not the silicothermic route. In this study, we calculated the composition of condensates using Gibbs energy minimisation to predict the species and compounds in the system at equilibrium, as a means of analysing the potential for producing high purity magnesium from a silicothermic process.

## 2 Overview of silicothermic processes

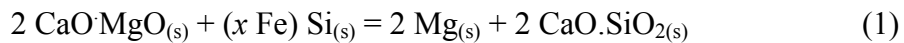
Silicothermic process involves a reduction reaction of magnesia or dolomite by silicon in the form of ferrosilicon to produce magnesium vapour which is then condensed in a condenser as magnesium solid metal. The detail of the processes, focusing on the thermochemistry of each process is explained in the following sub-sections.

### 2.1 The Pidgeon process

The raw materials for the Pidgeon process are calcined dolomite (CaO·MgO) and ferrosilicon (Fe-75wt% Si). The calcined dolomite and ferrosilicon are mixed and briquetted to improve the rates of heat transfer and the solid-state reaction. The briquettes are located inside a horizontal Ni-Cr



stainless-steel retort as shown in Figure 1 and the reduction is carried out at the operating conditions. The reaction of the Pidgeon process can be written as:



The magnesium vapour evolved from Reaction (1) is condensed on a removable sleeve in the throat of the retort [4]. Magnesium deposit is collected as a dense “crown” [3].

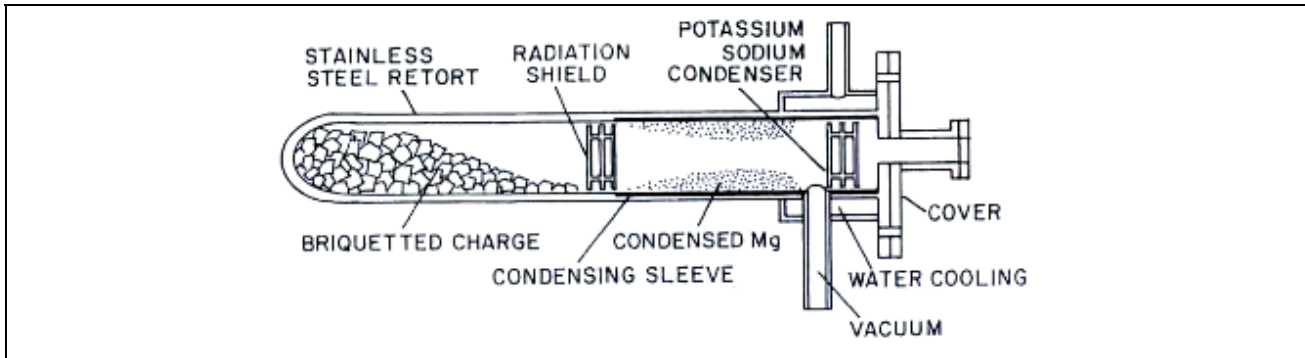


Figure 1: Schematic of the Pidgeon process retort [13]

Table 2: Reported impurities of the Magnesium produced from the Pidgeon process (in wt%)

Impurities	Laboratory scale [14]	Pilot Plant Scale [3]	Plant Scale [4]
Fe		0.002	0.003
Ni	0.002	< 0.001	< 0.005
Cu	0.0002	0.002	0.005
Si	0.07	0.003	0.008
Al	0.02	< 0.007	
Mn		< 0.001	0.001
Na		< 0.0005	< 0.005
Pb	0.06		
Ca	0.003		
Sn	0.002		
Zn	0.03		

Pidgeon and King [15] has measured the equilibrium vapour pressure of magnesium in Reaction (1) and reported a value of 1346 Pa at 1100°C. The magnesium vapour produced in the reaction zone is removed by applying low pressures of the order of 6 to 67 Pa. At these operating conditions, the major species in gas phase is magnesium; while the other species such as calcium oxide, magnesium oxide, silicon, and dicalcium silicates, have very low concentrations.

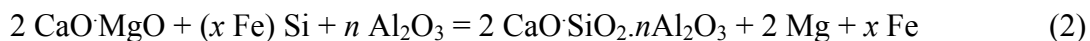
Table 2 provides data on the impurities of magnesium metal produced via the Pidgeon process. Some metal impurities such as Ni, Cu, Pb, Sn, Mn, and Zn come from volatilization of the oxide impurities in dolomite [3]. The amount and the composition of these impurities depend on the composition of starting materials. It can be seen that the Pidgeon process can produce magnesium with a very low level of impurity (>99.9 wt%). Post-oxidation of magnesium is often the major concern with impurities and not the intermetallic elements [16]. However, this process is labour intensive



and has low productivity [17] and there has been significant recent research on developing new process routes to magnesium [9, 12, 18].

## 2.2 The Magnetherm process

The development of thermal reduction of magnesium (which leads to the development of the Magnetherm process) began in France in 1948 [5] and continued production into the 1990s [19]. However, at present no industrial plant is operational. The process differs from the Pidgeon process in a number of ways [20]. The reduction is carried out in a liquid state, i.e. from a molten slag bath. Alumina/bauxite is used as a flux to form silico-aluminate slag, and the magnesium vapour produced is condensed to liquid state, before it is sent for refining. The main starting materials for production of magnesium at the Beudeant plant [5] using this process were calcined dolomite, ferro-silicon, and bauxite. The Magnetherm process involves a silicothermic reduction of MgO from the calcined dolomite (CaO.MgO) from a molten slag bath according the following overall reaction:



The process is operated at temperature of 1550°C and pressure of 5 kPa inside an electric arc furnace, as shown in Figure 2. The slag composition is maintained at 55 wt% of CaO, 25 wt% of SiO<sub>2</sub>, 14 wt% of Al<sub>2</sub>O<sub>3</sub>, and 6 wt% of MgO. At the operating temperature, the slag system is not fully molten, with 40% in the form of solid of dicalcium silicate (2CaO.SiO<sub>2</sub>) [6].

The simplified silicothermic reduction can be written as:



where ( ) refers to the component being dissolved in the molten slag. The key to this process is to promote a low silica activity in the liquid slag and maintain the composition of the slag on the dicalcium silicate and MgO periclase phase boundary in the quaternary CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO system [6]. The liquid magnesium oxide is kept at fully saturated, hence the activity of MgO is nearly unity.

The vacuum condition in the reactor results in a number of operational problems. The ingress of air during slag tapping was reported to cause the loss of 20% of the production due to the formation of MgO and Mg<sub>3</sub>N<sub>2</sub> in the condenser [7]. Another problem also comes from the oxidation of carbon from the reactor lining and electrode to form carbon monoxide, according to following reaction:



The direction of the Reaction (3) is reversed at lower temperature. Hence, at low temperature, the carbon monoxide vapour produced and taken along the magnesium vapour stream will re-oxidise the magnesium vapour forming magnesium oxide.

The magnesium vapour produced from the reaction is then condensed to liquid form in a condenser when it is cooled to a solid and sent for refining. Table 3 shows the impurities in the magnesium



after refining process as reported by Bowman [21]. It is suggested that the impurities in the magnesium originated from: (1) particulate matters that are carried over by magnesium vapour stream and condense in magnesium crucible as impurities, such as MgO and CaO; (2) physical and chemical interactions between species inside reactor; and (3) vaporization of volatilized materials, such as Mn, Zn, Pb, and Ni.

Table 3: Impurities in the magnesium produced from the Magnetherm process before and after refining (using MgCl<sub>2</sub> and KCl fluxes) process, in wt% [21]

Impurities	Initial	After refining
Calcium	0.77 – 1.05	0.005
Silicon	0.11 – 0.16	0.063 – 0.11
Aluminium	0.037 – 0.088	< 0.05

The details of the refining practice has been described by Bowman [21]. In this process the crude magnesium is remelted and flux containing 45% of MgCl<sub>2</sub> and 55% of KCl is added and stirred into the melt. At the end of the refining process, the fluxes are allowed to settle before molten magnesium is ladled and taken into casting. The chemical reaction in this refining stage can be written as:



Calcium present in a metallic form is consumed by the magnesium chloride flux. The flux also captures oxide inclusion and form a sludge of heavy oxy-chloride [22].

The refining practice can produce a magnesium ingot with a standard composition as required by ASTM B92. However, the refining stage means a higher production cost and less magnesium metal yield. There is about 5-8% magnesium loss in the refining stage [21].

Another silicothermic process that has been developed in Italy and Brazil is called the Bolzano process[23]. It employs an internally heated and brick-lined reactor. The briquette charge containing calcined dolomite and silicon is loaded inside the furnace. The process operates at 1200°C and a vacuum pressure at less than 400 Pa. Magnesium with a purity of 99.98-99.99% is obtained.

### 2.3 The Mintek process

There has been previous work by Cameron and co-workers and Christini on developing an atmospheric silicothermic route to magnesium [7, 19, 24], as a means of avoiding the difficulties associated with Magnetherm and productivity limitations of the Pidgeon process. Currently, Mintek are developing an atmospheric process based on Schoukens's patent [25]. The schematic of the Mintek process furnace is also shown in Figure 2. The key to this process relies on the utilization of aluminium in addition to ferrosilicon for the reduction of magnesium oxide at higher temperatures, 1700-1750°C. The process also utilizes slag that remains liquid in the temperature range. Thus, the magnesium vapour produced is much higher, at about 0.85 atm. Argon gas is used to maintain the atmospheric pressure inside the furnace. Aluminium is more expensive compared to ferrosilicon.



The work is still underway for finding the proper feed composition for the optimum production of magnesium [22].

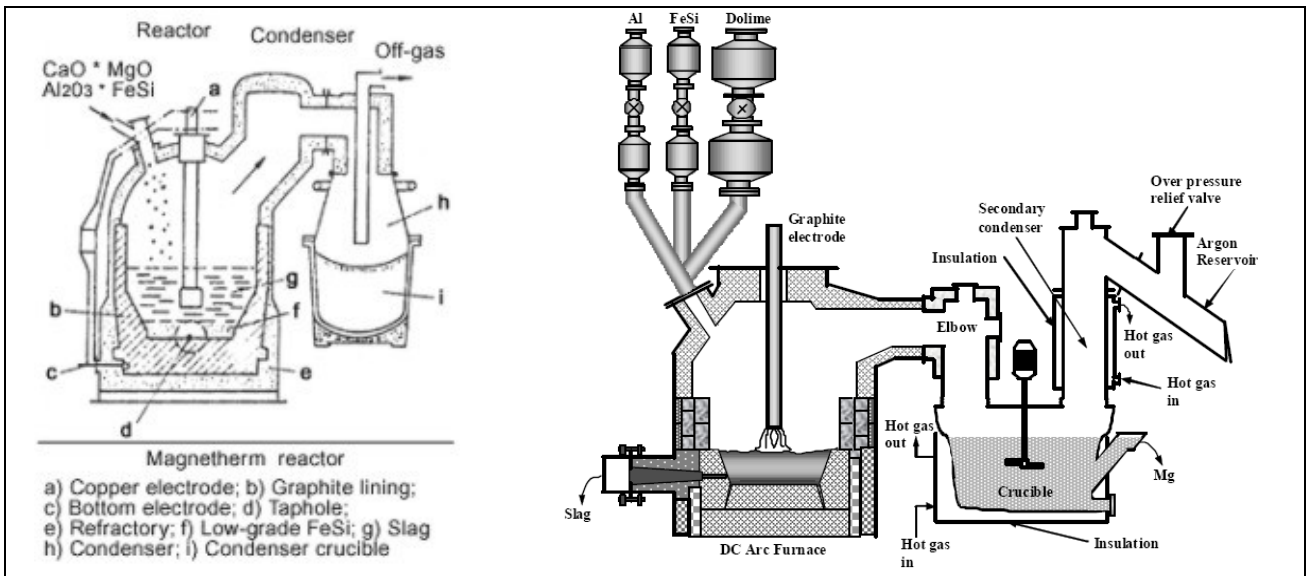


Figure 2: Schematic of the Magnetherm (left) [23] and Mintek (right) [26] processes

The main advantage of the Mintek process is its high productivity. It also operates at atmospheric pressure which gives a possibility of operating the process in a continuous way. The magnesium produced, however, has very high impurities compared to the other two previous processes, as shown in Table 1. For example, the calcium concentration (main impurity) in the magnesium is 0.385 wt%, which is much higher compared to calcium concentration in the magnesium produced by the Pidgeon process, i.e. 0.005%. The magnesium metal produced need to be remelted and further refined. Table 4 shows the impurities in the magnesium before and after refining stage. The total impurities concentration in the magnesium before refining may exceed 2 wt%.

The refining practice in the Mintek process consists of two stages [22]. In the first stage the magnesium is refined by adding MgCl<sub>2</sub>-KCl flux to remove the calcium impurity, as per Equation (5). This stage is similar to the refining practice in the Magnetherm process. In the second stage, the molten magnesium is treated by adding FeCl<sub>3</sub> to remove silicon impurity based on the following reaction:



Table 4: Impurities in the magnesium produced from the Mintek process before and after refining process, in (wt%) [22]

Element	ASTM B92 Grade 9980A	Crude Mg			Clean Mg		
		Avg.	Max	Min	Avg.	Max	Min
Aluminium	0.05 max	0.066	0.210	0.010	0.040	0.235	0.003
Silicon	0.05 max	0.281	1.010	0.100	0.095	0.500	0.014
Calcium	0.05 max	0.385	1.090	0.030	0.023	0.102	0.005
Iron	0.05 max	0.250	0.350	0.002	0.047	0.100	0.002



Abdellatif reported that the loss of magnesium in the refining stage in the Mintek process is about 9 % higher than that of the Magnetherm refining process, which ranges from 5 to 8% [22].

### 3 Thermodynamic analysis of silicothermic processes

There have been a number of studies on the thermodynamic analysis of the Pidgeon, the Magnetherm, and the Magnetherm atmospheric processes [6, 19, 24, 27]. However, there is limited information on the literature that focuses on the behaviour of the impurities present in magnesium. Knowledge on the distribution of the minor phases and impurities and their behaviour is important for the improvement of these processes.

In the present study, a thermodynamic analyses and calculations of the silicothermic processes, with an emphasis on the impurities distribution, were carried out using the FactSage thermodynamic package (version 5.0) [28]. FactSage is an integrated database computing system for chemical thermodynamic. This package has optimized database for solutions, such as metals, liquid and solid oxides, and slags. For pure components, the data are taken mostly from JANAF Thermochemical Tables [29], thermodynamic properties data from Barin [30], and from Berman *et.al.* [31]. The solution for liquid slag phase is taken from Eriksson *et.al* [32] using a modified quasi-chemical model for the oxide. In Equilib module, the Gibbs energy minimization technique is used to calculate the concentration of chemical species when specified elements or compounds are react to reach the state of equilibrium. Phases from the compound and solution databases are retrieved and listed as possible product in the equilibrium result. The appropriate optimised thermodynamic solution databases were used in the modelling, which include the solution databases for monoxide, liquid slag,  $\alpha$  and  $\alpha'$ -dicalcium silicate. In the current modelling, magnesium solid is considered as a single phase, i.e. no solid solution is considered inside the magnesium. In future work, a condensed metallic solution phase will be included in the calculation.

For the Pidgeon process equilibrium calculation, the input data including the calcined dolomite composition and the ratio of calcined dolomite to ferrosilicon were taken from Toguri's data [14] and is listed in Figure 4. The addition of  $\text{CaF}_2$  as catalyst as reported in the literatures [3, 14] was neglected as the catalyst is only affecting the kinetics but do not change the equilibrium. The equilibrium was evaluated at temperature of  $1160^\circ\text{C}$  and pressure of 67 Pa, replicating the practical operation conditions [3, 14]. The input data for the Magnetherm equilibrium calculation were taken from Faure and Marchal [5] and Christini, and is listed in Figure 5 [6]. The liquid slag solution database and alpha dicalcium silicate ( $\alpha\text{-Ca}_2\text{SiO}_4$ ) phase were included in the equilibrium calculation. The equilibrium was calculated at the operating conditions of the Magnetherm process, i.e. at temperature of  $1550^\circ\text{C}$  and pressure of 5 kPa. For equilibrium calculation of the Mintek process, the input data for the calcined dolomite, ferrosilicon, and aluminium were taken from one of the compositions from small-plant scale trials as reported by Abdellatif and listed in Figure 6 [26]. The calculation equilibrium was carried out at temperature and pressure of  $1750^\circ\text{C}$  and 85 kPa, respectively.



Further thermodynamic modelling was also undertaken to study the precipitation of solid impurities from the vapour phases produced upon cooling by carrying out a multi-stage equilibrium modelling using the same thermodynamic package. Figure 3 illustrates the multi-stage equilibrium modelling carried out in the present study. In Stage 1, the equilibrium at 1100°C was evaluated. The solid phases/impurities formed were then removed from the system and the vapour phases produced were cooled down to 1050°C; and the Stage 2 equilibrium calculation was then carried out. The procedure was repeated for the equilibrium calculations in the subsequent stages (where at each stage the temperature is decreased by 50°C) until the magnesium metal was condensed.

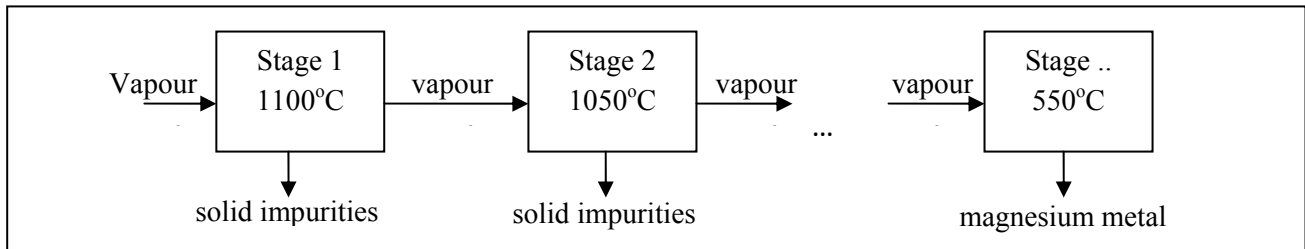


Figure 3: Schematic of a multi-stage equilibrium modelling carried out in the present study

## 4 Results and discussion

The one-stage equilibrium model was used to determine the possible phases and its composition in the equilibrium. Figure 4 shows the results of the equilibrium calculation for the Pidgeon process at 1160°C and 67 Pa. For this process, the solid phases at equilibrium were alpha prime dicalcium silicate ( $\alpha'$ -Ca<sub>2</sub>SiO<sub>4</sub>); monoxides which include single phase periclase (MgO) and calcined dolomite (CaO·MgO) containing Al<sub>2</sub>O<sub>3</sub>; ferrosilicon; and calcium aluminate. The vapour phase contained 99.68% Mg, and impurities which were mainly Ca and Fe. The presence of SiO vapour at relatively moderate temperature was very low, as suggested by Toguri and Pidgeon [33]. The vapour phase was then condensed to 550°C, a temperature that is lower than its melting point, i.e. 650°C. The pressure of the system was below the vapour pressure of Mg, thus it condensed to solid, as stated by Betcherman and Pidgeon [34]. At this temperature, the model predicted that the solid contain 99.32 wt% Mg. It also predicted that other elements end up as impurities, with the majority in the form of CaMg<sub>2</sub> intermetallic. In reality, the calcium is likely to be dissolved in the Mg, an aspect of the process not considered in this current model.

The equilibrium temperature of condensation of Mg under vacuum predicted in this model was in a good agreement with a previous study by Misra *et al.* [35], on the condensation characteristic of magnesium vapour from the Pidgeon process. According to their experimental study, the Mg metal condensed at temperatures below 590°C. At 470°C, the recovered deposit was coarse, while below 200°C it was very fine and pyrophoric.

The results of the equilibrium calculation for the Magnetherm process at 1550°C and 5 kPa are presented in Figure 5. In the Magnetherm process, the input charge includes dolomite, ferrosilicon and



bauxite. Slag in the reactor also involved in the reaction thus it is included in the input for the equilibrium calculation. At equilibrium, the predicted non-vapour phases present include liquid slag, alpha dicalcium silicate, and ferrosilicon. The predicted vapour phase contains 98.94% of Mg and other impurities which include Ca, Fe, and Al. The presence of SiO vapour predicted is significant compared to the case of Pidgeon process, i.e. 0.18% of the total vapour phase. The vapour phase was brought down to 650°C, i.e. temperature at the condenser. At this condition, the Mg was in a liquid form, 99.55% of the total material. The major impurity is Ca in the form of inter-metallic  $\text{CaMg}_2$ , which is similar to the case of the result from the calculation for the Pidgeon process.

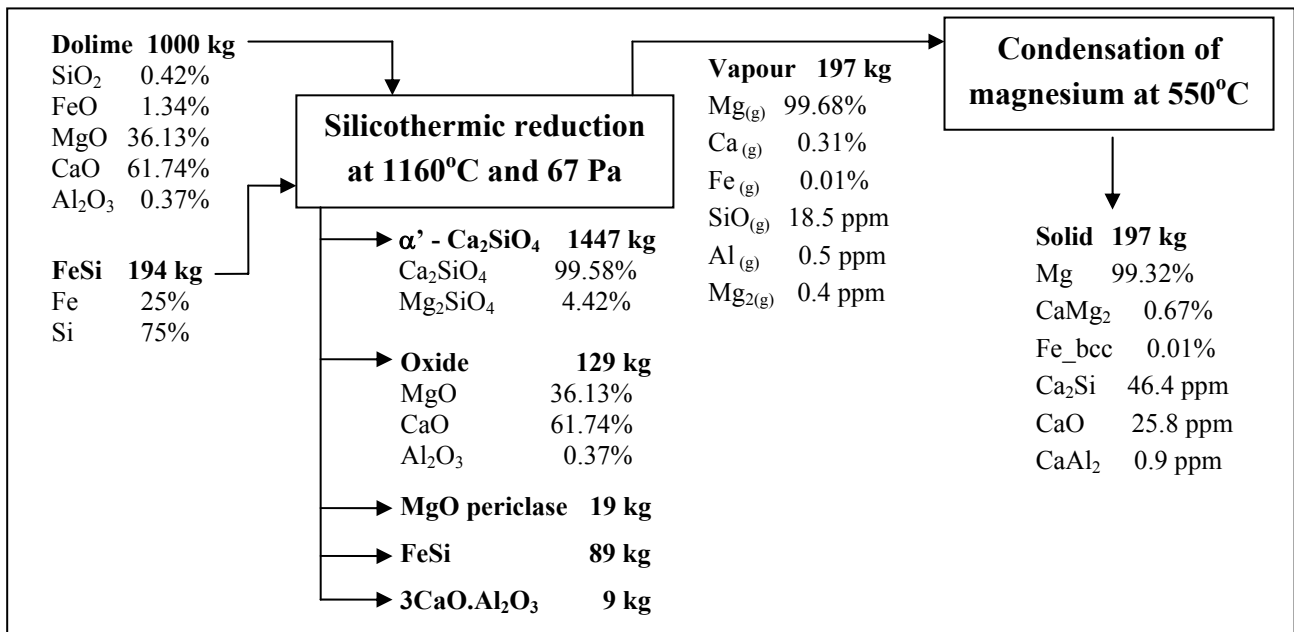


Figure 4: Equilibrium calculation for the Pidgeon process at 1160°C and 67 Pa.

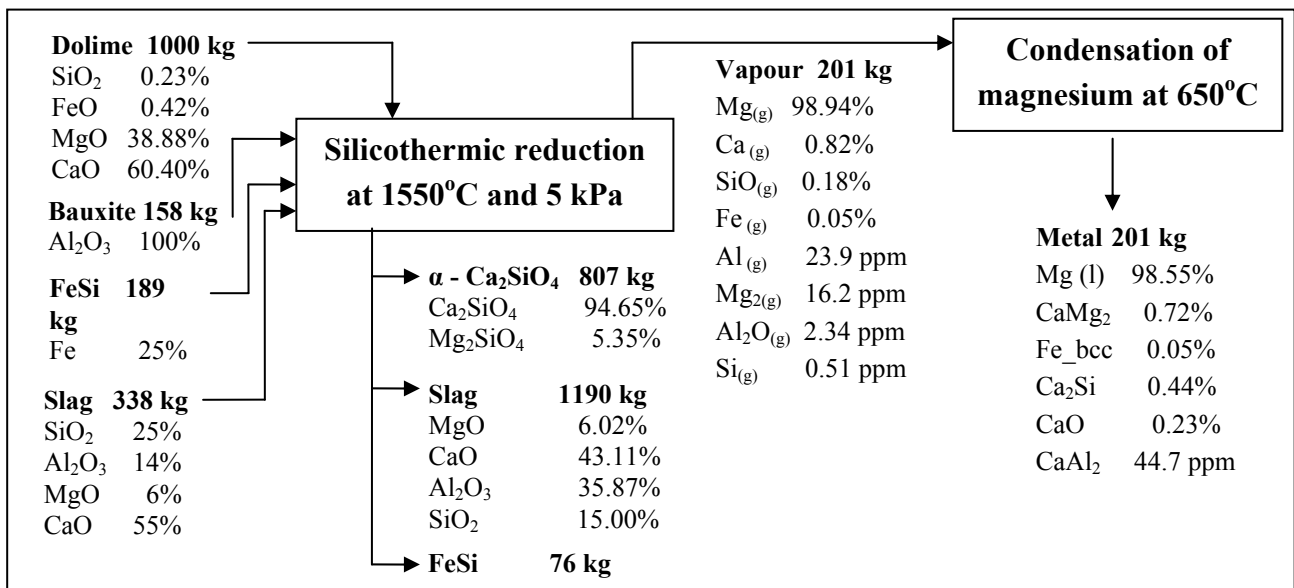


Figure 5: Equilibrium calculation for the Magnetherm process at 1550°C and 5 kPa.



The results of the equilibrium calculation for the Mintek process are shown in Figure 6. The predicted vapour phase contains 2.14 wt% of impurities, consisting of mainly Ca, followed by Mn and SiO vapour. For the Mintek process, the vapour is predicted to condense at 750°C and the Mg consists of 96.16% of the condensed phases. Similar to the other processes the major impurity predicted in this model is in the form of CaMg<sub>2</sub>.

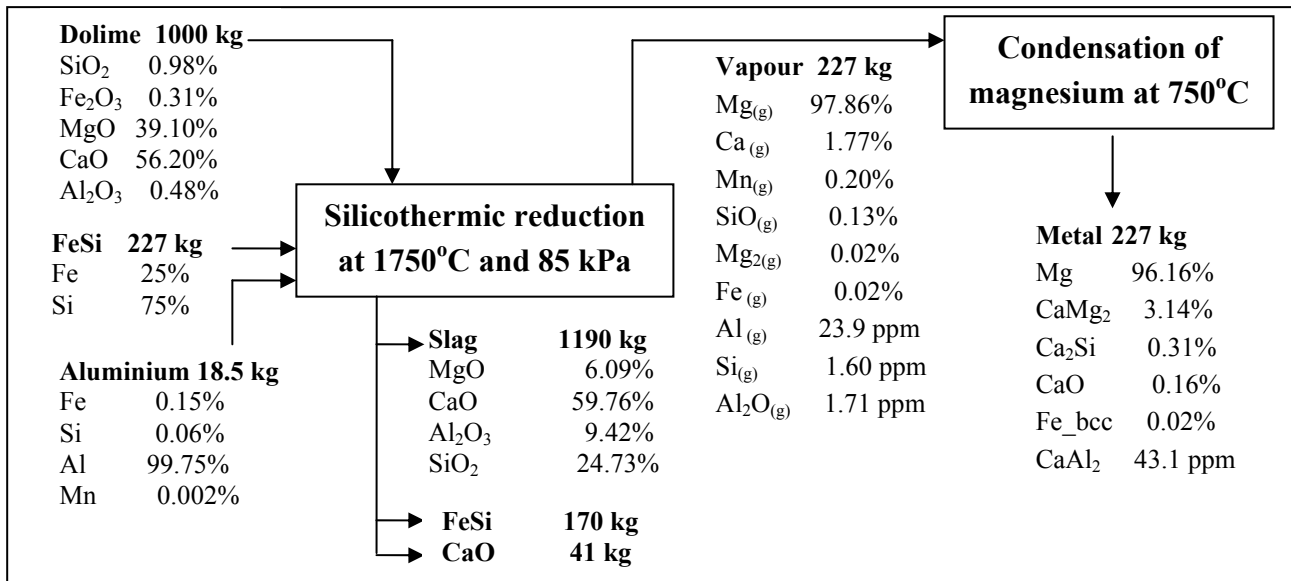


Figure 6: Equilibrium calculation for the Mintek process at 1750°C and 85 kPa.

The results of the multistage equilibrium modelling from the present study for the case of Pidgeon, Magnetherm and Mintek process are shown in Figures 7, 8, and 9, respectively. The mass fraction of solids precipitated during each equilibrium stage was plotted against the decreasing temperature. In the case of Pidgeon process, between 1100°C and 900°C, the major solid phases predicted to precipitate include CaO, Fe and FeSi; while various intermetallics were predicted to precipitate below 900°C, as shown in Figure 7. At temperature range between 900°C and 600°C, it was predicted that Mg and Ca are in equilibrium in the vapour phase, thus there was no solid precipitated at such range of temperature. The Ca vapour began to precipitate and interact with magnesium forming CaMg<sub>2</sub> at 600°C, and magnesium was predicted to condense with the impurity of CaMg<sub>2</sub>.

As can be seen in Figure 8, the major solid phase predicted to precipitate between 1500°C and 1300°C in the case of Magnetherm process were calcium orthosilicate and FeSi. At lower temperature, between 1250 and 1050°C, the metal impurities vapour was predicted to condense and formed oxide and intermetallic phases. Ca was still the main impurity in the vapour until the Mg metal condensed. In the case of Mintek process, calcium orthosilicate, FeSi and CaO were predicted to precipitate at temperature range of 1700°C-1600°C. From the model, it was found that intermetallics are precipitating below 1600°C, while Mg<sub>2</sub>SiO<sub>4</sub> is precipitating below 1000°C; see Figure 9.

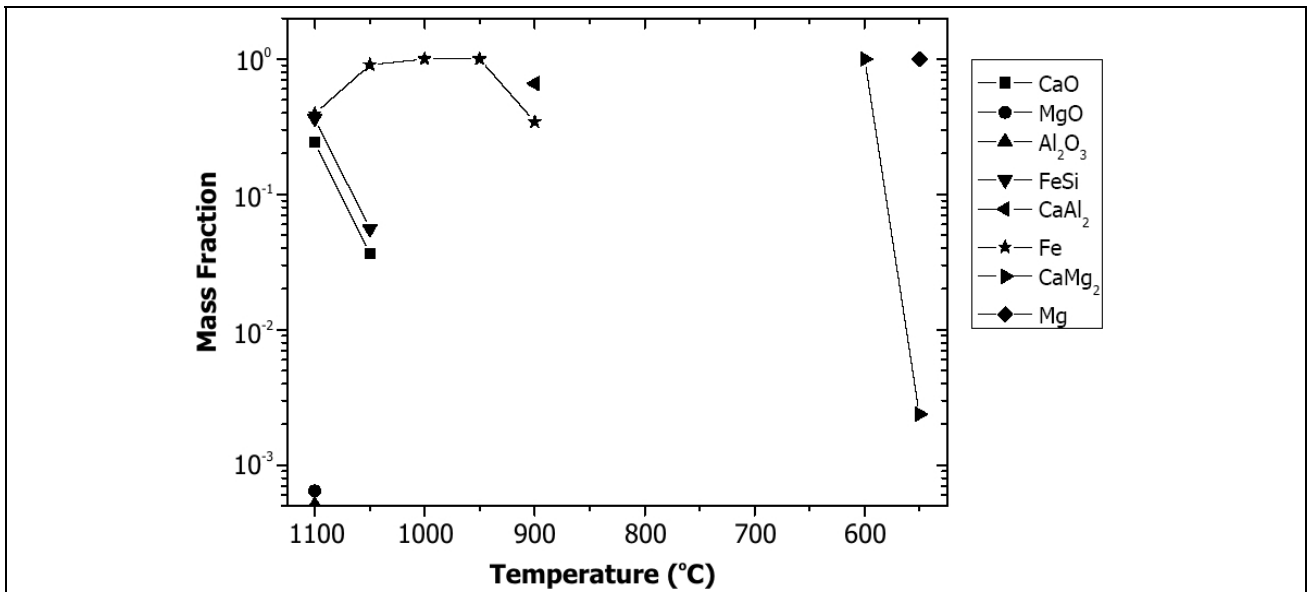


Figure 7: The mass fraction of solids precipitated from mixture of vapours produced from the Pidgeon process reaction (at 1160°C) at various temperatures step cooling of 50°C calculated from thermodynamic model.

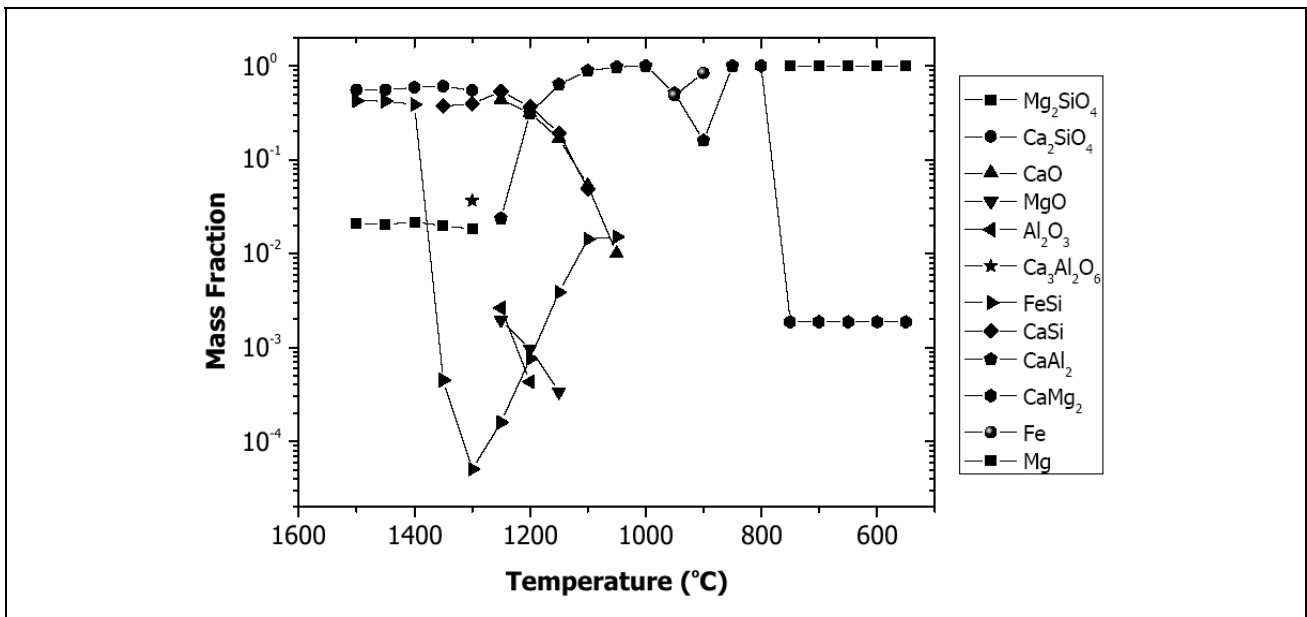


Figure 8: The mass fraction of solids precipitated from mixture of vapours produced from the Magnetherm process reaction (at 1550°C) at various temperatures step cooling of 50°C calculated from current thermodynamic model.

Elemental chemical analyses of the Mg produced from the silicothermic processes showed that the main impurity is Ca [17]. This is understandable as high amount of Ca is present in the reactant materials, i.e. dolomite. Ca vapour is present because of the reaction between CaO in dolomite and silicon, which can be written as:





The thermodynamic calculations from the present study suggested that calcium is the main impurity (assuming all the precipitated solids end up in magnesium product), which is in agreement with the chemical analysis results. The calcium was mainly present in magnesium metal collected in the form of calcium inter-metallic and calcium oxide [21].

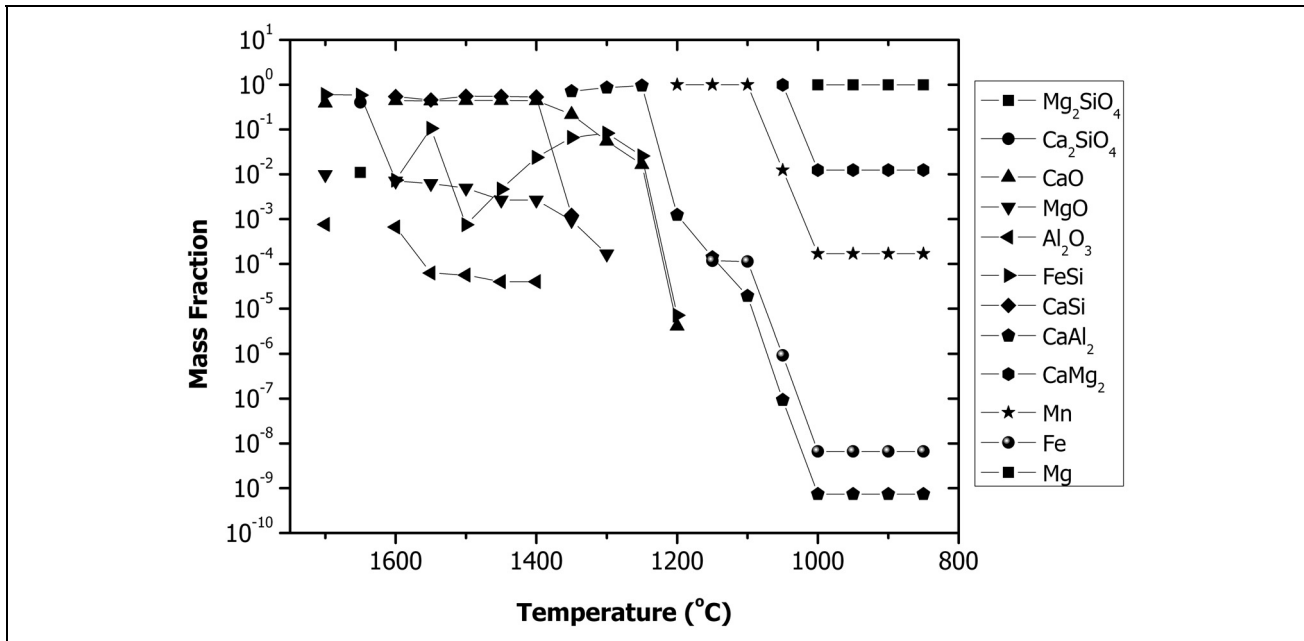


Figure 9: The mass fraction of solids precipitated from mixture of vapours produced from the Mintek process reaction (at 1750°C) at various temperatures step cooling of 50°C calculated from current thermodynamic model.

In the present study, the equilibrium has been evaluated by: (1) calculating equilibrium after direct cooling of the vapour to the Mg condensation temperatures, i.e. Model I; and (2) conducting multi-stage equilibrium calculations, i.e. Model II. In the Model I, all the impurities in the produced vapour end up in magnesium. This is not the case in the Model II as the solids condensed at higher temperatures do not advance with the rest of the vapour to the Mg condensation temperatures. Therefore, the total impurities (mainly calcium) in the magnesium calculated using Model I is higher compared to that calculated using Model II. Calcium impurity in the Mintek process predicted by Model II is 0.58%, much less than predicted by Model I, which is 1.77%.

Table 4 shows the Mg and the impurities (Ca, Si and Al) concentrations calculated from the present study, as well as the reported actual Ca impurity concentrations [17]. It can be seen from Table 4 that the Ca concentration calculated from Model I is about three to ten times higher compared to that from Model II. It can be seen from the Table 4 that, in the case of Pidgeon and Mintek process, Model I and Model II overestimate the Ca impurity concentration compared to the reported actual Ca concentration [22, 36]. The Ca concentrations from Model I and II are 0.31 and 0.11 wt% for the Pidgeon process model, still much higher compared to the actual data which is 0.02 – 0.06%. However, the result from Model I, in the case of Magnetherm process, lies in the reported actual Ca concentration range [21].



Table 4: Magnesium and calcium contents calculated from the present study (Model I and Model II), thermochemical study by Ritter and Sadoway [10], and from chemical analyses [14, 21, 22]

Element	Pidgeon	Magnetherm	Mintek
Magnesium (wt %)			
Model I	99.68	99.94	97.86
Model II	99.89	99.92	99.42
Calcium (wt %)			
Model I	0.31	0.82	1.77
Model II	0.11	0.08	0.58
Model by [10]	-	0.44 – 1.11	-
Actual	0.02 – 0.06	0.77-1.05	0.03 – 0.385
Silicon (wt %)			
Model I	0.002	0.11	0.08
Model II	N.A	N.A.	N.A
Model by [10]	-	0.44 - 1.19	-
Actual	0.03 – 0.07	0.11 – 0.16	0.1 – 1.1
Aluminium (wt %)			
Model I	0.0005	0.00256	0.00247
Model II	N.A	N.A	N.A.
Model by [10]	-	0.0012 – 0.0034	-
Actual	0.007 – 0.02	0.037 – 0.088	0.01 – 0.066

The result for the Magnetherm process is also compared to one specific study of analysis of impurities in the Magnetherm process by Ritter and Sadoway [10] using thermochemical databases. For calcium impurities, the Model I and II results agreed with their results.

The results presented provide information on the behaviour of species during condensation of vapour produced from silicothermic processes determined from chemical equilibrium reactions. In the actual process, the condensation of magnesium vapour is a very complex phenomena involving fluid and kinetics effects rather than idealized equilibrium process. The vapour may condense homogeneously in the vapour space or via heterogeneous nucleation on particles in the gas phase or along the walls of the condenser. The kinetics of cooling, connected to the heat transfer characteristics of the condenser and the fluid mechanics of the system, will affect the rate of nucleation of condensation. Other chemical interactions which are not associated with the main reactions, such as interaction of magnesium with air in the Magnetherm process, and the interaction of carbon lining and electrode with magnesium oxide are also not reflected in the models developed in this study. The equilibrium models developed in this study do not give information about kinetic phenomena but can identify the limits of the process and provide a starting point for more detailed studies of this system.

## 5 Conclusion

In the present article, a review of three silicothermic Mg productions and thermodynamic analyses of the processes with the emphasis on the formation of impurities and its distribution during con-



densation of Mg vapour have been presented. One-stage direct cooling and multi-stage equilibrium modelling have also been presented. The results from the multi-stage equilibrium model show that at equilibrium it should be possible to condense solid impurities before the majority of the magnesium vapour is condensed below 750°C, depending on the operating pressure of the system and the particular chemistry of the process. The model predicts that purities above 99.8wt% and 99.4wt% can be achieved for the Pidgeon and Mintek process, respectively. Without multi-stage condensation, the impurities in the metal are predicted to be significantly higher for the Mintek process (2.14 wt% compared to 0.6 wt%). These results are broadly consistent with existing industrial data.

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