

A THERMOCHEMICAL STUDY OF THE BEHAVIOR OF IMPURITIES IN THE MAGNETHERM PROCESS

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In the Magnetherm process magnesium is produced by metallothermic reduction through the reaction of dolime with ferrosilicon. The crude magnesium from the reactor contains both metallic and nonmetallic impurities. The behavior of each has been studied. Regarding metallic impurities, a thermodynamic model of the process has been constructed to use information from a variety of computerized thermochemical databases. For given sets of process inputs the thermodynamic model along with some kinetic considerations has predicted the concentrations of selected elemental impurities in the metal product. The results have been compared to available plant data for calcium, silicon, aluminum, and carbon. As for nonmetallic impurities, these are entrained in the product metal either as fines or as slag projections. An attempt has been made to explain the associated mechanisms.

INTRODUCTION

The Magnetherm process (1-7) was developed by Pechiney in the 1960's. The raw materials are calcined dolime (CaO-MgO), bauxite and ferrosilicon (75 wt % Si) which are charged continuously in a single-electrode electric furnace where the heat is generated by passing current through a resistive slag (Figure 1). The reaction takes place at high temperature (1550°C) and low pressure (0.05 atm). The magnesium is produced in the form of a vapor which is transferred to a separate vessel, known as a crucible, where it collects as a solid. The principal chemical reaction occurring in the furnace can be written as



where the underline denotes the solution of silicon in molten ferrosilicon. During the course of one cycle of operation, i.e., the time to fill the crucible with magnesium, it is necessary to tap the slag from the main reactor twice. This has important consequences for the purity of the metal product. Indeed, the crude magnesium obtained by this process is not pure enough for commercial applications (8) and must be remelted and fluxed to achieve impurity levels that meet industrial standards. Obviously, in order to improve the productivity of this process it is imperative that the purity of the crude metal produced in the Magnetherm reactor be improved.

This article reports the results of a study that attempted on the basis of a thermodynamic model along with some kinetic considerations to predict the

composition of the metal product. These predictions were compared with available plant data. The impurities fall into two categories: metallic and nonmetallic, or more precisely, elemental and compound.

LITERATURE

In the open literature the report by Bowman appears to be the only discussion of impurities in the Magnetherm process (8). That study gave average concentrations of metallic and nonmetallic calcium, silicon and aluminum in the crude magnesium.

In an unpublished report from Pechiney Electro-metallurgie, Lapostolle describes measurements made by sampling at different locations in a crucible of metal product (9).

RESULTS AND DISCUSSION

As the information reported in the study by Lapostolle was used extensively in the present study, for the convenience of the reader the data have been reproduced in Figures 2 through 5. Figure 2 is a schematic of the crucible and marks the sampling locations. Figures 3, 4, and 5 show the measured concentrations of calcium, silicon, and aluminum, respectively.

Each of these elements is known to be present in two different chemical forms: metallic and nonmetallic (8). For the present calculations it was assumed initially that the presence of metallic or elemental impurities was due exclusively to the formation of vapors in the reactor vessel which condense along with magnesium in the crucible. Furthermore, the rate of production of these impurities by this mechanism was assumed to be constant throughout the duty cycle of the furnace. For a given species the difference between the measured concentration reported in Figures 3, 4, and 5 and the estimated value for the metallic form was assigned to the value of the nonmetallic form. The total concentration was determined by graphical integration along the entire depth of the crucible.

For all three species, high concentrations are measured in the product that would have formed during the periods immediately following tapping of the slag from the furnace. As the reaction proceeds the concentrations are seen to decrease during the subsequent half-cycle and reach a minimum value. It

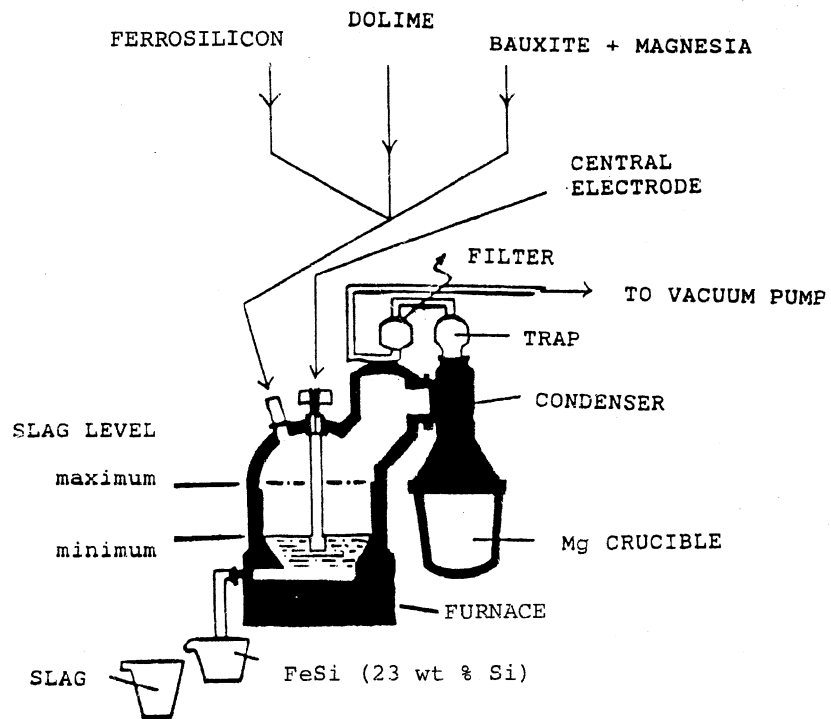


Figure 1. Schematic of the Magnetherm reactor.

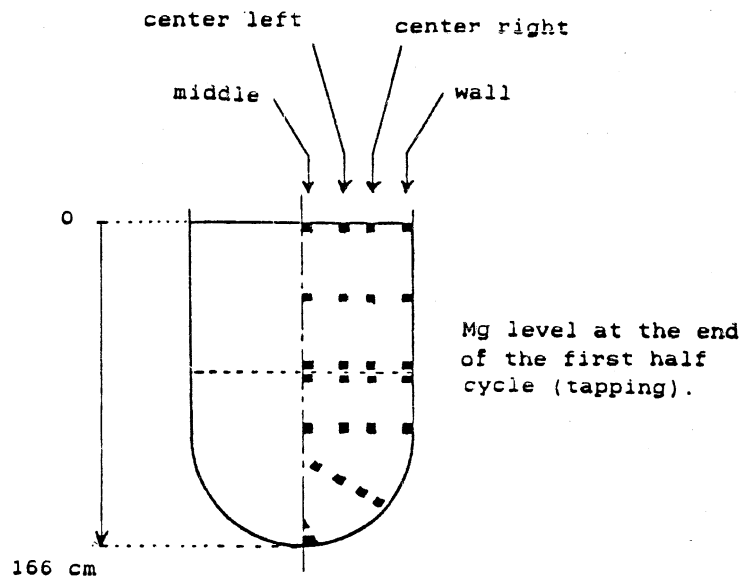


Figure 2. Schematic of the sampling locations in the crude magnesium crucible.

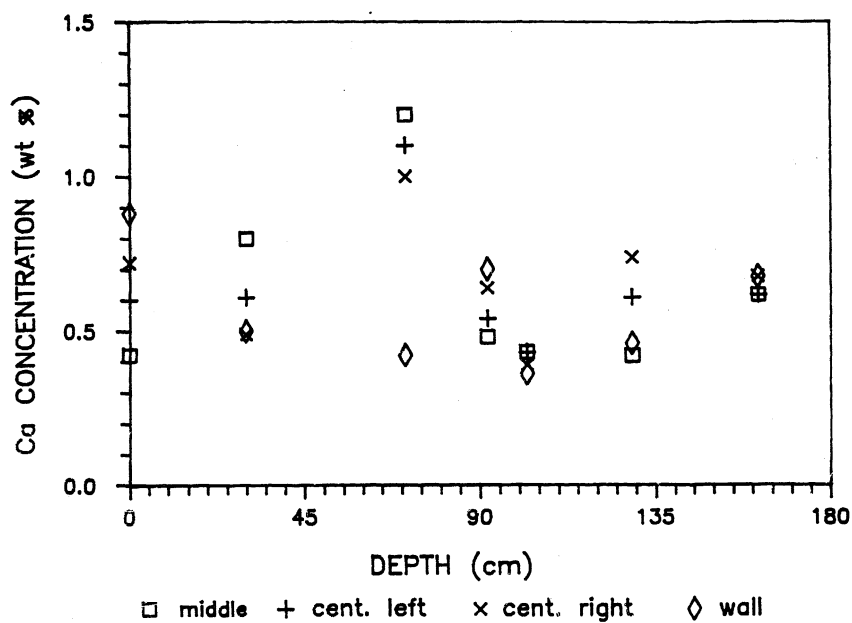


Figure 3. Calcium impurity levels in crude magnesium.

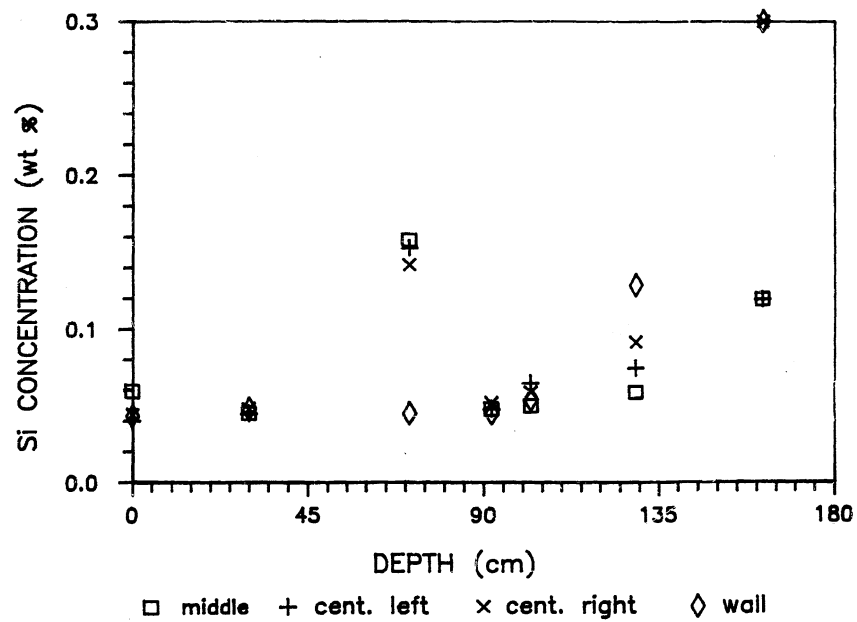


Figure 4. Silicon impurity levels in crude magnesium.

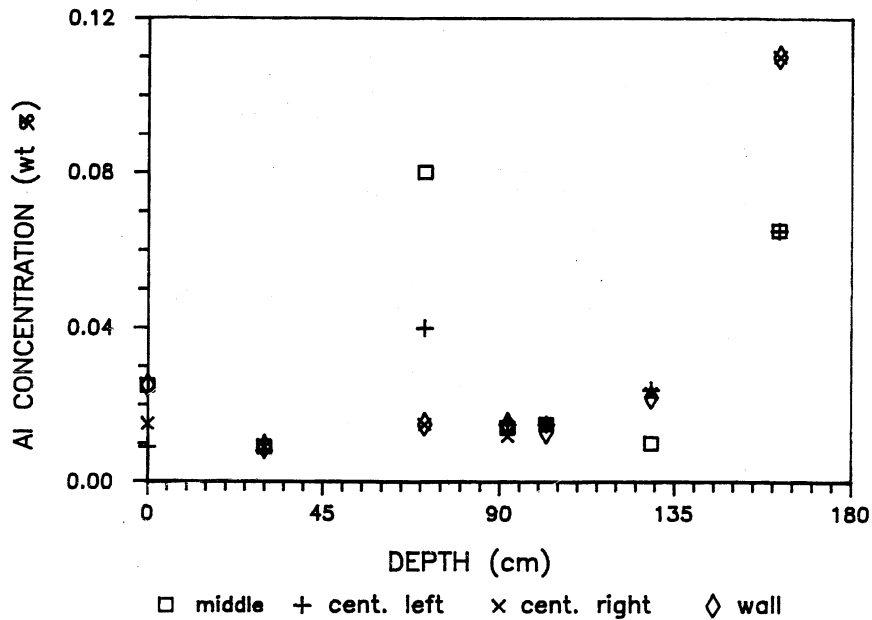


Figure 5. Aluminum impurity levels in crude magnesium.

is assumed that this minimum value corresponds to the level of metallic impurity; however, in the cases of aluminum and silicon this assumption does not take into account the metallic impurities coming from projections of ferrosilicon. The projection mechanism will be discussed below.

Elemental Impurities

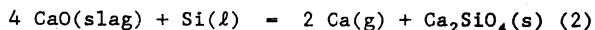
Calcium. The measured calcium level is given in Table I.

Table I. Measured Calcium Concentrations in Crude Magnesium

	Lapostolle	Bowman
Ca metallic (ppm)	4200	5900
Ca total (ppm)	6300	8500
metal/total	0.69	0.69

The results show that the levels of metallic and nonmetallic calcium in both studies are comparable. In particular, the ratio of metallic impurity to total impurity is identical.

The following reaction describes the formation of calcium vapor:



Assuming equilibrium, one can calculate the concentration of calcium in the gas phase above the slag. It is this concentration of calcium that is assumed to be the value of the calcium impurity level in the condensed magnesium. As equation 2 shows, this value

depends upon the activity of CaO in the slag which in turn is linked to the activity of MgO as seen in equation 1. Christini has compiled activity data for various slag components and has given a value of 0.4 for the activity of MgO (5). However, it should be noted that according to the phase diagrams of the quaternary system MgO-CaO-Al₂O₃-SiO₂ (10) under typical operating conditions the slag is expected to be nearly saturated with MgO, and so its activity may be much higher than 0.4. This uncertainty in the value of the activity of MgO gives rise to wide variation in the predicted values of impurity elements in the product crude metal. In consideration of the above in the present study calculations have been performed with the activity of MgO set at both extremes, 0.4 and 1.0. The concentration of metallic calcium in the crude magnesium as calculated herein is given in Table II.

Table II. Calculated Impurity Concentrations as a Function of MgO Activity

	0.4	1
a_{MgO}		
c_{Ca} (ppm)	11000	4400
c_{Si} (ppm)	11900	4400
c_{C} (ppm)	22	19

The level of calcium calculated by the model is in accordance with the experiments assuming that MgO is near saturation in the slag. This analysis also shows that to decrease the calcium content of the magnesium product the activity ratio of CaO to MgO should be minimized. At the same time, to maintain a high production rate of magnesium the activity of MgO in the slag should be maximized.

Silicon. The measured silicon level is given in Table III.

Table III. Measured Silicon Concentrations in Crude Magnesium

	Lapostolle	Bowman
Si metallic (ppm)	450	900
Si total (ppm)	660	1100
metal/total	0.68	0.81

The values in the two studies differ. The discrepancy can be explained by the fact that silicon may be introduced into the metal also by projection of slag or fines, which in this case refers to particles of ferrosilicon contained in the charge.

The metallic silicon finds its way into the crude magnesium by several mechanisms: formation of SiO vapor which is reduced by reaction with magnesium in the condenser, evaporation of elemental silicon from the furnace, and projection of ferrosilicon. These will each be discussed in turn.

The formation of SiO by the following reaction is allowed on thermodynamic grounds (11,12):

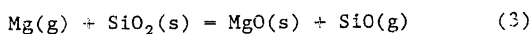
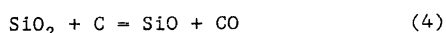


Table II gives values for the silicon concentration in the product magnesium by this reaction if one assumes complete conversion of SiO. These values are between 5 and 20 times too high. According to two Japanese studies on the interactions between a Magnetherm type slag and carbon, it seems that there may be kinetic limitations on reaction 3 (13,14). Instead, in the cited works SiO formation is explained by the following reaction:



In a Magnetherm furnace the only effective source of carbon for reaction 4 is the electrode. While the inner wall of the furnace is constructed of carbon, in practice there is a coating of oxide covering the structure and protecting it from chemical attack. With the kinetic data it is possible to calculate the amount of carbon monoxide and silicon monoxide formed during a cycle of operation. Assuming complete metallothermic reduction of these products by magnesium in the condenser, one can calculate the average concentrations of carbon and silicon in the crucible for the cycle. On this basis the concentration of silicon is calculated to be 30 ppm which is less than 10% of the measured value.

Evaporation of silicon from the furnace can be represented by the following reaction:



where the underline denotes solution in the molten ferrosilicon. If one assumes that the silicon in the product magnesium is at equilibrium with that in the ferrosilicon, one can calculate the concentration of silicon in the crucible. However, the silicon content

of the ferrosilicon is not constant, and there are no data for its precise variation. In the absence of such information the silicon concentration of the crucible has been calculated considering the two known extremes of 75 wt % silicon in the ferrosilicon charge and 23 wt % silicon in the tapped ferrosilicon. The results are reported in Table IV.

Table IV. Calculated Silicon Concentrations in Crude Magnesium due to Reaction (5)

wt % Si in FeSi	75	23
a_{Si} in FeSi	0.96	0.05
c_{Si} in Mg (ppm)	100	5

It is clear that evaporation is not the dominant mechanism for silicon contamination.

On the basis of the above it seems that projection of ferrosilicon is responsible for approximately 70 wt % of the silicon found in the product magnesium.

Aluminum. The measured aluminum level is given in Table V.

Table V. Measured Aluminum Concentrations in Crude Magnesium

	Lapostolle	Bowman
Al metallic (ppm)	80	50
Al total (ppm)	250	800
metal/total	0.32	0.06

The experimental data from the two studies are at variance.

The metallic aluminum finds its way into the crude magnesium by evaporation of elemental aluminum from the furnace and by projection of slag or fines, which in this case refers to particles of aluminum contained in the charge.

Evaporation of aluminum from the furnace can be represented by the following reaction:



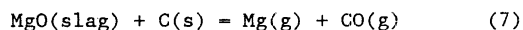
where the underline denotes solution in the molten ferrosilicon. As in the case of silicon, if one assumes that the aluminum in the product magnesium is at equilibrium with that in the ferrosilicon, one can calculate the concentration of aluminum in the crucible. However, the aluminum content of the ferrosilicon is not constant, and there are no data for its precise variation. In the absence of such information the aluminum concentration of the crucible has been calculated considering the two known extremes of 1.2 wt % aluminum in the ferrosilicon charge and 0.26 wt % aluminum in the tapped ferrosilicon. The activity of aluminum in the ferrosilicon was calculated using data from the binary system iron-aluminum (15). The results are reported in Table VI.

Table VI. Calculated Aluminum Concentrations in Crude Magnesium due to Reaction (6)

wt % Si in FeSi	75	23
wt % Al in FeSi	1.2	0.26
^a Al in FeSi	0.0008	0.0003
^c Al in Mg (ppm)	34	12

Under the circumstances the values calculated in Table VI should be considered in conformity with the measurements in Table V. Furthermore, projection of ferrosilicon in the amount calculated in the previous section is estimated to increase the values in Table VI by 5 to 12 ppm.

Carbon. Toshio *et al.* (13,14) studied the carbothermic reactions that could take place in a Magnetherm type slag. These reactions are given by equations 4 and 7.



As was stated above in the section on silicon, the only effective source of carbon in the Magnetherm furnace is the electrode. With the kinetic data in references 13 and 14 it is possible to calculate the amount of carbon monoxide formed. Assuming complete metallothermic reduction of CO by magnesium in the condenser, one can calculate the electrode consumption and the average carbon concentration in the product magnesium. Unfortunately, there are no plant data for either quantity. However, the calculated value of electrode consumption is 10% after three months which is the normal service lifetime of the electrode. In Table II the calculated values of carbon concentration in the product magnesium are shown.

Nonmetallic Impurities

Oxides. The measured levels of various oxides in the product magnesium are given in Table VII.

Table VII. Measured Oxides Concentrations in Crude Magnesium

	Lapostolle	Bowman
CaO (ppm)	2658	3637
SiO ₂ (ppm)	449	428
Al ₂ O ₃ (ppm)	283	1417

There is good agreement in the CaO and SiO₂ data. In contrast, the data for Al₂O₃ differ appreciably.

Table VIII displays the relative concentrations of the oxides as they are found in the charge, the furnace slag, and the product magnesium. While there are some similarities evident in the data, particularly with the CaO figures, no clear picture emerges from the results shown in Table VIII. There is no simple relationship between the oxide concentrations in the charge, slag, or combination of them and the concentrations in the product magnesium. This may be due in part to the uncertainties in the data themselves.

Table VIII. Relative Concentrations of Oxides in the Charge, Slag, and Crude Magnesium

	charge	slag	Lapostolle	Bowman
CaO	79%	60%	79%	66%
SiO ₂	3%	26%	13%	8%
Al ₂ O ₃	18%	14%	8%	26%

In the analysis of Lapostolle's data it was assumed above that the rate of production of metallic impurities was constant throughout the furnace cycle. As the total impurity concentrations of the various species were seen to vary with time, this must be due to variation in the rate of contamination by nonmetallic impurities. Figures 3, 4, and 5 show that contamination by nonmetallic impurities is high when the slag level in the furnace is low. At this time the degree of superheat in the slag is greatest, and this could result in more violent agitation of the furnace contents to promote projection into the crucible. To minimize this, one should attempt to control the heat transfer to the reaction zone more precisely. Additionally, perhaps it may be beneficial to modify the fluid flow in the furnace through the use of alternative electrical waveforms in the power supply which alter the electromagnetic forces acting on the melt (16).

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