Pressure Dependent Kinetics of Magnesium Oxide Carbothermal Reduction

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Abstract

The rate of MgO carbothermal reduction was studied at temperatures from 1350-1650°C and pressures from 0.1-100kPa based on product gas analysis at near isothermal conditions. For all temperatures the initial rate of carbothermal reduction increased inversely with pressure, and between conversions of 20-35% a transition occurred after which the reaction rate was maximum at 10kPa. Analysis of reacted pellets showed that the reaction stoichiometry, the ratio of C to MgO reacted, was less than unity and decreased with pressure indicating CO₂ generation was more prevalent at elevated pressures. SEM imaging revealed the dissolution of C and MgO contact with conversion, and isoconversional analysis points to a change in the rate determining step between 1 and 10kPa. The given experimental observations argue the importance of mass transfer and gaseous intermediates. A kinetic model is formulated based on a macroscopic species balance with CO₂ as the reaction intermediate.

Keywords

Carbothermal reduction; isoconversional; model-free; kinetics;

1. Introduction

Production of magnesium metal by carbothermal reduction of magnesium ore (namely magnesite and dolomite) is an attractive alternative to reduction by ferrosilicon (~42 kg CO_{2eq}/kg Mg [1]) or electrolysis of MgCl₂ (~24 kg CO_{2eq}/kg Mg [1]) due to its potential lower energy requirements and greenhouse gas emissions [2, 3]. Harnessing solar thermal radiation to provide some or all of the energy required for reduction has been proposed as a method to further lower GHG emissions [4]. In general, the carbothermal reduction reaction is written as,

and has been studied for a variety of metal oxides. Reaction (1) is highly endothermic and results in a large entropy increase due to the generation of gases from solids. Operating under vacuum, or using inert gas for dilution, increases the thermodynamic favorability of the reactions such that the process can operate at lower temperatures, and has been shown experimentally to increase the reaction rate [5-8]. The generation of CO₂ as a gaseous intermediate has been proposed as a mechanism since 1875 [9] and is described by reactions (2) and (3).

Other mechanisms, such as reaction through gaseous carbides[10] and hydrogen[11]intermediates as well as by the thermal dissociation of the metal oxide[12], have been proposed. The presence ofCO₂in the gaseous products [13-16] and an extent of reaction that exceeds the stoichiometric limit of reaction (1) [14] supports the mechanism described by reactions (2) and (3).Reaction (3) is considered by some [14, 15, 17, 18] to be the rate limiting step of carbothermal reduction due to the measured activation energy for the overall reaction being similar to that of carbon gasification (~200kJ/mol)[19-23] and due to experiments showing that catalysts used for carbon gasification also increase the rate of carbothermal reduction[15, 24]. The sum of reactions (1)-(3) is,

where λ is the reaction stoichiometrythat relates the extent of carbon oxidation to metal oxide reduction.

The rate of MgO carbothermal reduction has been measured by thermogravimetry[4, 6-8, 18, 25-28]and product gas analysis[29]using resistive, solar,and inductive heating.Since the rate of heating to the reaction temperatureis finite and strongly depends on the heating methods, high-temperature kinetic measurements are inherently non-isothermal. For carbothermal reduction, the contributions of reactions (1)-(3), the continually changing particle morphology, and the mass transfer of product gases out of the pellet or powder mixture results in the heating rate having a large effect on the measured rate of reaction. Thermogravimetric measurements have been carried out with fast heating rates using custom solar TG instruments where the pellet or powder mixture was exposed directly to concentrated radiation or indirectly through a heated wall[7, 30]. The concentrated radiation heats from one direction resulting in a temperature gradientwithin the pellet or powder mixture complicating kinetic analysis[31]. In this study, fast heating rates were achieved by dropping reactant pellets into a hot furnace.

The experimental space for previous MgO carbothermal reductionstudies and this work is shown in Figure 1.Previous investigations encompass a wide range of experimental conditions; however kinetic

Figure 1. Experimental space for studies of MgO carbothermal reduction, including this work

modeling exists exclusively through simple solid-state kinetic expressions[32] dependent only on temperature and conversion which do not take into account the immense effect of pressure on kinetics. In this work, the rate of MgO carbothermal reduction was calculated by product gas analysis at temperatures from 1350 to 1650°C under near isothermal conditions and pressures from 0.1 to 100kPa using a 2⁴ experimental design. A macroscopic species balance within a single pellet based on reactions (1)-(3) was formulated to continuously predict the reduction rate as a function of temperature, pressure, gas velocity, and conversion.

2. Thermodynamics

The thermodynamic favorability of reaction (1) can be represented by an Ellingham diagram. The Gibbs free energy change for Mg and C oxidation at product gas pressures of 1 and 100kPa are shown in Figure 2. Once ΔG_f^0 is more negative for carbon oxidation than Mg oxidation, reaction (1) is favored to proceed in the forward direction. The change in ΔG_f^0 with temperature for the half-reactions is primarily due to the change in entropy from the generation (C oxidation) or consumption (Mg oxidation) of gases. Lowering the partial pressure of product gases shifts the equilibrium such that reaction (1) is favored at lower temperatures. Based on Figure 2, reaction (1) is thermodynamically favored at 1350 and 1767°C for product gas pressures of 1 and 100kPa, respectively. For a detailed discussion on the thermodynamics of carbothermal reduction the reader is referred to Halmann et al. (2011)[33].

Figure 2. Ellingham Diagram for CO and MgO

3. Methods & Materials

3.1 Materials and Pelletization

Magnesium oxide ($D_p=10\mu\text{m}$) was obtained from Martin Marietta (MagOx Super Premium). Chevron Ace carbon black ($D_p=42\text{nm}$) was used as the carbon source, and PAYGEL[®] 290 pregelatinized wheat starch from ADM was used as a binder.

Carbon and magnesium oxide were mixed in a molar ratio of 2.0 (C/MgO) followed by the addition of 10wt% starch. Water was added to create a paste which was then pressed into 6.35mm spherical molds. The pellets were dried at 105°C in air for 12 hours and then pyrolyzed for 2 hours at 650°C in N₂. After pyrolysis, the final C/MgO molar ratio was 2.19 due to decomposition of starch binder, and the pellets shrunk to 5.5mm in diameter.

95 3.2 Reactor

96 The carbothermal reduction experiments were
 97 carried out using argon carrier gas in a sintered
 98 SiC crucible (Saint Gobain, 66cm long,
 99 ID=7.5cm) that was heated within a graphite
 100 furnace. A schematic of the reactor setup is
 101 shown in Figure 3. A 35 cm long graphite
 102 insert with two 2.5 cm diameter openings
 103 directed the gas flow through the crucible. The
 104 exit line in the graphite insert was lined with a
 105 removable graphite foil for the collection of
 106 condensable reaction products after which a
 107 paper filter was used for the collection of
 108 entrained particles. The reaction temperature
 109 was measured 1 cm from the bottom of the
 110 crucible with a C-type thermocouple. Pressure
 111 in the system was measured with an MKS
 112 Baratron absolute pressure transducer (Type
 113 626) and was controlled with an MKS throttle
 114 valve (Model T3BIB). The concentrations of the
 115 volatile reaction products (CO , CO_2) were
 116 measured with an NDIR gas analyzer (Nova 7905 AH) in the exhaust of a dry vacuum pump (Adixen
 117 Alcatel ACP15).

118 Pellets were loaded in a hopper above the crucible, separated from the hot zone by a ball valve, and the
 119 furnace was heated to the reaction temperature. Once temperature and pressure reached steady state at
 120 the desired reaction conditions, the ball valve holding C/MgO pellets was opened allowing pellets to fall
 121 into the hot crucible. 15 pellets ($\approx 1\text{g}$) were dropped in each experiment. The change in pressure due to
 122 the generation of gases from reaction was adequately controlled using the throttle valve. The reaction
 123 was observed until product gases were no longer detectable ($<0.005\text{ vol\%}$).

124
 125 The flow rate of argon carrier gas was adjusted such that the velocity through the graphite insert was
 126 $3.2\text{ m}\cdot\text{s}^{-1}$ for measurements at 0.1, 1 and 10 kPa and $0.32\text{ m}\cdot\text{s}^{-1}$ at 100 kPa. Higher flow rates at 100 kPa
 127 resulted in the formation of fine $\text{Mg}_{(s)}$ particles through homogenous condensation that clogged the
 128 particle filter at the reactor exit resulting in an uncontrollable increase of system pressure. The Reynolds
 129 number through the openings of the graphite insert varied between 1.83 and 202 due to the change in
 130 gas density with pressure.

132 3.3 Analytical Characterization and Compositional Analysis

133 Elemental carbon and oxygen composition in pellets before and after reaction was determined by IR
 134 detection of CO and CO_2 from oxidation by O_2 using a combustion analyzer (LECO C200) and by reduction

Figure 3. Reactor schematic

with carbon using a total oxygen analyzer (LECO TC600), respectively. Elemental magnesium was calculated assuming that all elemental oxygen is bound as magnesium oxide. Pellet and particle morphology was characterized by Field Emission Scanning Electron Microscopy (FESEM). Magnesium oxide and carbon particle surface area were calculated by BET analysis.

3.4 Calculations

Conversion, α , of MgO to Mg_(v) was determined from the composition of reacted pellets. Yield, Y , of Mg_(s) from Mg_(v) was determined by integration of CO and CO₂ flow according to the stoichiometry of reactions (1) and (2).

$$\alpha = \frac{N_{MgO, Initial} - N_{MgO, Final}}{N_{MgO, Initial}} \quad (5)$$

$$Y = \frac{\int_0^{t, final} (\dot{N}_{CO} + 2\dot{N}_{CO_2}) dt}{N_{MgO, Initial} - N_{MgO, Final}} \quad (6)$$

Dispersion of the reaction products due to the void space in the reactor affected the concentration measurements in the effluent (Figure 4). This effect was quantified with a tracer gas and corrected for using an nCSTR based dispersion model [34, 35] (Appendix D). Time dependent conversion was calculated from the effluent gas composition corrected for reversion by assuming that a constant fraction of Mg_(v) generated reverted to MgO,

$$\alpha(t) = \beta \cdot \frac{\int_0^t (\dot{N}_{CO} + 2\dot{N}_{CO_2}) dt}{N_{MgO, Initial}} \quad (7)$$

where β is the reversion coefficient assuming a total reaction order of 1 for reversion [29].

Figure 4. Dispersion correction for carbothermal reduction at T=1650°C and P=1 kPa

$$\beta = 1/Y \quad (8)$$

The reaction stoichiometry, defined by reaction (4), was calculated from the composition of the reacted pellets.

$$\lambda = \frac{N_{C, Initial} - N_{C, Final}}{N_{MgO, Initial} - N_{MgO, Final}} \quad (9)$$

The maximum absolute difference in duplicate experiments was 0.88% conversion at any given time point, and the overall mass balance for each experiment was closed to within 10%.

4. Results and Discussion

Carbothermal reduction experiments, as described in section 3, are assumed to be isothermal. An energy balance on a non-reacting pellet (Appendix C) suggests that the center of a pellet heated up to 95% of the reactor temperature in about 20 seconds, significantly less than the overall reduction time (see 4.3). Inspection of pellets after reaction indicated that pellets retained their shape throughout the experiment due to excess carbon. Experimental results are tabulated in Appendix A.

4.1 Pellet and Condensate Analysis

SEM images of C/MgO pellets before and after reaction are shown in Figure 5. Before reaction, magnesia particles were in intimate contact with surrounding carbon, while after reaction direct contact between magnesia particles and carbon was reduced. The narrowing of the XRD peaks for MgO shown in Figure 6 indicated an increase in crystallite size after reaction, likely due to sintering. The loss of C and MgO contact was seemingly due to reaction and/or sintering. Increasing C and MgO contact has been shown

Figure 5. SEM images of C/MgO pellets before (left) and after (right) reaction at 1450°C and 1 kPa. experimentally to increase the rate of carbothermal reduction [27, 36], so the decrease in contact likely

Figure 6. XRD spectra of C/MgO pellets before and after reaction at 1450°C and 1 kPa

Figure 7. Reaction stoichiometry, λ , and Mg yield vs. pressure. Bars represent variation with temperature

reduces the contribution of reaction (1) to the overall reduction rate. Figure 7 illustrates that the reaction stoichiometry, the relative amount of C to MgO reacted, decreased with pressure implying an increase in CO₂ production within the reacting pellet. This suggests that the contribution of gas-solid reactions, reactions (2) and (3), to the overall reduction rate increases with pressure. Variation with temperature appeared to be random, and is represented by bars. Magnesium yield correlated well with reaction stoichiometry up to 10 kPa indicating that the extent of reversion is related to CO₂ production from reaction as CO₂ oxidizes Mg more readily than CO[37]. With further increasing pressure, some reversion must occur by CO directly or indirectly through Boudouard reaction as the yield is less than the reaction stoichiometry. Figure 8 additionally illustrated that as the average CO partial pressure within the reaction chamber increases the yield of magnesium decreased.

Figure 8. Mg yield based on the average p_{CO} during reaction

Condensed magnesium, Figure 9, shows columnar growth similar to magnesium produced via the Pidgeon process. Magnesium oxide appears as aggregates with a dendritic structure indicative of homogeneous nucleation.

Figure 9. SEM image and EDS analysis of Mg and MgO condensate collected at a condenser temperature of 600°C from reaction at 1650°C and 0.1 kPa

4.2 Isoconversional Analysis

Isoconversional analysis was carried out using the integral method[38] to determine the change in activation energy with conversion. The method originates from,

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (10)$$

which after integration at constant pressure and temperature,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A_0 h(P) \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (11)$$

and rearrangement,

$$\ln(t_{\alpha,i}) = \ln\left(\frac{g(\alpha)}{A_0 h(P)}\right) + \frac{E_\alpha}{RT_i} \quad (12)$$

results in the equation for analysis where $t_{\alpha,i}$ is the time required to reach conversion α at temperature i . $E(\alpha)$ can be determined by linear regression of $t_{\alpha,i}$ vs $1/T$ at constant pressure. The integral method was used here because kinetic experiments were assumed to be isothermal, and the integral in equation (11) can be solved analytically at constant temperature.

Figure 10. Isoconversional analysis by integral method at constant pressure

Isoconversional analysis was carried out for conversions between 5 and 45% since reactions at low temperature did not reach high conversions, and linear regression results were deemed reliable only when $t_{\alpha,i}$ was available for all four temperatures studied.

The results in Figure 10 show that activation energy is relatively constant at a given pressure, but increases significantly from 1 to 10 kPa suggesting a change in the rate determining step. The change could result from mass transfer limitations and the influence of gas-solid reactions that become more prevalent at higher pressure, or possibly the change from a carbon limiting reaction to an MgO limiting reaction as the activation energy for carbon oxidation by CO_2 is $\sim 200 \text{ kJ/mol}$ [19-23].

4.3 Conversion as $f(T)_P$ and $f(P)_T$

Temperature and pressure dependent conversion curves are shown in Figures 11 and 12, respectively. Gas sampling was nearly continuous (1 Hz) relative to the overall reduction time, however only 10 data points are shown for clarity. Model predictions are shown as lines and will be discussed in section 5.

The effect of temperature at constant pressure was an increase in reduction rate with increasing temperature for which the Arrhenius dependence was evaluated in the previous section. At constant temperature, pressure had a dual effect on the reduction rate. At low conversions ($\alpha < 0.20$), the reduction rate increased with decreasing system pressure, while at conversions of 0.20-0.35 a transition occurs after which the reduction rate was maximum at 10 kPa. Reduction at 100 kPa resulted in the lowest rate for all temperatures. There exists an optimum pressure for maximum conversion within a given time interval. This phenomenon has been documented previously; Gulanzkii and Chizhikov (1955) [8]

determined that the reduction rate increased with decreasing pressure until ≈ 0.013 kPa below which the reduction rate slowed. As system pressure only affects the diffusivity of gaseous species within the pellet and reactor, the dual effect of system pressure on the reaction rate is thought to be due primarily to mass transfer of product gases from the pellet and the decrease of C and MgO contact with conversion.

Initially, C and MgO contact is greatest (Figure 5) so the initial rate of reduction is likely controlled primarily by reaction (1), the solid-solid reaction of C with MgO. The increase in initial reduction rate with decreasing pressure could be due to an increase in mass transfer of gaseous products out of the pellet, thus resulting in low partial pressures within the pellet that drive the reaction entropically.

As C and MgO contact decreases due to reaction and/or sintering, the rate of reaction (1) slows and the overall reduction may be propagated by gas-solid reactions. The calculated reaction stoichiometry indicates that the influence of gas-solid reactions increases with pressure. Thus, relatively high mass transfer rates, as a result of reduction at low pressures, may reduce the reduction rate by effectively sweeping CO and CO₂ out of the pellet resulting in low partial pressures that hinder the rates of reactions (2) and (3). The overall reduction consists of two parallel but coupled reactions: gas-solid and solid-solid. In this case, the change from solid-solid dominated kinetics to gas-solid was between $0.20 < \alpha < 0.35$ as suggested by experimental conversion curves, $f(P)_T$ (Figure 12). The optimum pressure for fast kinetics is inherently dependent on the reactivity of each species as well as mixing and pellet properties.

Figure 11. Temperature dependent conversion at pressures of 0.1kPa (a), 1kPa (b), 10kPa (c), and 100kPa (d). Data points represent experimental data and lines show the model fit

Figure 12. Pressure dependent conversion at temperatures of 1350°C (a) 1450°C (b) 1550°C (c) and 1650°C (d). Data points represent experimental data and lines show the model fit

5. Model Development

For the case of magnesium oxide, thermal dissociation is considered to be negligible due to the low equilibrium vapor pressure of O_2 . Only reactions (1)-(3) are considered.

The rate of the direct solid-solid reaction, reaction (1), is expressed as a reversible reaction, the rate of which is proportional to C and MgO contact area,

$$R_1 = k_1 A_{C-MgO} \left(1 - \frac{p_{CO} p_{Mg}}{K_1} \right) \quad (13)$$

where K_1 is the equilibrium constant and A_{C-MgO} is the C and MgO contact area. The rates of gas-solid reactions are expressed by Langmuir-Hinshelwood kinetics. The rate expressions are simplified assuming that CO is the dominant surface species.

$$R_2 = k_2 A_{CO-MgO} \frac{p_{CO} K_{2,CO}}{1 + p_{CO} K_{2,CO} + p_{CO_2} K_{2,CO_2} + p_{Mg} K_{2,Mg}} = k'_2 A_{CO-MgO} \frac{p_{CO}}{1 + p_{CO} K_{2,CO}} \quad (14)$$

$$R_3 = k_3 A_C \frac{p_{CO_2} K_{3,CO_2}}{1 + p_{CO} K_{3,CO} + p_{CO_2} K_{3,CO_2} + p_{Mg} K_{3,Mg}} = k'_3 A_C \frac{p_{CO_2}}{1 + p_{CO} K_{3,CO}} \quad (15)$$

R_2 and R_3 quantify the rates of reaction (2), MgO reduction by CO, and reaction (3), C gasification by CO_2 , respectively. Carbon gasification has been studied extensively [19, 20, 22, 39-41] so the parameters for reaction (3) are taken from Turkdogan & Vinters (1970) [19] as their results are similar to other works using relatively pure carbon [40, 41].

Given these rate expressions, a macroscopic species balance on a single pellet results in the following set of differential equations,

$$\frac{dN_{CO_{Pellet}}}{dt} = R_1 - R_2 + 2R_3 - 4\pi r_{pellet}^2 \varphi_s K_{d,CO} (C_{CO} - C_{CO_\infty}) \quad (16)$$

$$\frac{dN_{Mg_{Pellet}}}{dt} = R_1 + R_2 - 4\pi r_{pellet}^2 \varphi_s K_{d,Mg} (C_{Mg} - C_{Mg_\infty}) \quad (17)$$

$$\frac{dN_{CO_2_{Pellet}}}{dt} = R_2 - R_3 - 4\pi r_{pellet}^2 \varphi_s K_{d,CO_2} (C_{CO_2} - C_{CO_2_\infty}) \quad (18)$$

$$\frac{dN_{C_{Pellet}}}{dt} = -R_1 - R_3 \quad (19)$$

$$\frac{dN_{MgO_{Pellet}}}{dt} = -R_1 - R_2 \quad (20)$$

where K_d is the mass transfer coefficient at the surface of the pellet calculated using Frössling's correlation [42] and φ_s is the surface porosity. The partial pressures of product gases outside of the reacting pellet are considered to be negligible; however this may not be the case in a large reactor. The ideal gas law is used to relate concentration and pressure. The initial moles of C and MgO in

a single pellet are $1.4 \cdot 10^{-3}$ and $6.4 \cdot 10^{-4}$ moles, respectively, and the initial concentrations of gases are zero.

The importance of the direct solid-solid reaction on the overall reduction rate has been noted previously [27, 36], yet some models for carbothermal reduction of metal oxides only include the gas-solid reactions [15, 16, 43]. Here the solid-solid reaction is modeled based on a contracting area of contact. The total area of a magnesia particle is described by a shrinking core mechanism, and the area for solid-solid or gas-solid reaction is a fraction of the total area. Equations (21)-(23) describe the relation between surface area and reaction extent. The parameter k_p describes the rate of C and MgO contact loss and x_p describes the fraction of residual contact at high conversion. The parameter values ($k_p=7$, $x_p=0.05$) are estimated from SEM images. At $\alpha=0.30$, the area for gas solid reaction is maximum, which allows the model to predict the increased reactivity observed at 10 kPa.

Figure 13. MgO particle surface area reduction with conversion

$$A_{MgO} = SSA_{MgO} N_{MgO_i}^{\frac{1}{3}} N_{MgO}^{\frac{2}{3}} \quad (21)$$

$$A_{C-MgO} = SSA_{MgO} \left(N_{MgO_i}^{(1-k_p)} N_{MgO}^{k_p} (1-x_p) + N_{MgO_i}^{\frac{1}{3}} N_{MgO}^{\frac{2}{3}} x_p \right) \quad (22)$$

$$A_{CO-MgO} = A_{MgO} - A_{C-MgO} \quad (23)$$

The exposed surface area of carbon is assumed to not change significantly during the course of reaction as the pellets were made with an excess of carbon.

$$A_C = SSA_C N_{C_i} \quad (24)$$

ADamköhler number $\ll 1$ allows for a quasi-steady-state assumption of the gas phase. That is, the partial pressures of gases change much faster than the concentration of the solids such that equilibrium partial pressures exist for a given MgO and C concentration. Equations (16)-(18) are thus reduced to algebraic expressions and can be solved analytically, reducing the system of differential equations from 5 to 2. The analytical solution for (16)-(18) is incredibly complex and, thus, computationally expensive. A further assumption can be made that at low system pressure, the surface concentration of CO on C and MgO is low, therefore the reaction rate expressions given in equation (14) and (15) reduce to first order. Given this, the analytical solutions to the equilibrium partial pressures of product gases are greatly simplified and the overall reduction rate can be calculated by equation (25),

$$\frac{dn_{MgO_{Pellet}}}{dt} = -k_1 A_{C-MgO} \left(1 - \frac{p_{CO_{eq}} p_{Mg_{eq}}}{K_1} \right) - k_2' A_{CO-MgO} p_{CO_{eq}} \quad (25)$$

where $p_{CO_{eq}}$ and $p_{Mg_{eq}}$ are the equilibrium partial pressure of CO and Mg. The simplified model proved to be valid at pressures from 0.1 to 10 kPa, but over predicted the reduction rate at 100 kPa.

Table 1. Model Parameters

Full Model				Simplified Model			
Parameter	A_0		E [kJ·mol ⁻¹]	A_0		E [kJ·mol ⁻¹]	
k_1	14.8	[mol·m ⁻² ·s ⁻¹]	246	16.5	[mol·m ⁻² ·s ⁻¹]	243	
k'_2	$1.60 \cdot 10^{-4}$	[mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹]	187	$4.33 \cdot 10^{-6}$	[mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹]	166	
k'_3	$2.86 \cdot 10^{-1}$	[mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹]	243	$2.86 \cdot 10^{-1}$	[mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹]	243	
$K_{2,CO}$	$3.67 \cdot 10^{-3}$	[Pa ⁻¹]	-5.12	-		-	
$K_{3,CO}$	$4.35 \cdot 10^{-9}$	[Pa ⁻¹]	-137	-		-	

* Parameters taken from literature [19, 40, 41]

Model parameters in Table 1 are computed by non-linear least squares minimization of the difference in experimental and predicted conversion curves shown in Figures 11 and 12. The system of differential equations was solved using ode15s in MatLab. The solution for gas partial pressures quickly converged to equilibrium concentrations further validating a quasi-steady-state assumption. The predicted heat of adsorption of CO on MgO is near the range found in literature (12.5-41.4kJ) [44, 45]. To the knowledge of the authors, the reduction of MgO by CO has not been studied experimentally so experimental and predicted rate parameters cannot be compared.

Figure 14 shows representative predicted species concentrations within the reacting pellet. As the model predicts the production of CO₂, the overall molar conversion of MgO is greater than that of C. This relative conversion is the reaction stoichiometry, λ .

Figure 14. Model simulation at T=1350°C and P=1 kPa

The model represents the simplification of a complicated system of parallel multiphase reactions coupled to diffusion and mass transfer; thus, the rate of MgO carbothermal reduction is dependent on the pelletization method, internal pore structure, pellet size, C/MgO ratio as well as the particle size, grain

size, and SSA of C and MgO. Further, the addition of metals and other inorganic compounds has been shown to have pronounced catalytic effects[15, 24]. The proposed model takes some of these factors into account, and is able to describe the key phenomena in order to adequately predict the rate of MgO carbothermal reduction within the studied temperature and pressure range as is shown in Figures 11 and 12. A macroscopic species balance, as opposed to radial discretization, is used to reduce the number of differential equations required to represent the system kinetics, allowing the model to be implemented for scale-up calculations of pellets reacting in a moving bed or batch reactor.

Further work will be focused on measuring the intrinsic reaction rates for individual reactions (i.e. TGA for gas-solid reaction, dilatometry for SSA reduction). Independent measurement of the solid-solid reaction is extremely difficult without the interference of any gas-solid reaction.

6.0 Conclusion

The rate of MgO carbothermal reduction was studied in the range of 1350-1650°C and 0.1-100kPa. Pressure was shown to have a dual effect. At conversions less than 0.20 the reduction rate increased with decreasing system pressure, while at conversions of 0.20-0.35 a transition occurred after which the reduction rate was maximum at 10 kPa. The average activation energy at different pressures was analyzed using an integral isoconversional method and revealed a change in rate-determining step between 1 and 10kPa. The decrease in reaction stoichiometry with pressure implied an increase in CO₂ generation, and SEM imaging revealed the decrease of C and MgO contact with conversion. The evidence suggests that the importance of gas-solid reactions increases with pressure. At low conversion ($\alpha < 0.20$), the reduction rate is dominated by the direct solid-solid reaction between C and MgO resulting in an increase in reduction rate with vacuum due to low product gas partial pressures inside the pellet. As C and MgO contact degrade due to reaction and/or sintering the overall reaction must be propagated by gas-solid reactions. Relatively high mass transfer rates as a result of vacuum conditions limit the contribution of reactions (2) and (3) by removing CO and CO₂ from the pellet. The system consists of two parallel reaction, solid-solid and gas-solid, which results in an optimum reduction pressure for maximum conversion within a given time frame. A macroscopic species balance based on reactions (1)-(3) is developed and is able to predict the reaction rate within the studied range of temperature and pressure.

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Appendix A: Dispersion Correction

Table A1. Summary of Experimental Results

Temperature [°C]	Pressure [kPa]	Reactor Flow [LPM]	Time [s]	Conversion [%]	Yield [%]	Stoichiometry [λ]
1350	0.1	10	5444	51.9 ± 1.36	96.1 ± 2.36	0.96 ± 0.03
1450	0.1	10	8739	81.4 ± 1.18	100 ± 1.14	1.00 ± 0.02
1550	0.1	10	6498	98.4 ± 1.29	100 ± 0.95	0.92 ± 0.01
1650	0.1	10	3813	100 ± 1.30	100 ± 0.98	0.95 ± 0.01
1350	1	10	6158	62.0 ± 1.13	98.8 ± 1.56	0.83 ± 0.03
1450	1	10	4525	80.1 ± 1.18	93.1 ± 1.07	0.92 ± 0.02
1550	1	10	3600	99.8 ± 1.29	97.5 ± 0.89	0.98 ± 0.02
1650	1	10	3240	99.8 ± 1.30	92.8 ± 0.85	0.96 ± 0.01
1350	10	10	5084	55.0 ± 1.59	91.9 ± 2.52	0.79 ± 0.03
1450	10	10	4135	92.2 ± 1.26	86.7 ± 0.88	0.84 ± 0.01
1550	10	10	3927	99.9 ± 1.29	83.8 ± 0.77	0.91 ± 0.02
1650	10	10	1400	99.9 ± 1.29	75.2 ± 1.00	0.94 ± 0.01
1650	10	10	1415	99.9 ± 1.29	86.9 ± 0.80	0.95 ± 0.01
1350	100	1	8699	30.6 ± 3.12	57.0 ± 5.57	0.53 ± 0.05
1450	100	1	8553	64.9 ± 3.47	64.9 ± 2.86	0.86 ± 0.04
1550	100	1	7461	99.7 ± 4.10	79.6 ± 2.32	0.89 ± 0.03
1650	100	1	2995	99.8 ± 4.10	63.9 ± 1.86	0.86 ± 0.03

Appendix B: Additional Equations for Model Closure

The diffusivity of gaseous products is calculated based on kinetic theory. The binary diffusivity is calculated with respect to the carrier gas, argon.

$$\mathfrak{D}_{AB} = \frac{2}{3} \sqrt{\frac{k_B T}{\pi}} \sqrt{\frac{1}{2} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)} \frac{1}{\pi \left(\frac{1}{2} (d_A + d_B) \right)^2 n} \quad (\text{B1})$$

The viscosity of the gas is estimated to be that of argon at the reaction conditions using the Sutherland correlation[46].

$$\mu = \mu_0 \frac{T_0 + C}{T + C} \left(\frac{T}{T_0} \right)^{3/2} \quad (\text{B2})$$

For argon, $\mu_0 = 2.13 \cdot 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ and $C = 144.4 \text{ K}$.

The mass transfer coefficient is calculated using the Frössling correlation. Gas velocity is estimated based on flow through the graphite plug, essentially a 2.5cm diameter pipe.

$$Sh = 2 + 0.552Re^{1/2}Sc^{1/3} \quad (B3)$$

378 The values of thermodynamic functions were estimated using FactSage. Within the temperature range
 379 studied, the values of ΔH° and ΔS° were assumed to be constant. $\Delta H^\circ = 614.18 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 290.06 \text{ J}$
 380 $\text{mol}^{-1} \text{ K}^{-1}$.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (B4)$$

$$Keq = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad (B5)$$

382 **Appendix C: Estimation of Pellet Heating Time**

383 The time required for a pellet to heat to the reaction temperature was estimated by a 1-D heat transfer
 384 model of a spherical pellet without reaction.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{k_{eff}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \quad (C1)$$

$$T(t = 0, r) = 300K$$

$$k_{eff} \frac{\partial T}{\partial r} \Big|_{t, r=R_p} = \varepsilon \sigma (T_W - T(t, r = R_p))^4 + h (T_W - T(t, r = R_p))$$

$$\frac{\partial T}{\partial r} \Big|_{t, r=0} = 0$$

386 The heat transfer coefficient is calculated based on an analogous correlation to mass transfer[47].

$$Nu = 2 + 0.6Re^{1/2}Pr^{1/3} \quad (C2)$$

387 **Appendix D: Dispersion Correction**

388 For tracer gas measurements, the reactor was brought to reaction conditions using the same methods
 389 previously described, after which a step in CO flow was introduced at the reactor inlet. The dispersed
 390 gas signal was quantified by fitting parameters τ_{1-n} in equations[34, 35].

$$\tau_1 \frac{dC_1}{dt} = C_{in} - C_1 \quad (D1)$$

⋮

$$\tau_n \frac{dC_n}{dt} = C_{n-1} - C_n \quad (D2)$$

391 For the case of tracer gas measurements, C_{in} is the tracer gas flow defined by,

$$C_{in} = \frac{C_{max}}{2} (1 + \tanh(k_{MFC}(t - \theta))) \quad (D3)$$

where k_{MFC} was determined to be $6.7s^{-1}$ by fitting the valve response upon set point change in an MKS mass flow controller. Three CSTRs in series, $n=3$, was determined to be adequate for quantifying dispersion ($R^2 > 0.998$).

For carbothermal reduction, C_{in} is the CO concentration generated by C/MgO pellets within the reactor, and C_3 is the measured concentration. By the measurement of CO concentration, C_3 , and numerical approximations of C_3' , C_2' , and C_1' one can calculate the concentration of CO within the reaction, C_{in} .

419 **Nomenclature**

λ :	Overall reaction stoichiometry
α :	Conversion of MgO to Mg _(v)
N :	[mole]
$\dot{N}$:	Molar flow [mole s ⁻¹]
Y :	Yield of Mg _(s) from Mg _(v)
β :	Reversion Coefficient
τ :	CSTR space-time [s]
C :	Concentration [mole m ⁻³]
k_{MFC} :	Mass flow controller response constant [s ⁻¹]
θ :	Time delay [s]
R_i :	Rate of reaction i [mole s ⁻¹]
k_i :	Rate constant of reaction i [mole m ⁻² s ⁻¹]
k'_i :	Effective rate constant of reaction i [mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹]
p_i :	Partial pressure of component i [Pa]
K_i :	Equilibrium constant of reaction i
$K_{i,j}$:	Equilibrium adsorption constant for reaction i, component j [Pa ⁻¹]
A :	Surface area [m ²]
K_d :	Mass transfer coefficient [m s ⁻¹]
x_p :	Fraction of surface area decay by shrinking core = 0.05
k_p :	Surface area power decay coefficient = 7
A_0 :	Pre-exponential [mol m ⁻² s ⁻¹] or [mol s ⁻¹]
E :	Activation energy [kJ mol ⁻¹]
E_α :	Activation energy at conversion α [kJ mol ⁻¹]
$\mathcal{D}_{AB}$:	Binary gas diffusivity of A in B [mol m ⁻¹ s ⁻¹]
φ :	Pellet porosity = 0.4
φ_s :	Pellet surface porosity = 0.05
R_p :	Pellet radius 5·10 ⁻³ [m]
μ :	Gas viscosity [kg m ⁻¹ s ⁻¹]
μ_∞ :	External gas viscosity [kg m ⁻¹ s ⁻¹]
μ_0 :	Argon reference viscosity = 2.13·10 ⁻⁵ [kg m ⁻¹ s ⁻¹]
T_0 :	Reference temperature = 273.15 [K]
C :	Sutherland constant for argon = 144.4 [K]
D_p :	Average particle diameter [m]
C/MgO :	Carbon to magnesium oxide molar ratio
k_{MFC} :	Mass flow controller response constant = 6.7 [s ⁻¹]
ρ :	Porous pellet density = 650 [kg m ⁻³]
C_p :	Average pellet specific heat = 839 [J kg ⁻¹ K ⁻¹]
k_{eff} :	Porous pellet thermal conductivity = 0.27 [J m ⁻¹ K ⁻¹ s ⁻¹]
SSA_{MgO} :	Magnesium oxide specific surface area = 5965 [m ² mol ⁻¹]
SSA_C :	Carbon black specific surface area = 1025 [m ² mol ⁻¹]
N_{MgO_i} :	Initial moles of MgO in a pellet = 6.4·10 ⁻⁴ [moles]
N_{C_i} :	Initial moles of C in a pellet = 1.4·10 ⁻³ [moles]
ΔG :	Change in Gibbs free energy from reaction [J mol ⁻¹]
$f(\alpha)$:	Differential form of reaction model
$g(\alpha)$:	Integral form of reaction model
$h(P)$:	Pressure dependence on reaction model
$t_{\alpha,i}$:	Time to conversion α for temperature i
$f(T)_p$:	Reduction rate as a function of temperature at constant pressure
$f(P)_T$:	Reduction rate as a function of pressure at constant temperature

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422 References

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