Doctoral Thesis

On the Development of Magnesium Production via Carbothermic Reduction of Magnesium Oxide

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ON THE DEVELOPMENT OF MAGNESIUM PRODUCTION VIA CARBOTHERMIC REDUCTION OF MAGNESIUM OXIDE

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by

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Abstract

Magnesium (Mg) is considered an attractive construction material to substitute the 50% denser aluminum (Al) and the 4.6 times denser steel in order to lightweight vehicles and decrease their fuel consumption and CO$_2$eq emissions. Currently, Mg is primarily produced by the Pidgeon process in which ferrosilicon (Fe$_x$Si) reduces magnesium oxide (MgO). Compared to the process for making Al, however, the Pidgeon process consumes more than twice the energy and releases as much as three times more CO$_2$eq. Thus, in order to exploit the potential for the fuel consumption benefit enabled by lightweighting of vehicles with Mg, the energy and CO$_2$eq content embedded in Mg must be reduced. One way to accomplish this is to circumvent the highly energy consuming and CO$_2$eq emitting production of Fe$_x$Si by using the carbon (C) required for the Fe$_x$Si production directly to reduce MgO via carbothermic reduction (CTR) producing gaseous Mg and CO. It is the scope of this work to investigate and develop the CTR of MgO process as to bring it closer to commercial viability.

The reaction mechanism of CTR of MgO has been still controversially discussed in literature. It has been suggested that Mg$_{(g)}$ is being produced by either (i) MgO dissociation forming O$_2$ as the reaction intermediate or (ii) MgO$_{(s)}$-C$_{(s)}$ boundary reaction producing CO that then reduces MgO while forming CO$_2$ as the reaction intermediate. Either of the intermediates (O$_2$ or CO$_2$) are then consumed by C, which is necessary to sustain further Mg$_{(g)}$ production. Thus, to bring closure to this discussion, the prevailing reaction pathways were identified at the temperature and pressure ranges of 1375-1450°C and 1-2 kPa, respectively, and normalized reduction extents of up to 0.4. For that matter, O$_2$ or CO$_2$ were co-fed with Ar to reacting MgO-C blends with the intent to shift the equilibrium of one of the suspected Mg$_{(g)}$-producing reactions. After accounting for possible confounding effects of the C/MgO ratio in the reacting blend and CO concentration in the reaction atmosphere, it has been demonstrated that Mg$_{(g)}$
is produced via both MgO thermal dissociation and MgO reduction with CO that take place in parallel, while the former prevails with a ratio of 2:1 under the investigated conditions.

To identify the parameters controlling the production of Mg\(_{(g)}\) via MgO dissociation, its kinetics was investigated at a temperature of 1400°C and a total pressure of \(\sim\)2 kPa. Focus was given on studying the effect on the rate of CTR upon (i) increasing the initial MgO particle size and decreasing its specific surface area, (ii) varying the C/MgO molar ratio in the range of 1-4, (iii) diluting the solid reactants with Al\(_2\)O\(_3\), and (iv) replenishing MgO and C in the course of the CTR. It was observed that the CTR appears to pass two reaction stages that are reflected by (i) a high initial rate of CTR that quickly decreases during the first 5-10 min (stage 1) and (ii) a low rate of CTR that slowly decreases at reaction times > 5-10 min (stage 2). It has been shown that both, MgO dispersion and MgO surface area are the two key parameter controlling the rate of CTR during stage 1 of reaction. An increase in the MgO dispersion extent within the C bulk increases the rate of CTR as it increases the proximity of the MgO and C particles and thus facilitates the interparticle transport of O\(_2\) from MgO and C. A decrease in MgO surface area lowers the net O\(_2\) release rate from the MgO surface and thus decreases the rate of CTR. The decrease in MgO surface area being primarily induced by MgO sintering was considered responsible for the fast decrease in the rate of CTR. During stage 2 of reaction, is was speculated that Mg\(_{(g)}\) was primarily produced by reduction of MgO with CO, which in this work appeared to be controlled by the removal of the intermediate CO\(_2\) by C.

Equipped with these findings, a novel reactor concept was developed that is based on reducing MgO at high C/MgO ratios. The C/MgO ratio was considered a key for enhancing the production rate of Mg\(_{(g)}\), as with an increasing ratio the MgO dispersion extent within the C bulk increases thereby (i) facilitating the interparticle O\(_2\) transport and (ii) potentially reducing MgO sintering and the accompanied decrease in MgO surface area. In this reactor concept, the C is stored inside the hot zone of the reactor in form of a bath of C particles in order to avoid the extensive additional energy requirements brought in by heating the excess C. The MgO is continuously fed into the hot zone along with an equimolar amount of C as to account for its consumption by the CTR. The
feedstock is mixed with the C bath using a draught tube screw conveyor that recirculates the bath in vertical direction.

To evaluate this concept experimentally, a lab-scale prototype was designed and tested using either C powders (average size ~44 µm) or C granules (average size ~0.87 mm) as bath material and operating it at temperatures of 1500°C and total pressures in the order of 2-10 kPa. The tests, however, have shown that with both, C powders and granules the production rate of Mg_{(g)} was severely limited by an inefficient removal of the product gases Mg and CO.
Zusammenfassung

Im Leichtbau von Fahr- und Flugzeugen, der zum Ziel hat, deren Kraftstoffverbrauch und CO$_{2eq}$ Emissionen zu reduzieren, gilt Magnesium (Mg) als vielversprechendes Konstruktionsmaterial. Es wird an Stelle des 50% dichteren Aluminiums (Al) und des 4.6-fach dichteren Stahls eingesetzt. Heutzutage wird Mg hauptsächlich über den Pidgeon-Prozess hergestellt, der Magnesiumoxid (MgO) mit Ferrosilizium (Fe$_x$Si) reduziert. Im Vergleich zur Al-Produktion benötigt die Mg-Produktion jedoch mehr als die zweifache Menge an Energie und stösst die dreifache Menge an CO$_{2eq}$ aus. Um das Potential von Mg im Leichtbau auszunutzen, muss deshalb der eingebettete Energie- und CO$_{2eq}$-Gehalt im Mg reduziert werden. Eine Möglichkeit, dies zu erreichen, besteht darin, die stark energieverbrauchende und CO$_{2eq}$-emittierende Produktion von Fe$_x$Si zu umgehen, indem der dafür benötigte Kohlenstoff (C) direkt für die Reduktion von MgO genutzt wird. Das resultiert in der karbothermischen Reduktion (CTR) von MgO, welche gasförmiges Mg und Kohlenmonoxid (CO) produziert. Ziel dieser Arbeit ist die Erforschung und Entwicklung dieses CTR-Prozesses, um ihn näher an die kommerzielle Rentabilität zu bringen.

Der Reaktionsmechanismus der CTR von MgO wird in der Literatur zur Zeit immer noch kontrovers diskutiert. Vermutungen zufolge verläuft die Mg-Produktion entweder über (i) die Dissoziation von MgO, welche O$_2$ als Zwischenprodukt bildet, oder über (ii) eine MgO$_{(s)}$-C$_{(s)}$-Phasengrenzreaktion, welche CO produziert. Hier reagiert das produzierte CO mit MgO weiter, was CO$_2$ als Zwischenprodukt bildet. In beiden Fällen wird das Zwischenprodukt (O$_2$ oder CO$_2$) von C konsumiert, was die weitere Mg-Produktion antreibt. Um diese Diskussion aufzuklären, wurden die dominierenden Reaktionspfade im Temperatur- und Gesamtdruckbereich von 1375-1450°C und 1-2 kPa, sowie normalisierten MgO-Umsetzungsgraden von bis zu 0.4 identifiziert. Dazu wurden O$_2$-Ar- und CO$_2$-Ar-Gemische durch reagierende MgO-C-Mischungen...
geströmt, um das thermodynamische Gleichgewicht einer der vermuteten Mg-
produzierenden Reaktionen Richtung Reaktanden zu verschieben. Unter
Berücksichtigung möglicher Störfaktoren des C/MgO-Verhältnisses in der
Reaktandenmischung und der CO-Konzentration in der Reaktionsatmosphäre
konnte nachgewiesen werden, dass Mg sowohl über die MgO-Dissoziation, als
auch über die MgO-Reduktion mit CO produziert wird. Mit einem Anteil von
etwa zwei Dritteln dominiert dabei erstere Reaktion die Mg-Produktion.

Für die Identifikation der Parameter, welche die Kinetik der Mg-Produktion
kontrollieren, wurde die CTR von MgO bei einer Temperatur von 1400°C und
Gesamtdruck von ~2 kPa näher erforscht. Studiert wurden die Auswirkungen auf
die Kinetik der CTR resultierend von (i) einer Erhöhung der anfänglichen MgO-
Partikelgrösse und der Verringerung der spezifischen Oberfläche, (ii) der
Variation des C/MgO-Molverhältnis im Bereich von 1-4, (iii) der Verdünnung
der Reaktandenmischung mit Al₂O₃ und (iv) der Nachfüllung von MgO und C
im Laufe der CTR. Es wurde beobachtet, dass die CTR zwei Reaktionsstufen zu
durchlaufen scheint. Die Erste wird durch eine hohe Anfangsrate der CTR, die
während der ersten 5-10 min schnell abnimmt, reflektiert. Die Zweite beginnt bei
Reaktionszeiten > 5-10 min und wird durch eine niedrige Rate der CTR
reflektiert, die langsam abnimmt. Es hat sich gezeigt, dass sowohl die MgO-
Dispersion als auch die MgO-Oberfläche die Schlüsselparameter sind, welche
die Kinetik der CTR während Stufe 1 der Reaktion steuern. Eine Erhöhung des
MgO-Dispersionsgrades über die C-Partikel erhöht die Reaktionsrate der CTR:
MgO- und C-Partikel sind sich näher, was den interpartikulären Transport von
O₂ zwischen MgO und C erleichtert. Eine Verringerung der MgO-Oberfläche
senkt die Netto-O₂-Freisetzungsrate und verringert damit die Rate der CTR. Die
Abnahme der MgO-Oberfläche, die hauptsächlich durch das Sintern von MgO
hervorgerufen wird, wurde als Hauptursache für den schnellen Rückgang der
Mg-Produktionsrate angenommen. Des weiteren wurde spekuliert, dass während
Reaktionsphase 2, Mg in erster Linie durch die MgO-Reduktion mit CO
produziert wird. Deren Reaktionsrate scheint unter den beobachteten
experimentellen Konditionen durch die Konsumation des Zwischenprodukts
CO₂ mit C kontrolliert zu sein.
Ausgestattet mit diesen Erkenntnissen wurde ein neuartiges Reaktorkonzept vorgeschlagen, welches auf der Reduktion von MgO bei hohen C/MgO-Verhältnissen basiert. Das C/MgO-Verhältnis wurde als Schlüssel zur Steigerung der Produktionsrate von Mg angesehen. Mit zunehmendem Verhältnis nimmt die MgO-Dispersion über die C-Partikel zu. Dies führt (i) zu einer Erleichterung des interpartikulären O\(_2\)-Transportes und (ii) zu einer potentiellen Verlangsamung des Sinterns von MgO, wodurch die damit verbundene Abnahme der MgO-Oberfläche vermindert wird.

Im vorgeschlagenen Reaktorkonzept wird der Kohlenstoff in der heissen Zone des Reaktors in Form eines Bades aus festen Partikeln gelagert, um den hohen zusätzlichen Energiebedarf durch die Aufheizung des überschüssigen C zu vermeiden. Das MgO wird zusammen mit einer äquimolaren Menge von C kontinuierlich in den Reaktor eingespeist, wobei letzteres den Kohlenstoffverbrauch durch die CTR ausgleicht. Das kontinuierlich eingespeiste MgO-C-Gemisch wird mit Hilfe eines Schneckenförderers mit dem C-Bad vermischt.

Um dieses Reaktorkonzept experimentell zu beurteilen, wurde ein Prototyp im Labormassstab entworfen und getestet, der bei Temperaturen von 1500°C und Gesamtdrücken in der Größenordnung von 2-10 kPa betrieben wurde. Als Badmaterial wurde entweder C-Pulver (durchschnittliche Grösse ~44 µm) oder C-Granulat (durchschnittliche Grösse ~0,87 mm) verwendet. Mit beiden Badmaterialien war die Mg-Produktionsrate jedoch stark eingeschränkt, was auf ein ineffizientes Wegspülen der Produktgase Mg und CO zurückgeführt werden konnte.
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First of all, I thank Prof. Dr. Aldo Steinfeld for giving me the unique opportunity to conduct my doctoral thesis under his supervision at the professorship of renewable energy carriers (PREC) at ETH Zurich. It was a highly exciting and rewarding time. I express my sincerest gratitude to Dr. Zoran Jovanovic for his supervision, invaluable support, and the many critical, but very fruitful and encouraging discussions. I further thank Prof. Dr. Ing. Dr. h.c. Bernd Friedrich for acting as co-examiner of my thesis.

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Nomenclature

Latin characters

\( A_{\text{bath}} \) cross-sectional area of the annular bath section \( \text{mm}^2 \)

\( C_s \) clearance between a conveyor screw and its housing \( \text{mm} \)

\( D_o \) outer radius of a conveyor screw \( \text{mm} \)

\( D_c \) radius of the shaft of a conveyor screw \( \text{mm} \)

\( D_{\text{bath}} \) outer diameter of the annular bath section \( \text{mm} \)

\( \bar{d} \) volume-based mean particle size \( \mu\text{m} \)

\( E \) residence time distribution \((-)\)

\( f_r \) recirculation frequency of a vertically recirculating C bath \( \text{1/min} \)

\( h \) height of the bath or powdery heap \( \text{mm} \)

\( \Delta h^0 \) standard molar enthalpy of reaction \( \text{kJ/mol} \)

\( \Delta h^{1500^\circ C} \) molar enthalpy of reaction at 1500\(^\circ\)C \( \text{kJ/mol} \)

\( K_i \) equilibrium constant of reaction \( i \) \((-)\)

\( l \) length \( \text{mm} \)

\( l_c \) choke length of a vertical screw conveyor \( \text{mm} \)

\( m_j^0 \) initial mass of species, as-received material, or sample \( j \) \( \text{g} \)

\( m_j^f \) final mass of species, as-received material, or sample \( j \) \( \text{g} \)

\( m_{\text{ash}} \) mass of ash in sample \( s \) \( \text{g} \)

\( m_C^* \) mass of extra C layer on top of the felt \( \text{g} \)

\( m_{\text{bath}} \) mass of the bath \( \text{g} \)

\( m_{\text{C screw}} \) mass of C retained inside the conveyor screw after experiment \( \text{g} \)

\( m_{\text{reverse}} \) mass of produced MgO and C in the cooling zone \( \text{g} \)

\( m_{\text{deposits}} \) mass of deposits collected from the cooling zone \( \text{g} \)

\( m_{\text{Mg,final}} \) mass of Mg in the cooling zone \( \text{g} \)

\( m_{\text{cond}} \) mass of condensed volatile matter in the cooling zone \( \text{g} \)

\( M_j \) molar mass of species \( j \) \( \text{g/mmol} \)

\( N_j^0 \) initial amount of species \( j \) \( \text{mmol} \)

\( N_{\text{C,eff}}^0 \) effective initial amount of C \( \text{mmol} \)

\( N_j(t) \) temporal molar amount of species \( j \) \( \text{mmol} \)

\( \tilde{N}_j(t) \) temporal molar amount of species \( j \) in the absence of CTR \( \text{mmol} \)
\( N_{j,\text{dep}}(t) \) \( N_{\text{MgO}}^f \) \( N'_{j} \) \( N_{\text{Mg,final}} \) \( n \) \( \dot{n}_{j}^0(t) \) \( \dot{n}_{j}'(t) \) \( \dot{n}_{j}(t) \) \( \dot{n}_{\text{C,dep}}(t) \) \( \dot{n}_{\text{Mg,final}}(t) \) \( p \) \( p_{j} \) \( \dot{p}_{j} \) \( p_{\text{tot}} \) \( p_{\text{amb}} \) \( p_{\text{red}} \) \( Q_{\text{m}} \) \( Q_{s} \) \( R_{o} \) \( R_{c} \) \( R_{\text{eq}} \) \( r_{i} \) \( r_{i}^* \) \( r_{\text{heap}} \) \( S_{i} \) \( T \) \( T_{\text{ox}} \) \( T_{r} \) \( T_{\text{SP}} \) \( T_{\text{sint}} \) \( t \) \( t_{\text{flight}} \) \( t_{\text{bath}} \) \( t_{\text{drube}} \)

- Temporal molar amount of species \( j \) deposited as solid in the cooling zone, mmol
- Final molar amount of residual MgO after experiment, mmol
- Total molar amount of species \( j \) exiting the CTR zone, mmol
- Total molar amount of Mg retained in the cooling zone, mmol
- Rotational speed of a conveyor screw, rpm
- Temporal molar flow rate of species \( j \) at inlet, mmol/min
- Temporal molar flow rate of species \( j \) exiting the CTR zone, mmol/min
- Temporal molar flow rate of species \( j \) at outlet, mmol/min
- Deposition rate of C in the cooling zone, mmol/min
- Deposition rate of Mg in the cooling zone without undergoing oxidation, mmol/min
- Screw pitch, mm
- Partial pressure of species \( j \), Pa
- Partial pressure of species \( j \) in the absence of CTR, Pa
- Total pressure, Pa
- Ambient total pressure, Pa
- Reduced total pressure, Pa
- Mass throughput of a screw conveyor, g/min
- Sensible heat, kJ
- Outer radius of a conveyor screw, mm
- Radius of the shaft of a conveyor screw, mm
- Equivalent radius of a conveyor screw, mm
- Molar rate of reaction \( i \), mmol/min
- Molar rate of reverse reaction \( i \), mmol/min
- Radius of a powder heap, mm
- Absolute surface area of species \( i \), m²
- Temperature, °C
- Onset temperature of oxidation of C by co-fed oxidants, °C
- Onset temperature of CTR, °C
- Setpoint temperature of the furnace, °C
- Sintering temperature, °C
- Time, min
- (Outer) thickness of screw flights, mm
- Thickness of the annular bath section, mm
- Wall thickness of the draught tube, mm
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_b^i$</td>
<td>total bulk volume of a powdery material $i$</td>
<td>cm³</td>
</tr>
<tr>
<td>$V_{\text{screw}}$</td>
<td>total void volume of a conveyor screw</td>
<td>cm³</td>
</tr>
<tr>
<td>$V_p^i$</td>
<td>void volume of a conveyor screw in one pitch</td>
<td>cm³</td>
</tr>
<tr>
<td>$\dot{V}_S^0(t)$</td>
<td>temporal normal volume flow rate at inlet</td>
<td>L/N/min</td>
</tr>
<tr>
<td>$dV_{\text{bath}}$</td>
<td>relative increase in bath volume</td>
<td>%</td>
</tr>
<tr>
<td>$v_{\text{feeder}}$</td>
<td>speed of the feed screw</td>
<td>rpm</td>
</tr>
<tr>
<td>$v_{\text{recirculator}}$</td>
<td>speed of the recirculation screw</td>
<td>rpm</td>
</tr>
<tr>
<td>$v_{\text{bath,wall}}$</td>
<td>bath wall speed</td>
<td>cm/s</td>
</tr>
<tr>
<td>$W_0$</td>
<td>initial C/MgO molar ratio</td>
<td>(-)</td>
</tr>
<tr>
<td>$W_f$</td>
<td>final C/MgO molar ratio</td>
<td>(-)</td>
</tr>
<tr>
<td>$w_i^j$</td>
<td>mass fraction of compound $i$ in as-received material $j$</td>
<td>%$_{\text{wt}}$</td>
</tr>
<tr>
<td>$w_{\text{ash}}^j$</td>
<td>mass fraction of ash in the residual solid reactants</td>
<td>%$_{\text{wt}}$</td>
</tr>
<tr>
<td>$w_{\text{cond}}^C$</td>
<td>mass fraction of condensable volatile matter in as-received C</td>
<td>%$_{\text{wt}}$</td>
</tr>
<tr>
<td>$dX_i/dt$</td>
<td>conversion rate of species $i$</td>
<td>(-)</td>
</tr>
<tr>
<td>$X_i$</td>
<td>conversion extent of species $i$</td>
<td>(-)</td>
</tr>
<tr>
<td>$X_{\text{feed}}(t)$</td>
<td>temporal conversion of the MgO feed into Mg$_{(g)}$</td>
<td>(-)</td>
</tr>
<tr>
<td>$y_j^0(t)$</td>
<td>temporal molar fraction of species $j$ at inlet</td>
<td>(-)</td>
</tr>
<tr>
<td>$y_j(t)$</td>
<td>temporal molar fraction of species $j$ at outlet</td>
<td>(-)</td>
</tr>
<tr>
<td>$Z_{\text{Mg}}(t)$</td>
<td>temporal Mg reversion coefficient</td>
<td>(-)</td>
</tr>
<tr>
<td>$Z_{\text{CO}}$</td>
<td>fraction of CO consumed in the cooling zone</td>
<td>(-)</td>
</tr>
</tbody>
</table>

### Greek characters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha(r)$</td>
<td>screw helix angle</td>
<td>°</td>
</tr>
<tr>
<td>$\alpha_{\text{eq}}$</td>
<td>equivalent screw helix angle</td>
<td>°</td>
</tr>
<tr>
<td>$\delta$</td>
<td>interparticle O$_2$ transport distance between MgO and C</td>
<td>μm</td>
</tr>
<tr>
<td>$\theta_{\text{H}}$</td>
<td>half angle of hopper or cone (deviation from vertical direction)</td>
<td>°</td>
</tr>
<tr>
<td>$\lambda(r)$</td>
<td>helix angle of particle motion in a screw conveyor</td>
<td>°</td>
</tr>
<tr>
<td>$\lambda_{\text{eq}}$</td>
<td>equivalent helix angle of particle motion in a screw conveyor</td>
<td>°</td>
</tr>
<tr>
<td>$\phi_j$</td>
<td>molar reaction extent of reaction $j$ taking place in the cooling zone</td>
<td>mmol</td>
</tr>
<tr>
<td>$\phi_j^*$</td>
<td>molar reaction extent of reverse reaction $j$ taking place in the cooling zone</td>
<td>mmol</td>
</tr>
<tr>
<td>$\xi_j$</td>
<td>molar reaction extent of reaction $i$ taking place in the hot zone</td>
<td>mmol</td>
</tr>
<tr>
<td>$\xi_j^*$</td>
<td>molar reaction extent of reverse reaction $i$ taking place in the hot zone</td>
<td>mmol</td>
</tr>
</tbody>
</table>
\( \varepsilon \)  stoichiometric coefficient of the CTR proceeding via
dissociation of MgO  
\(-\)

\( \gamma \)  stoichiometric coefficient of the CTR proceeding via reduction
of MgO with CO  
\(-\)

\( \eta_{\text{max}} \)  maximum attainable energy conversion efficiency  
\(-\)

\( \eta_V \)  volumetric efficiency of a screw conveyor  
\(-\)

\( \eta_F \)  fullness efficiency of a screw conveyor  
\(-\)

\( \eta_{VR} \)  vortex efficiency of a screw conveyor  
\(-\)

\( \eta_{V\text{req}} \)  equivalent vortex efficiency of a screw conveyor  
\(-\)

\( \rho_b \)  bulk density of a powdery material  
g/cm\(^3\)

\( \phi_i \)  angle of repose of a powdery material  
\(\circ\)

\( \phi_s \)  angle of friction of a powdery material on the screw surface  
\(\circ\)

\( \mu_d \)  coefficient of friction of a powdery material at the draught tube  
\(-\)

\( \mu_i \)  particle-particle friction coefficient  
\(-\)

\( \mu_s \)  coefficient of friction of a powdery material on the screw surface  
\(-\)

\( \tau_{\text{ox}} \)  onset point of oxidation of C by co-fed oxidants  
min

\( \tau_I \)  onset point of CTR  
min

\( \tau_{II} \)  end point of CTR  
min

\( \tau_f \)  final point of test  
min

**Subscripts**

imp  impurity

N  normal (0°C and 101.3 kPa)

tot  total

vm  volatile matter

\( |_{O_2} \)  \( O_2\)-Ar sweep

\( |_{CO_2} \)  \( CO_2\)-Ar sweep

\( |_{\text{int}} \)  intermediate (\( O_2\)-Ar sweep or \( CO_2\)-Ar sweep)

\( |_{\text{high}} \)  high initial amount of C

\( |_{\text{low}} \)  low initial amount of C

**Abbreviations**

ATR  aluminothermic reduction
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller method</td>
</tr>
<tr>
<td>CTR</td>
<td>carbothermic reduction</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>LDS</td>
<td>laser diffraction spectroscopy</td>
</tr>
<tr>
<td>MTR</td>
<td>methanothermic reduction</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>SOM</td>
<td>solid-oxide membrane electrolysis</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>SSA</td>
<td>specific surface area</td>
</tr>
</tbody>
</table>


1 Introduction

As counteraction for the imminent global warming, policymakers around the world have decided to regulate and gradually decrease the greenhouse gas emissions of vehicles in the upcoming years.\textsuperscript{1, 2} For instance, the European Union and Switzerland have restricted the CO\textsubscript{2} emissions of passenger cars to 95 g/km by the year 2020.\textsuperscript{2, 3} One of the key measures considered to reduce the greenhouse gas emission of vehicles is to decrease their fuel consumption by lightweighting.\textsuperscript{4-8} Magnesium (Mg) is considered an attractive construction material to lightweight vehicles,\textsuperscript{4-8} because its density is only 65\% of that of aluminum and 22\% of that of iron.\textsuperscript{4} It is the eight most abundant element in the earth’s crust and is contained in numerous minerals (e.g. dolomite (MgCa(CO\textsubscript{3})\textsubscript{2}) or magnesite (MgCO\textsubscript{3})) and as third most plentiful element in seawater.\textsuperscript{9} In industry, magnesium is already primarily applied in aluminum alloys, die casting, desulfurization of iron and steel, and reduction of metals, e.g. titanium.\textsuperscript{4, 5, 9, 10} The material benefits from its excellent machinability,\textsuperscript{11} corrosion resistance,\textsuperscript{5, 11} and high strength-to-weight ratio.\textsuperscript{10, 11} Numerous vehicle components may be built of magnesium alloys, such as drivetrain parts (e.g. the engine block\textsuperscript{5, 6, 12}), interior parts (e.g. the seat frames\textsuperscript{6} or the steering wheel\textsuperscript{6, 7}), or chassis components.\textsuperscript{6} Estimations have shown that by substituting aluminum and/or steel with magnesium, a reduction in total vehicle weight of up to 15\% may be achieved.\textsuperscript{13}

1.1 Current Primary Mg Production

In the last two decades, the demand for magnesium metal in industry has significantly grown and the worldwide yearly primary production of Mg increased by ~270\% (from 368,000 metric tons in 1996\textsuperscript{[14]} to ~1,000,000 metric...

tons in 2016\textsuperscript{a, 9}). Furthermore, the majority of primary Mg production shifted from the US (36\% of the worldwide production in 1996\textsuperscript{[14]}) to China (~87\% of the worldwide production in 2016\textsuperscript{9}), primarily as a result of lower operational and capital costs of the Chinese plants\textsuperscript{8, 10} allowing a lower priced sale of the Mg metal. Nowadays, China produces Mg exclusively via the silicothermic route, i.e. the thermic reduction of MgO with ferrosilicon (Fe\textsubscript{x}Si) that is commonly known as the Pidgeon process.\textsuperscript{7, 15} In the US, Mg is being produced by electrolysis.\textsuperscript{9} Other countries that produce Mg commonly use either the Pidgeon process, electrolysis, or modifications thereof (e.g. the Magnetherm or the Bolziano process).\textsuperscript{7, 9}

1.1.1 Mg Production via the Silicothermic Route

The silicothermic route, i.e. the Pidgeon process commonly follows the process steps illustrated in Figure 1.\textsuperscript{7, 10, 16} First, mined dolomite is calcined at 1000-1300°C in a rotatory kiln\textsuperscript{7, 16} or in a vertical batch furnace\textsuperscript{16} in order to dissociate the dolomite into dolime (MgO\cdot CaO) and CO\textsubscript{2} according to

\[
\text{MgCa(CO}_3\text{)}_{2(s)} \rightleftharpoons \text{MgO} \cdot \text{CaO}_{(s)} + 2\text{CO}_{2(g)} \cdot \tag{1}
\]

In parallel, Fe\textsubscript{x}Si and the by-product CO is produced by reducing quartz (SiO\textsubscript{2}), together with iron oxides (Fe\textsubscript{x}O\textsubscript{y} from e.g. scrap iron or mill scale) with C in an electrical arc furnace at temperatures of 1600°C.\textsuperscript{10, 16} The dolime is then ground and blended with the reducing agent Fe\textsubscript{x}Si and with the catalyst calcium fluoride (CaF\textsubscript{2}) that resulting mixture is pressed to pellets. The pellets are filled into retorts that are heated to ~1200°C at total pressures in the order of 2\textsuperscript{[16]-70\textsuperscript{[10]}} Pa and left to react for ~8h\textsuperscript{16} to produce Mg gas according to

\[
2\text{(MgO} \cdot \text{CaO)}_{(s)} + \text{Fe}_x\text{Si}_{(s)} \rightleftharpoons 2\text{Mg}_{(g)} + \text{Ca}_2\text{SiO}_4_{(s)} + x\text{Fe}_{(s)} \tag{2}
\]

\textsuperscript{a} Produced quantities in the US are currently withheld to avoid disclosing company proprietary data. However, the total produced quantity with respect to worldwide production is considered small, as the total Mg production capacity was only 63’500 metric tons in 2016 [Bray, L., Magnesium, in 2016 Minerals Yearbook. 2018, U.S. Geological Survey.]
The Mg precipitates on a water-cooled condenser outside the furnace from which it is collected. Subsequently, the Mg is molten in a melting furnace, refined and casted into ingots. The molten Mg is prevented from burning using the cover gas sulphur dioxide (SO$_2$) or powdery sulphur (S) that is dispersed over the melt surface.

Figure 1. Overview of the commonly followed process steps in the silicothermic Mg production route.

### 1.1.2 Mg Production Via Electrolysis

In this route, Mg is produced by the electrolysis of magnesium chloride (MgCl$_2$) producing liquid Mg and chlorine gas at temperatures in the order 700-800°C. The process steps involved in the preparation of the MgCl$_2$ differ greatly depending on the Mg source. MgCl$_2$ is typically recovered from (i) sea
water or brines where it is present in its hydrated form (MgCl$_2$·12H$_2$O), (ii) from carnallite (MgCl$_2$·KCl·6H$_2$O), or (iii) from the ores dolomite (MgCa(CO$_3$)$_2$) or magnesite (MgCO$_3$).\textsuperscript{7,17}

1.1.3 The Problematic Energy Requirements and CO$_2$ Emissions Associated With Primary Mg Production

The Pidgeon process is considered a very energy consuming and CO$_2$ emissive process, especially as conducted in China.\textsuperscript{4,10,16} A cradle-to-gate life cycle assessment (LCA) of the Chinese Pidgeon process dating back to 2004 showed that the overall energy requirements and CO$_{2eq}$ emission were as high as 355 MJ and 42 kg CO$_{2eq}$ per kg Mg.\textsuperscript{16} The three most energy consuming and CO$_2$ emissive process steps were identified to be the reduction step (181.4 MJ/kg Mg and 15.9 kg CO$_{2eq}$/kg Mg), the production of Fe$_x$Si (113.5 MJ/kg Mg and 14.7 kg CO$_{2eq}$/kg Mg), and the calcination of dolomite (52.1 MJ/kg Mg and 10.1 kg CO$_{2eq}$/kg Mg). In the following decade, the Chinese Pidgeon process was improved primarily by exchanging the source of process heat from coal to fuel gases resulting in lower energy requirements (133 instead of 181.4 MJ/kg Mg for the reduction step alone) and lower overall CO$_{2eq}$ emissions (25.3 instead of 42 kg CO$_{2eq}$/kg Mg).\textsuperscript{7} Nevertheless, in comparison to the reported energy requirements and CO$_{2eq}$ emissions associated with the primary production of aluminum, the Chinese Pidgeon process still consumes more than twice the energy (133\textsuperscript{[7]} vs. 54\textsuperscript{[20]} MJ/kg Mg)a and releases as much as three times more CO$_{2eq}$ (25.3\textsuperscript{[7]} vs. 8.7\textsuperscript{[20]} CO$_{2eq}$/kg Mg). Also the electrolytic Mg production route is considered more energy consuming (100\textsuperscript{[7]} vs. 54\textsuperscript{[20]} MJ/kg Mg)a and CO$_2$ emissive (18.2\textsuperscript{[7]} vs. 8.7\textsuperscript{[20]} CO$_{2eq}$/kg Mg) than primary Al production.

Thus, the high energy requirements and CO$_2$ emissions associated with the production of primary Mg partially offset the fuel consumption benefits enabled by vehicle lightweighting with Mg. This problem is illustrated with an example of an LCA study reported by Ehrenberger et al.\textsuperscript{7}: manufacturing a steering wheel of a passenger car with Mg produced by the Pidgeon process instead of Al results

\textsuperscript{a} considering only the reduction and electrolysis step alone, respectively, as overall energy requirements are not available for all routes.
in the emission of additional \(\sim 3-4.5\) kg CO\(_{2eq}\). With the fuel savings generated by the substitution of Al with Mg, less CO\(_{2eq}\) is produced during the use of the passenger car. Thus, at the end of lifetime (at 200,000 km driving distance), the total amount of additionally emitted CO\(_{2eq}\) with the Mg steering wheel compared to the Al one decreases down to \(\sim (-1)\) kg CO\(_{2eq}\) (assuming no recycling of the Mg after end of lifetime). In this example, therefore, the generated benefits of using Mg instead of Al to lightweight vehicles on CO\(_{2eq}\) emissions are just offset by the additional amount of CO\(_{2eq}\) emitted during the production. Using Mg produced by electrolysis significantly improves the CO\(_{2eq}\) balance and up to 4 kg CO\(_{2eq}\) may be saved at the end of lifetime of the passenger car by the substitution of Al with Mg. Nevertheless, to superiorly exploit the benefits of lightweighting vehicles with Mg, the embedded energy and CO\(_{2eq}\) content in the primary Mg must be reduced. This may be accomplished by improving its production process.

### 1.2 Improving the Production of Primary Mg

Two general paths are considered that potentially improve the production of primary Mg in terms of energy requirements and CO\(_{2eq}\) emissions: (i) the Pidgeon process itself may be re-designed and improved, or (ii) an alternative Mg production route may be developed. An example for an improved Pidgeon process is given by the Gossan-Zuliani process that has been proposed recently.\(^{11}\) In contrast to the Chinese Pidgeon process, the reduction of MgO is to be conducted at 1600°C and ambient total pressure. Furthermore, natural gas is used as the source for process heat for dolomite calcination and hydroelectricity for Fe\(_x\)Si production and the MgO reduction step. It was estimated that overall CO\(_{2eq}\) emissions as low as 9.1 CO\(_{2eq}\)/kg Mg can be achieved with overall energy requirements as low as 170 MJ/kg Mg (i.e. 77 MJ/kg Mg considering the reduction step only).

Another method to lower the CO\(_{2eq}\) emissions of the Pidgeon Process has been suggested by Halmann et al.\(^{21}\). First, the CO\(_2\) and CO released in the process steps dolomite calcination and ferrosilicon production, respectively, are further used for the co-production of syngas. This can be accomplished by adding C and H\(_2\)O, or methane (CH\(_4\)) as to reduce the released CO\(_2\) to CO and co-produce H\(_2\).
Second, instead of using fossil fuels or hydroelectricity, concentrated solar energy is to be used as renewable source to provide the process heat for the three process steps dolomite calcination, Fe\textsubscript{x}Si production, and MgO reduction. Solar energy is considered as a very promising heat source, as (i) no CO\textsubscript{2} is produced during heat generation in comparison to combusting fossil fuels, and (ii) the incoming solar irradiation can be converted directly into heat instead of converting it first into electricity as compared to hydroelectricity.

In order to achieve high process temperatures with solar energy, the dilute terrestrial solar irradiation (~1 kW/m\textsuperscript{2}) needs to be collected and focused onto a central receiver using concentrating optical devices\textsuperscript{22}. An example for such a device is given in Figure 2 that shows a solar furnace located at the Paul Scherrer Institute (PSI) in Switzerland\textsuperscript{23}. A 124m\textsuperscript{2} heliostat reflects incoming sunlight onto a vertically aligned, parabolic concentrator of 8.5 m diameter. This concentrator focuses the sunlight with peak concentration ratios of over 5000 allowing to reach process temperatures as high as 2200°C.

Figure 2. High flux solar furnace at PSI, Switzerland\textsuperscript{24}. A heliostat (front) reflects sunlight onto a vertically aligned, parabolic concentrator located inside the building.
1.2.1 Alternative Mg Production Routes

The development of alternative Mg production routes focuses primarily on four different concepts: the aluminothermic reduction (ATR) of MgO, the solid-oxide membrane electrolysis (SOM) of MgO, the carbothermic reduction (CTR) of MgO, and the methanothermic reduction (MTR) of MgO.

1.2.1.1 Aluminothermic Reduction of MgO

The ATR of MgO uses Al as reducing agent and produces Mg\(_{(g)}\) and the by-product spinel (MgAl\(_2\)O\(_4\)) according to\(^{10}\)

\[
4\text{MgO}(s) + 2\text{Al}(s) \leftrightarrow 3\text{Mg}_{(g)} + \text{MgAl}_2\text{O}_4(s). \tag{3}
\]

Experimental studies have demonstrated the production of Mg at temperatures in the order 1200°C\(^{25,27}\) at reduced\(^{25,26}\) or ambient\(^{27}\) total pressure. It was observed that at 1300°C, ~5 Pa total pressure, and with dolomite as starting material, the conversion of MgO reached up to 80% within 10 minutes.\(^{28}\) The reduction of MgO with Al therefore appears to be significantly faster than the reduction with Si, which requires up to ~8h reaction time.\(^{16}\) The ATR of MgO has been considered to outperform the Chinese Pidgeon process in terms of potentially less energy requirements and CO\(_2\) emissions\(^{26}\) and lower amounts of solid product waste, since the spinel may be re-used,\(^{25,26,29}\) e.g. as refractory material.\(^{26}\) However, it is evident that this process is not able to outperform the production of primary Al in terms of energy requirements and CO\(_{2eq}\) emissions, since Al itself is used as reducing agent.

1.2.1.2 Solid-Oxide Membrane Electrolysis

In the SOM process, MgO is dissolved in a fluoride-based flux (MgF\(_2\)-MgO or MgF\(_2\)-CaF\(_2\)-MgO).\(^{30,32}\) By applying an electric current at temperatures in the order of 1150-1300°C, the MgO dissociates into Mg\(^{2+}\) and O\(^{2-}\). At an inert cathode placed into the flux, the Mg cations are reduced to Mg\(_{(g)}\) that evaporates from the flux and is collected in a separate condenser. The oxygen anions migrate
through a solid oxygen ion conducting membrane (i.e. yttria-stabilized zirconia (YSZ)) to an anode where they are oxidized. The oxygen is removed from the anode either directly as $O_2$ gas,\(^{31}\) or by the consumption with a reducing agent, e.g. $H_2$\(^{33}\) producing $H_2O(g)$, or solid C producing $CO$\(^{30}\). The membrane separates the flux from the anode and thus prevent its dissociation.\(^{30}\) The SOM process is considered as an attractive alternative for the currently conducted production of Mg via electrolysis, because the rather extensive preparation of MgCl$_2$ is not required.\(^{33}\) However, developing a long-term stable membrane has been shown to be challenging, since it may react with produced Mg\(_{(g)}\)\(^{30}\) or may degrade due to a diffusion of yttria into the flux.\(^{34}\)

1.2.1.3 Carbothermic Reduction of MgO

Significant attention has been brought to the CTR of MgO. In this route, Mg\(_{(g)}\) and the by-product CO is produced by the reduction of MgO with C that can be represented by the highly endothermic ($\Delta h^0 = 638$ kJ/mol\(^{35}\)) overall reaction\(^{36}\)

$$MgO(s) + C(s) \rightleftharpoons Mg(g) + CO(g). \tag{4}$$

The CTR of MgO process was originally invented by Hansgirg\(^{37}\) and some first industrial tryouts were already conducted during the 1940s.\(^{36, 38, 39}\) Thermodynamic calculations have shown that the temperature required for the overall reaction to proceed in forward direction is dependent on the pressure of the products Mg\(_{(g)}\) and CO.\(^{36, 40, 41}\) For example, Chubukov et al.\(^{41}\) have shown in their equilibrium calculations that a decrease of the total product pressure (Mg\(_{(g)}\) + CO) from 100 to 1 kPa decreases the onset temperature of the forward reaction from ~1750 to ~1350°C.

The CTR of MgO is considered an attractive alternative for primary Mg production. First estimates have projected the overall energy requirements and CO$_{2eq}$ emissions of the CTR process to values as low as 56 ($\pm 28$) MJ/kg Mg and 14 ($\pm 8$) kg CO$_{2eq}$/kg Mg.\(^{42}\) However, to achieve an overall energy requirement of ~56 MJ/kg Mg is suspected to be rather difficult considering that the standard molar enthalpy of the overall reaction is already as high as 26 MJ/kg Mg.
One of the major challenges in developing the CTR of MgO has been faced in suppressing the backward, i.e. reverse overall reaction (4): upon cooling the CTR product gas, the Mg reacts with CO forming MgO and C.\textsuperscript{36} Furthermore, cooling the product gas too rapidly may result in the formation of fine Mg powder that is pyrophoric and thus difficult to handle.\textsuperscript{36, 43, 44} Numerous attempts have been made to suppress the extent of the reverse overall reaction and/or to accomplish the collection of non-pyrophoric Mg:

- diluting and quenching the product gases by H\textsubscript{2}\textsuperscript{37, 45} or N\textsubscript{2}.\textsuperscript{46}
- diluting and quenching the product gases by hydrocarbon vapor, e.g. natural gas and promoting the formation of magnesium carbide (Mg\textsubscript{2}C\textsubscript{3} and/or MgC\textsubscript{2}) that was shown to decrease the pyrophoricity of the product condensate.\textsuperscript{47, 48} Recovery of Mg is conducted by vacuum distillation of the product condensate above the decomposition temperature of the magnesium carbide.
- shock-cooling the product gases with liquid Mg\textsuperscript{49} or MgCl\textsubscript{2}.\textsuperscript{50}
- lowering the product partial pressures by expanding the product gas through an orifice upon which the Mg product is condensed at a cooled surface.\textsuperscript{51}
- quenching the product gases supersonic by passing them through a Laval nozzle.\textsuperscript{43}
- condensing the Mg product under vacuum on a cooled surface that is in motion relative to a scraper, which continuously removes the Mg condensate from the cold surface.\textsuperscript{39}
- condensing the Mg product under vacuum in a multi-stage condenser.\textsuperscript{52-54}
- condensing the gaseous Mg product in a bed of moving particles, e.g. solid Mg, which allows a continuous removal of the Mg condensate.\textsuperscript{55}

However, neither of these methods have been commercially accepted so far to be a compelling solution for a large-scale industrial application. Nevertheless, high Mg yields above 90% have been observed by supersonic quenching\textsuperscript{43} or by lowering the CO partial pressure below 0.5 kPa\textsuperscript{56} demonstrating the feasibility for efficiently suppressing the reverse overall reaction.
Operating the CTR of MgO under vacuum is thus considered beneficial as (i) lower operating temperatures are required thereby reducing heat losses and the energy required to preheat the reactants, and (ii) the extent of the reverse overall reaction is decreased thereby increasing the Mg yield. It has to be evaluated, however, whether the benefits of vacuum operation for the amount of required process heat compensates for the additional pumping work required to maintain the low reaction pressures.

Concentrated Solar Energy as the Source of Process Heat

In order to further reduce CO$_{2eq}$ emissions of the CTR of MgO, it has been suggested to supply the process heat with concentrated solar energy.$^{40,57-61}$ Its applicability has already been successfully demonstrated in past research:

- Murray et al.$^{57}$ used a spherical receiver made of aluminum. In its center, a graphite crucible was placed comprising the powdery reactants MgO and C that were heated by a solar furnace providing 7 kW (at 850 W/m$^2$ ambient solar flux conditions) with peak concentration ratios of about 7000. Two 30-minute runs performed at temperatures and total pressures of ~1960°C and ~4 kPa, and ~1900°C and ~2 kPa, respectively, demonstrated the production of Mg that fractions in the solid product condensate (Mg, MgO, and C) were as high as 9 and 16%, respectively.

- Vishnevetsky et al.$^{60}$ demonstrated the CTR of MgO in a solar reactor comprising a graphite crucible for MgO-C pellets that was irradiated from the top and sealed by a quartz dome. Solar irradiation was provided by a 10 kW solar furnace at concentration ratios of up to 5000. Experimental tests at temperatures of 1530-1600°C, average CO partial pressures of ~3 Pa, and total reaction times of up to 3 hours resulted in MgO conversion extents of up to 70% and very high Mg fractions in the solid product condensate of up to 99%.

- Puig and Balat-Pichelin$^{59}$ used a 2 kW solar furnace having a concentration ratio of up to 11’000 to heat a solar reactor comprising a graphite crucible for MgO-C pellets, which was sealed by a quartz
dome. The highest MgO conversion extents (60%) were reached by slowly heating the reactants from 1500 to 1920°C within 50 min at 9 kPa total pressure resulting in Mg fractions in the solid product condensate of ~50%.

In conclusion, these experimental studies show that the use of concentrated solar energy as renewable source of process heat is a promising method for the production of Mg via the CTR of MgO.

1.2.1.4 Methanothermic Reduction of MgO

In the MTR of MgO, Mg\(_{(g)}\) is produced by the reducing agent methane (CH\(_4\)) according to\(^{62}\)

\[
\text{MgO (s)} + \text{CH}_4(\text{g}) \rightleftharpoons \text{Mg (g)} + \text{CO (g)} + 2\text{H}_2(\text{g})
\]  

Experimental studies have reported that at a temperature of 1400°C MgO conversions >50% can be achieved within a few seconds by finely dispersing MgO powders into a stream of CH\(_4\).\(^{62}\) Furthermore, the formation of magnesium carbides have been observed upon cooling and condensing the Mg product.\(^{63}\) However, the operation at temperatures as high as 1400°C also promotes extensive thermal decomposition of CH\(_4\) into solid C and H\(_2\).\(^{64}\) Thus, the development of the MTR of MgO without using a large excess of CH\(_4\) and/or endangering the clogging of the reactor by the formed C is considered challenging.

1.3 Thesis Outline

This thesis aims at developing the carbothermic reduction of MgO process for the production of Mg metal. The focus lies on investigating the prevailing reaction mechanism and the kinetics of the forward overall reaction that findings build the basis for the development of a suitable reactor, which is to be designed and experimentally tested.
Chapter 2 provides a background for presented work over current literature thereby focusing on the controversially discussed reaction mechanisms and on the kinetics of Mg production by the CTR. Furthermore, it provides a thermodynamic assessment on the expected equilibrium composition of the CTR. In chapter 3, the prevailing reaction pathway(s) are discriminated for the range of investigated conditions. Chapter 4 investigates the kinetics of the CTR and determines the key rate-controlling parameters using a novel experimental method to acquire kinetic data. Based on the key findings of chapter 4, a reactor concept is suggested in chapter 5. A following literature review provides the basis for designing the suggested reactor concept, which design is introduced in chapter 6. In chapter 7, the designed reactor is built and tested experimentally for its potential of producing Mg via the CTR of MgO. Chapter 8 gives a summary of the research findings and an outlook on the further development of the tested reactor concept and on further research in the production of Mg by the CTR of MgO.
2 Background

This chapter gives a review of current literature relevant for the CTR of MgO with focus on the suggested reaction mechanisms and on parameters affecting the kinetics of CTR. Furthermore, it provides a thermodynamic assessment on the expected equilibrium composition of the CTR.

2.1 The Controversially Discussed Reaction Mechanisms

At present, there is no consensus on the prevailing mechanism of the CTR of MgO. The reported findings gravitate around two hypotheses. The first one has been advocated by Komarek et al., who have proposed that MgO first dissociates into Mg\(_{(g)}\) and O and that the latter then diffuses to the C-surface where it reacts to form CO. The authors have not commented on excluding the recombination of the atomic oxygen from consideration, which is believed to be very fast at the temperatures of interest. This recombination transforms their proposed mechanism into its equivalent summarized as follows:

\[
\text{MgO}_{(s)} \rightleftharpoons \text{Mg}_{(g)} + 0.5\text{O}_{2(g)} \quad (6)
\]

\[
0.5\text{O}_{2(g)} + \text{C}_{(s)} \rightleftharpoons \text{CO}_{(g)} \quad (7)
\]

The findings of Komarek et al. have been supported by Hong et al. who also suspected that the CTR may proceed via MgO dissociation.

On the other hand, numerous authors have advocated the mechanism according to which MgO is being directly reduced by both C and CO. Namely, the Mg production is initiated by the MgO\(_{(s)}\)-C\(_{(s)}\) boundary reaction (4) that

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\(^{a}\) Material in this chapter was published in: A. Coray and Z.R. Jovanovic, “On the Prevailing Reaction Pathway during Magnesium Production via Carbothermic Reduction of Magnesium Oxide under Low Pressures”, Reaction Chemistry and Engineering, 2019, 4, p. 939-953
prevails up to MgO conversions of $X_{\text{MgO}} = 0.2^{[70]} - 0.25^{[67]}$. At conversions higher than these, the MgO is reduced mainly by CO

$$\text{MgO}_{(s)} + \text{CO}_{(g)} \rightleftharpoons \text{Mg}_{(g)} + \text{CO}_{2(g)} \quad (8)$$

as the contribution of the MgO(s)-C(s) boundary reaction to the total Mg(g) production decreases due to a loss in the MgO(s)/C(s) contact that has been attributed to (i) the decrease in the surface areas of the reactants due to CTR itself$^{70}$, (ii) sintering of MgO$^{70}$, or (iii) densification of MgO$^{67}$. The production of Mg(g) by reaction (8) is sustained by oxidation of C with CO$_2$

$$\text{CO}_{2(g)} + \text{C}_{(s)} \rightleftharpoons 2\text{CO}_{(g)} \quad (9)$$

which not only removes CO$_2$ from the reaction site but also replenishes the reducing agent CO. Beside of MgO conversion, the prevalence of the two pathways has also been distinguished by temperature when exploiting non-isothermal thermogravimetry$^{75}$, which conclusion was based on an observed inflection point in the rate of CTR upon reaching 1480°C. However, this inflection point may also have been confused by a change in rate control from thermodynamic equilibrium to any other form of control.

Experimental evidence supporting the significance of reaction (8) has been provided by Rongti et al.$^{67}$ and by Chubukov et al.$^{70}$. Rongti et al.$^{67}$ investigated the effect of CO concentration on the kinetics of MgO reduction by graphite. Exploiting non-isothermal thermogravimetry at atmospheric pressure, these authors have observed an increase in the Mg(g) production rate upon switching the reaction atmosphere from pure Ar to CO–Ar mixtures containing 10 or 20% CO. The authors have attributed this observation to the facilitating effect of an increase in the CO concentration on reaction (8). However, as also observed by other authors,$^{66, 76, 77}$ the reduction in pure CO was much slower than in pure Ar, which has been attributed to the suppressing effect of high CO concentrations on the removal of CO$_2$ from the reduction site via reaction (9). Chubukov et al.$^{70}$ studied the kinetics of MgO reduction with carbon black under isothermal/isobaric conditions at temperatures and total pressures in the range of 1350-1650°C and 0.1-100 kPa, respectively. Depending on the MgO conversion,
these authors observed a dual effect of decreasing the total pressure on the Mg\(_{(g)}\) production rate that they explained as follows:

1. At \(X_{\text{MgO}} < 0.2\), a decrease in the total pressure increases the reaction rate which was attributed to favoring the \(\text{MgO}(s) - \text{C}(s)\) boundary reaction (4).
2. At \(X_{\text{MgO}} > 0.35\), reducing total pressure decreases the reaction rate which was attributed to higher removal rates of CO and \(\text{CO}_2\) from the reaction zone. It, however, remains unclear why an increased removal rate of \(\text{CO}_2\) from the reaction zone would decrease the rate of CTR as it should actually favor reaction (8).

In contrast, it has also been suggested that MgO reduction with CO does not participate at all in the CTR, since no reduction of MgO was observed when flowing CO over MgO in the absence of C.\(^{78}\) However, these authors did not consider that without C there is no sink for \(\text{CO}_2\) that sustains Mg production making their interpretation rather inconclusive.

Other authors focused on fitting common kinetic models (e.g. Jander’s model or the shrinking core model) on their kinetic data and suggested that depending on the source of C,\(^{61}\) reaction extent,\(^{79}\) or reaction time\(^{59}\) different reaction pathways may prevail.

### 2.2 Effect of Reactant Morphology on the Rate of CTR

In past studies, it has been shown that the rate of CTR can depend on both, the morphology of MgO and C.

**Morphology of MgO**

Chubukov et al.\(^{41}\) have observed that the rate of CTR was significantly decreased when substituting MgO of high specific surface area (SSA) and small crystal size (147 m\(^2\)/g and \(~4\) nm) with MgO having a low SSA and large crystal size (0.6 m\(^2\)/g and \(~28\) nm). As already discussed, it has been suggested that a gradual sintering of MgO may be responsible for a loss in \(\text{MgO}(s)/\text{C}(s)\) contact leading to
a decrease in the rate of CTR.\textsuperscript{60,70} Sintering affects the morphology of a material substantial, as particles coalesce, which increases the particle and crystal size, and decreases the specific surface area.\textsuperscript{80,81} The sintering of MgO is an already well-documented phenomena.\textsuperscript{82-92} Experimental studies have observed an increase in crystallite size and an accompanied decrease in specific surface area already below 1000°C.\textsuperscript{82,90} The sintering kinetics are enhanced by e.g. water vapor in the atmosphere,\textsuperscript{82} solid additives,\textsuperscript{83} and activated carbon as dopant.\textsuperscript{84} Thus, it is very likely that sintering of MgO plays an important role in the control of the rate of CTR.

\textit{Morphology of C}

Several studies have shown that the rate of CTR can depend on the source of C,\textsuperscript{59,61,72,73} which effect was attributed to the amount and composition of impurities\textsuperscript{59,61} or morphology of C.\textsuperscript{72} As example, Chubukov et al.\textsuperscript{72} investigated the effect of using four different C sources on the rate of CTR. They observed that with the C source having the highest particle size and lowest SSA the rate of CTR was significantly decreased (~50\%) compared to the other sources and attributed this result to the low SSA of the C.

\subsection{2.3 Effect of Reactant Preparation on the Rate of CTR}

Generally, MgO-C mixtures may be prepared either as loose powder blends or in the form of pellets, while the latter has been the preferred option in the vast majority of the work dedicated to the CTR of MgO. However, there has been only very little research conducted so far on evaluating the effect of using pellets or loose powders on the rate of CTR. Only Rongti et al.\textsuperscript{67} and Yoshikawa et al.\textsuperscript{93} have shown by exploiting non-isothermal thermogravimetry and heating the reactants with microwave irradiation, respectively, that using pellets instead of loose powders increases the rate of CTR (by ~50\%). While in both studies the authors attributed this effect to an increase in the MgO\textsubscript{(s)}/C\textsubscript{(s)} contact, Yoshikawa et al.\textsuperscript{93} suggested that an enhanced reactant heating when using pellets may also have increased the rate of CTR. Thus, it is unclear whether also the results of Rongti et al.\textsuperscript{67} may have been confounded by higher heating rates of the pellets
with respect to loose powders. Therefore, further research is required to conclusively evaluate the effect of using pellets or loose powders on the rate of CTR. In addition, pelletization is an extra process step that requires an additional energy input. The potential beneficial effect of using pellets on the energy conversion efficiency of the CTR process must thus outweigh the energy required for pelletization.

Furthermore, it is important to note that a recent study\(^7\) has shown that the rate of CTR can be slightly affected by the method of pellet fabrication (extruding, briquetting, molding, and type of binder). It is therefore argued that the fabrication method should be considered when comparing results of different studies.

Milling of the MgO-C mixture prior to reaction has shown to significantly increase the rate of CTR\(^.\) This effect has been attributed to a decrease in MgO agglomerate and/or crystal size and an increase in the MgO-C mixing degree\(^.\)

### 2.4 Effect of Catalysts on the Rate of CTR

Solid catalysts have shown to potentially enhance the rate of CTR. Rongti et al.\(^6\) added either nickel (Ni), copper (Cu), cobalt (Co), or iron (Fe) to the MgO-C reactant mixture with a molar amount of 0.5 compared to MgO and C, respectively. With all four catalysts, they observed an increase in the rate of CTR that was the highest (factor ~2.5) when using Ni.

In contrast, Chubukov et al.\(^4\) observed an increase in the rate of CTR with the addition of either of seven tested catalysts when using an MgO source of low SSA and high crystal size and conducting the experiments at a total pressure of 10 kPa. Using an MgO source of high SSA and low crystal size, however, the tested catalysts (Fe and Ni) decreased the rate of CTR at total pressures of 10 kPa, while at total pressures of 0.1 kPa no significant effect was observed. They explained their results as follows: the catalysts catalyzed the reduction of MgO by CO (reactions (8) and (9)), but hindered the proceeding of the MgO\(_\text{(s)}\)-C\(_\text{(s)}\) boundary reaction (4) because of a decreased MgO\(_\text{(s)}\)/C\(_\text{(s)}\) contact by the interfering catalyst particles. Thus, with the high SSA and low crystal sized MgO source, the hindrance of the MgO\(_\text{(s)}\)-C\(_\text{(s)}\) boundary reaction outweighed the
catalysis of MgO reduction with CO therefore decreasing the net rate of CTR. With the low SSA and high crystal sized MgO source, the catalysis of MgO reduction with CO outweighed the hindrance of the MgO\(_{(s)}\)-C\(_{(s)}\) boundary reaction, which effect was more pronounced at a total pressure of 10 than at 0.1 kPa.

The observations made by Rongti et al.\(^{69}\) and Chubukov et al.\(^{41}\) indicate that the catalysis of the CTR of MgO induces rather complex phenomena that are difficult to reveal. Thus, further research is required to fully understand the catalysis of the CTR.

### 2.5 Equilibrium Composition of the CTR of MgO

This section provides an overview of the expected thermodynamic equilibrium composition of the CTR of MgO at a temperature and total pressure range of 1000-2000°C and 1-100 kPa, respectively. The equilibrium calculations were conducted using the HSC Outokumpu software code\(^{35}\) considering the species C\(_{(s)}\), C\(_{(g)}\), CO\(_{(g)}\), CO\(_2(g)\), O\(_2(g)\), Mg\(_{(g)}\), MgO\(_{(s)}\), and MgO\(_{(g)}\).

Figure 3 illustrates the temperature dependent equilibrium composition of the system MgO\(_{(s)}\) + C\(_{(s)}\) at total pressures of 1 (left), 10 (middle) and 100 kPa (right). As shown by this figure, a lower total pressure favors the CTR: while at 100 kPa complete conversion of MgO is reached at 1764°C, the required temperature to reach complete conversion of MgO decreases at 10 and 1 kPa to 1531 and 1350°C, respectively. In all three cases the product gas composition at complete MgO conversion extent comprised mainly Mg\(_{(g)}\) and CO\(_{(g)}\) in an approximately equimolar ratio. The amounts of the other considered gaseous species (i.e. C\(_{(g)}\), CO\(_2(g)\), O\(_2(g)\) and MgO\(_{(g)}\)) were always below 10\(^{-5}\) moles and thus neglected.

It should be noted that the temperature range between onset of CTR and full MgO conversion is very small (< 1°C). This observation can be attributed to the absence of significant amounts of gaseous species in the initial mixture. With higher initial gas amounts, this temperature range expands as shown in Figure 4 that illustrates the effect of inert gas (Ar) dilution in the range of 0-10 moles on the equilibrium extent of the CTR at an exemplary total pressure of 1 kPa.
Figure 3. Equilibrium composition of the system MgO\(_{(s)}\) + C\(_{(s)}\) as function of temperature at a total pressures of 1 (left), 10 (middle), and 100 kPa (right).

Figure 4. Equilibrium composition of the system MgO\(_{(s)}\) + C\(_{(s)}\) + x Ar\(_{(g)}\) with x = 0-10 moles at a total pressure of 1 kPa.
Furthermore, it is shown in Figure 4 that with higher amounts of inert gas in the system, the temperatures of CTR onset and of full conversion decrease and thus affect the CTR similar to when decreasing the total pressure.

*Effect of initial MgO-C stoichiometry*

The effect of initial MgO-C stoichiometry on the equilibrium composition of the CTR was studied at an exemplary total pressure of 1 kPa using the three systems \( \text{MgO}_\text{(s)} + \text{C}_\text{(s)} + \text{Ar}_\text{(g)} \), \( 10\text{MgO}_\text{(s)} + \text{C}_\text{(s)} + \text{Ar}_\text{(g)} \), and \( \text{MgO}_\text{(s)} + 10\text{C}_\text{(s)} + \text{Ar}_\text{(g)} \). The results are given in Figure 5 that shows the equilibrium molar amounts of \( \text{Mg}_\text{(g)} \) (top left), \( \text{CO}_\text{(g)} \) (top right), \( \text{O}_2\text{(g)} \) and \( \text{CO}_2\text{(g)} \) (bottom left), and \( \text{MgO}_\text{(g)} \) and \( \text{C}_\text{(g)} \) (bottom right) over the temperature range of 1000-2000°C.

As illustrated by this figure, using a 10:1 or 1:10 molar MgO-C ratio in the initial system instead of equimolar amounts of MgO and C only insignificantly affected the product gas composition:

- **10:1 molar MgO-C ratio**: having excess MgO in the system slightly favors the production of \( \text{Mg}_\text{(g)} \) at temperatures >1350°C. This can be attributed to (a) dissociation of MgO via reaction (6) as indicated by the increased amount of \( \text{O}_2\text{(g)} \) and (b) reduction of MgO with \( \text{CO} \) via reaction (8) as indicated by the increased amount of \( \text{CO}_2\text{(g)} \) and decreased amount of \( \text{CO}_\text{(g)} \) in the equilibrium composition. Furthermore, excess MgO favors the formation of \( \text{MgO}_\text{(g)} \) and consumption of \( \text{C}_\text{(g)} \).

- **1:10 molar MgO-C ratio**: having excess C in the system affects the equilibrium composition only at temperatures >1800°C, which is reflected by a favored production of \( \text{C}_\text{(g)} \) and consumption of \( \text{O}_2\text{(g)} \), \( \text{CO}_2\text{(g)} \), and \( \text{MgO}_\text{(g)} \). The potential effect on the equilibrium amounts of \( \text{Mg}_\text{(g)} \) and \( \text{CO}_\text{(g)} \), however, is too small to be graphically reflected.

Even though the addition of either excess MgO or C affects the equilibrium composition of the CTR, the effective impact is very small and may thus – at least for temperatures <1600°C at 1 kPa total pressure – be neglected.
Figure 5. Equilibrium molar amounts of Mg\textsubscript{(g)} (top left), CO\textsubscript{(g)} (top right), O\textsubscript{2(g)} and CO\textsubscript{2(g)} (bottom left), and MgO\textsubscript{(g)} and C\textsubscript{(g)} (bottom right) for the systems MgO\textsubscript{(s)} + C\textsubscript{(s)} + Ar\textsubscript{(g)}, 10MgO\textsubscript{(s)} + C\textsubscript{(s)} + Ar\textsubscript{(g)}, and MgO\textsubscript{(s)} + 10C\textsubscript{(s)} + Ar\textsubscript{(g)} in the temperature range of 1000-2000°C at an exemplary total pressure of 1 kPa.
3 The Prevailing Reaction Pathway(s)a

It is crucial for the development of a suitable reactor for the CTR of MgO to understand the prevailing reaction mechanism for which, however, there is no consensus in current literature. Thus, this chapter is dedicated to reconcile previously reported findings as to conclusively discriminate, which of the proposed pathways dominate the CTR of MgO.

3.1 Methodology

3.1.1 The Principle

The candidates for the prevailing reaction pathway discussed in the previous chapter may be distinguished by the gaseous intermediates they involve:

I. If Mg\textsubscript{(g)} is produced by the dissociation of MgO via reaction (6), O\textsubscript{2} acts as the key intermediate.
II. If Mg\textsubscript{(g)} is produced by the reduction of MgO with CO via reaction (8), CO\textsubscript{2} acts as the key intermediate.
III. If Mg\textsubscript{(g)} is produced by the MgO\textsubscript{(s)}-C\textsubscript{(s)} boundary reaction (4), no gaseous intermediate is formed.

It should be noted that in cases I and II involving the formation of gaseous intermediates the Mg\textsubscript{(g)}-producing reactions (6) and (8) do not significantly proceed without the removal of those intermediates from the reaction site by the reactions with C.

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This can be shown by comparing the equilibrium partial pressures of $\text{Mg}_{(g)}$ of MgO dissociation (reaction (6)) and MgO reduction with CO (reaction (8)) to the one of the overall reaction (4). They were calculated for the temperature range of 1000-2000°C by solving the equations

$$K_4(T) = p_{\text{Mg}}p_{\text{CO}}$$  \hspace{1cm} (10)  

$$K_6(T) = p_{\text{Mg}}p_{\text{O}_2}^{0.5}$$  \hspace{1cm} (11)  

$$K_8(T) = \frac{p_{\text{Mg}}p_{\text{CO}_2}}{p_{\text{CO}}}$$  \hspace{1cm} (12)  

using the equilibrium constants $K_i(T)$ that were extracted from the HSC database.\textsuperscript{35} Equation (10) was solved considering that $p_{\text{CO}} = p_{\text{Mg}}$, equation (11) considering that $p_{\text{O}_2} = 0.5p_{\text{Mg}}$, and equation (12) considering that $p_{\text{CO}_2} = p_{\text{Mg}}$ and assuming a $p_{\text{CO}}$ in the range of 0.1-10 kPa.

As shown in Figure 6, the equilibrium Mg partial pressure of the overall reaction (Figure 6a) is orders of magnitude higher than the ones of MgO dissociation (Figure 6b) and MgO reduction with CO (Figure 6c). For example, at 1600°C the equilibrium Mg partial pressure of the overall reaction is as high as $\sim$10 kPa, while the ones for MgO dissociation and MgO reduction with CO are as low as 0.04 Pa and 0.007-0.07 Pa, respectively.

In order to favor the production of $\text{Mg}_{(g)}$ via reactions (6) and (8), the $p_{\text{O}_2}$ and the ratio $p_{\text{CO}_2}/p_{\text{CO}}$, respectively, need to be reduced with respect to $p_{\text{Mg}}$. This effect is illustrated in Figure 7 that shows the equilibrium $p_{\text{O}_2}$ and $p_{\text{CO}_2}$ for given $p_{\text{Mg}} = p_{\text{CO}} = 1$-$100$ Pa, calculated via equations (11) and (12), respectively. The equality of $p_{\text{Mg}}$ and $p_{\text{CO}}$ is imposed by the overall reaction (4). As shown by this figure, the equilibrium $p_{\text{O}_2}$ and $p_{\text{CO}_2}$ are rather low. For example, at 1400°C the $p_{\text{O}_2}$ need to be as low as $10^{-14}$ to $10^{-10}$ Pa and $p_{\text{CO}_2}$ as low as $10^{-3}$ Pa (i.e. a $p_{\text{CO}_2}/p_{\text{CO}}$ ratio of $10^{-3}$-$10^{-5}$) in order to reach an equilibrium $p_{\text{Mg}}$ of 1-100 Pa.
Figure 6. Equilibrium partial pressure of Mg\(_{(g)}\) based on (a) reaction (4), (b) reaction (6), and (c) reaction (8).

This in turn implies that Mg\(_{(g)}\) production should be suppressed, if the partial pressures of those intermediates were increased above the values shown in Figure 7 thereby shifting the equilibria of both reactions (6) and (8) towards the reactants.
Therefore, the prevailing reaction pathway(s) may be discriminated by comparing the extents of CTR in the case when a reacting C/MgO blend is swept with an O\textsubscript{2}-Ar mixture and a CO\textsubscript{2}-Ar mixture with the extents of CTR in the cases when the same blend is reacted without adding any oxidants to the sweep and then implementing the logic outlined in Figure 8 as follows:

- The MgO dissociation is the prevailing pathway if the CTR is suppressed with the O\textsubscript{2}-Ar but not with the CO\textsubscript{2}-Ar sweep.
- The MgO reduction with CO is the prevailing pathway if the CTR is suppressed with the CO\textsubscript{2}-Ar but not with the O\textsubscript{2}-Ar sweep.
- The MgO\textsubscript{(s)}-C\textsubscript{(s)} boundary reaction is the prevailing pathway if the CTR remains unaffected by the presence of either O\textsubscript{2} or CO\textsubscript{2} in the sweep gas.
- If the CTR were suppressed with both the O\textsubscript{2}-Ar and the CO\textsubscript{2}-Ar sweeps, it would appear that both the MgO dissociation and MgO reduction with CO pertain to the Mg\textsubscript{(g)} production. However, this
conclusion may be confounded by an extra CO₂ production under the O₂-Ar sweep via reactions

\[
C\,(s) + O_2\,(g) \rightleftharpoons CO_2\,(g) \tag{13}
\]

\[
CO\,(g) + 0.5O_2\,(g) \rightleftharpoons CO_2\,(g) \tag{14}
\]

that may increase the ratio \( p_{CO_2} \big/ p_{CO} \), thereby shifting the equilibrium of reaction (8) towards the reactants. It would therefore be unclear whether the suppression of the CTR under the O₂-Ar sweep was the result of the equilibrium shifts of reactions (6) or (8) without information about the effective partial pressures of CO₂, CO, and Mg\,(g) in the reaction atmosphere.

![Diagram](image)

Figure 8. The logic for discriminating the prevailing reaction pathway.

It should be noted, however, that compared to the reference cases in which no oxidant is added into the gas sweeping a reacting C/MgO blend, the addition of O₂ or CO₂ into the sweep gas introduces two side-effects: (i) it increases the
consumption of C via reactions (7), (9), and (13) and (ii) it affects the effective $p_{CO}$ in the reacting atmosphere because of the additional CO production via reactions (7) and (9) and/or its consumption via reaction (14). Previous research has suggested that the rate of CTR decreases with a decrease in C/MgO molar ratio,\textsuperscript{66, 67} while it may either increase or decrease with an increase in $p_{CO}$.\textsuperscript{67, 70}

In addition, it has also been reported that the rate of CTR decreases with time, which has been attributed to a gradual sintering of MgO particles\textsuperscript{70} that may proceed at different rates dependent on the reaction atmosphere. Therefore, the addition of either of the suspected intermediates into the sweep gas may affect the Mg\textsubscript{(g)} production not only because of favoring reverse reactions (6) or (8) but also because of (i) the differences in the effective C/MgO ratios and CO partial pressures and (ii) the atmosphere-assisted sintering of the MgO particles.

3.1.2 Accounting for the Effects of Side-Reactions

Figure 9 qualitatively illustrates the expected temporal amounts of C in a MgO-C blend (top) and CO partial pressures over the same blend (bottom) when the blend is swept with Ar (Figure 9a) or Ar diluted with a suspected intermediate (Figure 9b) while subjected to a temperature program indicated by the dotted lines (middle) comprising three stages: (i) heatup ramp from ambient to a setpoint reaction temperature ($T_{SP}$), (ii) hold at $T_{SP}$, and (iii) cool-down ramp from $T_{SP}$ to the ambient temperature. As shown in the top part of Figure 9a, when pure Ar is used as the sweep gas the amount of C remains at its initial value $N_{C}^{0}$ until $t = \tau_{1}$ when the blend reaches the onset temperature of CTR ($T_{1}$), thus $N_{C}^{0} = N_{C}(\tau_{1})$ for $t < \tau_{1}$. With the further progress of the temperature program, C is being consumed solely by CTR until $t = \tau_{II}$ when the temperature drops below $T_{1}$ during the cool-down ramp. Therefore the amount of C remains at $N_{C}(\tau_{f})$ for $t \geq \tau_{II}$. However, if either $O_{2}$ or $CO_{2}$ is added to the sweep gas, it starts oxidizing C at a temperature $T_{ox}$ that is generally lower than $T_{1}$. This is illustrated by the top part of Figure 9b illustrating that within the time interval $\tau_{ox} \leq t < \tau_{1}$ C is being consumed by the reaction with the added oxidant before $T_{1}$ is reached, implying that the amount of C at the onset of CTR ($N_{C}(\tau_{1})|_{int}$) is lower than the initial amount ($N_{C}^{0}|_{int}$).
Figure 9. Qualitative temporal amounts of C in a reacting MgO-C blend (top) and CO partial pressures over the same blend (bottom) when it is swept with (a) Ar and (b) Ar diluted with O₂ or CO₂ as suspected intermediate (abbreviated as “int”) under the temperature program indicated by the dotted lines (middle). The dashed lines indicate the amounts of C and the partial pressures of CO that would be observed in the absence of the carbothermal reduction.
After this point of time, i.e., $\tau_1 \leq t \leq \tau_{II}$, C is being consumed by both the reaction with the added oxidant and by the CTR until the temperature drops below $T_1$. As the temperature decreases from $T_1$ to $T_{ox} (\tau_{II} < t \leq \tau_f)$ the amount of C continues to decrease because of the reaction with the oxidant to eventually stabilize at $N_c(\tau_f)|_{int}$ for $t \geq \tau_f$. Due to likely high rates of the oxidation reactions at the temperatures in question, the consumption of C by the added oxidant is expected to be mass-transfer limited, thereby occurring at a constant rate owing to a constant gas velocity and an insignificantly decreasing particle size. Accordingly, the amount of C that would be observed in the absence of the CTR, i.e. in the absence of MgO, is designated by the straight dashed line in the top sketch of Figure 9b ($\tilde{N}_c(\tau_f)|_{int}$). Therefore, the amount of C consumed by the CTR only is represented by $\tilde{N}_c(\tau_f)|_{int} - N_c(\tau_f)|_{int}$. The analogous description applies for the discussion of temporal CO partial pressures illustrated in the bottom parts of Figure 9. Again, the constant partial pressure of CO that would be observed in the absence of CTR ($\tilde{p}_{CO}|_{int}$) stems from the assumption that the consumption of C by the added intermediate is mass-transfer limited.

In general, the rates of C consumption and the resulting CO production by the side reactions of the suspected intermediates with C are specific to the oxidant added to the sweep gas. The dependence of these rates on the total sweep gas flow rate and/or the partial pressure of the oxidants can be assessed through a series of tests with pure C and/or C-(inert solid) blends swept with O$_2$-Ar and CO$_2$-Ar mixtures. The equal amounts of C available for the CTR regardless of which oxidant is fed with the sweep, i.e.,

$$\tilde{N}_c(\tau_1)|_{O_2} = \tilde{N}_c(\tau_1)|_{CO_2},$$

$$\tilde{N}_c(\tau_f)|_{O_2} = \tilde{N}_c(\tau_f)|_{CO_2},$$

(15)

can then be ensured by manipulating one or more of the following parameters: (i) the initial amounts of C ($N_{C|O_2}^0$ and $N_{C|CO_2}^0$), (ii) the flow rates of the O$_2$-Ar and CO$_2$-Ar sweep gas mixtures, and (iii) the partial pressures of O$_2$ and CO$_2$ in the sweep gas mixtures.

However, even when the feed rates and compositions of the O$_2$-Ar and the CO$_2$-Ar sweep gas mixtures are adjusted to ensure the same consumption rates
of C, the corresponding CO production rates are different because the oxidation of C with CO\textsubscript{2} produces twice as much of CO per mole of C. This results in $\tilde{P}_{\text{CO}|\text{CO}_2} > \tilde{P}_{\text{CO}|\text{O}_2}$, which may affect the extent of CTR through the effect of the CO partial pressure on the onset temperature of CTR and/or its rate. Moreover, even though satisfying the equation set (15) ensures that the amounts of C available for CTR under the O\textsubscript{2}-Ar and CO\textsubscript{2}-Ar sweeps are roughly the same at all times, the amount of C decreases with time faster in these cases than if no oxidant is added to the sweep. Therefore, the presence of oxidants in the sweep may result in a lower extent of the CTR merely because of a lower amount of C available for CTR but not because of suppressing forward reactions (6) and/or (8).

To account for the effects of the differences in both the amounts of C available for CTR and the effective CO partial pressures, one thus needs to establish a reference for comparing the extents of CTR obtained under sweep gas mixtures containing O\textsubscript{2} or CO\textsubscript{2} with those measured in the absence of either of the oxidants in the sweep. Such a referent range of the extents may be determined by using the initial amounts of C set at

$$N_{C|\text{high}}^0 = \bar{N}_C (\tau_i)$$

$$N_{C|\text{low}}^0 = \bar{N}_C (\tau_i)$$

(16) (17)

to react the same amount of MgO under (i) an Ar sweep and (ii) a CO-Ar sweep having the CO partial pressure in the sweep adjusted at $\tilde{P}_{\text{CO}|\text{CO}_2}$. This choice of the reaction conditions encompasses the expected effects of the extra consumption of C by the oxidants added to the sweep on the C/MgO ratios and CO partial pressures during the CTR. The pertinent reaction pathway(s) may then be conclusively identified if adding an oxidant to the sweep (i) has no effect on the extent of CTR or (ii) it results in a CTR extent that is below the referent range of the CTR extents. If, however, adding oxidant to the sweep suppresses the Mg production but the corresponding CTR extent is higher than that obtained with no oxidant in the sweep and with $N_{C|\text{low}}^0$, the decision cannot be made without considering the effective species partial pressures in the reaction atmosphere and/or the effect of the initial C/MgO ratio on the extent of CTR.
3.2 Experimental

3.2.1 Program

The methodology presented in the previous section was implemented through the experimental program comprising three phases as outlined in Appendix C.1.

The first phase involves experiments exploiting a standard temperature program under $O_2$-Ar sweep having the total inlet molar rate and composition set at $n^0|_{O_2}$ and $y^0_{O_2}$, respectively. It starts with the comparison experiment #1, which represents reduction of $N^0_{MgO}$ moles of MgO blended with $N^0_{C|O_2}$ moles of C to determine temporal amounts of the residual carbon in the blend ($N_C(t)|_{O_2}$) indicated by the solid line in the top sketch of Figure 9b. In the next step of this phase, the same initial amount of C ($N^0_{C|O_2}$) was oxidized under the same sweep gas mixture in the absence of MgO to quantify the C consumption in the absence of CTR, i.e., to determine the values of $\tilde{N}_C(t)|_{O_2}$ indicated by the dashed line in the top sketch of Figure 9b. With $\tilde{N}_C(t)|_{O_2}$ and $N^0_{C|O_2}$ at hand, one can determine $\tau_1$ and $\tau_f$ and, therefore, $\tilde{N}_C(\tau_1)|_{O_2}$ and $\tilde{N}_C(\tau_f)|_{O_2}$, as well as the extent of CTR during the comparison experiment #1.

Phase 2 repeats the same steps of phase 1 under the standard temperature program but under CO$_2$-Ar sweep mixtures. The initial goal of this phase is to identify a combination of $N^0_{C|CO_2}$, $n^0_{CO_2}$, and $y^0_{CO_2}$ that ensures the same C consumption in the absence of MgO as observed in phase 1 (i.e., $\tilde{N}_C(t)|_{CO_2} = \tilde{N}_C(t)|_{O_2}$ for $t \geq \tau_1$). Reaction of $N^0_{MgO}$ moles of MgO blended with $N^0_{C|CO_2}$ moles of C under the CO$_2$-Ar sweep gas mixture having the molar rate and CO$_2$ composition adjusted to satisfy the equalities imposed by equation (15) represents the comparison experiment #2.

Phase 3 involves the referent CTR experiments performed under the standard temperature program in the absence of either O$_2$ or CO$_2$ in the sweep. The reacting blends comprised $N^0_{MgO}$ moles of MgO and C in the amounts set according to equations (16) and (17), with $\tilde{N}_C(\tau_i)$ and $\tilde{N}_C(\tau_f)$ determined in phases 1 and 2. Each of these blends is then reacted under both (i) Ar sweep and (ii) the CO-Ar sweep having the flow rate and composition adjusted to ensure that the CO partial pressures during the experiments resemble those observed during the comparison experiment #2 ($p_{CO|CO_2}$).
The conclusive discrimination among the reaction pathways under consideration is based on establishing that the extent of CTR observed in the comparison experiments (#1 and/or #2) is either (i) unaffected by the presence of the oxidants in the sweep or (ii) lower than the lowest extent of the CTR observed in the referent experiments of phase 3. The former would imply the relevance of the MgO\(_{(s)}\)-C\(_{(s)}\) boundary reaction while the latter would point to reactions (6) and/or (8) as the Mg\(_{(g)}\) producing reactions.

### 3.2.2 Materials

Table 1 lists the sources, specific surface areas, volume-based mean particle sizes, and impurities contained in the as-received solid raw materials used in this study: MgO and C as reactants and Al\(_{2}\)O\(_{3}\) as inert diluent for the C oxidation experiments in the absence of MgO. The listed properties and impurity fractions were determined as outlined in Appendix A. The discrepancy between the ratios of the BET areas and the mean particle sizes of the MgO and C implies that these materials were either highly porous or that they comprised agglomerates of finer particles.

MgO and Al\(_{2}\)O\(_{3}\) powders contained H\(_{2}\)O and CO\(_{2}\) as impurities adsorbed from the surroundings. The MgO powder additionally contained both of these impurities chemically bonded in the forms of Mg(OH)\(_{2}\) and MgCO\(_{3}\) that begin to dissociate at 270°C and 350°C (at 1 bar total pressure)\(^{35}\) according to reactions (18) and (19), respectively.\(^{95, 96}\)

\[
\text{Mg(OH)}_2(s) \rightleftharpoons \text{MgO}_(s) + \text{H}_2\text{O}_{(g)} \tag{18}
\]

\[
\text{MgCO}_3(s) \rightleftharpoons \text{MgO}_(s) + \text{CO}_{2(g)} \tag{19}
\]

The as-received charcoal contained moisture, volatile matter, and ash.
Table 1. Properties and impurity fractions of the as-received solid materials.

<table>
<thead>
<tr>
<th>material</th>
<th>MgO</th>
<th>C</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>source</td>
<td>Sigma-Aldrich, # 342793</td>
<td>Fluka Analytical, # 05120</td>
<td>Sigma-Aldrich, # 265497</td>
</tr>
<tr>
<td>SSA (m²/g)</td>
<td>141±1</td>
<td>680±20</td>
<td>-</td>
</tr>
<tr>
<td>d (µm)</td>
<td>5.2</td>
<td>37</td>
<td>10(*)</td>
</tr>
<tr>
<td>impurities</td>
<td>H₂O + CO₂</td>
<td>H₂O volatiles</td>
<td>ash H₂O + CO₂</td>
</tr>
<tr>
<td>wt %</td>
<td>5.5</td>
<td>1.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

(*) As reported by the manufacturer

3.2.3 Apparatus

Figure 10 shows a schematic of the experimental apparatus. The reactant bed (a MgO-C blend, an Al₂O₃-C blend, or C alone) was placed into the assembly shown in more details on the left side of the figure. The reactant bed was poured over the graphite felt (Sigratherm® GFA5) protected with a C layer of $m_c^* = 0.23\ g$ to prevent the infiltration of the MgO into the felt, thereby allowing the complete recovery of the residual MgO after the reaction. Seven Al₂O₃ tubes (⌀10x2 mm, $l = 10\ mm$) separated the felt bottom from the support (Schupp ceramics, Ultraboard, mullite fibers, ⌀58 mm, $l = 20\ mm$) in order to prevent a reaction of the SiO₂ from the mullite support with the graphite felt. Seven boreholes (⌀4 mm) in the support allowed the removal of sweep and product gases. The packed bed assembly was placed into a reactor tube (Al₂O₃, ⌀70x5 mm, $l = 1200\ mm$) and held in place at the location of the hot zone by five support tubes (Al₂O₃, ⌀58x5 mm, $l = 100\ mm$). Heat was provided by an electrically heated tube furnace (Carbolite STF 16-450) equipped with an R-type thermocouple measuring the temperature in the furnace chamber at the height of the hot zone (location indicated by a dot in Figure 10). The part of the reactor tube below the furnace was cooled by surrounding air via natural convection and provided a cooling zone for precipitating the Mg(g) product.
Figure 10. Schematic of the experimental apparatus with the packed bed assembly situated in the hot zone. Components of the apparatus are: ① assembly wall, ② reactant bed, ③ extra C layer, ④ graphite felt, ⑤ alumina separator tubes, ⑥ mullite packed bed support, ⑦ alumina reactor tube, ⑧ alumina support tubes, ⑨ furnace, ⑩ thermocouple, ⑪ mass-flow controller MFC 1, ⑫ mass-flow controller MFC 2, ⑬ vacuum pump, ⑭ particle filter, ⑮ globe valve, ⑯ pressure sensor, ⑰ overpressure relief valve, and ⑱ gas chromatograph.
Sweep gas flow rates were controlled by calibrated mass flow controllers (11) and (12) (Bronkhorst EL-Flow Select series). The low-pressure environment was provided by a vacuum pump (13) (Adixen ACP15) protected by a particle filter (14) (Whatman, GF/F grade glass fiber filter). The pressure inside the reactor tube was monitored by a pressure sensor (16) (Kistler Instrumente AG, type 4045A1) positioned in the cold zone above the furnace and controlled via a globe valve (15) positioned in front of the vacuum pump. An overpressure relief valve (17) was set at 30 kPa overpressure relative to ambient pressure. The product gas composition was measured every 65 seconds by a gas chromatograph (18) (Agilent M200).

3.2.4 Procedure

The MgO-C blends were prepared by stirring $m_1^0$ grams of as-received MgO powder and $m_2^0$ grams of as-received charcoal powder with a spatula in a pill glass and occasionally breaking agglomerates until the blends appeared homogeneous. To investigate reaction of C with O$_2$ added to the sweep gas, the MgO was substituted with $m_3^0$ grams of as-received Al$_2$O$_3$ powder that does not react with C within the pressure and temperature ranges investigated$^{97}$. The effective amounts of the MgO, Al$_2$O$_3$ and C in the blends ($m_{\text{MgO}}^0$, $m_{\text{Al}_2\text{O}_3}^0$, and $m_{\text{C}}^0$, respectively) were calculated as

$$m_{\text{MgO}}^0 = m_1^0 \left(1 - w_{\text{impMgO}}\right)$$

$$m_{\text{Al}_2\text{O}_3}^0 = m_1^0 \left(1 - w_{\text{impAl}_2\text{O}_3}\right)$$

$$m_{\text{C}}^0 = m_2^0 \left(1 - w_{\text{H}_2\text{O}}^\text{C} - w_{\text{vm}}^\text{C} - w_{\text{ash}}^\text{C}\right)$$

(20)

The reaction of C with CO$_2$ added to the sweep gas was investigated using $m_2^0$ grams of as-received charcoal powder without diluting it with Al$_2$O$_3$.

The reactant beds (MgO-C, Al$_2$O$_3$-C, or C alone) were poured into the packed bed assembly after which the apparatus was sealed and the vacuum pump was started. Then, the globe valve in front of the vacuum pump was opened and total pressure inside the reactor was reduced to 0.8–1.9 kPa under 0.16–0.39 L$_{\text{N}}$/min of Ar sweep (Messer 4.6). After pressure equilibration, the furnace was heated
under continuing Ar flow to 1000°C at a 20°C/min ramp rate and held at 1000°C for 15 minutes to ensure the complete dissociation of Mg(OH)$_2$ and MgCO$_3$ contained in the starting MgO and the evaporation of volatile matter contained in the starting charcoal. In some experiments, the gas flow was then switched to one of the bottled gas mixtures - 5% O$_2$-Ar (Messer 5.0), 5% CO$_2$-Ar (Messer 4.8), or 5% CO-Ar (Messer 4.7) flowing at rates in the range of 0.16–0.39 L$_\text{N}$/min which resulted in the total pressure of 0.8-1.9 kPa and therefore the initial partial pressures of O$_2$, CO$_2$ and CO to 40-95 Pa. The furnace was then ramped at 20°C/min to the desired setpoint temperature ($T_{\text{sp}}$) of 1375, 1400 or 1450°C and held there for 30 minutes, after which the furnace was shut off and let cool off. When a gas mixture was used as the sweep, it was replaced by Ar when the furnace temperature reached 1250°C.

A possible deposition of C in the cooling zone via reverse Boudouard reaction (9)$^{98}$ was tested by feeding a 5% CO–Ar mixture into the empty reactor maintained at 1450°C under CO partial pressure of ~95 Pa and measuring the amount of produced CO$_2$ in the product gas.

### 3.2.5 Calculations

#### 3.2.5.1 Consumption of C and Generation of CO Owing to O$_2$ and CO$_2$ Added to the Sweep

The removal of C by the oxidants co-fed with the sweep was quantified exploiting the experiments performed in the absence of MgO based on the reactions listed in Table 2 and the corresponding C balance equations listed in Table 3. The molar extents of reactions occurring in the hot ($i$) and the cooling zone ($j$) are designated $\xi_i$ and $\varphi_j$, respectively. The extent $\varphi_9^*$ refers to the extent of the reverse reaction (9), i.e., $\varphi_9^* = -\varphi_9$. 
Table 2. Extents of the reactions \((i)\) and \((j)\) taking place (a) in the hot \((\xi_i)\) and (b) in the cooling zone \((\varphi_j)\) when C is swept with O\(_2\)-Ar and CO\(_2\)-Ar mixtures in the absence of MgO. Note: the extent \(\varphi_j^* \geq 0\) refers to the extent of the reverse reaction \((9)\).

<table>
<thead>
<tr>
<th>C source/sink</th>
<th>reactions</th>
<th>Phase 1</th>
<th>Phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>extent</td>
<td>stoichiometry</td>
<td>O(_2)-Ar</td>
</tr>
<tr>
<td>hot zone</td>
<td>(\xi_{13}) C(_s) + O(_2)(g) &amp; CO(_2)(g) \iff )</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>consumed by the</td>
<td>(\xi) C(_s) + CO(_2)(g) \iff 2CO(_g)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>oxidant added to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>the sweep</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cooling zone</td>
<td>(\varphi_j^*) 2CO(_g) \iff C(_s) + CO(_2)(g)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>deposited on the</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>column wall</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Species material balance equations for the reactions of C with O\(_2\) or CO\(_2\) added to the sweep gas in the absence of MgO.

<table>
<thead>
<tr>
<th>Amount of C</th>
<th>Phase 1: O(_2)-Ar</th>
<th>Phase 2: CO(_2)-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>remained in the hot zone (N_c)</td>
<td>(N_c^0 - \xi_{13} - \xi)</td>
<td>(N_c^0 - \xi)</td>
</tr>
<tr>
<td>removed as CO and CO(<em>2) in the product gas (N</em>{CO2})</td>
<td>(2\xi - 2\varphi)</td>
<td>(2\xi - 2\varphi^*)</td>
</tr>
<tr>
<td></td>
<td>(\xi_{13} - \xi + \varphi^*)</td>
<td>(N_{CO2, fed} - \xi + \varphi^*)</td>
</tr>
</tbody>
</table>

\(\tilde{N}_c(\tau_i)\) and \(\tilde{N}_c(\tau_i)\) (see Figure 9) were estimated by combining the balance equations \((21)\), \((23)\), and \((25)\) for the O\(_2\)-Ar sweep and equations \((22)\) and \((24)\) for the CO\(_2\)-Ar sweep as

\[
\tilde{N}_c(\tau_i)|_{O_2} = \left[ N_c^0 - N_{CO}(\tau_i) - N_{CO2}(\tau_i) - \varphi^*(\tau_i) \right]_{O_2} \quad \text{with} \quad i = I, f \quad (27)
\]

\[
\tilde{N}_c(\tau_i)|_{CO_2} = \left[ N_c^0 - 0.5 N_{CO}(\tau_i) - \varphi^*(\tau_i) \right]_{CO_2} \quad \text{with} \quad i = I, f \quad . \quad (28)
\]
In equations (27) and (28) \( N_i(\tau) \) represents the total molar amount of species \( i \) entrained with the product gas up to the point of time \( \tau \) calculated as

\[
N_i(\tau) = \int_{\tau_0}^{\tau} \dot{n}_i(t) \, dt
\]  

(29)

where the temporal molar flow rate of species \( i \) in the product gas was determined as

\[
\dot{n}_i(t) = y_i(t) \, \dot{n}(t).
\]  

(30)

\( y_i(t) \) and \( \dot{n}(t) \) represent the temporal mole fractions of species \( i \) determined by the gas chromatography and the temporal total molar rates of the product gas, respectively. The latter was calculated as

\[
\dot{n}(t) = \frac{\dot{n}_{Ar}(t)}{y_{Ar}(t)}
\]  

(31)

with

\[
y_{Ar}(t) = 1 - y_{O_2}(t) - y_{CO}(t) - y_{CO_2}(t)
\]  

(32)

and

\[
\dot{n}_{Ar}(t) = y_{Ar}^0 \, \dot{n}^0(t).
\]  

(33)

\( y_{Ar}^0 \) represents the mole fraction of Ar in the inlet sweep gas mixture. \( \dot{n}^0(t) \) is the total molar flow rate of the sweep gas

\[
\dot{n}^0(t) = \frac{p_N \, \dot{V}_N^0(t)}{R \, T_N}
\]  

(34)

based on the total volumetric inlet flow rate of the sweep gas \( \dot{V}_N^0(t) \) standardized with a flow definer (MesaLabs, Bios DryCal Definer 220) at \( p_N = 101.3 \, \text{kPa} \) and \( T_N = 0^\circ\text{C} \) for a given output to the mass-flow controller MFC 2.

The only remaining variable needed to calculate the temporal amounts of carbon via equations (27) and (28) are the extents of the Boudouard reaction (9)
As indicated by the temperature dependent equilibrium composition of 2 moles of CO at total pressures in the range of 0.1-10 kPa illustrated in Figure 11, solid C may form via the Boudouard reaction at temperatures $< 800^\circ$C. These calculations were conducted using the HSC Outokumpu software code$^{35}$ for the initial system $2\text{CO} \,(\text{g})$ considering the species $\text{C} \,(\text{s})$, $\text{CO} \,(\text{g})$, and $\text{CO}_2 \,(\text{g})$ in the calculation.

As the extent of the Boudouard reaction scales with the CO concentration in the cooling zone, it was evaluated by flowing a pilot CO-Ar stream through the setup kept at a typical reaction condition. This evaluation demonstrated the absence of $\text{CO}_2$ in the effluent at a CO partial pressure of 95 Pa, thereby allowing to consider that $\varphi_0^* = 0$ for $p_{\text{CO}} \leq 95$ Pa.

Under the $\text{CO}_2$-Ar sweep, temporal partial pressures of CO in the hot zone expected in the absence of CTR were approximated by the values that were observed during the C oxidation experiments in the absence of MgO as
\[ \tilde{p}_{\text{CO}|\text{CO}_2} = \left[ \tilde{y}_{\text{CO}}(t) \tilde{p}_{\text{tot}}(t) \right]_{\text{CO}_2}. \] (35)

Under the O_2-Ar sweep, however, the outlet rate of CO may not be representative of the CO rate coming from the hot zone because of CO oxidation via reaction (14) that may have proceeded in the cooling zone. However, as reaction (14) produces a mole of CO_2 per mole of CO, the rate of CO in the hot zone \( \left( \hat{n}'_{\text{CO}|o_2} \right) \) may be bound as

\[ \tilde{n}_{\text{CO}}(t)_{\text{o}_2} \leq \hat{n}'_{\text{CO}}(t)_{\text{o}_2} \leq \left[ \tilde{n}_{\text{CO}}(t) + \hat{n}_{\text{CO}_2}(t) \right]_{\text{o}_2} \] (36)

Owing to the high dilution of the product gas with Ar \( y_{\text{Ar}}(t) \approx 0.9-0.95 \) the total molar rate was not significantly different between hot zone and outlet, i.e. \( \hat{n}'(t) \approx \hat{n}(t) \), which results in \( \tilde{y}'(t) \approx \tilde{y}(t) \). Therefore, the partial pressure of CO in the hot zone is estimated as

\[ \left[ \tilde{y}_{\text{CO}}(t) \tilde{p}_{\text{tot}}(t) \right]_{\text{o}_2} \leq \tilde{p}_{\text{CO}}(t)_{\text{o}_2} \leq \left[ \left( \tilde{y}_{\text{CO}}(t) + \tilde{y}_{\text{CO}_2}(t) \right) \tilde{p}_{\text{tot}}(t) \right]_{\text{o}_2} \] (37)

3.2.5.2 Selecting the Initial Amounts of C and Partial Pressures of CO in the Sweep for the Reference CTR Experiments

As already discussed in section 3.1.2, the initial amounts of C in the reference CTR experiments performed in Phase 3 of the experimental program were selected according to equations (16) and (17). It should be noted that equations (16) and (17) account for the consumption of C not only from the reactant blend but also from both the extra layer of C and the graphite felt, thereby making the effective C/MgO ratios in the reference CTR experiments lower than their counterparts in the comparison runs of experimental phases 1 and 2. This could only have an adverse effect on the extent of CTR in the reference experiments. Therefore, if the CTR extents in the reference experiments are still higher than the CTR extent resulting from one of the comparison runs then the discrimination of the reaction pathway becomes only more conservative.

The composition and the flow rate of the CO-Ar sweep in the reference CTR experiments was selected such that the resulting \( p_{\text{CO}} \) observed in the absence of
CTR matched the highest CO partial pressures observed during the C oxidation experiments performed under O₂-Ar and CO₂-Ar sweeps in the absence of MgO.

### 3.2.5.3 The extents of CTR

In the absence of O₂ or CO₂ in the feed, the extent of CTR ($\xi_4$) was calculated from the MgO balance in the hot zone as

$$\xi_4 = N^0_{\text{MgO}} - N^f_{\text{MgO}} = \frac{m^0_{\text{MgO}} - m^f_{\text{MgO}}}{M_{\text{MgO}}}, \quad (38)$$

where $m^f_{\text{MgO}}$ designates the mass of the unreacted MgO in the residual reactant blend that was determined by thermogravimetry. The recovered residual reactant blend was first weighed to determine its mass ($m^f$) and then stirred well in a pill glass with a spatula. In the next step, a sample of the homogenized blend amounting to $m^0_s$ was heated under a 20% air-Ar atmosphere at a rate of 20°C/min to 900°C. The sample was held at this temperature until its mass stabilized at $m^f_s$, indicating that all the remaining C was oxidized thus leaving the retainer comprising only MgO and ash. The mass of the unreacted MgO in the residual reactant blend $m^f_{\text{MgO}}$ was then calculated as

$$m^f_{\text{MgO}} = m^f_s - \frac{m^0_s}{m^f_s} w^C_{\text{ash}} \left( \frac{m^0_s + m^*_{\text{C}}}{m^\text{ash}} \right) \quad (39)$$

The presence of O₂ or CO₂ in the sweep gas, however, precludes direct calculation of $\xi_4$ via equation (38) as some of the produced Mg(g) may re-oxidize within the hot zone via reverse reactions (6) or (8) to the extent that is not known. For this reason, the extents of CTR for the comparison runs of phases 1 and 2 were estimated exploiting the overall C balance based on the reactions listed in Table 4 and assuming that the amounts of C removed by the CTR is approximately equal to the amount of the reduced MgO as suggested by the overall reaction (4) (see Appendix B).
Table 4. Reactions involving C during the CTR experiments. Note: the extents $\Phi_4^* \geq 0$ and $\Phi_9^* \geq 0$ refer to the extents of the reverse reactions (4) and (9)).

<table>
<thead>
<tr>
<th>amounts of C</th>
<th>reaction extent and stoichiometry</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>consumed by the CTR</td>
<td>$\text{MgO}_s + C_s \rightleftharpoons \text{Mg}_g + \text{CO}_g$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>consumed by the oxidant added to the sweep</td>
<td>$C_s + \text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$</td>
<td>✔</td>
<td>✖</td>
<td>✖</td>
</tr>
<tr>
<td></td>
<td>$C_s + \text{CO}_2(g) \rightleftharpoons 2\text{CO}_g$</td>
<td>✔</td>
<td>✔</td>
<td>✖</td>
</tr>
<tr>
<td>deposited on the column wall</td>
<td>$\text{Mg}_g + \text{CO}_g \rightleftharpoons \text{MgO}_s + C_s$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td></td>
<td>$2\text{CO}_g \rightleftharpoons C_s + \text{CO}_2(g)$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

Based on the reactions listed in Table 4, this amount of C corresponds to the molar extent of reaction (4) expressed as

$$\xi_1|_{t = \tau_f} = \left[ N_{\text{CO}}(\tau_f) + N_{\text{CO}_2}(\tau_f) \right] - N_{\text{C,fed}}(\tau_f)$$

$$\text{amount of C entrained by the product gas}$$

$$- \left[ N_C^0 - \tilde{N}_C(\tau_f) \right] + N_{\text{C,dep}}(\tau_f)$$

$$\text{amount of C consumed by the oxidant in the sweep}$$

$$\text{amount of C deposited in the cooling zone}$$

(40)

with the individual terms defined as follows:

$$N_{\text{C,fed}}(\tau_f) = \left[ \left[ 0|_{\text{O}_2} \right]_{\text{CO}_2} \right]_{\text{CO}_2}$$

(41)

$$N_C^0 - \tilde{N}_C(\tau_f) = \left[ \left[ \xi_9(\tau_f) + \xi_{13}(\tau_f) \right]_{\text{O}_2} \right]_{\text{CO}_2}$$

(42)
The total amount of fed CO\textsubscript{2} was determined as

\[
N_{\text{CO}_2,\text{fed}}(\tau_f) = y_{\text{CO}_2}^0 \int_{\tau_{\text{ox}}}^{\tau_f} \dot{n}^0(t) \, dt
\]  

where \(y_{\text{CO}_2}^0\) represents the mole fraction of CO\textsubscript{2} in the inlet sweep gas mixture.

However, if either O\textsubscript{2} or CO\textsubscript{2} are present in the sweep gas, the five reaction extents listed in Table 4 cannot be calculated based on the measured CO and CO\textsubscript{2} outlet mole rates as the only information available. While the need for extents \(\xi_9\) and \(\xi_{13}\) can be conveniently circumvented by calculating the final amount of C in the absence of CTR \(N_C(\tau_f)\) according to equations (27) and (28), respectively, the final amount of deposited C \(N_{\text{C,dep}}(\tau_f)\) ranging as

\[
0 \leq N_{\text{C,dep}}(\tau_f) \leq \left[ \phi_4^*(\tau_f) + \phi_9^*(\tau_f) \right]
\]

cannot be calculated. However, this amount can be readily determined for the reference CTR experiments performed under Ar or an Ar-CO sweep for which the extent of CTR \(\xi_4\) is determined via the MgO balance equation (38). As in this case \(\xi_9 = \xi_{13} = 0\) and

\[
N_{C,\text{fed}}(\tau_f) = N_{\text{CO,fed}}(\tau_f) = y_{\text{CO}}^0 \int_{\tau_{\text{ox}}}^{\tau_f} \dot{n}^0(t) \, dt,
\]

equations (40), (42), (43), and (46) imply that

\[
\left[ \phi_4^*(\tau_f) + \phi_9^*(\tau_f) \right]_{\text{ref}} = \left[ N_{\text{CO,fed}}(\tau_f) + \xi_4(\tau_f) - N_{\text{CO}}(\tau_f) - N_{\text{CO}_2}(\tau_f) \right]_{\text{ref}}.
\]

As the amount of C deposited in the cooling zone increases with the increase in the partial pressures of Mg and CO, one of the reference experiments should be performed under conditions ensuring the highest \(\left[ \phi_4^*(\tau_f) + \phi_9^*(\tau_f) \right]_{\text{ref}}\) within the range of the conditions investigated. Using this value as the estimate of the higher limit for the amount of C deposited during the comparison runs of phases
1 and 2 will only inflate the extents of the CTR in those runs. Since the CTR mechanism can be discriminated if one of the CTR extents from the comparison runs is lower than the lowest CTR extent observed in the reference experiments of phase 3, this approach should make the decision only more conservative.

### 3.3 Results and Discussion

#### 3.3.1 Phase 1: O$_2$-Ar Sweep

**3.3.1.1 Detection of The Onset of CTR**

Table 5. The initial conditions for the tests under O$_2$-Ar sweep (phase 1 of the experimental program).

<table>
<thead>
<tr>
<th>sweep gas</th>
<th>$\dot{V}_N^0$</th>
<th>$P_0$ in the sweep</th>
<th>solids</th>
<th>$N_{\text{MgO}}^0$</th>
<th>$N_{\text{Al}_2\text{O}_3}^0$</th>
<th>$N_C^0$</th>
<th>$N_C^0/N_{\text{MgO}}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>53.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5% O$_2$-Ar</td>
<td>0.16</td>
<td>40</td>
<td>Al$_2$O$_3$-C</td>
<td>-</td>
<td>20.1</td>
<td>53.3</td>
<td>-</td>
</tr>
<tr>
<td>MgO-C</td>
<td>49.6</td>
<td>-</td>
<td>53.3</td>
<td>1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5 summarizes the initial conditions selected for the tests under O$_2$-Ar sweep. These conditions were implemented at three furnace setpoint temperatures $T_{sp} = 1375, 1400, \text{ and } 1450^\circ\text{C}$. Figure 12 compares the outlet CO, CO$_2$, and O$_2$ molar flow rates in the product gas from the experiments with the MgO-C and Al$_2$O$_3$-C blends at 1375°C; the results for the remaining two setpoint temperatures are shown in Appendix C.2. The onset of the CTR was identified at $\tau_1 \approx 22 \text{ min}$ by the inflection point of the CO molar rate observed with the MgO-C blend. The amount of Al$_2$O$_3$ for the Al$_2$O$_3$-C blend (20.1 mmol) was selected to match the heat capacity of the substituted MgO, thereby providing the equal sink for the heat released by the exothermic reaction (7). This resulted in a good agreement between the CO production rates with these two blends prior to the onset of CTR. This agreement could not be achieved with C alone (see Figure
91 of Appendix C.2) which has been attributed to the increase in the local temperature of the C bed due to exothermic reaction (7) \((\Delta h^0 = -110.5 \text{ kJ/mol})\). The CO\(_2\) observed in the outlet was attributed to reaction (13) taking place in the hot zone and/or reaction (14) taking place in the hot and/or cooling zone. Lower CO\(_2\) and O\(_2\) product flows in the test with MgO-C compared to those observed with Al\(_2\)O\(_3\)-C implied the re-oxidation of (i) Mg\(_{(g/l/s)}\) via reverse reactions (6) and (8) taking place in the hot and/or cooling zone and (ii) deposited C via reactions (7) and (13) taking place in the cooling zone only.

Figure 12. Outlet molar rates of CO, CO\(_2\), and O\(_2\) for MgO-C and Al\(_2\)O\(_3\)-C blends subjected to the O\(_2\)-Ar sweep (5% O\(_2\)-Ar; \(V^0_N = 0.16 \text{ L}_N/\text{min}\)) at \(T_{sp} = 1375^\circ\text{C}\). Note: the mole rate of CO\(_2\) is shown doubled to ease visual distinction from the mole rate of O\(_2\).

3.3.1.2 The Amounts of C Removed and CO Generated by Co-fed O\(_2\)

Following the procedure outlined in section 3.2.5.1, the amounts of C at the onset of CTR were found to be \(\tilde{N}_C(\tau_1)_{O_2} = 47.1 \pm 0.15 \text{ mmol}\) over the entire temperature range investigated. The final amount of C in the absence of CTR \(\tilde{N}_C(\tau_f)_{O_2}\) decreased from 31.6 at 1375°C to 26.6 mmol at 1450°C. This
decrease was attributed mainly to the increase in the durations of the heating and cooling temperature ramps that increased the total duration of O$_2$ co-feed from 60 min at $T_{sp} = 1375^\circ$C to 73 min at $T_{sp} = 1450^\circ$C. At the same time, the C consumption in the experiments with the Al$_2$O$_3$-C blend was essentially unaffected by an increase in $T_{sp}$ (see Appendix C.2). This, together with a roughly constant CO production rate once the temperature stabilized at $T_{sp}$, confirms that the oxidation of C in these experiments was controlled by film diffusion which for the typical C conversion of 12-17% implies essentially constant conversion rate$^{99}$. With the total $p_{tot}|_{O_2}$~0.8 kPa, $p_{CO}|_{O_2}$ was ranging between 55-65 Pa and 60-75 Pa at 1375°C and 1450°C, respectively.

3.3.2 Phase 2: CO$_2$-Ar Sweep

3.3.2.1 Detection of The Onset of CTR

Table 6. The initial conditions for the tests under CO$_2$-Ar sweep (phase 2 of the experimental program).

<table>
<thead>
<tr>
<th>sweep gas</th>
<th>$\dot{V}_N^0$ (L$_N$/min)</th>
<th>$P_{CO_2}$ in the sweep (Pa)</th>
<th>solids</th>
<th>$N_{MgO}^0$ (mmol)</th>
<th>$N_C^0$ (mmol)</th>
<th>$N_C^0/N_{MgO}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% CO$_2$-Ar</td>
<td>0.31</td>
<td>75</td>
<td>C</td>
<td>-</td>
<td>53.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgO-C</td>
<td>49.6</td>
<td>53.3</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 6 summarizes the initial conditions selected for the tests under O$_2$-Ar sweep. These conditions were implemented at three furnace setpoint temperatures ($T_{sp}$): 1375, 1400, and 1450°C. Figure 13 compares the outlet CO, CO$_2$, and O$_2$ molar flow rates in the product gas from the experiments with the MgO-C blend and C alone at 1375°C; the results for the remaining two setpoint temperatures are shown in Appendix C.2 and the repeatability of the experiments is demonstrated in Appendix C.3. The onset point of CTR was identified at $\tau_1 \approx 22$ min as the time stamp of the inflection point of the CO molar flow rate obtained with the MgO-C blend. Markedly, the good agreement between the data
sets for $t < \tau_1$ was achieved even without diluting C with Al$_2$O$_3$. This was attributed to the endothermic consumption of C by CO$_2$ via reaction (9) ($\Delta h^0 = +172.4$ kJ/mol$^{15}$). As it was the case for O$_2$-Ar sweep, the production of CO by the consumption of C with co-fed CO$_2$ was approximately constant once the temperature stabilized at $T_{sp}$, and essentially independent of $T_{sp}$ (see Appendix C.2). A decrease in the molar rate of CO$_2$ observed with the MgO-C during CTR compared to that observed during C oxidation experiments with C alone was attributed to the oxidation of Mg$_{(g/l/s)}$ and via reverse reaction (8) taking place in the hot and/or cooling zone.

![Figure 13. Outlet molar rates of CO and CO$_2$ for MgO-C and C alone subjected to the CO$_2$-Ar sweep (5% CO$_2$-Ar; $V_N^0 = 0.31$ L$_N$/min) at $T_{sp} = 1375^\circ$C.](image)

### 3.3.2.2 The Amounts of C Removed and CO Generated by Co-fed CO$_2$

Following the procedure outlined in section 3.2.5.1, the amounts of C at the onset of CTR were found to be $\tilde{N}_C(\tau_1)|_{CO_2} = 47.8 \pm 0.05$ mmol over the entire temperature range investigated. As it was the case for the tests under O$_2$-Ar sweep, the final amount of C in the absence of CTR $\tilde{N}_C(\tau_f)|_{CO_2}$ decreased with
increasing $T_{sp}$ from 32.6 mmol at 1375°C to 31.8 and 27.5 mmol at 1400°C and 1450°C, respectively, mainly because of the prolonged duration of the CO$_2$ co-feed. Compared to the O$_2$-Ar sweep experiments, the relative differences between calculated values of $\tilde{N}_C(\tau_1)$ and of $\tilde{N}_C(\tau_f)$ were $\leq 2\%$ and $\leq 4\%$, respectively, as shown in Figure 14. The set of the conditions listed in Table 6 therefore provided that $\tilde{N}_C(\tau_1)|_{CO_2} \approx \tilde{N}_C(\tau_1)|_{O_2}$ and $\tilde{N}_C(\tau_f)|_{CO_2} \approx \tilde{N}_C(\tau_f)|_{O_2}$ (see equation (15)) so no iterations with different CO$_2$-Ar sweep flow rates and/or compositions mentioned in section 3.1.2 and Appendix C.1 were needed. With $p_{tot}|_{CO_2} \approx 1.5$ kPa, $\tilde{p}_{CO}|_{CO_2}$ was approximately constant at $T_{sp}$ and ranged from 94 Pa ($T_{sp} = 1375^\circ$C) to 97 Pa ($T_{sp} = 1450^\circ$C) as shown in Figure 15.

Figure 14. Comparison of $\tilde{N}_C(\tau_1)$ and $\tilde{N}_C(\tau_f)$ under O$_2$-Ar and CO$_2$-Ar sweep as function of $T_{sp}$.
3.3.3 Phase 3: Ar and CO-Ar Sweeps

The initial conditions selected for the reference CTR experiments under CO-Ar and Ar sweeps are shown in Table 7. The starting amounts of C in the blends with MgO were selected to satisfy $N_C^0|_{\text{high}} \approx \bar{N}_C (\tau_1)$ and $N_C^0|_{\text{low}} \approx \bar{N}_C (\tau_f)$. To account for the observed decrease in $\bar{N}_C (\tau_f)$ with an increase in $T_{SP}$, $N_C^0|_{\text{low}}$ was adjusted to 32.9, 31.6, and 26.6 mmol for $T_{SP} = 1375, 1400,$ and $1450^\circ\text{C}$, respectively. The higher limit of CO partial pressure in the sweep was set to $p_{CO} = 95$ Pa to match $\bar{p}_{CO|_{\text{CO}_2}}$ that ranged from 94 to 97 Pa. This was accomplished by flowing a 5% CO-Ar mixture with a normal flow rate $V_N = 0.39$ L\text{N}/min, which resulted in $p_{\text{tot}} \approx 1.9$ kPa. The total normal flow rate of the Ar sweep was chosen to be the same as that of the CO-Ar sweep (0.39 L\text{N}/min) also resulting in $p_{\text{tot}} \approx 1.9$ kPa. The outlet gas in all the reference experiments comprised only Ar and CO. Figure 16 indicates remarkable similarity between the outlet CO molar rates observed during the comparison experiments under the CO$_2$-Ar sweep and the reference experiments under the CO-Ar sweep with $N_C^0|_{\text{high}}$. As
The Prevailing Reaction Pathway

expected, the outlet CO molar rates observed under the O₂-Ar sweep were lower. The results of the experiments performed under Ar sweep with \( N^0_{C|\text{high}} \) and the CO-Ar sweep with \( N^0_{C|\text{low}} \) are also available in Appendix C.2. In spite of the absence of CO₂ in the outlet gas during the experiments completed under CO-Ar and Ar sweeps, visual inspection of the cooling zone upon these experiments confirmed the presence of deposited C, MgO and/or Mg. This implies that C may have deposited as a consequence of the direct recombination of the products via the reverse reaction (4). The other possibility is that the condensed Mg\( _{(l/s)} \) may have catalyzed Boudouard reaction (as C deposition was not observed at up to \( p_{CO} \leq 95 \) Pa in the absence of CTR) but that the produced CO₂ was completely consumed by the Mg\( _{(g/l/s)} \) reoxidation via reverse reaction (8). This scenario would impose the equality of the extents of the reverse reactions (8) and (9), i.e. \( \varphi^*_8 = \varphi^*_9 \), thereby making the Boudouard reaction (9) only a step of the reverse overall reaction (4) as suggested by Hischier et al.\(^56\).

Table 7. The initial conditions for the reference tests completed under CO-Ar or Ar sweep (phase 3 of the experimental program).

| \( T_{SP} \) (°C) | sweep gas | \( V^0_N \) (L\( _N \)/min) | \( p_{CO} \) in the sweep (Pa) | solids | \( N^0_{\text{MgO}} \) (mmol) | \( N^0_{C|\text{high}} \) (mmol) | \( N^0_{C|\text{low}} \) (mmol) | \( \frac{N^0_C}{N^0_{\text{MgO}}} \) |
|-----------------|------------|------------------|-----------------|--------|----------------|-----------------|----------------|----------------|
| 1375            | 5% CO-Ar   | 0.39             | 95              | MgO-C  | 49.6           | -               | 32.9            | 0.67            |
| Ar              | 0.39       | -                | MgO-C           | 49.6   | 47.5           | -               | 32.9            | 0.67            |
| 1400            | 5% CO-Ar   | 0.39             | 95              | MgO-C  | 49.6           | -               | 31.6            | 0.64            |
| Ar              | 0.39       | -                | MgO-C           | 49.6   | 47.5           | -               | 31.6            | 0.64            |
| 1450            | 5% CO-Ar   | 0.39             | 95              | MgO-C  | 49.6           | -               | 26.6            | 0.54            |
| Ar              | 0.39       | -                | MgO-C           | 49.6   | 47.5           | -               | 26.6            | 0.54            |


Figure 16. CO molar rates observed at (a) $T_{sp}=1400^\circ C$ and (b) $1450^\circ C$ with $N_c^{0, high} \approx \bar{N}_c (\tau_1) = 47.5$ mmol and $N_{MgO}^{0} = 49.6$ mmol under CO-Ar (black solid line), CO$_2$-Ar (green dashed line) and O$_2$-Ar (blue dotted line). The comparison of the CO molar rates for $T_{sp}=1375^\circ C$ is shown in Appendix C.2.
3.3.4 Discrimination of the Prevailing Reaction Pathway

The extents of CTR calculated as outlined in section 3.2.5.3 are normalized by $N_{\text{MgO}}^0 = 49.6$ mmol and shown in Figure 17 as function of $T_{sp}$. The highest amount of the C deposited in the cooling zone, indicating the highest $\phi^*_4$ and $\phi^*_9$, is expected to be observed in the experiment performed with the higher initial amount of C $N_{C|\text{high}}^0 = 47.5$ mmol under the CO-Ar sweep as this experiment resulted in the highest Mg$_{(g)}$ production and the highest $p_{\text{CO}}$ in the cooling zone. Therefore, setting the maximum amount of deposited C to the amount calculated for this particular experiment, i.e.,

$$\max \left[ \phi^*_4 \left( \tau_f \right) + \phi^*_9 \left( \tau_f \right) \right] = \left[ \phi^*_4 \left( \tau_f \right) + \phi^*_9 \left( \tau_f \right) \right]_{\text{CO}, N_{C|\text{high}}^0}$$

allows for bounding the extents of CTR calculated for the comparison runs via equation (40) by the error bars reflecting the uncertainty of $N_{\text{C,dep}} \left( \tau_f \right)$ as

$$0 \leq N_{\text{C,dep}} \left( \tau_f \right) \leq \left[ \phi^*_4 \left( \tau_f \right) + \phi^*_9 \left( \tau_f \right) \right]_{\text{CO}, N_{C|\text{high}}^0}$$

The results presented in Figure 17 can be summarized as follows:

(A) The addition of CO to the sweep gas slightly suppresses the Mg production (data set II versus data set I); therefore, the runs performed under the CO-Ar sweep (data sets II and IV) may serve as a conservative reference for the CTR in the absence of the oxidants in the sweep.

(B) The extents of CTR in the comparison experiments performed under the O$_2$-Ar sweep with $N_{C|\text{high}}^0$ (data set V) were up to 60% lower than those obtained under the CO-Ar sweep with $N_{C|\text{low}}^0$ (data set IV).

(C) The extents of CTR in the comparison experiments performed under the CO$_2$-Ar sweep with $N_{C|\text{high}}^0$ (data set III) were lower than those obtained under the CO-Ar sweep with $N_{C|\text{high}}^0$ (data set II) but higher than those obtained under the CO-Ar sweep with $N_{C|\text{low}}^0$ (data set IV).
Figure 17. Normalized extents of CTR as function of $T_{sp}$ under (I) Ar sweep with $N_C^0 = N_{C|\text{high}}^0 = 47.5$ mmol (open circles), (II) CO-Ar sweep with $N_C^0 = N_{C|\text{high}}^0 = 47.5$ mmol (filled circles), (III) CO$_2$-Ar sweep with $N_C^0 = 53.3$ mmol corresponding to $\tilde{N}_C(\tau_f) = 47.8$ mmol $\approx N_{C|\text{high}}^0$ (open diamonds), (IV) CO-Ar sweep with $N_C^0 = N_{C|\text{low}}^0 = 32.9$ (1375°C), 31.6 (1400°C), and 26.6 mmol (1450°C) (filled squares), and (V) O$_2$-Ar sweep with $N_C^0 = 53.3$ mmol corresponding to $\tilde{N}_C(\tau_f) = 47.1$ mmol $\approx N_{C|\text{high}}^0$ (open triangles). The error bars for the comparison runs (III and V) represent the expected maximum of $N_{C,\text{dep}}(\tau_f)$ calculated via equation (47) for the experiments from the set (II) as the expected maximum of $N_{C|\text{high}}^0$. The dotted lines are added only to indicate trends.

As the addition of O$_2$ to the sweep showed no facilitating effect on the sintering of MgO (see Appendix C.4), the O$_2$-induced suppression of the Mg production in spite of a more favorable C/MgO ratio (observation B) can be attributed only to the equilibrium shifts of reactions (6) and/or (8) because of the potential increase in both $P_{O_2}$ and the ratio $P_{CO_2}/P_{CO}$. The former can be estimated from the outlet O$_2$ molar rates and then used to calculate the equilibrium partial pressures of Mg resulting from the MgO dissociation (reaction (6)) according to the analysis presented in Appendix C.6. These equilibrium partial pressures were five to six orders of magnitude lower than the
partial pressures of Mg estimated from the observed Mg productions as described in Appendix C.5. This implies that at $T_{sp}$ of 1375°C and 1400°C the MgO dissociation (reaction (6)) essentially did not contribute to the $Mg_{(g)}$ production under the O$_2$-Ar sweep (data set V). It should be noted that this claim cannot be extended to the experiment performed at $T_{sp} = 1450°C$ as the outlet O$_2$ molar rate was essentially zero during a part of this experiment hence the thermal dissociation could have taken place also. Using analogous reasoning outlined in Appendix C.6 to estimate $p_{CO_2}/p_{CO}$ ratios for the experiments under the CO$_2$-Ar sweep (data set III) indicates that the partial pressures of Mg estimated from the observed $Mg_{(g)}$ productions are ~ 20 to 4000 times higher than those predicted by the equilibrium of reaction (8). This implies that under the CO$_2$-Ar sweep (data set III) the MgO reduction with CO (reaction (8)) essentially did not contribute to the $Mg_{(g)}$ production.

A plausible explanation for the observed O$_2$ and CO$_2$ effects is that $Mg_{(g)}$ is produced via both (a) MgO thermal dissociation and (b) MgO reduction with CO that take place in parallel. The role of C is to remove the intermediates O$_2$ and CO$_2$ from the reaction sites, thereby favoring forward reactions (6) and (8). Markedly, at 1375°C and 1400°C the sums of the extents obtained under the CO$_2$-Ar (data set III) and O$_2$-Ar sweeps (data set V) are essentially equal to the extents obtained under the Ar-CO sweep (data set II); at 1450°C, the sum slightly exceeds the extent from the data set II which could be attributed to the Mg production under the O$_2$-Ar sweep partly to the MgO dissociation also. This implies that adding O$_2$ or CO$_2$ to the sweep allows to isolate one of the steps by preventing the other and to determine that at 1375°C and 1400°C roughly twice as much of Mg was produced via the MgO dissociation compared to the MgO reduction with CO.

The conclusion outlined above appears to contradict the claim by Chubukov et al. who have advocated that under the same reaction conditions the MgO$_{(s)}$-C$_{(s)}$ boundary reaction governs the Mg production rather than MgO dissociation. It should be noted that the disagreement may be existing only in the interpretation of the same reaction mechanism. Namely, the MgO dissociation (reaction (6)) is sustained by the removal of O$_2$ from the MgO surface via oxidation of C (reaction (7)) and the sum of these two steps results in the stoichiometry of the overall
reaction (4). However, there is no evidence supporting the relevance of a direct solid-solid reaction. In fact, the results of the comparison experiments presented in Figure 17 indirectly demonstrate that the contact between the materials is not a factor. Namely, the CTR experiments under the O$_2$-Ar and the CO$_2$-Ar sweeps (data sets III and V, respectively) were performed with the same initial amount of C, which was pre-oxidized to essentially the same extent before reaching the onset temperature of CTR (see Figure 14). Therefore, the pre-oxidation of C with O$_2$ and CO$_2$ should have affected the interfacial contact between the materials in the same way. Yet, the extents of the MgO reduction under the CO$_2$-Ar sweep are roughly twice as high compared to those observed under the O$_2$-Ar sweep.

### 3.4 Summary and Conclusions

This chapter discriminates the prevailing reaction pathways of the carbothermic reduction of MgO for normalized reduction extents of up to 0.4 achieved within the temperature and pressure ranges of 1375–1450°C and 1-2 kPa, respectively. It demonstrates that Mg$_{(g)}$ is produced in the ratio ~2:1 via (1) MgO thermal dissociation and (2) MgO reduction with CO that take place in parallel. These pathways generate O$_2$ (pathway 1) and CO$_2$ (pathway 2) as the intermediates that react with C, thereby sustaining the Mg production. It is also argued that the MgO dissociation pathway may have been confused with the MgO$_{(s)}$-C$_{(s)}$ boundary reaction advocated by previous investigators, which relies on the direct contact of the solid reactants. Therefore, our findings imply that the rate of the overall MgO reduction may be controlled by the diffusion of the intermediates from the MgO$_{(s)}$ surface to the C$_{(s)}$ surface and/or a loss of the MgO surface area due to sintering rather than by the loss of the direct contact between MgO$_{(s)}$ and C$_{(s)}$. 
4 Kinetics of Carbothermic Reduction of MgO Under Low Pressures\textsuperscript{a,b}

It has been conclusively shown in the previous chapter that at temperatures in the order of 1375-1450°C and total pressures of 1-2 kPa, Mg is produced by both dissociation of MgO and reduction with CO with the former being prevailing. The goal of the work in this chapter is to investigate the kinetics of the MgO dissociation pathway as to determine, which parameters control its rate. For that matter, the kinetics of CTR were investigated with powdery MgO-C blends under isothermal/isobaric (1400°C, ~2 kPa) conditions using a novel experimental method to measure the reaction kinetics. The discrimination of the rate-controlling reaction step(s) was accomplished by evaluating the effect on the rate of CTR when changing the C/MgO ratio, the MgO surface area and size, diluting MgO-C blends with inert Al\textsubscript{2}O\textsubscript{3}, and replenishing MgO-C blends with MgO and C, respectively, in the course of the CTR.

4.1 Experimental

4.1.1 Materials

Table 8 lists the as-received/prepared starting materials that properties and impurity fractions were determined according to the methods outlined in Appendix A.

\textsuperscript{a} Material in this chapter will be published as: A. Coray, L. Pusterla, and Z.R. Jovanovic, “On the Kinetics of Magnesium Production via Carbothermic Reduction of Magnesium Oxide under Low Pressures”, \textit{manuscript in preparation}.

\textsuperscript{b} Material in this chapter has been extracted from L. Pusterla “Kinetics of Carbothermic Reduction of Magnesium Oxide”, Master Thesis, ETH Zürich, 2016, directly supervised by A. Coray.
Table 8. Properties and impurity fractions of the as-received/prepared solid starting materials.

<table>
<thead>
<tr>
<th>material</th>
<th>as-received MgO</th>
<th>presintered MgO</th>
<th>purified C</th>
<th>as-received Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>source</td>
<td>Sigma-Aldrich, #342793</td>
<td>Sigma-Aldrich, #342793</td>
<td>Fluka Analytical, #05120</td>
<td>Sigma-Aldrich, #342688</td>
</tr>
<tr>
<td>$\bar{d}$ (µm)</td>
<td>12·10^{-3} (*)</td>
<td>151.3</td>
<td>37.6</td>
<td>29.9</td>
</tr>
<tr>
<td>SSA (m²/g)</td>
<td>141±1</td>
<td>9.9±0.1</td>
<td>493±18</td>
<td>-</td>
</tr>
<tr>
<td>bulk density (g/cm³)</td>
<td>0.45</td>
<td>1.75</td>
<td>0.42</td>
<td>1.80</td>
</tr>
<tr>
<td>impurities</td>
<td>type</td>
<td>H₂O</td>
<td>CO₂</td>
<td>H₂O+CO₂</td>
</tr>
<tr>
<td></td>
<td>wt %</td>
<td>3.5</td>
<td>2</td>
<td>negligible</td>
</tr>
</tbody>
</table>

(*): calculated from the SSA

As-received MgO

Based on the volume-based particle size distribution shown in Figure 19, it appears to imply that the as-received MgO consisted of particles in the order of 0.1-30 µm. However, the SEM photograph shown in Figure 18 indicates that these particles are only agglomerates of nanoparticles with effective particle sizes in the order of 12 nm as inferred from the measured SSA (assuming spherical, non-porous particles). The as-received MgO contained H₂O and CO₂ as impurities adsorbed from the surroundings and chemically bonded in the form of Mg(OH)₂ and MgCO₃, respectively. A removal of the contained H₂O and CO₂ from the MgO via calcination prior to its usage as reactant was, however, not practical as the freshly calcined MgO immediately re-adsorbed some H₂O and/or CO₂ upon getting in contact with surrounding air.

Presintered MgO

This material was prepared by sintering as-received MgO following the procedure discussed in section 4.1.4.1. The presintered MgO still appeared in powdery form, yet had a 14 times lower SSA and 4 times higher bulk density.
compared to the as-received MgO (9.9 vs. 141 m²/g and 1.75 vs. 0.45 g/cm³, respectively). Furthermore, the apparent particle size was significantly larger than of the as-received MgO (see Figure 19). Interestingly, TEM photographs shown in Appendix D.1 indicate that the grain size of the as-received and presintered MgO was not significantly different.

![Figure 18. MgO agglomerates (white) sitting on a C particle for better visualisation.](image)

**Purified C**

Before its usage as reactant for the CTR, as-received C was purified according to the procedure shown in section 4.1.4.2 in order to remove the contained moisture and volatile matter (1.6 and 2.4%, respectively) as to prevent a confounding of the reaction atmosphere by their volatilization during the CTR experiments. The particle sizes of the purified C ranged from ~5-500 µm as shown in Figure 20. The discrepancy between the mean particle size (37.6 µm) and the BET surface area (493 ± 18) indicates that the purified C was highly porous.

**As-received Al₂O₃**

In some experiments, as-received Al₂O₃ served as diluent of MgO-C blends. The mean particle size was similar as the purified C (29.9 vs. 37.6 µm), but the volume-based particle size distribution was significantly smaller (see Figure 20).
Figure 19. Volume-based particle size distribution of as-received and presintered MgO.

Figure 20. Volume-based particle size distribution of as-received Al₂O₃ and purified C.
4.1.2 Method for Kinetic Data Acquisition

Past studies that dealt with the CTR of MgO commonly acquired kinetic data by monitoring either the temporal weight of the solid reactants\textsuperscript{61, 66, 67, 73, 75} or the temporal product gas amount and composition.\textsuperscript{41, 70, 72, 79} The monitored product gas amount and composition further needed to be corrected for the confounding effect of the reverse overall reaction occurring in the cooling zone. To accomplish this, it was assumed that the fractions of produced Mg and CO that underwent reversion were constant,\textsuperscript{41, 70, 72, 79} i.e. in the reverse overall reaction, the reaction orders with respect to Mg and CO were assumed to be equal to unity. It has, however, not been conclusively shown so far that these reaction orders indeed equal unity questioning therefore the accuracy of this method.

In this work, a novel experimental method was developed that precluded the proceeding of the reverse overall reaction in the cooling zone. Kinetic data could therefore be acquired by monitoring the product gas amount and composition without requiring its correction for the confounding effect of the reverse overall reaction. Figure 21 schematically illustrates this method. Gaseous Mg and CO that are produced by the CTR a guided from the location of production (CTR zone) into a second zone, the Mg combustion zone. This zone is purged with CO\textsubscript{2} that combusted the gaseous Mg product according to reverse reaction (8). Fast combustion rates of Mg gas by CO\textsubscript{2} have been observed in past research,\textsuperscript{56, 101, 102} which supports the feasibility of the proposed method. Providing that the complete amount of Mg is combusted by CO\textsubscript{2} inside the Mg combustion zone, the product gas that is cooled down in the cooling zone is free of Mg. The proceeding of the reverse overall reaction in the cooling zone is therefore precluded.
4.1.3 Apparatus

Figure 22 schematically illustrates the experimental apparatus. At start of the measurement, a custom-made powder feeder ① that rotating paddle was driven by an electric motor ② (Lambda Instruments) dropped the solid reactants through a feed tube ③ (Al₂O₃, ø26x3 mm) swept with Ar into a cylindrical crucible ④ (Al₂O₃, ø58x5 mm, l = 100 mm) that is shown in more detail on the left side of the figure. Two graphite felts (Sigratherm GFA5) placed on the crucible top ⑤ and on the bottom ⑥, respectively, enclosed the crucible and prevented the removal of solid reactants from the CTR zone.
Figure 22. Schematic of the experimental apparatus. Components of the apparatus are: ① powder feeder, ② electric motor, ③ feed tube, ④ alumina crucible, ⑤ and ⑥ graphite felts, ⑦ boreholes, ⑧ thermocouple, ⑨ alumina reactor tube, ⑩ alumina support tubes, ⑪ furnace, ⑫ CO₂ injection tube, ⑬ mass-flow controller MFC 1, ⑭ mass flow controller MFC 2, ⑮ vacuum pump, ⑯ particle filter, ⑰ globe valve, ⑱ pressure sensor, ⑲ overpressure relief valve, and ⑳ gas chromatograph.
Six boreholes (7) (⌀4 mm) in the crucible bottom allowed the removal of sweep and product gases from the crucible. The temperature of the solid reactants was measured by a thermocouple (Conax Technologies, Type C, Al₂O₃ shielded, ⌀3.2 mm) (8) that reached into the solid reactant bulk. The crucible was located inside a reactor tube (9) (Al₂O₃, ⌀70x5 mm, l = 1200 mm) and held in place by five support tubes (10) (Al₂O₃, ⌀58x5 mm, l = 100 mm). Heat was provided by and electrically heated tube furnace (11) (Carbolite STF 16-450). The part of the reactor tube between crucible bottom and furnace insulation was designated as the Mg combustion zone that was purged with CO₂, which was injected through an injection tube (12) (Al₂O₃, ⌀6x1 mm). The part of the reactor tube below the furnace was cooled by surrounding air via natural convection and provided a cooling zone for precipitating the Mg(g) product. The flow rates of the sweep gas (Ar) and of CO₂ were controlled by calibrated mass flow controllers (13) and (14) (Bronkhorst EL-Flow Select Series). The low-pressure environment was provided by a vacuum pump (15) (Adixen ACP15) that was protected by a particle filter (16) (Whatman, GF/F grade glass fiber filter). Total pressure was controlled by a globe valve (17) positioned in front of the vacuum pump and monitored by a pressure sensor (18) positioned in the cold zone above the furnace. An overpressure relief valve (19) was set at 30 kPa overpressure relative to ambient pressure. The product gas composition at the outlet was measured every 60 seconds by a gas chromatograph (20) (Agilent M200).

4.1.4 Procedures

4.1.4.1 Presintering of As-Received MgO

The powder feeder was filled with as-received MgO, mounted into the apparatus that was sealed upon which the vacuum pump was started. Then, the flow rate of the Ar sweep (Messer 4.6) was set to 0.5 Lₐₙ/min and by opening the globe valve in front of the vacuum pump, total pressure inside the reactor was reduced to ~2 kPa. After pressure equilibration, the furnace was heated under continuing gas flow to the setpoint temperature $T_{SP} = 1400^\circ$C at a rate of 20°C/min and held there. Subsequently, the powder feeder was started with $v_{feeder} = 7.5$ rpm and the
as-received MgO was fed within 4 seconds into the crucible. After 30 minutes, the furnace was shut off and let to cool down. After cooling, the apparatus was opened and the sintered MgO was collected from the crucible.

4.1.4.2 Purification of As-Received C

The as-received C to be purified was poured into the crucible that was placed into the apparatus. After sealing the apparatus, the vacuum pump was started and by opening the globe valve in front of the vacuum pump, total pressure inside the reactor was reduced to ~2 kPa under 0.5 L/min of Ar sweep. After pressure equilibration, the furnace was heated under continuing Ar flow to the setpoint temperature $T_{SP} = 1500°C$ at a rate of 20°C/min and held there for 1 hour. The completed evaporation of the volatiles was indicated by the fractions of $H_2$ and $CO$ in the product gas composition approaching zero. Then, the furnace was shut off and let to cool down. After cooling, the apparatus was opened and the purified C was collected from the crucible.

4.1.4.3 CTR Experiments

The MgO-C blends were prepared by stirring $m^0_1$ grams of either as-received or presintered MgO powder with $m^0_2$ grams of purified charcoal powder with a spatula in a pill glass and, when using as-received MgO, occasionally disaggregating visible MgO agglomerates until the blends appeared to be homogeneously mixed. To investigate the effect of MgO-C blend dilution with $Al_2O_3$, $m^0_1$ grams of presintered MgO and $m^0_2$ grams of purified charcoal powder were stirred with a spatula in a pill glass. Upon reaching homogeneous appearance, $m^0_3$ grams of as-received $Al_2O_3$ was added and the powders were gently stirred again until the MgO-C-$Al_2O_3$ blend appeared to be homogeneously mixed. The effective amounts of the MgO, $Al_2O_3$ and C in the blends ($m^0_{MgO}$, $m^0_{Al_2O_3}$ and $m^0_C$, respectively) were calculated according to equation (20). The total masses of the blends to be fed were chosen such that the required sensible heat to preheat the reactants $(Q_s)$ was equal to 2.2 kJ thereby equilibrating the
heating time between different blends. The sensible heat for species \( i \) \( (Q_{s, i}) \) was calculated according to

\[
Q_{s, i} = N_i^0 \int_{T_{\text{amb}}}^{T_{sp}} c_p^i(T)\,dT
\]

with \( T_{\text{amb}} \) assumed to be equal to 293 K and \( c_p^i(T) \) as the specific heat capacity of species \( i \), which was extracted from the HSC database.\(^{35}\)

The prepared blends were filled into the powder feeder that was subsequently mounted into the apparatus. After sealing it, the vacuum pump was started. By opening the globe valve in front of the vacuum pump, total pressure inside the reactor was reduced to \( \sim 2 \) kPa under 0.5 L\text{N}/min of Ar sweep and 0.05 L\text{N}/min of CO\(_2\) (Messer 4.8). The experiment then followed the same procedure as followed for presintering MgO (section 4.1.4.1) until the furnace was cooled down. After cooling, the apparatus was opened, the support tubes were inspected for deposits, and the residual solid material was collected from the crucible.

In some experiments, the MgO in the residual solid material was further analyzed for the SSA. For that matter, the MgO was recovered from the residual solid material by heating a sample of it in a thermogravimetric analyzer (Netzsch 409 STA) under a 20% air-Ar atmosphere at a rate of 20°C/min to 900°C. Subsequently, the sample was held at this temperature until its mass stabilized indicating that the entire C was oxidized. The retaining mass comprised only MgO and ash, which fractions, however, could not be separated.

4.1.4.4 Replenishment of MgO or C in the course of CTR

The crucible was filled with an MgO-C blend that was prepared according to the same procedure as shown in section 4.1.4.3, except that total amounts were as high as \( m_{\text{MgO}}^0 = 2.0 \) g and \( m_C^0 = 0.6 \) g. The feeder was filled with either as-received MgO (\( m_{\text{MgO}}^0 = 2.0 \) g) or purified C (\( m_C^0 = 0.6 \) g). Then, the crucible and the feeder were mounted into the apparatus that was sealed afterwards. The vacuum pump was started and by opening the globe valve in front of the vacuum pump, total pressure inside the reactor was reduced to \( \sim 2 \) kPa under 0.5 L\text{N}/min of Ar sweep and 0.05 L\text{N}/min of CO\(_2\). Afterwards, the furnace was heated under
continuing gas flows at a rate of 20°C/min to the setpoint temperature $T_{sp} = 1400°C$ and held there for 30 minutes. Then, the feeder was started with $\nu_{feeder} = 7.5$ rpm and the feedstock was fed within 4 seconds into the crucible. The temperature was held constant for another 30 minutes until the furnace was shut off and let to cool. After cooling, the apparatus was opened, the support tubes were inspected for deposits, and the residual solid material was collected from the crucible.

4.1.5 Data Processing

4.1.5.1 Accounting for the Dissociation of Mg(OH)$_2$ and MgCO$_3$ Impurities

Right after the feed, the Mg(OH)$_2$ and MgCO$_3$ impurities dissociated (reactions (18) and (19)) releasing some H$_2$O and CO$_2$ from which a fraction further reacted via reactions (51) and (9), respectively.

$$\text{H}_2\text{O} + \text{C}_\text{(s)} \rightleftharpoons \text{H}_2\text{(g)} + \text{CO}_\text{(g)}$$  \hspace{1cm} (51)

During this time, the rate of CTR was not determinable as the additionally produced CO$_2$ and CO confounded the product gas composition. This distortion is exemplary illustrated in Figure 23 that shows the outlet molar rates of CO, CO$_2$, and H$_2$, temperature, and total pressure as function of time of a typical experiment. A temperature drop of ~20°C indicated the time of reactant feed (①). Simultaneously, an increase in total pressure of ~0.2 kPa was observed due to the production of gases and due to the partial filling of the crucible with reactants that led to an increase in the pressure drop over the crucible. The variation of total pressure due to the production of gases during the CTR was always < 0.1 kPa. The heating time of the reactants was determined to 50-55s, as indicated by the temperature trace. The dissociation of Mg(OH)$_2$ and MgCO$_3$ and the thereby induced reactions (51) and (9) was indicated in the outlet gas by the H$_2$ peak and the CO$_2$ rate being higher than the injected amount $\left(\dot{n}_{CO_2}^0\right)$, respectively. The dissociation of Mg(OH)$_2$ was completed within 60 seconds as indicated by the H$_2$ outlet rate approaching zero. The completion of MgCO$_3$
dissociation was similarly fast. This was confirmed by dropping as-received MgO alone under Ar sweep into the crucible and monitoring the CO and CO$_2$ outlet rates that approached zero within 60s. Therefore, the rate of CTR was determined starting from a reaction time of ~60s (2).

![Figure 23. Outlet molar rates of CO, CO$_2$ and H$_2$ in the outlet, temperature, and total pressure during a typical experiment. (1) solid reactant drop, (2) solid reactants fully heated and completion of Mg(OH)$_2$ and MgCO$_3$ dissociation. ($V_{N,Ar}^0 = 0.5$ L$_N$/min; $V_{N,CO}_2^0 = 0.05$ L$_N$/min; $T_{sp} = 1400^\circ C$)](image)

Furthermore, as reactions (51) and (9) consumed C, they lowered the effective initial amount of C ($N_{C,eff}^0$) that was available for CTR. However, the consumption extent of C by reactions (51) and (9) was not determinable. Therefore, the uncertainty range of $N_{C,eff}^0$ was bracketed by assuming that either none of the H$_2$O and CO$_2$ contained in the as-received MgO, or its complete amount reacted with C, i.e.
4.1.5.2 Determination of the Conversion Rates of MgO and C

The conversion rates of MgO \( \left( \frac{dX_{\text{MgO}}}{dt} \right) \) and C \( \left( \frac{dX_{\text{C}}}{dt} \right) \) were calculated according to

\[
\frac{dX_{\text{MgO}}}{dt} = \frac{r_4}{N_{\text{MgO}}^0}
\]

and

\[
\frac{dX_{\text{C}}}{dt} = \frac{r_4}{N_{\text{C,eff}}^0}
\]

with \( r_4 \) as the rate of CTR. This value was determined by a C material balance in the outlet, i.e. the summation of the molar product gas flow rates of CO \( \left( \dot{n}_{\text{CO}} \right) \) and CO\(_2\) \( \left( \dot{n}_{\text{CO}_2} \right) \) under the assumption that equal amounts of MgO and C were consumed by the CTR (see Appendix B). The flow rates \( \dot{n}_{\text{CO}} \) and \( \dot{n}_{\text{CO}_2} \) were determined according to equations (30)-(34) and corrected for gas dispersion by the method discussed in Appendix D.2. The potentially proceeding reactions are listed in Table 9. Reactions \( i \) designated with a star \( \left( r_i^* \right) \) refer to reactions proceeding into the reverse direction.

Table 9. Reactions taking place in the CTR, in the Mg combustion, and in the cooling zone. Reactions \( i \) proceeding reverse direction are designated with a star \( \left( r_i^* \right) \).
The CO and CO$_2$ material balances are given as

\[ \dot{n}_{\text{CO}} = r_4 + r_8^* - r_4^* - 2r_9^* \]  \hspace{1cm} (55)
\[ \dot{n}_{\text{CO}_2} = n_{\text{CO}_2}^0 - r_8^* + r_9^* \]  \hspace{1cm} (56)

that upon summation gives the C material balance in the outlet, i.e.

\[ \dot{n}_{\text{CO}} + \dot{n}_{\text{CO}_2} = r_4 + n_{\text{CO}_2}^0 - (r_4^* + r_9^*) \].  \hspace{1cm} (57)

The rates of reactions $r_4^*$ and $r_9^*$ (reverse overall reaction and reverse Boudouard reaction, respectively) reflect the rate of solid C deposition in the cooling zone, i.e.

\[ \dot{n}_{\text{C,dep}} = r_4^* + r_9^* \]  \hspace{1cm} (58)

Since the Mg$_{(g)}$ product is combusted inside the Mg combustion zone, the reverse overall reaction is precluded in the cooling zone, i.e. $r_4^* = 0$. Furthermore, the reverse Boudouard reaction was shown not to proceed on cooling zone walls made of Al$_2$O$_3$ and $p_{\text{CO}} \leq 95$ Pa (see section 3.2.5.1), i.e. $r_9^* = 0$. Thus,

\[ \dot{n}_{\text{C,dep}} = r_4^* + r_9^* = 0 \].  \hspace{1cm} (59)

Verification of equation (59) was given by visually inspecting the cooling zone walls after each CTR experiment. If any solid deposits (MgO, Mg, or C) would have been detected it would have been implied that either reaction $r_4^*$ and/or $r_9^*$ proceeded thereby falsifying equation (59). By combining equations (57) and (59), the molar rate of CTR ($r_4$) was calculated as

\[ r_4 = \dot{n}_{\text{CO}} + \dot{n}_{\text{CO}_2} - n_{\text{CO}_2}^0 \]  \hspace{1cm} (60)

4.1.5.3 Determination of the Conversion Extents of MgO and C

Final conversion extents of MgO ($X_{\text{MgO}}$) and C ($X_c$) were determined based on the composition of the residual reactant blend. When an MgO-C blend has an initial C/MgO molar ratio ($W_0$) unequal unity, the ratio changes with reaction
extent. The relation between the final C/MgO molar ratio \( W_f \) and the molar extent of CTR \( (\xi_4) \) is given as

\[
W_f = \frac{N_C^f}{N_{MgO}^f} = \left( \frac{N_{C,eff}^0 - \xi_4}{N_{MgO}^0 - \xi_4} \right)
\]  

(61)

Solving for \( \xi_4 \) and dividing it through \( N_{C,eff}^0 \) and \( N_{MgO}^0 \), respectively, results in the final conversion extents of MgO and C, i.e.

\[
X_{MgO} = \frac{W_0 - W_f}{1 - W_f}
\]  

(62)

\[
X_C = X_{MgO} \frac{1}{W_0}
\]  

(63)

The final C/MgO molar ratio \( W_f \) was determined by analyzing the composition of the residual solid reactants in a thermogravimetric analyzer (Netzsch 409 STA). The recovered residual reactant blend was first well stirred in a pill glass with a spatula. Then, a sample of the homogenized blend amounting to \( m_s^0 \) was heated under a 20% air-Ar atmosphere at a rate of 20°C/min to 900°C. The sample was held at this temperature until its mass stabilized at \( m_s^f \) indicating that all the remaining C was oxidized thus leaving the retainer comprising only MgO and ash. The recorded mass loss corresponded to the amount of C contained in the sample \( (m_s^C) \). The amount of MgO \( (m_{s,MgO}^f) \) in the retaining mass \( m_s^f \) was calculated according to

\[
m_{s,MgO}^f = m_s^f - \frac{w_{ash}^f m_s^C}{m_{s,ash}^f}
\]  

(64)

The final fraction of ash contained in the residual solid reactants \( (w_{ash}^f) \) was determined as follows: the total amount of ash \( (m_{ash}) \) in the reactant blend was considered constant with reaction extent and is calculated according to

\[
m_{ash} = w_{ash}^C m_s^0
\]  

(65)

However, the final weight fraction of ash \( w_{ash}^f \) in the residual solid reactants changes with reaction extent \( \xi_4 \) according to
\[
  w_{ash}^f = \frac{m_{ash}}{(m_{MgO}^0 - \xi_4 M_{MgO}) + (m_C^0 - \xi_4 M_C) + m_{ash}}
\]  

(66)

Thus, equations (61)-(64)-(66) needed to be solved iteratively. As initial guess for \( w_{ash}^f \), a value of 0.041 was assumed.

## 4.2 Results

### 4.2.1 Attestation of the Apparatus for Correct Kinetic Measurements

Prior to investigating the CTR kinetics, the apparatus was attested for its suitability for delivering correct kinetic measurements. It had to be ensured that the outlet gas was (a) not confounded by undesired side reactions or (b) by deposition of solid C in the cooling zone via reverse overall reaction (4) and/or the reverse Boudouard reaction (9). Furthermore, limitations in external heat transfer to the reactants had to be avoided to prevent an intrusion in the kinetic measurements.

#### 4.2.1.1 Testing the Potential Occurrence of Undesired Side Reactions

First, the MgO may react with the graphite felts enclosing the crucible. This would confound the C conversion rate and total conversions of MgO and C. The reaction of MgO with the graphite felt was tested by dropping as-received MgO alone under Ar sweep into the crucible at \( T_{sp} = 1400^\circ C \) and \( p_{tot} \approx 2 \) kPa. As the outlet molar rates of CO and CO\(_2\) approached zero after the completion of Mg(OH)\(_2\) and MgCO\(_3\) dissociation (~60 seconds after the MgO drop), it was concluded that a potential reaction of MgO with the graphite felts was below the measurable limit.

Second, the injected CO\(_2\) may diffuse upstream through the crucible boreholes and through the graphite felt into the reaction zone, where it consumes the reactant C via reaction (9). This would confound the product gas and also affect the kinetics of the CTR, since the reactant C is then consumed by two
oxidants, MgO and CO\textsubscript{2}. Therefore, the flow rates of Ar and CO\textsubscript{2} were selected such that a possible diffusion of CO\textsubscript{2} into the reaction zone was prevented. To find a proper flow rate setting, the reactor was brought to reaction conditions (1400°C and ∼2 kPa) and flow rates of Ar and CO\textsubscript{2} were varied in the range of 0.25-0.5 L\textsubscript{N}/min and 0.05-0.25 L\textsubscript{N}/min, respectively. The monitored CO and CO\textsubscript{2} flows in the outlet served as indicator for the upstream diffusion of CO\textsubscript{2} into the graphite felt, since it would be accompanied by oxidation of the graphite via reaction (9). The optimum Ar and CO\textsubscript{2} flow rates were selected to 0.5 and 0.05 L\textsubscript{N}/min, respectively, as for these values a reaction of CO\textsubscript{2} with the graphite felt was negligible \(X_{CO_2} < 1\%\). A subsequent drop of purified C into the crucible showed that no CO\textsubscript{2} diffused through the graphite felt, as the CO production and CO\textsubscript{2} consumption rates did not vary after the C drop.

4.2.1.2 Verifying the Absence of C Deposition in the Cooling Zone

As already discussed, the absence of C deposition by the reverse overall reaction or the reverse Boudouard reaction (9) was verified by visually screening the walls of the Mg combustion and the cooling zone for solid deposits after each experiment. Figure 24a schematically illustrates the location of observed deposits after a typical experiment, in which the Mg\textsubscript{(g)} product was combusted with CO\textsubscript{2}. Corresponding photographs of the Mg combustion and cooling zone are shown in Figure 25a and in Figure 25b, respectively. The upper part of the Mg combustion zone was covered with white deposits, while in the cooling zone no deposits were found. In order to identify the location and appearance of the deposits for the case, if some Mg\textsubscript{(g)} reached the cooling zone, a CTR experiment was conducted without combusting the Mg\textsubscript{(g)} product with CO\textsubscript{2}. The location of observed deposits for this case is shown in Figure 24b, while the corresponding photograph of the cooling zone is shown in Figure 25c. In this case, deposits of inhomogeneous dark gray to black appearance were found in the cooling zone indicating the presence of Mg, MgO, and/or C, while the combustion zone remained free of any deposits.
Figure 24. Location of solid deposits after a typical experiment (a) with and (b) without combusting the Mg product with CO$_2$.

These results verify that when the Mg product was combusted with CO$_2$, the deposition of C via the reverse overall reaction and/or reverse reaction (9) was absent in the cooling zone.
Figure 25. Photographs of support tubes after typical experiments. (a) MgO deposits in the Mg combustion zone and (b) the absence of deposit in the cooling zone when combusting the Mg\(_{(g)}\) product with CO\(_2\); (c) deposits of Mg, MgO, and/or C in the cooling zone when the Mg\(_{(g)}\) is not combusted with CO\(_2\).
4.2.1.3 Testing for External Heat Transport Limitations

A potential confounding effect of external heat transport limitations on the CTR was tested by comparing the rates of CTR of two MgO-C blends that had equal composition (C/MgO molar ratio equal to 2) but different initial amounts. The initial amount of one blend (blend 1) was chosen so that $Q_s$ equaled 2.2 kJ, while the initial amount of the other blend (blend 2) was chosen 1.5 times increased with respect to blend 1. The temporal MgO conversion rates of the two blends are shown in Figure 26. The rate was determined starting at a reaction time of ~100s, at which both blends were fully heated. As illustrated by this figure, the MgO conversion rates of the two blends showed remarkable similarity. This not only implies that the CTR was not confounded by external heat transport limitations, but also demonstrates a good repeatability of the experimental setup.

![Figure 26. Effect of total MgO-C blend amount on the MgO conversion rate at $T_{SP} = 1400^\circ$C and $p_{tot} \approx 2$ kPa.](image)

For blend 2, the maximum energy consumption rate by the CTR was determined to be ~6W. In all other experiments shown in this work except one, the maximum energy consumption rate was below this value and therefore free
of heat transfer intrusions, too. For the exceptional case (the MgO-C blend with initial C/MgO molar ratio equal to 4), the maximal energy consumption rate was about 11% higher (~6.6 W). A potential confounding effect of external heat transport limitations on the CTR, however, was assumed to be not significant.

4.2.2 Effect of MgO Particle Size and Surface Area

The effect of MgO particle size and surface area on the rate of CTR was investigated by substituting the as-received MgO in a MgO-C blend with presintered one using the same C source and same C/MgO ratio. A MgO-C blend prepared with presintered MgO significantly distinguished itself from a blend with as-received MgO of equal C/MgO ratio and same C source as shown by the SEM photographs in Figure 27 and Figure 28. Photographs with higher resolution are shown in Appendix D.1. The presintered MgO appeared separated from the C particles with apparent particle sizes as large as ~150 μm. In contrast, as-received MgO was well dispersed over the C particles with apparent particle/agglomerate sizes < 10 μm.

Figure 27. SEM photograph of an MgO-C blend prepared with presintered MgO with equimolar C/MgO ratio.
Figure 28. SEM photograph of an MgO-C blend prepared with as-received MgO with equimolar C/MgO ratio.

Figure 29 compares the conversion rates of MgO and C between MgO-C blends prepared with either as-received MgO or presintered one using the same C source and C/MgO molar ratio of 2. As illustrated by this figure, using presintered MgO decreased the rates are by ~50% over the complete monitored reaction time of 30 minutes. In both cases, however, the CTR appeared to pass through two stages. The first stage is reflected by a fast decrease in the rates during the first 5-10 minutes of reaction. The second stage is reflected by a slow decrease in the rates at reaction times > 5-10 minutes.
Figure 29. Comparison of the conversion rates of MgO (a) and C (b) for MgO-C blends prepared with either as-received MgO or presintered one using the same C source and C/MgO molar ratio of 2 ($T_{SP} = 1400^\circ$C and $p_{tot} \approx 2$ kPa).
4.2.3 Effect of C/MgO Ratio

To investigate the effect of C/MgO ratio on the rate of CTR, C/MgO molar ratio was varied within the range of 1 to 4. Figure 30 shows an SEM photograph of an MgO-C blend with C/MgO molar ratio of 4 that was prepared with as-received MgO. A photograph with higher resolution is shown in Appendix D.1. In comparison to an MgO-C blend with equimolar molar ratio of same MgO and C sources (Figure 28), it appeared that the concentration of MgO within the C bulk was reduced, i.e. the MgO was better dispersed within the C bulk.

Figure 30. SEM photograph of an MgO-C blend prepared with as-received MgO with C/MgO molar ratio equal to 4.

The temporal MgO and C conversion rates of MgO-C blends prepared with as-received MgO with C/MgO molar ratios in the range of 1 to 4 are shown in Figure 31, respectively. Figure 32 compares the conversion rates of MgO and C as function of their conversion extent. As illustrated by these figures, an increase in C/MgO ratio proportionally increased the conversion rate of MgO but left the conversion rate of C essentially unaffected. Furthermore, an increase in C/MgO ratio did not seem to significantly affect the presence of the two reaction stages. As shown in Figure 32, the two stages were clearly distinguishable and for all tested C/MgO ratios the transition point between the stages appeared to be at $X_C \approx 0.07$. The SSA of the residual MgO were as low as $\sim 2.6-4.7$ m$^2$/g (see
Table 10) and thus by a factor of ~30-54 reduced compared to the SSA of as-received MgO.

Figure 31. Comparison of the temporal conversion rates of MgO (a) and C (b) for MgO-C blends prepared with as-received MgO using the same MgO and C sources and C/MgO molar ratios ranging from 1 to 4 ($T_{sp} = 1400^\circ$C and $p_{tot} \approx 2$ kPa).
It is important to note, however, that these values were only qualitative, since the residual MgO also contained some ash (up to 10% \text{wt}). Interestingly, the apparent grain/particle sizes of the residual MgO shown in the TEM photographs in Appendix D.1 seemed to be significantly larger compared to as-received and presintered MgO, respectively.

![Comparison of the conversion rates of MgO (a) and C (b) as function of total conversion for MgO-C blends prepared with as-received MgO using the same MgO and C sources and C/MgO molar ratios ranging from 2 to 4 \((T_{sp} = 1400^\circ\text{C} \text{ and } p_{tot} \approx 2 \text{ kPa})\).]

**Figure 32.**

<table>
<thead>
<tr>
<th>C/MgO molar ratio (-)</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA ((\text{m}^2/\text{g}))</td>
<td>2.6</td>
<td>2.8</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Table 10.** SSA of residual MgO of the reacted MgO-C blends with C/MgO molar ratios ranging from 2 to 4.

As illustrated in Figure 33, the effect of C/MgO ratio on the rate of CTR remained the same when the MgO-C blends were prepared with presintered MgO instead of as-received one: the conversion rate of MgO proportionally increased when...
increasing C/MgO molar ratio from 1 to 2, while the conversion rate of C essentially remained unaffected.

Figure 33. Comparison of the conversion rates of MgO (a) and C (b) for MgO-C blends prepared with presintered MgO and C/MgO molar ratios of 1 and 2 ($T_{sp} = 1400^\circ C$ and $p_{tot} \approx 2 kPa$).
4.2.4 Effect of MgO and C Replenishment in the Course of CTR

As already discussed in section 4.1.4.4, to investigate the effect of MgO and C replenishment in the course of CTR, as-received MgO and purified C, respectively, were dropped onto reacting MgO-C blends of equimolar C/MgO ratio that first had been slowly heated (20°C/min) to 1400°C and left to react for 30 minutes at constant temperature. The dropped MgO and C, respectively, were left to react on top of the MgO-C blend for another 30 minutes at 1400°C. As reference test, an MgO-C blend with equimolar C/MgO ratio was heated to 1400°C and left to react for 60 min at constant temperature without replenishing it with MgO or C. Figure 34 compares the molar rates of CTR (a) when replenishing MgO and (b) when replenishing C in comparison to the reference test. Up to the point of MgO or C replenishment, the conversion extents of MgO and C reached ~19%. Right after the replenishment, the release of H$_2$O and CO$_2$ from the MgO and re-adsorbed moisture from the C, respectively, confounded the rates of CTR. The corresponding measurement points (3 and 0.14 mmol/min for the MgO and C replenishment, respectively) were therefore omitted in Figure 34. When replenishing MgO, the reaction rate initially increased by a factor of ~3. With progressing time the rate decreased fast until it approached the same value as observed when nothing was replenished. Up to this point, however, only ~5% of the dropped MgO was converted. In contrast, when replenishing C the reaction rate only increased by a factor of ~1.15. With progressing time, the reaction rate remained increased as compared to when nothing was replenished resulting in a final conversion extent of the replenished C of ~1%.

4.2.5 Effect of MgO-C Blend Dilution With Al$_2$O$_3$

The effect of Al$_2$O$_3$ dilution on the rate of CTR was investigated using an MgO-C-Al$_2$O$_3$ blend that was prepared with presintered MgO with an Al$_2$O$_3$-C bulk volume ratio $V_b^{\text{Al}_2\text{O}_3}/V_b^C = 0.33$ and a C/MgO molar ratio of 1.5. As shown in Figure 35b, the dilution with Al$_2$O$_3$ decreased the C conversion rate during stage 1 of the CTR. During stage 2, however, the conversion rate of C appeared unaffected.
Figure 34. Replenishment of MgO-C blends of equimolar C/MgO ratio with (a) as-received MgO and (b) purified C after their 30 min exposure to 1400°C at ~2 kPa total pressure.
Figure 35. Effect of Al$_2$O$_3$ dilution on the conversion rate of MgO (a) and C (b) for MgO-C blends prepared with presintered MgO and C/MgO molar ratios in the range of 1 to 2 ($T_{sp} = 1400^\circ$C and $p_{tot} \approx 2$ kPa).
Similarly, the MgO conversion rate (Figure 35a) did not proportionally increase with increasing C/MgO ratio during stage 1 as it would be expected from the previous observations (see Figure 33a) implying that the Al₂O₃ dilution adversely affected the rate of CTR.

4.3 Discussion

As already elaborated on, the temporal rate of CTR seemed to pass through two reaction stages that were reflected by (i) a fast decrease in the rate of CTR during the first 5-10 min (stage 1) and (ii) a slow decrease in the rate of CTR at reaction times > 5-10 min (stage 2). The investigation primarily focused on elucidating the origin of the fast decrease in the rate in stage 1 that was considered the key controlling factor of the CTR rate.

4.3.1 Discriminating the Rate-Controlling Parameters During Stage 1

During stage 1, the rate of CTR may be controlled by either (i) the release of O₂ by MgO, and/or (ii) the removal of O₂ by C. A control by the removal of the product gases Mg(g) and CO was excluded beforehand, as their partial pressures did not reach their equilibrium values.

The release of O₂ by MgO is represented by reaction (6) that kinetics was considered to be very fast at the investigated temperature and total pressure (1400°C and ~2 kPa) and thus in thermodynamic equilibrium, i.e. the partial pressure of O₂ is constant at the MgO surface. The net O₂ release rate \( \dot{n}_{O_2} \) therefore scales with the total surface area of MgO \( \left( S_{MgO} \right) \) according to

\[
\dot{n}_{O_2} = S_{MgO} J_{O_2},
\]

where \( J_{O_2} \) represents the O₂-diffusion flux at the MgO surface.

The removal of O₂ by C further comprised (i) the transport of O₂ from MgO to C (interparticle mass transport) and (ii) the consumption of O₂ by C via reaction (7). With a constant \( p_{O_2} \) at the MgO surface, the O₂ transport rate scales with the extent of MgO dispersion within the C bulk. With higher MgO dispersion extents, a larger fraction of MgO is in proximity with C, thus the effective O₂ transport distance from MgO to C \( (\delta) \) is reduced. This leads to an increase in \( J_{O_2} \) that may be represented by the diffusion equation, i.e.
\[ J_{O_2} = \left( \frac{D_{O_2}}{\delta} \right) \Delta c_{MgO-C} \]  

\((D_{O_2} = O_2 \text{ diffusion coefficient}; \ \Delta c_{MgO-C} = \text{ concentration difference of } O_2 \text{ between MgO and C}). \) The consumption of \( O_2 \) by C is summarized by the overall kinetics of reaction (7) without distinguishing between intrinsic kinetics and intraparticle heat/mass transport effects. Therefore, for a given C source, the \( O_2 \) consumption rate scales with the amount of C, i.e. C surface \( S_C \).

The controlling parameters of the MgO dissociation pathway comprise thus either \( S_{MgO} \), MgO dispersion, (i.e. \( \delta \)), and/or \( S_C \).

### 4.3.1.1 Effect of MgO Presintering

As shown in Figure 27, the apparent particle size of MgO in a MgO-C blend was significantly higher than of as-received MgO blended with C of equal source and C/MgO ratio (Figure 28). Furthermore, the specific MgO surface area of presintered MgO was by a factor of \(~14\) reduced compared to as-received MgO. Thus, substituting as-received MgO with presintered one using the same C source and C/MgO ratio (i) lowered the MgO dispersion extent, i.e. \( \delta \) and (ii) decreased \( S_{MgO} \). The decreased MgO and C conversion rates that were observed with presintered MgO compared to as-received one (see Figure 29) were thus attributed to either the increased \( \delta \) and/or the decreased \( S_{MgO} \).

These results also imply that the overall kinetics of \( O_2 \) consumption by C (reaction (7)) was not rate-controlling, since the source of C and C/MgO ratio and thus \( S_C \) with respect to MgO was the same in both MgO-C blends. Therefore, the partial pressure of \( O_2 \) at the C-surface was in equilibrium and thus constant.

Furthermore, it is interesting to note that the SSA of presintered MgO was at least two times higher than the SSA of residual MgO recovered from reacted MgO-C blends (see Table 10), even though in both cases the MgO had been subjected to the same temperature (1400°C) for the same amount of time (30 minutes). This observation indicates that either the presence of C (as also suggested by Xie et al.\(^{84}\)) and/or the CTR enhances the kinetics of MgO sintering.
4.3.1.2 Effect of C/MgO Ratio

Increasing the C/MgO ratio increased (a) the total amount of C and therefore $S_c$ with respect to MgO, and (b) the dispersion extent of MgO as indicated by the comparison of the SEM photographs shown in Figure 28 and Figure 30. Therefore, the observed increase in the MgO conversion rate with increasing C/MgO ratio could be attributed to (i) the decrease in the effective O$_2$ transport distance $\delta$ and/or (ii) the increase in $S_c$. However, as discussed before, the overall kinetics of O$_2$ consumption by C (reaction (7)) was not rate-controlling. Therefore, the increase in MgO conversion rate with increasing C/MgO ratio was solely attributed to the increase in MgO dispersion, i.e. decrease in $\delta$.

Furthermore, the observed increase in MgO conversion rate manifests that the overall kinetics of MgO dissociation were not rate-controlling and thus justifies the assumption that reaction (6) was in equilibrium.

4.3.1.3 Effect of MgO and C Replenishment in the Course of CTR

As shown in Figure 34, the replenishment of an MgO-C blend passing through reaction stage 2 with as-received MgO, i.e. $S_{MgO}$, appeared to reactivate stage 1 of the CTR. In contrast, the replenishment of C, i.e. $S_C$, did indeed slightly increase the rate of CTR but did not seem to reactivate stage 1 of the CTR. This results show that the rate of CTR during stage 1 is highly dependent on $S_{MgO}$.

4.3.1.4 Effect MgO-C Blend Dilution with Al$_2$O$_3$

Diluting an MgO-C blend with Al$_2$O$_3$ increases the total blend volume and thus increases the effective O$_2$ transport distance $\delta$, while $S_{MgO}$ and $S_C$ remained unaffected. The decrease in the MgO and C conversion rates during stage 1 (see Figure 35) when diluting an MgO-C blend with Al$_2$O$_3$ was therefore attributed to the increased $\delta$ manifesting the importance of O$_2$ transport from MgO to C in the CTR.
4.3.1.5 The Key Rate-Controlling Parameters

Based on the effects observed by varying $S_{\text{MgO}}$, $\delta$, and/or $S_\text{C}$, it was concluded that the rate controlling parameters of CTR during stage 1 of reaction are both, MgO dispersion and $S_{\text{MgO}}$. On the one hand, an increase in the MgO dispersion extent within the C bulk, i.e. a decrease in $\delta$ increases the rate of CTR because the $O_2$-flux $J_{O_2}$ is increased. On the other hand, the decrease in the rate of CTR during stage 1 was primarily induced by the decrease in $S_{\text{MgO}}$ due to MgO sintering that decreases the net $O_2$ release rate $\dot{n}_{O_2}$.

4.3.2 Speculations About the Rate-Controlling Parameters During Stage 2

The considered key rate-controlling parameter $\delta$ and $S_{\text{MgO}}$ do not conclusively explain two of the observations made during stage 2 of the CTR:

a) Replenishing C (i.e. $S_\text{C}$) during stage 2 (see Figure 34) resulted in an increase in the rate of CTR that remained increased with progressing time in comparison to the reference test. However, neither $\delta$ nor $S_{\text{MgO}}$ were considered to be significantly affected by the C replenishment. Therefore, if only $\delta$ and $S_{\text{MgO}}$ would be controlling the CTR during stage 2, a replenishment of $S_\text{C}$ should not have affected the rate of CTR.

b) By diluting an MgO-C blend prepared with presintered MgO with $\text{Al}_2\text{O}_3$, the C conversion rate decreased during stage 1, but appeared to be unaffected during stage 2 (see Figure 35). Assuming that this observation was not a result of limited experimental accuracy, the unaffected C conversion rate during stage 2 indicates that $\delta$ was no longer a key rate-controlling parameter. Otherwise, the rate of CTR of the diluted MgO-C-$\text{Al}_2\text{O}_3$ blend would have been similarly decreased compared to the undiluted MgO-C blend as in reaction stage 1.

Therefore, it was speculated that the rate of CTR during stage 2 is dominated by MgO reduction with CO (reactions (8) and (9)). For the examined MgO and C sources in the form of powdery blends and experimental conditions (1400°C,
The rate of this pathway appears to be controlled by the consumption of CO\(_2\) by C (reaction (9)). With MgO reduction by CO being the prevailing pathway, the two above discussed observations can be conclusively explained:

a) Replenishing C during stage 2 increases the consumption of CO\(_2\) by C (reaction (9)) due to the increased \(S_C\) and thus the rate of CTR is higher.
b) The C conversion rate during stage 2 remains unaffected when diluting an MgO-C blend with Al\(_2\)O\(_3\), since the rate of CTR is controlled by reaction (9) and not by interparticle CO\(_2\) transport.

### 4.4 Summary and Conclusions

This chapter explores the rate-controlling parameters of the MgO dissociation pathway that prevails the carbothermic reduction of MgO at temperatures in the order of 1375-1450°C and total pressures of 1-2 kPa. For that matter, powdery MgO-C blends were subjected to a temperature of 1400°C and ~2 kPa total pressure for 30-60 min. The gaseous Mg product was combusted with CO\(_2\) before cooldown in order to preclude the proceeding of the reverse overall reaction in the cooling zone. This procedure allowed the acquisition of kinetic data by monitoring the product gas amount and composition without requiring its correction for the confounding effect by the reverse overall reaction. The key rate-controlling parameters were discriminated by evaluating the effect on the rate of CTR when (i) changing the C/MgO molar ratio, (ii) changing the initial MgO surface area and particle size, (iii) diluting MgO-C blends with Al\(_2\)O\(_3\), and (iv) replenishing MgO-C blends with MgO and C, respectively, in the course of reaction.

It was observed that the CTR seemed to pass two reaction stages that were reflected by (i) a fast decrease in the rate of CTR during the first 5-10 min (stage 1) and (ii) a slow decrease in the rate of CTR at reaction times > 5-10 min (stage 2). It was found that during stage 1, both MgO dispersion and the surface area of MgO were key parameter controlling the rate of CTR. While the rate of CTR scaled with MgO dispersion, i.e. effective interparticle O\(_2\) transport distance, the
fast decrease in the rate of CTR in stage 1 was a result of MgO sintering that reduced the MgO surface area and thus the net $O_2$ release rate. During stage 2, the CTR was speculated to be dominated by MgO reduction with CO that rate appeared to be controlled by the consumption of $CO_2$ by C.
As next step in assessing the viability of Mg production via the CTR of MgO for commercial use, a suitable, potentially scalable reactor concept needed to be developed, designed, and tested. However, the so far obtained rates of CTR in this work were rather low and complete MgO conversion was not achieved within the investigated experimental conditions. Thus, prior to developing the reactor concept, a suitable method needed to be found to substantially enhance the rate of CTR as to obtain complete MgO conversion in a reasonable amount of time. As first estimate, a total reaction time of $\leq 30$ minutes was anticipated, since such times have already been reported in literature$^{41,70}$ and were therefore considered feasible to achieve.

### 5.1 Enhancing the Rate of CTR of MgO

The two key parameter regarded to enhance the rate of CTR were MgO dispersion and MgO surface area $S_{\text{MgO}}$. It was considered that for given MgO and C sources the two parameter can be tuned primarily by two means:

- milling the MgO-C reactant mixture.
- increasing the C/MgO ratio of the MgO-C reactant mixture.

A milling of the MgO-C reactant mixture decreases the MgO and C agglomerate and/or particle sizes and thus increases the dispersion of MgO within the C bulk$^{41}$, as well as the surface areas $S_{\text{MgO}}$ and/or $S_{\text{C}}$. An increase in the C/MgO ratio of the MgO-C reactant mixture increases the MgO dispersion extent within the C bulk as shown in the previous chapter. Although the initial surface area of

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MgO $S_{\text{MgO}}$ remains the same, an increase in the MgO dispersion extent potentially reduces the sintering of the MgO particles in the course of the CTR resulting in a slower MgO particle size increase and thus a slower reduction in $S_{\text{MgO}}$.

The beneficial effect of reactant milling on the rate of CTR has already been conclusively demonstrated by Chubukov et al.\textsuperscript{41} and Nusheh et al.\textsuperscript{75} both using pellets instead of powdery blends. Therefore, reactant milling is considered a suitable method for enhancing the rate of CTR. However, as already discussed, this method suffers from the disadvantage that the potentially beneficial effect on the reactor efficiency may be offset by the additional amount of energy required for the milling step.\textsuperscript{41} In contrast, the effect of using C/MgO molar ratios above 4 on the rate of CTR has not been investigated so far and may potentially outperform the already demonstrated benefits of reactant milling. Therefore, the potential benefit of high C/MgO ratios on the rate of CTR was experimentally assessed using MgO-C blends with C/MgO molar ratios ranging from 1 to 35 that were subjected for 30 minutes to 1400 and 1500°C, respectively, at total pressures in the order of ~2 kPa. The details of the experiments (MgO and C sources, apparatus, procedures) are outlined in chapter 4. The experiments were performed without combusting the Mg product and the MgO conversion extents were calculated according to equation (62). The obtained MgO conversion extents are shown in Figure 36 as function of C/MgO molar ratio. At a temperature of 1400°C, an increase of the C/MgO molar ratio above 4 did not substantially increase the MgO conversion extent. It was speculated that this observation may be attributed to (i) an under-proportional increase in MgO dispersion with increasing C/MgO ratio, and/or (ii) the kinetics of MgO dissociation (reaction (6)) that may start to control the rate of CTR. At a temperature of 1500°C, the obtained MgO conversion extents were substantially higher than at 1400°C. It was speculated that the increased MgO conversion resulted not only from the increased kinetics of the MgO dissociation pathway, but also due to a more pronounced contribution of the reduction of MgO with CO (reactions (8) and (9)).

Complete MgO conversion was achieved within 20 minutes using a C/MgO molar ratio of 35. Compared to Chubukov et al.\textsuperscript{41} who achieved reaction times
for complete MgO conversion of ~10 minutes when milling the MgO-C reactant mixture with C/MgO molar ratio of 2, the reaction time of 20 minutes obtained in this work when using a C/MgO molar ratio of 35 is still twice as long. It is important to note, however, that this comparison is lacking as Chubukov et al.\textsuperscript{41} also used (i) different MgO and C sources, (ii) pellets instead of powdery blends, (iii) a five times higher total pressure (10 instead of 2 kPa), and (iv) a 50°C higher temperature (1550 instead of 1500°C). Nevertheless, it was assumed that by using high C/MgO ratios reaction times of 10 minutes and lower may easily be achieved by increasing the C/MgO ratio above 35 and/or increasing temperature $> 1500°C$. Therefore, it was concluded that increasing the C/MgO ratio of the MgO-C reactant mixture may potentially be a more beneficial method to enhance the rate of CTR than reactant milling. Thus, it was decided to base the reactor concept on the method of using high C/MgO ratios for producing Mg.

![Graph](image_url)

Figure 36. MgO conversion extents of powdery MgO-C blends with initial C/MgO molar ratios in the range of 1 to 35 subjected for 30 minutes to ($T_{sp} = 1400$ and 1500°C, respectively, at $p_{tot} \approx 2$ kPa). Note: the details of the experiments (MgO and C sources, apparatus, and procedure) are outlined in chapter 4.
5.2 Development of the Reactor Concept

Using high C/MgO molar ratios for the CTR of MgO, however, results in the following problem: performing the CTR with a mixture of e.g. 1 mol MgO and X moles C results in (X-1) moles of residual C upon complete MgO conversion. Nevertheless, these (X-1) moles of C need to be heated to reaction temperature even though they do not participate in the reaction. Thus, when using a large excess of C, a substantial amount of additional sensible energy is required lowering the maximum possible energy conversion efficiency of the reactor. To illustrate this problem, the maximum possible energy conversion efficiency $\eta_{\text{max}}$, for this example defined as

$$\eta_{\text{max}} = \frac{\Delta h_{1500^\circ C}}{Q_s + \Delta h_{1500^\circ C}} ,$$

was determined as function of initial C/MgO molar ratio. $Q_s$ denotes the amount of sensible energy required to heat a mixture of 1 mole of MgO + X moles of C to 1500°C and was calculated according to equation (50). $\Delta h_{1500^\circ C}$ denotes the enthalpy of the overall reaction as to convert 1 mole of MgO into Mg(g) that value was extracted from the HSC database.35 The maximum possible energy conversion efficiency $\eta_{\text{max}}$ is shown in Figure 37 as function of C/MgO molar ratio (= X). As illustrated by this figure, with increasing C/MgO molar ratio the maximum possible energy conversion substantially decreases and approaches a value of 0.2 at a C/MgO molar ratio of 50.

This problem can be circumvented by using a concept schematically shown in Figure 38. Instead of heating and cooling the excess C, it is stored inside the hot zone of the reactor in form of a bath of C particles. The reactant MgO is fed into this hot C bath and is mixed with it by a mixing system, while a co-feed of C accounts for the consumption of C by the CTR. Downstream the reactor a cooled Mg precipitation zone separates the Mg from the CO. This concept allows a continuous Mg production with high C/MgO molar ratios. The only additional sensible energy required is used for the initial heating of the C bath, which effect on the energy conversion efficiency diminishes with increasing run time of the reactor.
Figure 37. Effect of molar ratio C/MgO on the maximum possible energy conversion efficiency.

Figure 38. Schematic of the suggested reactor concept.
Beside of efficiency-related advantages of this concept, also an increase in the CTR reaction kinetics is suspected: the MgO inside the hot zone is continually mixed with C that may lead to an additional dispersion of MgO agglomerates. Furthermore, loosely sintered MgO particles may be broken by the action of the mixer thus suppressing its sintering.

5.3 Selection of the Particle Feeding System

This section gives a brief overview of common feeding system concepts that were assessed for selecting the optimum feeding system. Two means of material transport were regarded:

- fluidized bed feeders that feed the material via fluidization with a carrier gas.
- mechanical feeder that feed the material by mechanical means.

5.3.1 Fluidized Bed Feeders

In fluidized bed feeders a carrier gas flows upwards through the solid feedstock bed and fluidizes it. Feeding is accomplished by partially entraining the feedstock where the entrained particles are discharged through a tube that brings them to the location of feed. The feed rate is controlled by the carrier gas velocity. Fluidized bed feeders primarily come into application, if at the location of feed a dispersed cloud of particles is desired, or for delivering combustible material to the location of combustion. The feed of fine Geldart C classified powders, however, is challenging without the addition of larger particles serving as fluidization agent, as the fluidization of those powders is very difficult to accomplish.

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* Material in this section has been extracted from K. Blum “Design, Fabrication, and Test of a Powder Feeder”, Master Thesis, ETH Zürich, 2017, directly supervised by A. Coray.
5.3.2 Mechanical Feeders

Mechanical feeders that transport material by mechanical means exist in various forms. The considered concepts are schematically illustrated in Figure 39.

Figure 39. Schematics of considered mechanical feeder concepts: (a) table feeder, (b) belt feeder, (c) vibration feeder, (d) wheel feeder, (e) rotary feeder, and (f) screw feeder.
- **Table feeder:** A horizontally aligned rotating turntable transports the feedstock from a hopper to a scraper that removes the material from the table to the location of feed. The feed rate is controlled by either the rotational speed of the turntable and/or the radial position of the scraper.\(^{109}\)

- **Belt feeder:** A belt transports the feedstock from a hopper to the location of feed. The feed rate is controlled by either the belt speed and/or the opening position of the gate.\(^{109}\)

- **Vibration feeder:** The feedstock is transported from a hopper to the location of feed by a plate or tube that is vibrating\(^{109, 110}\). The feed rate is usually controlled by the vibrational frequency.

- **Wheel feeder:** A rotating wheel collects the feedstock from a hopper in slots or holes in the wheel and transports it to the location of feed.\(^{111}\) Carrier gas sweeping the slots/holes may be used to aid removing the material from the wheel. The feed rate is controlled by the rotational speed of the wheel.

- **Rotary feeder:** The feedstock is collected from the hopper in the void space of a rotor rotating inside a housing that transports the material to the location of feed. The feed rate is controlled by the rotational speed of the rotor.\(^{111-113}\)

- **Screw feeder:** A conveyor screw rotating inside a housing transports the feedstock from a hopper to the point of feed, while the feed rate is controlled by the rotational speed of the screw.\(^{109, 113}\)

### 5.3.3 Conclusion

The optimum feeding system for the given application was selected based on the following criteria:

- **Suitable for feeding powdery and cohesive feedstocks as well as granular ones:** allows to select the feedstock morphology with regard to optimize the Mg production rate.
• **Uniform and controllable feed rate**: enables a steady-state operation of the reactor.

• **Broad feeding rate range between 100-5000 mg/min**: allows to adjust the C/MgO molar ratio of the bath inside the reactor in a wide range.

• **Suited for the operation at total pressures as low as 1 kPa**: allows to operate the reactor at reduced total pressure.

• **Independent operation from total pressure**: allows to operate the reactor with temporally changing total pressure without affecting the feed rate.

• **Can be swept with inert gas**: allows to remove the air from the feeding system that otherwise contaminates the reactor atmosphere during the feed.

Since the criteria request the suitability of the feeding system to feed powdery and cohesive feedstocks, a fluidized bed feeder was considered not applicable. Furthermore, since the feed rate of fluidized bed feeders is controlled over the carrier gas velocity, a temporally changing total pressure may affect the gas velocity and therefore the feed rate. Consequently, a mechanical feeder was chosen. The feed rate of table, belt, and vibration feeders was considered very difficult to control with feed rates as low as 100 mg/min. Furthermore, it was suspected that the gas sweep through the feeder that velocity was considered rather high at reduced total pressures may entrain some of the feedstock on the turntable/belt and flood the feeder. Rotary and wheel feeder were considered difficult to design: to achieve a quasi-continuous feed, high rotational speeds and/or a large number of rotor blades/slots would be required. However, to achieve a feed rate as low as 100 mg/min, the void volume of the rotor blades/slots would need to be rather small that in turn endangers a clogging of the cohesive feedstock. Therefore, a screw feeder was considered to be the optimum particle feeding system for the given application. Theoretically, a feed rate may be achieved that is – independently of rotational speed – continuous.
5.4 Selection of the Mixing System

To choose the optimum mixing system, existing particle mixing concepts were assessed for its suitability in the given application. They can be divided into two groups that differ in the means of particle agitation:

- fluidized bed mixer that mix the feedstock with the bath by fluidization.
- mechanical mixer that mix the feedstock with the bath by mechanical means.

5.4.1 Fluidized Bed Mixer

A particle bed is fluidized, when the velocity of a carrier gas stream penetrating the bed in upward direction is high enough, such that the drag force induced by the gas on the particles counterbalances their gravitational force. Fluidized beds benefit from a rapid mixing of the particulate matter and thus from high heat and mass transfer rates between the carrier gas and the particles. However, as already discussed, the fluidization of fine, Geldart C classified particles is difficult to accomplish.

5.4.2 Mechanical Mixer

Current literature distinguishes between three different mixing mechanisms that may prevail in mechanical mixers.

- **Convection:** groups of particles, i.e. clumps are displaced with respect to each other by the action of the mixer. This mechanism increases mainly the macroscopic homogeneity of a particle bulk, i.e. the mixing degree between different clumps of particles.
- **Diffusion:** individual particles are rearranged within the particle bulk, e.g. by a distribution of particles over a surface induced by the mixer action. This mechanism increases mainly the microscopic homogeneity of a particle bulk as it promotes the mixing on the length scale of the particles. It is not to be confused with the molecular diffusion in a fluid.
• **Shear**: particle groups that move against each other or against other surfaces are subjected to shear strain. As a result, the particle groups deform and the area of contact between the borders increase, which is considered an effective mechanism to break up agglomerates.

The considered mixer concepts are illustrated in Figure 40 with two of them having a horizontal axis of rotation and two of them have a vertical one.

- **Rotating drum mixer**: In a rotating drum mixer the shell rotates and the material tumbles around inside. Depending on the filling degree and on the rotational speed of the drum, six different flow patterns can be observed that range from a slipping of the particle bulk along the drum wall at low rotational speeds up to a centrifuging of the particles at the drum wall at high rotational speeds.\(^{116-118}\) The prevailing mixing mechanisms in this mixer are considered to be shear and diffusion.\(^{115}\) The mixing of the particles in radial direction is considered high, while the mixing in axial direction is considered significantly slower.\(^{114, 117, 119}\)

- **Paddle, ploughshare, or ribbon mixer**: These mixer concepts use a horizontally rotating agitator comprising a shaft with attached paddles, ploughshares or ribbons to mix the particle bulk.\(^{118, 120}\) The prevailing mixing mechanisms are considered to be convection and shear.\(^{118}\) The mixing in axial direction is considered slower than in radial direction, yet faster than the axial mixing in a rotating drum.\(^{119}\)

- **Draught tube screw mixer**: In draught tube screw mixers a vertically aligned conveyor screw collects material from the vessel bottom and transports it to the surface of the particle bulk. The material is then discharged from the conveyor screw and recirculated back to the vessel bottom.\(^{114, 120, 121}\) The recirculation time of a particle is considered to be a function of its radial position in the annular bulk provoking axial mixing,\(^{114}\) i.e. convective mixing. A mixing in radial direction proceeds primarily via a dispersion of the discharged particles onto the bulk surface, i.e. diffusion acts here as the prevailing mixing mechanism.\(^{114}\)

- **Vertical impeller/paddle mixer**: A vertically aligned impeller\(^{109, 114, 115}\) or a shaft with inclined paddles\(^{122, 123}\) transports the particles along the
vessel wall to the bulk surface that then flow down in the center of the vessel. The prevailing mixing mechanisms are convection\textsuperscript{115} and shear.\textsuperscript{122} This mixer concept is considered to be very effective in the breaking of agglomerates,\textsuperscript{115, 121} however, requires high speeds (e.g. in the order of 1500 rpm for a one liter vessel\textsuperscript{122}) and power consumption.\textsuperscript{121}

Figure 40. Schematics of considered mechanical mixer concepts: (a) rotating drum mixer, (b) paddle/ploughshare/ribbon mixer, (c) draught tube screw mixer, (d) vertical impeller/paddle mixer
5.4.3 Conclusion

The mixing concept was chosen with regard to construct a prototype that ensures the highest chance for successful operation. It is empathized that other mixing concepts may be suitable as well. The optimum mixer concept was selected based on following criteria:

- *Fast mixing of the feedstock with the C bath (~1 min):* allows to establish the desired particle bulk homogeneity with the desired C/MgO molar ratio before the MgO surface that is required to achieve high rates of the CTR is significantly reduced.

- *Suitable for mixing powdery material as well as granular one:* allows to select the morphology of the C with regard to optimize Mg production.

- *Suitable for the operation at temperatures of up to 1600°C and total pressures as low as 1 kPa:* allows to evaluate the CTR under these conditions.

- *Manufacturing as simple as possible:* increases the chance of success.

- *Removal of the product gas without the entrainment of solid material into the outlet:* A significant loss of the solid reactants lowers the energy conversion efficiency of the process, as the entrained material was heated without undergoing reaction.

- *Preferably shear as prevailing mechanism:* enhances the dispersion of cohesive particulate (i.e. MgO) in the bulk.

- *Preferably high heat transfer through the particle bulk:* decreases a cooling of the bath due to the energy consumed by the endothermic CTR reaction.

- *Preferably high filling fraction of the vessel:* improves the volume-based reaction rate of the CTR that helps to keep the reactor small.

The advantages and disadvantages of each considered mixer concept with regard to the listed guidelines are shown in Table 11.
<table>
<thead>
<tr>
<th>Mixer</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidized Bed</td>
<td>- rapid mixing</td>
<td>- Difficult to prevent particle entrainment due to the constantly changing particle sizes by (i) MgO sintering, (ii) MgO and C consumption by the CTR.</td>
</tr>
<tr>
<td></td>
<td>- high heat transfer rates</td>
<td>- Difficult to fluidize fine powders (Geldart C classified ones).</td>
</tr>
<tr>
<td></td>
<td>- simple construction (no moving parts required)</td>
<td>- Poor axial mixing compared to the radial one.</td>
</tr>
<tr>
<td>Rotating Drum</td>
<td>- Shear as prevailing mechanism.</td>
<td>- Difficult to construct the rotational joints as along the rotational axis an inlet for solids and sweep gas on one side and a gas outlet and a Mg precipitation zone on the other side is required.</td>
</tr>
<tr>
<td></td>
<td>- May be upgraded by a grinding medium (milling balls) that aid agglomerate dispersion.</td>
<td>- Difficult to construct a robust, heat-resistant agitator</td>
</tr>
<tr>
<td>Paddle/Ploughshare/Ribbon</td>
<td>- Shear as prevailing mechanism.</td>
<td>- Shear not a prevailing mechanism.</td>
</tr>
<tr>
<td></td>
<td>- Improved axial mixing compared to the rotating drum</td>
<td>- Potentially poor gas sweep/removal from the bulk.</td>
</tr>
<tr>
<td></td>
<td>- High filling fraction possible.</td>
<td>- Potentially poor heat transfer in radial direction</td>
</tr>
<tr>
<td>Draught tube screw</td>
<td>- Good axial mixing due to the continuous enrichment of the vertically rotating C bath with feedstock.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Simpler construction of the screw compared to the agitator of paddle, ploughshare, or ribbon mixers</td>
<td></td>
</tr>
<tr>
<td>Vertical impeller/paddle</td>
<td>- Very effective to break agglomerates</td>
<td>- Difficult to construct robust, heat-resistant impeller/paddles that rotate at high speeds.</td>
</tr>
<tr>
<td></td>
<td>- High filling fraction possible.</td>
<td>- High energy input compared to other concepts.</td>
</tr>
</tbody>
</table>
Fluidized bed mixers were considered less suitable for the given application due to the expected difficulties in the prevention of particle entrainment and in achieving a homogeneous fluidization. Amongst the mechanical mixers, the draught tube screw mixer was decided to be the best suitable one. The pivotal advantages were (i) a faster mixing in comparison to the rotational drum mixer, and (ii) a potentially simpler and more robust construction of the conveyor screw in comparison to the agitator in paddle, ploughshare, ribbon, or impeller mixers.
6 Lab-Scale Reactor Design

To evaluate the CTR of MgO with the suggested reactor concept, a lab-scale prototype was developed and constructed that is schematically shown in Figure 41. Photographs of some of the reactor components are shown in Appendix F.

Figure 41. Schematic of the developed prototype comprising the components particle feeding system, reactor head, bath recirculation system, Mg precipitation zone and reactor bottom, and furnace chamber.

\(^a\) Material in this chapter will be published as: A. Coray, K. Blum, S. Kull, and Z.R. Jovanovic “A Novel Reactor Concept for the Production of Mg Metal via Carbothermic Reduction of Magnesium Oxide”, manuscript in preparation.
The key components of this prototype are summarized as follows:

- the particle feeding system that allows a continuing feed of material into the bath recirculation system.
- the reactor head comprising the screw drive chain and inlets for sweep gas and solid feed.
- the bath recirculation system that mixes the feed with the C bath.
- the Mg precipitation zone that collects the Mg product, and the reactor bottom that contains a sweep gas inlet for the cooling zone and the gas outlet.
- the heat source in form of e.g. an electrical furnace, which encases either the bath recirculation system alone or, in case produced Mg is being combusted by CO\textsubscript{2} in a separate combustion zone as to acquire kinetic data (see section 4.1.2), both, the recirculation system and part of the Mg precipitation zone (as illustrated in Figure 41).

### 6.1 The Particle Feeding System\(^a\)

The developed particle feeding system is schematically shown in Figure 42. The feed screw (aluminum, dimensions shown in Table 12) was mounted by two NBR-sealed groove ball bearings (Schaeffler Schweiz, 2HRS, \(32\) mm) inside a round housing (steel 1.4301, \(60\) mm, \(l = 240\) mm). At the drive shaft, gas tightness was ensured by two O-rings (FKM) that were placed at the inner and outer ring of the ball bearing. At the bearing of the screw tip, gas tightness was ensured by an O-ring (FKM) placed inside a groove in the housing and pressed together by a lid (steel 1.4301, \(60\) mm) that was screwed to the housing. A hopper (steel 1.4301) containing the feedstock was screwed to the housing that connection was sealed by a rubber cord placed inside a groove. A rectangular hopper outlet was chosen as it has been suggested in literature\(^{124, 125}\) that the hopper half angles required to prevent material arching at the outlet are by 10-12°\(^{125}\) smaller than in a circular hopper outlet. The chosen outlet size of 30 × 90

\(^a\) Material in this section has been extracted from K. Blum “Design, Fabrication, and Test of a Powder Feeder”, Master Thesis, ETH Zürich, 2017, directly supervised by A. Coray.
mm was considered sufficiently large to avoid material arching, while the optimum hopper half angles $\theta_{H,\alpha}$ and $\theta_{H,\beta}$ were determined during testing of the feeding system. The top of the hopper was closed by a lid (steel 1.4301) and sealed by a rubber cord placed inside a groove in the lid. Two gas inlets allowed a sweeping of the feeder with Ar. Inlet #1 was used to remove air from the hopper that otherwise may have contaminated the reaction zone during feeding. Inlet #2 was used to entrain the feed and transport it pneumatically into the reaction zone.

Figure 42. Schematic of the particle feeding system.
6.1.1 Design Aspects of the Feed Screw

As illustrated in Figure 43, the design of the feed screw comprised the selection of following parameters:

- the shaft radius \( R_c \)
- the outer screw radius \( R_o \)
- the pitch length \( p \)
- the flight shape
- the outer flight thickness \( t_{flight} \)

![Figure 43. Design parameter of the feed screw.](image)

The chosen parameters of the feed screw are listed in Table 12 that selection is discussed in the following section.

*Screw Radius*

The diameter of the feed screw was chosen to be 25 mm, i.e. \( R_o = 12.5 \text{ mm} \), which was 5 mm smaller than the hopper outlet width of 30 mm. It was assumed that the resulting gap between screw and the housing wall allowed a better distribution of feedstock over the screw surface.
Table 12. Selected design parameters for the feed screw.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_o$</td>
<td>12.5 mm</td>
</tr>
<tr>
<td>$R_c$</td>
<td>10.5 mm</td>
</tr>
<tr>
<td>$p$</td>
<td>8 mm</td>
</tr>
<tr>
<td>flight shape</td>
<td>elliptical</td>
</tr>
<tr>
<td>$t_{flight}$ at $R_o$</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

**Flight Shape**

The flight shape was chosen based on the work of Dalenjan et al.\(^{126}\), who investigated the performance of different flight shapes for feeding fine ZnO powders. From screws with either rectangular or trapezoidal shape, or circular shaped screws with either thick or thin flights, the circular shaped screw with thin flights performed the best in terms of stable feed rates and minimal material clogging between the flights. In this work, an elliptical flight shape (see Figure 42) instead of a circular one was used for further reducing the likelihood of the material to clog between the flights.

**Shaft Radius, Pitch, and Outer Flight Thickness**

The outer flight thickness $t_{flight}$ was chosen to be as thin as possible, i.e. 1 mm, to reduce the likelihood of particle jamming between the flight surface and the housing. The optimum pitch $p$ and the shaft radius $R_c$ were determined under consideration of following guidelines:

- For having freedom in operating the reactor, the range of achievable feed rate should be as high as possible, while the minimum rate being the critical parameter in feed screw design. As minimum, a feed rate in the order of $Q_m = 100 \text{ mg/min} \left( \frac{n^{0}_{\text{MgO}}}{\text{min}} \approx 2 \text{ mmol/min} \right)$ was chosen to be sufficient.
- The minimum screw speed \( v_{\text{feeder}} \) should be as high as possible to reduce a potential fluctuation in the feed rate.
- The ellipsoidal flight shape should be as flat as possible in order to reduce the likelihood of material clogging, i.e. the flight-distance-to-depth ratio \( \left( \frac{p-t_{\text{flight}}}{(R_o-R_c)} \right) \) should be as high as possible.
- The flight depth \( (R_o-R_c) \) should be as deep as possible, as it was assumed that deeper flight depths promote an efficient filling of the flight voids with feedstock.

Thus, in order to find the optimum pitch \( p \) and the shaft radius \( R_c \), the two values were varied within the range of 2-10 and 7.5-12 mm, respectively, and the flight-distance-to-depth ratio and flight depth were calculated as function of the screw speed \( v_{\text{feeder}} \) and constant \( Q_m = 100 \text{ mg/min} \). The mass throughput \( Q_m \) was calculated according to the conveyor model reported by Yu and Arnold\(^{127} \) (see Appendix E). Thereby, it was assumed that the screw was completely filled with material, i.e. the fullness efficiency \( \eta_f \) equaled unity. This assumption was based on the work of Yu and Arnold\(^{127} \) who suggested that at low screw speeds \( \eta_f \approx 1 \).

The calculated flight depth \( (R_o-R_c) \) and flight-distance-to-depth ratio \( \left( \frac{p-t_{\text{flight}}}{(R_o-R_c)} \right) \) are shown in Figure 44 as function of pitch \( p \) for \( v_{\text{feeder}} \) ranging from 0.5 – 2 rpm. Based on the guidelines shown above, chosen values were \( R_c = 10.5 \text{ mm} \) and \( p = 8 \text{ mm} \). With those values, the flight depth was \( \approx 2 \text{ mm} \) and flight-distance-to-depth ratio equaled 3.5. Because \( R_c \) and \( p \) were rounded to full numbers to ease manufacturing, the minimum achievable feed rate \( Q_m \) with \( v_{\text{feeder}} = 0.5 \text{ rpm} \) was 120 mg/min that, however, was considered sufficient.
Figure 44. Flight depth (a) and flight-distance-to-depth ratio (b) as function of pitch for screw speeds ranging from 0.5 - 2 rpm with constant $Q_m = 100$ mg/min.
6.2 The Bath Recirculation System

Figure 45 shows a schematic of the bath recirculation system. The C bath (not shown) is contained inside the reactor tube (Al$_2$O$_3$, φ70x5 mm). The recirculator is located in the center of said tube and comprised the recirculation screw (graphite, dimensions shown in Table 13) that rotates inside a draught tube (Al$_2$O$_3$, φ30x4 mm). The fraction of the screw that is not encased by the draught tube (51 mm) plus the 9 mm gap between screw tip and the bath floor is referred to as the choke section (60 mm) and allows the collection of bath material. The conveyed material is discharged through three discharge windows (15x20 mm) that were cut into the draught tube at the top of the bath container. The recirculation screw is connected to a hollow shaft (Al$_2$O$_3$, φ14x2 mm) by two transverse bolts (Al$_2$O$_3$, φ4 mm) at right angles to each other. The bolts are held in place by a clutch made of graphite (R4550, φ23 mm, l=59 mm). The tip of the clutch is conically shaped (θ$_h$ = 30°) to guide conveyed material out of the discharge windows. The feed enters the bath container through a feed tube (Al$_2$O$_3$, φ14x2 mm) that is supported by the container lid (graphite R4550, φ59x14 mm, l= 20 mm). This lid is held in place by three transverse bolts (graphite, φ4 mm) reaching into boreholes (φ4 mm) drilled into the draught tube. Two thermocouples (Conax Technologies, Type C, Al$_2$O$_3$ shielded, φ3.2 mm) measure the temperature at two latitudes (85 and 185 mm distance from bath floor). The bottom part of the bath is of conical shape (graphite R4550, φ58 mm, cone half angle θ$_h$ to be determined during experimentation) in order to guide the bath material into the screw choke section and is held in place by a support tube (Al$_2$O$_3$, φ58x4 mm). A graphite felt ring (Sigratherm® GFA5), placed between the bottom part and support tube prevents a loss of particulate matter through the gap between bottom part and reactor tube. Two configurations shown in Figure 46 allow the removal of sweep and product gases from the recirculation system.

a) A removal through boreholes (7x φ4 mm) in the bath floor. A graphite felt (Sigratherm® GFA5) covering the boreholes serves as particle filter. This configuration is further referred to as configuration A.
b) A removal from above the bath through a gas bypass that opens below the bath bottom. The boreholes in the bath bottom are enclosed in this configuration by a graphite disc that is gas tightened using Al₂O₃ refractory paint (Alfa Aesar, aerosol spray). This configuration is further referred to as configuration B.

Both configurations can be used at the same time by having the gas bypass implemented and the boreholes in the bath floor left open.
6.2.1 Design Aspects of the Recirculation Screw

As illustrated in Figure 43, the design of the feed screw comprised the selection of following parameters:

- the outer screw diameter $D_o$
- the shaft diameter $D_c$
- the pitch length $p$
- the flight thickness $t_{\text{flight}}$
- the screw clearance $C_s$
- the choke length to pitch ratio $l_c/p$

Figure 47. Design parameter of a conveyor screw. $D_o =$ outer screw diameter; $D_c =$ shaft diameter; $p =$ pitch; $t_{\text{flight}} =$ flight thickness; $C_s =$ screw clearance; $l_c/p =$ choke length to pitch ratio.

The selected dimensions of the recirculation screw are shown in Table 13.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_o$</td>
<td>24 mm</td>
</tr>
<tr>
<td>$D_c$</td>
<td>11 mm</td>
</tr>
<tr>
<td>$p$</td>
<td>17 mm</td>
</tr>
<tr>
<td>$t_{\text{flight}}$</td>
<td>2.5 mm</td>
</tr>
<tr>
<td>$C_s$</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>$l_c/p$</td>
<td>3</td>
</tr>
</tbody>
</table>
Their selection was guided by numerous restrictions and guidelines inferred from different sources. Literature served with following guidelines:

- The shaft diameter $D_c$ should be larger than a third of the screw diameter $D_o$ in order to avoid a powder slip back near the shaft where the screw helix angle, i.e. inclination of the screw flight is high, i.e. $D_c \geq D_o/3$.¹²⁸
- The choke length $l_c$ of the screw is preferably at least 3 pitches long in order to increase the fullness efficiency, i.e. $l_c/p \geq 3$.¹²⁹
- For the pitch to screw diameter ratio $(p/D_o)$ different guidelines were found:
  1. Some manufactures use a ratio of 0.5-0.67 for inclined screw conveyors.¹³⁰,¹³¹
  2. According to Rakitsch¹³² usual values are in the range of 0.6 to 1. Higher values result in lower fullness efficiencies $\eta_F$.
  3. According to Robert et al.¹²⁹ the highest conveyor rate at given screw speed and $\eta_F$ is reached at a value of 1.2.

To enable the manufacturing of the screw, the manufacturer¹³³ required that

- The screw shaft diameter $D_c$ has to be at least 11 mm thick.
- The flight thickness $t_{\text{flight}}$ has to be at least 2-2.5 mm.

Furthermore, following guidelines applied:

- The screw diameter $D_o$ should be as small as possible to maximize the radial thickness of the annular C bath ($t_{\text{bath}}$). It was assumed that with a higher $t_{\text{bath}}$, the likelihood of the bath to arch between draught tube and reactor wall is lower.
- The screw diameter $D_o$ should be large enough to allow a recirculation of the C bath within 1 minute to ensure a proper dispersion of the feedstock, i.e. the recirculation frequency $f_r$ should be $\geq 1$.
- Low screw speeds ($\nu_{\text{recirculator}}$) are preferred as to reduce the mechanical loads on the recirculator.
Shaft Diameter, Flight thickness, Screw Clearance, and Choke Length

The shaft diameter $D_c$ and the flight thickness $t_{flight}$ were chosen to match the requirements given by the manufacturer, i.e. $D_c = 11$ mm and $t_{flight} = 2.5$ mm. The screw clearance $C_s$, i.e. the gap between screw flight and draught tube was selected to be 0.5 mm, while the choke length to pitch ratio $l_c/p$ was selected to be equal to 3 as guided by literature.

Pitch-to-Diameter Ratio

To find the optimal pitch-to-diameter ratio $p/D_o$, its effect on the mass throughput of the recirculator $Q_m$ was evaluated as function of rotational speed $v_{recirculator}$. The mass throughput $Q_m$ was determined with the model given by Roberts$^{134}$ (see Appendix E). Figure 48 shows $Q_m$ as function of rotational speed for $p/D_o$ ranging from 0.5 to 1.2 with an exemplarily screw diameter $D_o = 20$ mm. For the fullness efficiency $\eta_F$, a constant and conservative value of 0.25 was assumed.

Figure 48. Mass throughput $Q_m$ of the recirculation screw as function of rotational speed for $p/D_o$ ranging from 0.5 to 1.2.
As shown by this Figure, $Q_m$ increases with increasing $p/D_0$ with the optimum being reached at a value of 1.2, as suggested by Roberts et al.\textsuperscript{129} also. However, it was suspected that lower $p/D_0$ ratios may promote a higher fullness efficiency. Therefore, an intermediate value of $p/D_0 = 0.7$ was selected.

\section*{Outer Screw Diameter}

The outer screw diameter $D_o$ was optimized such that a recirculation frequency $f_r$ of 1/min was achieved with (i) a radial C bath thickness $t_{bath}$ as large as possible, (ii) a C bath amount $m_{bath}$ as large as possible, and (iii) $v_{recirculator}$ as low as possible. Inferred from the schematic shown in Figure 49, $t_{bath}$ is calculated according to

$$t_{bath} = 0.5D_{bath} - t_{dtube} - 0.5D_o$$ \hfill (68)

with $D_{bath}$ being the diameter of the C bath, i.e. the inner diameter of the reactor tube and $t_{dtube}$ the draught tube thickness that was chosen to be 2.5 mm.

![Figure 49. Cross-section of the reactor at around middle height of the recirculation system.](image)

The recirculation frequency $f_r$ was defined as
\[ f_r = \frac{Q_m(D_o)}{m_{bath}(D_o)} \]  

with the mass throughput \( Q_m \) determined by the model of Roberts \(^{134} \) (see Appendix E) assuming \( \eta_F = 0.25 \). The C bath amount \( m_{bath} \) was calculated according to

\[ m_{bath} = \rho_b h_{bath} \pi \left( \left( \frac{D_{bath}}{2} \right)^2 - \left( \frac{D_o}{2} + C_s + t_{dube} \right)^2 \right) \]  

with \( h_{bath} \) as the height of the C bath. The diameter of the C bath \( D_{bath} \) and the bath height \( h_{bath} \) were inferred from the restricting dimensions of the electrical furnace (Carbolite, STF 450) that was used for the experiments: into this furnace a tube with outer diameter of 70 mm could be mounted that was heated for a length of 450 mm. With a chosen reactor tube thickness of 5 mm, \( D_{bath} \) equals 60 mm. The total height of the bath container was chosen to be 250 mm, approximately the upper half of the heated length. The lower half of the heated length was reserved for the potential equipment of the reactor with an Mg combustion zone (see section 4.1.2). For determining the optimum \( D_o \), the bath height \( h_{bath} \) was chosen to be 120 mm, i.e. approximately the half of the total bath container height (250 mm), as it also needed to be considered that some space inside the container was required for the implementation of the cone-shaped bottom part that geometry was not yet determined, two thermocouples, and potentially the gas bypass.

Figure 50a shows the C bath amount \( m_{bath} \) and the annular bath thickness \( t_{bath} \) as function of the inner draught tube diameter \( (D_o + 2C_s) \), while Figure 50b shows the required \( v_{recirculator} \) to match \( f_r = 1 \) at given \( (D_o + 2C_s) \). The screw diameter \( D_o \) was chosen to be 24 mm (+ 1 mm clearance gap \( C_s \)). At this value, \( t_{bath} \) was still 15 mm, \( m_{bath} \) as high as 56 g, and the required \( v_{recirculator} \) to reach \( f_r = 1 \) was only 535 rpm.
Figure 50. Calculated C bath size $m_{\text{bath}}$ and bath thickness $t_{\text{bath}}$ (a), and required $v_{\text{recirculator}}$ to match $f_r = 1$ (b) as function of $D_o + 2C_s$. 
6.3 The Reactor Head

Figure 51 shows a schematic of the reactor head. The hollow shaft driving the recirculation screw is connected by two transverse blind screws (M4) to the steel drive shaft. The drive chain is supported by an angular and a groove ball bearing (SKF, NBR-sealed, $\varnothing 32$ mm), respectively, and gas tightened by two shaft seals (SKF, ecorubber). The seals are greased by a temperature-resistant grease (Osixo 600 G) that was filled into the chamber between the shaft seals. The draught tube is attached to the reactor head by three screws (M5) and held stiff by three blind screws (M4) that could be adjusted to allow a centering of the draught tube. The two thermocouples are connected at the reactor lid by packing glands (Conax Technologies). A skewed steel tube (steel 1.4301, $\varnothing 12\times2$ mm) with a funnel shaped opening connects the feeding system with the $\text{Al}_2\text{O}_3$ feed tube. The reactor tube is connected to the lid by a connector (steel 1.4301). O-rings (FKM) seal the contacts of the connector with the reactor tube and with the lid. Two gas inlets (#3 and #4) mounted into the connector allow the insertion of sweep gas and the mounting of a pressure sensor and an overpressure relief valve, respectively.

6.4 The Mg Precipitation Zone and the Reactor Bottom

Figure 52 shows a schematic of the Mg precipitation zone and the reactor bottom. The sweep and product gases originating from the recirculation system are guided through the precipitation tube ($((\text{Al}_2\text{O}_3, \varnothing 33\times2.5$ mm, $l = 448$ mm) and leave the reactor at the outlet. The gaseous Mg product is condensed and deposited inside the precipitation tube along the axial thermocline brought in by the cooling of the reactor bottom by the surrounding air via natural convection. At the precipitation tube inlet, the product gas is diluted by either the Mg combustion gas CO$_2$ (see section 4.1.2) or Ar as inert substituent that is introduced through inlet #5. A dilution with CO$_2$ would additionally require a coating of the graphite bottom part of the recirculation system with $\text{Al}_2\text{O}_3$ refractory paint (Alfa Aesar, aerosol spray) as to prevent the reduction of CO$_2$ with the graphite bottom via reaction (9).
Figure 51. The reactor head comprising the screw drive chain and inlets for gases and the solid feed.
Figure 52. The Mg precipitation zone and the reactor bottom.
7 Experimental Testing of the Lab-Scale Reactor\textsuperscript{a,b,c}

To experimentally evaluate the designed reactor, a prototype was built and tested with two types of C reactant: (i) powdery C and (ii) granular C. With each C reactant, following procedure was applied for testing the prototype:

1. Test, optimize and calibrate the feeding system at ambient and reduced total pressure.
2. Test and optimize the recirculation system at (i) ambient temperature (cold-flow tests) and ambient total pressure, (ii) ambient temperature and reduced total pressure, and (iii) elevated temperatures (hot tests) and reduced total pressure.
3. Evaluate the Mg production performance of the reactor.

7.1 Materials

The used as-received solid materials are shown in Table 14 where the listed properties and impurity fractions were either given by the manufacturer or determined according to the methods outlined in Appendix A.

7.1.1 Preparation of the Reactant C

As listed in Table 15, the C was used in three different purification degrees in the different steps the reactor tests: as-received, free of moisture (dried), and free of moisture and volatile matter (purified). Dried C was prepared by heating the as-

\textsuperscript{a} Material in this chapter will be published as: A. Coray, K. Blum, S. Kull, and Z.R. Jovanovic “A Novel Reactor Concept for the Production of Mg Metal via Carbothermic Reduction of Magnesium Oxide”, \textit{manuscript in preparation}.

\textsuperscript{b} Material in this section has been extracted from K. Blum “Design, Fabrication, and Test of a Powder Feeder”, Master Thesis, ETH Zürich, 2017, directly supervised by A. Coray.

\textsuperscript{c} Material in this section has been extracted from S. Kull “Construction and Test of a Novel Reactor to Produce Mg Metal via Carbothermic Reduction of MgO”, Master Thesis, ETH Zürich, 2018, directly supervised by A. Coray.
received material in air to 110°C in a desiccation furnace (Binder APT Line Series FD 53) and left at constant temperature for two hours. Purified C was prepared according to the procedure discussed in section 7.2.3.1. Both dried and purified C were stored in plastic flasks purged with Ar (Messer 4.6) to prevent a remoistening of the C during storage.

Table 14. Properties of the as-received solid materials.

<table>
<thead>
<tr>
<th>material</th>
<th>source</th>
<th>SSA</th>
<th>$\bar{d}$</th>
<th>impurities</th>
<th>type</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>powdery MgO</td>
<td>Sigma-Aldrich, # 342793</td>
<td>(-)</td>
<td>(-)</td>
<td>H$_2$O</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$O</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>powdery C</td>
<td>Fluka Analytical, # C5510</td>
<td>793.5±35</td>
<td>43.5</td>
<td>volatiles</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ash</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>powdery Al$_2$O$_3$</td>
<td>Fluka Analytical, # 06285</td>
<td>(-)</td>
<td>(-)</td>
<td>H$_2$O + CO$_2$</td>
<td>&lt; 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$O</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>granular C</td>
<td>Chemviron Carbon, Aquacarb 607C 14x40</td>
<td>1100$^b$</td>
<td>868.6</td>
<td>volatiles</td>
<td>~2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ash</td>
<td>&lt; 1$^b$</td>
<td></td>
</tr>
<tr>
<td>rod-shaped C</td>
<td>Chemviron AP3-60</td>
<td>(-)</td>
<td>Ø3000$^b$</td>
<td>(-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rod-shaped C</td>
<td>Norit RB2 H2</td>
<td>(-)</td>
<td>Ø1000$^b$</td>
<td>(-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>granular C</td>
<td>Envirocarb 207C</td>
<td>(-)</td>
<td>3400$^b$</td>
<td>(-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>granular C</td>
<td>Chemviron type 33</td>
<td>(-)</td>
<td>1120</td>
<td>(-)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ assumed to be similar as in other batches (see Table 1)

$^b$ as reported by the manufacturer
The contact with ambient air during handling of the dried/purified C was not avoidable. A potential moistening of the C during handling, however, was considered not significant. When using granular C as feedstock component, it was slightly milled for 2 min in a mortar before usage in order to prevent a potential particle jamming between the feed screw and the feeder housing. The volume-based particle size distribution that typically resulted from the milling is exemplarily illustrated Figure 53 in comparison to the as-received C. The mean particle size $\bar{d}$ of the milled granulate was usually in the order of $\sim$500 µm.

Table 15. Purification degree of C used in the different steps of the reactor tests.

<table>
<thead>
<tr>
<th>usage</th>
<th>feedstock component</th>
<th>bath material</th>
</tr>
</thead>
<tbody>
<tr>
<td>test sequence</td>
<td>optimization</td>
<td>calibration/ hot tests</td>
</tr>
<tr>
<td>powders as-received/ dried</td>
<td>purified</td>
<td>as-received/ dried</td>
</tr>
<tr>
<td>granules (-)</td>
<td>purified</td>
<td>as-received/ dried</td>
</tr>
</tbody>
</table>

Figure 53. Volume-based particle size distribution of milled C granulate in comparison to the as-received one.
7.1.2 Preparation of the MgO-C Feedstocks

The MgO-C feedstocks were prepared by stirring $m_1^0$ grams of as-received MgO powder and $m_2^0$ grams of dried or purified C with a spatula in a beaker and occasionally breaking agglomerates until the blends appeared homogeneous. The effective amounts of MgO and C in the feedstock ($m_{\text{MgO}}^0$ and $m_{\text{C}}^0$) were calculated according to equation (20).

7.2 Experimental Setups and Procedures

7.2.1 Feeding System Tests and Calibration

The feeding system was tested and calibrated using the experimental setup schematically shown in Figure 54. The feed screw was driven by an electric motor (micro motors, E192 series). Fed material was collected in a steel pipe (KF25, $l = 100 \text{ mm}$) with a paper filter bottom (Whatman GF/F glass microfibre filter) that was connected to the feeder outlet. For the tests at reduced total pressure, a vacuum pump (Adixen ACP15), protected by a particle filter was connected to the feedstock collector. Ar sweep gas was supplied through inlets #1 and #2 that were interconnected to prevent a pressure difference between the hopper and the feeder outlet. Flow rate of Ar was controlled by a calibrated mass flow controller (Bronkhorst EL-flow Select series), while total pressure was monitored by an absolute pressure sensor (Kistler Instrumente AG, Type 4045A1) that was mounted next to inlet #2. For tests at ambient pressure, the Ar supply tubing, the pressure sensor, and the vacuum pump were disconnected from the system.

Furthermore, the feeding system could be equipped with test hoppers for studying the effect of hopper geometry on the feeding performance. These test hoppers of freely selectable form consisted of bended steel sheets that were held together and mounted on the feeder with adhesive tape.
7.2.1.1 Test Procedure

First, the hopper was filled with feedstock with amounts ranging from 20-50 g. Then, the feed screw was run for 5 min with \( v_{feeder} = 5 \) rpm in order to fill the screw with material and to stabilize the feed rate. The collected material was then re-charged into the hopper that was enclosed afterwards. When testing under reduced total pressure \( (p_{red}) \), the vacuum pump was started and the pressure in the system was reduced within 2 minutes to a total pressure in the range of 1-2 kPa and the Ar flow rate (Messer 4.6) was set to 0-0.1 \( \text{LN}/\text{min} \). When testing at \( p_{amb} \), no Ar flow was applied. Then, the feed screw was turned on with \( v_{feeder} \) ranging from 1-60 rpm. After a feed interval of 5-10 minutes, the feeder was slowly re-pressurized within 2 minutes and the fed material was collected and weighted. Up to 3-6 feed intervals were conducted per hopper charge corresponding to a feed time of 15-30 minutes in total.
7.2.2 Cold Flow Tests of the Bath Recirculation System

Figure 55 illustrates schematics of the experimental setups for the cold flow tests of the bath recirculation system. The recirculation performance of powdery C material at $p_{\text{amb}}$ was examined with the setup shown in Figure 55a. The bath container ($\varnothing 70 \times 5 \text{ mm}$, $l = 250 \text{ mm}$) was built of Plexiglas to allow a visual inspection of the bath flow. Optionally, a tilted Plexiglas tube could be inserted through an opening in the container enclosing one of the three discharge windows and collecting the bath material being discharged through it (see Figure 114). The recirculator comprised (i) a metallic screw instead of the graphite one (handcrafted with dimensions shown in Table 13, except $D_o = 10 \text{ mm}$ and $t_{\text{flight}} = 0.75 \text{ mm}$), and (ii) a draught tube made of Plexiglas ($\varnothing 30 \times 2 \text{ mm}$) instead of $\text{Al}_2\text{O}_3$ allowing the visual inspection of the powder flow. This recirculator is further referred as cold flow conveyor. The cone-shaped bottom part was made of modelling clay (FIMO) with freely selectable cone half-angles $\theta_H$. The clay surface was coated with boron nitride (Proline, 427 BN) to reduce friction.

The recirculation performance of powdery C material at $p_{\text{red}}$ and of granular C material at both, $p_{\text{amb}}$ and $p_{\text{red}}$ was investigated with the setup shown in Figure 55b. Also here, the bath container was built of Plexiglas ($\varnothing 70 \times 5 \text{ mm}$, $l = 525 \text{ mm}$). The apparatus could be equipped with two different recirculators, both driven by an electric motor (Orientalmotor BLH230KC-5).

- the cold flow recirculator comprising the metallic screw and the Plexiglas draught tube.
- the heat-resistant recirculator comprising the graphite screw (dimensions shown in Table 13) and the $\text{Al}_2\text{O}_3$ draught tube ($\varnothing 30 \times 2.5 \text{ mm}$) at which the container lid and the feed tube were attached.

The flow rate of Ar was controlled by a calibrated mass flow controller (Bronkhorst EL-flow Select series) connected to inlet #3, while total pressure was monitored by an absolute pressure sensor (Kistler Instrumente AG, Type 4045A1) connected to inlet #4. A vacuum pump (Adixen ACP15) that was protected by a particle filter provided the low pressure environment. A globe valve allowed the manual control of total pressure inside the recirculation system.
Figure 55. Schematic of the experimental setups for the cold flow tests of the bath recirculation system; a) with powdery C at $p_{amb}$, and b) with powdery C at $p_{red}$ and with granular C at $p_{amb}$ and $p_{red}$.
The cone-shaped bottom part consisted either of modelling clay (FIMO) with freely selectable half-angles \( \theta_H \) or of graphite with \( \theta_H = 22^\circ \).

### 7.2.2.1 Test Procedure

First, either as-received or previously dried C material amounting to \( m_{\text{bath}} = 20-70 \) g was filled into the recirculation system by either removing the lid of the bath container (in setup shown in Figure 55a) or by pouring it through the feed inlet (in setup shown in Figure 55b). When testing at \( p_{\text{red}} \), the vacuum pump was started and the pressure in the system was then slowly reduced within 2-3 minutes to total pressures ranging from 1-15 kPa and the Ar flow rate (Messer 4.6) was set to 0-0.5 L\text{N}/\text{min}. The recirculation screw was started with \( v_{\text{recirculator}} = 20-600 \) rpm either before, during, or after reaching the desired \( p_{\text{rot}} \). When testing at \( p_{\text{amb}} \), the vacuum pump and the Ar flow tubing was disconnected from the system and the recirculation screw was directly started with \( v_{\text{recirculator}} = 20-600 \) rpm. At both \( p_{\text{amb}} \) and \( p_{\text{red}} \), the bath recirculation was run up to 30 minutes during which the bath flow was visually observed.

The bath recirculation performance at \( p_{\text{amb}} \) was quantified for the rate of material throughput by the conveyor screw \( Q_m \), recirculation frequency \( f_r \), fullness efficiency \( \eta_f \), and speed of the bath at the reactor wall \( v_{\text{bath, wall}} \). These quantities were obtained by following methods.

- Material throughput \( Q_m \) was measured using the bath withdrawal tube inserted into the container. The bath recirculation was run for 10-30 s after which the material collected in the withdrawal tube was weighted and refilled into the bath container. The measurement was repeated three times for each of the three windows and the overall material throughput was calculated by triplicating the average of all nine measurements.
- The recirculation frequency of the bath \( f_r \) was calculated according to equation (69).
• The fullness efficiency \( \eta_F \) was calculated according to

\[
\eta_F = \frac{m_{\text{screw}}^C}{V_{\text{screw}} \rho_b}
\]

with \( V_{\text{screw}} \) as the void space of the recirculation screw that can be filled with material and \( m_{\text{screw}}^C \) as the amount of C on the screw flights. \( m_{\text{screw}}^C \) was determined by running the recirculator for 2-3 minutes and subsequently collecting and weighing the material from the screw flights by emptying the recirculator in a separate vessel. Each measurement was repeated three times and averaged.

• The bath speed at the container wall \( v_{\text{bath,wall}} \) was measured by visually tracing the movement of a particle/agglomerate and recording the time that it required to travel a 5 cm vertical distance along the outer wall. Measurements were taken at two radial positions: one at the middle position of a discharge window and the other one between two discharge windows \( (90^\circ \text{ displaced}) \). Measurements were repeated eight times for each point and averaged.

The bath recirculation at \( p_{\text{red}} \) was studied by visually observing the bath flow at the reactor walls. The quality of the bath flow was rated in terms of flow uniformity: the bath flow was considered (i) uniform, when the complete bath was in motion, (ii) non-uniform, when a fraction of the bath was stagnant, and (iii) blocked, when the complete bath was stagnant and the recirculator run empty.

7.2.3 Hot Tests

The hot tests were conducted using the experimental setup schematically shown in Figure 56. Heat was delivered by an electrical furnace (Carbolite STF 450). Ar was inserted using calibrated mass flow controllers (Bronkhorst EL-flow Select series) (i) into the feeder, (ii) into the reactor head, and (iii) into the Mg precipitation zone from the reactor bottom. The equipment for vacuum operation
(pump, filter, and pressure sensor) was the same as used in the cold flow test setup (section 7.2.2). Downstream the vacuum pump, a gas chromatograph (Agilent 490 Micro GC) measured the composition of the effluent with a sampling frequency of 95 s.

![Figure 56. Schematic of the experimental setup for the hot tests.](image)

Some experiments investigated the Mg production in the absence of the C bath in the recirculation system. In some of these tests, the recirculation screw, the bottom part, and the precipitation tube were removed from the reactor and replaced by a cylindrical crucible (Al₂O₃, ø58x5 mm) with 7 boreholes (ø4 mm) in the crucible bottom (Figure 57). The bottom of the crucible was covered by a graphite felt to retain the solid reactants in the hot zone. A conical graphite ring (R4550, ø58x5 mm, θᵢ = 30°) was added at the top of the crucible to prevent an accumulation of feedstock on top of the crucible wall.
7.2.3.1 Test Procedures

**Preparation of Purified C**

For preparing thermally purified C, the material was poured via the feed inlet into the recirculation system after which the setup was enclosed and the vacuum pump was started. Then, total pressure was reduced under Ar flow ($V_{N,MFC_2}^0 = 0.5\ \text{L}_N/\text{min}$, and $V_{N,MFC_3}^0 = 0.28\ \text{L}_N/\text{min}$) by opening the globe valve in front of the vacuum pump to $p_{tot} \approx 2\ \text{kPa}$ after which the reactor was heated under continuing Ar flow with a rate of $20^\circ\text{C}/\text{min}$ to $1500^\circ\text{C}$. Subsequently, the temperature was kept constant until the C was free of moisture and volatile matter as indicated by the CO and H$_2$ flows in the outlet approaching zero. Then, the furnace was shut off and left to cool. After cooling, the precipitation tube was removed from the reactor, weighed, and cleaned with a brass spatula from possible condensed volatile matter that was collected and weighed also. Subsequently, the C bath was removed from the recirculation system by pulling...
the support tube and the attached bottom part out of the reactor and directly into a Plexiglas tube (⌀70x5 mm) that was pressed against the bottom opening of the reactor. The bath was then visually inspected and weighed.

**Testing the Bath Recirculation System**

*C powders* – For testing the recirculation performance of powdery material, a bath of as-received C powder amounting to $m_{\text{bath}} = 50$ g was poured into the recirculation system and the feeder was filled with ~80 g of Al$_2$O$_3$ powders. The Al$_2$O$_3$ served as mixing tracer in order to visually observe the degree of mixing between the white Al$_2$O$_3$ feedstock and black C bath after experimentation. Then, the feed screw was turned 25 rounds to fill the screw with material, while the fed material was collected and recharged into the hopper. The feeder was enclosed, mounted onto the reactor and by opening the globe valve in front of the vacuum pump, $p_{\text{tot}}$ was then slowly reduced under Ar sweep ($\dot{V}_{N, \text{MFC 1}} = 0.05$ L$_{N}$/min, $\dot{V}_{N, \text{MFC 2}} = 0.35$ L$_{N}$/min, and $\dot{V}_{N, \text{MFC 3}} = 0.4$ L$_{N}$/min) within 2-3 minutes to ~9 kPa. Then, the reactor was heated with a rate of 20°C/min under continuing Ar flow to 1500°C. After temperature equilibration, the bath recirculation was initiated following the procedure that was developed in the cold flow tests: the globe valve was closed in front of the vacuum pump until $p_{\text{tot}}$ increased to ~25 kPa. Then, the globe valve was reopened to its original position and while the recirculator was started with $v_{\text{recirculator}} = 600$ rpm. While $p_{\text{tot}}$ was still decreasing, the feeder was started with a speed of 5 rpm and a total amount of ~20 g of mixing tracer Al$_2$O$_3$ was fed within 5 min into the recirculating bath. After the feed, the recirculation of the bath was stopped and the furnace was shut off. After cooling, the feeder was dismounted, disassembled, cleaned, and the residual feedstock inside the feeder was collected and weighed. Then, the reactor head was pulled out of the reactor and the recirculator was visually inspected for residues of bath material on the screw flights. Finally, the bath was withdrawn by pulling the support tube and the attached bottom part out of the reactor and directly into a Plexiglas tube (⌀70x5 mm) that was pressed against the bottom opening of the reactor. The bath was then visually inspected and weighed.
C granules – When using granular material, the functionality the recirculation system was evaluated after each test by checking whether residual bath material was stored inside the conveyor after experimentation. If the bath recirculation would have stopped working during the test, the conveyor would have discharged the material inside and would have been empty afterwards.

Evaluating the Mg production performance of the reactor

First, either thermally pretreated C powders or as-received C granules serving as bath material and amounting to $m_{\text{bath}} = 50\text{-}70$ g was poured via the feed inlet into the recirculation system. The feeder was filled with an equimolar mixture of MgO and C powders or granules with total masses of ~40 g. Then, the feed screw was turned 25 rounds to fill the screw with material, while the fed material was collected and recharged into the hopper. Subsequently, the feeder was enclosed and mounted onto the feed inlet, the vacuum pump was started and by opening the globe valve in front of the vacuum pump $p_{\text{tot}}$ in the system was slowly reduced within 2-3 minutes to values ranging from 3-9 kPa. During the pressure reduction, the Ar flow rates were set to the desired values ($\dot{V}^{0}_{\text{N,MFC},1} = 0.05 \text{ LN/min}$, $\dot{V}^{0}_{\text{N,MFC},2} = 0.1 \text{ LN/min}$, $\dot{V}^{0}_{\text{N,MFC},3} = 0.28\text{-}0.38 \text{ LN/min}$). The precipitation zone was swept with Ar alone as it was renounced to combust the produced Mg with CO$_2$. Subsequently, the reactor was heated with a rate of 20°C/min to the set point temperature of 1500°C. When using as-received C as bath material, a 60 min waiting period at 1500°C was applied before starting the bath recirculation as to ensure the complete evaporation of volatile matter in the as-received material that was indicated by the CO and H$_2$ outlet flows approaching zero. When using C granules as bath material, the bath recirculation was started with $v_{\text{recirculator}} = 450$ rpm and after 10-15 minutes of recirculation, the feeding was commenced with $v_{\text{feeder}} = 2.8\text{-}5$ rpm. When using C powders as bath material, the bath recirculation was started by (1) closing the globe valve in front of the vacuum pump and letting $p_{\text{tot}}$ increase to ~25 kPa, (2) reopening the valve, (3) start the recirculation with $v_{\text{recirculator}} = 600$ rpm, and (4) start the feeder with $v_{\text{feeder}} = 2.8\text{-}5$ rpm while $p_{\text{tot}}$ was still decreasing (see section 7.3.2.2.3 for further discussion). Total feed time ranged from 15 to 30 minutes. 5-10 minutes after the feed, the bath recirculation was stopped and the furnace was turned off. After
cooling, the precipitation tube was removed from the reactor, weighed, and cleaned with a brass spatula from deposits that were collected and weighed also. The collection of residual feedstock and bath material followed the same procedure as discussed in the bath recirculation test procedure.

_Evaluating the Mg production performance in the absence of the C bath_

To evaluate the Mg production performance in the absence of the C bath, the feeder was filled with an MgO-C mixture with either C powders or granulates of molar ratio C/MgO = 10. Then, the feed screw was filled with feedstock by turning the screw 25 times, the fed material was recharged to the hopper, and the feeder was enclosed and mounted. Subsequently, $p_{\text{tot}}$ was reduced under Ar flow ($V_{N, MFC \, 1}^0 = 0.05 \text{ L}_N/\text{min}$, $V_{N, MFC \, 2}^0 = 0.1 \text{ L}_N/\text{min}$, and $V_{N, MFC \, 3}^0 = 0-0.2 \text{ L}_N/\text{min}$) within 2-3 min to ~2 kPa by opening the globe valve in front of the vacuum pump. Then, the reactor was heated under continuing Ar flow with a rate of 20°C/min to 1500°C. After temperature equilibration, the feeding was commenced with $v_{\text{feeder}} = 3.95 \text{ rpm}$. After a total feed time of 30 min, the furnace temperature was held constant for another 10-15 min after which the furnace was turned off. Material collection and reactor inspection after cooling followed the same procedure as for the tests with equimolar feedstock except for when the crucible (Figure 57) was used. In this case, the deposits in the cooling zone were collected from the cone support tube, as the precipitation tube was not included.

### 7.2.3.2 Calculations

**Estimation of the Feed Conversion**

MgO feed conversion ($X_{\text{feed}}$), i.e. the fraction of MgO in the feed ($\dot{n}_{\text{MgO}}^0$) converted to Mg(g) by the CTR ($\dot{n}_M^0$) served as indicator to evaluate the Mg production performance of the reactor and was calculated according to

$$X_{\text{feed}}(t) = \frac{\dot{n}_M(t)}{\dot{n}_{\text{MgO}}^0(t)}.$$  \hspace{1cm} (72)
The estimation of the Mg production rate \( \dot{n}_{\text{Mg}} \) required the material balances of Mg, CO, CO\(_2\), and H\(_2\) that were based on the reactions proceeding inside the recirculation system and in the Mg precipitation zone, respectively. They are listed in Table 16. Reactions proceeding in reverse direction are denoted with a star, i.e. \( r_i^* \). Beside of the CTR of MgO (reaction (4)), some amounts of H\(_2\)O and CO\(_2\) contained in the MgO were released via reactions (18) and (19). The released H\(_2\)O and CO\(_2\) then further consumed C via reactions (51) and (9), respectively, and may also have consumed some of the Mg\(_{\text{(g)}}\) product via reaction (73) and reverse reaction (8).

\[
\text{Mg}_{\text{(g)}} + \text{H}_2\text{O}_{\text{(g)}} \rightleftharpoons \text{MgO}_{\text{(s)}} + \text{H}_2\text{(g)} \tag{73}
\]

Furthermore, the water-gas shift reaction may have proceeded according to

\[
\text{CO}_{2\text{(g)}} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO}_{\text{(g)}} + \text{H}_2\text{O}_{\text{(g)}} \tag{74}
\]

Concerning the Mg precipitation zone, it was assumed that (i) no H\(_2\)O or CO\(_2\) produced by reactions (18) and (19) was transported into the precipitation zone, and (ii) all CO\(_2\) produced by the potentially catalyzed reverse Boudouard reaction (9) was consumed by reverse reaction (8) (as observed in chapter 3). Therefore, only the reverse overall reaction proceeded at that location.

The location-dependent Mg material balances are given as follows:

- The effective Mg production rate by the CTR is given as
  \[
  \dot{n}_{\text{Mg}}(t) = r_4. \tag{75}
  \]

- The amount of produced Mg that was transported into the Mg precipitation zone \( \dot{n}'_{\text{Mg}} \) is defined as
  \[
  \dot{n}'_{\text{Mg}}(t) = r_4 - r_{73} - r_8^*. \tag{76}
  \]

- The amount of produced Mg\(_{\text{(g)}}\) that deposited as Mg\(_{\text{(s)}}\) without being re-oxidized by the reverse overall reaction \( \dot{n}_{\text{Mg,final}} \) is given by
  \[
  \dot{n}_{\text{Mg,final}}(t) = r_4 - r_{73} - r_8^* - r_4^*. \tag{77}
  \]
Table 16. Reactions taking place in the recirculation system and in the Mg precipitation zone, respectively.

<table>
<thead>
<tr>
<th>location</th>
<th>reaction description</th>
<th>equation</th>
<th>#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recirculation system</td>
<td>CTR of MgO</td>
<td>( \text{MgO}<em>{(s)} + \text{C}</em>{(s)} \rightleftharpoons \text{Mg}<em>{(g)} + \text{CO}</em>{(g)} )</td>
<td>( r_4 )</td>
</tr>
<tr>
<td></td>
<td>Release of ( \text{H}_2\text{O} ) and ( \text{CO}_2 ) from MgO</td>
<td>( \text{Mg(OH)}<em>{2(s)} \rightleftharpoons \text{MgO}</em>{(s)} + \text{H}<em>2\text{O}</em>{(g)} )</td>
<td>( r_{18} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{MgCO}<em>{3(s)} \rightleftharpoons \text{MgO}</em>{(s)} + \text{CO}_{2(g)} )</td>
<td>( r_{19} )</td>
</tr>
<tr>
<td>Recirculation system</td>
<td>Reduction of ( \text{H}_2\text{O} ) and ( \text{CO}_2 ) with C</td>
<td>( \text{H}<em>2\text{O}</em>{(g)} + \text{C}_{(s)} \rightleftharpoons \text{H}_2(g) + \text{CO}_g )</td>
<td>( r_{51} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{CO}_{2(g)} + \text{C} \rightleftharpoons 2\text{CO}_g )</td>
<td>( r_9 )</td>
</tr>
<tr>
<td>Mg precipitation zone</td>
<td>Reduction of ( \text{H}_2\text{O} ) and ( \text{CO}_2 ) with Mg</td>
<td>( \text{Mg}<em>{(g)} + \text{H}<em>2\text{O}</em>{(g)} \rightleftharpoons \text{MgO}</em>{(s)} + \text{H}_2(g) )</td>
<td>( r_{73} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Mg}<em>{(g)} + \text{CO}</em>{2(g)} \rightleftharpoons \text{MgO}_{(s)} + \text{CO}_g )</td>
<td>( r_8^* )</td>
</tr>
<tr>
<td></td>
<td>water-gas shift</td>
<td>( \text{CO}_{2(g)} + \text{H}_2(g) \rightleftharpoons \text{CO}_g + \text{H}<em>2\text{O}</em>{(g)} )</td>
<td>( r_{74} )</td>
</tr>
</tbody>
</table>

Combining equations (75) and (77) leads to

\[
\dot{n}_{\text{Mg}} (t) = \dot{n}_{\text{Mg,final}} (t) + r_{73} + r_{8^*} + r_{4^*}.
\]  

(78)

The individual terms of equation (78) were determined as follows:

- The final Mg fraction \( \dot{n}_{\text{Mg,final}} \) was determined by solving the material balances of CO, CO\(_2\) and \( \text{H}_2 \) in the outlet that are given as

\[
\dot{n}_{\text{CO}} (t) = r_4 + r_{51} + 2r_9 + r_{8^*} + r_{74} - r_{4^*},
\]  

(79)
Experimental Testing of the Lab-Scale Reactor

\[ \dot{n}_{\text{CO}_2} (t) = r_{19} - r_9 - r^*_8 - r_{74}, \]  

(80)

\[ \dot{n}_{\text{H}_2} (t) = r_{51} + r_{74} - r_{74}, \]  

(81)

where the molar flow rates of species \( i \) \( (\dot{n}_i (t)) \) in the outlet were determined according to equations (30)-(34) from their temporal fractions in the product gas \( (y_i (t)) \) acquired by gas chromatography. Solving for \( \dot{n}_{\text{CO}_2} + 2\dot{n}_{\text{CO}_2} - \dot{n}_{\text{H}_2} \) and combining with equation (77) gives

\[ \dot{n}_{\text{Mg, final}} (t) = \dot{n}_{\text{CO}_2} (t) + 2\dot{n}_{\text{CO}_2} (t) - \dot{n}_{\text{H}_2} (t) - 2r_{19} \]  

(82)

with \( r_{19} \) being equal to the molar feed of \( \text{CO}_2 \) contained in the \( \text{MgO} \) that was calculated as

\[ r_{19} = \frac{M_{\text{MgO}}}{M_{\text{CO}_2}} \cdot w_{\text{CO}_2} \cdot \frac{\dot{n}_{\text{MgO}} (t)}{\dot{n}_{\text{MgO}} (t)}. \]  

(83)

- The rate of reverse reaction \( r^*_4 \) was defined by combining equations (76) and (77) that results in

\[ r^*_4 = \dot{n}'_{\text{Mg}} (t) - \dot{n}_{\text{Mg, final}} (t). \]  

(84)

With the temporal reversion coefficient \( (Z_{\text{Mg}} (t)) \) that is defined as the fraction of re-oxidized \( \text{Mg(g)/s} \) by the reverse overall reaction of the amount of \( \text{Mg(g)} \) that entered the cooling zone, i.e.

\[ Z_{\text{Mg}} (t) = 1 - \frac{\dot{n}_{\text{Mg, final}} (t)}{\dot{n}'_{\text{Mg}} (t)} \]  

(85)

the rate of the reverse overall reaction \( r^*_4 \) can be expressed by combining equations (84) and (85) as

\[ r^*_4 = \dot{n}_{\text{Mg, final}} (t) \left( \frac{1}{1 - Z_{\text{Mg}} (t)} - 1 \right). \]  

(86)
However, the temporal values of \( Z_{Mg}(t) \) could not be determined. Therefore, it was assumed that \( Z_{Mg}(t) \) was approximately constant with time and thus equal to the final value \( Z_{Mg} \) given by

\[
Z_{Mg} = 1 - \frac{N_{Mg,\text{final}}'}{N_{Mg}'}.
\] (87)

The final reversion coefficient \( Z_{Mg} \) was determined according to the following procedure: the total amount of deposited Mg \( N_{Mg,\text{final}}' \) was determined by integrating equation (82) over the total reaction time of CTR, i.e.

\[
N_{Mg,\text{final}}' = \int_0^{t_f} \dot{n}_{Mg,\text{final}}(t) dt
\] (88)

The total amount of Mg that entered the cooling zone \( N_{Mg}' \) was determined by the Mg material balance in the cooling zone given by

\[
N_{Mg}' = N_{Mg,\text{final}}' + \xi_4'^*
\] (89)

The extent of the reverse reaction \( \xi_4'^* \) is expressed as

\[
\xi_4'^* = \frac{m_{\text{reverse}}}{(M_{\text{MgO}} + M_C)}
\] (90)

with \( m_{\text{reverse}} \) as the total mass of produced MgO and C by the reverse reaction. This amount was determined from a mass balance of deposited material in the precipitation zone that is written as

\[
m_{\text{reverse}} = m_{\text{deposits}} - m_{Mg,\text{final}} - m_{\text{cond}}
\] (91)

with \( m_{\text{deposits}} \) being the total amount of collected deposits from the Mg precipitation tube and \( m_{\text{cond}} \) being deposits of other species than Mg, MgO, and C, i.e. volatiles of C that condensed in the cooling zone. The amount of condensed volatile matter was determined by

\[
m_{\text{cond}} = \omega_{\text{cond}} C m_{\text{bath}}
\] (92)
with \( w_{\text{cond}}^C \) as the weight fraction of condensable volatile matter in the as-received C. When using purified C as bath material, \( w_{\text{cond}}^C \) equaled zero. When using as-received C as bath material, \( w_{\text{cond}}^C \) was determined from the amount of deposits that were collected when preparing purified C in the absence of MgO (see section 7.2.3.1), in which case
\[
w_{\text{cond}}^C = \frac{m_{\text{deposits}}}{m_{\text{bath}}}.
\]
- The rates of reaction (73) and reverse reaction (8) were not quantifiable and therefore bracketed by their minimum and maximum possible extent: it was assumed that either none or all of the \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) reacted with produced Mg, i.e.
\[
0 \leq r_{73} + r_{8}^* \leq n_{\text{MgO}}^0(t) \left( w_{\text{H}_2\text{O}}^{\text{MgO}} M_{\text{MgO}} + w_{\text{CO}_2}^{\text{MgO}} M_{\text{MgO}} \right) \frac{1}{n_{13} + n_{14}} \tag{93}
\]

The effective MgO feed rate \( n_{\text{MgO}}^0(t) \) was determined from the molar flow rate of \( \text{H}_2 \) \( (\dot{n}_{\text{H}_2}(t)) \) in the outlet, i.e.
\[
n_{\text{MgO}}^0(t) = \frac{1}{w_{\text{H}_2\text{O}}^{\text{MgO}} M_{\text{MgO}}} \dot{n}_{\text{H}_2}(t) \tag{94}
\]

**Estimation of the CO partial pressure in the recirculation system**

The CO partial pressure in the recirculation system was estimated according to
\[
p_{\text{CO}}(t) = \frac{1}{1 - Z_{\text{Mg}}} y_{\text{CO}}(t) p_{\text{tot}}(t) \tag{95}
\]

with \( y_{\text{CO}}(t) \) as the temporal molar fraction of CO in the outlet.
7.3 Results and Discussion

7.3.1 Feeding System Tests

7.3.1.1 Optimization of the Hopper Geometry

The operation of the feeding system at $p_{\text{amb}}$ with powdery, equimolar MgO-C feedstock and using a test hopper with $\theta_{H,\alpha} = -10^\circ$ and $\theta_{H,\beta} = 10^\circ$ (symmetrical form) resulted in the formation of a cohesive arch over the screw surface as schematically illustrated in Figure 58. Usually, this arch developed within the first few turns of the feed screw eventually blocking the material flow into the screw entirely. Variation in screw speeds within 6 – 60 rpm did not significantly influence the development of said arch. In addition, arching within the hopper was observed sometimes.

![Figure 58. Formed arch during operation of the feeding system at $p_{\text{amb}}$ with powdery, equimolar MgO-C feedstock.](image)

Hopper arching was prevented by tilting the hopper against rotational direction and selecting $\theta_{H,\alpha}$ and $\theta_{H,\beta}$ equal to 2 and $10^\circ$, respectively. Variation of $\theta_{H,\alpha}$ and $\theta_{H,\beta}$, however, did not prevent the development of the arch over the screw surface shown in Figure 58. For eliminating the formation of said arch, brushes were placed at the hopper outlet as schematically shown in Figure 59. They were kept in front-and-back movement by the rotating screw flights and acted as moving walls. Steel sheets covered the brush clamps to allow a stepless transition between hopper walls and brush section. Different brush lengths of 10 mm and 35 mm, respectively, allowed the positioning of the narrowest hopper
section to a point where one wall was covered by a brush thereby preventing an arching at that position. Furthermore, bended and negative tapered front and rear walls with $\theta_{H,\gamma} = 20^\circ$ prevented a clogging of material at the edges of the hopper and a ratholing of the feedstock.

Figure 59. Schematic of the particle feeding system equipped with brushes.

7.3.1.2 Calibration of the Feeding System

The operation with the brushes resulted in an approximately uniform and stable feed rate at both $p_{\text{amb}}$ and $p_{\text{red}}$ for both feedstock types (with powdery or granular C). The calibration runs with equimolar MgO-C feedstock using powdery, purified C material are shown in Figure 60. As illustrated by Figure 60a, the mass accumulation appeared to be linear with feed time and repetitive runs were almost identical to each other. However, regarding the feed rates normalized by $v_{\text{feeder}}$ as illustrated in Figure 60b, fluctuations in temporal feed uniformity of up to 10% were observed. It was assumed that these fluctuations may have been induced by an intermittent blocking of material in the brush
section or intermittent clogging in the feed screw flights as observed in previous research.\textsuperscript{113} Furthermore, except for the run at 10 rpm, operation at $p_{\text{amb}}$ resulted in up to 20\% lower feed rates than at $p_{\text{red}}$. This observation was attributed to a feedstock compression at $p_{\text{red}}$ resulting in a higher bulk density and therefore in a higher mass feed rate compared to $p_{\text{amb}}$. An increase in Ar flow rate to 0.1 L\textsubscript{N}/min showed no effect on feed rate. Additional pertinent observations are as follows:

- the feed rate started to decrease with $\leq 10$ g residual feedstock inside the hopper, because part of the screw was not covered by material anymore.
- the feed screw did not clog significantly over the course of feeding one hopper charge; however, feed screw and hopper needed to be cleaned between two consecutive charges in order to prevent a progressing clogging.
- feedstocks with C/MgO molar ratio of 10 showed better feed uniformity by trend than equimolar feedstocks, because the concentration of the cohesive MgO was lower that led to higher feedstock fluidity.
- the normalized rate of the feed predicted with the conveyor model (0.24 g/(min\cdot rpm)) was up to 30\% higher compared to the measured feed at $p_{\text{amb}}$. This deviation was presumably caused by either (i) non-ideal filling of the screw with material that lowered $\eta_{\text{F}}$, (ii) a slight sticking of the cohesive material on the screw surface lowering $\eta_{\text{VR}}$, or (iii) inaccuracies in powder property measurements.

The calibration runs with equimolar MgO-C feedstock using granular, purified C are illustrated in Figure 61. Similar fluctuations in feed uniformity (Figure 61b) were observed as to the ones observed using powdery C material as feedstock component (Figure 60b). In contrast to powdery MgO-C feedstock, no effect of total pressure on feed rate was observed. Further pertinent observations are as follows:

- in contrast to powdery feedstock, the feed screw did not clog over 4 consecutive hopper charges without cleaning the feeder in between.
- feedstocks with molar ratio C/MgO of 10 showed better feed uniformity by trend than equimolar ones.

Figure 60. Temporal mass accumulation (a) and normalized feed rate (b) for powdery, equimolar MgO-C feedstock at \( P_{\text{amb}} \) and \( P_{\text{red}} = 1-2 \) kPa. Error bars show the maximum deviation between the available repetitions.
Figure 61. Temporal mass accumulation (a) and normalized feed rate (b) for equimolar MgO-C feedstock using C granulates at $p_{amb}$ and $p_{red} = 1-2$ kPa. Note: the calibration point at 30 min for 3 rpm at $p_{amb}$ is omitted, as the hopper was emptied during calibration thereby distorting the results.
7.3.2 Cold Flow Tests of the Bath Recirculation System – C Powders

7.3.2.1 Tests at Ambient Pressure

The cold flow tests at $p_{\text{amb}}$ with dried, powdery C and a clay cone with $\theta_H = 20^\circ$ showed that the onset screw speed for stable bath recirculation was dependent on $m_{\text{bath}}$ (Figure 62). Below the onset speed, bath recirculation was unstable and the bath flow often blocked before 5 min of operation. A blocked bath could seldom be de-blocked by changing $v_{\text{recirculator}}$ and/or restarting the recirculator. Usually, a vigorous stirring with a stick was required for de-blocking. At $m_{\text{bath}} \geq 40\text{g}$, onset speed was constant at 180 rpm, while at $m_{\text{bath}} < 40\text{g}$, onset speed increased up to 540 rpm. In accordance to this observation, the maximum throughput rate $Q_m$ ($v_{\text{recirculator}} = 600 \text{rpm}$) increased with higher bath amounts starting to approach a steady state value of $\sim 300 \text{g/min}$ at $m_{\text{bath}} > 50\text{g}$.

![Figure 62. Onset screw speed and maximum throughput $Q_m$ as function of $m_{\text{bath}}$ for a dried, powdery C bath with a clay cone of $\theta_H = 20^\circ$. Error bars in $Q_m$ indicate the standard deviation of measurement points.](image)

It was concluded that the observed behavior was dependent on the location of the bath surface level. At $m_{\text{bath}} < 40 \text{g}$, the choke section of the recirculation
screw was not entirely covered with material. Some of conveyed material was therefore thrown from the screw flights before entering the draught tube thereby decreasing the screw fullness efficiency. It should be noted that during the throughput measurements with \( m_{\text{bath}} = 40 \text{ g} \), the bath level fell below the draught tube inlet level during operation distorting the results slightly.

Furthermore, at \( v_{\text{recirculator}} > 420 \text{ rpm} \), an aeration of the bath was observed increasing the bath surface level and therefore the occupied volume of the bath container. Upon stopping the recirculation, the bath surface level decreased to its original level with air bubbles leaving the bath surface. The increase in bath volume \( (dV_{\text{bath}}) \) that was inferred from the location of the bath surface level, is shown in Figure 63 as function of \( v_{\text{recirculator}} \) for \( m_{\text{bath}} = 55 \text{ g} \). Bath aeration was strongly influenced by the moisture content in the C material. When using as-received instead of dried C, bath aeration was not visible and the bath sometimes blocked even at \( v_{\text{recirculator}} > 180 \text{ rpm} \). This observation was attributed to the increasing cohesiveness of the material with increasing moisture content.\textsuperscript{113, 125}

![Figure 63](image_url)

**Figure 63.** Relative increase in bath volume \( (dV_{\text{bath}}) \) for a dried, powdery C bath amounting to \( m_{\text{bath}} = 55 \text{ g} \) using a clay cone with \( \theta_H = 20^\circ \).
Further characterization of the bath recirculation system was conducted using a dried C bath with $m_{\text{bath}} = 55 \text{ g}$. The measured $\eta_F$ is shown in Figure 64a as function of $v_{\text{recirculator}}$. Measured values were in the range of 73-95%, which were ~3-4 times higher than first assumed while designing the conveyor screw (25%, see section 6.2.1). $\eta_F$ decreased with increasing $v_{\text{recirculator}}$, presumably because the material intake rate of the recirculation screw in the choke section could not follow the potential increase in conveying capacity. This observation is in accordance to the reported work in literature.\textsuperscript{134} The measured $Q_m$ and the corresponding $f_r$ is illustrated in Figure 64b. With increasing $v_{\text{recirculator}}$ from 180 to 600 rpm, $Q_m$ increased approximately linear from ~80 up to 300 g/min, which corresponds to $f_r$ in the range of 1.6 to 5.7. This is an over 5 times higher value than predicted ($f_r=1$, see section 6.2.1) and can be attributed to the higher effective $\eta_F$. The $Q_m$ predicted with the conveyor model that is illustrated in same figure was calculated using the measured $\eta_F$ (Figure 64a), and the friction properties of C on Plexiglas and steel, respectively (see Table 21). The modelled and measured $Q_m$ fit very well at $v_{\text{recirculator}} \geq 480 \text{ rpm}$, while at lower speeds the model significantly underestimated the measurements. Nevertheless, it was concluded that the model fit remarkably good considering that (i) measured powder properties may have been inaccurate, and (ii) the model assumes free-flowing and non-cohesive material that was not the case for the used C powder.
Figure 64. Fullness efficiency $\mu_f$ a) and measured and modelled mass throughput $Q_m$ and recirculation frequency $f_r$ b) for $m_{\text{bath}} = 55$ g using a clay cone with $\theta_{\text{n}} = 20^\circ$. Error bars indicate the standard deviation of the measurements.
The measured bath speed at the wall is shown in Figure 65. As illustrated, the speed is similar at both measured locations confirming the uniformity of the bath flow profile in circumferential direction. Regarding the bath flow profile in radial direction, it was suspected that bath flow was faster near the reactor wall than near the draught tube, as the calculated throughput inferred from \( v_{\text{bath, wall}} \) \((Q_m = \rho_b v_{\text{bath, wall}} A_{\text{bath}})\) was by 20-50% higher than the measured one shown in Figure 64b. This assumption is in accordance to Bridgwater\textsuperscript{114} who suggested that the recirculation time of a particle is a function of the radial position in the annular bath.

![Figure 65. Bath speed at the reactor wall (\( v_{\text{bath, wall}} \)) below a discharge window and 90° displaced between two windows for dried, powdery C amounting to \( m_{\text{bath}} = 55 \text{ g} \) using a clay cone with \( \theta_h = 20° \). Error bars indicate the standard deviation of the measurements.](image)

Effect of the Cone Half Angle

Variation in \( \theta_h \) resulted in following observations using as-received C of \( m_{\text{bath}} = 40\text{g} \):
• Using a cone with $\theta_H = 15^\circ$, the observed bath flow was similar to when using a cone with $\theta_H = 20^\circ$.

• Using a cone with $\theta_H = 30^\circ$, a stagnating layer was built over the cone surface with up to 20 mm thickness at the reactor wall resulting in a funnel flow pattern of the C bath. At $v_{\text{recirculator}} < 180$ rpm, bath blockage seemed to occur earlier than with $\theta_H$ of 20$^\circ$ and 15$^\circ$, respectively.

*Effect of the Gas Bypass*

Operating the recirculation system (dried C, $m_{\text{bath}} = 50$ g) with the gas bypass mounted into the clay cone did not significantly affect the bath flow while the bath was aerated ($v_{\text{recirculator}} > 420$ rpm). However, with $v_{\text{recirculator}} < 420$ rpm, a stagnation zone formed around the bypass with a width of up to $\sim 1/3$ of the bath circumference as shown in Figure 66. This figure illustrates a circumferential view of the bath flow along the wall of the reactor tube. Due to the nontransparent clay cone, the choke section of the conveyor screw was visually not accessible.

![Figure 66. Schematic of the circumferential view of the bath flow along the wall of the reactor tube.](image)
7.3.2.2 Tests at Reduced Pressure

The performance of the recirculation system was examined at $p_{\text{red}}$ in order to (i) specify recommendations and restrictions in operational conditions ($\dot{V}_N^0$, $p_{\text{tot}}$, $v_{\text{recirculator}}$, and $m_{\text{bath}}$) by evaluating their effect on bath flow and (ii) improve the bath flow if required by studying the effects of geometrical adaptions. First, the bath flow was examined and optimized using the cold flow recirculator. Upon reaching a satisfying uniformity, the recirculator was replaced with the heat-resistant one and bath flow uniformity was once more examined and improved if required.

7.3.2.2.1 Performance with the Cold Flow Recirculator

*Step 1: Selection of the Optimal Gas Removal Location*

The effect of gas removal location on bath flow was investigated using a clay cone with $\theta_H = 20^\circ$ and dried $C$ of $m_{\text{bath}} = 50$ g and $v_{\text{recirculator}} = 540-600$ rpm. Figure 68 schematically illustrates the bath flow uniformity of the different configurations as function of $\dot{V}_N^0$ in the range of 0-0.5 $L_N/\text{min}$.

*Withdrawal Through the Bath Floor (Configuration A)* – Operating the recirculation system without a sweep gas flow ($p_{\text{tot}} \approx 0.1$ kPa) resulted in an uniform bath flow even though the reduction in $p_{\text{tot}}$ resulted in a decrease in bath volume due to compression by up to $\approx 25\%$. However, after setting sweep the flow rate to 0.05 $L_N/\text{min}$, the bath immediately blocked. Blockage also occurred when starting the gas sweep before starting the bath recirculation. It was assumed that this behavior was caused either by the impulse of the gas that compressed and consolidated the bath thereby blocking the bath flow, and/or a downwards entrainment of material inside the conveyor preventing its transport in upward direction. Furthermore, the gas permeability of the C bath appeared to be very low as it took a multiple of time (several minutes) to achieve a steady-state pressure ($\approx 1$ kPa) than with the empty system. Starting the bath recirculation already during reduction in $p_{\text{tot}}$ did not significantly affect the pressure gradient implying that the gas permeability of the bath did not change while being in motion.
Withdrawal Through the Gas Bypass (Configuration B) — When testing configuration B, a particle filter was placed on top of the bypass tube (see Figure 67) to prevent a removal of particles from the bath container. When no sweep gas was applied, the bath flow was uniform. However, upon setting the sweep flow to 0.05 L/min ($p_{\text{tot}} \sim 5$ kPa), the bath flow was non-uniform, since a stagnation zone formed around the bypass similar to the one shown in Figure 66. With increasing $\dot{V}_N^0$ up to 0.5 L/min ($p_{\text{tot}} \rightarrow 10$ kPa), the size of the stagnation zone increased by trend, which was accompanied by a decrease in recirculator throughput as visually indicated by the material stream through the discharge windows that appeared to be lower. With $\dot{V}_N^0 > 0.5$ L/min, the bath often completely blocked after some minutes. Furthermore, it was observed that with decreasing $v_{\text{recirculator}}$ the stagnation zone increased by trend.

![Figure 67. Schematic of the particle filter placed on top of the bypass tube.](image)

Furthermore, the bath flow responded very sensitive to temporal pressure gradients:

- While total pressure was temporally decreasing, the bath expanded resulting in a uniform and stable bath flow. The extent of bath expansion correlated with the slope of the pressure gradient and with too high values the bath surface level increased even above the discharge windows. Furthermore, a bath that has been previously blocked could be immediately brought to flow again by decreasing total pressure. This behavior was presumably caused by the removal of gases inside the bath from above, which fluidized the material. However, it is interesting to
note that bath expansion was not observed when the recirculator did not run, which implies that initial bath motion was required to bring it to fluidization.

- While total pressure was temporally constant, no bath expansion was observed and the stagnation zone at the gas bypass started to develop.
- While total pressure was temporally increasing, the bath started to compress resulting in an increase in stagnation zone size. With too high pressure gradients the bath completely blocked. This behavior was presumably caused by a filling of the bath container with gas that caused a pressure difference between container and bath bulk, which compressed the material.

![Figure 68. Effect of gas withdrawal configuration on bath flow uniformity.](image)

*Withdrawal From Both Locations (Configurations A and B)* – When the sweep gas was withdrawn through both, the bath floor and the gas bypass, temporal pressure gradients resulted in a bath expansion/compression behavior similar as observed with configuration B. However, the bath flow was more sensitive to
without sweep gas added to the system, the bath flow was uniform. Increasing $\dot{V}_N^0$ to 0.05 L_N/min resulted in the development of the stagnation zone, which increased in size with $\dot{V}_N^0 = 0.1$ L_N/min. Complete bath blockage was observed at $\dot{V}_N^0 \geq 0.15$ L_N/min.

**Final Choice** – Comparing the three gas withdrawal methods to each other implied that configuration B showed by far the most stable bath flow with changing $\dot{V}_N^0$. Therefore, this configuration was chosen for further experimentation.

**Step 2: Improving the Bath Flow**

Unless otherwise specified, the tests for improving the bath flow uniformity were conducted using a clay cone with $\theta_H = 20^\circ$, dried C material of $m_{\text{bath}} = 60$ g, and $v_{\text{recirculator}} = 600$ rpm.

**Effect of the Bypass Particle Filter** – The influence of the bypass particle filter on bath flow uniformity was studied by using either no filter on the gas bypass, or a version (Figure 69) with a higher filter area compared to the original filter (Figure 67).

![Figure 69. Schematic of the high-area particle filter.](image)

In comparison to the original particle filter, it was observed that

- without a particle filter on the gas bypass, the bath flow was less sensitive towards changes in $\dot{V}_N^0$ as illustrated in Figure 70. In the range...
of $\dot{V}_N^0 = 0 - 0.35 \text{ L}_N/\text{min}$, the bath flow was uniform ($p_{tot} = 0.7 - 8.5 \text{ kPa}$). With higher $\dot{V}_N^0$ of up to $0.5 \text{ L}_N/\text{min}$ ($p_{tot} \sim 12.5 \text{ kPa}$), the complete bath was still in motion. However, the bath speed near the gas bypass was significantly decreased. Furthermore, some material (estimated 2-3 g) was withdrawn from the bath through the gas bypass and collected by the particle filter in front of the vacuum pump. This material withdrawal was also indicated by a slight, approximately constant increase in $p_{tot}$ with progressing run time due to a beginning filling of the filter in front of the vacuum pump with bath material.

- with the high-area filter (Figure 69), the bath flow was uniform in the range of $\dot{V}_N^0 = 0 - 0.2 \text{ L}_N/\text{min}$. With higher $\dot{V}_N^0$ in the range of 0.2-0.5 L$_N$/min, the bath flow was non-uniform by trend: the stagnating zone around the bypass formed that, however, was only marginally stable and sometimes still in motion.

![Figure 70. Effect of different particle filters on bath flow uniformity.](image)

It was assumed that the improving effect of having a higher filter area or no filter at all on bath flow uniformity was caused by the difference in pressure drop
over the bypass section. With an increasing pressure drop, a higher fraction of sweep gas was withdrawn from the bath container through the gap between clay cone and reactor tube that was not gastight. For entering this gap, the gas needed to flow through the bath thereby presumably compressing it.

**Effect of total pressure** – It was observed that a higher $p_{tot}$ positively affected bath flow uniformity by trend. Operating the recirculation system with $\dot{V}_N^0 = 0.5$ LN/min and using the high-area filter on the bypass showed that at $p_{tot} \geq 8$ kPa the bath flow was quasi uniform, while at $p_{tot} \leq 5$ kPa a stagnation zone formed around the bypass tube leading to a non-uniform bath flow. It was speculated that the beneficial effect of $p_{tot}$ was induced by a difference in the bath bulk density, as the bath was presumably less compressed by trend with higher $p_{tot}$.

**Effect of Draught Tube Vibration** – The draught tube was brought to vibration by losing the screws of the connection to the reactor head. The moving screw then brought the draught tube into a slight stirring motion with a frequency corresponding to the screw speed. These vibrations resulted in uniform bath flow within $\dot{V}_N^0 = 0-0.5$ LN/min, even when using the high-area filter at $p_{tot}$ as low as 5 kPa. It was assumed that the stirring motion of the draught tube kept the complete bath in movement thereby preventing the development of a stagnation zone around the bypass.

**Effect of Outer Bath Diameter** – The outer bath diameter was reduced by inserting a Plexiglas tube ($\varnothing 60x4$ mm) into the reactor tube. It was observed that with the smaller outer bath diameter ($\varnothing 52$ mm), the bath flow uniformity was improved: operation with dried C material of $m_{bath} = 40$ g, $\nu_{recirculator} = 480-600$ rpm, using a clay cone with $\theta_{cl} = 20^\circ$ and the high-area particle filter, the bath flow was uniform within $\dot{V}_N^0 = 0-0.5$ LN/min. Only for $\nu_{recirculator} < 480$ rpm the bath flow was non-uniform with a stagnation zone being similar to the one illustrated in Figure 66. It was speculated, that this improvement was caused by a more efficient material intake of the recirculation screw that relative size compared to the bath container was larger.
7.3.2.2.2 Performance with the Heat-Resistant Recirculator

Operating the recirculation system (dried C, \( m_{\text{bath}} = 50 \text{ g} \), \( v_{\text{recirculator}} = 600 \text{ rpm} \), clay cone with \( \theta_H = 20° \)) with the heat-resistant recirculator significantly deteriorated bath flow uniformity. Without a particle filter on the gas bypass and \( \dot{V}_N^0 = 0.5 \text{ L_N/min} \), the majority of the bath was stagnating. The bath flow into the choke section of the conveyor screw was restricted to about 1/5 of the annular bath, accompanied by a significantly decreased recirculator throughput compared to the throughput with a free flowing bath. With the high-area particle filter, the stagnating zone even extended with run time and the bath flow often blocked completely after 5-10 minutes. This decrease in bath flow quality was attributed to the increased friction coefficient \( \mu_d \) of the C particles at the draught tube, which was higher when using a draught tube made of alumina instead of Plexiglas (0.7 vs. 0.6, see Table 21).

**Improving the Bath Flow**

Unless otherwise specified, the tests for bath flow improvements were conducted using dried C material of \( m_{\text{bath}} \approx 50 \text{ g} \), \( v_{\text{recirculator}} = 600 \text{ rpm} \), \( \dot{V}_N^0 = 0.5 \text{ L_N/min} \), \( p_{\text{tot}} \approx 8-12 \text{ kPa} \), and using a clay cone with \( \theta_H = 20° \).

**Effect of Draught Tube Vibration** – Bringing the Al\(_2\)O\(_3\) draught tube to vibration showed no improvement in bath flow, which was a different result compared to the operation with the cold-flow recirculator. It was assumed that due to either (i) the increased weight and stiffness of the alumina draught tube or (ii) the replacement of the metallic screw with the graphite one, the vibration intensity was decreased resulting in a less distinct stirring movement. Furthermore, it was observed that the graphite screw was worn at the tip due to the rubbing movement against the wall of the cone making this method unsuitable with the chosen component materials.
**Effect of bypass geometry** – The different bypass geometries were constructed using either cardboard and/or graphite felt (Sigratherm® GFA5). For these tests, the clay cone was replaced by the graphite bottom part ($\theta_{h} = 22$). This replacement did not seem to affect the bath flow. The tested bypass geometries and the observed bath flows are schematically shown in Figure 71. Except for Figure 71e, the tests were conducted without the implementation of a particle filter on top of the bypass tube. The measured sizes of the bath flow regions are only exemplarily shown pointing out trends to ease the comparison of the effect of different bypass forms. These values were not always constant and varied with run time and test repetition, respectively.

The bath flow of the original bypass form is shown in Figure 71a. As already discussed, the flow into the choke section was restricted to ~1/5 of the annular bath area. The location of the free flowing region was not always on direct opposite side of the bypass, but wandered in circumferential direction with increasing run time. It was observed that the bath flow could be significantly manipulated by modifying the bypass geometry:

- Partially replacing the stagnant zone with a triangular shaped cardboard insert (Figure 71b) did not significantly decrease the dimension of the stagnation zone. Furthermore, the location of bath flow into the choke section wandered with run time resulting in a bath flow appearance similar to when using the tubular bypass (Figure 71a).
- Including a segmenting wall (Figure 71c) resulted in a stagnating zone of helical form. The direction of this helix was opposite of the clockwise running conveyor screw. Only a small fraction of the bath was flowing and entered the choke section at one side of the segmenting wall. This observation indicates that in a free flowing bath the direction of flow inside the bath was not strictly vertical like at the bath wall, but also had a velocity component in circumferential, clockwise direction. Segmenting the bath then led to an accumulation of material at the segmenting wall. It is important to note that a similar bath flow was observed when operating this system at $p_{\text{amb}}$ and $V_{N}^{0} = 0$.
- To promote free bath flow in circumferential direction, a rectangular cardboard was inserted (Figure 71d) that smoothened the transition of
bypass tube to wall. However, this geometry led to the formation of a stagnation zone similar to when using the tubular bypass form. It was assumed that the decreased radial bath thickness at the bypass location promoted a compression of material between bypass and draught tube that subsequently stagnated at that location.

- Guiding the bath material into the choke section by using a trapezoidal cardboard insert (Figure 71e) appeared to improve bath flow on the side with the overhanging section. The stagnating region on that side was similarly wide as the cardboard insert. On the other side, however, there was still a significant accumulation of material at the bypass.

- Inserting an inverse triangular cardboard insert (Figure 71f) significantly improved the bath flow as the majority of the bath was fast flowing. Below the insert, a fraction of the bath was only moving very slowly, which motion was marginally stable and sometimes even stagnant. It was speculated that this improvement in bath flow arised from (i) a promoted guidance of material into the choke section by the overhanging cardboard on the right side, and (ii) the generation of a void in the bath below the overhanging cardboard on the left side, inside which the material from the gap between bypass and draught tube was able to flow downwards. Interestingly, with a wider triangular form (70 mm wide, $\theta_l = 18.5^\circ$), the width of the slow moving region was proportionally increased, too. Constructing the inverse triangular insert out of heat-resistant graphite felt slightly worsened bath flow by trend, presumably due to the increased friction of bath material at the graphite felt. This deterioration in bath flow quality, however, was not significant. When using the inverse triangular insert in combination with the high-area particle filter (Figure 71g), however, the bath flow was significantly worse than without the filter. A stagnation zone formed around the bypass that increased with run time and eventually blocked bath flow entirely. Also the insertion of the thermocouples ((Figure 71h) deteriorated bath flow and the fraction of the bath between bypass and thermocouple was stagnant.
Figure 71. Schematic views of the bath flow for different bypass forms: a) tubular, b) triangular \( (\theta_T \approx 15^\circ) \), c) segmenting wall, d) rectangular, e) trapezoidal, f) inverse triangular \( (\theta_T \approx 15^\circ) \), g) inverse triangular with the bypass particle filter included, and h) inverse triangular with the thermocouples included. Flow speed is denoted in (i) light blue and arrows with solid lines for fast flowing material (estimated \( v \approx 1 \text{ cm/s} \)), (ii) dark blue and arrows with dotted lines for slow flowing material \( (v \approx 0.1 \text{ cm/s}) \), and (iii) gray without arrows for stagnant material. Distances are shown in mm.
Effect of Outer Bath Diameter – With a smaller outer bath diameter (⌀52 mm) and without using the bypass particle filter, the bath flow was non-uniform with a stagnation zone being developed of similar form as the one observed in Figure 71a. However, the stagnation zone appeared to be smaller than with the larger bath diameter (⌀60 mm) and bath flow was therefore slightly improved. Using the high-area bypass particle filter did not significantly deteriorate the bath flow.

Effect of Reactor Tube Material – The effect of reactor tube material was studied by lining the inner surface of the Plexiglas tube with a paper that was coated with Al$_2$O$_3$ refractory paint (Alfa Aesar, aerosol spray). A 20 mm vertical gap between the graphite cone and the paper allowed a visual observation of the bath flow above the choke section.

- With the small reactor tube (⌀60x4 mm), bath flow was intermittent and frequently blocked completely due to material arching between reactor and draught tube. This observation was attributed to the increased friction of the C at the reactor wall.
- With the large reactor tube (⌀70x5 mm) and the inverse triangular bypass geometry, the bath flow was not significantly affected, except that the flow speed appeared to be slightly temporally fluctuating.

7.3.2.2.3 Final Geometry and Operational Recommendations

The extensive study of the effects of operational and geometrical changes on the bath flow quality resulted in following geometrical adaptions and operational recommendations for the hot tests.

1. In the hot tests, sweep and product gases should be solely removed from above the bath through the gas bypass (configuration B). Using only this configuration, however, endangers that the reaction products of the CTR Mg$_{(g)}$ and CO$_{(g)}$ may not be efficiently swept from the bath bulk as the sweep gas Ar was bypassed. Therefore, the rate of CTR may be
controlled by external mass transfer, i.e. by the thermodynamic equilibrium.

2. The chosen bypass geometry should be the inverse triangular one with $\theta = 15^\circ$ made of graphite felt.

3. The implementation of a particle filter on top of the gas bypass should be renounced in order to stabilize bath flow. This decision results in the drawback that some of the bath material may be removed from the bath recirculation system during testing. Moreover, a fraction of the removed bath material may deposit on the surface of the Mg precipitation tube confounding the deposit mass balance (91) and consequently precluding the determination of the reversion coefficient $Z_{Mg}$.

4. The long thermocouple reaching into the bath should be removed as it significantly distorts the bath flow. Consequently, bath temperature can be only measured by the short thermocouple that should be placed into the material discharge stream of one of the discharge windows.

5. The draught tube should not be brought to vibration as it does not significantly improve the bath flow when using the heat-resistant conveyor and wears the screw in addition.

6. The outer bath diameter should be kept at a value of 60 mm, as a smaller diameter ($\varnothing 52$ mm) leads to an arching of the bath between reactor wall and draught tube when they are made of $\text{Al}_2\text{O}_3$.

7. The bath recirculation should be initiated as follows to ensure a functioning bath recirculation at feed start:
   
   1. Close the globe valve in front of the vacuum pump and let $p_{\text{tot}}$ increase to 25 kPa.
   2. Start the recirculation with $v_{\text{recirculator}} = 600$ rpm.
   3. Reopen the globe valve to its original position to reduce $p_{\text{tot}}$ to initial value that results in bath expansion.
   4. Start the feeder while $p_{\text{tot}}$ is still decreasing.

8. Total sweep gas flow rate $V_N^0$ should be kept $\leq 0.5$ L$_N$/min.

9. Total pressure $p_{\text{tot}}$ should be kept $\geq 8$ kPa.

10. Initial bath amount $m_{\text{bath}}$ should be $\geq 50$ g.
7.3.3 Cold Flow Tests of the Bath Recirculation System – C Granules

7.3.3.1 Selection of the C Material

The granular C material was selected based on the two criteria (i) highest purity as possible, and (ii) a particle size that is as high as possible to increase the gas permeability of the bath, yet small enough to be transported by the recirculator. To find the optimum particle size, different materials listed in Table 14 were tested for their recirculation ability.

Testing the rod-shaped C (Chemviron AP3-60 and Norit RB2 H2) showed that both materials were conveyable in principle, yet jammed inside the draught tube. This jamming resulted in an extensive vibration of the recirculator that was accompanied by loud, hammering noises. It was suspected that the conveying action of these rods exposed the recirculator to significant mechanical stresses that may lead to its rupture. Therefore, C rods were considered unsuitable in general. Similar to the rod shaped material, the granular material with \( d = 3.4 \) mm (Envirocarb 207C) exposed the recirculator to significant vibrations and mechanical stresses making this material unsuitable as well. The recirculation ability of the granular material with \( d = 1.12 \) mm (Chemviron type 33) was significantly better compared to the other materials in terms of jamming and noise generation. However, particle size measurements after recirculating the material for 10 and 20 min, respectively, at \( \nu_{\text{recirculator}} = 400 \) rpm revealed a significant grinding of the material by the conveyor screw as illustrated in Figure 72. After 10 min of recirculation, \( d \) decreased from 1.12 mm to 0.50 mm. Interestingly, a further recirculation of another 10 min did not further grind the material significantly (\( d = 0.49 \) mm). This observation implied that particles primarily got grinded when they jammed between the draught tube wall and the flight tip that nominal screw clearance \( C_s \) was 0.5 mm. Consecutive tests at \( p_{\text{red}} \) revealed that the grinding action by the conveyor screw adversely affected the bath flow and the removal of the sweep gas through the bath floor (configuration A). Using the heat-resistant conveyor and the bottom bath part made of graphite (\( \theta_l = 22^\circ \)), recirculating a bath of \( m_{\text{bath}} = 80 \) g under a sweep of \( V_N^0 = 0.5 \) LN/min resulted in an increase in \( p_{\text{tot}} \) from \( \sim 3 \) to \( \sim 27 \) kPa. This pressure increase was attributed to the accumulation of fines on the bath floor that were produced by
the grinding process. Furthermore, a major fraction of the first uniform flowing bath stagnated resulting in a non-uniform, yet temporally stable bath flow. It was assumed that the non-uniformity was caused by the sweep gas that channeled through the bath at one location thereby promoting a one-sided bath flow.

![Graph showing particle size distribution](image)

Figure 72. Effect of C material grinding on the volume-based particle size distribution.

Based on the observed adverse effects of the grinding process on the recirculation performance, it was concluded that the optimum particle size for the selected material should be equal to the screw clearance $s$ of the recirculator screw (0.5 mm) in order to minimize the grinding progress. The selected material that matched the two criteria (purity and particle size) at best was given by the material Aquacarb 207C 14x40 with the properties shown in Table 14.

### 7.3.3.2 Tests at Ambient Pressure

The recirculation performance of the granular C bath (Aquacarb 207C 14x40) at $p_{amb}$ was investigated using the heat-resistant recirculator and the bottom bath part made of graphite ($\theta_n = 22^\circ$). The recirculation onset speed was evaluated
for $m_{\text{bath}} = 20\text{--}80 \text{ g}$. A bath with $m_{\text{bath}} = 20 \text{ g}$ was not conveyable, as the bath did not fill the entire choke section resulting in the discharge of transported material below the draught tube inlet. With $m_{\text{bath}} = 40 \text{ g}$ the choke section was almost entirely covered (distance of the bath level to the draught tube inlet $\sim 0.5 \text{ cm}$) and the bath started to recirculate at $v_{\text{spinning}}$ of 300 rpm. With amounts of $m_{\text{bath}} \geq 60 \text{ g}$ the onset speed decreased down to surprisingly low values of 20 rpm, the minimum limit of $v_{\text{recirculator}}$.

The determined bath speeds at the reactor wall are shown in Figure 73 as function of $v_{\text{recirculator}}$ for a granular C bath amounting to $m_{\text{bath}} = 110 \text{ g}$.

![Figure 73. Bath speed at the reactor wall below a discharge window with a granular C bath amounting to $m_{\text{bath}} = 110 \text{ g}$. Error bars indicate the standard deviation of the measurements.](image)

As illustrated by this Figure, the bath speed linearly increases with $v_{\text{recirculator}}$ from 0.1 (60 rpm) to 1.4 cm/s (600 rpm). The bath speed at location between two discharge windows was not measured, since the bath flow appeared to be uniform in circumferential direction. It interesting to note, however, that the temporal bath speed was fluctuating with a frequency appearing to be similar to $v_{\text{recirculator}}$. These
fluctuations were attributed to the wobbling screw inside the draught tube that presumably resulted in intermittent material intake.

7.3.3.3 Tests at Reduced Pressure

The recirculation performance of the granular C bath at $p_{rod}$ was examined using the heat-resistant recirculator and the bottom bath part made of graphite ($\theta_H = 22^\circ$). The sweep gas was removed through the bath floor (configuration A). Testing the recirculation ($v_{recirculator} = 400$ rpm) of a dried, granular C bath of $m_{bath} = 70$ g without the injection of sweep gas resulted in a uniform bath flow at a temporally stable $p_{tot}$ of $< 0.5$ kPa. Restarting the recirculation system after setting $\dot{V}_N^0$ to $0.15$ L$_N$/min ($p_{tot} \approx 0.9$ kPa) did not appear to change the bath flow that was still uniformly flowing over the whole bath circumference. However, total pressure started to increase with recirculation time as illustrated by Figure 74.

![Figure 74](image)

Figure 74. Increase in $p_{tot}$ over recirculation time for a granular C bath of $m_{bath} = 70$ g under a sweep of $\dot{V}_N^0 = 0.15$ L$_N$/min.
Starting from 0.9 kPa, $p_{\text{tot}}$ increased up to 7.6 kPa within 10 min recirculation time and only slowly started to approach a temporally stable value. A further increase in $\dot{V}_N^0$ of up to 0.5 L$_{\text{N}/\text{min}}$ resulted in a further increase in $p_{\text{tot}}$ to $>20$ kPa. Nevertheless, the bath flow was still uniform and did not seem to be affected by the increase in $\dot{V}_N^0$.

Similar to the material selection tests (section 7.3.3.1), the inspection of the bath floor after experimentation revealed a layer of compressed C fines on the felt. Therefore, the observed increase in $p_{\text{tot}}$ (Figure 74) was attributed to a temporal accumulation of these fines. As without any sweep gas flow $p_{\text{tot}}$ was temporally stable and no fines accumulated on the bath floor, it was concluded that the segregation of the fines observed at $\dot{V}_N^0 > 0$ was induced by the sweep gas flowing through the C bath bulk. As observed in the material selection tests (section 7.3.3.1), it was assumed that the segregating C fines originated from a grinding process of the C granules by the conveyor screw. Confirmation was given by recirculating a C bath of $m_{\text{bath}} = 70$ g in 10 min intervals at $p_{\text{amb}}$. Between each interval, a sample of the C bath (~2 g) was collected and analyzed for volume-based particle size distribution. The determined particle size distributions are shown Figure 75 in comparison to as-received C. After the first 10 min interval, the particle size decreased by about 0.1 mm (from $\bar{d} = 0.869$ to 0.773 mm) confirming a progressing grinding of the C by the recirculation screw. However, the grinding rate decreased with recirculation time ($\bar{d} = 0.755$ at 20 min and $\bar{d} = 0.751$ at 30 min) resulting in $\bar{d}$ starting to approach a constant value. Interestingly, the final mean particle size $\bar{d}$ approached a higher value in comparison to the material selection tests (section 7.3.3.1) that final $\bar{d}$ was only $\sim0.5$ mm. This observation was attributed to a gradual wearing of the recirculation screw resulting in a continuing increase of the tip clearance that, at the point of these tests was already as high as 0.75 mm.

Furthermore, the bath flow was uniform over the whole tested range of flow rates ($\dot{V}_N^0 = 0-0.5$ L$_{\text{N}/\text{min}}$), while with the material Chemviron type 33 (section 7.3.3.1) the bath flow was strongly non-uniform. This difference was attributed to the amount of fines in the C bath bulk that fraction presumably correlated with the extent of particle grinding. Support of this assumption was given by adding 3.5 g of C powders (5%$_{\text{w}}$ of $m_{\text{bath}}$) to the previously uniformly flowing C bath
that then switched the bath flow pattern to a strongly non-uniform one implying that bath flow uniformity was strongly affected by the fraction of fines inside the bath bulk.

![Graph showing particle size distribution](image)

Figure 75. Volume-based particle size distribution of the C granules illustrating the effect of particle grinding by the recirculation screw.

7.3.3.4 Comparison of the Recirculation Performances of C Powders vs. Granules

In the tests at $p_{\text{amb}}$, the most significant difference in the recirculation ability of powdery vs. granular C material was given by the onset $v_{\text{recirculator}}$. The comparison of the onset $v_{\text{recirculator}}$ of the two materials is illustrated in Figure 76 as function of bath volume $V_{\text{bath}}$. As shown by this Figure, the onset speed with C granules was up to 250 rpm lower. It was suspected that this difference could be attributed to a lower friction of the granular C on the screw surface compared to the powdery C. The lower the friction, the lower the required $v_{\text{recirculator}}$ to induce a relative motion between the screw flights and the conveyable material. Further indication of a lower friction was given by following observation: when
the recirculator filled with C granules was lifted above the bath surface level, the recirculator most of the time self-discharged; when it was filled with C powders, a vigorous shaking of the recirculator was required to discharge the material.

![Figure 76. Onset \( v_{\text{recirculator}} \) for stable bath recirculation of C powders and granules as function of \( V_{\text{bath}} \).](image)

Also at reduced total pressure \( p_{\text{red}} \) the recirculation ability of granular C was significantly better compared to the powdery C: a recirculating granular bath never blocked even though the sweep gas was directed through the C bulk (configuration A), while a powdery bath subjected to the gas sweep could not be recirculated at all with this gas removal configuration. Furthermore, with granular C no bath expansion/compression was observed with a temporally changing \( p_{\text{tot}} \).

In terms of recirculation ability, therefore, C granules were the preferable material choice. However, the partial grinding of the C granules by the recirculation screw brought the disadvantage of a clogging of the bath floor thereby severely restricting the lowest achievable \( p_{\text{tot}} \).
7.3.4 Hot Tests

7.3.4.1 Testing the Bath Recirculation System

The visual inspection of the bath after experimentation revealed a whitish layer on top of a black one implying that some of the feedstock (Al₂O₃, white) did not mix with the C bath (black). Both of the layers were slightly solidified and needed to be squished in order to return them to a powdery form. Regarding the Al₂O₃ layer, this solidification was attributed to a sintering of the fed material that is well known to proceed at temperatures as high as 1500°C.¹³⁵ The solidification of the C, however, was atypical since when the test was repeated without feeding Al₂O₃ into the recirculation system, the C bath retained in its powdery form after the experiment (see Figure 77).

Figure 77. Samples of recirculated and heated C baths diluted with Al₂O₃ (left) and undiluted (right).

Therefore, the solidification of the C bath was attributed to a presence of Al₂O₃ inside the bath that sintered during the test. To manifest the presence of Al₂O₃ in the C bath, the elemental composition of a sample of the consolidated bath was analyzed by EDS. Since the element Al was found inside the sample, the presence of Al₂O₃ in the C bath seemed confirmed. The dispersion of some of the fed Al₂O₃ within the bath implied that the bath recirculation must have functioned at feed start and only stopped after the fed Al₂O₃ sintered and
solidified the bath. The rest of the feed was then accumulated on top of it resulting in the two layers that were observed after the experiment. Therefore, one can conclude that a) the bath recirculation system passed the test because it worked until the bath solidified, and b) sintering of the feedstock potentially solidifies the bath and stops it from recirculating. This may also be true when the feedstock is comprised of an MgO-C mixture instead of Al₂O₃.

7.3.4.2 Evaluation of the Mg Production Performance of the Reactor

7.3.6.2.1 Mg Production Performance with Powdery C

The Mg production performance with powdery C reactant was evaluated by feeding an equimolar MgO-C mixture with a setpoint MgO feed rate of 19.3 mmol/min (v_{feeder} = 5 rpm) for 15 min into a recirculating bath of powdery, pretreated C with amount of m_{bath} = 50 g. Sweep and product gases were removed from the recirculation system through the bypass (configuration B).

The inspection of the reactor after experimentation revealed that ~50-75% of the bath and/or feedstock was removed from the recirculation system and retained in the Mg precipitation tube. Therefore, the Mg reversion coefficient Z_{Mg} was not determinable and estimated to be equal to 0.2. It was assumed that the removal of the material from the recirculation system was presumably a result of its fluidization by produced H₂ and CO.

The temporal amounts of H₂ and CO in the outlet as well as the recorded temperature trace are shown in the top part of Figure 78, while the effective MgO feed rate \( \dot{n}_{MgO}^0 \), the total pressure \( p_{tot} \) and the estimated range of the feed conversion \( X_{feed} \) are illustrated in the bottom part of Figure 78. The start of the bath recirculation (1) is shown by \( p_{tot} \) that was elevated from ~9 to 25 kPa and subsequently decreased again to its original value while the recirculation screw was turned on. The feed (2) was commenced immediately after start of the bath recirculation, thus (1) \( \approx \) (2). As a result of the commencing bath recirculation, the temperature – measured with the short thermocouple placed into the material stream – increased by ~ 5°C.
Figure 78. Outlet molar rates of CO and H₂, and measured temperature (top part), effective MgO feed rate $\dot{n}_{\text{MgO}}^0$, total pressure $p_{\text{tot}}$, and estimated MgO feed conversion $X_{\text{feed}}$ (bottom part) as function of feed time $t$ for a 15 min feed of an equimolar MgO-C mixture with a nominal MgO feed rate of 19.3 mmol/min into a recirculating, powdery C bath of $m_{\text{bath}} = 50$ g. ①: recirculation start; ②: feed start; ③: feed stop (Ar flow rates: $\dot{V}_{N,MFC\ 1}^0 = 0.05$ L N/min, $\dot{V}_{N,MFC\ 2}^0 = 0.35$ L N/min, and $\dot{V}_{N,MFC\ 3}^0 = 0.4$ L N/min. $T_{\text{SP}} = 1500^\circ\text{C}$).
It should be noted that the measurement location of the was at the top of the furnace chamber at which location the temperature was usually ~20°C lower, i.e. 1480°C than $T_{sp}$ of 1500°C. The increase in temperature after commencing the bath recirculation was thus attributed to a heating of the thermocouple by the slightly warmer conveyed C bath.

The effective MgO feed rate $\dot{n}_{MgO}$ was rather poor: the setpoint value of 19.3 mmol/min was reached only after ~5 min and subsequently fluctuated by up to 30% until it was stopped (③). The estimated MgO feed conversion $X_{feed}$ was very low and appeared to be constant in the range of ~0-0.14. This is also indicated by the temporal amounts of H₂ and CO in the outlet that were similar to each other. This implies that most of the produced CO originated from the reactions of C with H₂O and CO₂ (reactions (51) and (9)), respectively. It was assumed that the low MgO feed conversion was a result of (i) the removal of C bath and feedstock from the hot zone, and/or (ii) an inefficient removal of the products of the CTR ($Mg(g)$ and $CO(g)$) from the bath bulk, i.e. the CTR was in thermodynamic equilibrium.

**Prevention of Bath/Feedstock Removal from the Recirculation System**

In order to prevent a removal of material from the recirculation system, the test was repeated with the high-area bypass particle filter (Figure 69) implemented. After the feed start, however, the filter immediately started to clog resulting in an increase in $p_{tot}$ from ~10 to 85 kPa within the 15 min feed. Even with the particle filter implemented, some bath/feedstock material (~5g) was found in the cooling zone. The estimated range of the MgO feed conversion ($Z_{Mg}$ estimated equal to 0.2) was in the order of ~0-0.14, similarly to the test without the bypass particle filter (see Figure 78).

**Testing the Product Gas Removal Efficiency via the Gas Bypass**

In order to investigate the efficiency of the product gas removal when the gases were withdrawn from the recirculation system via the bypass (configuration B), tests in the absence of the C bath were conducted.
• In the first test, a MgO-C mixture with molar ratio C/MgO = 10 was fed for 30 min into the empty reactor with a setpoint MgO feed rate of 3.7 mmol/min ($v_{\text{feeder}} = 3.95$ rpm). The excess C in the feedstock accounted for the absent C bath. Sweep gas flow rates of $V_{N,\text{MFC}1} = 0.05$ L$_N$/min, $V_{N,\text{MFC}2} = 0.1$ L$_N$/min, and $V_{N,\text{MFC}3} = 0.2$ L$_N$/min were chosen and a bypass particle filter was implemented as to prevent a potential removal of the solid reactants from the hot zone.

• For the second test, the graphite bottom part was substituted by the cylindrical crucible (Figure 57) as to guide the sweep gas ($V_{N,\text{MFC}1} = 0.05$ L$_N$/min and $V_{N,\text{MFC}2} = 0.1$ L$_N$/min) through the reactant bulk and to increase the gas removal rate in comparison to the bypass configuration. The same feedstock composition, setpoint rate, and duration was chosen as the first test in order to be able to directly compare the observed kinetics of CTR.

In both tests, however, some unreacted feedstock was found along the walls of the Mg precipitation tube precluding the determination of $Z_{Mg}$ that was therefore assumed to be equal to 0.2. The estimated range of $X_{\text{feed}}$ of the first test is shown in Figure 79 along with the effective MgO feed rate $\dot{n}_{\text{MgO}}$ and the total pressure $p_{\text{tot}}$. As illustrated by this figure, $X_{\text{feed}}$ was low (~0-0.18) and did not significantly increase over feed time, similarly to the test with the equimolar MgO-C feed (see Figure 78). Total pressure increased with feed time from ~2 to 3 kPa that was attributed to a slight clogging of the bypass particle filter. When the sweep gas was guided through the reactants by using the cylindrical crucible (test 2, Figure 80), $X_{\text{feed}}$ first increased within the first 15 min and approached an approximately constant range of ~0.25-0.4. Also $p_{\text{tot}}$ increased in the course of the feed from ~2 up to 5 kPa, which was attributed to a filling of the crucible with feedstock thereby increasing the pressure drop between the recirculation system and the precipitation zone.

The comparison of $X_{\text{feed}}$ between the two tests (Figure 79 and Figure 80) showed that when the sweep was directed through the reactant bulk (test 2) instead of the bypass (test 1), the rate of CTR was approximately 3 times higher. This observation showed that rate of CTR was dependent on the gas removal rate.
and it was concluded that a removal of the product gases through the bypass (configuration B) was insufficient. Therefore, in all tests that used this gas removal configuration, the CTR was controlled by the thermodynamic equilibrium.

Figure 79. Effective MgO feed rate \( \dot{n}_{\text{MgO}}^0 \), total pressure \( p_{\text{tot}} \), and estimated MgO feed conversion \( X_{\text{feed}} \) as function of feed time \( t \) for a 30 min feed of an MgO-C mixture with molar ratio C/MgO = 10 at a nominal MgO feed rate of 3.7 mmol/min into the empty reactor. Sweep and product gases were withdrawn through the gas bypass (Ar flow rates: \( V_{\text{N,MFC1}}^0 = 0.05 \, \text{L}_N/\text{min}, \, V_{\text{N,MFC2}}^0 = 0.1 \, \text{L}_N/\text{min}, \) and \( V_{\text{N,MFC3}}^0 = 0.2 \, \text{L}_N/\text{min}. \) \( T_{\text{SP}} = 1500^\circ\text{C} \))

It is interesting to note that when the sweep was directed through the reactant bulk (test 2), \( X_{\text{feed}} \) reached a constant temporal value well below unity at feed times > 15 min. This observation indicated an approach to equilibrium control of the CTR even though the estimated \( p_{\text{CO}} \) (calculated with \( Z_{\text{Mg}} = 0.2 \) and \( p_{\text{tot}} = 5 \, \text{kPa} \)) in the recirculation system was significantly lower than the equilibrium value (≈1.1 vs. 3.4 kPa). The equilibrium control may therefore be explained by the filling of the crucible with reactants that forced the sweep gas to flow around the crucible through the gap between crucible and reactor wall. The gas composition inside the reactant bulk may therefore have been different from what
was measured in the effluent implying that the local partial CO pressure inside the reactant bulk may indeed have approached values as high as the equilibrium value of 3.4 kPa.

Figure 80. Effective MgO feed rate \( n^0_{\text{MgO}} \), total pressure \( p_{\text{tot}} \), and estimated MgO feed conversion \( X_{\text{feed}} \) as function of feed time \( t \) for a 30 min feed of an MgO-C mixture with molar ratio C/MgO = 10 at a nominal MgO feed rate of 3.7 mmol/min into a cylindrical crucible replacing the graphite bottom part. The sweep gas was directed through the reactant bulk and was withdrawn with product gases through the crucible bottom (Ar flow rates: \( \dot{V}_{\text{N, MFC 1}}^0 = 0.05 \text{ L}_N/\text{min} \) and \( \dot{V}_{\text{N, MFC 2}}^0 = 0.1 \text{ L}_N/\text{min} \). \( T_{\text{SP}} = 1500^\circ\text{C} \))

7.3.6.2.2 Mg Production Performance with Granular C

The Mg production performance with granular C reactant was evaluated by feeding equimolar MgO-C mixtures and setpoint MgO feed rates of 4, 5.5, and 11 mmol/min (\( v_{\text{feeder}} = 0.94, 1.4, \) and 2.8 rpm), respectively, for 30 min into recirculating granular baths amounting to \( m_{\text{bath}} \approx 70 \text{ g} \). The sweep gas flow rates were set to \( \dot{V}_{\text{N, MFC 1}}^0 = 0.05 \text{ L}_N/\text{min} \), \( \dot{V}_{\text{N, MFC 2}}^0 = 0.1 \text{ L}_N/\text{min} \), and \( \dot{V}_{\text{N, MFC 3}}^0 = 0.28 \text{ L}_N/\text{min} \) and were withdrawn along with the product gases through the bath floor (configuration A). In all tests, neither feedstock nor bath material appeared to have been withdrawn from the recirculation system allowing to determine the Mg reversion coefficient to values of \( Z_{\text{Mg}} = 0.15-0.21 \). Furthermore, the
recirculator was always filled with material after the tests implying that the bath was recirculating during the whole time the recirculator was running. The effective MgO feed rates $\dot{n}_{\text{MgO}}^0$, total pressures $p_{\text{tot}}$, and the range of the MgO feed conversions $X_{\text{feed}}$ are illustrated in Figure 81, Figure 82, and Figure 83 for the three setpoint MgO feed rates (4, 5.5, and 11 mmol/min). In addition, the top part of Figure 81 exemplary shows the outlet molar rates of H$_2$ and CO, and the measured temperature trace for the test with the setpoint MgO feed rate of 4 mmol/min.

In all three tests, similar observations were made:

- After the start of the bath recirculation (①) $p_{\text{tot}}$ significantly increased from ~3-7 kPa to ~9-11 kPa.
- The measured temperature increased after commencing the bath recirculation by ~5-10°C (exemplary shown in the top part of Figure 81).
- After the feed start (②), $p_{\text{tot}}$ further increased up to 15-17 kPa that was sometimes followed by pressure fluctuations/drops.
- The effective MgO feed rate $\dot{n}_{\text{MgO}}^0$ was low at the beginning and approached the setpoint rate only within 5-15 min after the feed start.
- The MgO feed conversion $X_{\text{feed}}$ was initially as high as ~0.6-1 but significantly decreased in the course of the feed approaching a range in the order of ~0.05-0.2 that was approximately constant with time.
- After feed stop (③) $p_{\text{tot}}$ decreased again by 3-4 kPa up to the bath recirculation stop (④).
- After the recirculation stop, the temperature decreased by ~3-5°C before the furnace was cooled down (as reflected by a fast temperature drop exemplary shown in Figure 81 at $t \sim 44$ min).
- After the tests, accumulated feedstock was discovered (i) at the wall of the funnel-shaped connection between the feeding system and the reactor head, and (ii) as a compressed layer on top of the bath floor (see Figure 119 in Appendix F).
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Figure 81. Outlet molar rates of CO and H₂, measured temperature (top Figure), effective MgO feed rate \( \dot{n}_{\text{MgO}}^0 \), total pressure \( p_{\text{tot}} \), and estimated MgO feed conversion \( X_{\text{feed}} \) (bottom Figure) as function of feed time \( t \) for a 30 min feed of an equimolar MgO-C mixture with a nominal MgO feed rate of 4 mmol/min into a recirculating, granular C bath amounting to \( m_{\text{bath}} \approx 70 \text{ g} \). ①: recirculation start; ②: feed start; ③: feed stop; ④: recirculation stop (Ar flow rates: \( V_{N,\text{MFC 1}}^0 = 0.05 \text{ L}_N/\text{min} \), \( V_{N,\text{MFC 2}}^0 = 0.1 \text{ L}_N/\text{min} \), and \( V_{N,\text{MFC 3}}^0 = 0.28 \text{ L}_N/\text{min} \). \( T_{\text{sp}} = 1500^\circ\text{C} \).
Figure 82. Effective MgO feed rate $n_{\text{MgO}}^0$, total pressure $p_{\text{tot}}$, and MgO feed conversion $X_{\text{feed}}$ as function of feed time $t$ for a 30 min feed of an equimolar MgO-C mixture with a nominal MgO feed rate of 5 mmol/min into a recirculating, granular C bath amounting to $m_{\text{bath}} \approx 70$ g. ①: recirculation start; ②: feed start; ③: feed stop; ④: recirculation stop (Ar flow rates: $\dot{V}_{N,\text{MFC 1}} = 0.05$ L\textsubscript{N}/min, $\dot{V}_{N,\text{MFC 2}}^0 = 0.1$ L\textsubscript{N}/min, and $\dot{V}_{N,\text{MFC 3}}^0 = 0.28$ L\textsubscript{N}/min. $T_{\text{SP}} = 1500^\circ \text{C}$)

Based on the given observations, following course of events was concluded: After the start of the bath recirculation (①) fines from the C bath accumulated on the bath floor led to the increase in $p_{\text{tot}}$ (as observed in the cold flow tests at reduced pressure). Then, the feed was commenced (②) and part of the feedstock that entered the recirculation system reacted, while part of the feedstock segregated from the bath and started to accumulate on the bath floor. It was assumed that at this point majority of the sweep gas flowed through the bath bulk and removed the product gases from the reaction zone through the bath floor.
Figure 83. Effective MgO feed rate $\dot{n}^0_{\text{MgO}}$, total pressure $p^0_{\text{tot}}$, and MgO feed conversion $X^0_{\text{feed}}$ as function of feed time $t$ for a 30 min feed of an equimolar MgO-C mixture with a nominal MgO feed rate of 11 mmol/min into a recirculating, granular C bath amounting to $m_{\text{bath}} \approx 70 \text{ g}$.  

1: recirculation start; 2: feed start; 3: feed stop; 4: recirculation stop

(Ar flow rates: $V^0_{N,\text{MFC 1}} = 0.05 \text{ L N/min}$, $V^0_{N,\text{MFC 2}} = 0.1 \text{ L N/min}$, and $V^0_{N,\text{MFC 3}} = 0.28 \text{ L N/min}$. $T_{SP} = 1500^\circ \text{C}$)

High MgO feed conversions $X^0_{\text{feed}}$ indicated that the rate of CTR was kinetically controlled. The low MgO feed rates $\dot{n}^0_{\text{MgO}}$ at the beginning were the result of partial feedstock deposition at the wall of the funnel-shaped connection between the feeding system and the reactor head. With increasing feed time, more feedstock accumulated on the bath floor as implied by a further increase in $p^0_{\text{tot}}$ that gradually enclosed the gas outlet and the sweep gas was redirected through the gap between the graphite bottom part and the reactor wall thereby bypassing the major fraction of the bath bulk. Consequently, the CTR product gases were not swept anymore from the bath bulk resulting in a decrease in the MgO feed conversion $X^0_{\text{feed}}$ as the CTR became controlled by external mass transfer, i.e. the CTR was in thermodynamic equilibrium. Support of this assumed course of events was given by the comparison between $X^0_{\text{feed}}$, increase in $p^0_{\text{tot}}$ from feed start $\left( p^0_{\text{tot}} (t) - p^0_{\text{tot}} (0) \right)$, and effective MgO feed rate $\dot{n}^0_{\text{MgO}}$ (Figure 84).
Figure 84. Comparison of the effective MgO feed rates $\dot{n}_{\text{MgO}}^0$, MgO feed conversions $X_{\text{feed}}$, and increases in total pressure from feed start $p_{\text{tot}}(t) - p_{\text{tot}}(0)$ for the three tests with setpoint MgO feed rates of 4 (green, solid lines/triangles), 5 (black, dashed lines/squares), and 11 mmol/min (blue, dotted lines/circles).

With higher $\dot{n}_{\text{MgO}}^0$, more feedstock accumulated on the bath floor resulting in a faster increase in $p_{\text{tot}}$ and therefore in a faster decrease in product gas removal rate as indicated by the faster decrease in $X_{\text{feed}}$. The fluctuations/drops in $p_{\text{tot}}$ in the course of the feed were attributed to the formation of gas channels in the gap between graphite bottom part and reactor tube or in the annular felt ring thereby increasing the sweep gas removal rate from the recirculation system.
The decrease in $p_{\text{tot}}$ after feed stop (3) (Figure 81, Figure 82, and Figure 83) was attributed to (i) a decrease in gas production because of the vanishing reactants $\text{H}_2\text{O}$ and $\text{CO}_2$ and (ii) further formation of gas channels increasing the gas removal rate from the recirculation system.

### 7.4 Summary and Conclusions

A novel reactor was designed and tested for the production of Mg metal via CTR at temperatures as high as 1500°C and total pressures as low as 2 kPa. The reactor consisted of a heated bath of either powdery (average size $\sim 44$ µm) or granular C (average size $\sim 0.87$ mm) into which an equimolar MgO-C mixture was fed by a screw feeder. The feedstock was mixed with the C bath using a draught tube screw conveyor that recirculated the bath in vertical direction. Below the recirculation system, a cooling zone allowed the precipitation of the gaseous Mg product. The screw feeder was designed for allowing a feed of mixtures of cohesive MgO in powdery form and C in the form of either powders or granulates with C/MgO molar ratios ranging from 1 – 10 at total pressures in the order of $\sim 1$ kPa. The feeder comprised a novel method to achieve accurate feeding rates: two brushes were attached at the hopper outlet that were kept in front-and-back movement by the screw. The brushes acted as moving walls and prevented an arching of the feedstock over the screw surface. Testing the bath recirculation system at ambient temperature and pressure showed high bath recirculation rates up to six times per minute while the vertical bath speed appeared to be uniform in circumferential direction with both powdery and granular C materials. The tests at reduced total pressure (1-10 kPa) showed that when using C powders as bath material, the sweep gas needed to be bypassed around the bath to prevent a blockage of the bath due to powder compression. This bypass, however, disturbed the bath flow provoking the development of a bath stagnation zone around the bypass that progressed with run time and eventually led to bath recirculation stop. With an optimized bypass geometry, this stagnation zone could be kept small and non-progressing. When using C granules as bath material the sweep gas could be directed through the bath without stopping the bath recirculation. However, a partial grinding of the granules by the recirculation
screw resulted in a segregation of fines that gradually clogged the gas outlet and restricted the lowest achievable total pressure to \( \sim 10 \) kPa. Testing the bath recirculation system at 1500°C and \( p_{\text{tot}} \approx 2-10 \) kPa showed a functioning bath recirculation for both, C powders and C granules. The evaluation of the Mg production performance of the reactor using C powders as bath material and feedstock component showed that a bypassing of the sweep gas resulted in an insufficient product gas removal and the CTR was consequently in thermodynamic equilibrium with MgO feed conversions as low as 0-0.14. Using C granules as bath material and feedstock component, high initial MgO feed conversions of 0.6-1 were observed that however decreased down to 0.05-0.2 in the course of the feed. It was assumed that the decrease in MgO feed conversion was a result of insufficient product gas removal that decreased with feed time due to a redirection of the sweep gas around the bath bulk, as the gas outlet of the recirculation system gradually clogged by segregated feedstock.
8 Summary and Outlook

8.1 Summary

This work examines the production of Mg metal via the carbothermic reduction of MgO. It has been shown that within the temperature and pressure range of 1375–1450°C and 1-2 kPa, respectively, Mg(g) is produced via MgO dissociation and MgO reduction with CO while the former prevails the reaction with a ratio of ~2:1. These pathways generate O₂ and CO₂ as the intermediates that diffuse and react with C, thereby sustaining the Mg production. It is also argued that the MgO dissociation pathway may have been confused with the MgOₙ₋₁-C(s) boundary reaction advocated by previous investigators, which relies on the direct contact of the solid reactants.

In order to explore the rate-controlling parameters of the MgO dissociation pathway, powdery MgO-C blends were subjected to a temperature of 1400°C and ~2 kPa total pressure for 30-60 min. The gaseous Mg product was combusted with CO₂ before cooling in order to preclude the proceeding of the reverse overall reaction in the cooling zone. This procedure allowed the acquisition of kinetic data by monitoring the product gas amount and composition without requiring its correction for the confounding effect of the reverse overall reaction. It was observed that the CTR seemed to pass through two reaction stages that were reflected by (i) a fast decrease in the rate of CTR during the first 5-10 min (stage 1) and (ii) a slow decrease in the rate of CTR at reaction times > 5-10 min (stage 2). It was found that during stage 1, both MgO dispersion and the surface area of MgO were key parameter controlling the rate of CTR. While the rate of CTR scaled with MgO dispersion, i.e. effective interparticle O₂ transport distance, the fast decrease in the rate of CTR in stage 1 was a result of MgO sintering that reduced the MgO surface area. During stage 2, the CTR was speculated to be dominated by MgO reduction with CO that rate appeared to be controlled by the consumption of the intermediate CO₂ by C.
Equipped with these findings, a novel reactor concept was designed and tested for the production of Mg metal via CTR at temperatures as high as 1500°C and total pressures as low as 2 kPa. The reactor consisted of a heated bath of either C powders (average size ~44 µm) or C granules (average size ~0.87 mm) into which an equimolar MgO-C mixture was fed by a screw feeder. The feedstock was mixed with the C bath using a draught tube screw conveyor that recirculated the bath in vertical direction. Below the recirculation system, a cooling zone allowed the precipitation of the gaseous Mg product. Using C powders as bath material and feedstock component resulted in MgO feed conversions as low as 0-0.14, because the product gases Mg and CO were only insufficiently removed, i.e. the CTR was in thermodynamic equilibrium. Using C granules as bath material and feedstock component, high initial MgO feed conversions of 0.6-1 were observed that however decreased down to 0.05-0.2 in the course of the feed. It was assumed that the decrease in MgO feed conversion was a result of insufficient Mg and CO product gas removal that decreased with feed time due to a redirection of the sweep gas around the bath bulk, as the gas outlet of the recirculation system gradually clogged by segregated feedstock.

8.2 Outlook

8.2.1 Reaction Mechanism and Kinetics

It has been conclusively shown that at temperatures around 1400°C and 1-2 kPa total pressure, Mg is produced via dissociation of MgO and reduction of MgO with CO that reactions are sustained by the removal of the intermediate O₂ and CO₂ with C. However, while MgO dissociation was the prevailing source of Mg under the conditions investigated, it remains unclear whether at higher temperatures and/or pressures, still MgO dissociation or MgO reduction with CO dominates total Mg production. Thus, it would be of great interest to further investigate in that matter. Similarly, investigating the kinetics of CTR led to the successful identification of the key rate-controlling parameters MgO surface and MgO dispersion. However, this investigation was restricted to a temperature of 1400°C, total pressures of ~2 kPa, C/MgO molar ratios in the order of 1 to 4, and
using only one source of C. Thus, it would be of great importance for the further development to identify the key rate-controlling parameters in a wider range of temperatures, pressures, C/MgO molar ratios, and C sources.

Moreover, it still has not been conclusively shown so far, which of the two considered methods to enhance Mg production – reactant milling or using high C/MgO ratios – is the preferred route as to achieve the lowest overall energy requirements of the CTR. To decide between these two routes, it would be very beneficial to further develop the suggested reactor concept in order to explore the potential of using high C/MgO ratios for Mg production. If the method of high C/MgO ratios would be dismissed, it would be of great importance to further investigate the effect of using pellets or loose powder blends on the rate of CTR.

8.2.2 Further Development of the Suggested Reactor Concept

The tested reactor suffered primarily from a) a non-uniform bath flow when using C powders and b) an inefficient removal of the product gases due to (i) sweep gas bypassing when using C powders, and (ii) gas outlet clogging when using C granules.

It is suggested that the bath flow may be significantly improved by using a screw with conical tip as schematically illustrated in Figure 85a. In this case, the C bath sits on the rotating screw instead of the stationary, conical-shaped bath bottom. Thus, partial bath blockage may be effectively prevented. In order to improve the removal of the product gases, porous bath walls may be incorporated as shown in Figure 85b. This brings the advantage that the product gases can be removed in radial instead of axial direction reducing the product gas transport distance through the bath. Thus, the gas bypass may not be required. However, the pore size of the bath wall is considered a critical parameter: selecting the pore size to large may result in a removal of particles from the bath. Selecting the pore size to small may lead to pore clogging by fines that hinders the product gas removal.

Moreover, the selection of a different mixing system may be of interest. Most promising would be a horizontally aligned mixer that uses paddles, ploughshares, or ribbons to agitate and mix the bath, as in this case bath blockage would not
occur. However, care must be taken in preventing a potential clogging of the particle filter at the outlet, which may be accomplished by continuously cleaning it with the agitator.

Furthermore, providing that the suggested modifications or other methods bring the reactor to a reasonable Mg production performance, a heat and mass transfer model could be developed for optimizing the reactor design and its scaling.

![Figure 85](image_url)

Figure 85. Reactor modification with a conical screw (a) and in combination with gas permeable (porous) bath walls (b).

8.2.2.1 Reactor Scale-Up

Under the assumption that with the suggested modifications shown in Figure 85 or with other methods the reactor provides a promising Mg production performance, it may be scaled up according to the schematic outlined in Figure 86. The reactor is split into multiple tubes that are interconnected at top and bottom. One tube comprises the recirculator, while the others contain the C bath. The reactant feed enters the reactor from the top. The bath-containing tubes are
made of porous material in order to remove the product gases in radial direction. The product gas removal may be supported by sweep gas added through e.g. injection lances reaching into the bath tubes.

Figure 86. Schematic view of the scaled reactor

With this multi-tube arrangement, the reactor may be scaled up without significantly increasing the diameter of the tubes. Thus, the heat transfer and product gas removal is enhanced as compared to a one-tube reactor concept. Theoretically, a multi-tube arrangement may also be achieved by just multiplying the number of recirculation systems. However, this would also require a multiple of recirculators and feeders thus significantly complicating the reactor design.

Another problem is faced when it comes to long-term operation of the reactor. With increasing operational time, solid impurities contained in the MgO and C
reactants may accumulate gradually diluting the C bath. Thus, if no way is found to remove these impurities from the bath, it needs to be regularly replaced.

Finally, the use of concentrated solar energy as source of the process heat should be investigated requiring thus a suitable reactor design allowing to be heated by concentrated solar radiation.
Appendix A

Methods Employed for the Analysis of Solid Materials

A.1 Weight Fraction of Impurities in the Solid Materials

Magnesium Oxide and Aluminum Oxide

The weight fractions of H$_2$O and CO$_2$ in MgO and in Al$_2$O$_3$ were determined in a thermogravimetric analyzer (Netzsch 409 STA). Samples of the materials were heated in Ar up to 1000°C at a rate of 20°C/min and held at this temperature until a constant final sample mass was obtained. The amount of released CO$_2$ ($m_{CO_2}$) was calculated from the temporal mole fraction of CO$_2$ entrained in the product gas ($y_{CO_2}(t)$) (see equations (30)-(34)) that was measured with a gas chromatograph (Varian CP-4900). The amount of released H$_2$O ($m_{H_2O}$) was determined according to

$$m_{H_2O} = m_{imp} - m_{CO_2}$$  \hspace{1cm} (96)

where $m_{imp}$ corresponded to the measured mass loss, i.e. the total mass of released H$_2$O and CO$_2$.

Carbon

The as-received charcoal contained moisture, volatile matter, and ash. To determine their weight fractions, a sample of as-received charcoal was placed into a thermogravimetric analyzer (Netzsch 409 STA), heated to 105°C in Ar at a rate of 20 °C/min, and then kept at this temperature for 30 minutes. The measured mass loss corresponded to the mass of moisture contained in the as-received material. Then, the temperature was increased to 1000°C at a rate of 20 °C/min and then maintained constant for 30 minutes to determine the mass loss due to evaporation of the volatile matter. The atmosphere was then switched to a 20% Ar-air and kept until the sample mass stabilized indicating the mass of ash after the complete oxidation of C.
A.2 Properties of Solid Materials

Properties of solid materials that were determined by commonly applied methods using commercially available devices were:

- **specific surface area**: BET (Micrometrics TriStar 3000 N\textsubscript{2} adsorption analyzer)
- **volume-based mean particle size and distribution**: LDS (HORIBA LA-950 laser scattering analyzer)
- **visual appearance**: SEM (Hitachi TM-1000) and TEM (JEOL JEM-1400 Plus)
- **elemental composition**: EDS (Hitachi TM-1000)

Further properties were determined as follows:

- **bulk density**: The bulk density of a powdery material was calculated by loosely filling a vessel (e.g. a pill glass) with material and dividing its amount through the vessel volume. The vessel volume was either known (i.e. written on the vessel) or determined by filling it with water and dividing its mass with the known density (0.998 g/cm\textsuperscript{3} at 20°C\textsuperscript{136}).

- **kinematic friction angle and coefficient**: The kinematic friction angle and coefficient between a powder and a flat ground of certain material was estimated using a custom-made apparatus shown in Figure 87. First, a powder sample (MgO-C mixture or C alone) was placed on a flat block of ground material (aluminum, alumina, or graphite) and slightly pressed into rectangular form with a spatula. Then, the angle of the mobile arm was stepwise increased and at each step, the powder sample was gently pushed downwards as to overcome the static friction. The angle at which the powder continued to move downwards after the gentle push corresponded to the kinematic friction angle ($\phi$) and was recorded on the board behind the arm. The kinematic friction coefficient was then calculated according to

$$
\mu = \tan(\phi)
$$

(97)
It is evident, however, that this method has a limited accuracy. Thus, each angle measurement was repeated 10 times, averaged, and reported within an uncertainty range that shows the standard deviation of the measurements.

Figure 87. Photograph of the apparatus used to determine the kinematic friction angle and coefficient between a powdery material and a flat ground material.

- angle of repose and particle-particle friction coefficient: To estimate the angle of repose \( \phi_i \), the powdery material was poured through a funnel onto a flat surface in order to form a heap. The angle of repose was then calculated from the heap radius \( r_{\text{heap}} \) and heap height \( h_{\text{heap}} \) according to

\[
\phi_i = \tan^{-1}\left( \frac{h_{\text{heap}}}{r_{\text{heap}}} \right),
\]  

(98)

while the particle-particle friction coefficient \( \mu_i \) was calculated by

\[
\mu_i = \tan(\phi_i)
\]  

(99)
The accuracy of this method was limited because of the cohesiveness of the powdery material. Therefore, each measurement was repeated 5 times, averaged, and reported within an uncertainty range that shows the standard deviation of the measurements.
Appendix B

The Limits for Unequal MgO and C Consumption by the CTR

The overall reaction of the CTR (reaction (4)) assumes that equal amounts of MgO and C are consumed by the CTR, i.e. the rates of the individual reaction steps are equal:

$$r_6 = r_7 \quad (100)$$

$$r_8 = r_9 \quad (101)$$

However, this assumption was false if substantial amounts of the intermediates O$_2$ and CO$_2$, respectively, were removed by the product gas resulting in lower extents of reactions (7) and (9) with respect to reactions (6) and (8), i.e.

$$\frac{r_7}{r_6} = \epsilon \quad (102)$$

$$\frac{r_9}{r_8} = \gamma \quad (103)$$

with $\epsilon$ and $\gamma$ as stoichiometric coefficients relating the rates of the reaction steps to each other. In this case, reaction (4) would not accurately describe the overall reaction for the CTR. Assuming that the CTR proceeds via the MgO dissociation pathway (reactions (6) and (7)), the overall reaction would then needed to be rewritten as

$$\text{MgO}_\text{(s)} + \epsilon \text{C}_\text{(s)} \Leftrightarrow \text{Mg}_\text{(g)} + 0.5(1-\epsilon)\text{O}_2\text{(g)} + \epsilon\text{CO}_\text{(g)} \text{ with } \epsilon \in \{0,1\} \quad (104)$$

Under the assumption that the CTR proceeds via MgO reduction with CO (reactions (8) and (9)), the overall reaction would then be given as

$$\text{MgO}_\text{(s)} + \gamma \text{C}_\text{(s)} \Leftrightarrow \text{Mg}_\text{(g)} + (1-\gamma)\text{CO}_2\text{(g)} + (2\gamma-1)\text{CO}_\text{(g)} \text{ with } \gamma \in \{0.5,1\} \quad (105)$$
However, the differences between the rates of reactions (6) and (7) and between the rates of reactions (8) and (9) can be neglected, if the stoichiometric coefficients $\varepsilon$ and $\gamma$ do not deviate significantly from unity, which maximum allowable deviation was selected to be 1%, i.e.

$$\varepsilon \geq 0.99$$ \hfill (106)

$$\gamma \geq 0.99$$ \hfill (107)

For given partial pressures of Mg and CO, the minimum limits of $\varepsilon$ and $\gamma$ can be calculated as follows: the differences between reactions (6) and (7) and between reactions (8) and (9) are expressed by the O$_2$ balance and CO$_2$ balance, respectively, given as

$$r_5 - r_6 = 2\dot{n}_{O_2}$$ \hfill (108)

$$r_7 - r_8 = \dot{n}_{CO_2}$$ \hfill (109)

Reformulation with

$$y_i = \frac{\dot{n}_i}{\dot{n}_{tot}} = \frac{p_i}{p_{tot}},$$ \hfill (110)

with $r_5 = \dot{n}_{Mg}$, $r_7 = \dot{n}_{Mg}$, and combination with (102) and (103), respectively, results in

$$\varepsilon = 1 - 2\frac{p_{O_2}}{p_{Mg}}$$ \hfill (111)

$$\gamma = 1 - \frac{p_{CO_2}}{p_{Mg}}$$ \hfill (112)

The minima of $\varepsilon$ and $\gamma$ are reached with maximum, i.e. equilibrium $p_{O_2}$ and $p_{CO_2}$, respectively, that are determined by solving the equation set

$$K_6(T) = p_{Mg} p_{O_2}^{0.5}$$ \hfill (113)
\[ K_8(T) = \frac{p_{\text{Mg}}p_{\text{CO}_2}}{p_{\text{CO}}} \] (114)

using the equilibrium constants \( K_i(T) \) that were extracted from the HSC database\textsuperscript{35}. Thus combining equations (111)-(113) and (112)-(114) results in

\[ \varepsilon = 1 - 2 \frac{K_6(T)^2}{p_{\text{Mg}}} \] (115)

\[ \gamma = 1 - \frac{K_8(T)p_{\text{CO}}}{p_{\text{Mg}}} \] (116)

**B.1 Extent of the Stoichiometric Coefficient \( \varepsilon \)**

The extent of the stoichiometric coefficient \( \varepsilon \) is shown in Figure 88 as function of temperature \( (T) \) and partial pressure of Mg \( (p_{\text{Mg}}) \). As illustrated by this figure, in the range of the experimental conditions used in this work \( (T \leq 1500^\circ\text{C} \text{ and } p_{\text{Mg}} \geq \sim 10 \text{ Pa in average}) \), \( \varepsilon \) is significantly higher than the selected limit of 0.99 implying approximately equal consumptions of MgO and C by the CTR. Thus, the usage of reaction (4) as overall reaction for the CTR is in this case justified.

**B.2 Extent of the Stoichiometric Coefficient \( \gamma \)**

*Equal Mg and CO partial pressures*

Under a sweep comprising Ar alone, equations (105) implies that \( p_{\text{Mg}} \) is always equal or higher than \( p_{\text{CO}} \). To assess the minimum limit of \( \gamma \) one may thus assume that the two partial pressures are equal (see equation (116)), i.e.

\[ p_{\text{CO}} = p_{\text{Mg}}. \] (117)

The extent of \( \gamma \) for this case is shown in Figure 89 as function of temperature and Mg partial pressure. As illustrated by this figure, under the conditions relevant for this work \( (T \leq 1500^\circ\text{C} \text{ and } p_{\text{Mg}} \geq \sim 10 \text{ Pa in average}) \), \( \gamma \) is always
higher than the selected limit of 0.99. Thus, also in this case it is justified to use reaction (4) as overall reaction for the CTR, since approximately equal amounts of MgO and C are consumed by it.

*Elevated CO partial pressure with respect to Mg*

With an oxidant (O$_2$ or CO$_2$) or CO present in the sweep, the CO partial pressure was elevated by up to 95 Pa with respect to the Mg partial pressure (see section 3.3.2.2), i.e.

\[
p_{\text{CO}} = p_{\text{Mg}} + 95 \text{ Pa}
\]  

(118)

This elevation facilitates the consumption of MgO by the CTR with respect to C and thus leads to extents of $\gamma$ as illustrated in Figure 90 that are significantly lower at a given $p_{\text{Mg}}-T$ set compared to equal Mg and CO partial pressures (see Figure 89). Nevertheless, under the conditions relevant for this work ($T \leq 1450^\circ\text{C}$ and $p_{\text{Mg}} \geq \sim 10$ Pa in average), $\gamma$ is still higher than the selected limit of 0.99 justifying the usage of reaction (4) as the overall reaction of the CTR.

![Figure 88. Extent of the stoichiometric coefficient $\varepsilon$ as function of temperature and partial pressure of Mg ranging from 1 to 100 Pa.](image-url)
Figure 89. Extent of the stoichiometric coefficient $\gamma$ as function of temperature and partial pressure of Mg with the partial pressure of CO assumed equal to Mg.

Figure 90. Extent of the stoichiometric coefficient $\gamma$ as function of temperature and partial pressure of Mg with the partial pressure of CO elevated by 95 Pa compared to Mg.
Appendix C

Supporting Information for Chapter 3

C.1 Experimental Program

Phase 1

Objectives

For a selected set of \( N_{\text{C}}^0 \), \( N_{\text{MgO}}^0 \), and the flow rate and the composition of the \( \text{O}_2-\text{Ar} \) sweep determine

1. \( \tau_{\text{t} \text{O}_2} \),
2. \( \tilde{N}_{\text{C} \text{O}_2} \left( \tau_{\text{t}} \right) \) and \( \tilde{N}_{\text{C} \text{O}_2} \left( \tau_{\text{t}} \right) \),
3. \( \tilde{P}_{\text{CO} \text{O}_2} \),
4. the extent of CTR

Materials

MgO-C blend and C in the absence of MgO.

Method

1. Set the fraction of \( \text{O}_2 \) in the sweep.
2. Set the flow rate of the \( \text{O}_2-\text{Ar} \) sweep.
3. Set the initial amount of C to \( N_{\text{C}}^0 \).
4. Set the initial amount of MgO to \( N_{\text{MgO}}^0 \).
5. Blend \( N_{\text{C} \text{O}_2}^0 \) with \( N_{\text{MgO}}^0 \).
6. Subject the MgO-C blend prepared in step 5 to the standard temperature program.
7. Determine the temporal amounts of CO in the product gas and the extent of CTR.
8. Subject \( N_{\text{C} \text{O}_2}^0 \) alone to the standard temperature program but in the absence of MgO.
9. Determine the temporal amounts of CO in the product gas.
10. Compare the temporal amounts of CO in the product gas acquired in steps 7 and 9.

11. Locate the onset of CTR (τ₁|O₂) as the moment at which the temporal amounts of CO acquired in steps 7 and 9 start deviating from each other.

12. Determine \( \tilde{N}_{C|O_2}(\tau_i), \tilde{N}_{C|O_2}(\tau_f), \) and the partial pressure of CO (\( \tilde{p}_{CO|O_2} \)) from the test exploiting C in the absence of MgO (step 8).

**Phase 2**

**Objectives**

1. Establish a combination of the (i) the initial amount of C (\( N^0_{C|CO_2} \)) and (ii) \( CO_2-Ar \) sweep gas mixture flow rate and composition that for the selected temperature program defined in phase I leads to \( \tilde{N}_{C|CO_2}(\tau_i) \approx \tilde{N}_{C|O_2}(\tau_i) \) and \( \tilde{N}_{C|CO_2}(\tau_f) \approx \tilde{N}_{C|O_2}(\tau_f) \) (see Figure 3).

2. Quantify the CO partial pressure (\( \tilde{p}_{CO|CO_2} \)) for the previously established combination of reaction conditions.

3. Determine the extent of CTR

**Materials**

MgO-C blend and C in the absence of MgO.

**Method**

1. Set the initial fraction of \( CO_2 \) in the sweep.
2. Set the initial flow rate of the \( CO_2-Ar \) sweep.
3. Set the initial amount of C to \( N^0_{C|CO_2} \).
4. Set the initial amount of MgO to \( N^0_{MgO} \) (the same value used in step 4 of phase 1).
5. Blend \( N^0_{C|CO_2} \) with \( N^0_{MgO} \).
6. Subject the MgO-C blend prepared in step 5 to the standard temperature program.
7. Determine temporal amounts of CO in the product gas.
8. Subject \( N^0_{C|CO_2} \) alone to the standard temperature program but in the absence of MgO.

10. Compare the temporal amounts of CO in the product gas acquired in steps 7 and 9.

11. Locate the onset of CTR ($\tau_{i}^{\text{CO}_2}$) as the moment at which the temporal amounts of CO acquired in steps 7 and 9 start deviating from each other.

12. Determine $\tilde{N}_{C|\text{CO}_2}^{\tau_{i}}$ and $\tilde{N}_{C|\text{CO}_2}^{\tau_{f}}$ from the test exploiting C in the absence of MgO (step 8).

13. Check if $\tilde{N}_{C|\text{CO}_2}^{\tau_{i}} \approx \tilde{N}_{C|\text{CO}_2}^{\tau_{f}}$ and $\tilde{N}_{C|\text{CO}_2}^{\tau_{i}} \approx \tilde{N}_{C|\text{CO}_2}^{\tau_{f}}$. If not, go back to steps 1-3 and vary the CO$_2$ fraction, and/or the sweep flow rate, and/or $\Lambda_{C|\text{CO}_2}^{\text{MgO}}$.

14. For the initial amount of C, the CO$_2$ fraction in the sweep, and the flowrate of the CO$_2$-Ar sweep identified at steps 1-3, determine the partial pressure of CO ($\tilde{p}_{\text{CO}|\text{CO}_2}$).

15. Blend $\Lambda_{\text{MgO}}^{\text{MgO}}$ with the $\Lambda_{C|\text{CO}_2}^{\text{MgO}}$ identified in step 3.

16. Subject the MgO-C blend prepared in step 15 to the standard temperature program under the CO$_2$-Ar sweep gas mixture flow rate and CO$_2$ fraction identified at steps 1 and 2.

17. Determine the extent of CTR.

**Phase 3**

**Objectives**

Quantify the extent of CTR in the absence of any oxidant in the sweep to account for the effects of

1. the consumption of C by the oxidants observed at step 12 of phase 1, and
2. the difference in the partial pressures of CO observed in step 12 of phase 1 and step 14 of phase 2.

**Materials**

MgO-C blends.
Method

1. Prepare two pairs of MgO-C blends, each by mixing the initial amount of MgO selected in phase 1 with the initial amounts of $C \cdot \tilde{N}_C(\tau_1)$ and $\tilde{N}_C(\tau_f)$ identified in Phase 1.

2. Subject each of the prepared blends to the same temperature program under the Ar sweep and the CO-Ar sweep having the CO partial pressure equal to $\tilde{p}_{\text{co}}|_{\text{co}_2}$ observed in step 14 of phase 2.

C.2 Outlet Molar Rates of Product Gases

![Graph showing outlet molar rates of CO, CO$_2$, and O$_2$ for MgO-C and C alone subjected to the O$_2$-Ar sweep at $T_{sp}=1375^\circ$C.]

Figure 91. Outlet molar rates of CO, CO$_2$, and O$_2$ for MgO-C and C alone subjected to the O$_2$-Ar sweep at $T_{sp}=1375^\circ$C.
Figure 92. Outlet molar rates of CO, CO$_2$, and O$_2$ for MgO-C and Al$_2$O$_3$-C blends subjected to the O$_2$-Ar sweep at $T_{sp}$ = 1400°C.

Figure 93. Outlet molar rates of CO, CO$_2$, and O$_2$ for MgO-C and Al$_2$O$_3$-C blends subjected to the O$_2$-Ar sweep at $T_{sp}$ = 1450°C.
Figure 94. Outlet molar rates of CO and CO$_2$ for MgO-C and C alone subjected to the CO$_2$-Ar sweep at $T_{sp}=1400^\circ$C.

Figure 95. Outlet molar rates of CO and CO$_2$ for MgO-C and C alone subjected to the CO$_2$-Ar sweep at $T_{sp}=1450^\circ$C.
Figure 96. Outlet molar rates of CO at $T_{SP} = 1375^\circ C$ for (a) Ar alone with $N_C^{0,1} \approx \tilde{N}_C(\tau_1) = 47.5$ mmol and (b) CO-Ar sweep with $N_C^{0,1} \approx \tilde{N}_C(\tau_f) = 32.9$ mmol.
Figure 97. Outlet molar rates of CO at $T_{sp} = 1400^\circ$C for (a) Ar alone with $N_{C\text{high}}^{\text{r}} \approx \dot{N}_C(\tau_1) = 47.5$ mmol and (b) CO-Ar sweep with $N_{C\text{low}}^{\text{r}} \approx \dot{N}_C(\tau_f) = 31.6$ mmol.
Figure 98. Outlet molar rates of CO at $T_{sp} = 1450^\circ C$ for (a) Ar alone with $N_{C_{\text{high}}}^0 \approx \dot{N}_C(\tau_I) = 47.5$ mmol and (b) CO-Ar sweep with $N_{C_{\text{low}}}^0 \approx \dot{N}_C(\tau_f) = 26.6$ mmol.
Figure 99. CO molar rates observed at $T_{SP}$ =1375°C with $N_{C_{ref,1}}^0 \approx \tilde{N}_c(\tau_1) = 47.5$ mmol and $N_{MgO}^0 = 49.6$ mmol under CO-Ar (black solid line), CO$_2$-Ar (green dashed line) and O$_2$-Ar (blue dotted line).

C.3 Repeatability of the Experimental Setup

The repeatability of the experimental setup was inspected by reacting two MgO-C blends prepared in the same way as described in section 3.2.4 under the same experimental conditions. The results are shown in Figure 100.
C.4  Effect of Atmosphere on MgO Sintering

The effect of atmosphere on MgO sintering was evaluated by subjecting samples of the as-received MgO powder (Sigma Aldrich, no. 342793, see Table 1 in section 3.2) to the temperature program illustrated in Figure 101 (Netzsch 409 STA thermogravimeter) as follows. First, the sample was heated under 0.1 L N/min N\(_2\) (Messer 4.7) with a rate of 20°C/min to a desired temperature \(T_{\text{sint}}\) ranging from 900-1200°C and kept there for 5 min to ensure the complete dissociation of the Mg(OH)\(_2\) and MgCO\(_3\) impurities from the samples. The samples were then sintered for additional 15 min under 0.1 L\(_N\)/min of N\(_2\) (Messer 4.7), 20.5% O\(_2\)-N\(_2\) (synthetic air, Messer) or 20.5% CO\(_2\)-N\(_2\) (obtained by mixing N\(_2\) (Messer 5.0) with CO\(_2\) (Messer 4.8)). Upon the completion of the sintering step, the samples were cooled at a rate of 20°C/min. The SSA’s of the samples were analyzed using the BET method (Micrometrics TriStar 3000 N\(_2\) adsorption analyzer) in Figure 102. While this figure does indicate a significant decrease
from the SSA of the as-received MgO (141 m$^2$/g) with an increase in the sintering temperature, the sintering atmosphere does not seem to have an effect.

Figure 101. MgO sintering conditions.

Figure 102. Effect of O$_2$ and CO$_2$ on MgO surface area during sintering.
C.5 Assessment of the Average Effective Partial Pressures of Mg in the Hot Zone Based on the Experimentally Observed Mg Production

The average partial pressures of Mg in the hot zone during the comparison runs under the O$_2$-Ar and CO$_2$–Ar sweeps ($\bar{p}_{Mg}\mid_{int}$) were assessed based on the average production rate of Mg by the CTR ($\bar{n}_{Mg}\mid_{int}$) calculated as

$$\bar{n}'_{Mg}\mid_{int} = \left[\frac{\xi_{i} (\tau_{f})}{\tau_{f} - \tau_{i}}\right]\mid_{int} \quad (119)$$

where $\xi_{i} (\tau_{f})\mid_{int}$ is the extent of the CTR and $(\tau_{f} - \tau_{i})\mid_{int}$ is the total reduction time. Because of the high dilution of the product gas with Ar ($y_{Ar}(t) \approx 0.9-0.95$), the total molar rate did not change significantly between the hot zone and the outlet, i.e.

$$\dot{n}(t) \approx \dot{n}'(t) \quad (120)$$

which allowed calculating the average partial pressure of Mg in the hot zone as

$$\bar{p}_{Mg}\mid_{int} = \left[\frac{\bar{n}'_{Mg}}{\bar{n}} \bar{p}_{tot}\right]\mid_{int} \quad (121)$$

As the extents of CTR were only approximated within the uncertainty range bound by the maximum possible amount of deposited C, the corresponding ranges for $\bar{p}_{Mg}\mid_{int}$ are listed in Table 17.

Table 17. Uncertainty ranges of the average partial pressures of Mg in the hot zone under the O$_2$-Ar and CO$_2$-Ar sweep.

<table>
<thead>
<tr>
<th>$T_{sp}$ ($^\circ$C)</th>
<th>$\bar{p}<em>{Mg}\mid</em>{O_2}$ (Pa)</th>
<th>$\bar{p}<em>{Mg}\mid</em>{CO_2}$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1375</td>
<td>10-16</td>
<td>25-31</td>
</tr>
<tr>
<td>1400</td>
<td>12-19</td>
<td>27-34</td>
</tr>
<tr>
<td>1450</td>
<td>16-22</td>
<td>28-35</td>
</tr>
</tbody>
</table>
C.6 Assessment of the Partial Pressures of Mg in the Hot Zone Expected from the Equilibrium of MgO Dissociation and MgO Reduction with CO

\( O_2\)-Ar sweep

The high limit of the equilibrium partial pressures of Mg in the hot zone resulting from reaction (6)

\[
\begin{align*}
  p_{\text{Mg,eq}} |_{O_2} &= \left[ \frac{K_6 (T)}{(p_{O_2})^{0.5}} \right] \left|_{O_2} \right. \\
  (122)
\end{align*}
\]

can be estimated under the \( O_2\)-Ar sweep using the outlet molar rates of \( O_2 \) shown in Figure 12 and Figure 93 considering that these rates could only be lower than the \( O_2 \) molar rates in the hot zone because of the potential additional consumption of \( O_2 \) in the cooling zone via reactions (13) and (14). Therefore, as the outlet \( O_2 \) molar rates can be considered as a lower limit of the \( O_2 \) molar rates in the hot zone, i.e. \( \dot{n}_{O_2}(t) |_{O_2} < \dot{n}'_{O_2}(t) |_{O_2} \), and invoking equation (120) one may bound the \( O_2 \) partial pressure in the hot zone as

\[
\begin{align*}
  p_{O_2}(t) |_{O_2} \geq \left[ \frac{\dot{n}_{O_2}(t)}{n(t)} p_{\text{tot}}(t) \right] |_{O_2} \\
  (123)
\end{align*}
\]

The results of the calculations via equations (122) and (123) are shown in Table 18. One should note that no result could be reported for \( T_{sp} = 1450^\circ C \), as the partial pressure of \( O_2 \) may have been zero for a part of the experiment.
Table 18. Low limits of the O\textsubscript{2} molar rates in the hot zone and the corresponding high limits of the equilibrium partial pressures of Mg of reaction (6) in the hot zone under the O\textsubscript{2}-Ar sweep.

| \(T_{SP} \) (°C) | \(p_{O_2|O_2} \) (Pa) | \(p_{Mg,eq|O_2} \) (Pa) |
|------------------|------------------|------------------|
| 1375             | 1.7              | \(9\cdot10^{-6} \) |
| 1400             | 0.2              | \(5.4\cdot10^{-5} \) |
| 1450             | 0                | (-)              |

**CO\textsubscript{2}-Ar sweep**

Under the CO\textsubscript{2}-Ar sweep, the equilibrium partial pressures of Mg\textsubscript{(g)} \(p_{Mg,eq|CO_2} \) resulting from reaction (8) may be estimated based on equation (12) that was reformulated as

\[
p_{Mg,eq|CO_2} = K_8(T) \left[ \frac{p_{CO}}{p_{CO_2}} \right]_{CO_2}
\]  

(124)

However, the additional consumption of both CO and CO\textsubscript{2} in the cooling zone via reverse reactions (4) and (8) precludes the direct determination of the \(p_{CO|CO_2} \) and the \(p_{CO_2|CO_2} \) based on the outlet molar rates. These partial pressures could still be estimated as follows.

- Compared to the outlet molar CO rate \(\left( \dot{n}_{CO} \right)_{CO_2} \), the molar rate of CO in the hot zone \(\left( \dot{n}'_{CO} \right)_{CO_2} \) may have been either (i) higher due to the consumption of CO in the cooling zone by the reverse reaction (4) depositing C, or (ii) lower due to the production of CO via reverse reaction (8) proceeding either in the hot and/or cooling zone. The molar rates of CO in the hot zone were the highest under the assumption that reverse reaction (8) proceeded in the hot zone only. In this case, the material balance of CO between hot zone and outlet is given as

\[
\dot{n}_{CO} \big|_{CO_2} \left( t \right) = \left[ \dot{n}'_{CO} \left( t \right) - \dot{n}_{C,dep} \left( t \right) \right]_{CO_2}.
\]  

(125)
with \( \dot{n}_{\text{C,dep}}(t)|_{\text{CO}_2} \) as the deposition rate of C (i.e. the consumption rate of \( \text{CO} \)) in the cooling zone. Assuming that \( \dot{n}_{\text{C,dep}}(t)|_{\text{CO}_2} \) scales proportionally with \( \dot{n}'_{\text{CO}}(t)|_{\text{CO}_2} \), i.e. the reaction order of the reverse reaction (4) is unitary with respect to \( \text{CO} \), \( \dot{n}_{\text{C,dep}}(t)|_{\text{CO}_2} \) can be written as

\[
\dot{n}_{\text{C,dep}}(t)|_{\text{CO}_2} = \left[ Z_{\text{CO}} \cdot \dot{n}'_{\text{CO}}(t) \right]_{\text{CO}_2},
\]  

(126)

with \( Z_{\text{CO}} \) as the fraction of \( \dot{n}'_{\text{CO}}(t)|_{\text{CO}_2} \) consumed that is constant with time. Solving equation (126) for \( \dot{n}'_{\text{CO}}(t)|_{\text{CO}_2} \) and combining with equation (125) yields

\[
\dot{n}_{\text{CO}}(t)|_{\text{CO}_2} = \left[ \dot{n}_{\text{C,dep}}(t) \left( \frac{1}{Z_{\text{CO}}} - 1 \right) \right]_{\text{CO}_2}.
\]  

(127)

By integrating equation (127) over the total time of the CTR \((\tau_\text{II} - \tau_1)\), and considering that

\[
\left[ N_{\text{C,dep}}(\tau_\text{II}) - N_{\text{C,dep}}(\tau_1) \right]_{\text{CO}_2} = N_{\text{C,dep}}(\tau_f)|_{\text{CO}_2},
\]  

(128)

allows evaluating the fraction \( Z_{\text{CO}} \) as

\[
Z_{\text{CO}} = \left[ \frac{N_{\text{C,dep}}(\tau_f)}{N_{\text{CO}}(\tau_\text{II}) - N_{\text{CO}}(\tau_1) + N_{\text{C,dep}}(\tau_f)} \right]_{\text{CO}_2}.
\]  

(129)

The molar rate of \( \text{CO} \) in the hot zone can be estimated by combining equations (125) and (126)

\[
\dot{n}'_{\text{CO}}(t)|_{\text{CO}_2} = \left[ \left( \frac{1}{1 - Z_{\text{CO}}} \right) \dot{n}_{\text{CO}}(t) \right]_{\text{CO}_2}
\]  

(130)

resulting in the values shown in Table 19.

- The molar rate of \( \text{CO}_2 \) in the hot zone \( \dot{n}'_{\text{CO}_2}(t)|_{\text{CO}_2} \) could have only been higher than the outlet \( \text{CO}_2 \) molar rates \( \dot{n}_{\text{CO}_2}(t)|_{\text{CO}_2} \) because reverse reaction 4 consumes \( \text{CO}_2 \). Thus, the low limit of \( \dot{n}'_{\text{CO}_2}(t)|_{\text{CO}_2} \) are given as (see Table 19)


\[ n'_{\text{CO}_2}(t)|_{\text{CO}_2} \geq \dot{n}'_{\text{CO}_2}(t)|_{\text{CO}_2}. \] (131)

With \( p_{\text{CO}}/p_{\text{CO}_2} = \dot{n}'_{\text{CO}}/\dot{n}'_{\text{CO}_2} \), the values of \( p_{\text{Mg,eq}}|_{\text{CO}_2} \) calculated via equation (124) are listed in Table 19.

Table 19. Fractions of CO spent on the depositing C in the cooling zone, high limits of molar CO rates in the hot zone, low limits of molar CO\(_2\) rates in the hot zone, and corresponding high limits of the reaction (8) equilibrium partial pressures of Mg\(_{\text{(g)}}\) expected in the hot zone under the CO\(_2\)-Ar sweep.

| \( T_{\text{SP}} \) (°C) | \( Z_{\text{CO}} \) (-) | \( \dot{n}'_{\text{CO}}|_{\text{CO}_2} \) (mmol/min) | \( \dot{n}'_{\text{CO}_2}|_{\text{CO}_2} \) (mmol/min) | \( p_{\text{Mg,eq}}|_{\text{CO}_2} \) (Pa) |
|----------------|----------------|----------------|----------------|----------------|
| 1375           | 0.041          | 1.7            | 0.023          | 0.07           |
| 1400           | 0.042          | 1.9            | 0.013          | 0.24           |
| 1450           | 0.045          | 2.0            | 0.007          | 1.18           |
Appendix D

Supporting Information for Chapter 4

D.1 Additional SEM and TEM Photographs

Figure 103. TEM photograph of as-received MgO

Figure 104. TEM photograph of presintered MgO.
Figure 105. SEM photograph of an MgO-C blend prepared with presintered MgO with equimolar C/MgO ratio.

Figure 106. SEM photograph of an MgO-C blend prepared with as-received MgO with equimolar C/MgO ratio.
Figure 107. SEM photograph of an MgO-C blend prepared with as-received MgO with C/MgO molar ratio equal to 4.
Figure 108 TEM photographs of residual MgO recovered from MgO-C blends prepared with as-received MgO with initial C/MgO molar ratios of (a) 2, (b) 3, and (c) 4.

D.2 Correction of the Product Gas for Gas Dispersion

Generally, elements of a gas flow passing through a vessel may spend different amounts of time inside the vessel before exiting as they get axially dispersed. The temporal distribution of these elements exiting the vessel is commonly referred to as residence time distribution (E) of the gas. Thus, the product gas flow traces \( \dot{n}_{\text{CO}} \) and \( \dot{n}_{\text{CO}_2} \) acquired at the reactor outlet needed to be corrected for their dispersion in order to correctly determine the rate of CTR. Mathematically, the modification of a gas flow rate of species \( i \) exiting the CTR
zone \( \left( \dot{n}'_i \right) \) by the residence time distribution \( E \) can be expressed by the convolution integral \(^99\), i.e.

\[
\dot{n}_i = E \ast \dot{n}'_i
\]  

(132)

with \( \dot{n}_i \) representing the flow rate of species \( i \) in the outlet. Knowing \( \dot{n}_i \) and \( E \), the gas flow rate at the CTR zone exit \( \dot{n}'_i \) can be calculated by deconvoluting \( \dot{n}_i \) with \( E \). This operation was performed using Matlab (R2015b), while the residence time distribution \( E \) was determined experimentally using CO\(_2\) as tracer gas.

To determine \( E \), total pressure of the reactor was first reduced by opening the globe valve in front of the vacuum pump and setting Ar and CO\(_2\) flow rates to 0.5 and 0.05 L\(_N\)/min, respectively. Subsequently, the reactor was heated under continuing gas flow at a rate of 20\(^\circ\)C/min to the setpoint temperature \( T_{sp} = 1400\(^\circ\)C \) and held there. Then, the inlet CO\(_2\) flow rate was increased by 0.025-0.05 L\(_N\)/min with the mass flow controller MFC 2 that resulted in a step in the CO\(_2\) flow rate at the CTR zone exit \( \left( \dot{n}'_{CO_2} \right) \). The step in \( \dot{n}'_{CO_2} \) was assumed to be ideal, since the residence time of the CO\(_2\) in the injection tube was estimated < 1 second. At a given time \( t \) after the step in \( \dot{n}'_{CO_2} \), the product gas composition was analyzed with the gas chromatograph and \( \dot{n}_{CO_2} \) was determined according to equations (30)-(34). Proper temporal resolution of \( \dot{n}_{CO_2} \) was attained by repeating the procedure and varying the time \( t \) of the product gas composition analysis. The residence time distribution \( E \) then corresponded to the derivative of the temporal increase in the outlet CO\(_2\) flow rate brought into dimensionless form, which is called the \( F\)-curve\(^99\).

The determined \( E \) and \( F \) curves are shown in Figure 109 for a step in \( \dot{n}'_{CO_2} \) by 0.025 L\(_N\)/min at time \( t = 0 \). As illustrated by this figure, the complete amount of CO\(_2\) that entered the reactor exited within ~55 seconds.
Figure 109. Normalized increase in $\dot{n}_{CO_2}$ (F-curve) and residence time distribution $E$ in the outlet for a step in the CO$_2$ flow rate at CTR zone exit ($\dot{n}'_{CO_2}$) of 0.025 L$_N$/min.

Effect of Volume Flow Rate on the Residence Time Distribution

The residence time distribution $E$ in a particular experimental setup, however, changes with gas velocity that in turn is a function of the total volume flow rate $\dot{V}_{tot}$

$$\dot{V}_{tot} = \frac{\dot{n}_{tot}RT}{P_{tot}}.$$  \hspace{1cm} (133)

Thus, with a change in total molar flow rates ($\dot{n}_{tot}$), total pressures ($P_{tot}$), or temperature ($T$) the residence time distribution $E$ may change accordingly.

To evaluate the effect of an increase in total molar flow rate $\dot{n}_{tot}$ on $E$, the size of the step in $\dot{n}'_{CO_2}$ was increased to 0.05 L$_N$/min that resulting $F$-curve is illustrated in Figure 110. As illustrated by this figure, an increase in $\dot{n}_{tot}$ did not affect the $F$-curve implying that $\dot{V}_{tot}$ and therefore $E$ was unaltered. This
observation was attributed to the total pressure $p_{\text{tot}}$ that increased proportionally with an increase in $n_{\text{tot}}$, thus

$$\frac{\dot{n}_{\text{tot}}}{p_{\text{tot}}} = \text{constant} \quad (134)$$

The linear relationship between $\dot{n}_{\text{tot}}$ and $p_{\text{tot}}$ can be explained by regarding the pumping speed curve (given in m$^3$/h) as function of inlet pressure of the used vacuum pump (Pfeiffer Vacuum, ACP15), which data is provided by the manufacturer$^{137}$. In the range of $\sim$0.04-1 kPa, the pumping speed, i.e. $V_{\text{tot}}$ is approximately constant implying that in this range $\dot{n}_{\text{tot}}$ and $p_{\text{tot}}$ are linearly dependent at a given temperature (see equation (133). It is important to note that at the CTR zone exit, the range of $p_{\text{tot}}$ being linearly dependent on $\dot{n}_{\text{tot}}$ is at a higher level than at the inlet of the vacuum pump, because the particle filtration system and piping components between CTR zone exit and vacuum pump inlet introduced a pressure drop in direction of flow.

![Figure 110. Effect of total molar flow rate and temperature on gas dispersion](image-url)
To evaluate the effect of \( T \) on \( E \), the measurements were repeated with a step in \( \dot{n}_{CO}^{'} \) of 0.025 L\textsubscript{N}/min with the reactor being at ambient temperature (\( T_{amb} \)). As illustrated in Figure 110, the effect of \( T \) on the \( F \)-curve and therefore on \( E \) was small. Thus, in the CTR experiments comprising both, a non-isothermal and an isothermal section (see section 4.1.4.4), the difference of \( T \) on \( E \) was neglected and the product gas was corrected using the \( E \) curve acquired at \( 1400^\circ \text{C} \).

**Effect of Gas Dispersion on the Product Gas Flow**

The effect of dispersion on the product gas flow is shown in Figure 110 that compares the molar rate of CO in the outlet (\( \dot{n}_{CO} \)) to the calculated rate at CTR zone exit \( \dot{n}'_{CO} \). Because of the small time scales of \( E \) (< 1 min) with respect to total CTR reaction time (30 min), the two molar CO rates \( \dot{n}_{CO} \) and \( \dot{n}'_{CO} \) are very similar.

![Figure 111. Effect of gas dispersion of \( \dot{n}'_{CO} \) on \( \dot{n}_{CO} \) at \( T_{sp} = 1400^\circ \text{C} \).](image-url)
Appendix E

Prediction of the Conveyor Throughput Rates

To predict the material throughput rates of both the feed screw and the recirculation screw, existing conveyor models from literature\textsuperscript{134, 138, 139} were used. Generally, the mass throughput rate of a conveyor screw ($Q_m$) is defined as

$$ Q_m = \eta_v V_p \rho_b n $$

(135)

with $\eta_v$ as the volumetric efficiency, $V_p$ as the volume of the conveyor screw per pitch, $\rho_b$ as the bulk density of the conveyed material, and $n$ as the screw revolution speed. The volumetric efficiency $\eta_v$ is given as

$$ \eta_v = \eta_f \eta_{VR} $$

(136)

where $\eta_f$ corresponds to the fullness efficiency, i.e. the fraction of screw volume $V_p$ filled with material, and $\eta_{VR}$ corresponds to the vortex efficiency. Generally, the vortex efficiency $\eta_{VR}$ is dependent on screw radius $r \in [R_c, R_s]$ and is defined by the helix angle of particle motion ($\gamma (r)$) and the screw helix angle ($\alpha (r)$), i.e.

$$ \eta_{VR} (r) = \frac{\tan (\lambda (r))}{\tan (\alpha (r)) + \tan (\lambda (r))} $$

(137)

as inferred from the velocity diagram of element motion.\textsuperscript{134, 138, 139} The screw helix angle $\alpha (r)$ is given as

$$ \alpha (r) = \frac{p}{2 \pi r} $$

(138)

while the helix angle of particle motion $\lambda (r)$ was calculated differently for the feed screw and the recirculation screw, respectively. The overall vortex efficiency is then determined by integrating $\eta_{VR} (r)$ over the screw radius according to \textsuperscript{134}
\[ \eta_{VR} = \frac{2}{\left( R_o^2 - R_c^2 \right)} \int_{R_c}^{R_o} \eta_{VR}(r) r dr \]  

(139)

**Feed Screw**

For the feed screw, the model of Yu and Arnold\textsuperscript{138} was used. This model also simplifies the determination of \( \eta_{VR} \); instead of integrating the radially dependent \( \eta_{VR}(r) \) over the screw radius, an average, i.e. “equivalent” value \( \eta_{VReq} \) was calculated at radius position \( r = R_{eq} \) defined as\textsuperscript{138,139}

\[ R_{eq} = R_o \sqrt{\frac{1 + \left( \frac{R_c}{R_o} \right)^2}{2}}. \]  

(140)

Equation (137) is thus transformed into

\[ \eta_{VReq} = \frac{\tan(\lambda_{eq})}{\tan(\alpha_{eq}) + \tan(\lambda_{eq})} \]  

(141)

with \( \alpha_{eq} = \alpha(R_{eq}) \) determined by equation (138) and \( \tan(\lambda_{eq}) \) given as

\[ \tan(\lambda_{eq}) = \frac{\pi(R_o + R_c) - \mu_s p}{p + \pi \mu_s (R_o + R_c)} \]  

(142)

which equation is inferred from a force component analysis of material on the flight surface.\textsuperscript{138} The coefficient \( \mu_s \) corresponds to the friction coefficient of material on the flight surface.

**Recirculation Screw**

For the recirculation screw, the helix angle of particle motion \( \lambda(r) \) was calculated using the model of Roberts\textsuperscript{134}. Inferred from a force component analysis of material on the flight surface, \( \lambda(r) \) can be determined from
\[
\frac{r \omega^2}{g} = \left[ 1 + \frac{\tan(\lambda(r))}{\tan(\alpha(r))} \right] \frac{k_r \sin(\alpha(r) + \phi_s)}{\mu \cos(\alpha(r) + \phi_s + \lambda(r)) - k_s} - k_s
\]  

(143)

with \( k_r = (1 - \mu_b k_s) \) and \( k_s = 2k_j q_f (p/2R_o) \). The radial-to-vertical pressure ratio \( k_j = p_r/p_v \) ranging from \(-0.4 – 1\)\(^{134}\) was assumed to be equal to 0.5. The coefficient \( \mu_b \) denotes the friction coefficient of material at a boundary, which corresponds (i) for \( r < R_o \) to the particle-to-particle friction coefficient denoted as \( \mu_i \), and (ii) for \( r = R_o \) to the friction coefficient of material at the draught tube, denoted as \( \mu_d \). The coefficient \( \phi_s \) corresponds to the friction angle of material at the screw surface.

**Material Properties**

The required material properties for calculating \( Q_m \) of the feed and the recirculation screw are listed in Table 20 and Table 21, respectively. They were experimentally determined according the methods outlined in Appendix A using either powdery, equimolar MgO-C feedstock or dried, powdery C, respectively.

Table 20. Material properties of powdery, equimolar MgO-C feedstock required to calculate \( Q_m \) of the feed screw.

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk density ( \rho_b )</td>
<td>0.32 g/cm(^3)</td>
</tr>
<tr>
<td>kinematic coefficient of friction ( \mu_s ) on aluminum</td>
<td>0.9 ± 0.1</td>
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<table>
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<th>property</th>
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<tr>
<td>bulk density $\rho_b$</td>
<td>0.22 g/cm$^3$</td>
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<tr>
<td>kinematic friction coefficient $\mu_d$ on Al$_2$O$_3$</td>
<td>0.7±0.1</td>
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<tr>
<td>kinematic friction coefficient $\mu_d$ on Plexiglas</td>
<td>0.6±0.1</td>
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<tr>
<td>kinematic friction angle $\phi_s$ on graphite</td>
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<tr>
<td>kinematic friction angle $\phi_s$ on steel</td>
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</tr>
<tr>
<td>particle-particle friction coefficient $\mu_i$</td>
<td>0.78±0.06</td>
</tr>
</tbody>
</table>
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<table>
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  - Feed start; 
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1: recirculation start; 2: feed start; 3: feed stop; 4: recirculation stop

(Ar flow rates: \( \dot{V}_{\text{N,MFC } 1}^0 = 0.05 \text{ L}_N/\text{min} \), \( \dot{V}_{\text{N,MFC } 2}^0 = 0.1 \text{ L}_N/\text{min} \), and \( \dot{V}_{\text{N,MFC } 3}^0 = 0.28 \text{ L}_N/\text{min} \). \( T_{\text{SP}} = 1500^\circ \text{C} \))

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1: recirculation start; 2: feed start; 3: feed stop; 4: recirculation stop

(Ar flow rates: \( \dot{V}_{\text{N,MFC } 1}^0 = 0.05 \text{ L}_N/\text{min} \), \( \dot{V}_{\text{N,MFC } 2}^0 = 0.1 \text{ L}_N/\text{min} \), and \( \dot{V}_{\text{N,MFC } 3}^0 = 0.28 \text{ L}_N/\text{min} \). \( T_{\text{SP}} = 1500^\circ \text{C} \))

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1: recirculation start; 2: feed start; 3: feed stop; 4: recirculation stop

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