Magnesium Production by the Pidgeon Process Involving Dolomite Calcination and MgO Silicothermic Reduction: Thermodynamic and Environmental Analyses

M. Halmann,* A. Frei,† and A. Steinfeld‡§

Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Rehovot 76100, Israel, Solar Technology Laboratory, Paul Scherrer Institute, 5232 Villigen, Switzerland, and Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

Thermochemical equilibrium calculations indicate the possibility of considerable fuel savings and CO2 emission avoidance in the three steps of the Pidgeon process: (a) calcination of dolomite; (b) production of ferrosilicon from quartz sand, coal, and iron oxide; (c) silicothermic reduction of calcined dolomite by ferrosilicon to magnesium. All three steps should benefit from application of concentrated solar energy as the source of high-temperature process heat, while the first two steps may be adapted to the coproduction of syngas. For the production of ferrosilicon, an experimental study was carried out by thermogravimetry as a model for a solar-driven process. The net reaction at 1823 K was shown to be represented by Fe2O3 + 4SiO2 + 11C → 2FeSi(s) + 10CO(g) + SiC(s) + SiO2(g), confirmed by gas chromatographic analysis of the evolved CO and by XRD identification of the solid products FeSi and SiC. This product mixture agrees with that predicted for the thermochemical equilibrium, but differs from that reported in the literature for the electric arc process.

1. Introduction

The use of metallic magnesium is growing very rapidly, mainly for the production of light metal alloys. The silicothermic reduction of calcined dolomite, CaMg(CO3)2, to metallic magnesium using the abundantly available dolomite mineral was pioneered by Lloyd M. Pidgeon in Canada during World War II. This process has subsequently been replaced, mainly in the U.S.A., Canada, Russia, and Israel, by the electrochemical reduction of fused magnesium chloride, derived from brines or seawater. A potential alternative method of magnesium production would involve the carbothermic reduction of MgO at temperatures above 1773 K, which results in the formation of Mg(g), CO, and CO2. A main technological challenge of this path is to avoid the recombination of Mg with the carbon oxides. However, the vacuum carbothermic reduction of CaO–MgO (calcined dolomite) to Mg has been reported using a moderate vacuum of 1.3 × 10−3 bar at about 1673 K. During the past 20 years the Pidgeon process achieved a strong revival, particularly in China as the major producer of Mg, reaching 72.5% of the world primary production of this metal, which in 2006 amounted to 726 000 tons. The advantages of this silicothermic process are, besides the plentiful occurrence of dolomite, its relative simplicity and the formation of high-purity Mg. However, this process is plagued by severe environmental pollution along with heavy CO2 emissions. Its global warming impact has been estimated by a detailed life-cycle study to be 42 kg of CO2-eq/kg of Mg ingot. The Pidgeon process is based on three reaction steps.

(a) Conversion of dolomite by calcination to “dolime”, a mixture of MgO and CaO. This step, carried out at 1573 K, is highly endothermic, and releases CO2 both from the reaction itself and from the fuel combusted for process heat:

\[
\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \quad (1)
\]

(b) The production of the alloy ferrosilicon for the reduction of dolime. It is produced via a carbothermic reaction by applying an electric arc on a mixture of quartz sand, carbon (coke, petcoke, or coal), and iron oxide (hematite). The equation reported for this reaction is:

\[
\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} \rightarrow 2\text{FeSi(s)} + 10\text{CO(g)} + \text{SiC(s)} + \text{SiO}_2(g) \quad (2)
\]

The theoretical electric energy input amounts to 23.18 MJ to produce 1.19 kg of ferrosilicon, which is needed to form 1 kg of Mg. The actual required electric energy is twice as much. This reaction requires the safe disposal of the toxic carbon monoxide.

(c) The reduction of MgO by silicon, in the form of ferrosilicon. The preferred composition of the ferrosilicon is 75% Si to 25% Fe by weight. The overall reaction has been described by Toguri and Pidgeon:

\[
2\text{MgO} + 2\text{CaO} + (\text{FeSi}) \rightarrow 2\text{Mg(g)} + \text{Ca}_2\text{SiO}_4(s) + \text{Fe} \quad (3)
\]

This endothermic reaction, carried out at 1473–1773 K in horizontal externally heated evacuated steel retorts, is catalyzed by CaF2. It results in the formation of the slag of dicalcium silicate, and in the release of gaseous Mg (mp 923 K, bp 1380 K), which condenses in steel sleeves in the cooler part of the retorts as “crown magnesium”. The distillation step, carried out under reduced pressure (less than 0.1 mmHg), provides high-purity Mg (99.97%), because its vapor pressure is much higher than that of the metal contaminants in the dolomite ore and in the other reactants. The final step is the remelting of Mg under a protective atmosphere and its casting into ingots. The process heat for the reduction of dolime is usually provided by the combustion of coal. The theoretically required energy is 13.67 MJ/kg Mg ingot. However, since the energy efficiency is only about 12%, the amount of coal actually required is 180 MJ/kg Mg ingot. A proposed mechanism assumes the formation of...
gaseous silicon monoxide as an intermediate, followed by its reaction with CaO to form dicalcium silicate:6,7

\[
\text{MgO} + \text{Si} \rightarrow \text{Mg(g)} + \text{SiO(g)} \quad (4)
\]

\[
2\text{SiO(g)} + 2\text{CaO} \rightarrow \text{Ca}_2\text{SiO}_4(s) + \text{Si} \quad (5)
\]

In the present study, the thermodynamic limits were determined for attaining both fuel savings and CO2 emission avoidance in the three steps of converting dolomite to magnesium. Thermochemical equilibrium calculations were made using the CET85 and the FactSage program codes.9,10 Process heats were computed using the data of NIST11 to determine the enthalpy changes between the reactants at 300 K and the products at the reaction temperature, usually at 1 bar. C(gr) was taken as the model for the carbon source (coal, coke, or pet coke), and Fe(s) and Si(s) were the models for the alloy ferrosilicon. The proposed process variations have been based on the data reported for the actual industrial process steps.4

For the calcination of dolomite and the silicothermic reduction of dolime, external heating by combustion of fossil fuel is usually applied, and therefore the change to heating by concentrated solar energy is relatively straightforward. However, the high-temperature production of ferrosilicon, as noted above, is normally carried out by internal heating, using electric discharges. In order to define the conditions for external heating by concentrated solar energy, an exploratory experiment of ferrosilicon production was carried out using thermogravimetry coupled with gas chromatography and X-ray diffraction analysis of the solid products.

2. Calcination of Dolomite

The thermodynamics of the calcination of dolomite was examined under a variety of conditions: dolomite decomposition, or dolomite calcination in the presence of carbon, carbon + oxygen, carbon + water, or methane.

**Calcination of Dolomite.** Thermochemical equilibrium compositions as a function of temperature in the range of 600–1300 K and at 1 bar for an initial amount of 1 mol of dolomite are presented in Figure 1. The onset of calcination of MgCO3 starts already at 800 K, while that of CaCO3 starts only at 1100 K. Therefore, the evolution of CO2 occurs in two steps. At 1200 K and 1 bar, the reaction can be represented by the equation

\[
\text{CaMg(CO}_3\text{(CO}_3\text{)}_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \quad (6)
\]

Table 1. Fuel Consumption and CO2 Emission in the Calcination of Dolomite, Based on the Thermoneutral Equilibrium at 1200 K and 1 bar for the Reaction of CaMg(CO3)2 = CaO + MgO + 2CO2, with \(\Delta H = +471\) MJ/kmol CaMg(CO3)2

<table>
<thead>
<tr>
<th>Component</th>
<th>kg/kg Mg</th>
<th>MJ/kg Mg</th>
<th>CO2 (kg/kg Mg)</th>
<th>MgO (kg/kg Mg)</th>
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</thead>
<tbody>
<tr>
<td>Dolomite feed</td>
<td>11.6</td>
<td>29.67</td>
<td>9.90</td>
<td>5.54</td>
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<td>5.54</td>
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<td>5.54</td>
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<td>1.00</td>
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<tr>
<td>Mg production</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Designed to produce 1 kg of Mg ingot from initial 11.6 kg of dolomite (as in ref 4), using either coal combustion or concentrated solar energy for process heat. * Assuming coal combustion (HHV = 25 MJ/kg) is used for process heat. * Assuming 95% yield in the calcination of dolomite. * Assuming 55% overall yield of magnesium from dolomite.

The reaction is highly endothermic, with \(\Delta H = +471\) and +551 kJ/mol MgO at 1200 and 1300 K, respectively. Such a reaction may approximate the dolomite calcination in current industrial practice. In Table 1, the fuel inputs and the CO2 emissions are compared for this reaction carried out either with coal combustion or with concentrated solar energy for process heat. The energy consumption of conventional dolomite calcination has been reported to be 52.1 MJ/kg Mg ingot, while the total CO2 emission, both from the reaction itself and from the combustion of coal for process heat, amounts to 10.1 kg of CO2 per kg of Mg ingot.4 Theoretical, no fuel input would be necessary with solar energy except for auxiliary devices (e.g., for loading and discharging materials), and therefore the fuel saving should approach 100%. The CO2 emission avoidance with concentrated solar energy relative to coal combustion would be 44.0%.

**Dolomite Calcination Combined with Carbon Gasification.** The equilibrium composition for the initial mixture of CaMg(CO3)2 + 2C in the temperature range 700–1500 K is shown in Figure 2 (for clarity, the reactant dolomite and product lime are not shown). By carrying out the calcination of dolomite in the presence of carbon, the emitted CO2 is predicted to achieve the gasification of the carbon. At 1200 K and 1 bar, the required process heat is +829 kJ/mol MgO. The net reaction can be represented by the equation

\[
\text{CaMg(CO}_3\text{(CO}_3\text{)}_2 + 2\text{C} \rightarrow \text{CaO} + \text{MgO} + 3.85\text{CO} + 0.073\text{CO}_2 + 0.073\text{C(gr)} \quad (7)
\]

Thus, most of the CO2 will be reduced to CO, which may be further processed via water gas shift to methanol or hydrogen. As shown in Table 2, the coproduction of 1 kg of pure Mg ingot and of 2.328 kg of CH3OH would require, according to eq 7 and assuming solar process heat, 49.58 MJ of coke (or...
petcoke) for the reaction. The CO₂ emission would amount to 7.317 kg. The conventional methanol production via methane steam reforming (MSR) requires 44.5 MJ/kg methanol, and releases 0.837 kg of CO₂/kg of methanol. Thus, for the production of 2.328 kg of methanol, the energy requirement would be 103.6 MJ and the CO₂ emissions would be 1.95 kg of CO₂. Therefore, the conventional separate production of the above amounts of dolomite and methanol would require 155.7 MJ, and would result in the emission of 12.05 kg of CO₂. The fuel saving of the proposed coproduction of dolime and methanol relative to the conventional separate processes would be 68.1%, and the corresponding CO₂ emission avoidance would be 39.3%. If instead of solar energy the process heat for the above coproduction was supplied by the combustion of coal, the additional fossil energy input would be 52.23 MJ/kg Mg ingot, resulting in a total energy input of 101.81 MJ. The additional CO₂ release from coal combustion would be 7.66 kg, resulting in a total CO₂ release of 14.98 kg of CO₂/kg of Mg ingot. In this case, the fuel saving would be only 28.1%. In addition, there would be an excess CO₂ emission of 19.6% for the coproduction relative to the conventional processes. Experimental tests will be required to check if the reaction of eq 7 proceeds at an adequate rate, or if catalysts will be necessary.

**Dolomite Calcination Combined with Carbon Gasification and Partial Oxidation.** In analogy to previous studies on the calcination of limestone to lime, the calcination of dolomite can be converted to a thermoneutral process by adding a calculated amount of carbon and oxygen to CaMg(CO₃)₂. The equilibrium composition as a function of temperature for an initial mixture of CaMg(CO₃)₂ + 4C + 2.3O₂ is shown in Figure 3. This resulted at 1200 K in a slightly endothermic process, with ΔH = -17.6 kJ/mol CaMg(CO₃)₂, and with oxidation of carbon to CO and CO₂ according to the net reaction:

\[
\text{CaMg(CO}_3\text{)}_2 + 4\text{C} + 2.3\text{O}_2 \rightarrow \text{CaO} + \text{MgO} + 3.4\text{CO} + 2.6\text{CO}_2
\]

In this case, there would not be a need for solar process heat. The amount of O₂ required to achieve such a thermoneutral reaction was found by trial and error to be 2.3 mol of O₂ per mole of CaMg(CO₃)₂, as shown in eq 8. The decrease in CO₂ concentrations between 800 and 1000 K can be explained by the Boudouard equilibrium, i.e., the simultaneous consumption of C(gr) and formation of CO. The second increase of CO₂ above 1100 K, coincides with the decomposition of CaCO₃.

The combined calcination of dolomite with the conversion of CO to syngas followed by methanol synthesis requires a fuel (coke) input of 99.0 MJ/kg Mg ingot, and discharges 13.5 kg of CO₂/kg of Mg ingot (see Table 3). The total energy consumption of dolomite calcination by itself has been reported to be 52.1 MJ/kg Mg ingot, and the total CO₂ emission, both from the process heat and from reaction (1) amounts to 10.1 kg of CO₂/kg of Mg ingot. For the conventional production of 2.06 kg of methanol, the energy requirement would be 91.7 MJ, and the CO₂ emission would be 1.72 kg of CO₂. Therefore, the conventional separate calcination of 11.6 kg of dolomite and production of 2.06 kg of methanol would require a total of 143.8 MJ/kg Mg ingot, and would result in the emission of 11.8 kg of CO₂/kg of Mg. The fuel saving by the proposed coproduction of dolime and methanol would thus be 31.2%. The excess of CO₂ emission by coproduction vs the conventional separate processes would be 12.6%.

Experimental tests will be required to check if the reaction of eq 8 proceeds at an adequate rate. Air may be used instead of pure O₂ to eliminate the additional costs of an air separation unit. In such a case, the predicted equilibrium composition can be represented by the net reaction, in which 2.3O₂ + 8.6N₂ approximate the ratio of O₂/N₂ in air:

\[
\text{CaMg(CO}_3\text{)}_2 + 4\text{C} + 2.3\text{O}_2 + 8.6\text{N}_2 \rightarrow \text{CaO} + \text{MgO} + 3.4\text{CO} + 2.6\text{CO}_2 + 8.6\text{N}_2
\]
The enthalpy change increases, reaching +224 kJ/mol CaMg(CO₃)₂, due to the additional heat required for heating N₂ from 300 to 1200 K.

**Dolomite Calcination Combined with Carbon Gasification and Steam Reforming.** Using an excess of carbon and added water, the calcination of dolomite should result in the production of both dolime and syngas. This reaction would involve, in part, the gasification of carbon. The equilibrium composition as a function of temperature for an initial mixture of CaMg(CO₃)₂ + 20C + 40H₂O is shown in Figure 4. The reaction at 1050 K can be represented by

\[
\text{CaMg(CO}_3\text{)}_2 + 20\text{C} + 40\text{H}_2\text{O} \rightarrow \text{MgO} + \text{CaO} + 26.26\text{H}_2 + 13.54\text{CO} + 13.64\text{H}_2\text{O} + 8.41\text{CO}_2 + 0.05\text{CH}_4, \text{ with } \Delta H = +43,325 \text{ MJ/kmol CaMg(CO}_3\text{)}_2
\]

This reactant composition was determined by trial and error to arrive at a product molar ratio of H₂/CO = 1.94, thus forming a syngas suitable for methanol or Fischer−Tropsch syntheses. The enthalpy of the reaction is considerable, +4325 kJ/mol MgO, mainly due to the steam gasification of carbon. Nonetheless, the drawback of the large excess of carbon input may be offset by the production of the valuable syngas. Such a reaction could be attractive when obtaining coal from a coal−water slurry. As shown in Table 4 and according to eq 10, the coproduction of 1 kg of Mg ingot and 23.8 kg of methanol would require the consumption of 495.8 MJ/kg Mg of coke, and the release of 23.3 kg of CO₂/kg of Mg. If coal combustion was used for process heat, the additional fuel consumption would amount to 272.5 MJ/kg Mg, resulting in a total fuel use of 768.3 MJ/kg Mg ingot. The additional CO₂ emission would be 39.95 kg of CO₂/kg of Mg, resulting in a total release of 63.26 kg of CO₂/kg of Mg ingot. Conventional separate production of the above amounts of magnesium and methanol would require 52.1 and 1059 MJ/kg Mg, or a total of 1111 MJ/kg Mg, and would result in the release of 10.1 and 19.92 kg of CO₂/kg of Mg, or a total of 30.0 kg of CO₂/kg of Mg. The fuel saving by the coproduction, with coal combustion for process heat, relative to the separate processes, would be 30.8%, and the CO₂ emission excess would be 52.6%. With solar energy, the fuel saving would be 55.4%, and the CO₂ emission avoidance would be 22.3%. Experimental tests will be required to check if the reaction of eq 10 proceeds at an adequate rate.

**Dolomite Calcination Combined with Dry Reforming of Methane.** In this proposed reaction, the CO₂ evolved by the calcination reaction could achieve the dry reforming of CH₄. The variation of the equilibrium composition with temperature at 1 bar is shown in Figure 5. At 1200 K, the net reaction can be represented by

\[
\text{CaMg(CO}_3\text{)}_2 + 4\text{CH}_4 \rightarrow \text{MgO} + \text{CaO} + 2.01\text{C(gr)} + 7.77\text{H}_2 + 3.88\text{CO} + 0.08\text{CH}_4 + 0.02\text{CO}_2
\]

This reactant composition was again derived by trial and error. The syngas produced has a H₂/CO molar ratio of 2.00, suitable for Fischer−Tropsch reactions to hydrocarbons, or for direct methanol synthesis. The reaction enthalpy at 1200 K is +1387 kJ/mol. Experimental proof will be necessary to confirm if the gas−solid reaction according to eq 11 proceeds at a satisfactory rate.

As shown in Table 5 and according to eq 11, the coproduction of 1 kg of Mg ingot and of 7.04 kg of methanol, when carried out with solar process heat, would require the consumption of 224.5 MJ of natural gas, and would result in the release of 0.0554 kg of CO₂. If coal combustion was used for process heat, the additional fuel input would be 87.4 MJ, or a total of 311.9 MJ/kg Mg. The additional CO₂ release would be 12.80 kg, or a total of 12.855 kg of CO₂/kg of Mg. The separate production of 1 kg of Mg and 7.04 kg of methanol would require 52.1 and 313.3 MJ, respectively, or a total of 365.4 MJ/kg Mg, and would release 10.1 and 5.89 kg of CO₂, or a total of 16.0 kg of CO₂/kg of Mg. By comparison with the conventional separate production of the same amounts of these materials, the fuel saving would be 38.6% with concentrated solar energy and
Table 5. Fuel Consumption and CO2 Emission in the Calcination of Dolomite Combined with the Partial Oxidation of NG (Natural Gas), Followed by Conversion of Syngas to Methanol, Based on the Thermochemical Equilibrium at 2000 K and 1 bar for the Reaction of Fe2O3 + 4SiO2 + 2/3 CO to 2FeSi + SiC + CO2.

<table>
<thead>
<tr>
<th>Fe2O3 feed (kg/kg Mg)</th>
<th>coke feed (kg/kg Mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.252</td>
<td>0.355</td>
</tr>
</tbody>
</table>

Table 6. Fuel Consumption and CO2 Emission in the Production of Ferrosilicon by the Reduction of Fe2O3 and Silica with Coal, Followed by WGS of 2/3 CO to H2 and Conversion of Syngas to Methanol, Based on the Thermochemical Equilibrium at 2000 K and 1 bar for the Reaction of Fe2O3 + 4SiO2 + 11C to 2FeSi + 4H2O + 11C.

```
Fe2O3 + 4SiO2 + 11C → 2FeSi + 4H2O + 11C (12)
```

**3. Production of Ferrosilicon**

**Production of Ferrosilicon with Carbon.** The equilibrium composition of the system Fe2O3 + 4SiO2 + 11C as a function of temperature at 1 bar is shown in Figure 6. The reaction above about 1900 K may represent the conditions of the actual industrial production, usually carried out in an electric arc. At 2000 K, the net calculated reaction can be described by

```
Fe2O3 + 4SiO2 + 11C → 2FeSi + 10CO + SiC + 4H2O (12)
```

with an enthalpy change of \( \Delta H = +2096 \text{ kJ/mol Fe}_2\text{O}_3 \). Large amounts of CO are produced, as well as smaller amounts of solid SiC and gaseous SiO. These predicted reaction products shown in eq 12 are different from those reported in the literature.

```
Fe2O3 + 4SiO2 + 11C → 2FeSi + 3CO(g) (2)
```

**Possibly the discrepancy between our calculated equilibrium composition above 2000 K in Figure 6 and eq 12 and that reported in the literature could be due to a different reaction mechanism under electric discharges, which may include electronic excitations. The calculated equilibrium composition is independently supported by the present thermogravimetric experiment (see below, section 4).**

As shown in Table 6, the coproduction of 1.19 kg of ferrosilicon and 0.258 kg of methanol requires, when driven by solar process heat, 11.65 MJ/kg Mg due to the coke consumed, and results in the emission of 0.789 kg of CO2/kg of Mg. In the conventional electric arc process, the total required energy is 113.5 MJ/kg Mg, and the total global warming impact is 14.7 kg of CO2-eq/kg of Mg. Together with the conventional production of 0.258 kg of methanol via MSR, which would require 11.5 MJ, and would emit 0.22 kg of CO2, the total conventional energy use would be 125.0 MJ/kg Mg, and the greenhouse gas release would be 14.9 kg of CO2/kg of Mg ingot. Thus, the potential fuel saving by applying concentrated solar energy and coproducing methanol could reach 90.7%, and the CO2 emission avoidance could reach 94.7%.

**Ferrosilicon Production with Carbon and Water.** The addition of water to the above reactant mixture of Fe2O3 + 4SiO2 + 11C was examined in order to check if partial water gas shift of CO to H2 concurrently with the ferrosilicon production may be thermodynamically possible. For the thermochemical calculation, the unstable metasilicic acid, \( H_2SiO_3 \), was taken as a proxy for \( SiO_2 + H_2O \) at the initial temperature of 300 K, and the temperature dependence of the equilibrium composition for the system \( Fe_2O_3 + 4SiO_2 + 4H_2O + 11C \) at 1 bar pressure is presented in Figure 7. For clarity of the figure, the data for SiO2(s), C(gr), and SiO(g) have been omitted. A sharp onset of ferrosilicon formation and CO release occurs between 1630 and
1640 K. At 1800 K, the process heat is +3614 kJ/mol Fe2O3, and the reaction can be represented by the equation

\[
\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 4\text{H}_2\text{O} + 11\text{C} \rightarrow 2.0\text{FeSi(s)} + 11.0\text{CO(g)} + 4.0\text{H}_2(g) + 2.0\text{SiO}_2(s) + 0.02\text{SiO}(g) \tag{13}
\]

The main change from the reaction without H2O (eq 12) is the replacement of SiC(s) and most of SiO(g) formation by the appearance of unreacted SiO2. It is yet unclear how this change would affect the further use of the ferrosilicon for the reduction of calcined dolomite. By water gas shift of 55% of the resulting CO to H2, a syngas mixture with a molar ratio of H2/CO = 2 may be obtained, suitable for methanol synthesis.

The coproduction of 1.19 kg of ferrosilicon and 0.465 kg of methanol, as shown in Table 7, using concentrated solar energy would require 11.65 MJ/kg Mg for the coke consumed, and would result in emissions of 0.710 kg of CO2/kg of Mg. In the conventional electric arc process, the total required energy is 113.5 MJ/kg Mg, and the total global warming impact is 14.7 kg of CO2/kg of Mg. Together with the conventional production of 0.465 kg of methanol via MSR, which would require 20.7 MJ and would emit 0.39 kg of CO2, the total conventional energy use would be 134.2 MJ, and the total greenhouse gas release would be 15.1 kg of CO2 per kg of Mg ingot. The potential fuel saving from both the application of concentrated solar energy and of methanol coproduction could reach 91.3%, and the CO2 emission avoidance could reach 95.4%. The presence of the above amount of water in the initial reactant mixture for ferrosilicon production should significantly enhance the resulting syngas quality, and thus improve the economics of the whole process.

A different equilibrium composition of the major products is predicted when applying orthosilicic acid, H4SiO4, as a proxy for SiO2 + 2H2O with a molar ratio SiO2/Fe2O3 = 2. As shown in Figure 8 for the temperature dependence, the onset of FeSi formation occurs at 1630 K. Between 1650 and 1800 K, the reaction can be represented by the equation

\[
\text{Fe}_2\text{O}_3 + 2\text{SiO}_2 + 4\text{H}_2\text{O} + 11\text{C} \rightarrow 2.0\text{FeSi(s)} + 11.0\text{CO(g)} + 4.0\text{H}_2(g) + 0.004\text{SiO(g)} + 0.002\text{C(gr)} \tag{14}
\]

In this case, the FeSi produced should be essentially free of nonvolatile contaminants. The process heat for reaction 14 at 1800 K is +2968 kJ/mol Fe2O3. The reactions according to eqs 13 and 14 require experimental confirmation.

**Production of Ferrosilicon with Methane.** The equilibrium composition of the system Fe2O3 + 4SiO2 + 11CH4 as a function of temperature and at 1 bar is presented in Figure 9. For clarity, SiC and SiO have been omitted. At 1900 K, the net reaction can be represented by

\[
\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{CH}_4 \rightarrow 2\text{FeSi} + 21.98\text{H}_2 + 10.00\text{CO} + \text{SiC} + \text{SiO}, \ \Delta H = +3050\text{kJ/mol Fe}_2\text{O}_3 \tag{15}
\]

forming syngas with a H2/CO molar ratio of 2.20. The reaction is strongly endothermic, with \(\Delta H = +3050\text{kJ/mol Fe}_2\text{O}_3\). Experimental proof will be required for the occurrence of this gas−solid reaction.

As shown in Table 8, the coproduction of 1.19 kg of ferrosilicon and 0.775 kg of methanol, when driven by solar
process heat, would require 26.4 MJ/kg Mg due to the natural gas consumed, and in theory would not result in any CO₂ emission. In the conventional electric arc process, the total required energy is 113.5 MJ/kg Mg, and the total global warming impact is 14.7 kg of CO₂eq/kg of Mg. Together with the conventional production of 0.775 kg of methanol via MSR, which would require 34.5 MJ and would emit 0.649 kg of CO₂, the total conventional energy use would be 148.0 MJ, and the total greenhouse gas release would be 15.3 kg of CO₂/kg of Mg ingot. Thus, the potential fuel saving by applying concentrated solar energy and coproducing methanol could reach 82.2%, and the CO₂ emission avoidance could reach 95.7%.

4. Thermogravimetric Experiment on Ferrosilicon Production

A 71.0 mg sample of a mixture of Fe₂O₃ (Johnson Matthey, 99.999%), SiO₂ (Sigma s-5631, 99%), and active carbon (Fluka 5105, ca. 85%) in the molar ratio Fe₂O₃:SiO₂:C = 1:4:11, was placed in the sample holder of a high-temperature thermogravimeter (Netzsch STA 409). Under a constant Ar flow of 200 mL/min, the temperature was increased at a rate of 20 K/min until 1823 K, and then maintained for about 200 min. Evolved gases were sampled every 3 min for gas chromatography (MTI Micro CG P200, equipped with a MS 5A column and a TC detector). The calculated weight loss due to the release of gaseous CO and SiO required by the equation

Fe₂O₃ + 4SiO₂ + 11C → 2FeSi(s) + 10CO(g) + SiC(s) + SiO(g) (12)

is 60.9%.

Table 9. Calculated Pressure Dependence of the Onset Temperature of Mg Production by the Reaction of 2MgO + 2CaO + Si = 2Mg + Ca₂SiO₄

<table>
<thead>
<tr>
<th>pressure, bar</th>
<th>onset temp, K</th>
</tr>
</thead>
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<tr>
<td>0.1</td>
<td>1602</td>
</tr>
<tr>
<td>1.0</td>
<td>1837</td>
</tr>
</tbody>
</table>

Figure 10. Thermogravimetry coupled with gas chromatography for the reaction of Fe₂O₃ + 4SiO₂ + 11C.

Figure 11. XRD spectrum of the solid product of the reaction of Fe₂O₃ + 4SiO₂ + 11C.
Table 10. Potential Fuel Savings and CO₂ Emission Avoidance in the Pidgeon Process by Concentrated Solar Energy Combined with Conversion of Syngas (If Formed) to Methanol, vs Conventional Processes

<table>
<thead>
<tr>
<th>process steps</th>
<th>fuel savings, %</th>
<th>CO₂ emission avoidance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite Calcination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaMg(CO₂)₃ = CaO + MgO + 2CO₂</td>
<td>100⁺</td>
<td>44⁺</td>
</tr>
<tr>
<td>CaMg(CO₂)₃ + 20C + 4H₂O = CaO + MgO + 26.3H₂ + 13.5CO + 13.6H₂O + 8.4CO₂</td>
<td>55.4⁺ 30.8⁺</td>
<td>22.3⁺ 52.6⁺</td>
</tr>
<tr>
<td>CaMg(CO₂)₃ + 4C₁H₂ = CaO + MgO + 7.8H₂ + 3.9CO + 2C(gr)</td>
<td>38.6⁺ 14.6⁺</td>
<td>99.7⁺ 19.6⁺</td>
</tr>
<tr>
<td>CaMg(CO₂)₃ + 2C = CaO + MgO + 3.85CO + 0.073CO₂</td>
<td>68.1⁺ 28.1⁺</td>
<td>39.3⁺ 19.6⁺</td>
</tr>
<tr>
<td>CaMg(CO₂)₃ + 4C + 2.3O₁ = CaO + MgO + 3.4CO + 2.6CO₂</td>
<td>31.2⁺</td>
<td>-12.6⁺</td>
</tr>
</tbody>
</table>

Ferrosilicon Production

| Si + 2MgO + 2CaO = 2Mg(g) + Ca₂SiO₄(s)               | 99.2             | 100                        |

a Negative values of CO₂ emission avoidance mean excess emissions vs conventional processes. b Assuming process heat from concentrated solar energy. c Assuming process heat from coal combustion. d Thermoneutral reaction.

As shown in Figure 10, the observed weight loss was 59.1%. The difference relative to the above calculated weight loss is within experimental error. The weight loss curve shows three inflections that may be ascribed to the successive stages of Fe₂O₃ reduction, i.e., Fe₃O₄, FeO, and Fe. Simultaneously, the CO chromatograph was 30.7 mg. The X-ray diffraction (XRD) spectrum of the nonvolatile product of the above reaction is presented in Figure 11, showing the presence of FeSi (PDF No. 38-1397) and SiC (PDF No. 2-1050). These measurements were performed using a Philips X’Pert MPD/DY636 instrument. Identification of peaks was carried out with the Philips Analytical Software for XRD.

5. Silicothermic Reduction of Calcined Dolomite

The industrial silicothermic reduction of calcined dolomite is carried out with ferrosilicon alloy as the reducing agent. The iron does not participate in the reaction, similar to the reduction with elementary silicon.⁶,⁷ The equilibrium composition of the system Si + 2MgO + 2CaO as a function of temperature at 1 bar is shown in Figure 12. At 1838 K MgO(s) (periclase) is transformed to gaseous Mg, while CaO is transformed to solid dicalcium silicate Ca₂SiO₄. At 1900 K and 1 bar, the net reaction can be represented by

\[
\text{Si} + 2\text{MgO} + 2\text{CaO} \rightarrow 1.990\text{Mg(g)} + 0.997\text{Ca}_2\text{SiO}_4(s) + 0.009\text{MgO(s)} + 0.006\text{Ca(g)} + 0.003\text{SiO(g)}
\]  (16)

As shown in Figure 13, the onset of the equilibrium in the silicothermic reduction is strongly shifted to lower temperatures at decreased pressure. At 2 × 10⁻⁵ bar, the onset occurs at 1084.8 K. At 10⁻³ bar, the onset occurs already at 1060 K. At this temperature, the net reaction can be represented by

\[
\text{Si} + 2\text{MgO} + 2\text{CaO} \rightarrow 1.998\text{Mg(g)} + 0.999\text{Ca}_2\text{SiO}_4(s) + 0.002\text{MgO(s)} + 0.0005\text{CaSi(s)} + 0.0005\text{Ca(g)}
\]  (17)

Calculated onset temperatures for the formation of Mg as a function of pressure are presented in Table 9. These computed equilibrium results are consistent with the experimental kinetic observations of Toguri and Pidgeon.⁵,⁶ In industrial practice, the evacuated retorts for the reduction of calcined dolomite by ferrosilicon are heated to 1433–1438 K. The energy input by coal combustion for this reduction step was reported to be 180 MJ/kg Mg ingot, and the total energy input to be 191.4 MJ/kg Mg ingot, while the global warming impact was estimated at 15.9 kg of CO₂eq/kg of Mg ingot.⁴

If the coal combustion was replaced by concentrated solar energy, the fuel saving would theoretically be 99.2%; the CO₂ emission avoidance would also approach 100%.

6. Discussion

Previous relevant thermochemical processes for the extraction of metals from their metal oxides effected with concentrated solar energy include the carbothermal reductions of Fe₃O₄, MgO, and ZnO with C(gr) and CH₄ to produce Fe, Mg, and Zn, respectively.
respectively. 17–21 A review of the solar concentration and the solar reactor technologies indicate the feasibility of effecting these high-temperature processes at a large (megawatts) scale. 22 Thermochemical equilibrium calculations show that the calcination of dolomite occurs in two stages, with the MgO being formed at a lower temperature than the CaO. Fully calcined or half calcined dolomites are widely studied as reversible high-temperature sorbents for CO2 and H2S (e.g., for coal-burning power plants). The two-stage kinetics of CO2 release had been observed previously in thermogravimetric experiments on the calcination of dolomite, with MgO being released first, with an onset of about 923 K, and CaO released from about 1223 K. 23 All three steps in the Pidgeon process, namely dolomite calcination, ferrosilicon production, and silicothermic reduction of calcined dolomite, have the potential for achieving significant fuel saving and CO2 emission avoidance by using concentrated solar energy as the source of high-temperature process heat. Table 10 summarizes the estimated fuel savings and CO2 emission avoidance calculated in Tables 1–8 and discussed in detail in the various above sections.

The world production of Mg in 2006 amounted to 726 ktons, of which China, Canada, Russia, U.S.A., Israel, and Kazakhstan produced 526, 50, 50, 43, 28, and 20 ktons, respectively. 24 Assuming that the global warming impact of the world Mg production is similar to that reported for the Chinese production, i.e., 42 tons of CO2eq/ton of Mg, 4 the global greenhouse gas emissions from this industry should be about 25.2 × 10^6 tons of CO2eq, representing 0.1% of the global anthropogenic CO2 emissions of 24 Gtons of CO2 in the year 2000. 25 For the calcination of dolomite, additional fuel savings and CO2 emission mitigation can be predicted by combining this endothermic process with the exothermic partial oxidation of carbon, thus attaining a thermoneutral process. Also, if for the calcination of dolomite or the production of ferrosilicon either methane or carbon and water are used as reducing agents, the predicted coproduct could be valuable syngas (leading to methanol, hydrogen, ammonia, and other synthetic chemical commodities), which may significantly improve the economics of the whole process. The coproduction of metals and syngas should result in considerable overall mitigation of CO2 emissions. 26

**Nomenclature**

HHV = high heating value
NG = natural gas
MSR = methane steam reforming
PDF = powder diffraction file
ton = metric ton
WGS = water gas shift

**Literature Cited**


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