Co-Production of Syngas and Metals or Lime

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Several high-temperature endothermic chemical reactions are major contributors to the anthropogenic CO$_2$ emissions:

1. The reforming of natural gas to syngas and various chemicals and fuel.
2. The calcination of limestone to produce lime and cement, CaCO$_3$ = CaO + CO$_2$.
3. The production of metals from their ores,
   a) Fe$_2$O$_3$ + 3C = 2Fe + 3CO
   b) Al$_2$O$_3$ + 3C = 2Al + 3CO
   c) 2MgO-CaO + FeSi = 2Mg + Ca$_2$SiO4 + Fe
Causes of CO$_2$ Emissions

CO$_2$ emissions from these processes are due:

1. Partly from the chemical reactions themselves.
2. Partly from fossil fuel combustion for process heat.

Considerable fuel savings and CO$_2$ emission avoidance are expected by modifying these reactions.

The sequestration of CO$_2$ is usually very expensive – unless its cost is offset by a profitable process – such as enhanced oil recovery.
1) **Tri-Reforming by Combining Endothermic and Exothermic Reactions**

The combination of heat releasing and heat absorbing reactions had been applied successfully to the catalytic reforming of natural gas to syngas

By simultaneously reacting natural gas with steam and with carbon dioxide,

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &= \text{CO} + 3\text{H}_2 & \Delta H &= 206 \text{ kJ/mol} \quad (1) \\
\text{CH}_4 + \text{CO}_2 &= 2\text{CO} + 2\text{H}_2 & \Delta H &= 247 \text{ kJ/mol} \quad (2)
\end{align*}
\]

which are both strongly heat consuming reactions, and also with oxygen by a heat releasing reaction,

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2 & \quad \Delta H = -38 \text{ kJ/mol} \quad (3)
\]

an overall thermo-neutral process of *tri-reforming* could be achieved, which (once started) does not require an input of external heat by combustion of fossil fuel.

Tri-Reforming for Rapid Hydrogen Production

A mixture of CH₄ – CO₂ – H₂O – O₂

(60 : 10 : 10 : 20%)

Passed at 700° C over the 4-component catalyst

Ni – Ce₂O₃ – Pt – Rh (6.6 : 3.9 : 2.2 : 0.2 wt%)

supported on ceramic fibers,

resulted in 90% methane conversion

with a contact time of 5 ms and a

space-time yield of 12.2 kmol H₂ L⁻¹ h⁻¹

The inclusion of O₂ in the gas feed provided the heat

required for the reforming reactions

Inui, Appl. Organometal. Chem. 15, 87, 2001
Tri-reforming of power station flue gases

Tri-reforming has been proposed for the utilization of the power station flue gases for syngas production.

Using specific catalysts, the high-temperature reaction of the flue gases with natural gas results in the combined steam/CO₂ reforming and partial oxidation of methane.

Song and Pan, Catal. Today, 98, 463, 2004
# Major Components of Flue Gases

*Chunshan Song, Chemical Innovation, 31, 21, 2001*

<table>
<thead>
<tr>
<th></th>
<th>Coal-Fired Boilers</th>
<th>Gas-Fired Boilers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>12-14%</td>
<td>8-10%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>8-10%</td>
<td>18-20%</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3-5%</td>
<td>2-3%</td>
</tr>
<tr>
<td>N$_2$</td>
<td>72-77%</td>
<td>67-72%</td>
</tr>
</tbody>
</table>
Tri-Reforming of Flue-Gas from Coal- or Gas-fired burners

*How to produce syngas suitable for methanol synthesis?*

(1) Added air is necessary to achieve an overall thermoneutral process.

(2) An excess of methane is necessary to obtain syngas useful for both hydrogen and ammonia synthesis.

_Halmann and Steinfeld, Energy, 31, 3171, 2006_
Conclusions on Trireforming of Flue Gases

(a) CO$_2$ Consumed for Production of Syngas;
(b) N$_2$ Consumed for Production of Ammonia;
(c) Decreased CO$_2$ Emission by Tri-Reforming;
(d) Increased CO$_2$ Emission by Coal Gasification;
(e) Fuel Saving, particularly by Coal Gasification;
(f) Favorable Economics;

But: For Significant CO$_2$ Emission Mitigation by Tri-Reforming - the World Proved Reserves of Natural Gas would be Insufficient.

2) Proposed Thermo-Neutral Co-Production of Lime and Syngas

To Combine the *Endothermal* Decomposition of Limestone to Lime,

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \Delta H_{298} = +178 \text{ kJ/mol} \]

and the *Endothermal* CH\(_4\)/CO\(_2\) Reforming,

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + \text{CO} \quad \Delta H_{298} +247 \text{ kJ/mol} \]

with the *Exothermal* Partial Oxidation of CH\(_4\)

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2 \quad \Delta H_{298} -38 \text{ kJ/mol} \]

to achieve an Overall *Thermo-neutral* Reaction

*Halmann, Steinfeld, Energy & Fuels, 17, 774 (2003)*

*Halmann, Steinfeld, Energy, 31, 1533 (2006)*
Equilibrium Composition vs. Temperature for Initial Mixture at 300 K and 1 bar of
\[ \text{CaCO}_3 + 4\text{CH}_4 + 2\text{H}_2\text{O} + 8.7\text{N}_2 + 2.3\ \text{O}_2 \]
Fuel Economy and CO₂ Emission Avoidance by Co-Production of Lime and Methanol

Assume Thermochemical Equilibrium at 1100 K and 1 bar:

\[
\text{CaCO}_3 + 4\text{CH}_4 + 2\text{H}_2\text{O} + 8.68\text{N}_2 + 2.32\text{O}_2 = \text{CaO} + 7.56\text{H}_2 + 3.79\text{CO} + 2.44\text{H}_2\text{O} + 1.21\text{CO}_2 + 8.68\text{N}_2
\]

By Proposed Co-Production followed by Methanol Synthesis:

- Fuel Saving by Co-Production = 29%
- CO₂ Emission Avoidance by Co-Production = 88%
Calculated CO₂ Emission Avoidance by Co-Production of Lime and Ammonia or Urea

Assume Thermochemical Equilibrium at 1100 K and 1 bar

\[
\text{CaCO}_3 + 4\text{CH}_4 + 2\text{H}_2\text{O} + 2.3\text{O}_2 + 8.7\text{N}_2 = \\
\text{CaO} + 7.6\text{H}_2 + 3.8\text{CO} + 2.4\text{H}_2\text{O} + 1.2\text{CO}_2 + 8.7\text{N}_2
\]

By Proposed Lime and Syngas Co-Production followed by Water-Gas Shift and Ammonia Synthesis:

\[
\text{CO}_2 \text{ Emission Avoidance by NH}_3 \text{ Co-Production} = 23\%
\]

If Ammonia is Converted to Urea: \(2\text{NH}_3 + \text{CO}_2 = \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}\)

\[
\text{CO}_2 \text{ Emission Avoidance by Urea Co-Production} = 47\%
\]
Why Choose Ammonia as Preferred Product from Syngas?

Ammonia and urea essential as fertilizers in agriculture.

Expected world demand exceeds world capacity.

Ammonia production uses 3% of world energy consumption.

Ammonia production would consume part of flue-gas nitrogen.

Ammonia could become important as a hydrogen carrier for ammonia fuel cells.

Urea production consumes over 70% of CO₂ generated from ammonia production.
Conclusions on Co-Production of Lime and Syngas

1. Syngas and CaO Production in Single Reactor
2. Much Decreased CO₂ Emission
3. Fuel Saving by Thermo-Neutral Process
4. Attractive Economics
5. But: Requires further Experiments, Particularly on the Reaction Kinetics
3) Solar Furnace Fe$_3$O$_4$ Reduction by Methane

At 1300 K and 1 atm, Fe$_3$O$_4$, fluidized in CH$_4$, was converted into Fe and syngas

\[
\text{Fe}_3\text{O}_4 + 4\text{CH}_4 = 3\text{Fe} + 8\text{H}_2 + 4\text{CO}
\]

\[\Delta H = 978 \text{ kJ/mol}\]

Steinfeld, Kuhn, and Karni, Energy, 18, 239 (1993)

**Advantage:** Process heat supplied by solar energy.

**Drawback:** For continuous processing requires a hybrid solar–fossil fuel energy supply.
Metals and Syngas Co-Produced
in Thermoneutral Reactions by Combining the
Endothermic Reduction of Metal oxides by CH₄
with the Exothermic Partial Oxidation of CH₄ by O₂

ZnO + CH₄ = Zn + CO + 2H₂ \[\Delta H_{298K} = 315 \text{ kJ/mol}\]

Fe₃O₄ + 4CH₄ = 3Fe + 4CO + 8H₂ \[\Delta H_{298K} = 976 \text{ kJ/mol}\]

Fe₂O₃ + 3CH₄ = 2Fe + 3CO + 6H₂ \[\Delta H_{298K} = 717 \text{ kJ/mol}\]

CH₄ + 1/2O₂ = CO + 2H₂ \[\Delta H_{298K} = -36 \text{ kJ/mol}\]

Halmann, Frei, Steinfeld, Energy, 27, 1069, 2002
Thermoneutral Carbothermic Reduction of $\text{Fe}_2\text{O}_3$

Thermochemical Equilibrium Composition vs. Temperature for the System: 
$\text{Fe}_2\text{O}_3 + 6.5\text{C} + 2.55\text{O}_2$
Equilibrium Composition for the System

Fe$_2$O$_3$-CH$_4$-O$_2$ (molar ratio 1 : 4.9 : 3.5)
Thermogravimetric experiments with ~100 mg Fe$_2$O$_3$ under 3.6% O$_2$ in Argon. After equilibration at 1400°K, 5.1% CH$_4$ was introduced.

Halmann, Frei and Steinfeld, Energy, 27, 1069, 2002
Emission Avoidance and Fuel Saving by Co-Production of Iron and Methanol

Thermochemical Equilibrium at 1400K, 1 bar:

\[
\text{Fe}_2\text{O}_3 + 6.5\text{C} + 2.6\text{O}_2 = 2\text{Fe} + 4.9\text{CO} + 1.6\text{CO}_2
\]

followed by partial water-gas shift of CO to H₂,

and methanol synthesis.

By Proposed Co-Production:

**CO₂ Emission Avoidance by Co-production:** 50%

**Fuel Saving by Co-Production:** 27%
Thermogravimetric Experiment
100 mg ZnO / 5.5% CH₄ / 3.9% O₂ / 1400 K
Conclusions on Co-Production of Syngas and Iron or Zinc

1. Co-Production of Syngas and Metal in Single Reactor;
2. Thermo-Neutral Reaction Achieved by Presence of O₂;
3. Added Catalyst Possibly not Needed;
4. Coking Avoidance by Presence of O₂;
5. Syngas Quality Improved by H₂O Addition (*in situ* water-gas shift);
6. **But:** Much Further Work Required, Particularly on the Reaction Kinetics.
Efforts on Carbothermic Reduction of $\text{Al}_2\text{O}_3$ to Al Metal

The current electrochemical Hall-Héroult process suffers from high energy requirement and large greenhouse gas emissions.

With carbon or $\text{CH}_4$ as reducing agents, the overall desired reactions are:

\[
\text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO} \quad \Delta H_{298}^\circ = 1344.1 \text{ kJ mol}^{-1}
\]

\[
\text{Al}_2\text{O}_3 + 3\text{CH}_4 = 2\text{Al} + 3\text{CO} + 6\text{H}_2 \quad \Delta H_{298}^\circ = 1568.7 \text{ kJ mol}^{-1}
\]

Halmann, Frei, Steinfeld, Energy, 32, 2420, 2007
Equilibrium Distribution vs. Temperature for the System $\text{Al}_2\text{O}_3 + 3\text{C}$ at 1 bar

Halmann, Frei, Steinfeld, Energy, 32, 2420, 2007
Induction Furnace Carbothermic Reduction of Alumina

The production of \( \text{Al} \) and \( \text{CO} \), as well as the aluminum carboxides \( \text{Al}_2\text{OC}, \text{Al}_4\text{O}_4\text{C} \), and the carbide \( \text{Al}_4\text{C}_3 \) was achieved by heat pulses from an induction furnace on mixtures of \( \text{Al}_2\text{O}_3 \) and activated carbon in an Ar stream.

The formation of these species was proven by gas chromatography for the \( \text{CO} \), and by XRD analysis for the solid products on the cold reactor wall, as shown in the next slide:
Conclusions on Carbothermic Co-Production of Al and CO

1. The Carbothermic Al Production is Complicated by Co-Production of Al-Carbide and Al-Oxy-Carbides.

2. Further Work Required to Obtain Al without these Carbides.

3. The Conversion of the CO Product to Syngas should Improve the Economics of the Process.

4. The Carbothermic Production of Al would avoid the Environmental Problems and High Energy Consumption of the Electrolytic Hall-Héroult Process.

5. A Successful Solar Carbothermic Process for Al and Methanol Co-Production could potentially achieve up to ~52% decrease in CO₂ Emissions and up to ~ 81% Fuel Savings.
Industrial Production of Magnesium:

1. Silicothermic Reduction of Calcined Dolomite, \( \text{CaMg(CO}_3\text{)}_2 \), Pioneered by Loyd M. Pidgeon in Canada during World War II.

   Afterwards replaced by the

2. Electrochemical Reduction of Fused Magnesium Chloride, derived from Brine Lakes, such as the Dead Sea, or from Seawater – mainly in the U.S.A., Russia, Canada, and Israel.
World Primary Magnesium Production – about 726,000 Ton/year (in 2006)

Of these produced in:
China: 526,000 Ton
Canada: 50,000 Ton
Russia: 50,000 Ton
U.S.A. 43,000 Ton
Israel: 28,000 Ton
Kazakhstan: 20,000 Ton

www.intlimag.org
The Three Steps of the Pidgeon Process

1. Calcination of Dolomite,

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

2. Ferrosilicon Alloy Production,

\[ \text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} = 2(\text{Fe})\text{Si}_2 + 11\text{CO} \]

3. Silicothermic Reduction of MgO by Ferrosilicon,

\[ 2\text{MgO} + 2\text{CaO} + (\text{Fe})\text{Si} = 2\text{Mg(g)} + \text{Ca}_2\text{SiO}_4(s) + \text{Fe} \]

Energy Consumption and Greenhouse Gas Emissions in the Industrial Pidgeon Process

From Ramakrishnan, Koltun, Resources, Conservation & Recycling, 42, 49, 2004

<table>
<thead>
<tr>
<th>Reaction Steps</th>
<th>Energy Consumption MJ/kg Mg Ingot</th>
<th>Global Warming Impact kg CO$_{2eq}$/kg Mg Ingot</th>
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<tbody>
<tr>
<td>Dolomite Calcination</td>
<td>52.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Ferrosilicon Production</td>
<td>113.5</td>
<td>14.7</td>
</tr>
<tr>
<td>MgO Reduction by Ferrosilicon</td>
<td>181.4</td>
<td>15.9</td>
</tr>
</tbody>
</table>
The 1st Step of the Pidgeon Process

Calcination of Dolomite, at ~1300° C,

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

Highly Endoothermic Reaction,
\( \text{CO}_2 \) Released both from the Reaction, and from Fuel Burned for Process Heat.
Equilibrium Composition vs. Temperature for the Calcination of CaMg(CO$_3$)$_2$
initially at 300 K and 1 bar

The 2nd Step of the Pidgeon Process

Ferrosilicon Alloy Production

by Electric Arc through Mixture of Hematite, Quartz Sand, and Coal.
Extremely Endothermic Reaction;
Emits Toxic CO.

*Literature Reported Reaction:*

\[ \text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} = 2(\text{Fe})\text{Si}_2 + 11\text{CO} \]
Equilibrium Composition vs. Temperature for the System

$\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C}$ at 1 bar

[Graph showing the changes in mole fractions of various products (C(gr), CO, FeSi, SiO, SiO2) with temperature (1500 to 2000 K).]
Thermogravimetric Experiment

Purpose of experiment:

To test if for Ferrosilicon Production, the Customary Internal Heating by an Electric Arc could be Replaced by External Heating, Potentially with Concentrated Solar Energy.

Expected Reaction from Literature:

Fe₂O₃ + 4SiO₂ + 11C = 2(Fe)Si₂ + 11CO

A mixture of hematite, quartz sand and active carbon was heated under constant Ar flow in a high-temperature thermogravimeter.

Observed Reaction in Present work:

Fe₂O₃ + 4SiO₂ + 11C = 2FeSi+10CO+SiC+SiO

Evolved gases measured by gas chromatography.
Solid products analyzed by X-ray diffraction.

XRD of the Solid Product of the Reaction

\[ \text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} = 2\text{FeSi} + \text{SiC} + 10\text{CO} + \text{SiO} \]

Identified \text{FeSi} and \text{SiC}
The 3rd Step of the Pidgeon Process

Silicothermic Reduction of MgO by Ferrosilicon,

at ~1200-1500°C under Vacuum.

Highly Endothermic Reaction,

\[
2\text{MgO} + 2\text{CaO} + (\text{Fe})\text{Si} = 2\text{Mg}(g) + \text{Ca}_2\text{SiO}_4(s) + \text{Fe}
\]

Products: Gaseous Mg and Slag of Dicalcium Silicate.
Equilibrium Composition vs. Temperature at $10^{-5}$ bar for the System

$\text{Si} + 2\text{MgO} + 2\text{CaO}$

<table>
<thead>
<tr>
<th>Process Steps</th>
<th>Fuel Savings, %</th>
<th>CO₂ Emission Avoidance, %</th>
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</thead>
<tbody>
<tr>
<td><strong>Dolomite Calcination</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaMg(CO₂)₃ = CaO+MgO+2CO₂</td>
<td>100</td>
<td>44.0</td>
</tr>
<tr>
<td>CaMg(CO₂)₃+20C+40H₂O=CaO+MgO+26.3H₂+13.5CO+13.6H₂O+8.4CO₂</td>
<td>55.4</td>
<td>22.3</td>
</tr>
<tr>
<td>CaMg(CO₂)₃ + 4CH₄ = CaO+MgO+7.8H₂+3.9CO+2C(gr)</td>
<td>38.6</td>
<td>99.7</td>
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<tr>
<td><strong>Ferrosilicon Production</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃+4SiO₂+11C = 2FeSi+10CO+SiC+SiO</td>
<td>90.7</td>
<td>94.7</td>
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<tr>
<td><strong>Reduction of Calcined Dolomite</strong></td>
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</tr>
<tr>
<td>Si + 2MgO + 2CaO = 2Mg(g) + Ca₂SiO₄(s)</td>
<td>99.2</td>
<td>100</td>
</tr>
</tbody>
</table>
Conclusions on Modifications to Pidgeon Process


2. For Dolomite Calcination, and for Ferrosilicon Production, Additional Fuel Saving and CO₂ Emission Avoidance Possible by using CH₄ or C + H₂O as Reductant, resulting in Co-Production of Syngas.

3. Half-Calcined Dolomite, CaCO₃-MgO, is useful for Reversible Moderate-Temperature (~800K) Capture of CO₂ and SO₂.
Ammonia Production by a Cyclic Process via Alumina and Aluminum Nitride

The production of NH₃ by a two-step cyclic process was tested as an alternative to its current industrial production by the Haber-Bosch process.

The first, endothermic step, is the production of AlN by the reduction of Al₂O₃ with carbon in a N₂ atmosphere above 1300°C:

\[ \text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO} \]

The CO may be “water-gas” shifted to syngas.

The second, exothermic step, is the steam-hydrolysis of AlN to produce NH₃ and reform Al₂O₃ below 375°C; the latter is recycled to the first step:

\[ 2\text{AlN} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 2\text{NH}_3 \]

**Advantages:**
1) No need for high pressure;
2) No need for expensive catalysts;
3) Petcoke or charcoal as feedstock instead of hydrogen;

**But:**
Pure N₂ required as feedstock.


Conclusions: Principles of Process Improvements

1. Combining heat absorbing and heat releasing chemical reactions.

2. Combining CO$_2$ emitting and CO$_2$ consuming reactions.

3. Lowering the temperature required for gas-releasing reactions by decreased gas pressure.

Scope for Collaboration of Different Industries on Carbon Management

1. Between the Petrochemical and Metallurgical Industries on the Co-Production of Metals and Syngas;

2. Between the Petrochemical and Lime (and Cement) Industries on the Co-Production of Lime and Syngas;
