

Global Climate and Energy Project (GCEP)
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Workshop on Carbon Management in Manufacturing Industries

Co-Production of Syngas and Metals or Lime

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Outline

Several high-temperature endothermic chemical reactions are major contributors to the anthropogenic CO₂ emissions:

- 1. The reforming of natural gas to syngas and various chemicals and fuel.**
- 2. The calcination of limestone to produce lime and cement, $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$.**
- 3. The production of metals from their ores,**
 - a) $\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}$**
 - b) $\text{Al}_2\text{O}_3 + 3\text{C} = 2\text{Al} + 3\text{CO}$**
 - c) $2\text{MgO-CaO} + \text{FeSi} = 2\text{Mg} + \text{Ca}_2\text{SiO}_4 + \text{Fe}$**

Causes of CO₂ Emissions

CO₂ 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 CO₂ emission avoidance are expected by modifying these reactions.

The sequestration of CO₂ 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,



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



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.

Ashcroft et al, Nature, 352, 225,1991

Tri-Reforming for Rapid Hydrogen Production

A mixture of $\text{CH}_4 - \text{CO}_2 - \text{H}_2\text{O} - \text{O}_2$

(60 : 10 : 10 : 20%)

Passed at 700°C over the 4-component catalyst

$\text{Ni} - \text{Ce}_2\text{O}_3 - \text{Pt} - \text{Rh}$ (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 $12.2 \text{ kmol H}_2 \text{ L}^{-1} \text{ h}^{-1}$

The inclusion of O_2 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

	Coal-Fired Boilers	Gas-Fired Boilers
CO₂	12-14%	8-10%
H₂O	8-10%	18-20%
O₂	3-5%	2-3%
N₂	72-77%	67-72%

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) CO₂ Consumed for Production of Syngas;
- (b) N₂ Consumed for Production of Ammonia;
- (c) Decreased CO₂ Emission by Tri-Reforming;
- (d) Increased CO₂ Emission by Coal Gasification;
- (e) Fuel Saving, particularly by Coal Gasification;
- (f) Favorable Economics;

But: For Significant CO₂ Emission Mitigation by Tri-Reforming - the World Proved Reserves of Natural Gas would be Insufficient.

Halmann and Steinfeld, Catal. Today, 115, 170, 2006

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

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



and the **Endothermic** CH₄/CO₂ Reforming,



with the **Exothermic** Partial Oxidation of CH₄

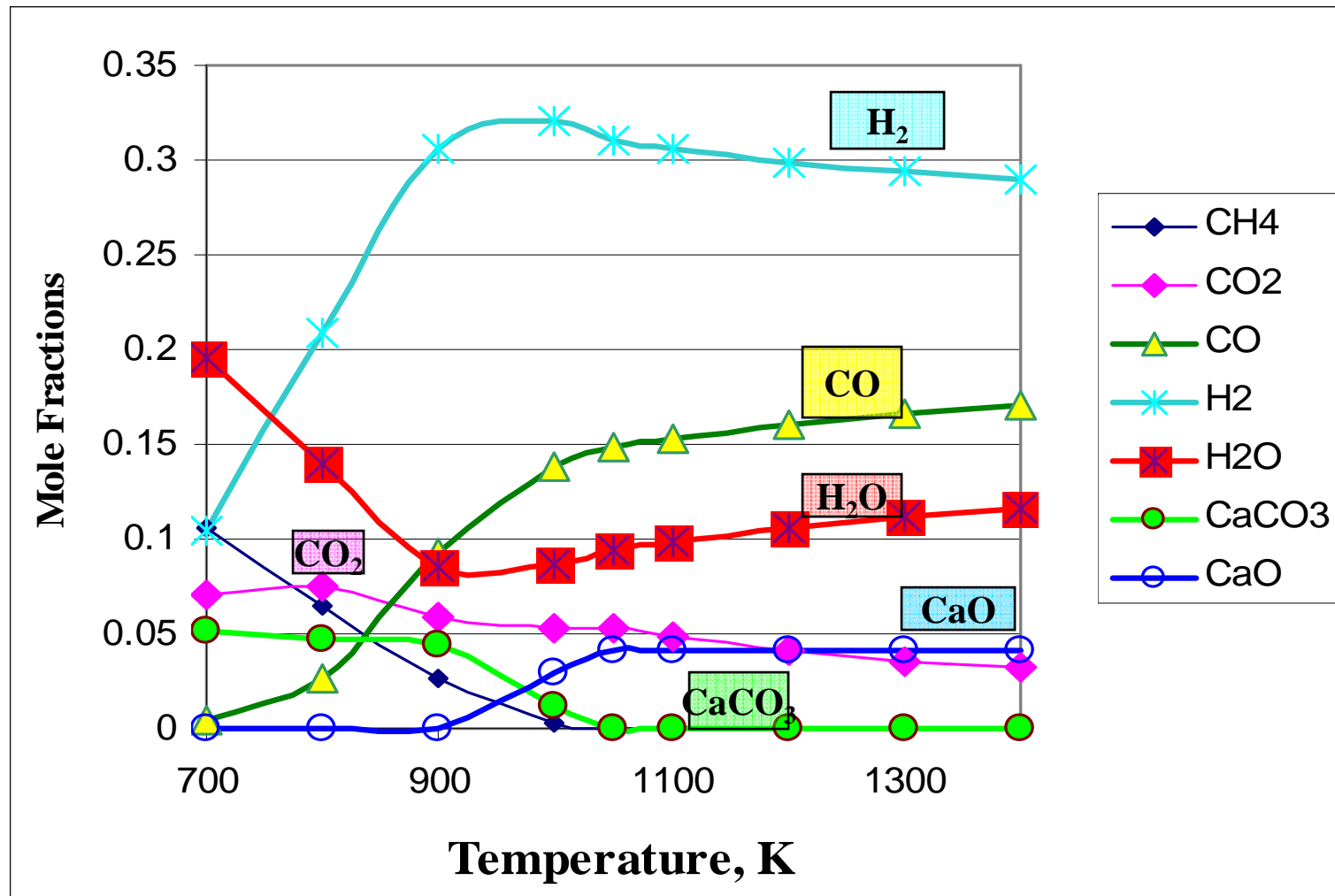


to achieve an Overall **Thermo-neutral** Reaction

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

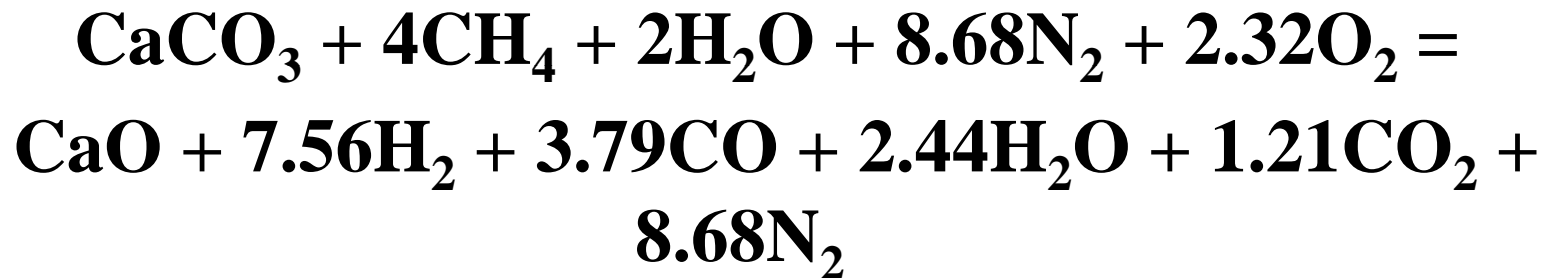
Halmann, Steinfeld, Energy, 31, 1533 (2006)

**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:**



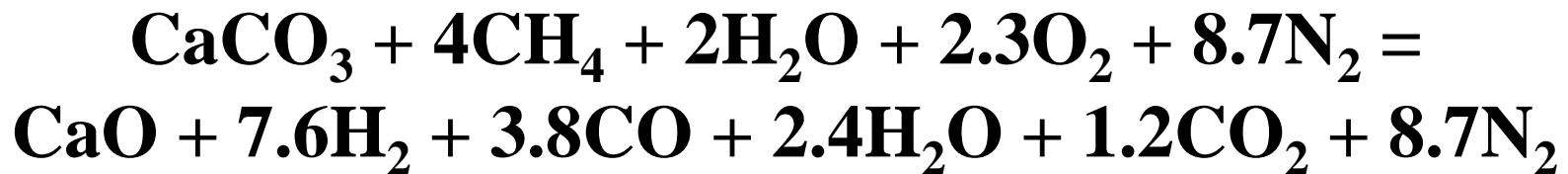
By Proposed Co-Production followed by Methanol Synthesis:

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



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

CO₂ Emission Avoidance by NH₃ Co-Production = 23%

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

CO₂ 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**.

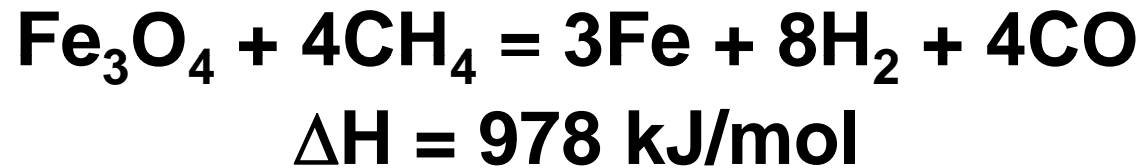
Urea production consumes over 70% of CO₂ generated from ammonia production.

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 Fe₃O₄ Reduction by Methane

At 1300 K and 1 atm, Fe₃O₄, fluidized in CH₄, was converted into Fe and syngas



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.

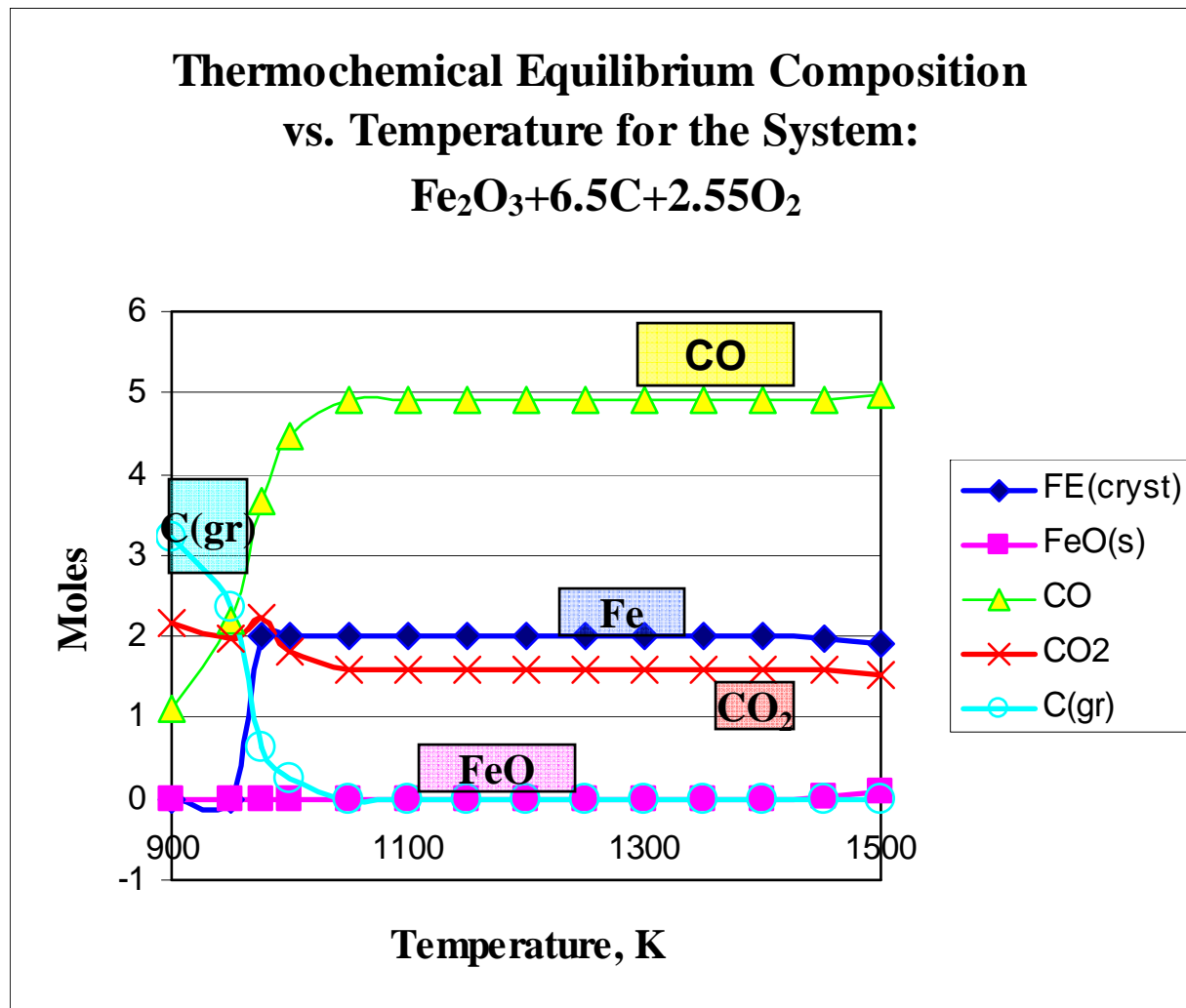
Metals and Syngas Co-Produced

in Thermoneutral Reactions by Combining the
Endothermic Reduction of Metal oxides by CH₄
with the Exothermic Partial Oxidation of CH₄ by O₂



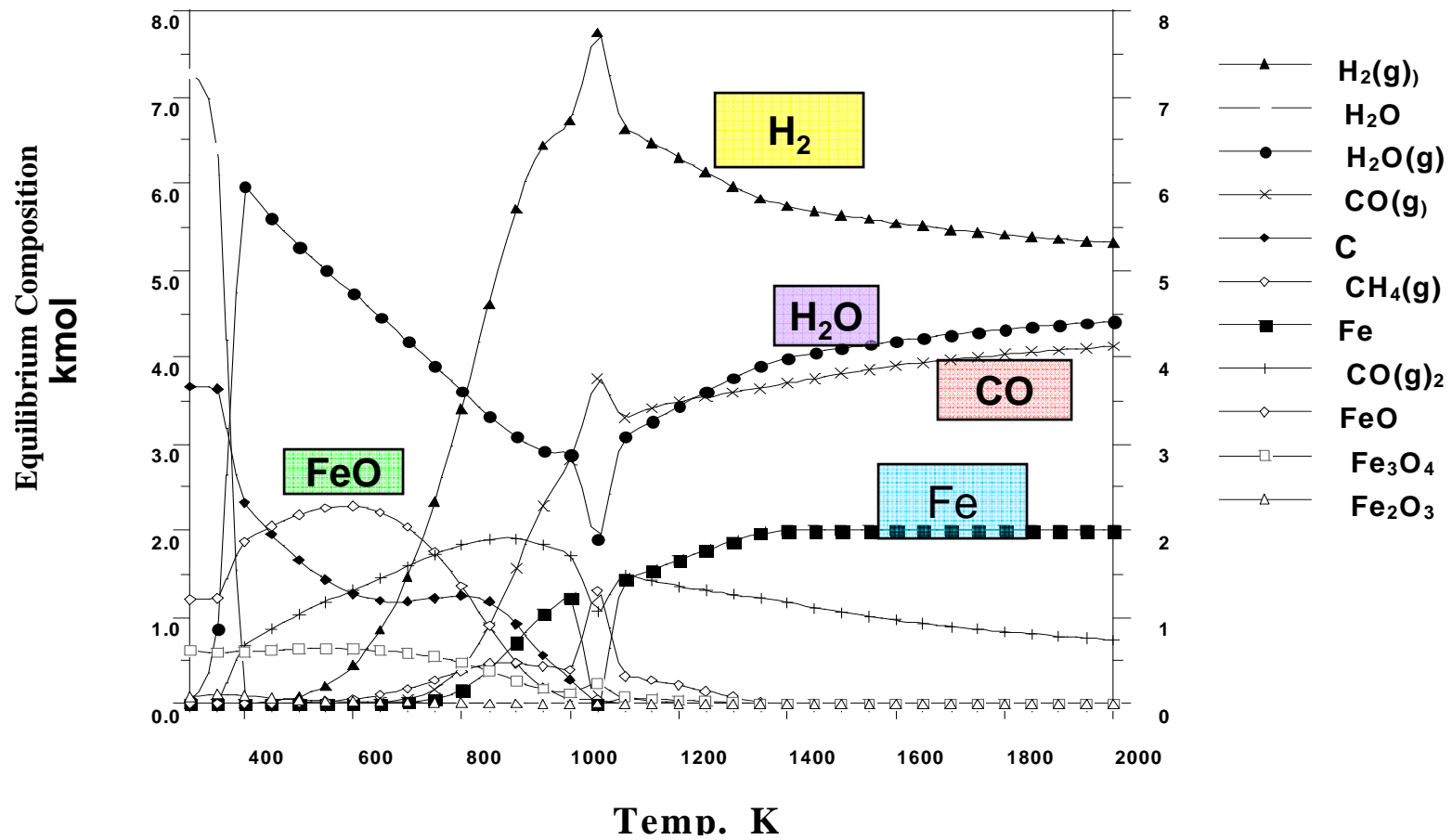
Halmann, Frei, Steinfeld, Energy, 27, 1069, 2002

Thermoneutral Carbothermic Reduction of Fe_2O_3



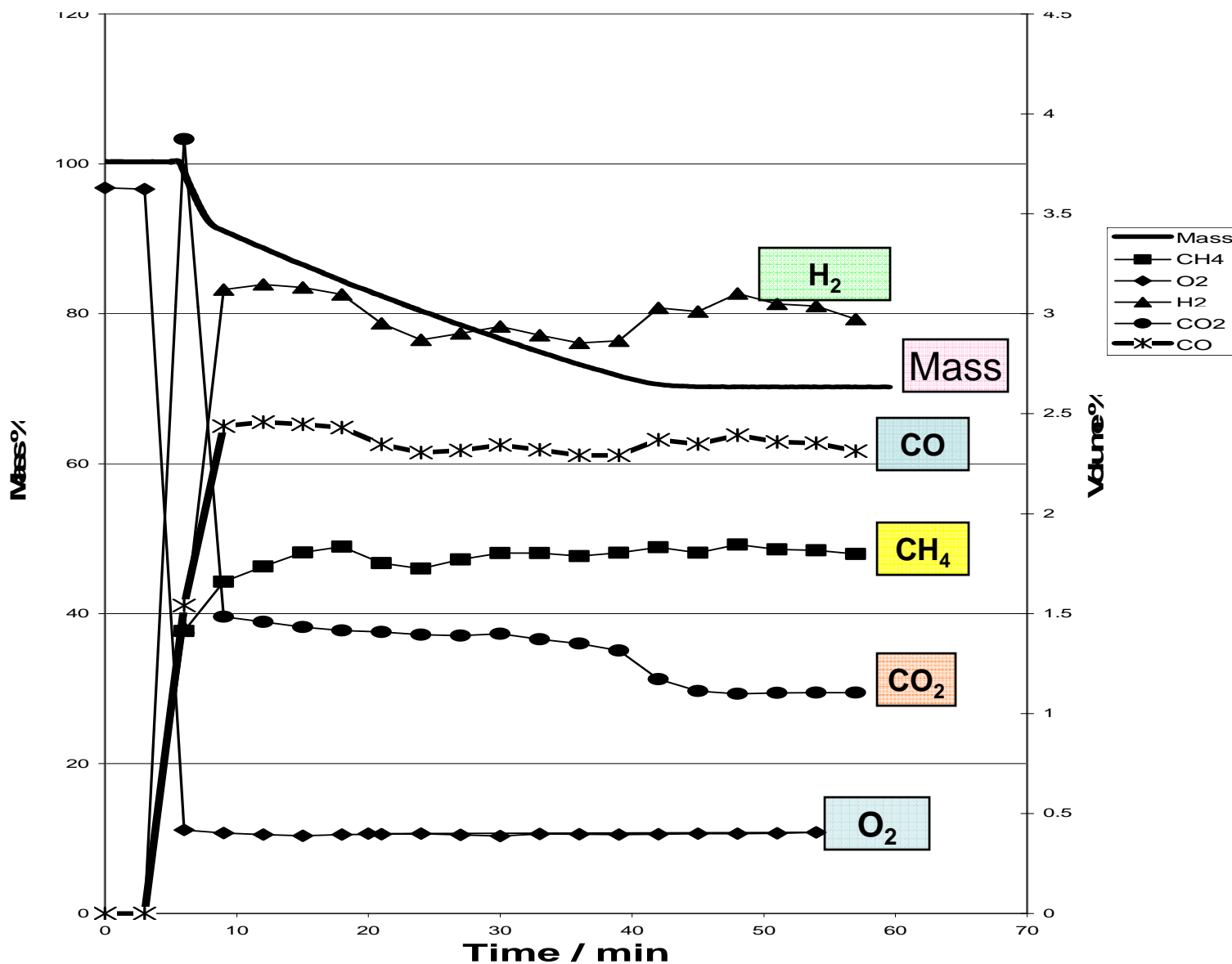
Equilibrium Composition for the System

Fe₂O₃-CH₄-O₂ (molar ratio 1 : 4.9 : 3.5)



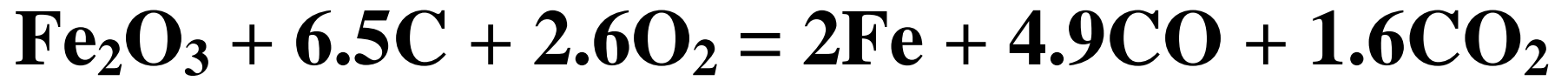
Thermogravimetric experiments with ~100 mg Fe₂O₃ under 3.6% O₂ in Argon. After equilibration at 1400°K, 5.1% CH₄ was introduced.

Halmann, Frei and Steinfeld, Energy, 27, 1069, 2002



CO₂ Emission Avoidance and Fuel Saving by Co-Production of Iron and Methanol

Thermochemical Equilibrium at 1400K, 1 bar:



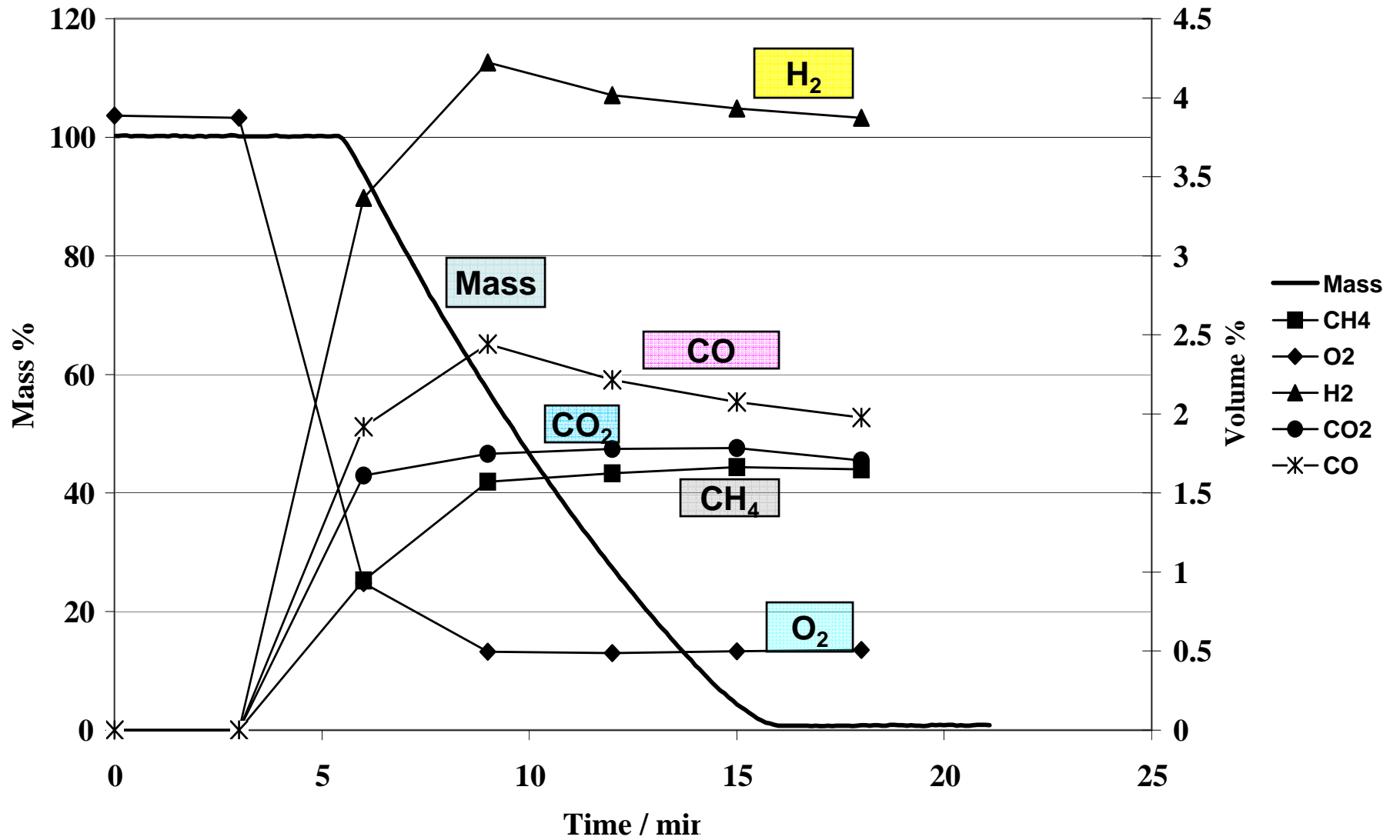
**followed by partial water-gas shift of CO to H₂,
and methanol synthesis.**

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



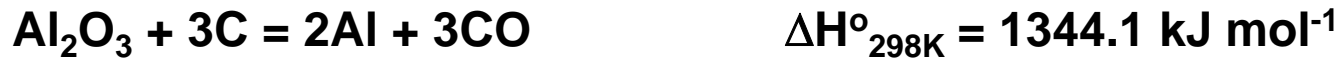
Conclusions on Co-Production of Syngas and Iron or Zinc

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 Al₂O₃ to Al Metal

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

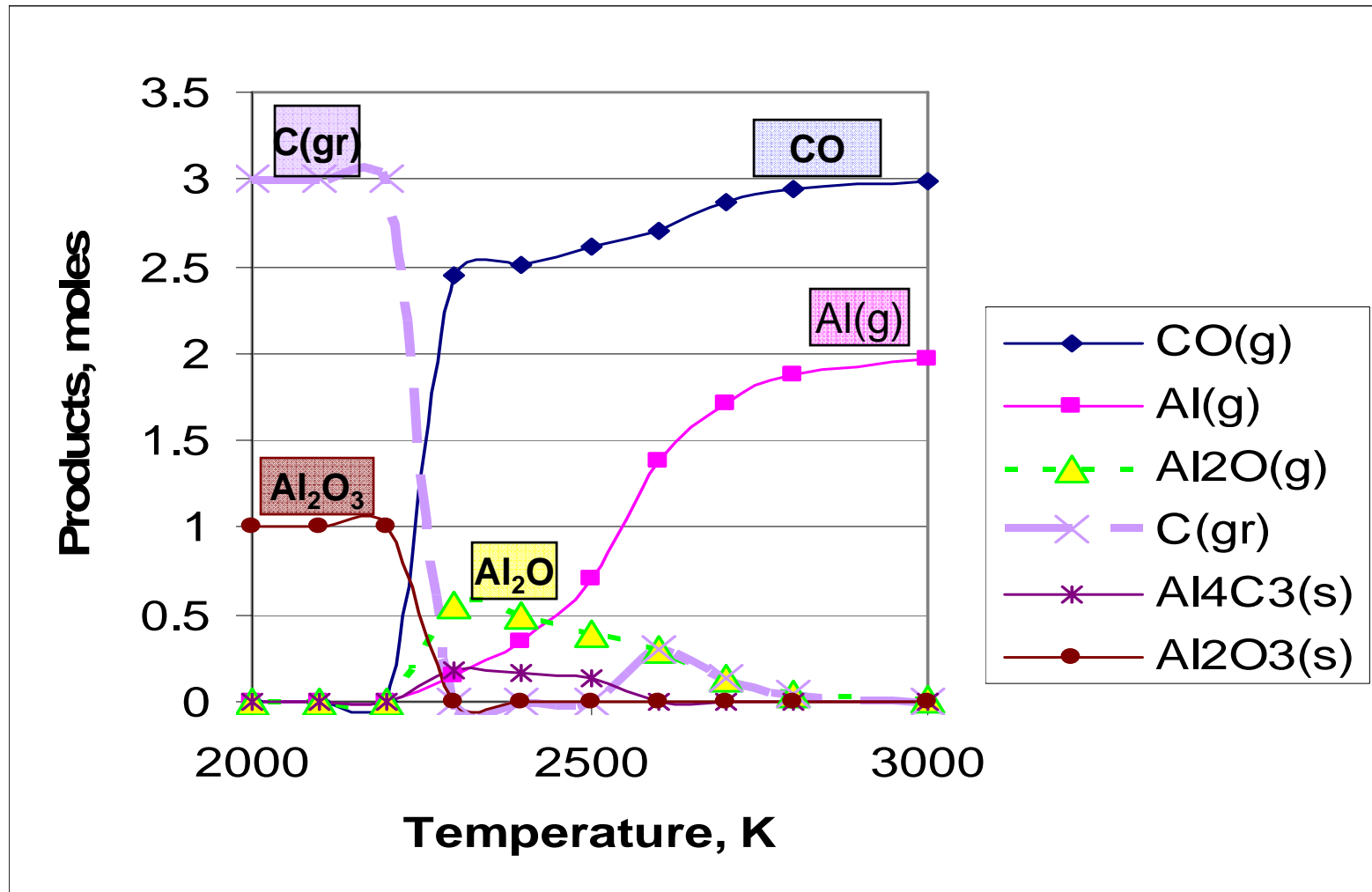
With carbon or CH₄ as reducing agents, the overall desired reactions are:



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

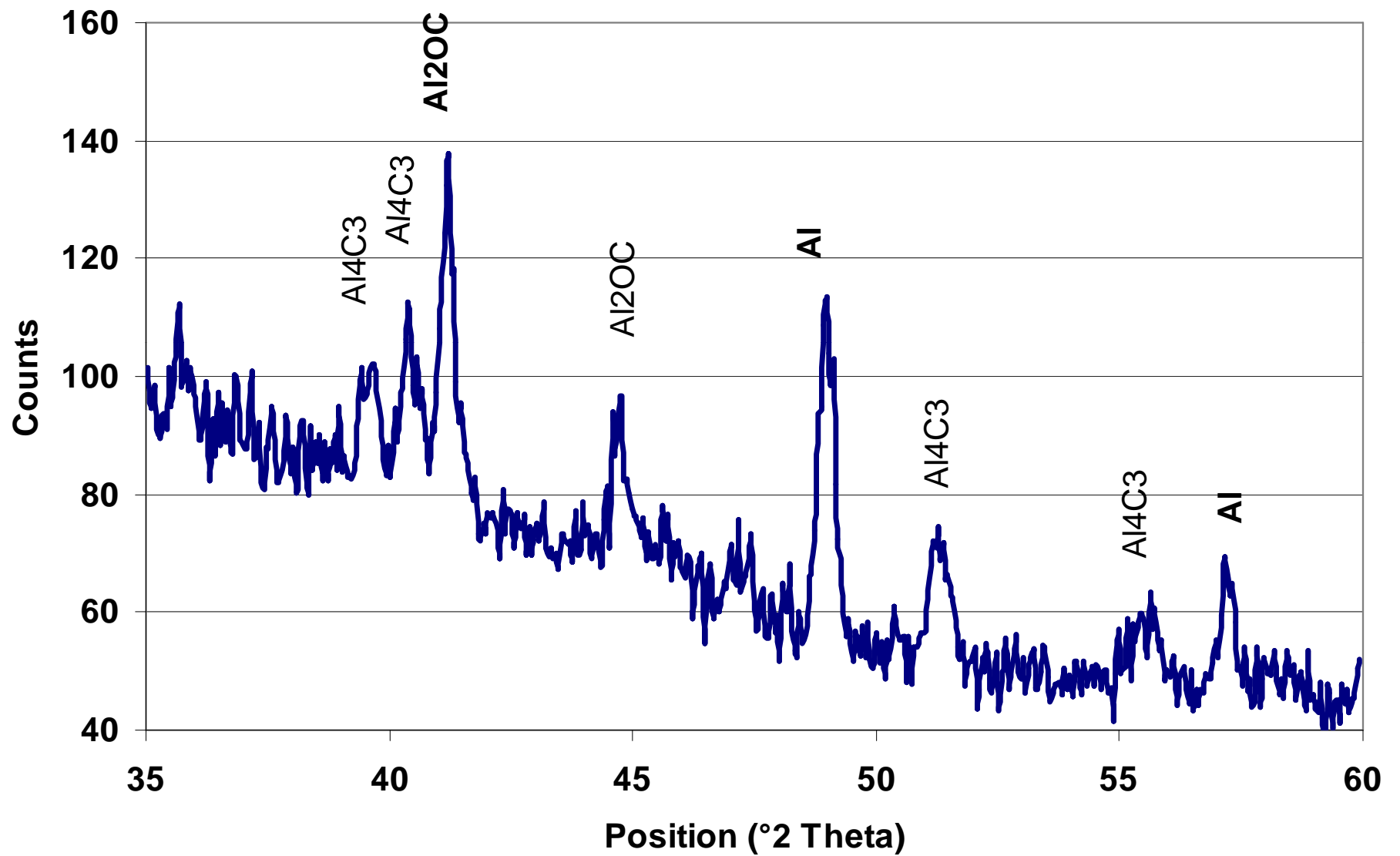
Halmann, Frei, Steinfeld, Energy, 32, 2420, 2007



Induction Furnace Carbothermic Reduction of Alumina

The production of **Al** and **CO**, as well as the aluminum carboxides **Al₂OC**, **Al₄O₄C**, and the carbide **Al₄C₃** was achieved by heat pulses from an induction furnace on mixtures of Al₂O₃ and activated carbon in an Ar stream.

The formation of these species was proven by gas chromatography for the 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, $\text{CaMg}(\text{CO}_3)_2$, 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

U.S.Geological Survey, 2007
www.intlmag.org

The Three Steps of the Pidgeon Process

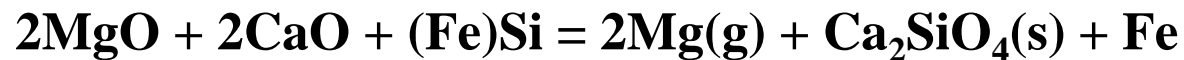
1. Calcination of Dolomite,



2. Ferrosilicon Alloy Production ,



3. Silicothermic Reduction of MgO by Ferrosilicon,



Toguri and Pidgeon, Can. J. Chem., 40, 1769 (1962)

Energy Consumption and Greenhouse Gas Emissions in the Industrial Pidgeon Process

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

Reaction Steps	Energy Consumption MJ/kg Mg Ingot	Global Warming Impact kg CO_{2eq}/kg Mg Ingot
Dolomite Calcination	52.1	10.1
Ferrosilicon Production	113.5	14.7
MgO Reduction by Ferrosilicon	181.4	15.9

The 1st Step of the Pidgeon Process

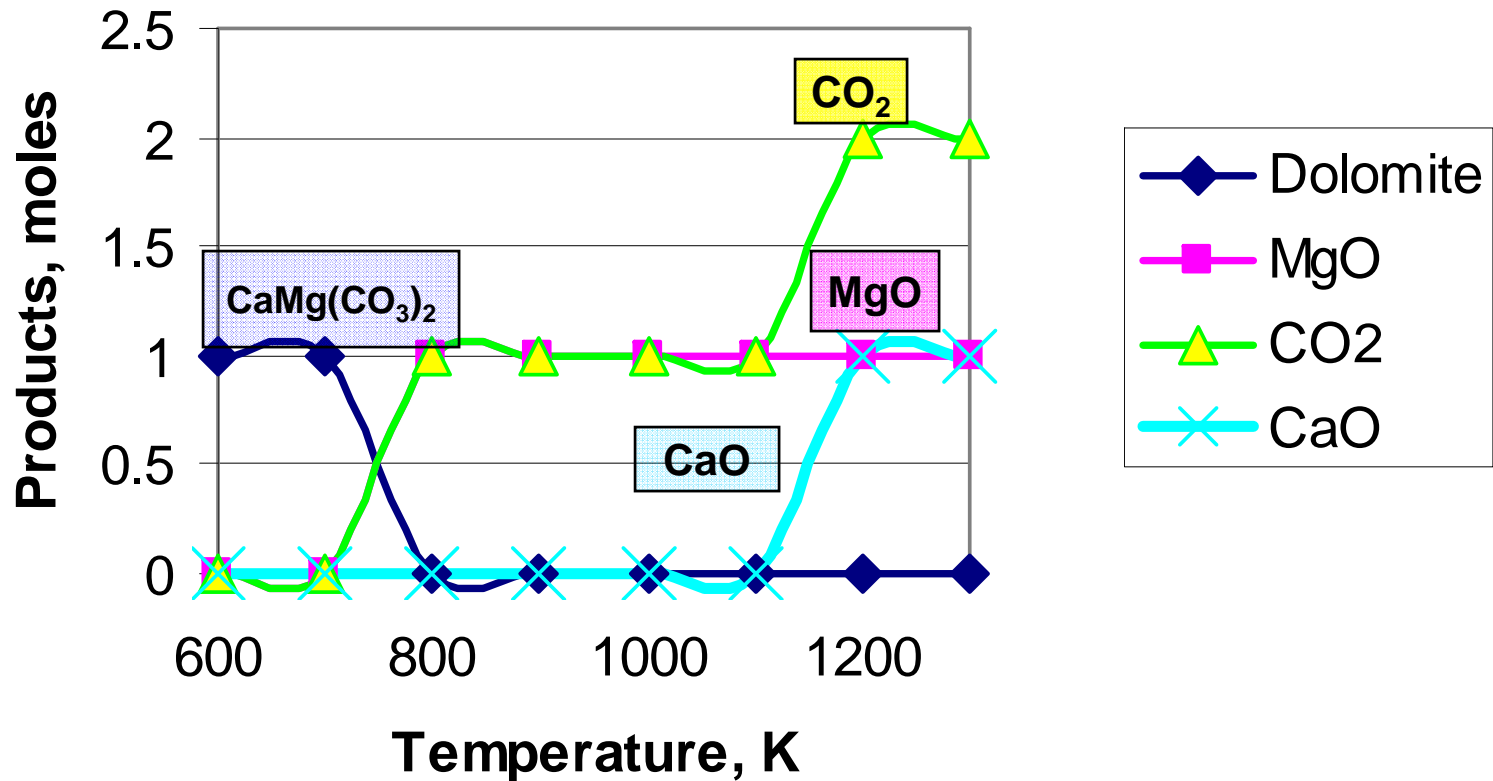
**Calcination of Dolomite,
at ~1300° C,**



**Highly Endothermic Reaction,
CO₂ Released both from the Reaction,
and from Fuel Burned for Process Heat.**

Equilibrium Composition vs. Temperature
for the Calcination of $\text{CaMg}(\text{CO}_3)_2$
initially at 300 K and 1 bar

Halmann, Frei, Steinfeld, Ind. Eng. Chem. Res., 47, 2146, 2008



The 2nd Step of the Pidgeon Process

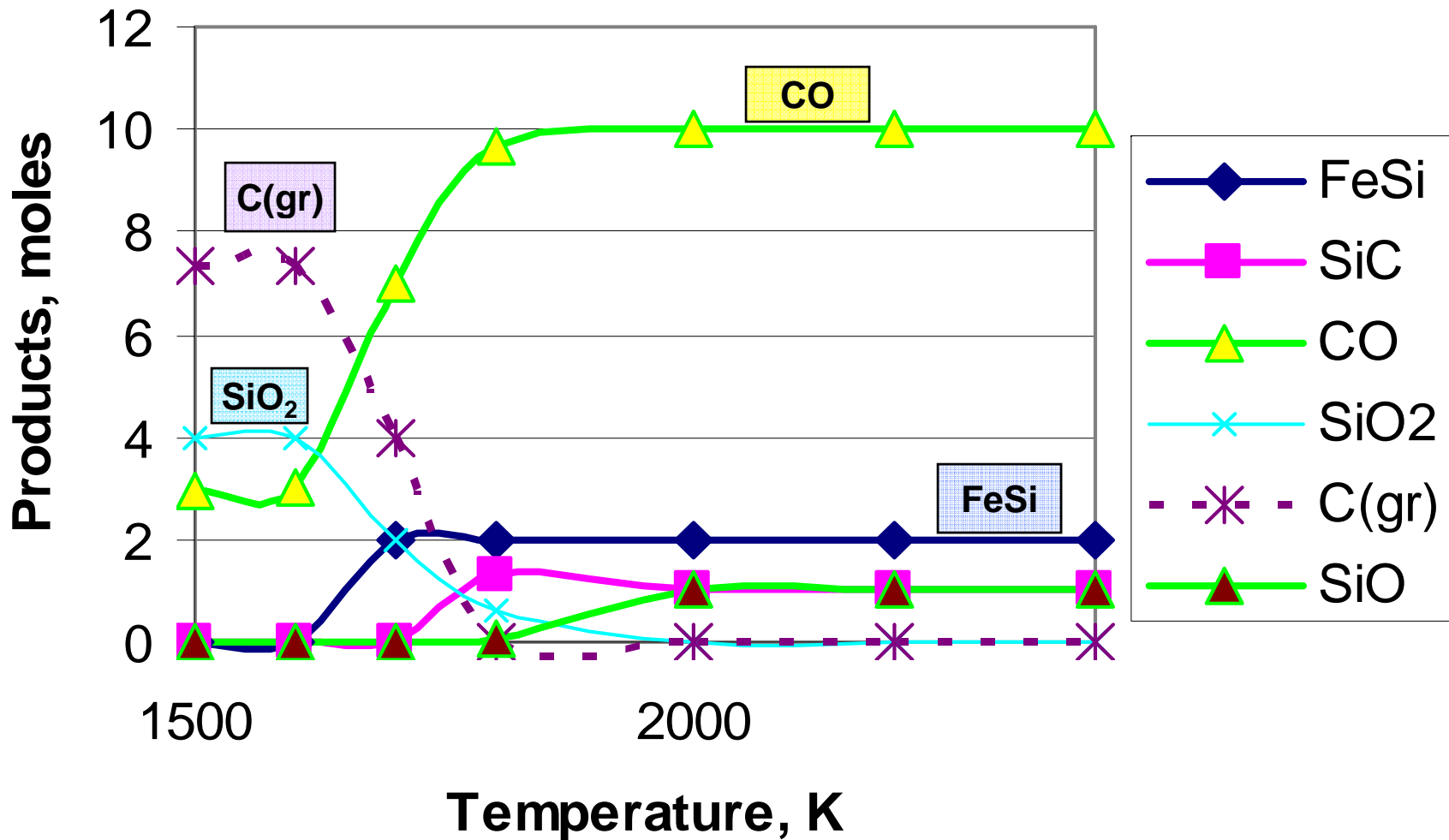
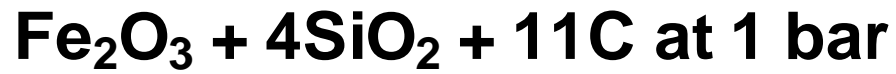
Ferrosilicon Alloy Production

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

Literature Reported Reaction:



Equilibrium Composition vs. Temperature for the System



Thermogravimetric Experiment

Purpose of experiment:

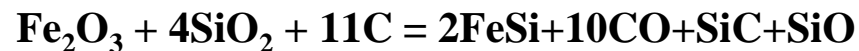
To test if for Ferrosilicon Production, the Customary **Internal Heating** by an Electric Arc could be Replaced by **External Heating**, Potentially with Concentrated Solar Energy.

Expected Reaction from Literature:



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:



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

Halmann, Frei, Steinfeld, Industrial Eng. Chem. Res., 47, 2146, 2008

The 3rd Step of the Pidgeon Process

**Silicothermic Reduction of MgO by
Ferrosilicon,**

at ~1200-1500°C under Vacuum.

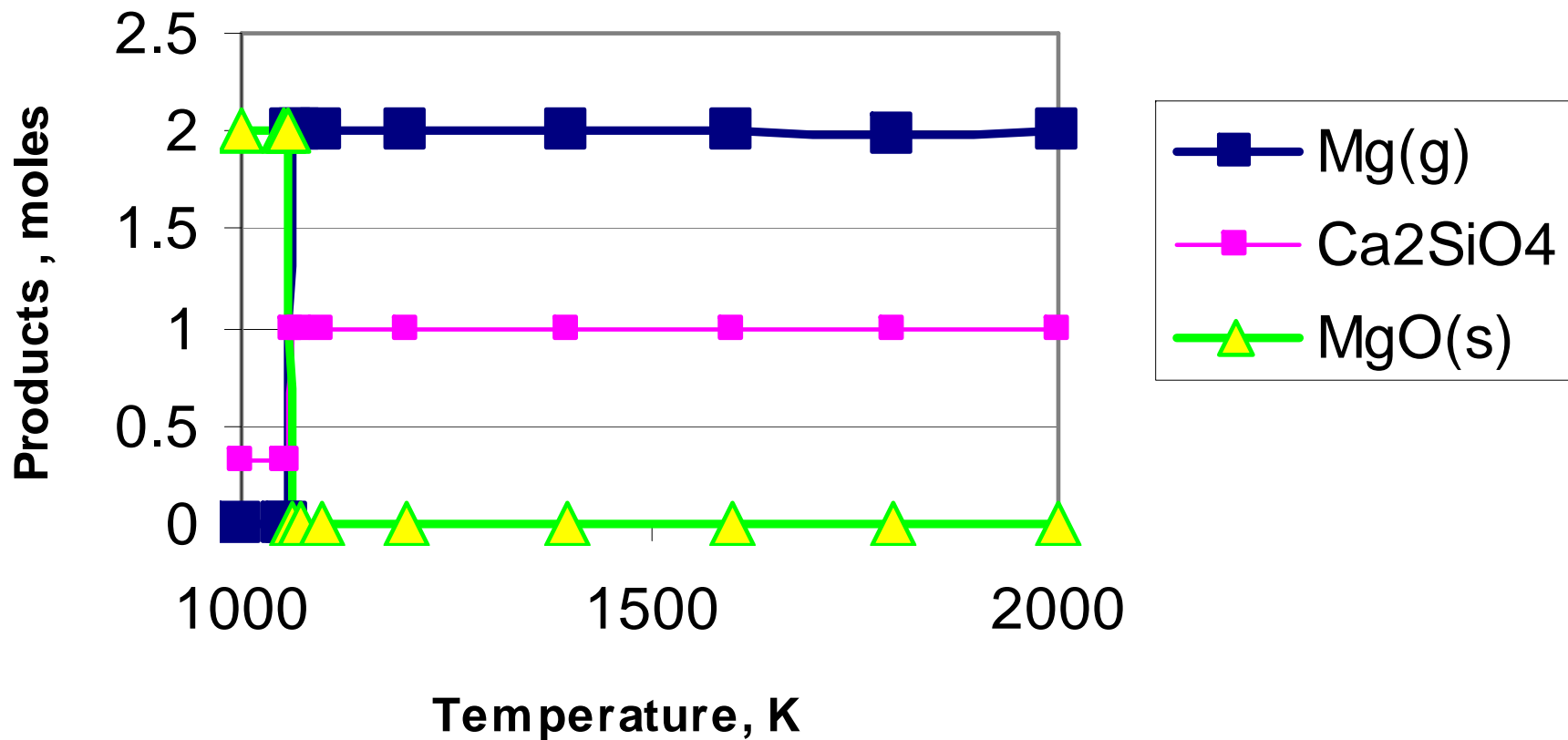
Highly Endothermic Reaction,



Products: Gaseous Mg and

Slag of Dicalcium Silicate.

Equilibrium Composition vs.
Temperature at 10^{-5} bar for the System
Si + 2MgO + 2CaO



Potential Fuel Savings and CO₂ Emission Avoidance in a Solar Pidgeon Process Combined with Conversion of Syngas (if formed) to Methanol – vs. Conventional Processes.

Process Steps	Fuel Savings, %	CO ₂ Emission Avoidance, %
Dolomite Calcination		
$\text{CaMg}(\text{CO}_2)_3 = \text{CaO} + \text{MgO} + 2\text{CO}_2$	100	44.0
$\text{CaMg}(\text{CO}_2)_3 + 20\text{C} + 40\text{H}_2\text{O} = \text{CaO} + \text{MgO} + 26.3\text{H}_2 + 13.5\text{CO} + 13.6\text{H}_2\text{O} + 8.4\text{CO}_2$	55.4	22.3
$\text{CaMg}(\text{CO}_2)_3 + 4\text{CH}_4 = \text{CaO} + \text{MgO} + 7.8\text{H}_2 + 3.9\text{CO} + 2\text{C}(\text{gr})$	38.6	99.7
Ferrosilicon Production		
$\text{Fe}_2\text{O}_3 + 4\text{SiO}_2 + 11\text{C} = 2\text{FeSi} + 10\text{CO} + \text{SiC} + \text{SiO}$	90.7	94.7
Reduction of Calcined Dolomite		
$\text{Si} + 2\text{MgO} + 2\text{CaO} - 2\text{Mg}(\text{g}) + \text{Ca}_2\text{SiO}_4(\text{s})$	99.2	100

Conclusions on Modifications to Pidgeon Process

- 1. Considerable Fuel Savings and CO₂ Emission Avoidance Predicted in all Three Steps of the Pidgeon Process by using Concentrated Solar Energy for Process Heat.**
- 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

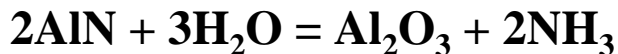
The production of NH_3 by a two-step cyclic process was tested as an alternative to its current industrial production by the Haber-Bosch process.

The first, **endothermic step**, is the production of AlN by the reduction of Al_2O_3 with carbon in a N_2 atmosphere above 1300°C :



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

The second, **exothermic step**, is the steam-hydrolysis of AlN to produce NH_3 and reform Al_2O_3 below 375°C ; the latter is recycled to the first step:



Advantages:

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

But:

Pure N_2 required as feedstock.

Gálvez, Halmann, Steinfeld, Ind. Eng. Chem. Res. 46, 2042, 2007

Gálvez et al, Ind. Eng. Chem. Res. 47, 2231, 2008

Conclusions: Principles of Process

Improvements

- 1. Combining heat absorbing and heat releasing chemical reactions.**
- 2. Combining CO₂ emitting and CO₂ consuming reactions.**
- 3. Lowering the temperature required for gas-releasing reactions by decreased gas pressure.**
- 4. Substituting concentrated solar energy instead of fuel combustion for process heat.**

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;**
- 3. Between the Automobile and Electrochemical Industries on the Development of Ammonia Fuel Cells for Carbon-Free Emissions.**

