CO₂ Capture in the Steel Industry
Review of the Current State of Art

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IEA Greenhouse Gas R&D Programme
Cheltenham, UK

Industry CCS Workshop
Vienna, Austria
28th April 2014
IEAGHG Activities on CCS for the Iron & Steel Industry

**Reports**

- 2013-04 – “Understanding the Economics of Deploying CO₂ Capture Technologies in an Integrated Steel Mill”


**Stakeholders Engagement**

- 1ˢᵗ Workshop (Nov. 2011) Dusseldorf, Germany in collaboration with VDeH, Swerea MEFOS

- 2ⁿᵈ Workshop (Nov. 2013) Tokyo, Japan in collaboration with IETS, World Steel, Swerea MEFOS

**Total Cost of the Study:** ~ £ 440,000

**IEA GHG Contribution:** ~ £ 120,000
Presentation Overview

• Brief Introduction
  • Global Steel Industry
  • Overview to the Steel Production

• Capture of CO₂ from Blast Furnace Gas
  • ULCOS Programme – Oxygen Blown BF with TGR
  • COURSE50 Programme – Chemical Absorption & Physical Adsorption
  • POSCO / RIST Programme – Chemical Absorption

• Capture of CO₂ from Alternative Ironmaking Process
  • Direct Reduction Ironmaking
    o MIDREX, ENERGIRON (HYL), ULCORED
  • Smelting Reduction Ironmaking
    o COREX, FINEX, HISARNA

• Summary / Concluding Remarks
World Crude Steel Production
(Data and Figure from World Steel)

• Total Crude Steel Production has reached 1.545 Billion Tonnes of crude steel in 2012.
  • As compared to 2002 (905.2 million tonnes), crude steel production has increased by ~70%.

• Global CO$_2$ Emissions from the steel industry is roughly at ~2.3-2.5Gt/y

• Major Steel Producing Regions
  • China (716.5 million tonnes)
  • EU27 (168.6 million tonnes)
  • N. America (121.6 million tonnes)
  • CIS (111.0 million tonnes)
  • Japan (107.2 million tonnes)
  • India (77.6 million tonnes)
Overview of Steel Production
(Picture from VDEH)
World Crude Steel Production

Data estimated from WSA & VDEH statistics (2012)

- **BOF Steel** (70%)
- **EAF Steel** (29%)
- **OHF Steel** (1%)
- **DRI / HBI** (4.5%)
- **Scrap Metal** (30%)
- **Hot Metal – Corex/Finex** (0.5%)
- **Hot Metal – Blast Furnace** (65%)

Crude Steel Production

 Metallic Charge

~1735
OVERVIEW OF STEEL PRODUCTION VIA BF/BOF ROUTE

NOTE:

• Presentation is derived from the results of IEAGHG Study (Report No. 2013-04)
Integrated Steelmaking Process (BF/BOF)

- **Raw Materials Preparation Plants**
  - Coke Production
  - Ore Agglomerating Plant (Sinter Production)
  - Lime Production

- **Ironmaking**
  - Blast Furnace
  - Hot Metal Desulphurisation

- **Steelmaking**
  - Basic Oxygen Steelmaking (Primary)
  - Secondary Steelmaking (Ladle Metallurgy)

- **Casting**
  - Continuous Casting

- **Finishing Mills**
  - Hot Rolling Mills (Reheating & Rolling)
Point Source Emissions
(Results of IEAGHG Study – An Example)

CO₂ Emissions are released at various stacks within the integrated steel mill.

<table>
<thead>
<tr>
<th>UNT</th>
<th>Source of CO₂ Emissions</th>
<th>Emissions (kg/t HRC)</th>
<th>Annual Emission (t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Coke oven flue gas</td>
<td>191.37</td>
<td>765,495</td>
</tr>
<tr>
<td>100</td>
<td>Coke oven gas flare</td>
<td>3.30</td>
<td>13,196</td>
</tr>
<tr>
<td>200</td>
<td>Sinter plant flue gas (CO₂ + CO)</td>
<td>288.46</td>
<td>1,157,825</td>
</tr>
<tr>
<td>300</td>
<td>Hot Stove flue gas</td>
<td>415.19</td>
<td>1,680,769</td>
</tr>
<tr>
<td>400/1300</td>
<td>PCI, Coal drying, torpedo car and ladle heating (HM Desulphurisation) diffuse emissions</td>
<td>7.76</td>
<td>31,042</td>
</tr>
<tr>
<td>300</td>
<td>Blast Furnace Gas flare</td>
<td>19.73</td>
<td>78,331</td>
</tr>
<tr>
<td>500/600</td>
<td>Basic Oxygen Furnace gas flared and system losses, SM diffuse Emissions</td>
<td>51.02</td>
<td>204,089</td>
</tr>
<tr>
<td>700</td>
<td>Continuous Casting - diffuse emissions (from slab casting)</td>
<td>0.90</td>
<td>3,188</td>
</tr>
<tr>
<td>800</td>
<td>Reheating Furnace flue gas</td>
<td>57.71</td>
<td>236,833</td>
</tr>
<tr>
<td>900</td>
<td>Höt Rolling Mills - diffuse emissions (from cutting and scarfing)</td>
<td>0.04</td>
<td>179</td>
</tr>
<tr>
<td>1000</td>
<td>Lime Plant flue gas</td>
<td>71.62</td>
<td>286,430</td>
</tr>
<tr>
<td>1200</td>
<td>Power Plant flue gas</td>
<td>982.13</td>
<td>3,928,513</td>
</tr>
<tr>
<td>1300</td>
<td>Ancillaries transport fuel emissions (trucks and rails)</td>
<td>4.00</td>
<td>16,000</td>
</tr>
</tbody>
</table>

Total Emissions: 2084.14 t CO₂ / 8,376,554 t CO₂
Carbon Balance of Ironmaking Process
(Results of IEAGHG Study)

Direct CO₂ Emissions of an Integrated Steel Mill (REFERENCE)
Producing 4 MTPY Hot Rolled Coil
2090 kg CO₂/t HRC (2107 kg CO₂/thm)

<table>
<thead>
<tr>
<th>Carbon Input (kg C/thm)</th>
<th>Carbon Output (kg C/thm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke 312.4</td>
<td>Hot Metal 47.0</td>
</tr>
<tr>
<td>Limestone 1.5</td>
<td>BF Screen Undersize 6.3</td>
</tr>
<tr>
<td>PCI Coal 132.2</td>
<td>Dust &amp; Sludge 8.0</td>
</tr>
<tr>
<td>COG 1.3</td>
<td>BFG Export 266.4</td>
</tr>
<tr>
<td>Hot Stove’s Flue Gas</td>
<td>BFG Flared 5.4</td>
</tr>
<tr>
<td><strong>Total</strong> 447.5</td>
<td><strong>Total</strong> 447.2</td>
</tr>
</tbody>
</table>

80-90% of the carbon that caused to the CO₂ emissions of the steel production.
## Composition of Off-Gases
(Results of IEAGHG Study – An Example)

<table>
<thead>
<tr>
<th>Wet Basis (%vol.)</th>
<th>Coke Oven Gas (COG)</th>
<th>Blast Furnace Gas (BFG)</th>
<th>Basic Oxygen Furnace Gas (BOFG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>23.2</td>
<td>- NA -</td>
<td>- NA -</td>
</tr>
<tr>
<td>H₂</td>
<td>60.1</td>
<td>3.6</td>
<td>2.6</td>
</tr>
<tr>
<td>CO</td>
<td>3.9</td>
<td>22.1</td>
<td>56.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.0</td>
<td>22.3</td>
<td>14.4</td>
</tr>
<tr>
<td>N₂</td>
<td>5.8</td>
<td>48.3</td>
<td>13.8</td>
</tr>
<tr>
<td>O₂</td>
<td>0.2</td>
<td>- NA -</td>
<td>- NA -</td>
</tr>
<tr>
<td>H₂O</td>
<td>3.2</td>
<td>3.2</td>
<td>12.2</td>
</tr>
<tr>
<td>Other HC</td>
<td>2.7</td>
<td>- NA -</td>
<td>- NA -</td>
</tr>
</tbody>
</table>

| LHV (MJ/Nm³) – wet basis | 17.5 | 3.2 | 7.5 |

### Users of the Off-Gases
- Hot Stoves, Coke Ovens, Lime Kilns, Reheating Furnaces and others
- Hot Stoves, Power Plant
- Power Plant
**CAPTURE OF CO$_2$ FROM BLAST FURNACE GAS (BFG)**

<table>
<thead>
<tr>
<th>Treated BFG (Components)</th>
<th>Units</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>%(v/v) – dry</td>
<td>17 - 25</td>
</tr>
<tr>
<td>CO</td>
<td>%(v/v) – dry</td>
<td>20 - 28</td>
</tr>
<tr>
<td>H$_2$</td>
<td>%(v/v) – dry</td>
<td>1 – 5</td>
</tr>
<tr>
<td>N$_2$ / Ar</td>
<td>%(v/v) – dry</td>
<td>45 - 55 (balance)</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>mg/Nm$^3$</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>mg/Nm$^3$</td>
<td>1 – 10</td>
</tr>
<tr>
<td>Heavy Metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>mg/Nm$^3$</td>
<td>0.10 - 0.29</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/Nm$^3$</td>
<td>0.01 – 0.05</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/Nm$^3$</td>
<td>0.03 - 0.17</td>
</tr>
</tbody>
</table>

**NOTE:**

- Blast Furnace is a reduction process.
- CO$_2$ capture from BFG cannot be classified as post-combustion or oxy-combustion.
**The 4 ulcos process routes**

<table>
<thead>
<tr>
<th>Coal &amp; sustainable biomass</th>
<th>Natural gas</th>
<th>Electricity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Revamped BF</td>
<td>Greenfield</td>
<td>Revamped DR</td>
</tr>
<tr>
<td>ULCOS-BF</td>
<td>Hlsarna</td>
<td>ULCORED</td>
</tr>
<tr>
<td>Pilot tests (1.5 t/h)</td>
<td>Pilot plant (8 t/h) start-up 2010</td>
<td>Pilot plant (1 t/h) to be erected in 2013?</td>
</tr>
<tr>
<td>Demonstration under way</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Carbon Balance of Ironmaking Process
Results from IEAGHG Study – Case 3: OBF with MDEA/Pz CO₂ Capture

Direct CO₂ Emissions of an Integrated Steel Mill (with OBF & MDEA CO₂ Capture)
Producing 4 MTPY Hot Rolled Coil
1115 kg CO₂/t HRC (1124 kg CO₂/thm)

Carbon Balance of Ironmaking Process

<table>
<thead>
<tr>
<th>Carbon Input (kg C/thm)</th>
<th>Carbon Output (kg C/thm)</th>
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<td>Coke 227.7</td>
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</tr>
<tr>
<td>PCI Coal 132.2</td>
<td>Dust &amp; Sludge 8.0</td>
</tr>
<tr>
<td>Natural Gas 12.0</td>
<td>OBF PG Export 64.5</td>
</tr>
<tr>
<td></td>
<td>PG Heater Flue Gas 12.0</td>
</tr>
<tr>
<td></td>
<td>CO₂ Captured 236.3</td>
</tr>
<tr>
<td><strong>Total 372.7</strong></td>
<td><strong>Total 372.4</strong></td>
</tr>
</tbody>
</table>
Blast Furnace (TGR BF)

Raw Top Gas
- CO: 46-49%
- CO₂: 37-38%
- H₂: 8 - 9%
- Balance: N₂

Recycled Top Gas
- CO: 73-75%
- CO₂: ~3%
- H₂: 14-15%
- Balance: N₂

CO₂ Removal evaluated by ULCOS consists of:
- PSA, VPSA
- VPSA or PSA + Cryogenic Separation
- Chemical Absorption

Concentration of CO₂ depends on capture technology used

Expected C-savings
- 25%
- 24%
- 21%
ULCOS BF
(Experimental Results from Lulea’s EBF Work)
Data courtesy of Tata Steel
LKAB’s EBF Trial

Schedule: 16th April ~ 11th May, 2012

Ferrous Material: Sinter 70% - Pellet 30%
Coke, PC: from SSAB

- [Probing, Sampling]
- [Operational Data, Analyzing]

- Upper shaft Tuyere
- Lower shaft Tuyere
- [Hot Top Gas Injection]
- [Reformed COG Injection]
- [COG Injection]

Figures are quoted from Swerea/MEFOS and LKAB brochure
COURSE50 Programme
CO₂ Capture Pilot Plants

**CAT-1 & CAT-10**
*at Nippon Steel Kimitsu Works*

**CAT-1**
1 t/d CO₂ for solvent testing

**CAT-30**
30 t/d CO₂ for process improvement evaluation

**ASCOA**
*at JFE Steel Fukuyama Works*

**ASCOA-3** *(JFE Steel Fukuyama Area)*
*Advanced Separation System by Carbon Oxides Adsorption*

Capacity: 3tons-CO₂/day
Plant Area: 21m x 25m

Start: March 2011

Pictures & Info from Osame et al (2011) – Nippon / JFE Steel
POSCO – RIST Programme

CO₂ Emissions:
- Hot Milling: 4%
- Cold Milling: 3%
- Steel-making: 1%
- Iron-making: melting/reduction: 91%

Research Scope:
1. Power Plant
2. Hydrocarbons
3. CO₂ Production

Process:
- Coal → Cokes
- Iron Ore → Sinter Process
- BFG
- CO → Hydrocarbons
CO₂ Capture Using Aqueous Ammonia (II): Milestones

☐ R&D history
  • Lab-scale research (2006~2007)
  • 1st stage pilot plant research (2008-2010): 50 Nm³-BFG/hr (Dec. 2008)
  • 2nd stage pilot plant research (2010-2014): 1,000 Nm³-BFG/hr
    - One-site pilot tests are on-going (May 2011-), Purification/Liquefaction facilities integrated (Apr. 2012-)

☐ 2nd Pilot Plant Spec.

<table>
<thead>
<tr>
<th>Item</th>
<th>Spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Gas</td>
<td>BFG (Blast Furnace Gas, CO₂ ~ 22%)</td>
</tr>
<tr>
<td>Feed Gas Flow rate</td>
<td>1,000Nm³/h</td>
</tr>
<tr>
<td>Absorbent Sol.</td>
<td>&lt;10% NH₃</td>
</tr>
<tr>
<td>Product CO₂</td>
<td>10 t-CO₂/d, 0.5MW power plant</td>
</tr>
<tr>
<td>Purity of product CO₂</td>
<td>&gt;95% (Gas)</td>
</tr>
<tr>
<td></td>
<td>&gt;99.8% (Liquid)</td>
</tr>
</tbody>
</table>

☐ Test Results
  • CO₂ recovery > 90%, L-CO₂ purity > 99.5%

☐ Further Plan
  • Long-term continuous operation
  • Additional pump around and higher NH₃ concentration in absorbent solution
  • Basic engineering design for commercial scale
CO₂ Conversion using COG Reforming (I) : Concept/Feature

- **Background**
  - Need for the conversion of capture CO₂ and the utilization in steel industry

- **Steel-industry-specific CO₂ conversion and utilization**

  - **Captured CO₂**
    - H₂O
    - COG
  - COG = coke oven gas (55% H₂, 27% CH₄, 3% CO, etc)
  - Fuel
  - Energy
  - Waste heat recovery from molten slag
  - Reformed COG (H₂, CO)
  - BF or/and FINEX

  - **[COG reforming]**
    - \( \text{CH}_4 + x\text{H}_2\text{O} + y\text{CO}_2 \rightarrow \text{CH}_2 + d\text{CO} \)

  - Reduce coke consumption in iron-making process !!

  - Conceptual scheme for production and utilization of the reducing gas in the steel process

- **Mass production of the H₂ and/or CO rich gases by using COG reforming with steam and CO₂**
  - Require highly coking-resistant catalyst for the COG reforming
  - Require optimization of reaction condition, heat integration, and scale-up by using reactor modeling
CAPTURE OF CO₂ FROM ALTERNATIVE IRONMAKING PROCESS

• Direct Reduction Ironmaking Process
• Smelting Reduction Ironmaking Process
Direct Reduction Ironmaking

70 Process Developments

From “Aachener Drehofen” to “Zam Zam” Process

Only Midrex & Energiron (HYL) reached successful commercialisation
MIDREX Plant w/o CO$_2$ Removal
(Picture Courtesy of MIDREX)

Reduction:
- $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$
- $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

Carburization:
- $3\text{Fe} + \text{CO} + \text{H}_2 \rightarrow \text{Fe}_3\text{C} + \text{H}_2\text{O}$
- $3\text{Fe} + \text{CH}_4 \rightarrow \text{Fe}_3\text{C} + 2\text{H}_2$

Reforming:
- $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$
- $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
MIDREX Plant with CO₂ Removal
MIDREX PLANT with CO₂ Removal Reference Plant
(Picture Courtesy of Siemens VAI & Essar Steel)

• NO standalone Midrex Plant that removes CO₂ from the DRI shaft reactor’s off-gas.

• However, ESSAR Steel employed partial removal of CO₂ using VPSA at their Hazira Steelworks (India).
  • Steelworks is hybrid plant where COREX gas is used as fuel to the reformer of the MIDREX plant.
  • 2 Midrex modules (#5 & #6) equipped with CO₂ removal system
    o VPSA off gas is mixed with NG as feedstock to the reformer. This reduces NG consumption.
    o VPSA tail gas with ~60% CO₂, ~20% CO, ~5%H₂ is used as heating fuel within the steelworks
ENERGIRON – HYL Technology

In-situ Reforming
\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]
\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \]

Reduction
\[ Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \]
\[ Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \]

Carburization
\[ 3Fe + CH_4 \rightarrow Fe_3C + 2H_2 \]
ENERGIRON WITH CO₂ CAPTURE REFERENCE PLANTS

• CO₂ removal system used by Energiron / HYL is a competition between Chemical Absorption (i.e. MDEA) vs Physical Adsorption (VPSA / PSA)

• List of Reference Plants with CO₂ Capture
  • Mexico
    o AM Lazaro Cardenas (2 modules) – food grade CO₂ – 2007/2009
    o Ternium 4M, 2P (2 modules) – food grade CO₂
  • India
    o Welspun Maxsteel (1 modules – food grade CO₂ - 2009
  • Abu Dhabi
    o Emirate Steel (2 modules) – EOR grade CO₂ – under construction
Smelting Reduction Ironmaking

45 Process Developments

From “AISI Direct Steelmaking” to “VOEST” Process
Only COREX & FINEX reaching commercialisation
COREX Process

- CO: 42 - 47%
- CO$_2$: 29 - 32%
- H$_2$: 19 - 22%
- CH$_4$: 1 – 3%
- Balance: N$_2$
COREX with CO\textsubscript{2} Removal
Commercially Operated Plant based on VPSA or PSA

- No standalone COREX plant that removes CO\textsubscript{2} from their export gas.
- However, 2 Plants with COREX gas used as feedstock to Midrex do remove the CO\textsubscript{2}.
  - Saldanha Steelworks, S. Africa (1 module commissioned in 2000)
  - JSW Vijayanagar Steelworks, India (2 modules, commissioned in 2013)
Future of FINEX with CCS
HISARNA (ULCOS Programme)

3. The HIsarna pilot plant

- Reactor building
- Incinerator
- Gas Cooler
- Coal / lime silos
- Hot Metal / Slag pot

But who will be the winner???
Concluding Remarks
(Figures adapted from VDEH)

- **So many ways to produce steel…**
- **What is the right way to reduce CO$_2$ emissions depends on so many factors…**
  - Raw materials (coke, iron ore, scrap,…)
  - Energy availability
  - Cost (Economics)
- **It has been recognised that CCS will play an important role in reducing GHG emissions. To successfully deploy CCS, issues regarding MARKET COMPETITIVENESS should be addressed**
Nucor Louisiana Project in the U.S.A. (2.5Mt/y)

Original Plan BF

- Iron Ore
- Coke Oven
- Hot Metal
- Basic Oxygen Furnace
- Rolling Mill
- Shale Gas

Current Plan Gas-DR

- Iron Ore
- Pellet Plant
- DRI
- EAF
- Rolling Mill
- Gas-Based DR Plant

- Lower capital cost of a DRI plant – around half that for an equivalent blast furnace
- Lower greenhouse gas emissions

- Reduction Cost Evaluation
  - Coke rate: 17.68
  - Gas: 46 million BTU
  - BF: 14 MTC
  - Gas-DR: 4 MTC
  - Cost: 1.5 MTC

- With the cheap shale gas, construction of the large-sized gas DR plant was started in the U.S. instead of construction of the BF

Voestalpine constructing MIDREX direct reduction plant in Texas, USA

- The decision on the construction of the Voestalpine direct reduction plant in North America has been made.
- The plant will be constructed on just outside the city of Corpus Christi, Texas, USA.
- The planned facilities are designed for an annual capacity of around 2 million tons of HBI and DRI.
- The investment volume is around EUR 550 million.
- The plant is due to begin operations in early 2016.
- This will provide the Austrian steel production sites in Linz and Donawitz with access to cost-efficient and environmentally-friendly HBI and DRI pre-materials, ensuring their competitiveness over the long-term.
Thank You

Stanley Santos
IEA Greenhouse Gas R&D Programme

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