# Development of alternative raw material and by-product diversity of metallurgical coke manufacture

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- Ore based iron and steel making at SSAB Raahe steel works  
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Major environmental challenge of ore based carbon steel industry

- About 70% of steel (annual production about 1.665 billion tons) is produced from mainly virgin raw materials with the integrated blast furnace (BF) –basic oxygen furnace (BOF) route;
- On average, 1.8 tons of CO₂ are emitted for every ton of BF-BOF steel produced;
- The whole iron and steel industry accounts for approximately 6.7% of total world CO₂ emissions.

*World steel association 2014*
SSAB Raahe steel works produces high quality hot strip and plate products with a maximum steelmaking capacity of 2.8 Mt/a;

The SSAB Raahe Steel Works is also the largest CO₂ point source in Finland emitting approximately 4 Mt/a;

Specific CO₂ emissions (1.63 tons/1 ton steel) means that emissions are quite near the technical minimum that can be reached with present process technology.

SSAB Raahe steel works is already high efficient industrial production park.

Ore-based carbon steelmaking at SSAB Raahe steel works

Modified from Lilja 2014 and Mäkikyrö 2015
EU nations are working hard to cut its greenhouse gas emissions substantially while encouraging other nations and regions to do likewise.

According to Paris Climate agreement Energy intensive industries in EU could cut emissions by more than common target 80% below 1990 level by 2050. => The technologies used will get cleaner and more energy-efficient.

The basic objectives of current EU waste policy are to prevent waste formation and promote re-use, recycling and recovery, which means transition to circular economy society and demand to raise the recovery rate of waste.

The EU and other developed countries will continue to support climate action to reduce emissions and build resilience to climate change impacts in developing countries. (What this possibly means? See next slide.)

Results from least-cost energy-economic modeling approach

• Provide a good proxy for likely domestic emission reductions needed

• Finland would need to achieve about a 60% reduction below 1990 levels by 2030.
  • Present 2°C goal -40% by 2030

• By 2050, domestic emissions would need to become negative in Finland with reductions of 135% below 1990 levels.
  • Present 2°C goal -80% by 2050

• Taking into account equity considerations, larger reductions in emission allowances are needed, reflecting the need for mitigation abroad
  • -60% by 2030 and -150% by 2050
1. The development of radical new steel making technologies with a lower carbon footprint,

OR/AND

2. It is needed revolutionary ideas to take a mega jump in technological and economic efficiency by totally eliminating waste streams and fully exploiting synergies with other related industrial technologies and society

In case 2. it must be remembered the basic principle based on the OPTIDUST project 1999 – 2000 “The primary production chain of the ore based steel making should not be disturbed”

Szekely 1996 and Pöyliö et al. 2002
Natural reserves of coking coal are limited and the standards for blast furnace iron making are becoming increasingly strict, encouraging steel producers to implement environmentally friendly and economical processes.

Besides concentrating on the main properties of metallurgical coke (e.g., strength and reactivity), the coking process requires innovative use of secondary (plastics, car tyres, waste oils, etc.) or bio based reducing agents recovered from household, industry and other appropriate sources.
Metallurgical coke was prepared in laboratory scale coke ovens (see next slide) by coking coal without and with varying amounts of most widely used plastic – high density polyethylene (HDPE), \((C_2H_4)_n\).

Before coking both plastics and coals were grinded to < 5.

In mini coking process samples were warmed to 1200 °C.

Coke compression strength was measured by Zwick 100 kN Tensile test machine.

Image analysis by optical microscopy was performed to study textures and porosity of coke.

ASAP 2020 Pore size analyser was used to measure porosity and surface area (BET) of coke (pores < 78.8 nm)
The 9 cylindrical coke crucibles (H 60 mm and D 20 mm) and coking battery were made of graphite.

The total weight of one sample was 10.39 g.

The crucibles were covered with graphite flakes to protect the samples from air.
Cold compression strength of coke as a function of HDPE plastic addition in RI coal
Cold compression strength, pore volume and BET area results of coke with zero and with varying amounts of HDPE plastics addition to RI coal

<table>
<thead>
<tr>
<th>Coke + HDPE, %</th>
<th>Strength</th>
<th>RTC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Pore vol</th>
<th>RTC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET area</th>
<th>RTC&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>%</td>
<td>mm&lt;sup&gt;3&lt;/sup&gt;/g</td>
<td>%</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;/g</td>
<td>%</td>
</tr>
<tr>
<td>RI 0</td>
<td>13.5</td>
<td>100.0</td>
<td>1.57</td>
<td>100.0</td>
<td>0.923</td>
<td>100</td>
</tr>
<tr>
<td>RI 2.5</td>
<td>18.3</td>
<td>135.7</td>
<td>2.04</td>
<td>129.8</td>
<td>0.965</td>
<td>104.5</td>
</tr>
<tr>
<td>RI 5</td>
<td>16.2</td>
<td>120.3</td>
<td>2.09</td>
<td>133.1</td>
<td>1.032</td>
<td>111.8</td>
</tr>
<tr>
<td>RI 7.5</td>
<td>9.8</td>
<td>72.3</td>
<td>2.75</td>
<td>174.9</td>
<td>1.326</td>
<td>143.6</td>
</tr>
<tr>
<td>RI 10</td>
<td>8.5</td>
<td>63.1</td>
<td>2.40</td>
<td>152.9</td>
<td>1.187</td>
<td>128.6</td>
</tr>
<tr>
<td>RI 12.5</td>
<td>6.2</td>
<td>45.7</td>
<td>2.99</td>
<td>190.6</td>
<td>1.577</td>
<td>170.8</td>
</tr>
</tbody>
</table>

- RTC means relative to coke made using coal with no plastic
- Pore volumes and BET are measured from pores < 78.8 nm
Wavelet-based image analysis of experimental metallurgical coke (isotropic—green, mosaic—red, banded—yellow, and pores—blue)

(a,c) 100% coal and (b,d) 87.5% coal and 12.5% HDPE

### Amount of textures in samples of experimental coke

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>HDPE content by mass / %</th>
<th>Texture amount (area fraction) / %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mosaic</td>
<td>Isotropic</td>
</tr>
<tr>
<td>RI100</td>
<td>0.0</td>
<td>18.93</td>
<td>65.31</td>
</tr>
<tr>
<td>RI97.5–HDPE2.5</td>
<td>2.5</td>
<td>20.04</td>
<td>67.71</td>
</tr>
<tr>
<td>RI95–HDPE5</td>
<td>5.0</td>
<td>18.73</td>
<td>65.88</td>
</tr>
<tr>
<td>RI92.5–HDPE7.5</td>
<td>7.5</td>
<td>14.21</td>
<td>74.05</td>
</tr>
<tr>
<td>RI90–HDPE10</td>
<td>10.0</td>
<td>16.07</td>
<td>64.81</td>
</tr>
<tr>
<td>RI87.5–HDPE12.5</td>
<td>12.5</td>
<td>12.65</td>
<td>73.63</td>
</tr>
</tbody>
</table>

Note: normalized to 100% after exclusion of the amount of pores.

Variations in mosaic texture of experimental coke vs. HDPE content

Relationship between coke carbon texture and coke strength and reactivity properties (Cheng 2001)

<table>
<thead>
<tr>
<th>Carbon texture</th>
<th>Mechanical strength</th>
<th>Resistance to CO₂ attack</th>
<th>Resistance to alkali attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic Mosaic</td>
<td>Weak</td>
<td>Weak</td>
<td>Strong</td>
</tr>
<tr>
<td>Flow-type</td>
<td>Medium</td>
<td>Strong</td>
<td>Medium</td>
</tr>
<tr>
<td>Strong</td>
<td></td>
<td>Weak</td>
<td>Weak</td>
</tr>
</tbody>
</table>

- According to Cheng (2001) coke with a higher amount of anisotropic texture generally has a lower CRI value, whereas isotropic parts generally have higher reactivity towards CO₂, which increases the CRI value.
- Because low CRI values are directly related to high CRS values, the increase of anisotropic texture also improves the CSR value of coke (Sharma et al. 2005).
- The reactivity and cold compression strength of any given coke can be indirectly assessed by quantitative wavelet based image analysis, with measurement of the amount of isotropic and anisotropic textures (Gornostayev et al. 2014)
The share of raw materials and main products in coal and HDPE plastic co-carbonisation process to get equal amount of metallurgical coke.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Raw material</th>
<th>Coke</th>
<th>COG</th>
<th>Tar+Hydrocarbon oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>kg</td>
<td>kg</td>
<td>kg</td>
<td>kg</td>
</tr>
<tr>
<td>Coal 100</td>
<td>Coal 1000</td>
<td>780</td>
<td>160</td>
<td>45</td>
</tr>
<tr>
<td>Coal 97.5+HDPE 2.5</td>
<td>Coal 996+HDPE 26</td>
<td>780</td>
<td>174</td>
<td>52</td>
</tr>
<tr>
<td>Coal 95.0+HDPE 5.0</td>
<td>Coal 992+HDPE 52</td>
<td>780</td>
<td>189</td>
<td>60</td>
</tr>
</tbody>
</table>
The cold strength results of coke manufactured up to 5% of HDPE plastics addition to RI coal were as high or higher than coke with no plastics.

When the amount of HDPE plastic in RI coal is more than 5%, strength values decrease distinctively.

Pore (< 78.8 nm) volume increase in coke manufactured from HDPE plastic and RI coal, with an increasing amount of plastics in coal.

The addition of plastics less than 5% do not have significant influence on the mosaic texture thus balancing the weakening effect of increased porosity.

Mosaic carbon texture in coke is usually less reactive with carbon dioxide compared to isotropic carbon texture, thus improving the CRI and CSR values of coke to be used in blast furnace.

Increased rounded macro pores observed in texture analysis, decrease the weakening effect.

The reactivity and cold compression strength of any given coke can be indirectly assessed by quantitative wavelet based image analysis, with measurement of the amount of isotropic and anisotropic textures.
Advantages

- Using plastics as a secondary raw material in coke making besides reducing CO₂ emissions also utilisation of municipal waste will be improved.

- The yield of coal coking, depending of coal quality, is 75%-80% coke, 14-17.5% coke oven gas (COG) and 6-7.5% tar and light oils. The yield of HDPE plastic coking is appr. 12% coke, 58% COG and 30% tar and light oils.

- To get maximum advantage of plastic and coal co-carbonisation in coke ovens it is required also a sustainable management of COG to utilise valuable gases (H₂ and CH₄) and light oil components in more sophisticated way.

- Low investment costs because existing coke oven and by-product plant facilities can be used. Plastic crushers and agglomerators are the only extra devices needed in the basic utilisation process.

- When hydrogen and other valuable elements are recovered from COG, existing and proven technology from other industrial fields can be used.

- When hydrogen is produced by using different feedstock, COG has the lowest energy consumption level and in terms of CO₂ emissions, COG is superior to other options.
Ideas for near future

- Maximise the amount recycled and/or biomass-based raw material to produce high quality metallurgical coke and COG in existing coke ovens to be used as a reductant in the blast furnace to reduce the environmental burden of ore based carbon steel making.
- The preliminary evaluation of reactivity and cold compression strength of any given coke can be made based on their textural properties (isotropic and anisotropic).
“The best time to plant a tree was 20 years ago. The second best time is now.”
- Chinese aphorism -

Photosynthesis is the process, where plants convert light energy to chemical energy and storing it in the bonds of sugar. Trees need light energy, CO₂, and H₂O to make sugar.

Future acts to reduce carbon footprint of iron and steel industry

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