Reduction swelling behaviour of iron ore pellets
Dynamic vs. isothermal conditions

Research seminar
29.5.2012, Oulu
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  – Dynamic vs. isothermal reduction
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Background of research

• Research is a part of PEMAS (Pellettimasuuni) project
  – English project name: ”Flexible transition to 100% pellet burden in BF operation”

• Project duration
  – 1.3.2009 - 30.4.2012
  – I as a scientist from 11.1.2011 and as a responsible scientist from 1.2.2011

• Industrial need of project
  – Preparing to transition from sinter/pellet mixture to 100% pellet burden in both blast furnaces at the end of 2011 in Ruukki Metals Oy at Raahe Steel Works
Introduction

• Blast furnace shaft operation is greatly affected by the mechanical properties of burden materials
  – Upwards rising gases follow the easiest path they can have
  – Areas of low permeability in BF shaft leads to uneven gas distribution in shaft and uneven reduction behaviour of burden material
    • Low energy efficiency (low utilization rate of top gas)
• Swelling and disintegration of pellets in burden can have effect on shaft operation
• Swelling can be categorized into normal swelling, up to 20% in volume, and abnormal, i.e. catastrophic swelling, which may exceed 400% in volume at worst
Introduction

• In literature, swelling of pellets has been studied extensively
  – Mainly under isothermal conditions, but also under dynamic conditions
  – With different variables
    • Reducing conditions
      – Reduction rate, reduction temperature, reduction time, reducing gas atmosphere, partial pressure of reducing gases, total gas flow rate, impurities in the reducing gas (sulphur and potassium), isothermal / non-isothermal reduction
    • Pellet properties
      – Porosity, basicity, gangue content
  – With different measuring methods
    • Optical (Optical dilatometer)
    • Mechanical (diameter determination)
• In this study, the reduction swelling behaviour of olivine and SiO₂-rich pellets has been studied under simulated BF shaft conditions
  – Both dynamically and isothermally (comparative study)
  – Additionally, optically (on-line imaging) and mechanically (diameter determination)
Devices and procedures - BFS

**BFS, Blast Furnace gas phase Simulator:**

- Reduction tube with inner diameter of 95 mm
- Adjustable partial pressured of N\(_2\), CO, CO\(_2\), H\(_2\), H\(_2\)O, S\(_2\) and K gases
- Time-temperature dependent atmosphere profiles
- Heat resistant steel tube (max 1100 °C)
- Online measurement of sample weight
- Camera recording system
- Many variables can be studied at the same time (RSI vs. RD)

**Furnace**
1. Reduction tube
2. Sample basket
3. Thermocouple
4. Electrically heated furnace
5. Gas inlet
6. Transparent lid with cooling gas inlet and reducing gas outlet

**Gas supply system**
7. Gas containers
8. Mass flow controllers
9. Potassium generator
10. Sulphur generator
11. Water vapour generator

**Camera recording system**
12. Light source
13. Mirror
14. Camera

**Auxiliary instruments**
15. Scale for TGA
16. Computer system

RSI = Reduction Swelling Index
RD = Reduction Degree
Devices and procedures - Atmospheres

- Dynamic experiments:

- Isothermal experiments:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>t [min]</th>
<th>T [°C]</th>
<th>N₂ [vol-%]</th>
<th>CO [vol-%]</th>
<th>CO₂ [vol-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron A</td>
<td>120</td>
<td>1100</td>
<td>55</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>ISO 4698</td>
<td>60</td>
<td>900</td>
<td>70</td>
<td>30</td>
<td>-</td>
</tr>
</tbody>
</table>

- Gas composition in BF shaft is followed according to literature and thermodynamic calculations

Total gas flow rate 10 l/min
ISO 4698: Iron ore pellets for blast furnace feedstocks - Determination of the free-swelling index

Free swelling

- **NOTE!** ISO 4698 standard swelling test has no CO₂ gas component and the sample is put into a pre-heated furnace
  - This leads to high reduction rate at the beginning of experiment

ISO 4698

- 18 pellets is heated to 900°C and then exposed to reducing gas 30/70 %CO/N₂
- The sample is isothermally reduced during 60 min
- Main result: volume increases (%)
Devices and procedures - Measurements

**Optical online measurement**
- Measurement can be made in one direction
  - Unisotropic changes cause scattering
- Reference line of known basket holes to compensate optical distortions

**Static ”before and after experiment” measurement**
- More accurate in case of unisotropic dimension changes
- Used to verify the validity of optical measurement
- Average pellet diameter was calculated and spherical form was assumed on both of the cases
Defined parameters

\[ \text{Degree of reduction} = \frac{\Delta W_f}{\Delta W_T} \times 100\% \]

where
\( \Delta W_f \) is the weight loss of sample at time [g]
\( \Delta W_T \) is the total possible weight loss due to the removal of oxygen from the pellets [g]

\[ \text{RSI} = \frac{V_1 - V_0}{V_0} \times 100\% = \left[ \left( \frac{d_1}{d_0} \right)^3 - 1 \right] \times 100\% \]

where
\( V_0 \) is the volume of the pellet before reduction
\( V_1 \) is the volume of the pellet after reduction
\( d_0 \) is the diameter of the pellet before reduction [mm, pix]
\( d_1 \) is the diameter of the pellet after reduction [mm, pix]
Test materials - Pellet classification

Olivine (MPBO) pellets and acid (KPH) pellets were tested

Classification of test pellets
10.0 – 12.7 mm

- Magnetic separation
- Surface area measurement
  - Differences probably due to different firing conditions during sintering

### Chemical analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂ rich reference pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“LoMag”</strong></td>
<td>0.1%</td>
<td>1.69%</td>
<td>0.30%</td>
<td>0.71%</td>
<td>1.25%</td>
<td>0.30%</td>
<td>n.a. not analyzed</td>
</tr>
<tr>
<td><strong>“MeMag”</strong></td>
<td>0.2%</td>
<td>1.71%</td>
<td>0.30%</td>
<td>0.71%</td>
<td>1.26%</td>
<td>0.30%</td>
<td>n.a. not analyzed</td>
</tr>
<tr>
<td><strong>“HiMag”</strong></td>
<td>2.9%</td>
<td>1.76%</td>
<td>0.31%</td>
<td>0.70%</td>
<td>1.30%</td>
<td>0.31%</td>
<td>5.34%</td>
</tr>
<tr>
<td><strong>RefPellet</strong></td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Pellet grade</th>
<th>Low magnetite</th>
<th>Medium magnetite</th>
<th>High magnetite</th>
<th>SiO₂ rich reference pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“LoMag”</strong></td>
<td>25 wt.%</td>
<td>61 wt.%</td>
<td>14 wt.%</td>
<td>n.a. not analyzed</td>
</tr>
<tr>
<td><strong>“MeMag”</strong></td>
<td></td>
<td></td>
<td></td>
<td>n.a. not analyzed</td>
</tr>
<tr>
<td><strong>“HiMag”</strong></td>
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<th>“HiMag”</th>
<th>RefPellet</th>
</tr>
</thead>
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<tr>
<td>BET-area (m²/g)</td>
<td>0.20</td>
<td>0.21</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Results - Pellet cracking

- Dynamic reduction
  - The high magnetite fraction of olivine pellets cracked most significantly
  - Acid pellets cracked less than olivine pellets
  - In dynamic reduction, some large cracks intruding to the pellet core were formed, while in isothermal reduction minor cracks were observed

- Isothermal reduction
  - The high magnetite fraction of olivine pellets cracked most significantly
  - Acid pellets cracked less than olivine pellets
  - ISO 4698
    - RD 42 %
    - RSI 20 %
  - RD 85 %
  - RSI 44 %
Dynamic vs. isothermal reduction

- Pellets swelled significantly more under constant temperature and gas composition conditions than under dynamic simulated BF conditions (red oval)
- However, standard reduction swelling tests, such as ISO 4698, are conducted under isothermal conditions
- Results indicate that the test method itself has big influence on the test result
- The amount of swelling increases as reduction reactions proceed (blue rectangle)
- Amount of swelling under dynamic conditions is limited (for tested pellets – olivine and acid pellets – so called normal swelling)
Dynamic reduction – Cracking and swelling mechanism

- LOM image of a high-magnetite olivine pellet reduced dynamically by 80%
- Cracking is found to locate to the boundary between original magnetite nucleus and hematite shell

- FESEM micrograph of a medium-magnetite olivine pellet surface reduced dynamically by 90%
- Surface is somewhat fibrous
- No iron whiskers were detected in dynamic experiments
Dynamic reduction – RSI and RD

- When reduced to iron, olivine pellets swelled and acid pellets shrunk.
- Acid pellets swelling tendency at "Magnetite" and "Wüstit" stages was followed by volume contraction at "Iron 1" and "Iron 2" stages.

Mikko Iljana | Prosessimetallurgian laboratorio
LTD – Low Temperature Disintegration

- LTD test gives a relative measure for evaluating the disintegration of the iron burden materials when hematite is reduced to magnetite in the low-temperature reduction zone of a blast furnace
- LTD values indicates the percentage of the +6.3 mm fraction after stressing the pellet sample isothermally at 500°C in a CO-CO₂-H₂-N₂ atmosphere
- The bigger the LTD value is, the better the strength during reduction is

- As stated earlier, olivine pellets with a large magnetite nucleus crack most significantly and that causes an intensification of fines formation, which is verified in the LTD standard test
Isothermal reduction

- In ISO 4698 experiment, acid pellets swelled the same as amount than olivine pellets, although there was a considerable difference in dynamic reduction.
- THUS, implications drawn from ISO 4698 test results can be misleading when comparing different pellet grades.

- Most of the pellet swelling occurs at the beginning of the test, coinciding with the highest reduction rate.
Pellet microstructure after dynamic and isothermal reduction (core)

- Intensive swelling during isothermal reduction is shown as a more porous microstructure
Validity of the developed method

- Accuracy of the image analysis method ± 10 percentage points
  - This IS enough when swelling tendency is studied
Conclusions

• The developed method involving a camera recording system and image analysis was found to be appropriate for studying the swelling tendency.
• The test method itself has big influence on the test result.
• The dynamic swelling of iron ore pellets in a simulated blast furnace atmosphere is considerably more restrained than the corresponding static swelling. Thus, the reduction swelling behaviour of iron ore pellets should preferably be studied DYNAMICALLY under simulated blast furnace conditions to obtain the most realistic results.
• Implications drawn from the isothermal swelling tests, such as ISO 4698, can even be misleading.
• In olivine pellets, the amount of swelling and the number and size of cracks will increase as the reduction reactions propagate.
• Cracking of pellet structure was found to be more pronounced in the olivine pellets having a large magnetite nucleus causing an intensification of fines formation, as verified in the LTD standard test.
• The boundary between the original magnetite nucleus and the hematite shell acts as the source of cracks.
• Tested acid pellets swell and crack considerably less than olivine pellets, probably due to their higher gangue content and cohesive slag bonds.
• However, the average amount of swelling in tested pellets was minor and so called normal swelling.
Additional research

- The effect of gaseous $S_2$, K and $H_2$-$H_2O$ on dynamic reduction swelling behaviour of olivine and acid iron ore pellets in CO-CO$_2$-N$_2$ atmosphere has been studied and results will be published in another journal article.
  - Sulphur and potassium are circulating elements in blast furnace.
  - Hydrogen and water vapour is generated from injected materials via tuyeres.
Thank You!

• These results will be published in:
  – Mikko Iljana¹, Olli Mattila², Tuomas Alatarvas¹, Jari Kurikkala³, Timo Paananen² and Timo Fabritius¹ (2012) Dynamic and isothermal reduction swelling behaviour of olivine and acid iron ore pellets under simulated blast furnace shaft conditions, *ISIJ International*, Vol. 52, No. 7, pp. 1265-1273.

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