EFFECT OF LIMESTONE ADDITION ON THE METALLURGICAL PROPERTIES OF IRON ORE PELLETS

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BACKGROUND

• This presentation is based on a manuscript *Effect of Limestone Addition on the Metallurgical Properties of Iron Ore Pellets* by Mikko Iljana a, Antti Kemppainen a, Timo Paananen b, Olli Mattila b, Erkki Pisilä b, Mikhail Kondrakov c and Timo Fabritius a submitted to *the International Journal of Mineral Processing* on 31th May 2014.
  
a Research Group of Process Metallurgy, University of Oulu, Finland
b Ruukki Metals Oy, Raahe, Finland
c Karelsky Okatysh, Severstal Resources, Kostomuksha, Russia

• The manuscript will be the third article in my doctoral thesis.

• Published articles:
  

INTRODUCTION

- Iron ore pellets are used for the production of hot metal in blast furnaces and DRI/HBI in direct reduction processes.
- A blast furnace is a shaft furnace, which is charged with iron bearing materials (pellets, sinters and/or lump ore), reducing agents (metallurgical coke) and additives (limestone, quartz, BOF slag). Metallurgical coke and auxiliary reducing agents (coal, oil, natural gas) are used to reduce iron oxides and melt the charge materials.
- Main types of pellets
  - Acid
  - Basic
  - Fluxed
- Some additives are often used to make better the metallurgical properties (reducibility, softening and melting properties, slag formation) of the iron ore pellets
  - Limestone CaCO$_3$
  - Magnesite MgCO$_3$
  - Dolomite (Ca,Mg)CO$_3$
  - Olivine Mg$_2$SiO$_4$
- In this study, the focus is on limestone as an additive.
- There are a lot of standard tests for iron ore pellets. Additionally steel companies and specialized research institutes have their own tests.

HBI = Hot Briquetted Iron
DRI = Direct Reduced Iron
MATERIALS

- Iron ore pellets were manufactured by Severstal Resources in Karelia (Russia).
- Not commercial grade, but test pellets produced in a laboratory-scale pelletizing drum and fired in sample baskets in the same production line as the commercial blast furnace pellets.
- “Non-fluxed” and “fluxed” with similar SiO$_2$ content.

### Chemical analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Non-fluxed</th>
<th>Fluxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{tot}$</td>
<td>65.6</td>
<td>63.8</td>
</tr>
<tr>
<td>FeO</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.51</td>
<td>3.20</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>4.62</td>
<td>4.61</td>
</tr>
<tr>
<td>MgO</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.38</td>
<td>0.34</td>
</tr>
<tr>
<td>S</td>
<td>0.011</td>
<td>0.061</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.109</td>
<td>0.100</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>0.061</td>
<td>0.052</td>
</tr>
<tr>
<td>CaO/SiO$_2$</td>
<td>0.11</td>
<td>0.69</td>
</tr>
</tbody>
</table>

### Size distribution

![Size distribution graph](image)

### Internal structure (LOM image)

![Internal structure images](image)
METALLURGICAL TESTS FOR IRON ORE PELLETS

Standard tests
Isothermal

Cold Crushing Strength, CCS, ISO 4700 (handling, charging, screening)

Low-temperature disintegration, LTD, ISO 13930 (disintegration as hematite reduces to magnetite at the top of the shaft)

25°C

500°C

Modified tests
Dynamic

Reducibility (without load in the shaft area)
Max. 1100°C

Reduction swelling behaviour (without load in the shaft area)
Max. 1100°C

Advanced Reduction under Load, ARUL (temperature and reduction degree in the cohesive zone)
Max. 1100–1350°C

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TESTS CARRIED OUT IN OULU UNIVERSITY

- Reducibility test:
  - Total of 26 pellets
    - Total weight: 120 g
    - Size: 12.5-16 mm
    - Well-fired pellets with nil to small-sized magnetite nucleus
  - "No additives” test (CO-CO$_2$-N$_2$ gas)

- Reduction swelling test:
  - 2 pellets of a certain grade, total of 4 pellet grades
    - Weight: 4.7±0.2 g (each pellet)
    - Size: 12.5-16 mm
    - Round-shaped
    - Well-fired pellets with nil to small-sized magnetite nucleus
  - ”No additives”, ”Medium-S” and ”High-K” tests
BLAST FURNACE GAS PHASE SIMULATOR (BFS)

Unique laboratory device to test the effect of $S_2(g)$ and $K(g)$

- Reduction tube with inner diameter of 95 mm
- Adjustable partial pressures 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. T 1100 °C)
- Online measurement of sample weight
- Camera recording system
- Inert purging gas ($N_2$) to cool the sample quickly
- Many variables can be studied at the same time

\[
\begin{align*}
K_2CO_3(s) + 2C(s) &= 2K(g) + 3CO(g) \\
2SO_2(g) + 2C(s) &= S_2(g) + 2CO_2(g)
\end{align*}
\]

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
12. Light source
13. Mirror
14. Camera

Auxiliary instruments
15. Scale for TGA
16. Computer system
• Reduction conditions (temperature and gas composition) in the blast furnace shaft were simulated
  • CO-CO$_2$-N$_2$ gas ("No additives" test)
  • From ambient temperature (25°C) up to 1100°C
  • Gas composition was also adjusted during the tests.
  • Total gas flow rate 10 l/min

"No additives" experiment
REDUCTION CONDITIONS (2/2)

- Effect of gaseous sulphur and potassium on the swelling was also studied.
  - "Medium-S" test with CO-CO$_2$-N$_2$-S gas
    - max 0.1 vol-% S(g)
  - "High-K" test with CO-CO$_2$-N$_2$-K gas
    - max. 0.03 vol-% K(g)
- The circulation of S and K in the BF shaft were simulated.
REDUCIBILITY AND REDUCTION SWELLING BEHAVIOUR

• Reducibility test:
  ✓ Non-fluxed: 59.4 % RD
  ✓ Fluxed  63.5 % RD

• Reduction swelling test:

RD = Reduction Degree
RSI = Reduction Swelling Index
REDUCTION-SOFTENING TEST (ARUL)

Advanced Reduction Under Load (ARUL)
Compression with graphite contacts
Feed and measured gases: CO, CO$_2$, H$_2$, N$_2$
Material ”Quality indexes”: TDP20, TK50, Reducibility
Provides information of material state forming the cohesive zone in the blast furnace (reduction degree, temperature etc.)

Wüstite
Metallic iron

Gases
CONDITIONS IN THE ARUL EXPERIMENTS

• Initial sample H 90 mm and D 70 mm (W ~600–700 g)
• BF conditions are simulated under CO-CO$_2$-N$_2$ gas
• Total gas flow 23 l/min
• The test is ended as the pressure difference across the sample exceeds 70 mbar or temperature rises up to 1350°C (=cohesive zone).

Note that the conditions are similar to the reducibility and reduction swelling tests up to 1100°C!
SOFTENING BEHAVIOR (ARUL)

• In the top part of the ARUL sample pellets are somewhat flattened themselves due to the load showing softened structure.
• At the end of the ARUL experiment, melt has started to squeeze through the top holes in the graphite crucible.
• The lower part is better reduced than the upper part.
• The periphery of individual pellets is better reduced than the core.

Light grey: metallic iron
Dark grey: wüstite
SOFTENING BEHAVIOR (ARUL)

- Pressure difference curve indicates the ability of gases to penetrate through the pellet cake.
- TDP20, TDP50 and TDP70 values are temperature when pressure difference across the sample is 20, 50 and 70 mbar.
- Fluxed pellets started to soften at lower temperatures, however the final reduction degree was higher compared to the non-fluxed pellets.

<table>
<thead>
<tr>
<th></th>
<th>Non-fluxed</th>
<th>Fluxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDP20 [°C]</td>
<td>1122</td>
<td>1087</td>
</tr>
<tr>
<td>TDP50 [°C]</td>
<td>1137</td>
<td>1112</td>
</tr>
<tr>
<td>TDP70 [°C]</td>
<td>1140</td>
<td>1130</td>
</tr>
<tr>
<td>TDP70 – TDP20 [°C]</td>
<td>18</td>
<td>43</td>
</tr>
<tr>
<td>Compression [%]</td>
<td>48.4</td>
<td>50.5</td>
</tr>
<tr>
<td>RD_final [%]</td>
<td>45.9</td>
<td>50.2</td>
</tr>
</tbody>
</table>
The reason for forming gas impermeable structure is apparently linked to the increase of inter-particle melt with olivine composition allowing wüstite grains to move in relation to each other under the mechanical stress.
Chemical composition of the inter-granular slag was plotted to the composition section of $2\text{CaO} \cdot \text{SiO}_2 - 2\text{FeO} \cdot \text{SiO}_2$.

**Hypothesis:** In the fluxed pellets, primary slag with composition near eutectic liquid has formed in the ARUL experiment and the composition of the primary slag has changed to contain less FeO due to reduction reactions proceeding during softening.
The LTD value indicates the percentage of the +6.3 mm fraction after stressing the pellet sample isothermally at 500°C in a CO-CO₂-H₂-N₂ gas.

“Recommendations” for blast furnace use:
- CCS > 220 daN
- LTD > 55 %

Limestone addition slightly decreased the “quality indexes” CCS and LTD.

However, the CCS and the LTD values for the fluxed pellets are estimated to be enough high for blast furnace use.

Discussion:
- Effect of divalent iron content

<table>
<thead>
<tr>
<th>Component</th>
<th>Non-fluxed Content [wt-%]</th>
<th>Fluxed Content [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
DISCUSSION

• Blast furnace burden materials have strict requirements
  ➢ All metallurgical “quality indexes” must be at acceptable level
• In a real blast furnace also other slag forming elements, such as alkalis, sulphur and ash particles from metallurgical coke and alternative reducing agents, are captured by iron ore materials. The effect of alkalis, sulphur and ash particles to inter-granular slag formation was not taken into account in the softening test (ARUL). Possible problems may arise from the high sulphur load leading to partial melt formation of FeO-FeS at temperatures higher of 915°C.
• The numerical results of ARUL experiments cannot be taken as direct measure of the softening temperature of the iron-bearing charge in a real blast furnace, but it shows the difference between different burden materials (=suitable for comparative studies).
CONCLUSIONS

- Limestone addition increased the reducibility of the pellets.
- Swelling and cracking of the pellets during dynamic reduction was slightly increased with limestone addition.
- The final reduction degree was higher in the reduction-softening test named ARUL with the fluxed pellets compared to the non-fluxed ones, although softening began in a lower temperature with the fluxed pellets compared to the non-fluxed ones.
- Limestone addition slightly decreased the cold crushing strength of the acid pellets and increased the fines formation in the hematite to magnetite reduction stage in the LTD test. However, the CCS and the LTD values for the fluxed pellets are estimated to be high enough for blast furnace use.
Thank You for Your Interest!

Now is Time for Questions!

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