Preheating manganese ore in a pilot-scale rotary kiln

PROMETIA – 10 December 2020

PREMA - Energy efficient, primary production of manganese ferroalloys through the application of novel energy systems in the drying and pre-heating of furnace feed materials
Overview

1. Mn production and PREMA project
2. Pre-heating of Mn ores
3. Conclusions
Mn production and PREMA project
PREMA - Energy efficient, primary production of manganese ferroalloys through the application of novel energy systems in the drying and pre-heating of furnace feed materials

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 820561

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Mn process

Manganese source = Ores
Reductant = Coke
Fluxes = Dolomite

2 options for decreasing CO₂ emissions and improve furnace efficiency:

• Make Boudouard's reaction negligible by playing on kinetics and raw materials
• Carry out the pre-reduction reactions in the absence of C outside the EAF

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PREMA: A H2020 European project

Energy efficient, primary production of manganese ferroalloys through the application of novel energy systems in the drying and pre-heating of furnace feed materials

PREMA objectives

- Capture CO from the EAF furnace
- Pre-reduce the ore in absence of C with CO gas from furnace
- Transfer hot blend to the furnace

4 years project: 2018-2022

Outotec
Screening process to select pre-treatment unit technology
- Rotary kiln & Shaft furnace

Eramet Ideas
Rotary kiln pilot campaign
- Pre-heating & pre-reduction

SINTEF
Melting & reduction

MINTEK
Pretreatment, melting & reduction

Design, engineering and business plan

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Pilot campaigns goals

**Goals**
- Determine the level of pre-reduction / decomposition achievable on different ores
- Evaluate the effectiveness of the pre-reduction with different types of solid reducers
- Assess the impact of this pretreatment on the load (particle size, permeability)
- Estimate the efficiency of the operation at the thermal level
- Collect data for sizing industrial equipment

**Pre-heating campaign**
- Pre-heating of manganese ore alone in air
- Decomposition of Mn oxides in air in the range 700-800°C
- Comparison of Mn ores behavior to preheating

**Pre-reduction campaign**
- Pre-reduction of manganese ore in presence of reductant to generate CO
- Obtain calcined ore temperature similar to the first campaign: 700-800°C
- Comparison of Mn ores behavior to prereduction

*Predominance diagram for Mn-C-O system*
Vernon Rotary kiln

Vernon rotary kiln
- Tube length: 4 m
- Tube diameter: 0.48 m
- Rotation speed: from 1 to 6 rpm
- Slope: from 0 to 4%
- Burner (natural gas): 220 kW

Calcination mode
- Counter current flow
- Gradual heating
- Insulated with refractory
- No dams or bed disturbers

Rotary kiln principle

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Mn ores used for the campaign

Selected ores
- Comilog, MMA grade, highly oxidized ore
- Assmang, Nchwaning grade, semi-carbonated ore

<table>
<thead>
<tr>
<th>Compositions (%) by mass</th>
<th>Al2O3</th>
<th>CaO</th>
<th>FeO</th>
<th>MgO</th>
<th>SiO2</th>
<th>Mn</th>
<th>x in MnOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assmang</td>
<td>0,33</td>
<td>6,91</td>
<td>12,5</td>
<td>1,93</td>
<td>5,37</td>
<td>45,82</td>
<td>1,4</td>
</tr>
<tr>
<td>Comilog</td>
<td>6,27</td>
<td>0,32</td>
<td>4,34</td>
<td>0,18</td>
<td>4,55</td>
<td>49,31</td>
<td>2</td>
</tr>
</tbody>
</table>

Chemical analysis

Qemscan images

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Pre-heating Mn ore
Tests performed: March 11-14, 2020

Goals

- Decomposition of Mn oxides in air in the range 700-800°C
- Comparison of Mn ores behavior to preheating

**Burner start**
- Obtaining thermal stability of the furnace (empty)

**Optimization of parameters on Comilog**
- Obtain a calcined ore between 600-700°C

**Production**
- Preparation of a ton of Comilog with the optimized parameters

**Transition**
- Change of ore for Assmang and stabilization

**Production**
- Preparation of one ton of Assmang with the parameters set during the Comilog tests

**Test**
- Change of parameters on Assmang

**Transition**
- Change of ore for Comilog and stabilization

**Test**
- Change of parameters on Comilog

Adjustment of the filling ratio and parameters of the burner

Comparison of Mn ores to preheating with production calcined ore for SINTEF

Study of the influence of parameters
Temperatures and thermal profiles

**Production settings**
- $P_{\text{burner}} = 120$ kW
- Filling ratio = 13%
- Residence time = 45 min

**Thermal profile & Temperatures**
- Assmang tends to heat higher than Comilog for the same set of parameters
  - Calcined Assmang = 863°C +/- 2°C
  - Calcined Comilog = 728°C +/- 15°C
- Thermal profile = Higher temperatures deeper in the furnace for Assmang
Physical properties

Particule size distribution: Calcined ore + dusts

- Assmang ore: Raw material with coarse particles: 50% of 10-20 mm compared to 41% of 10-40 mm for Comilog
- Comilog ore: Raw material with more fines: 33% < 6.3mm compared to 15% for Assmang
- Decrepitation of both ores with more impact on Assmang

Dust take-off

- More important on MMA than Assmang

<table>
<thead>
<tr>
<th>Ore</th>
<th>Loading (kg)</th>
<th>Calcined (kg)</th>
<th>fine dust (kg)</th>
<th>Take-off rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comilog</td>
<td>1847</td>
<td>1431</td>
<td>148</td>
<td>8%</td>
</tr>
<tr>
<td>Assmang</td>
<td>2085</td>
<td>1648</td>
<td>90</td>
<td>4%</td>
</tr>
</tbody>
</table>

Permeabilities

- Comilog: Lowest permeability at first but best results after calcination
- Assmang: Slight improvement of permeability
Chemical properties

- Analyzes carried out at Eramet and Norlab

- Elementary analysis
  - Close results for both lab
  - No major differences before and after calcination: little chemical degradation
  - Incomplete decarbonation for Assmang

- Determination of Mn valence
  - Reducing potential of the ore expressed as MnOx
  - Same method for both laboratories but differences for Assmang
  - Comilog: Decomposition of Mn oxides
  - Assmang: No impact of calcination

![Graph showing carbon analysis before and after calcination for both ores](image)

- Reducing potential expressed as MnOx

![Graph showing reducing potential expressed as MnOx](image)
**Chemical properties - XRD**

Before and after pre-heating
- **Braunite** = Mn$^{3+}$
- **Haussmannite** = Mn$^{2+}$/Mn$^{3+}$
- **Iron manganese oxide** = Mn$^{3+}$

Before pre-heating
- **Pyrolusite** = Mn$^{4+}$
- **Lithiophorite** = Mn$^{4+}$

After pre-heating
- **Manganese oxide** = Mn$^{3+}$
Conclusions
Conclusions (1/2) – First campaign

Comparison of Mn ores behavior to pre-heating in the same conditions

- **Comilog**
  - Calcined ore temperature = 728°C +/- 15°C
  - Slight decrepitation and blow off ultrafines
  - Improved permeability
  - Decomposition of MnO₂ into Mn₂O₃

- **Assmang**
  - Calcined ore temperature = 863°C +/- 2°C with higher temperatures inside the kiln and thus different thermal profile
  - Important decrepitation
  - Slight improvement of permeability
  - No decomposition of Mn₂O₃ into Mn₃O₄

**Thermal decomposition in air**

- **Comilog**
  - Mn⁴⁺ rich (pyrolusite and lithiophorite)
  - Heating and decomposition
  - Rotary kiln (Ore = 750-850°C)
  - No further decomposition available at this temperature range

- **Assmang**
  - Mn³⁺/²⁺ rich (Braunite and Haussmanite)
  - Heating
  - Not hot enough to decompose it

**Goal achieved:** Data collection to size a rotary kiln and study of parameters influence

- More potential for Comilog than Assmang
- Boudouard reaction still present
Conclusions (2/2) - Second pilot campaign

Aim of the campaign

• Evaluate the extent of the pre-reduction reachable in a rotary kiln
• Provide data for design and dimensioning

Experimental set-up

• Addition of reductant to generate reducing atmosphere
• Higher constraints on the inerting of the calcined ore because of CO generation and potentially re-oxidation of MnO

Reductant used

• Coal: Silero 1-7mm from Enerco
  Typical use: reducing agent in the production of elemental metallic silicon from silicon dioxide by application of extreme temperatures
• Charcoal: 5-20 mm briquettes from Valbois
  Typical use: Barbecue

Tests performed in November

• Date processing in progress

Reductant pictures: Coal (above) and Charcoal (below)
Thank you for your attention

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