Evaluation of a BOF Slag Recovery Treatment combining Experimental and Simulation Studies

Ismael Matino\textsuperscript{1}, Teresa Annunziata Branca\textsuperscript{1}, Erika Alcamisi\textsuperscript{1}, Valentina Colla\textsuperscript{1}, Lea Romaniello\textsuperscript{2}

\textsuperscript{1} Scuola Superiore Sant’Anna \textsuperscript{2} ILVA S.p.A.

TINOS 2015 ♦ Tinos Island, July 2-4, 2015
Contents

1 Introduction
2 Objectives
3 Approach
4 Experimental Design
5 Process Modelling and Simulation (PM&S)
6 Case study simulation
7 Conclusions
8 Future work
Introduction

Environmental Sustainability: Waste and By-Products

Why?

- Greater sensitiveness to environmental issues
- More stringent legislation
- Increase of landfill and disposal costs

By-products and Waste Reuse and Recycling

Increase of Environmental Sustainability

Landfills Minimization
Introduction
Main Products, By-Products and Waste in Steelworks

External Recovery
- Construction material
- Road building
- Concrete aggregate
- Thermal insulation

Internal Recovery
- Reuse in main process as raw materials
Introduction

Slags in Steelmaking Plants - Types, Components and Possible Reuses

### Slag Types
- Blast Furnace (BF) Slag
- Basic Oxygen Furnace (BOF) Slag
- Electric Arc Furnace (EAF) Slag
- Secondary Metallurgy (SM) Slag

### Slag Main Components
- Silica
- Calcium Oxide
- Magnesium Oxide
- Aluminium Oxide
- Iron Oxides
- Metal Iron (10 – 40% wt)

### Possibilities of BOF Slag Recycle and Reuse
- reactant for $CO_2$ chemical absorption
- agriculture purpose
- construction field
- raw material in internal pellettization process

TINOS 2015 — Evaluation of a BOF Slag Recovery Treatment combining Experimental and Simulation Studies
Introduction
Tinos Island, July 2-4, 2015
Objectives

Obtain Information about BOF Slag Features
- Chemical composition
- Mineralogy
- Physical Properties

Evaluation of BOF Slag Management, Treatment and Recovery

Providing a preliminary proof of BOF slag reuse
- Agriculture
- Pelletization
Contents

1 Introduction

2 Objectives

3 Approach

4 Experimentatal Design

5 Process Modelling and Simulation (PM&S)

6 Case study simulation

7 Conclusions

8 Future work
Approach

Proposed Recovery Treatment
Approach

Main Phases

**Experimental Design**

- BOF slag **characterization**
- Preliminary **laboratory tests** of the proposed process

**Process Modelling and Simulation (PM&S)**

- **Modelling** of treatment phases
- **Simulation** of BOF slag fraction recovery in different scenarios (different qualities of BOF slag or different operating condition)
Contents

1 Introduction
2 Objectives
3 Approach
4 Experimentatal Design
5 Process Modelling and Simulation (PM&S)
6 Case study simulation
7 Conclusions
8 Future work
Three qualities of BOF slag where selected in Taranto steelworks, each regarding production of a different steel grade

<table>
<thead>
<tr>
<th>Compound</th>
<th>Slag I [% wt]</th>
<th>Slag II [% wt]</th>
<th>Slag III [% wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_{tot}</td>
<td>22.2</td>
<td>17.4</td>
<td>23.2</td>
</tr>
<tr>
<td>CaO</td>
<td>40.5</td>
<td>46.6</td>
<td>42.0</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>12.6</td>
<td>12.4</td>
<td>12.1</td>
</tr>
<tr>
<td>MnO</td>
<td>3.4</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>P_{2}O_{5}</td>
<td>0.1</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>MgO</td>
<td>6.0</td>
<td>7.8</td>
<td>6.5</td>
</tr>
<tr>
<td>V</td>
<td>0.08</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>TiO_{2}</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>0.19</td>
<td>0.17</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Experimental Design
BOF slag characterization - Microcompounds

Microcompounds and Heavy Metals Analyses (EPA 3501A 2007)

- total Chromium: $1 - 1.7 \text{mg} \cdot \text{kg}^{-1}$
- Vanadium: $0.7 - 1.5 \text{mg} \cdot \text{kg}^{-1}$


- total Chromium: $12 \mu\text{g} \cdot \text{l}^{-1}$
- Vanadium: $< 0.10 \mu\text{g} \cdot \text{l}^{-1}$
## Experimental Design

**BOF slag characterization - Mineralogy through XRD**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Slag I [% wt]</th>
<th>Slag II [% wt]</th>
<th>Slag III [% wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larnite</td>
<td>55</td>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>Srebodolskite</td>
<td>25</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Wüstite</td>
<td>&lt;5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Magnesiowüstite</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Magnetite</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Free Lime</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Periclase</td>
<td>5</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>
Experimental Design

BOF slag characterization - SEM analyses

BOF slag is **polyphasic** and composed of **complex oxides** similar to the calcium silicate.

<table>
<thead>
<tr>
<th>Element</th>
<th>wp min [% wt]</th>
<th>wp max [% wt]</th>
<th>bp min [% wt]</th>
<th>bp min [% wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.7</td>
<td>10.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>38.4</td>
<td>49.7</td>
<td>21.7</td>
<td>22.9</td>
</tr>
<tr>
<td>Si</td>
<td>14.7</td>
<td>16.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>2.7</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>20.9</td>
<td>27.6</td>
<td>1.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>12.7</td>
<td>16.3</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>8.3</td>
<td>10.8</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>11.5</td>
<td>48.7</td>
<td>54.4</td>
</tr>
</tbody>
</table>
Slag grain size distribution (PSD)
ISO 4701:2008

Results

- **Calcium** and **Iron** are main slag components
- other interesting compounds: **Phosphorous oxides**
- ad-hoc physical treatments can be required to **separate slag in its two main fractions**:
  - **iron rich fraction** to be fed in pellettization unit
  - **calcium and phosphorous rich fraction** to be used as fertiliser
Experimental Design

Laboratory scale tests

The tests have been carried out on different slag qualities

Tests Steps

1. **Air-cooling stage** of 24 hours at atmospheric conditions
2. **Aging phase** of some days
3. **Milling** with a lab jaw crusher equipment and **Sieving**:
   - coarse fraction (PSD > 1mm)
   - finer fraction (PSD < 1mm)
4. Manual **magnetic separation** of coarse and finer fractions with a neodymium magnet:
   - two similar fractions (similar iron content) derived from finer fraction
   - magnetic coarse fraction (iron rich)
   - non-magnetic coarse fraction
5. **Mixing** of finer fractions and magnetic coarse fraction
Main Results

- **Different techniques of magnetic separation are supposed to be more suitable:**
  - the **finer fraction** is not adequately separated as the iron particles are bonded to the fine grains of slag

- **Two main fractions have been obtained:**
  - **non-magnetic coarse slag** to be tested as fertiliser
  - **iron rich fraction** to be tested in sintering process
Contents

1 Introduction
2 Objectives
3 Approach
4 Experimental Design
5 Process Modelling and Simulation (PM&S)
6 Case study simulation
7 Conclusions
8 Future work
PM&S
Model Development

Heuristic Excel-based sub-models have been developed to represent in detail the pre-tested slag treatment

Data for modelling, tuning and validation steps

- Literature data
- Real data from preliminary experimentation

Main aims

- Evaluation of process behaviour in different operating scenarios:
  - different BOF slag qualities
  - different operating conditions
- Investigation of possible treatment modifications
- support for lab tests instead of executing plant on-line applications
PM&S
Model Development - Cooling Stage

Model Foundations
- Newton’s law of cooling
- Fourier equation for conductivity

Model Operating Principles
1. **Discretization** of the global BOF slag heap in several layers
2. **Iterative computation of external layer temperature** by evaluation of global heat transfer coefficient (convective, conductive and radiant)
3. **Estimation of temperature of each internal conductive layer** by evaluation of conductive heat transfer coefficient
4. **Estimation of heat losses**

Model aim
**Monitor temperature** (external and core) and **heat losses** on the basis of the cooling time
### Model Development - Cooling Stage

**INPUT VARIABLES**
- **F**: kg, 200000.00, Slag mass
- **Tin**: °C, 1600.00, Initial slag temperature
- **Ta**: °C, 25.00, Ambient temperature
- **h**: m, 2.00, Height of slag heap
- **t**: min, 1440.00, Cooling time

**CALCULATED VARIABLES**
- **Tin**: K, 1873.15, Initial slag temperature
- **Ta**: K, 298.15, Ambient temperature
- **V**: m³, 606.06, Slag Volume
- **L**: m, 17.41, Length of slag heap
- **S**: m², 442.29, External area of slag heap
- **t**: s, 86400.00, Cooling time

**REFERENCE AND AUXILIARY DATA**
- **PM**: g/mol, 1.82E+02, Mean molar weight of slag
- **rho**: kg/m³, 3.30E+03, Slag density
- **ε**: -, 7.50E-01, Slag emissivity
- **c**: J/(mol*K), 5.97E+01, Slag specific heat
- **c slag**: J/(m⁺K), 1.50E+00, Slag conductivity
- **K**: J/(m⁺K⁺s), 1.00E-02, Air thermal conductivity
- **σ**: W/(m²*K), 5.68E-08, Stefan-Boltzmann constant
- **δ**: m, 5.00E-03, Thickness of the conductive layer in external fraction of slag
- **s**: m, 0.10, Thickness of each conductive layer in internal fraction of slag

**OUTPUT VARIABLES**
- **Vrad**: m³, 43.46, Volume of the external radiant layer of the slag
- **Fext**: kg, 143407.88, Mass of the external radiant layer of the slag
- **n**: -, 9.00, Maximum number of conductive layers in internal part of slag
- **Tcore**: °C, 920.24, Final temperature of core slag
- **Text**: °C, 25.00, Final temperature of external slag
- **Qloss**: GJ, 488.07, Heat Losses
PM&S
Model Development - Grinding and Sieving

Model Foundations
- Grindability, tenacity, hardness (Mohrs scale) and work index of slag compounds
- Bond’s law of comminution

Model Operating Principles
1. Composition analysis data normalization (if required)
2. Reduction of the BOF slag size by specific factor using fixed grinding grade
3. Allocation of each fraction in the relative partition of the new PSD using fixed distribution efficiencies
4. Estimation of mill energy consumption

Model aim
Provide the composition of each fraction obtained through grinding process and estimate the mill energy consumption
Model Foundations

- Magnetic properties of slag compounds

Model Operating Principles

1. Composition analysis data normalization (if required)
2. Allocation of compounds between magnetic and non-magnetic fractions using separation efficiencies based on magnetic properties of slag compounds

Model aim

Provide the composition of magnetic and non-magnetic fractions
PM&S
Model Development - Magnetic Separation

TINOS 2015 — Evaluation of a BOF Slag Recovery Treatment combining Experimental and Simulation Studies
Process Modelling and Simulation (PM&S)
Tinos Island, July 2-4, 2015
Contents

1 Introduction

2 Objectives

3 Approach

4 Experimental Design

5 Process Modelling and Simulation (PM&S)

6 Case study simulation

7 Conclusions

8 Future work
Case Study Simulation

- The developed sub-models can be used in sequence to analyse the proposed treatment behaviour with different qualities of BOF slag or under different operating conditions.

- A case study is presented regarding one BOF slag quality.
Case Study Simulation

Global model input

### IN COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>60.00</td>
</tr>
<tr>
<td>Siliciclastic</td>
<td>40.00</td>
</tr>
</tbody>
</table>

### IN PSD

<table>
<thead>
<tr>
<th>Size Range</th>
<th>mm</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.063</td>
<td>2</td>
<td>2.36</td>
</tr>
<tr>
<td>0.063 - 0.106</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>0.106 - 0.125</td>
<td>3.35</td>
<td></td>
</tr>
<tr>
<td>0.125 - 0.15</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>0.15 - 0.212</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>0.212 - 0.25</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>0.25 - 0.5</td>
<td>8.95</td>
<td></td>
</tr>
<tr>
<td>0.5 - 1</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>1 - 1.4</td>
<td>10.16</td>
<td></td>
</tr>
<tr>
<td>1.4 - 2</td>
<td>39.40</td>
<td></td>
</tr>
<tr>
<td>&gt; 2</td>
<td>24.80</td>
<td></td>
</tr>
</tbody>
</table>

### OTHER

<table>
<thead>
<tr>
<th>Input Data</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of the slag to be treated</td>
<td>t</td>
<td>2000</td>
</tr>
<tr>
<td>Initial slag temperature</td>
<td>°C</td>
<td>1600</td>
</tr>
<tr>
<td>Atmospheric temperature</td>
<td>°C</td>
<td>25</td>
</tr>
</tbody>
</table>
**Input**

- Cooling conditions: *atmospheric temperature and pressure*
- Cooling time: 24 hours

**Output - Results**

- External temperature of BOF slag heap: 25°C
- Internal core temperature of BOF slag heap: 920°C
- Heat losses: $488\text{GJ}$ Possibilities for energy recovery can be evaluated
Case Study Simulation
Grinding and Sieving

**FINAL PSD**

<table>
<thead>
<tr>
<th>mm</th>
<th>mm</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.045</td>
<td>0.045</td>
<td>6.38</td>
</tr>
<tr>
<td>0.045</td>
<td>0.063</td>
<td>7.20</td>
</tr>
<tr>
<td>0.063</td>
<td>0.09</td>
<td>7.04</td>
</tr>
<tr>
<td>0.09</td>
<td>0.125</td>
<td>8.92</td>
</tr>
<tr>
<td>0.125</td>
<td>0.25</td>
<td>11.78</td>
</tr>
<tr>
<td>0.25</td>
<td>0.5</td>
<td>13.40</td>
</tr>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>13.52</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>6.97</td>
</tr>
<tr>
<td>&gt; 1</td>
<td>1</td>
<td>24.79</td>
</tr>
</tbody>
</table>

**COMPOSITION OF EACH PARTICLE SIZE FRACTION**

- Mill energy: **17.5 MWh**
- Fractions with PSD < 0.25mm: + Calcium compounds - Ferrous compounds
- Fraction with PSD > 0.25mm: + Phosphorus
Case Study Simulation
Magnetic Separation

Input
- According to the proposed global treatment, only the coarse fraction is fed to the magnetic separation.

Output - Results
- Magnetic fraction: 46% wt.
  - Hypothetically suitable to be fed in pelletization unit.
- Non-magnetic fraction: 54% wt.
  - Probably suitable as fertiliser.
Mixing Step

The magnetic coarse fraction and the fine portion of the BOF slag are mixed to be then fed to pelletizing unit.

Observations

The content in larnite (calcium compound) is not negligible so better separation is required.
Main remarks

- huge energy losses in BOF slag cooling stage
- non-magnetic coarse fraction of BOF slag is calcium and phosporous rich appear suitable to be used as fertiliser
- the obtained part of BOF slag to pelletize is still reach in larnite
- an additional and better magnetic separation including slag finer fraction could result in:
  - a higher amount of slag to be reused as fertiliser
  - a fraction with higher iron content and less calcium more suitable for the sinter plant
Conclusions

**What**
- Investigation of **BOF slag recovery** option

**How**
- Combining **experimental data collection** and **process simulation**

**Why**
- To find appropriate treatments and suitable operating conditions to recover two main slag fractions with features that fit with requirements for a possible reuse as:
  - fertiliser
  - pelletization operations

**Outcomes**
- Similar results between experimental and simulation tests preliminary prove the possibility of BOF slag valorisation after the proposed recovery process
- Simulation results suggest **adjustments in magnetic separation operation**
Contents

1 Introduction
2 Objectives
3 Approach
4 Experimentatal Design
5 Process Modelling and Simulation (PM&S)
6 Case study simulation
7 Conclusions
8 Future work
Future works

Future

- Analyses of possibilities of energy recovery
- Investigation of suggested process modifications
- Further simulation analyses on different qualities of slag
- Pelletization tests with obtained fraction
- Fertilisation tests, in particular specific soil column tests to evaluate how the obtained BOF slag fraction with higher content of Calcium and Phosphorous affects soil features
Acknowledgements

The work described in the present paper has been developed within the projects entitled Efficient use of resources in steel plants through process integration (Contract No. RFSR-CT-2012-00039) and Removal of Phosphorus from BOF-slag (RFSR-CT-2013-0032) and that have received funding from the Research Fund for Coal and Steel of the European Union. The sole responsibility of the issues treated in the present paper lies with the authors the Commission is not responsible for any use that may be made of the information contained therein.
Thank you!

Comments and suggestions are welcome.

Evaluation of a BOF Slag Recovery Treatment combining Experimental and Simulation Studies

I. Matino, T.A. Branca, E. Alcamisi, V. Colla, L. Romaniello
i.matino@sssup.it

3rd International Conference on Sustainable Solid Waste Management • Tinos Island, July 2-4, 2015