Recent progress of hot stage processing for steelmaking slags in China considering stability and heat recovery

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Crude Steel Production / Mt

- China Rude Steel Production

Ratio of China Rude Steel Production in World Total

Year
In 2005, the total waste heat energy of China’s steel industry was 288 kgCE (kilogram of coal equivalent) per tonne of steel. The average recovery ratio was less than 26%.

Furthermore, the recovery ratio of sensible heat in all kinds of molten slags was only 1.6%.

In 2009, the total quantity of steelmaking slag was 90 million tonnes in China.

In 2010, the total quantity of steelmaking slag was 99 million tonnes in China.
Introduction

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The current hot stage processing of BOF slags

- Pyrolytic Self-slaking process
- Baosteel’s Slag Short Flow (BSSF)
- Instantaneous slag chill process (ISC)
- Water-granulation process
- Wheel-granulation process (HK)
Pyrolytic Self-slaking process

- The hot slag within a temperature range of 300~800°C is poured into a tank with a cover, while water is sprayed into the tank and thus steam will be generated that reacts with the free lime and magnesia in the slag.

Bayuquan steel works of An-Ben Steel
- 700,000 tons/a for 3×260 t BOF

Tiantie:
- 600,000 tons/a for 2×180 t BOF

Shaogang:
- 500,000 tons/a
**Instantaneous slag chill process (ISC)**

Invented by Nippon Steel and imported by Baosteel in 1980s
Jinan Steel has been using this process for BOF slag granulation since 1978 for their 25 ton BOF. To avoid explosion, the flow rate of quenching water and molten slag must be well controlled.
Wheel-granulation process (HK)
HK process was first applied in Benxi Steel in 2004 for $3 \times 120t$ and $3 \times 150t$ BOF. In total 4 units were built. In 2006, Liuzhou Steel built 2 units for their $3 \times 100t$ BOF.
BSSF-A
Distribute

Wheel granulation

BSSF—B

BSSF—RC
## Comparison of steelmaking slag granulation processes

<table>
<thead>
<tr>
<th>Process</th>
<th>pyrolytic Self-slaking</th>
<th>Air-granulation</th>
<th>Water-granulation</th>
<th>HK</th>
<th>ISC</th>
<th>BSSF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Suitability for slag</strong></td>
<td>All slag</td>
<td>Low viscosity</td>
<td>Low viscosity</td>
<td>Low viscosity</td>
<td>All slag</td>
<td>All slag</td>
</tr>
<tr>
<td><strong>Ratio of process</strong></td>
<td>100%</td>
<td>90%</td>
<td>50%</td>
<td>80~85%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td><strong>safety</strong></td>
<td>high</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>Relative high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Processing ability</strong></td>
<td>20~40 heats/3 days/box</td>
<td>2~2.5t/min</td>
<td>1.5t/min</td>
<td>1.5~3 t/min</td>
<td>0.03t/min/trolley</td>
<td>1~3 t/min</td>
</tr>
<tr>
<td><strong>Processing cycle</strong></td>
<td>≥12 h</td>
<td>1~2 min</td>
<td>5~6 min</td>
<td>6~8 min</td>
<td>≥2 h</td>
<td>1~2 min</td>
</tr>
<tr>
<td><strong>Size of granulated slag</strong></td>
<td>≤10 mm, ≥60%</td>
<td>&lt; 6 mm</td>
<td>≤5 mm, ≥90%</td>
<td>≤12.5 mm, ≥95%</td>
<td>≤300 mm</td>
<td>≤19 mm, ≥90%</td>
</tr>
<tr>
<td><strong>Water/Slag ratio (t/t slag)</strong></td>
<td>0.25~0.6</td>
<td>-</td>
<td>10:1</td>
<td>3:1</td>
<td>~0.3:1</td>
<td>1:1</td>
</tr>
<tr>
<td><strong>Pressure of media (MPa)</strong></td>
<td>0.3</td>
<td>0.35~0.6</td>
<td>&gt;0.25</td>
<td>0.3</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Water supply (t/h)</strong></td>
<td>20</td>
<td>100 circulation</td>
<td>624 circulation</td>
<td>430~480 circulation</td>
<td>circulation</td>
<td>100~180 circulation</td>
</tr>
<tr>
<td><strong>Environm. impact</strong></td>
<td>Steam, dust emission</td>
<td>100 dB Noise</td>
<td>Steam emission</td>
<td>Steam emission</td>
<td>Steam emission</td>
<td>Steam emission</td>
</tr>
</tbody>
</table>
For BOF slag treatment, above mentioned pyrolytic self-slaking, HK, and BSSF processes are being accepted.

No process considered the heat recovery from molten slag during granulation processes.

Large scale application of stabilised steel slag powder in construction is a good way for steel slag valorisation.

The practical feasibility, applicable in large scale, low cost is very important for slag valorisation processes.
Treating and heat recovery system for steelmaking slag in Shougang Group

Four key problems to be solved:
- Flexibility to various slag properties;
- Interrupting input and continuous output of slag;
- Continuous and stable heat exchange with hot slag;
- Fast stabilisation of free lime.
Currently, a testing system for steelmaking slag treatment and energy recovery is being built in the Shougang Group.

It has the capacity to treat 1 million tonne of slag per year.
Fast stabilisation of free lime

Fig. Effect of 1 h dry ball milling on the content of f-CaO

Fig. Effect of wet ball milling on the content of f-CaO

Fig. DTG curves of steel slag after 1 h dry ball milling

Fig. DTG curves of steel slag after wet ball milling for different times
The advantages of this technique are:

- Either a liquid slag with good fluidity or a liquid/solid slag mixture can be treated;
- There is no danger of explosion as the molten slag does not contact water directly;
- Gas (air, CO₂ and steam) is only used as heat exchange medium and lime stabiliser but not as granulating energy, thereby lowering the energy consumption;
- The heat energy of molten slag can be recovered efficiently and slag can be stabilised quickly, the metal can be recycled and the tailings can be utilised.
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Dry treating method based on steelmaking slag composition modification

- The Wuhan Research Institute of Metallurgical Construction developed this slag granulation method considering that the conventionally treated slag cannot be fully utilised due to the lower cementitious activity caused by water treatment.

- Process:
  - Homogenising and composition modifying the molten slag;
  - Water quenching and granulation;
  - Dry the granulated slag powders by high temperature steam recovered from water quenching and granulation;
  - Dry magnetic dressing to separate metal;
  - Utilisation of slag powders.
Reactions may occur during composition modification of slag:

\[
4 \text{FeO} + \text{O}_2 = 2 \text{Fe}_2\text{O}_3 \\
\text{Fe}_2\text{O}_3 + n\text{CaO} = n\text{CaO} \cdot \text{Fe}_2\text{O}_3 \\
4\text{CaO} \cdot \text{FeO} + \text{O}_2 = 4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \\
4\text{CaO} \cdot \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 = 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \ (C_4\text{AF}) \\
2\text{CaO} + \text{SiO}_2 = 2\text{CaO} \cdot \text{SiO}_2 \ (C_2\text{S}) \\
2\text{CaO} \cdot \text{SiO}_2 + \text{CaO} = 3\text{CaO} \cdot \text{SiO}_2 \ (C_3\text{S}) \\
3\text{CaO} + \text{Al}_2\text{O}_3 = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \ (C_3\text{A})
\]

The analysis confirmed that the quantity of main high early strength minerals such as \( C_4\text{AF}, C_3\text{A}, \) and \( C_3\text{S} \) increased, while the quantity of free lime and free magnesia obviously decreased. Hence, the slag after compositional modification becomes a Portland cement clinker with high early strength and stable properties.
The advantages of this process

- Continuous production;
- Small number of processing steps;
- The investment and space requirements are 30% lower than conventional slag treatment processing;
- Expanded range of applications. free lime and other unbeneficial components is less than 1%. As the strength of construction materials made of treated slag powders are improved over 40%.

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**Table 1: Separated products of steelmaking slags.**

<table>
<thead>
<tr>
<th>Products</th>
<th>Diameter (mm)</th>
<th>T. Fe (wt %)</th>
<th>Magnetic Fe (wt %)</th>
<th>Ratio (%)</th>
<th>Water (%)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel powder</td>
<td>&lt; 1</td>
<td>&gt; 50</td>
<td>--</td>
<td>10~14</td>
<td>&lt; 2</td>
<td>Sintering</td>
</tr>
<tr>
<td>Steel grain</td>
<td>1~10</td>
<td>&gt; 90</td>
<td>--</td>
<td>3~7</td>
<td>&lt; 1</td>
<td>Steelmaking</td>
</tr>
<tr>
<td>Slag powder</td>
<td>&lt; 0.1</td>
<td>--</td>
<td>&lt; 2</td>
<td>68~78</td>
<td>&lt; 2</td>
<td>Construction material</td>
</tr>
<tr>
<td>Slag grain</td>
<td>0.1~5</td>
<td>--</td>
<td>&lt; 2</td>
<td>5~15</td>
<td>&lt; 1</td>
<td></td>
</tr>
</tbody>
</table>
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- **Fundamental Studies**

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**Fundamental Studies**

- National Natural Science Foundation of China (NSFC) project: “Fundamental study on key techniques for the preparation of high value products by utilisation of both heat and slag”.

- The process proposed targets the modification of the slag composition by:
  - Carbothermic reduction to reduce iron oxides in the molten slag.
  - Waste refractory materials containing silica and alumina are added into the molten slag to lower the viscosity and adjust the slag composition making it suitable for making glass ceramics.
  - The liquid slag is air granulated and heat can be recovered.

- Component modification of steelmaking slag in an air quenching process to improve grindability was reported.
**Table 2:** Composition of modification agents and original BOF slag (wt %)

<table>
<thead>
<tr>
<th>Component</th>
<th>T. Fe</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>S</th>
<th>f-CaO</th>
<th>FeO</th>
<th>M-Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>1.53</td>
<td>5.3</td>
<td>0.78</td>
<td>21.53</td>
<td>67.27</td>
<td>0.47</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.59</td>
</tr>
<tr>
<td>Mill tailings</td>
<td>15.79</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>63.42</td>
<td>1.53</td>
<td>--</td>
<td>--</td>
<td>0.71</td>
<td>--</td>
</tr>
<tr>
<td>Steel slag</td>
<td>17.28</td>
<td>44.73</td>
<td>8.46</td>
<td>4.6</td>
<td>14.53</td>
<td>0.045</td>
<td>9.54</td>
<td>21</td>
<td>8.45</td>
<td>--</td>
</tr>
</tbody>
</table>

**Fig.** Particle volume fraction of slag modified by 9% fly ash and original slag

**Fig.** Cumulative undersize distribution of steel slag with different ratios of fly ash
**Fig.** SEM images of slag without fly ash added: 1, 3, 6—\(3\text{CaO} \cdot \text{SiO}_2\); 2, 4, 5—RO; 7—CaO\cdot\text{SiO}_2; 8—CaO\cdot\text{Fe}_2\text{O}_3; 9—f-CaO

**Fig.** Micrographs of slag with 5% fly ash added: 1, 2, 3, 4—CaO\cdot\text{SiO}_2; 5, 7—2CaO\cdot\text{SiO}_2; 6—CaO\cdot\text{FeO}\cdot\text{SiO}_2; 8—RO
Experiments about cooling and pulverising the molten steel slag and blast furnace (BF) slag by a high pressure water jet of 8 to 10 MPa were conducted on a self-made slag melting and high pressure water cooling system.
Fig. Particle size distribution of jetted steel slag

Fig. Comparison of compressive strength of cement samples from jetted and original steel slag
Preparation of glass–ceramics from liquid steel slag

- 40% EAF slag was melted at 1724 K and then mixed with 60% melting additives (containing silica, alumina and sodium oxide), subsequently heated to 1773 K for 1 hour. Then the modified slag was cast, annealed and transformed to glass–ceramics.

**Fig.** XRD patterns of glass-ceramics

**Fig.** SEM image of glass-ceramics
Simulation on heat recovery in dry granulation process of steelmaking slag

Fig. Schematic diagram of the system of granulation heat exchange
The temperature of output granulated slag will be 900 K if the input slag temperature is 1673 K. The temperature of room temperature blown air was increased to 693 K after heat exchange with molten slag. The flow rate of air in the range of 80000 to 100000 m³/h results in slag cooling and heat recovery efficiently.
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Problems of sensible heat recovery of molten slag:

- There are two solid phase: crystal phase and glass, the heat conductivity is different:
  - Liquid slag: 0.1~0.3W/m²K, Glass: 1~2W/m²K, Crystal: ~7W/m²K;
- Fast granulate to small particles is precondition.
- Most developed or under developing methods are physical methods based on air, steam or hot water as heat recovering medium; the quality of recovered heat is poor;
- The energy conversion are multi-steps;
- **Low exergy efficiency** of sensible heat recovery from molten slag is the key problem.
Conclusions

- According to the pilot-scale experiments and fundamental studies on hot stage steelmaking slag treatment recently carried out in China, heat recovery from molten slag in the slag granulating process must consider the massive application of treated slag products and engineering possibility of the process.

- No matter what process is selected, molten slag with suitable fluidity is essential for smooth and continuous processing. For this reason, slag modification in composition and temperature are necessary in some cases. Slag modification in composition is also a measure to decrease the basicity of slag, enlarge the application areas of steel slag products.

- Completely dry treatment is impossible to eliminate free lime. Therefore, water quenching, steam treatment, or wet milling, carbonating must be included in the process.

- Making use of the sensible heat of molten slag and decreasing the energy input during molten slag treatment should be acceptable instead of net energy recovery.
Thank you for your attention!