UPDATE OF IRON AND STEEL SLAG IN JAPAN AND CURRENT DEVELOPMENT FOR VALORISATION

Tomo ISAWA, Nippon Slag Association
Contents

- Activity of Nippon Slag Association
- Statistics: production and sales of iron and steel slag
- Laws, environmental criteria, sales management
- Development of BOF slag for marine use
Nippon Slag Association

FOCUS: Iron and steel slag
TARGET: to create Recycling-oriented Society

The primary objectives are:
- to promote a better understanding of iron and steel slag,
- to position the slag as a viable commercial product and
- to pave the way for its stable supply.

MEMBERS
- Iron and Steel manufactures (4), and the Assoc./Group of manufactures (2)
- Cement and BF cement companies (5)
- Slag processing companies (15)

Established in 1978

Annual production of ‘slag’ in Japan (2011)

<table>
<thead>
<tr>
<th>Source</th>
<th>Ferrous</th>
<th>Non-Ferrous</th>
</tr>
</thead>
<tbody>
<tr>
<td>from metal manufacture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granulated BF slag</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>Air-cooled BF slag</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Steelmaking slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOF slag</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>EAF slag</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Copper-, Ferronickel-slag etc</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>from waste treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat-treated, melted/fused waste, sewage sludge</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>
Slag and steel production in Japan

- Blast furnace slag: 24 million tonnes/yr (≈300kg-slag/t-HM)
- Steelmaking slag: 13 million tonnes/yr (≈120kg-slag/t-steel)
Iron and Steel slag in steel manufacture

Integrated mill
eg. BF-BOF-RH/LF-CC/IC

EAF steelmaking
eg. EAF-LF/RH-CC/IC

Iron ore

Blast Furnace

BOF

Hot metal pre-treatment
+scrap

TPD Injection
KR de-S

RH degasser

post refining
comp. fine control
temp. adjustment

LF

Continuous Caster

Ingot Casting

Steelmaking slag (BOF, EAF slag)

carried-over BF slag (SiO₂, CaO, Al₂O₃, MgO)
oxides of hot metal ingredient (Si, Mn and P)
burnt lime as a flux and iron oxide for refining

BF slag

ash from coke
gangue of ore
limestone
## Chemical compositions of ferrous slag

### Typical chemical compositions of various ferrous slag (%)

<table>
<thead>
<tr>
<th>Blast furnace</th>
<th>Granulated / air-cooled</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>FeO</th>
<th>S</th>
<th>P$_2$O$_5$</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace</td>
<td>Granulated / air-cooled</td>
<td>42</td>
<td>34</td>
<td>13</td>
<td>7.4</td>
<td>&lt;0.5</td>
<td>0.8</td>
<td>&lt;0.1</td>
<td>%CaO/%SiO$_2$ =1.2</td>
</tr>
<tr>
<td>BOF SMS</td>
<td></td>
<td>46</td>
<td>11</td>
<td>2</td>
<td>6.5</td>
<td>17.4</td>
<td>0.1</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Pre de-S</td>
<td></td>
<td>50</td>
<td>10</td>
<td>2-10</td>
<td>2</td>
<td>7</td>
<td>1.5</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>Pre de-P</td>
<td></td>
<td>35</td>
<td>25</td>
<td>5</td>
<td>5</td>
<td>15-25</td>
<td>&lt;0.2</td>
<td>2.5-5.0</td>
<td></td>
</tr>
<tr>
<td>BOF</td>
<td></td>
<td>45</td>
<td>15</td>
<td>3</td>
<td>5</td>
<td>15-20</td>
<td>&lt;0.1</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>LF, etc</td>
<td></td>
<td>30-40</td>
<td>10-15</td>
<td>15-35</td>
<td>5-10</td>
<td>10-25</td>
<td>&lt;0.1</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>EAF</td>
<td>Oxydising</td>
<td>23</td>
<td>12</td>
<td>7</td>
<td>6.8</td>
<td>29.5</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reducing</td>
<td>55</td>
<td>19</td>
<td>17</td>
<td>7.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Rock: Andesite</td>
<td></td>
<td>6</td>
<td>60</td>
<td>17</td>
<td>2.8</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Portland Cement</td>
<td></td>
<td>64</td>
<td>22</td>
<td>6</td>
<td>1.5</td>
<td>3.0</td>
<td>2.0</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Portland Cement: reference
Breakdown of BF slag usage

**Characteristics** | **Main Uses (JIS Nos.)**
---|---
Hydraulicity | Road building (A 5015)  
| Cement (R 5211, R 5210, A 6206)
Lightweight, Permeability, Latent hydraulicity | Soil improvement  
| Backfills in civil engineering
Stability, anti-alkalinity | Aggregates for concrete (A 5011-1)
Low content of Na₂O, K₂O | Clay as a raw material of cement clinkers
Fertilising ingredient | CaO and SiO₂ source for fertilizer

**Merit of BFS cement use in CO₂ emission (kg-CO₂/t)**

<table>
<thead>
<tr>
<th>Items</th>
<th>Portland Cement</th>
<th>PBFC</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>77</td>
<td>55</td>
<td>22</td>
</tr>
<tr>
<td>de-CO₂ (limestone)</td>
<td>510</td>
<td>294</td>
<td>216</td>
</tr>
<tr>
<td>Combustion</td>
<td>271</td>
<td>159</td>
<td>112</td>
</tr>
<tr>
<td>Delivery, etc</td>
<td>38</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Total CO₂ emission</td>
<td>896</td>
<td>526</td>
<td>370</td>
</tr>
</tbody>
</table>

Breakdown of steelmaking slag usage

- **Characteristics**
  - Hardness, anti-wearing + Hydraulicty
  - Large angle of internal friction
  - Ingredient (CaO, SiO₂, Al₂O₃)
  - Stability (EAF slag)
  - Fertilising ingredient

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Main Uses (JIS Nos.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, anti-wearing</td>
<td>Aggregate for asphalt concrete (A 5011-1)</td>
</tr>
<tr>
<td>+ Hydraulicty</td>
<td>Road building (A 5015)</td>
</tr>
<tr>
<td>Large angle of internal friction</td>
<td>Civil engineering, soil improvement (SCP)</td>
</tr>
<tr>
<td>Ingredient (CaO, SiO₂, Al₂O₃)</td>
<td>Raw material for cement clinker</td>
</tr>
<tr>
<td>Stability (EAF slag)</td>
<td>Aggregates (anti alkali-silica reaction) (A 5011-4)</td>
</tr>
<tr>
<td>Fertilising ingredient</td>
<td>CaO and SiO₂, MgO, FeO, (P₂O₅) source</td>
</tr>
</tbody>
</table>

- Slag ratio of BOF and EAF is about 120kg/t-steel
- Percentage of reclamation is 2% (40% in 1980)
- For several cases, a risk of the expansion and the alkali risk should be considered depending on a use.
Management of slag expansion

Expansion of BOF slag in service causes trouble on road surface

Measurement of expansion
Evaluation of expansion and standardisation as an engineering material
road building material
Management and suppression of the expansion
steam ageing for accelerated treatment

JIS A 5015 (revised March 2013)
1) Accelerated test
2) Criteria for expansion stability
   for road base: less than 1.5%
   for asphalt aggregate: less than 2.0%

Expansion measuring equipment

Expansion of BOF slag in service causes trouble on road surface

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Evaluation of expansion and standardisation as an engineering material
road building material
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Expansion measuring equipment

Steam ageing
Legal Position of Iron and Steel Slag

Basic Environment Law
the Basic Law for Establishing the Recycling-based Society

Waste Management and Public Cleaning Law (1970),
definition: ‘Waste is a filthy or discarded object in a solid or liquid form …’
category: general waste and 19 industrial wastes, including “slag”

Whether “waste or not” is to be evaluated by comprehensive consideration of 5 factors:
1) properties of the object, 2) states and conditions when discharged,
3) procedure of handling, 4) economical value, and 5) intention of possessor.
(Notifications for the application of law, by Ministry of the Environment, ’71, ’05, ’05)

Law of Promotion of Effective Utilisation of Resources (2000):
Promotion of 3Rs: reduce, reuse and recycle
Steel industry is one of “5 designated resources-saving Industries”, and is required to promote the reduction of, and the effective use of ferrous slag as by-products.

Nippon Slag Association takes the situation that
Iron and Steel slag is not a waste as far as it is used commonly, effectively and environmentally correctly.
Quality Standards for Environment

Standard for primary heavy metals:

<table>
<thead>
<tr>
<th>substance</th>
<th>CaO for soil pollution</th>
<th>harbour use only Elution</th>
<th>for seabed [mg/litre]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Content [mg/kg]</td>
<td>Elution [mg/litre]</td>
<td></td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>150</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Total cyanide (t-CN)</td>
<td>50</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>150</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Chromium hexavalence (Cr⁶⁺)</td>
<td>250</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>150</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Total Mercury (t-Hg)</td>
<td>15</td>
<td>0.0005</td>
<td>0.0015</td>
</tr>
<tr>
<td>Alkylmercury (R-Hg)</td>
<td>-</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>150</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Fluorine (F)</td>
<td>4,000</td>
<td>0.8</td>
<td>15</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>4,000</td>
<td>1</td>
<td>20</td>
</tr>
</tbody>
</table>

Interim criteria is applied to harbour use
Sales management

Social requirement to slag products is not optimistic.

- Disagreement of supply/demand balance
- Decrease of public construction investment
- Competition with other recycle materials
- Actualisation of environmental risks
- Lack of understanding of the slag and its quality control
- Unfavourable feeling to recycle material
- Environmentally consciousness of public
- Need for communication of slag information

Not only R&D for new applications and technology of quality assurance, but also sales management are necessary; ensuring the appropriate utilisation of ferrous slag product, and preventing problems arising from it.

The Guide Line includes:

- Quality Control and Assurance Methods for Slag Products
- Compliance for Order Acceptance & Delivery of the products
- Evaluation of environmental influence around the site before sales
- Judgment as to the adequacy of Utilisation
- Customer follow-up during construction and after use
- Countermeasures in case of problems
- Internal and external audit for confirmation of compliance
New application of steelmaking slag

The situation of slag sales in Japan

Blast furnace slag has established a stable position for cement industry. Its availability is well known, though the public education is still necessary.

Steelmaking slag need further development of new applications to compete with other recycle materials. These are the tasks that we should intensively settle while confirming the environmental impacts:

- to utilise the characteristics of slag to the maximum
- to overcome the disadvantageous points of slag, and
- to educate the advantage of slag to the public with practical examples.
## Characteristics for steelmaking slag

<table>
<thead>
<tr>
<th>characteristic</th>
<th>explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.2 – 3.7 g/cm³ Higher than natural aggregate</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>CaO, SiO₂, FeO, Al₂O₃ Similar to natural aggregate Possible expansion and pH increase due to free lime (CaO)</td>
</tr>
<tr>
<td>Hydraulicity</td>
<td>Weak cement property when contacting with water</td>
</tr>
<tr>
<td>Environmental aspects</td>
<td>Fulfill the environmental requirement (heavy metals)</td>
</tr>
<tr>
<td>Expansion</td>
<td>Consideration may be necessary depending on application</td>
</tr>
<tr>
<td>Clarification effect</td>
<td>Strong affinities with Phosphate and sulphide</td>
</tr>
<tr>
<td>Improvement of dredged soil strength</td>
<td>BOF slag containing high concentration of free lime improves mechanical strength of dredged soil</td>
</tr>
<tr>
<td>Influence of alkali</td>
<td>Untreated BOF slag may cause rapid increase of pH, though alkali is mitigated by magnesium ions in seawater in long-term.</td>
</tr>
</tbody>
</table>
Clarification effect: P and S absorption

Phosphate:
positive relation between absorption and f-CaO content

Sulphide:
negative effect of f-CaO on the suppression of H₂S
Improvement in mechanical properties of dredged soil

Physical effect:
- decrease in moisture content of the mixture
- improvement in particle distribution

Chemical reaction: in short period hydro reaction

Initial fluidity: 10cm(left), 15cm(mid), 20cm(right)
Influence on pH and white turbidness

Possible influence of BOF slag for the marine application

High pH near the slag

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- 
\]

White turbidness during construction

\[
\text{Mg}^{2+} (\text{in seawater}) + 2 \text{OH}^- \rightarrow \text{Mg(OH)}_2 
\]

In order to reduce environmental impact of alkali
decrease the area contacting with water
lower the activity of free CaO

<table>
<thead>
<tr>
<th></th>
<th>Size control</th>
<th>Particle distribution</th>
<th>Elimination of powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>carbonation</td>
<td>Marine block</td>
<td>Rapid Carbonation</td>
</tr>
<tr>
<td>reaction with soil</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>coarse</th>
<th>fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reaction with soil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Basic characteristic

<table>
<thead>
<tr>
<th></th>
<th>coarse</th>
<th>fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reaction with soil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Steel Slag Hydrated Block / Stone

Production of hydrated block and its usage

- BOF slag
  - aggregate
- GGBFS
  - binder
- Else
  - flyash
  - alkali stimulus

Mixing

- BOF slag
- GGBFS
- Else

Concreting

- Pre-cast frame

Crushing

- Yard

Curing

- Ferroform™
- Frontier rock™
- Frontier stone™

Wave breaker
- Ferroform
- Artificial stone/rock
- Algae construction
Algae block of carbonated slag matrix

Restoration of the marine environment

Production of marine block™

Microstructure of MB

Sediment: soft clay

Shallow mound

Embarkment

Seaweed bed

Coral bed
Properties control of dredged clay

Dredged clay
\[ q_u = 0 \text{ kN/m}^2 \]

BOF slag
high f-CaO

Improvement in strength

Dehydration by free lime
Decrease in fluidity by C-S-H formation

Mitigation of pH impact

\[ \text{pH} = 9.8 \text{ in seawater} \]
\[ \text{pH} = 8.2 \]
C-S-H reaction consumes f-CaO

Clarification effect (experimentally confirmed);
absorption of excess nutrition (phosphate)
suppression of harmful gas (\( \text{H}_2\text{S} \))
Influence on pH of the construction

Shallows construction with continuous mixing with dredged soil and dumping to the site

Mixture: soil and slag

pH increase last several hours and recovered soon
Backfill of the depression at seabed

For the restoration deep depression at sea bed

Loss of *Philippinarum*

<table>
<thead>
<tr>
<th>Date</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 1985</td>
<td>30,000 t</td>
</tr>
<tr>
<td>September 1986</td>
<td>1,400 t</td>
</tr>
<tr>
<td>August 1988</td>
<td>4,200 t</td>
</tr>
<tr>
<td>September 1994</td>
<td>2,700 t</td>
</tr>
</tbody>
</table>

by Chiba Pref. Fisheries Exper.Sta.

Imagination of marine environment
Suppression of $\text{H}_2\text{S}$ odour in harbour

Construction area: Fukuyama inner harbour (100 m width x 2.2 km length x 2-4 m depth)
Experimental site 24 m x 18 m

Steelmaking slag: a particle size adjusted to 5-25 mm
JFE Steel West Japan Works (Fukuyama)

<table>
<thead>
<tr>
<th>T. Fe</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>29.3</td>
<td>33.0</td>
<td>6.0</td>
<td>8.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>3.8</td>
<td>1.2</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Experimental area
Control plot

Schematic view of measuring positions

Interstitial of sediment
Interstitial of slag

Fukuyama
Tokyo

Control plot (sea side)

Distance from the center (m)

Constructed on August 2011.

2013/4/2
Water qualities (sulphide concentration and ORP of the water) are remarkably improved and the effects last for 10 months. The pH above the seabed are constant (ca. pH=7.3) through the experiment.
Mechanism of sulphide capture

Cross section of suspended solid

SEM image of suspended particles

The area sulphur concentrate corresponds to the area iron exists, though Ca has weak correspondent to sulphur. Particles of iron sulphide were detected from solid suspension in seawater.

EPMA : Eectoron Probe MicroAnalyzer
Sulphide capture by BOF slag

with Fe, pH=8:
FeS / FeS₂ in low ORP, and S/SO₄²⁻ in high ORP.

(a) S=20 ppm, Fe=0 ppb
(b) S=20 ppm, Fe=5 ppb

Sulphide capture by BOF slag

\[
\begin{align*}
\text{HS}^- + \text{Fe}^{2+} &\rightarrow \text{FeS} + \text{H}^+ \\
\text{HS}^- + 2\text{Fe}^{3+} &\rightarrow \text{S}^0 + 2\text{Fe}^{2+} + \text{H}^+
\end{align*}
\]
Restoration of the marine environment

Artificial seaweed bed, shallow bottoms, tidal flats

Formation of seaweed beds, shallow bottoms & tidal flats makes cradle of fish and shellfish
Concluding remarks

In order to contribute the realisation of recycling-oriented society, our activity is focusing on:

to promote a better understanding of iron and steel slag,
to position the slag as a viable commercial product and
to pave the way for its stable supply.

The restoration of the marine environment with BOF slag is a big approach that substantiate the maximum utilization of slag's characteristics. Development of seashore and prevention of disasters were the principal objectives, but the restoration of lost sea area environment will be recognised as an important theme in future as well. These developments and proposals meet social needs, and they promote public confidence for the slag.

Nippon Slag Association contributes to sustainable growth of steelmaking industry through these activities.

Thank you for your attention.

Acknowledgement: Figures of the marine use were used thanks to the permission of JISF.