Slag Analysis by X-ray Fluorescence Spectrometry
Welcome

Today’s topics

• Why analyze slag?
  o EAF furnace
  o How slag is formed
  o Foaming
  o Modeling

• Slag Analysis
  o XRF fundamentals
  o Instrumentation

• Summary

• Q & A

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XRF Technical Sales Specialist
Bruker AXS Inc.
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Today’s Panelists

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Product Manager, XRF
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Why Analyze Slag?

Alexander Seyfarth
Slag – What is it?

Metallurgy relies on “slag” to:
- remove unwanted elements from the metal
- purify the metal by forming oxides and floating them off the molten metal

Slag usually consists of metal oxides and acts as
- a destination for impurities
- a thermal blanket (stopping excessive heat loss)
- an erosion reducer for the refractory lining of the furnace

Effective steel production goes hand-in-hand with effective slag control
- production capacity (number of heats)
- Refractory wear
- Energy consumption
- Additive consumption
- Quality of metal (grade)
The EAF furnace

- “Standard furnace” for Mini-Mill production of steel as pioneered by NUCOR (see also Wikipedia - EAF)

(PD) Wikipedia Image
High-tech refractory

- Slag Line Brick
- "Hot Spot" Brick Pad
- EBT Tap Hole Assemblies
- Lower Wall Brick
- MgO Safety Brick
- Monolithic Materials for New Installations and Repairs

Bruker AXS
EAF Slag

- Oxidation of Si, Al & Mn in scrap
- Ash in charge & injection C
- Gangue & FeO in DRI/HBI
- Dirt in scrap (gangue)
- Refractory wear
- Flux: lime & dolomite
- Residual slag in EAF
- Oxidation of Si & Mn in Pig Iron
- FeO/rust on scrap
- Oxidation of Fe => FeO
EAF Slag – Main Requirements

- **Compatibility with the refractories**
  - MgO saturated since most slag lines consist of magnesia-carbon refractories

- **Good “foaming” properties and correct viscosity**
  - Foam at the right time and long enough to enable to achieve optimal refining capabilities

- **Lower energy consumption**

- **Lower metal loss**

- **Metal cleaning/refining**
Raw Materials

- High Calcium Lime (Ca source)
- Dolomitic Lime (Ca, Mg source)
- Pre-blended Lime Mixes (Met Grade) Ca Mg mix
- MgO – Carbon Briquettes (Proslag™) (Mg and C source)
- Pig iron – Fe, Mn to counter high Ni, Cu, Cr scrap
### EAF slag composition – analytical requirements

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>8%</td>
</tr>
<tr>
<td>CaO</td>
<td>43%</td>
</tr>
<tr>
<td>FeO</td>
<td>26%</td>
</tr>
<tr>
<td>MnO</td>
<td>6%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13%</td>
</tr>
</tbody>
</table>

- **Refractory Oxides**
  - CaO: 43%
  - FeO: 26%
  - MnO: 6%

- **Fluxing Oxides**
  - MgO: 8%
  - Al₂O₃: 4%
  - SiO₂: 13%
Slag formation in the EAF – meltdown

- Slag formers are either charged with the scrap or blown into the furnace.
- The Si and Al in the scrap are oxidized first to form SiO$_2$ and Al$_2$O$_3$ (fluxing oxides).
- As oxygen is blown into the furnace, the principal flux (FeO) is generated.
- The "slag balance" now starts to shift and the slag becomes more liquid.
Carbon and additive injection

Lime Injection
Carbon Injection
Slag

Lime injection through sidewalls of Electric Arc Furnace

Courtesy Carmeuse Technical Training
Slag Formation in the EAF – flat bath and then hitting the spot

- Carbon (in the form of coke or coal) is lanced into the slag layer, partially combusting to form carbon monoxide gas
- This causes the slag to foam
  - achieving greater thermal efficiency
  - better arc stability
  - better electrical efficiency
- The slag blanket also covers the arcs, preventing damage to the furnace roof and sidewalls from radiant heat.
Slag formation in the EAF

Effective foaminess/viscosity vs Time (Amount of FeO generated)

- Too Crusty
- Optimum Foaming
- Too Liquid
The dynamics of the FeO balance

FeO is generated by oxygen injection:

\[ \text{Fe} + \frac{1}{2} \text{O}_2 (g) = \text{FeO} \]

FeO is reduced by carbon injection:

\[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} (g) \]

The rate of FeO generation must be balanced by carbon injection

- To achieve a stable foam, the reaction of C with FeO is more effective than the reaction of C with O
- A good foamy slag reduces radiant heat loss from the bath and improves the efficiency of electrical power input to the bath
- Slag foaming also allows for higher rates of electrical energy input to the bath without risking damage to the furnace roof, shell and side walls
Slag variables and impact on viscosity

- **FeO content** (fluxing component)
  - Increasing the FeO decreases slag viscosity

- **MgO content** (refractory component)
  - Increasing the MgO increases slag viscosity

- **Temperature**
  - Increasing temperature decreases viscosity

- **Slag basicity**
  - Slag basicity *controls* the timing and the extent of foaming
The “right” slag

- **Optimum slag viscosity**
  - The most important factor affecting slag viscosity is the presence of suspended second phase particles (MW & C2S) in the slag

- **FeO content of the slag**
  - Sufficient FeO in the slag is required to react with carbon and generate CO gas bubbles
  - Too much FeO is equated with iron loss

- **MgO content of the slag**
  - Sufficient MgO “in solution” is required to minimize refractory wear and prolong foaming

Modeling by means of thermodynamic data based on the major oxides enables fast tuning of the slag and optimizing the slag just in time.
% MgO vs basicity for dual saturation

**Dual Saturation:**
- Di-Calcium Silicate $\text{Ca}_2\text{SiO}_4$ [C2S]
- Magnesio-Wustite $(\text{Fe},\text{Mg})\text{O}_{ss}$ [MW]

![Graph showing the relationship between % MgO and basicity for dual saturation.](image_url)
Slag Formation in the EAF

Bas = 1.5
% MgO = 12.6

Bas = 2.0
% MgO = 9.2

Bas = 2.5
% MgO = 7.7
Modeling of the slag

- Four variables:
  - MgO content
  - FeO content
  - Temperature
  - Basicity

By fixing basicity and temperature, the phase relations as a function of MgO and FeO content can be determined and modeled.

The MgO content can be optimized for a particular basicity to sustain foaming and minimizing refractory wear...

...to hit the so-called "sweet spot"
Analytical requirements to hit the sweet spot...

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>11 – 13 %</td>
<td>Refractory Oxide</td>
</tr>
<tr>
<td>CaO</td>
<td>26 - 30 %</td>
<td>Refractory Oxide</td>
</tr>
<tr>
<td>FeO</td>
<td>25 - 32 %</td>
<td>Fluxing Oxide</td>
</tr>
<tr>
<td>MnO</td>
<td>4 - 8 %</td>
<td>Fluxing Oxide</td>
</tr>
<tr>
<td>SiO2</td>
<td>10 - 15 %</td>
<td>Fluxing Oxide</td>
</tr>
<tr>
<td>Al2O3</td>
<td>4 - 6 %</td>
<td>Fluxing Oxide</td>
</tr>
<tr>
<td>V-ratio</td>
<td>1.8 – 2.1</td>
<td>CaO / SiO2</td>
</tr>
<tr>
<td>B3-ratio</td>
<td>1.3 – 1.6</td>
<td>CaO / SiO2 + Al2O3 + TiO2</td>
</tr>
</tbody>
</table>
Factors for slag analysis

In order to maximize steel production, it is critical to effectively control the slag condition in the furnace.

- Increase the life of the furnace
- Reduce energy consumption
- Reduce the amount of additives needed
- Improve the quality of steel

One of the most important tools for slag control is the fast, reliable slag analyzer, which allow quick and reproducible analysis of all the oxides in the slag.
Factors for slag analysis

- Total time from sampling to result < 15 min!
  - Get the data while heat is still on!

- Repeatable and fit-for-purpose results
  - Accuracy for Mg and Al, Si important
  - Ratios to be calculated with analysis (B3 and V or more)

- Modeling compliant data

- Rugged system: to be close to the EAF

- Easy to use
Introduction to XRF and Slag Analysis

Dan Pecard
Audience Poll

Please use your mouse to answer the question on your screen:

What method(s) do you currently use to analyze slag? Check all that apply:

- None
- External lab (non-routine)
- XRF – energy-dispersive
- XRF – wavelength-dispersive
- OES
- Other
X-ray Fluorescence Analysis
Energy Dispersive XRF (EDXRF)

- **Energy of X-ray photons:**
  - element
  - qualitative analysis

- **Number of X-ray photons at a given energy:**
  - concentration
  - quantitative analysis
X-ray Fluorescence Analysis
Wavelength Dispersive XRF (WDXRF)

- An analyzer crystal separates the various wavelengths. $\lambda$ (energies)
- The detector records only the number. N. of X-ray photons at a given wavelength (energy)
WDXRF technology

- Process grade WDXRF
  - Lab setting -> smaller unit
  - Less demand on infrastructure
  - Direct loading for uptime
  - Auto samplers...
  - Backup for OES (steel!)
  - Fluorine

- BUT not in the control room...
## EDXRF detector options

<table>
<thead>
<tr>
<th>Detector</th>
<th>Typical Resolution (eV)*</th>
<th>Relative Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportional Counter</td>
<td>~ 1000</td>
<td>low</td>
</tr>
<tr>
<td>PIN Diode</td>
<td>~ 180</td>
<td>medium</td>
</tr>
<tr>
<td>Si(Li)</td>
<td>~ 150 max 20,000 cts</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>LN2 or electrically cooled</td>
<td></td>
</tr>
<tr>
<td>Si Drift (SDD)</td>
<td>~ 150 (High rate)</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>electrically cooled</td>
<td></td>
</tr>
</tbody>
</table>

* for Mn Ka$_1$ and low count rates
Standard detector vs Bruker XFlash® 410

Energy resolution of Cu $K_\alpha$ at different count rates
Peak separation and element sensitivity at 100,000 cps
Sample Preparation
Sample taken manually or by robot
Sample crushed to ensure homogeneity

Before

After
Sample taken by robot as stick sample approx 70-100 g per sampling

Quartered down manually to approx 20 g
Sample Preparation:
Dose – Grind – Press

- Crush sample
- Grind sample
- Press powder into tablet
Remove “iron” from powder
Please use your mouse to answer the question on your screen:

How do you most frequently prepare your samples?

- None
- Loose powder
- Pressed pellet
- Fusion
- Graphite for OES
- Other
Bruker SLAG QUANT
The solution for the mill!

- LMF, EAF analysis conditions and methods
- EAF calibration from international reference samples
- Tuned with local samples
- Drift correction sample (monitor) - special stable conditioned glass
- V and B3 ratio calculation included
- SOP and QA/QC to use in customer QA/QC system
S2 RANGER: All-in-one design
Sample Preparation Repeatability
10 pressed pellets

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average wt%</th>
<th>Std.Dev. wt%</th>
<th>Rel.Std.Dev. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>9.78</td>
<td>0.05</td>
<td>0.46%</td>
</tr>
<tr>
<td>Al2O3</td>
<td>6.76</td>
<td>0.04</td>
<td>0.58%</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>1.04</td>
<td>0.00</td>
<td>0.34%</td>
</tr>
<tr>
<td>CaO</td>
<td>31.01</td>
<td>0.08</td>
<td>0.25%</td>
</tr>
<tr>
<td>MgO</td>
<td>6.76</td>
<td>0.11</td>
<td>1.65%</td>
</tr>
<tr>
<td>MnO</td>
<td>4.94</td>
<td>0.02</td>
<td>0.37%</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.5</td>
<td>0.00</td>
<td>0.00%</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.47</td>
<td>0.01</td>
<td>2.06%</td>
</tr>
<tr>
<td>S</td>
<td>0.12</td>
<td>0.00</td>
<td>1.80%</td>
</tr>
<tr>
<td>FeO</td>
<td>34.18</td>
<td>0.09</td>
<td>0.26%</td>
</tr>
<tr>
<td>B3 Ratio</td>
<td>1.8</td>
<td>0.01</td>
<td>0.38%</td>
</tr>
<tr>
<td>V-Ratio</td>
<td>3.2</td>
<td>0.01</td>
<td>0.45%</td>
</tr>
</tbody>
</table>

NOTE: LOOSE POWDER WILL NOT YIELD THIS ACCURACY
Accuracy and Repeatability (EAF) (n=10 on same sample)

<table>
<thead>
<tr>
<th>E A F Compound</th>
<th>Avg. error of calibration (SEC) (wt%)</th>
<th>Stability as Std. Dev. (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.58</td>
<td>0.04</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>0.23</td>
<td>0.13</td>
</tr>
<tr>
<td>MnO</td>
<td>0.12</td>
<td>0.01</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.005</td>
<td>0.00</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.71</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Long term stability…
S2 RANGER with XFlash™

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average (n=526)</th>
<th>abs. std. dev.</th>
<th>rel. std. dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (%)</td>
<td>8.54</td>
<td>0.08</td>
<td>0.9%</td>
</tr>
<tr>
<td>Al2O3 (%)</td>
<td>4.47</td>
<td>0.03</td>
<td>0.8%</td>
</tr>
<tr>
<td>SiO2 (%)</td>
<td>12.21</td>
<td>0.06</td>
<td>0.5%</td>
</tr>
<tr>
<td>P2O5 (%)</td>
<td>0.58</td>
<td>0.01</td>
<td>1.0%</td>
</tr>
<tr>
<td>SO3 (%)</td>
<td>0.53</td>
<td>0.01</td>
<td>1.3%</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>28.49</td>
<td>0.10</td>
<td>0.4%</td>
</tr>
<tr>
<td>TiO2 (%)</td>
<td>0.45</td>
<td>0.00</td>
<td>1.1%</td>
</tr>
<tr>
<td>Cr2O3 (%)</td>
<td>1.01</td>
<td>0.01</td>
<td>0.5%</td>
</tr>
<tr>
<td>MnO (%)</td>
<td>3.92</td>
<td>0.01</td>
<td>0.3%</td>
</tr>
<tr>
<td>Fe2O3 (%)</td>
<td>39.78</td>
<td>0.19</td>
<td>0.5%</td>
</tr>
<tr>
<td>V-Ratio-furnace</td>
<td>2.33</td>
<td>0.01</td>
<td>0.3%</td>
</tr>
<tr>
<td>B3 Ratio</td>
<td>1.66</td>
<td>0.01</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

Glass sample using EAF calibration on a lab system
S2 RANGER: SLAG ANALYZER with XFlash™

- All-in-one design for EDXRF
- Pd X-ray tube operated up to 50 Watts, air cooled
- Silicon Drift Detector 4th generation XFlash with 145 eV at 100,000 cps (MnKα1)
- Integrated vacuum pump
- Direct Access Sample compartment
- Touchcontrol™
- Built-in printer
Direct access for sample – cleaning no problem!
Touchcontrol™
Select application: EAF or LMF
Touchcontrol™
Type in sample ID: heat number
Touchcontrol™
Measure sample
Touchcontrol™
Wait 3-4 minutes
Touchcontrol™
Get results
Touchcontrol™
It’s that easy
Connectivity…
Networked via TCP/IP

On Demand via WebEx
S2 RANGER SLAGANALYZER

- Total time from sample prep to results: < 15 min
- Repeatable and fit-for-purpose results
- Easy to use
- Results transmittable to Level 2
- Rugged all-in-one design
What does all this mean to you?

- The S2 RANGER SLAGANALYZER is the ideal analyzer to establish slag analysis in your plant.
- It’s the right tool for the metallurgist and the operators:
  - No compromises
  - Fast quantification with accurate results
- The S2 RANGER SLAGANALYZER enables the implementation of the foamy slag model, as well as optimized operation with specialized additives such as Proslag™.
- Developed in cooperation with NUCOR steel.
- Fielded in North America with over 20 installations.
- X-ray spectrometry solution scalable to your plant’s needs.
Summary

Arkady Buman
Why slag analysis?

- New furnace refractory linings enable more heats between maintenance intervals
  - e.g. dry monolithic bottom material instead of brick
  - Specialized zone-based lining with customized bricks
- Slag is used to protect refractory material
  - Less repair and downtime
  - More heats in combination with refractory optimization
- Slag properties impact energy consumption
- Control of additives to create effective slag
  - Additives for Mg and Ca
  - Additives for C
  - Additives for Al, Si flux
- Slag optimization for better alloy quality
XRF Slag Analyzer from Bruker

- Dedicated instrument right in the melt shop
- Pre-calibrated and easy to use
- Fast and reliable analysis
- Small, rugged benchtop unit
- Results are transmitted to control room/Level 2
Payback of slag control

- Use of monolithic patching material decreased from 7.0 to 5.5 lb per ton of steel produced
- Gunning material consumption decreased from 2.4 to 0.7 lb per ton
- Furnace brick life doubled
- Energy consumption per heat decreased from 339 to 323 kW/ton
- Tons per hour increased from 113 to 119.5

With the right slag control this would have been your PAYBACK
Thank you for attending!

Please type any questions you may have in the Q&A panel.

Copies of this presentation and related XRF resource materials will be emailed to you.
Visit us at:

Canadian Mineral Analysts (CMA)
Bathurst, New Brunswick, Sep 15-19

MINExpo International
Las Vegas, Nevada, Sep 22-24

Material Science & Technology (MS&T)
Pittsburgh, Pennsylvania, Oct 5-9

XRF for YOU Seminar
Denver, Colorado, Oct 10