Selected Aspects of Graphite Applications in Ferrous Metallurgy.

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Agenda

- Introduction
- EAF Electrods
- Macro scale experiments
- Micro scale experiments
- Future experiments/possibilities
- Summary
Introduction

One of the basic units for steel production is an electric arc furnace.

However, one of the most important elements of its construction are graphite electrodes.

The graphite electrode consumption is an essential component of the cost of steel production in EAF.
Consumption of graphite electrode is related to different parameters of steel production technology and electrical parameters of supply system. Average consumption of electrodes is measured in kg of electrode per ton of steel and has widely range:

from less than 1 kg/t up to 5 kg/t (in special cases up to 10 kg/t)

Assuming consumption of 1-2 kg per ton of world steel production the demand of electrode is about 2 million tons per year.

The graphite electrodes production is a big market.
Mechanisms of Electrode Consumption

The mechanisms of graphite electrode consumption fall into two basic categories termed:

- “contin-uous consumption” and
- “discontinuous consump-tion”.

Continuous consumption is further defined as losses due to tip sublimation and sidewall oxidation.

Discontinuous consumption is characterized by losses due to various forms of breakage, butt losses and spalling.
Mechanisms of Electrode Consumption

Tip sublimation

of graphite electrodes occurs at temperatures at or above 3000°C. These very high temperatures exist only when an arc is present. Within milliseconds after the arc is extinguished, sublimation loss stops. During sublimation, graphite is converted directly from a solid to a gas (carbon monoxide), without ever achieving a liquid state.
Numerous factors affect the rate of sublimation:

- Magnitude of the current passing through the electrode when arcing.
- Cross-sectional diameter of the arc spot at the tip of the electrode.
- Duration of time current is passing through the electrode (power-on time).
- Resistivity of the graphite electrode.
- Arc stability (good arc stability is essential to proper EAF operation).
By using higher voltages and lower currents (long arc operation), the losses due to sublimation will be reduced while also improving the scrap melting. When running under long arc operation, the conical arc impacts a larger area of the scrap and tends to cut the scrap from the furnace walls much more efficiently.
Mechanisms of Electrode Consumption

- **Calculation of Continuous Graphite Consumption (Sublimation)**

\[
C_{\text{Tip}} = R_{\text{Sub}} \frac{I^2 \cdot t_{po}}{0.454 \cdot P}
\]

where
- \(C_{\text{Tip}}\) = graphite sublimation (lbs/ton),
- \(R_{\text{Sub}}\) = graphite sublimation rate (kg-hr/kA²),
- \(I\) = current per phase (kA),
- \(t_{po}\) = power-on time (hours) and
- \(P\) = productivity (tons/heat).
sidewall oxidation
Multiple fac-tors influence the magnitude of sidewall oxidation:
- graphite electrode density and resistivity
- tap-to-tap time,
- Temperature - arc current,
- gas flowing parameters inside furnace.
Mechanisms of Electrode Consumption

Calculation for Graphite Electrode Consumption (Oxidation)

\[ C_{\text{Slide}} = R_{0x} \times \frac{A \times t_{\text{tap}}}{P} \]

where
- \( C_{\text{Side}} = \) graphite oxidation (lbs/ton),
- \( R_{0x} = \) average oxidation rate in (lbs/ft\(^2\)-hr),
- \( A = \) oxidizing electrode surface area (ft\(^2\)),
- \( t_{\text{Tap}} = \) tap-to-tap time (hours) and
- \( P = \) productivity (tons/heat).

1 lb = 0,45 kg
ft\(^2\) = 0,09 m\(^2\)
Mechanisms of Electrode Consumption

Normally, when electrodes sublime and oxidize, there will be a release of carbon monoxide (CO) gas.

The CO film around the electrode reduces the effect of oxygen attack to the graphite.

Anything that affects that protective film will accelerate the oxidation losses.
Mechanisms of Electrode Consumption

- Calculation for Sidewall Oxidation

\[ SWO = \frac{(D^2 - d^2)}{D^2} \]

where
- \( SWO = \text{sidewall oxidation (pounds)}, \)
- \( D^2 = \text{virgin diameter of graphite electrode and} \)
- \( d^2 = \text{measured diameter of graphite electrode.} \)
share of tip sublimation to sidewall oxidation

\[ SWO = \frac{(D^2 - d^2)}{D^2} \]
Mechanisms of Electrode Consumption

The discontinuous consumption includes various forms of: breakage, such as socket breaks, pin breaks, body breaks, butt losses and spalling.

The most frequent cause of breakage and butt losses is improper electrode additions techniques. The second most frequent cause of breakage and butt losses is improper scrap mixes and poor scrap loading. Improper scrap mixes can include charging non-conductive material.
Mechanisms of Electrode Consumption

In a properly operating shop, with good electrode addition and scrap practices:

- the continuous consumption should account for approximately 95% and

- discontinuous consumption for 5% of the total graphite electrode usage.
Some examples of electrode consumption
Some examples of electrode consumption
Some examples of electrode consumption
Some examples of electrode consumption
Subjects of interest.
Why we are working at?

Lining corrosion of blast furnace hearth.

Tap hole
Past experiments – macro scale experiments

Cylindrical samples of material submerged in liquid metal under a rotary movement:
- temperature: 1500°C
- atmosphere: protection by Ar, final Ar, CO, CO₂ (\(p_{O_2} = 5.10^{-10}\)at) due to oxidation of graphite tube
- crucible: alumina (99.5 % Al₂O₃)
- metal phase: Fe – approx. 2% C
- rotation speed: 80 rpm
Past experiments

Orienting experiments in time range 0.5–2 h in purpose to choosing the proper time of exposure to metal.

- Corrosion of material occurred rather by removing of grains from the body of sample.
- Formation of a ‘neck’ in the place of contact of liquid and gas phase is visible for such material.

Time of experiments limited to 1 hour because:

- progress of disintegration (weight change) for time over 1 hour is rather small
- analysed concentration of carbon in iron after the experiments reached a value of about 3.3% for the time of about 1 hour and remained nearly constant for a longer time of experiment.
- time of residence of pig iron in blast furnace is usually not longer than 1 hour (if periodic tapping in every 2 hour = 1 hour residence and ~ 1 hour of tapping)
Past results

Generally:
Grain extraction from the surface of sample seems to be depend mainly on basic as anthracite and/or graphite, grain size, ceramic additives and porosity.
Mixtures components:

- **Sample I**
  - mixture of chrome slag (50) + scale (20) + pure SiO₂ (20) + pure Al₂O₃ (10)

- **Sample II**
  - mixture of chrome slag (48) + converter slag (24) + scale (9.5) + pure SiO₂ (9.5) + pure Al₂O₃ (9)

- **Sample III**
  - mixture of converter slag (50) + scale (24) + pure SiO₂ (14) + pure Al₂O₃ (12)

- **Sample IV** – chrome slag

- **Sample V** – BOF slag

- **Sample VI** – synthetic slag melted from pure oxide components (SiO₂, Al₂O₃, MgO, CaO)
### Chemical compositions – Spectrometer Twin-X.

<table>
<thead>
<tr>
<th>Sample I</th>
<th>Sample II</th>
<th>Sample III</th>
<th>Sample IV</th>
<th>Sample V</th>
<th>Sample VI</th>
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</thead>
<tbody>
<tr>
<td>MgO</td>
<td>1.63</td>
<td>MgO</td>
<td>2.86</td>
<td>MgO</td>
<td>3.23</td>
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<tr>
<td>Al₂O₃</td>
<td>12.51</td>
<td>Al₂O₃</td>
<td>13.52</td>
<td>Al₂O₃</td>
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<td>SiO₂</td>
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<td>SiO₂</td>
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<tr>
<td>P₂O₅</td>
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<td>P₂O₅</td>
<td>0.20</td>
<td>P₂O₅</td>
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<tr>
<td>K₂O</td>
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<td>K₂O</td>
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<td>K₂O</td>
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<td>CaO</td>
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<td>CaO</td>
<td>30.96</td>
<td>CaO</td>
<td>25.80</td>
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<td>TiO₂</td>
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<td>TiO₂</td>
<td>0.73</td>
<td>TiO₂</td>
<td>0.12</td>
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<tr>
<td>Cr₂O₃</td>
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<td>Cr₂O₃</td>
<td>4.81</td>
<td>Cr₂O₃</td>
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<tr>
<td>MnO</td>
<td>1.11</td>
<td>MnO</td>
<td>1.08</td>
<td>MnO</td>
<td>1.21</td>
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<tr>
<td>FeO</td>
<td>19.21</td>
<td>FeO</td>
<td>22.02</td>
<td>FeO</td>
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<tr>
<td>B₁</td>
<td>0.89</td>
<td>B₁</td>
<td>1.16</td>
<td>B₁</td>
<td>0.98</td>
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Equipment – Hightemp microscope - Hesse Instruments

1 - halogen lamp  2 - specimen t.c.  3 - furnace with double t.c.  
4 - CCD-camera  5 - specimen carriage
Results - Images of samples.
## Analysis of SEM

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Al.</th>
<th>Si</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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</thead>
<tbody>
<tr>
<td>Area of analysis near by right edge of bigger “crater”</td>
<td>48,34</td>
<td>22,86</td>
<td>0,66</td>
<td>2,28</td>
<td>12,08</td>
<td>0,30</td>
<td>1,57</td>
<td>0,76</td>
<td>7,04</td>
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<tr>
<td>Area of analysis near by left edge of bigger “crater”</td>
<td>19,41</td>
<td>23,72</td>
<td>1,86</td>
<td>6,24</td>
<td>10,11</td>
<td>22,81</td>
<td>0,35</td>
<td>3,93</td>
<td>1,44</td>
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<tr>
<td>Area of analysis bottom of bigger “crater”</td>
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<td>30,82</td>
<td>0,32</td>
<td>0,95</td>
<td>2,29</td>
<td>3,58</td>
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<tr>
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<td>31,9</td>
<td>0,02</td>
<td>0,33</td>
<td>0,51</td>
<td>1,83</td>
<td>0</td>
<td>0,07</td>
<td>0,04</td>
<td>0,83</td>
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<tr>
<td>Area of analysis bottom of smaller “crater”</td>
<td>52,43</td>
<td>31,86</td>
<td>0,27</td>
<td>-</td>
<td>3,10</td>
<td>8,73</td>
<td>0,00</td>
<td>0,17</td>
<td>0,00</td>
<td>3,44</td>
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</tbody>
</table>
Pictures of samples (experiments and results of investigation)
Area changes of samples
Slag/graphite wetting angles
Equipment – Thermal expansion - Future

The main elements of the high temperature rheometer

$F_N$ – Normal Forces are control.
Summary.

We still did not solve a lots of problem with graphite and carbon at ferrous metallurgy.

There are many challenges and ideas and we are open for it.
Thank you for your attention