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The Ohio Journal of Science. v77, n4 (July-August, 1977), 186-188
http://hdl.handle.net/1811/22465

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BRIEF NOTE

X-RAY FLUORESCENT ANALYSIS OF AN EARLY OHIO BLAST FURNACE SLAG

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OHIO J. SCI. 77(4): 186, 1977

In the summers of 1975 and 1976, archaeological excavations were carried out at the Eaton-Hopewell Furnace near Struthers, Ohio. These excavations were carried out primarily to recover information on early ironmaking in the Western Reserve. The Eaton-Hopewell Furnace, considered to be the earliest blast furnace west of the Alleghenies, was built in 1802 and lasted for 10 years until 1812. The excavations lasted a period of 10 weeks and led to the recovery of hundreds of artifacts and several major structural features. Among the more ubiquitous cultural remains recovered from the site were the fragments of heavily incrusted iron scrap and slag.

The slag phase in ironmaking has always been a critical one as indicated by the industrial maxim "take care of the slag, and the steel will take care of itself". Nowadays, the steelman is a technologist, enlisting the aid of a wealth of accrued information in slag chemistry, his predecessor in the early 19th century was more an artisan, guided by a feel for his trade. Now, as then, the slag characteristics of concern to the metallurgist are its fusibility (the slag should be completely liquid at ironmaking temperatures) and fluidity (the liquidus should have relatively low viscosity, that is, favorable diffusion properties). Muan and Osborn (1964) add to these the properties of optimum composition and a high sulfur-removing capacity. Analysis of slag for the information it can provide is especially important in the historical or archaeological context where there is a

1Manuscript received October 1, 1976 and in revised form as a note April 1, 1977 (#76-77).
**Table 1**

*Percentage composition by X-ray spectroscopy of Eaton-Hopewell slags.*

<table>
<thead>
<tr>
<th>Specimen*</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Blue</td>
<td>Green</td>
<td>Black</td>
<td>Turquoise</td>
<td>Green</td>
<td>Turquoise</td>
<td>Green</td>
<td>Black</td>
<td>Grey-Black</td>
</tr>
<tr>
<td>MgO</td>
<td>6.1</td>
<td>6.1</td>
<td>5.1</td>
<td>6.2</td>
<td>3.3</td>
<td>2.70</td>
<td>2.90</td>
<td>2.40</td>
<td>4.30</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.3</td>
<td>16.2</td>
<td>14.8</td>
<td>16.3</td>
<td>14.5</td>
<td>15.00</td>
<td>13.10</td>
<td>14.40</td>
<td>16.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>51.6</td>
<td>51.8</td>
<td>53.5</td>
<td>53.2</td>
<td>55.3</td>
<td>55.80</td>
<td>55.00</td>
<td>55.00</td>
<td>58.00</td>
</tr>
<tr>
<td>S</td>
<td>0.4</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
<td>0.35</td>
<td>0.28</td>
<td>0.38</td>
<td>0.28</td>
</tr>
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<td>CaO</td>
<td>18.2</td>
<td>16.6</td>
<td>20.2</td>
<td>15.4</td>
<td>19.0</td>
<td>17.80</td>
<td>19.30</td>
<td>16.20</td>
<td>16.50</td>
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<tr>
<td>MnO</td>
<td>3.2</td>
<td>4.1</td>
<td>2.6</td>
<td>4.1</td>
<td>2.9</td>
<td>2.86</td>
<td>3.74</td>
<td>3.05</td>
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<tr>
<td>TiO₂</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
<td>0.7</td>
<td>0.6</td>
<td>0.61</td>
<td>0.90</td>
<td>0.90</td>
<td>0.70</td>
</tr>
<tr>
<td>FeO</td>
<td>0.5</td>
<td>1.0</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.66</td>
<td>1.94</td>
<td>2.32</td>
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<tr>
<td>CaO+MgO</td>
<td>36.9</td>
<td>33.3</td>
<td>37.4</td>
<td>31.9</td>
<td>32.9</td>
<td>29.3</td>
<td>33.3</td>
<td>26.2</td>
<td>20.0</td>
</tr>
</tbody>
</table>

CaO+MgO/Al₂O₃ (desulfurization index)

*Specimens 1, 2, 3, and 4 were collected from the surface of the slag pile. They were selected specifically by color and/or texture. Specimen 5 was recovered from the tipple area at a depth of 20 cm. Specimens 6 and 8 were recovered from the casting floor area at a depth of 25 cm. Specimen 7 was recovered from the slag pile at a depth of 75 cm. Specimen 9 was recovered from the slag pile at a depth of 120 cm.*

Furnace slags increases in the order SiO₂ < Al₂O₃ < MgO < CaO. The optimum compositional ratio for desulfurization has a low SiO₂-Al₂O₃ content and a high CaO-MgO content. The desulfurization index can be determined by dividing the combined percentages of CaO and MgO by the combined percentages of SiO₂ and Al₂O₃. To a point, at least, the higher the index, the greater the sulfur retaining capacity. The index for Eaton-Hopewell slags was between a very low 0.20 and 0.37 (average 0.31). For comparison purposes, slags from 8 other historic blast furnaces (dating from 1650 to 1850) were analyzed. These ranged from a low index of 0.28 (from Hammersmith on the Saugus, the earliest blast furnace in the United States) to a high of 0.54 (from the original Hopewell in Berks County, Pennsylvania). In terms of desulfurizing property, the Eaton-Hopewell slag could not be considered particularly effective even for its time.

The need for effective sulfur retention capacity is more critical in those situations where coke or raw coal were used as a fuel than in cases where charcoal was relied upon. Just such a need may have been called for at the Eaton-Hopewell Furnace but history has left no written record of the fuel used. It has been common to credit the "Mary" Furnace in Lowellville, Ohio with being the first blast furnace in the United States (built in 1842) to use coal in the melting of iron ore. Archaeological findings and subsequent metallurgical analysis leads to the inevitable conclusion that this historical footnote will have to be modified. Archaeological excavations undertaken in the tipple area of the Eaton-Hopewell Furnace (located on the cliffs above the blast furnace) turned up an abundance of high quality bituminous coal mixed with fragments of charcoal and kidney ore. In addition, analysis of the finished Eaton-Hopewell irons revealed larger amounts of sulfur (between 0.060% and 0.22%) than one might expect with simple charcoal reduction (White 1976). In short, the Eaton-Hopewell Furnace used combination of charcoal and raw coal as fuel. Its date almost 40 years earlier than the "Mary" supports the site's claim as representative of a transition stage between the sole use of charcoal and the sole use of coal.

Fortunately, the very same qualities that develop optimum desulfurization also provided for low viscosity. CaO and MgO aid in the breaking down the
polymerized silicon-aluminum-oxygen tetrahedra. To a point (at which very low SiO$_2$ content leads to the formation of merwinite or periclase crystals suspended in the liquidus) viscosity decreases with the increase of CaO and MgO.

Using the 15% Al$_2$O$_3$ plane of the CaO-MgO-Al$_2$O$_3$-SiO$_2$ tetrahedron designed by Osborn and co-investigators (1954), the Eaton-Hopewell slags were found to fall within the isotherms of 1300°C. This is appreciably cooler than the temperature of modern blast furnace slags (fig. 1). Technical analyses such as these give archaeologists and historians insights into early industry and they may ultimately supply the critical clues on pioneering operations which lasted only a short time.

Acknowledgments. The author wishes to thank Youngstown Sheet and Tube Company for their cooperation and contributions of time and expertise. Particular thanks must go to Frank Galletta, John Stubbles and Dick Huber for their analysis and comments. In addition, my sincerest thanks to Daniel Mamula and Dominic Russo of STEEP for the opportunity to excavate the site.

LITERATURE CITED


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