BRIEF NOTE

X-RAY FLUORESCENT ANALYSIS OF AN EARLY OHIO BLAST FURNACE SLAG[1]

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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 ubiguitous 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 absence or paucity of written information.

Fragments of slag (9) were selected from various stratigraphic levels and from different horizontal locations. The samples consisted of slags of different colors and textures and were analyzed by specialists at the Youngstown Sheet and Tube Company in Youngstown, Ohio using a Vacuum X-ray Quantometer. The instrument was calibrated using previously analyzed samples of modern blast furnace slags of known constituency. In the case of the Eaton slags, the critical calibration was for SiO_2 where the range was in the 50 percentile. Modern test samples in this high silica range are not common but samples are available.

Slags produced through a charcoal blast furnace normally are of a viscid character and have a high silica content. Lord's (1884) early work on Ohio iron manufacturing and his analysis of slags from charcoal furnaces in the Hanging Rock region seem to bear this out. The Eaton-Hopewell slags were no exception. X-ray fluorescent analysis of 9 specimens of slag indicated a high percentage of SiO_2 ranging between 51.6 and 58.0 and with an average of 54.5 (table 1).

The Eaton-Hopewell slag is apparently typical of slags produced in the blast furnace environment. At the low oxygen pressures prevailing, only those oxides which are very stable thermodynamically were present. The oxides of magnesium (MgO), aluminum (Al_2O_3), silica (SiO_2), and calcium (CaO) were the most important. Manganese (MnO) also was present in appreciable quantities (table 1).

The sulfur-removing ability of blast

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TABLE 1

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

Specimen*	1	2	3	4	5	6	7	8	9
Color	Blue	Green	Black (glassy)	Tur-quoise	Green-Tur-quoise	Green (glassy)	Black	Grey-Black (porous)	Green-Black-(porous)
Constituents									
MgO	6.1	6.1	5.1	6.2	3.3	2.70	2.90	2.40	4.30
Al_2O_3	15.3	16.2	14.8	16.3	14.5	15.00	13.10	14.40	16.30
SiO_2	51.6	51.8	53.5	53.2	55.3	55.80	55.00	56.00	58.00
S	0.4	0.5	0.3	0.4	0.4	0.35	0.28	0.38	0.28
CaO	18.2	16.6	20.2	15.4	19.0	17.80	19.30	16.20	10.50
MnO	3.2	4.1	2.6	4.1	2.9	2.86	3.74	3.05	4.40
TiO_2	0.7	0.7	0.5	0.7	0.6	0.61	0.60	0.60	0.70
FeO	0.5	1.0	0.4	0.6	0.6	0.66	1.94	2.32	1.75
$\frac{CaO+MgO}{SiO_2+Al_2O_3}$ (desulfurization index)	.36	.33	.37	.31	.32	.29	.33	.26	.20

*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 cms. Specimen 9 was recovered from the slag pile at a depth of 120 cm.

furnace slags increases in the order $SiO_2 < Al_2O_3 < MgO < CaO$. The optimum compositional ratio for desulfurization has a low SiO_2–Al_2O_3 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 SiO_2 and Al_2O_3. 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 cliffside 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

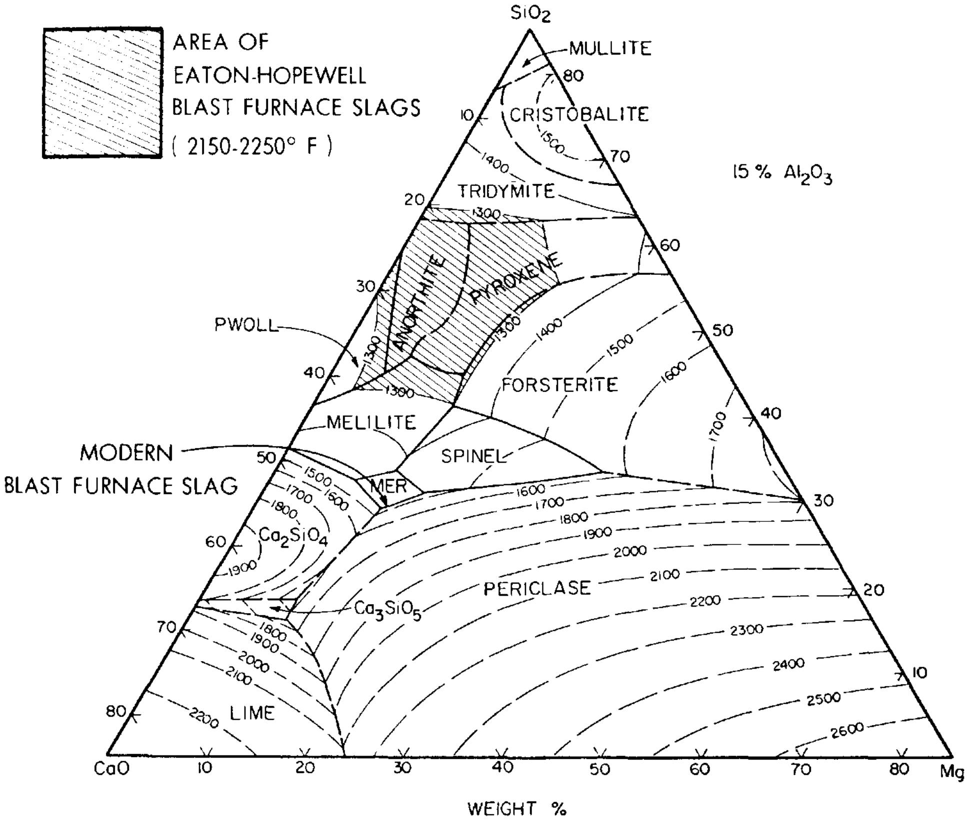

FIGURE 1. Phase relations at liquidus temperatures in the 15% Al_2O_3 plane of the CaO–MgO–Al_2O_3–SiO_2 system, showing position of Eaton-Hopewell Furnace slags in relation to those of a modern blast furnace. Temperature in degrees Celcius.

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_2O_3 plane of the CaO-MgO-Al_2O_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.

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