Brief introduction to blast furnaces

The example of a blast furnace at Pine Grove Furnace was built in the 1770s, and continued "in blast" to April 1895: in other words, it made iron from around the time of the American Revolution to exactly 30 years after the Civil War. Iron production via **blast furnaces** played an important early role in the development of our industrial civilization (the "Industrial Revolution"). Blast furnaces are a *continuous industrial process* resulting in vast quantities of ferrous metals – a major building block of modern industry. This technique is only one of several ways that metallic iron was obtained historically, but other methods (such as **bloomery forges** to convert raw ore directly into wrought iron) produced much smaller quantities at a time because they were *batch processes*.

Bloomeries, and techniques that make the special ferrous metal we call steel, are ancient technologies. Evidence of ironand steel-making can be found in the archaeologic record in multiple places in sub-Saharan Africa, the Middle East and East Asia. However, until the modern era the amount of iron or steel that could be produced was relatively small. The blast furnace as we know it today derives from 14th to 15th century European developments, but other cultures had similar technology even earlier. The blast furnace remains the first step in new steel production in modern times. Differences between a blast furnace of medieval times *vs.* today are size, automation and quality control... but <u>the underlying</u> <u>chemistry is exactly the same</u>.

The purpose of a blast furnace is *smelting* ore to produce crude iron. We use the word *smelting* (not merely *melting*) to describe a high-temperature, high-volume *chemical process*. Three raw materials – **iron ore**; **flux** such as limestone to bind elements other than **Fe**; and a **carbon source** such as charcoal made from wood, or mineral coal such as anthracite or coke – are continuously loaded in layers into the top of the stack. The visible masonry encloses a hollow vertical column lined with heat-resistant refractory bricks. The vertical space is essentially a large counter-current reactor where solids become liquid and descend, and hot gases ascend. Air **blast** is forced into the bottom via pipes and nozzles called **tuyeres**. The carbon burns energetically, chemical reactions occur as explained below, and **Fe** is liberated from oxygen and other elements it is bound to in the raw iron ore. This reaction is a *carbothermic reduction*. The reduced metal in the furnace is above its melting point of ~1538 °C (2800 °F), so as a liquid it drips down and collects in the circular bottom or "crucible." It is periodically drained into an attached building, the "casting house" with a layer of sand as its floor.

In liquid form, the resulting crude iron is called **hot metal**; when solidified, it is **pig iron**. An operation such as Pine Grove Furnace produced bars about 4 feet long called "pigs," or alternatively the iron flowing from the furnace could be directly cast in molds to form useful shapes such as pots, Dutch ovens and stove plates. Inclusion of as much as 5% carbon from smelting in direct contact with fuel, sometimes called "iron carbide dissolved in iron" (**Fe₃C** in **Fe**), gives pig iron a microscopic structure prone to fracturing. Pig iron is very strong in compression, but is also brittle – even thick pieces can be broken by a sharp blow such as with a hammer. Look for broken feet on the bottom of cast pots as a typical historical example. Other elements such as phosphorus and sulfur play an often undesirable role in the characteristics of the final cast metal. Details of iron-carbon and other alloys are beyond the scope of this brief introduction.

Blast furnaces can be seen as the first step in the "indirect" process of making workable iron. To be useful to a blacksmith or in a rolling mill, brittle pig iron must be transformed into **wrought iron**, which has an extremely low carbon content. This transformation involves first *decarburizing* the pig (burning out the carbon), and then violently squeezing out slag inclusions. The altered crystalline structure of the wrought ("worked") iron yields very different properties from pig iron: it is flexible and can be hammered into various shapes, or squeezed to make plates, and it can be welded. The conversion was performed in a **finery forge** which had massive "helve hammers" with stone & iron heads weighing many hundreds of pounds. Pigs produced in the furnace here were hauled two miles to Laurel Forge, built in 1830 as part of the combined operation called an "iron works." Laurel Lake in the modern State Park is a legacy of the need to provide water power for the finery forge; it was not originally built for swimming, fishing and boating! This two-step process – pig iron made in a furnace, then converted to wrought iron at a forge – yielded "bar iron" that could be sold for four times the price of pigs.

A modern "integrated hot metal plant" takes iron from a blast furnace and immediately transports it as a liquid in special "torpedo" rail cars to a steel converter nearby in the same facility, thus preserving almost all the thermal energy in the metal. Steel was not made at Pine Grove Furnace and we will not discuss that aspect of metallurgy in great detail today.

Chemistry of iron smelting

Iron ores of industrial importance include **hematite** (Fe_2O_3) and **magnetite** (Fe_3O_4). In the South Mountain region of Pennsylvania, available ore is hematite or a closely related form, limonite; no magnetic ores are found around Pine Grove Furnace. (The closest magnetite deposits are to the south, or eastward in PA around Dillsburg. An advantage of magnetic ore is that it can be pulverized, then strong magnets separate and concentrate the material before it is added to a furnace. This technology is used today to make **taconite pellets** in the upper Great Lakes region from relatively low-concentration ore deposits. Pellets are also easy to transport and load in a furnace with automatic machinery.)

Here are the essential reactions that occur in a blast furnace:

Oxygen (in the air blast) enters the furnace via the tuyeres. The carbon fuel is ignited in a familiar exothermic reaction:

 $C + O_2 \rightarrow CO_2 + heat$

This reaction occurs in the presence of excess carbon at high temperatures; carbon dioxide is reduced to carbon monoxide: $CO_2 + C \rightarrow 2CO$

The resulting carbon monoxide is a critical reactant in the reduction of iron ore, as shown in the table:

(1) 3 Fe ₂ O ₃ + CO \rightarrow CO ₂ + 2 Fe ₃ O ₄	Begins at ~450 °C (850 °F)
(2) Fe ₃ O ₄ + CO \rightarrow CO ₂ + 3 FeO	Begins at ~590 °C (1100 °F)
(3) FeO + CO \rightarrow CO ₂ + Fe or FeO + C \rightarrow CO + Fe	Begins at ~700 °C (1300 °F)

At the same time that the iron oxides are undergoing these purifying reductions, they are also beginning to soften and melt until they finally trickle as a liquid down to the crucible area at the bottom of the furnace.

Products of the blast furnace other than pig iron

Meanwhile, the limestone flux loaded into the furnace undergoes its first reaction as follows:

 $CaCO_3 \rightarrow CaO + CO_2$

This reaction requires energy and starts at about 870 °C (1600 °F).

CaO is useful because it binds with unwanted elements that might give the finished metal undesirable characteristics. For example, calcium oxide combines with silicon dioxide in the ore. SiO_2 is a major component of the earth's crust:

$CaO + SiO_2 \rightarrow CaSiO_3$

It also helps to remove some of the sulfur that might be present in the iron ore:

 $FeS + CaO \rightarrow CaS + FeO$

Similar **CaO** reactions involve alumina (Al₂O₃), magnesia (MgO) and other minerals commonly present in the ore.

The products of these reactions are given the general name **slag**, a waste product of smelting. In the high temperatures of the furnace, slag is a liquid that trickles toward the bottom of the furnace. It floats atop the molten iron, because it is less dense. Periodically slag is drained out of the furnace, allowed to cool and solidify, and is carted away to form huge "cinder piles," or used as road fill or as ballast in railroad construction. Pieces of slag are still readily observed on trails (formerly wagon haul roads) throughout the Michaux State Forest today.

Slag can vary considerably in color depending on the details of the acid-base chemistry and temperature at which it formed in the furnace, as well as small impurities. For example, at Pine Grove Furnace a brilliant sky-blue slag resulted from abundant manganese in iron ore obtained from two quarries just southeast of Laurel Forge. In general, a dull grey or dull green slag represented proper activity inside the furnace. These dull colors would make the old-time iron makers happy: they were unaware of all the chemistry going on, and had to adjust their smelting process as an art, not a science.

Finally, a large volume of waste gas or "flue gas" is produced – being very hot, it ascends to the top of the stack (through small gaps between the reactants being loaded into the top, or it bubbles through the liquids). The composition of this gas varies with different furnaces, raw materials and fuels, but will be approximately 56% nitrogen compounds, 25% CO, 17% CO₂, 2% H₂, and a little water vapor. Notice that smelting creates significant amounts of "greenhouse gases."

This gas has a considerable energy value. In a modern furnace it is saved as it emerges from the top of the furnace stack so that it can be burned as a fuel in "regenerative stoves" to preheat the air that will be forced into the furnace as "hot blast." Preheating air reduces the amount of carbon fuel needed, thus saving money. Moreover, it is necessary to preheat the blast for furnaces being fueled with anthracite or coke, or air used in converting hot metal into steel, typically to > 900 °C (1600 °F). Modern hot metal operations preheat air to even higher temperatures.

A very large flow of air is needed to smelt iron or make steel. Oxygen is a fourth hidden but critical raw ingredient. Consider the technical problem of how to rapidly heat a large volume of continuously flowing air that is forced under pressure into a furnace. This challenge was not easy to solve in the early days of "hot blast" iron-making.