10.2.2 Smelting Iron

Remember?

Maybe you read the module about smelting science, may be you didn't. If you read it, you probably forgot most of what you read. I'm constantly amazed myself on what I find in all those modules because I forgot it - and I actually wrote them.

Then there are the copper smelting modules. Remember this picture? I thought so.

For those of you with slight guilt feelings by now, here are the links plus a short description of the contents.

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Smelting Science 1 **Furnace and Fire**	How hot? Economy of size. Air flow stuff. Different fuels. Furnace examples	**Smelting Science 2** **Charcoal Technology**	Charcoal properties. Size counts! Tree type too. The dual role of charcoals.
Smelting Science 3 **Smelter Technology**	The ideal smelter. The real smelter. Tuyeres and air flow. There are many important temperatures!	**Smelting Science 4** **Air Supply**	Air supply is everything! Blowpipe limits. Natural draft and wind. Only bellows allow good smelting!
Smelting Science 5 **Slag; Tricks**	Size limits. How hot should it be? No good slag, no good smelting. Crucible smelting without CO.	**Smelting Science 6** **Serious Iron Smelting**	Boudouard equilibrium Baur-Gaessler diagram Why smelters produce *only* wrought iron Why they don't
Smelting Light **Smelting copper**	How it works for copper. The gases in a smelter. Primitive copper smelting in salad bowls. Progress with time		Don't despair! There is light a the end of the tunnel (and my wife). Innards of Ephesus amphitheatre

For those of you who couldn't pay attention because they had to get some beer or do some gender mainstreaming, I will now repeat the essentials by a direct comparison of copper and iron smelting. Below is a very schematic picture of a smelter. On the right we go for copper, on the left for iron.

Comparison of copper and iron smelting
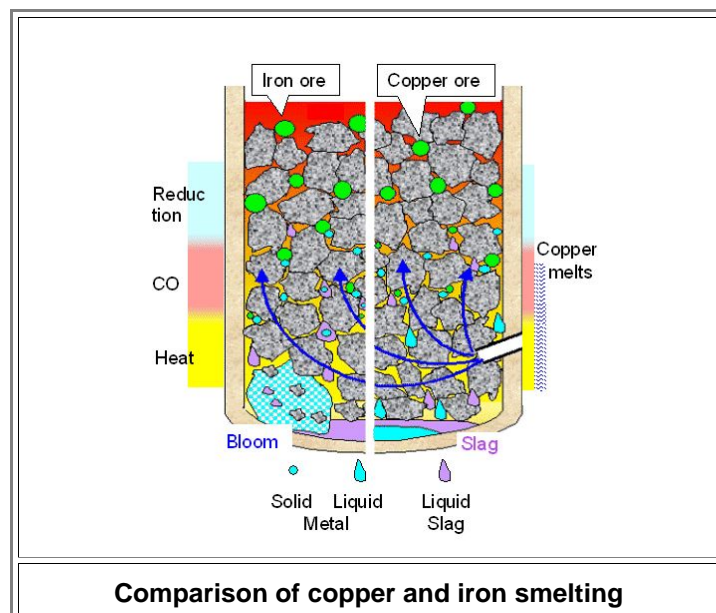
Let's see what both smelting experiments have in common:

- We need to produce a lot of *heat* = energy, and for that we *burn* = oxidize charcoal at the bottom part in the heat generating zone or **oxidizing zone**. We need to supply a lot of air through a "tuyere" for this, and it must be just the right amount. Not too much because all the oxygen (O_2) in the air supply needs to be used up after a few layers of charcoal, and not too little because we need to get the temperature up quite a bit. The combustion products of the "burning" charcoal layer is hot *carbon dioxide* (CO_2; according to $C + O_2 \Rightarrow CO_2 + energy$) plus hot nitrogen ($N_2$) from the air.
- The charcoal layer *above* the burning layer can't burn because there is no more oxygen. If it gets sufficiently heated by the hot gases flowing through, it will produce (hot) *carbon monoxide* (CO; according to $C + CO_2 + energy \Rightarrow 2CO$). This reaction does *not* produce energy but consumes quite a bit, meaning it *cools* the gases.
- Ideally, the burning layer should be at least at 1200 ⁰C (2192 ⁰F) and the carbon monoxide producing layer at least at 800 ⁰C (1472 ⁰F) if the smelter is supposed to work efficiently for both copper and iron. That is not all that difficult to achieve - provided you have a decent air supply, always necessitating bellows.
- We now add a certain amount of ore (and maybe "flux") to the charcoal and feed that mix (called "**burden**") into the smelter from above. The flux is supposed to generate slag, together with all the other stuff in the smelter including "**gangue**" (the "rock" fragments coming with the ore) and often the clay from the smelter wall material.
- The hot carbon monoxide "reduces" the ore, i.e. turns it into pure metal (abbreviated "M"); most simply according to $MO + CO + energy \Rightarrow M + CO_2$. All that chemistry simply states that both metal and carbon monoxide fight for oxygen. The carbon *mono*xide likes to have more oxygen (turning it into carbon *di*oxide) and the metal ores like to keep the oxygen it has attached to the metal atoms. The carbon monoxide wins the battle for oxygen against *some* (not all) metal ores if the temperature is high enough. For copper and iron it always wins. This **reduction reaction** (= stealing of the oxygen) starts already at rather low temperatures around 400 ⁰C (752 ⁰F) for copper and for some iron ores. The reduction uses up energy and thus cools the smelter. Reducing iron takes substantially more energy than reducing copper and altogether needs somewhat higher temperatures.
- In both cases the ore is turned into the metal with everything being *solid all the time*. The reduction process fragments the ore pieces into many small and "spongy" metal particles. We now have small metal particles relatively high up in the smelter, mixed with not yet fully reduced ore. The flux materials have also started to react to what we find later in the slag but everything is still solid. At best some glassy very viscous goo is formed.
- As the charcoals at the bottom part get turned into gases, the whole burden moves slowly down - charcoal, ore, metal particles, flux material, slag goo - getting hotter all the time. If that would be all, the metal particles would start to re-oxidize as soon as they move into the oxidation zone and *no metal would be produced!*
- The slag, after turning liquid, collects in the bottom (as in the picture above). It also might be tapped every once in a while through a tap hole in the "right " position. Accordingly, you produce "**production slag**", a sort of cylindrical cake found in the bottom pits of furnaces, or **tap slag** outside the furnace, irregular pieces often with a flow pattern; see below.
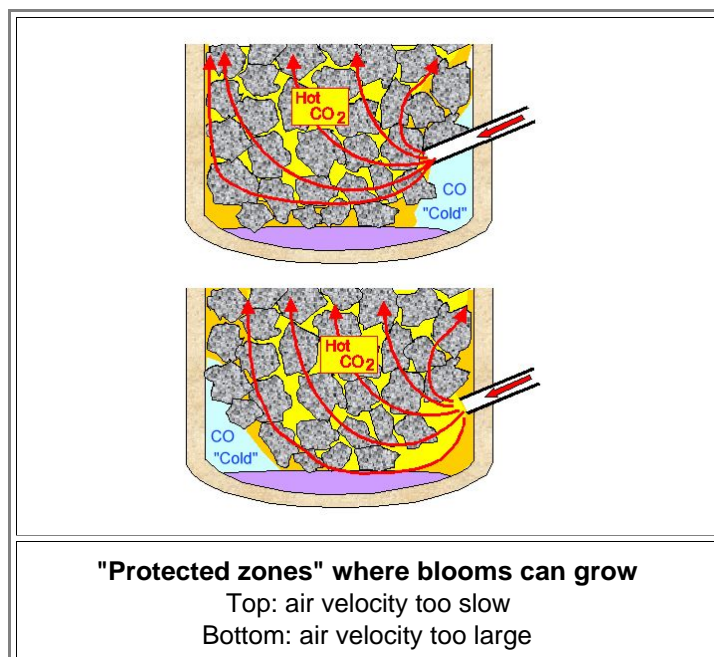

Left: Production slag (about 200 kg, Denmark, 200 AD - 500 AD)
Right: Tap slag (unspecified)

Source: Left: Photographed in Copenhagen museum. Left: English Heritage, May 2011; open access Internet

A first conclusion emerges. The metal must go through the oxidation zone quickly. That is easiest if something is liquid:

> # If we want to produce metal we need to liquefy something *above* the oxidation zone so it can move down quickly. Either the metal, the slag or - best of all - both!

Now to the *differences* in copper and iron smelting. This will also make clear why something liquid is needed:

- Reducing iron ore generally takes more energy than reducing copper ore. You must therefore increase the ratio of charcoal to ore since you need to burn more charcoal to supply more energy.
- In the almost unavoidable presence of silicates (typical gangue material or the stuff coming with the ore), iron oxide or iron ore is a good flux material. That's why copper smelting was routinely done with iron oxide as flux material. It is then no wonder that iron was produced accidentally every now and then during copper smelting. In fact, as copper smelting techniques progressed, this became a problem.
- Iron smelting thus can be a "self-fluxing" process, meaning you do not have to add flux material as long as the ubiquitous silicates from the gangue were around. Early iron smelters indeed did not use flux materials. Self-fluxing also means that your smelting efficiency goes down, since quite a bit of your ore ends up in the slag as "fayalite", an iron silicate and a major part of slag. With bad luck, slag might have been the only thing you produced in your supposed iron smelting.
- The metallic *copper* particles are produced in the *solid state*, just as the iron particles (or any other metal particle in normal smelting). They will *melt*, however, while still above the hottest part of the smelter, the oxidizing zone where the charcoals *burn* because there is oxygen. Being *liquid*, the copper now can trickle down much faster than the whole burden moves down, and thus pass through the very hot oxidizing zone without becoming re-oxidized again. It collects as a *liquid* at the very bottom, protected by a liquid layer of slag that collects on top of it.
- The metallic *iron* particles will *not* melt. They would move down slowly with the burden and re-oxidize in the hot oxidation zone - if they don't become part of the liquid slag. Sorry. No liquid slag - no solid iron!
  Solid iron is *only* produced as a **bloom** if liquid **slag** envelops the iron particles *above* the oxidizing zone and sweeps them down quickly to a half-way protected place. There a bloom will grow because iron-particle containing slag is raining down on it, and the iron particles stick together.
- However, in a "badly" run smelter, some iron particles produced close to the edge of a smelter may make it down on their own because they might happen to move through "cool" oxygen-deprived places in the oxidation zone. Such a "protected place", with some CO around that's made right there, might be *behind the tuyere* , in particular if it sticks too far into the smelter and the air flows out *too rapidly*. Alternatively, it might be on the opposite side of the tuyere, in particular if the air flows out of the tuyere *too slowly* and doesn't quite make it to the other side. This is schematically illustrated below. Of course, a bit of liquid slag also helps. Mulling this over it becomes clear that the exact geometry of the tuyere (height, angle, diameter, penetration depth into smelter) will be important.

"Protected zones" where blooms can grow
Top: air velocity too slow
Bottom: air velocity too large

This is an extremely simplified description of what is going on inside a smelter. I bet that you had no idea that it would be that complicated, even in the most simplified version. I'm now going to answer a few of your questions.

Question: "It seems that reduction to metal always takes place in the solid state, and that melting the metal *above* the oxidizing zone is good. So why don't we just increase the temperature in iron smelting to well above the melting point of iron? That should be no problem with present-day technology."
Answer : True enough. It just won't work. The problem is that liquid iron trickling though hot coals and exposed to carbon monoxide at least on parts of its way down will incorporate so much carbon (and whatever else might be around) that you don't get *pure* liquid iron all the way down but dirty *cast-iron*! You simply cannot make *clean* liquid iron in a carbon smelter.
Question: "Excuse me, but why do I get clean liquid copper then?"
Answer: You don't, actually. It just so happens that copper does not incorporate a lot of carbon (look at its phase diagram!). It can and will dissolve a lot of other stuff that happens to be around, however - iron, for example! That *is* a problem! But when you *melt* the dirty copper again, getting it ready for alloying and casting, you automatically purify it to some extent.
Question: "Why do we get mostly *wrought iron*, i.e. rather carbon-free iron in *solid* iron smelting as I read almost everywhere? After all, the *solid* particles of rather hot iron could also incorporate some carbon on their way down, even if they hang on to liquid slag! "
Answer: First, in contrast to public opinion and quite involved theory, typical iron smelting throughout the ages did *not* produce just wrought iron. A bloom with a wild mix of low-carbon wrought iron and all kinds of carbon steel is produced most of the time if you do not run your smelter in an optimized way. However, the iron produced by reduction below about 700 ºC (970 ºF), has no choice but to be rather pure. If you manage to keep it that way on its way down the smelter, you do end up with wrought iron. But that does not happen "automatically"; you need to know how to achieve that. More details can be found here.
Question: "Why do archeometallurgists, including the ones whose papers I particularly enjoy reading, often mention iron that has been "carburized" if they discuss steel artifacts? Don't they know that you cannot increase the *volume* carbon concentration of a solid piece of iron by *any* reasonable treatment? In other words there is no such thing as "carburization"! Then they talk a lot about "primitive small smelters" in the iron age. Don't they know that smelter technology at the beginning of the iron age around 1200 BC was already highly developed?"
Answer: You are right and I don't know the answers. There is indeed a lot of confusion in the general literature about how to make wrought iron, steel and cast iron. As far as the intricacies of smelter technology and the iron-carbon system are concerned - those were and are mysteries to almost all. That's why I'm writing this Hyperscript, after all. Since all and sundry were inclined to believe that bloomeries could *only* produce wrought iron, you had to assume that some "carburization" was done later if you actually dug up steel.
"Primitive smelters" may simply refer to dug-up facts. Smelters might well have been more primitive for iron than they had been for copper. After the fall of the (Western) Roman empire, bath-room facilities were rather more primitive for about 1500 years than Roman standards, for example, and the same might have happened to metal technology in some places for a while. However, the technology for making the **Colossus of Rhodes** around 300 BC from bronze and iron / steel was certainly not primitive, to give a counter example.

More to that in the next sub-chapter. First I will look a little more closely into what is going on inside an iron smelter

Inside an Iron Smelter

Let's assume that carbon monoxide (CO) is around and that it is hot enough for things to happen. Now let's give that a closer look. One of the things that could happen is that you killed yourself because carbon monoxide is rather poisonous, and some of it always comes out at the upper end of your smelter.
Carbon monoxide reduces iron ores in stages. Before that happens, some changes in the ore may take place by roasting. It goes like that:

	Roasting		
Goethite / Limonite	$2\ FeO(OH)$	$\Rightarrow$	$Fe_2O_3 + H_2O$
Siderite	$FeCO_3$	$\Rightarrow$	$FeO + CO_2$
	Smelting		
Magnetite	$Fe_3O_4 + CO$	$\Rightarrow$	$3\ FeO + CO_2$
Hematite	$Fe_2O_3 + CO$	$\Rightarrow$	$2\ FeO + CO_2$
Wüstite	$FeO + CO$	$\Rightarrow$	**$Fe + CO_2$**

● No, I didn't break my promise of "no equations". Those are just chemical reaction "equations". We don't count those among serious mathematical equations. They are just abbreviations for long names.

What we see is that the various iron oxides are turned into iron in several steps, always producing FeO or **wüstite** first. The first two reactions (roasting) you can do separately from smelting, you sort of condition your ore.

Reduction of the wüstite is the final reaction in the smelter, it produces the elemental iron.

Far more reactions occur then the ones listed above, including, for example, direct reduction with carbon and not carbon monoxide.

We must also consider that some of the carbon dioxide (CO_2) produced by reducing the ore is turned into carbon monoxide ($C + CO_2 + energy \Rightarrow 2CO$) as long as it is hot enough, helping the reduction process. That is good. On the other hand, some of the carbon monoxide produced will turn to carbon dioxide and carbon in the form of soot; not so good.

Where the main processes happen inside the smelter can be seen in this link

How *fast* one of these reaction proceeds depends on many things. Essential is always the available surface area of the ore because whatever happens takes place at the surface. A bunch of small ore particles react much faster than just one lump of the same weight. So crush your ore - but don't make the pieces too small, this would restrict the flow of gases too much. A porous ore particle full of microcracks has a larger surface than a compact one of the same size. Crumbly limonite thus might be better than solid magnetite.

▶ Now let's look at some not-so-good things that will also happen.

● First, cementite (Fe_3C) is formed; either from an oxide or from the freshly generated iron. Cementite formation reduces efficiency because it takes out some of the iron supplied by the ore.

3 FeO + 2C	$\Rightarrow$	**Fe_3C + CO**
3 Fe + 2 CO	$\Rightarrow$	**Fe_3C + CO_2**

● We are not yet done. Besides carbon and iron ore, we have all kinds of "dirt" inside the smelter, not to mention the flux we added, and the walls of the smelter that will also participate in all kinds of reactions. We might, for example "smelt" a few more elements by accident, for example phosphorous (P), nickel (Ni) and copper (Cu) if some compounds happen to be around:

P_2O_5 + 5 CO	$\Rightarrow$	**2 P + 5 CO_2**
NiO + CO	$\Rightarrow$	**Ni + CO_2**
Cu_2O + CO	$\Rightarrow$	**2 Cu + CO_2**
......	**.....**	**.....**
All of the above is possible and will happen in an antique bloomery if the stuff is around. The elements produced can end up in the iron		
SiO_2+ 2 CO	$\Rightarrow$	**Si + 2 CO_2**
MnO_2 + 2 CO	$\Rightarrow$	**Mn + 2 CO_2**
…..	**.....**	**.....**
Possible in principle but *not* happening in an antique bloomery. Manganese oxide in your ore thus will *not* put beneficial manganese (Mn) into your iron		

So some of the constituents of the unavoidable "dirt" in your smelter may or may not end up in the iron you produce. If they do end up in the iron, they do influence its properties. In a major way like [phosphorous](#), where small quantities below 1 % make a big difference, or just a little bit like nickel (Ni), where 1 % or so is hardly felt. But sorry - all those manganese-oxide rich iron ores do not help *directly* to make better iron because some beneficial manganese makes it into your product as is often assumed.
However, stuff that does not imbue the iron with manganese, silicon, or other "good" elements may nevertheless be quite important for other reasons:

1. It may influence or even dominate slag formation like silicon dioxide (SiO_2) or change the properties of the slag. The slag, for example, might become fluid at a somewhat lower temperature because of some "dirt" and that is rather good.
2. It influences the ability of the iron to pick up carbon on its way down to the bloom. Manganese oxide (MnO) is reported to do this, for example; although I'm not sure I understand how that is supposed to happen.

The message is loud and clear:

The kind and "quality" of your ore, gangue and flux matters very much!

Making good iron is easier if you can command clean oxides or carbonates. If you are stuck with ["bog iron"](#) , you still can make good iron but you must adjust and optimize your process chain - from the pre-treatment of your ingredients, via the smelting process, to special processing tricks for the product. Your way of making a steel sword "from scratch" could then be quite different from that of the more lucky people with clean ore.

I'm not done yet. We still need to produce slag. No slag - no efficient iron smelting! If we use the ore as flux in a kind of self-fluxing process, we are looking at (simplified) reactions like:

SiO_2 (quartz) + 2 FeO **solids**	⇒	**Fe_2SiO_4** **Fayalite, main component of slag, viscous liquid**
$CaCO_3$ (limestone) **SiO_2 + CaO (quicklime)** **solids**	⇒	**$CaO + CO_2$** **$CaSiO_3$** **slag component**
………..	⇒	**………..**

The first reaction takes place between silicates always containing SiO_2 and iron oxide (= iron ore). It produces an **iron-silicate** , Fe_2SiO_4, called **fayalite**, a [major component](#) of pretty much all antique **slags**. SiO_2 is pure quartz or "silica", rather common by itself, but most silicates and thus most "rocks" will also do.
The second reaction uses calcium oxide (CaO) or **quicklime**, something you don't find but must make by [burning limestone](#) right in your smelter. While quicklime making was already known to stone-age people, its use for iron smelting had to await the advent of the blast furnace around 1400 / 1500 AD where limestone is used for flux.
In any case, these reactions (plus plenty of others) occurred between crystalline *solids* because your primary flux materials, like your ores, would never liquefy in antique (or modern) smelters. Only some reaction products are *glassy* or amorphous materials that do not melt but turn from solid to viscous to liquid as the temperature goes up, sort of like honey. Around 1200 ºC (2192 ºF) your slag is liquid enough to "run".

I'm going to stop here. I'm sure you got the point

What happens inside a smelter is very complex indeed!

Today we might be able to model the whole thing by using appropriate and very involved theory. With very big computers one might get useful results. That is pretty much the only way to "look" inside a smelter. Any direct way of "looking", or approaching the task experimentally, is well-nigh impossible. You simply cannot watch a piece of ore making its way down the smelter and record in great detail what is going on.

What we can do, however, is to make special experiments in the laboratory. Expose a small piece of pure iron oxide to carbon monoxide in a retort at precisely known and controlled temperatures and you can "see" and measure what is going on. That will give you data like the ones [displayed here](#).

All that the early iron engineers *could* do was to go by trial and error. What they actually *did* do, we don't know. First, only a very small part of all the iron things made have survived and were found. Second, the results from unsuccessful smelting runs are almost never found because you can't find iron if none was produced. In a similar vein, it is not likely that we find many objects that were made from "bad" iron, e.g. copper-rich iron, because at best a few small objects like rings were ever made.

In 2000 years from now archeologists are going to find zillions of silicon devices but at best a few that were made from germanium. The very first electronic devices, however, have been made from germanium only. The experiments concerning silicon and the many "bad" silicon devices actually made during the germanium time (and then thrown out), will not show up in the future archeological records at all.