Smelting Science

5. Slag and Different Ways of Smelting

More to Smelting

We will look briefly at four topics here:

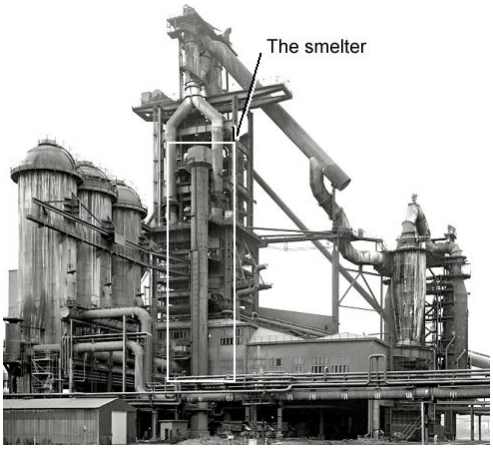
1. What limits the **size of a smelter**? How hot should it get?
2. The role of **slag**. Can one smelt without producing slag and why is this not necessarily desirable? How does one optimize slag?
3. How did the often alluded to "messy and inefficient" **ancient smelting** work? How did smelting develop? Are there ways to smelt without carbon monoxide?
4. What is different between, for example, *copper and iron smelting*? Could a well-designed efficient copper smelter also produce iron if charged with iron ore?

Let's look at these topics one by one

Limits to the Size of a Smelter

From ~~the aforementioned provisions~~ (sorry, but I'm forced to read a lot of legal stuff a present) what you learned in the preceding modules, the limits to the size of a smelter become clear as soon as we look at what it takes to run a big one:

1. *Air supply.* You need a hell of a lot of air to run a large modern blast furnace. When you look at one of these giants, most of what you see is actually there to ensure the air supply; look a the picture below. And you need far more power for moving the air around than a water wheel could supply.



Modern blast furnace.
Most of what you see is for the air supply

2. *Mechanics and logistics.* Huge smelters need stable constructions and thus a lot of steel, concrete, and so on. You just could not built one only with stones, clay and wood. They also need to be fed with huge amounts of ore, fuel, and flux. That is simply not possibly without an extensive system of railroads and the like.
3. *Operation.* Big smelters need more people for keeping them running. This implies that at some point you need people for supervising those who actually work. You need people to run the infrastructure, to find ways for minimizing taxes, to threaten your customers to pay their bills or else, and so on. You need some hierarchy and structure to keep everybody (reasonably) happy while still making a profit. Not an easy thing to do.
4. *Risks.* If something goes wrong with a big smelter, the financial losses are huge. You can't rebuilt or repair it quickly, and every day it doesn't operate puts you back a lot.
5. *Output.* You produce a lot of (cast) iron, and you must be able to handle it.
6. *Bloom size.* If you don' run a cast iron producing smelter but a **bloomery**, you can almost forget all of the above because now you have a very simple and basic limitation: Your bloom, the spongy piece of solid iron with inclusions of slag, charcoal and whatnot, *must not be too big*! Otherwise you can`t handle or process it!

First of all, if the bloom is too large, you can't get it out of the smelter. Tearing down the smelter after one use is fine as long as it is relatively small and easy to rebuild. You don't want to tear down a large smelter every time you produced a

bloom, however.
Second, you must process your bloom while it is still hot. Processing simply means to bang it with a hammer, compacting it by contact-welding, and squeezing out the slag as long as it is still liquid. If you have only one measly manpower at your disposal, wielding one regular hammer, your bloom shouldn't be larger than about larger two fists. Otherwise you just can't hit it hard enough to do the job.

- People did cut blooms in half with an axe right after one was extracted from the furnace. That necessitates to employ two smiths for the following banging up. You might conceive a few other tricks but nothing helps as long as you work with man-power: A bloomery is very limited in size.
  Your only way out to some extent is to use big hammers driven by water power, like this mother. Add "power bellows" and you can produce 50 kg blooms. But the end is near. Bloomeries bottomed out around 1770, when almost 1 ton (1000 kg) blooms were produced with huge efforts. Blast furnaces produced far more cast iron with far less effort by then.

How Hot Should it Get?

The nature of your fuel determines the maximum temperature that can be obtained under the best possible conditions. For good charcoal this was $T_{max} \approx$ **2000 °C (3600 °F)**. The supply of oxygen (not the same thing as "air"!) and the thermal insulation determines the maximum temperature you can reach in your specific set-up.

- The blow-pipe limit is around 1 200 °C (2 192 °F) and that temperature can be seen as the limit for early metallurgy. It is high enough for *melting* metals like lead, tin, copper, bronze, gold and silver and just about enough for (messily) *smelting* copper, tin and lead, but marginal for smelting iron and only able to fully melt *cast iron*.
  With bellows and a well-designed smelter you can easily get 1 500 °C (2 732 °F). Natural draft or wind furnaces might also be able to get that far.
  Do temperatures that high solve all smelting / melting problems?

No! Very high temperatures cause problems

Two issues concerning very high temperatures are shared by all pyrotechnical equipment:

1. The material used for building the equipment may not withstand very high temperatures or will not have a long service life. It also might react with the load, like becoming "fluxed". This is rather serious when you aim for 1 500 °C (2 732 °F) or beyond. The term "*refractory materials*" carries a lot of weight here.
2. Costs go up pretty much exponentially with every degree Celsius you add.

Other problems encountered are specific for the material you try to process. In what follows a few examples are given.

Copper smelting involves almost always iron. Some iron ore is either part of the gangue or was intentionally added because it is a good "flux" and generally used when slag is intentionally made, i.e. whenever copper is smelted in quantities, see below. It is almost unavoidable that some iron is produced during copper smelting. **Iron** is soluble in liquid copper to a small extent at temperatures around the melting point of copper, but its solubility increases rapidly with increasing temperature.
If your temperature is too high, you get iron-rich copper - and that is not good! Copper - iron alloys do not have desirable properties and must be avoided.

For the first two millennia of serious *iron* smelting, most operators aimed for "wrought iron" or iron with a relatively low carbon content. What needed to be avoided was the accidental production of cast iron. Only the Chinese begged to be different.
If your temperature is too high, maybe because you charcoal to ore ratio was too large, or because you worked your bellows to vigorously, you produced either cast iron, a bloom with a too high carbon concentration, or even both simultaneously. That was not good for "Western" metal workers before 1500 or so. They neither could deal with high-carbon steel like the "Indians" nor with cast iron like the Chinese. And why should they? Their technology to work with wrought iron and mild steel was second to none, after all. The Celts, Romans, "Dark-Age" knights, Crusaders and so on did win a lot of sword fights and battles, and if they lost, it was not because their steel was inferior.

- Much more could be added but I'm sure you get the idea!

The Role of Slag

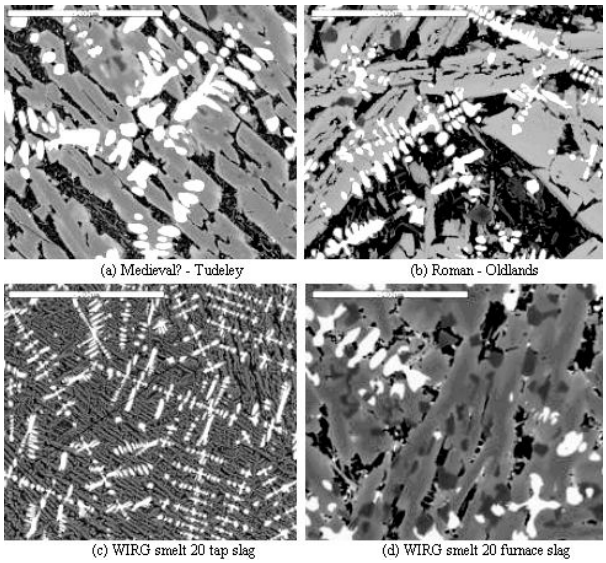
The topic "slag" has come up a lot in the preceding modules, and the two points following should be pretty clear already:

1. Producing slag during smelting is almost unavoidable.
2. Slag, if produced "right", is not only good but essential for efficient smelting.

Let's look at the first point. Why is slag production "almost" unavoidable, you might ask? The basic smelting reaction **$Me_yO + CO \Rightarrow y\ Me + CO_2$** need *only* ore and carbon monoxide (CO) and doesn't produce slag. If I see to it that I only feed clean ore and charcoal in my smelter, why should slag be produced?

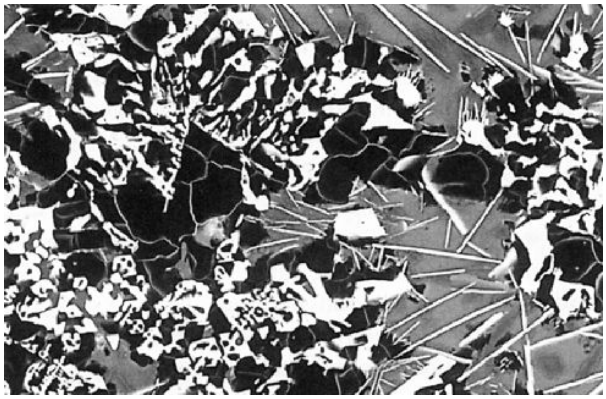
You are certainly right. If you do just that, *no* slag will be produced. You also will *not* produce slag - stuff that was rather liquid once - if your temperature on average is too low (below about 1.100 ^oC (2 012^oF). You might still produce some copper, though, because of the occasional "hot spots" you produce while working with your blow pipe.
Actually, very early copper smelting seems to have been rather "slagless". I have this piece of information and much of what is described here and in related modules from Andreas Hauptmann's book: "The archeometallurgy of copper", a veritable treasure trove (but not all that easy to read) and Rehder's book, already mentioned.
Slagless smelting causes a certain problem because archeologists are trained to look for slag if they look for smelting. It is easy to overlook signs of smelting if there is no or only very little slag. And it is virtually impossible to find out if a 5 000 year old crucible was used for "slagless" *s*melting or just for melting some copper.

Now to the second point. What, exactly, *is* slag and what is it good for? The answer, of course, is: it depends. On what kind of metal you are trying to smelt, what kind of ore you use (there are many different kinds!), the kind of gangue that ore is mixed-up with, and on what is going on inside your smelter. Hopeless? Not quite!
There are a few points that are rather universal in principle, if rather different in detail. I'll give them to you one by one.
First let's look at the microstructure of some slag:



Microstructure of some slag from iron smelting
Field find slags and WIRG experimental slags
White: wüstite FeO; light grey: fayalite Fe_2SiO_2; black: glassy
anorthite $CaO/Al_2O_3/2SiO_2$

Source: Internet pages of WEALDEN IRON RESEARCH GROUP (WIRG) - Thanks!



Microstructure of some slag from copper smelting

Source: Hauptmann's wonderful book

The "copper slag" right above is from early copper smelting in the Fayan / Jordan area. A sample from a neighboring piece might look quite different. The white stuff is magnetite, mixed in with cristobalite and tridymite (black). In between is a glassy matrix (grey) and columnar delafossite.
No, I won't explain. Believe me: *you* don't want to know particulars about slag. It is good enough to know that there are people out there who know (almost) all there is to know about slag. Let's focus on what slag does for us.

1. *Liquid* slag *transports the metal* to where you want it.

The reduction process typically takes place at medium temperatures. The ore gets reduced to a porous metal that coats the ore body, and this composite still is encrusted with gangue. The metal produced occupies a smaller volume than the ore, and that will cause stress and possibly cracking, exposing more ore to the reducing gas. Eventually all ore particles are reduced and you have small porous or spongy metal particles and metal-gangue pieces still hanging together.
What you want to happen now is that your metal particles move through the oxidizing hot zone of your smelter *without becoming oxidized* and, in the case of iron, heavily carburized. If they do that as solids, moving down with the slow speed of the burden, chances are slim that they make it through the oxidizing zone without being completely oxidized again.
If the metal should get liquefied already in the reduction zone, it will trickle down and that is much faster. Parts of the liquid metal then may make it to the bottom and collect there in the liquid state. That might happen for copper and is almost sure to happen for lead and tin. Nevertheless, you are going to loose some of the metal produced. It will get oxidized and end up in the slag.
If you smelt iron, it will not become liquid. But the small iron particles produced in the upper part of the smelter still need to move down to below the tuyere, where they collect and sinter together in a kind of self-driven powder metallurgy process. They can do that as long as they are quite hot and their surface is "clean" and not oxidized. This is what needs to happen if a "bloom" is to form.
As a metal particle, you cannot avoid some oxidation in the hot and still oxygen-rich zone around the tuyere. If you move by quickly you might avoid complete oxidation, though. Moving fast would require that the *residence time* of your process must be short. But how to do this? The residence time of a well-running process is pretty much fixed and you can't change it at will. Moreover, if you move too fast through the hot zones, your metal may not melt or become sufficiently superheated to stay molten. Any way you look at it, you have a problem

Here is the solution to the problem: Enclose your metal in something liquid that protects it *and* moves it down more quickly than the burden moves. That "something liquid" is slag, of course.
Take a bucket, put a lot of small holes in the bottom, fill it with regular barbecue charcoal, and put some water on top. What will trickle out at the bottom is rather dirty water since it took all the little pieces of charcoal with it as it percolated down. If you look closely, you also note that the small dust particles inside a water droplet become fused together, the cling to each other. Same thing with metal particles inside liquid slag. Inside a liquid drop they tend to ball up because that reduces their surface and thus surface energy. It doesn't matter much if the metal particles are solid or liquid; it works in either case. The key word is "surface tension" but I won't go into this here.

It's time to make two points about smelting that are rarely mentioned in the literature. Let's assume we have optimum slag conditions and modern equipment without limitation as to temperature. So, can we:

1. Make a *solid* bloom of copper? In other words smelt copper without liquefying it? The answer is: *No!* Solid copper particles will not weld together, even if very hot. You can't fire or hammer weld copper either. That is probably also true for many more metals.
2. Make *liquid* wrought iron? The answer is: *No!* If you get your smelter up to temperatures that are sufficient to melt the iron produced in the reduction zone, it would dissolve so much carbon on its way down that you will always end up with carbon-rich cast- iron.

2. *Slag gets rid of the gangue*.

This is a bit trivial - but consider: How would your smelter work if the gangue is not liquefied but stays solid? You would collect more and more "stones" and stone dust inside your smelter. You smelter would not work very well after some time and would stop altogether after a while. If you liquefy the gangue you can remove it by periodically tapping the slag or by just letting it run out naturally. The German word for "to run" is "rennen" and that's why ***bloomeries*** are called "**Rennöfen**" ("Running ovens"), just like ter are "running noses" in English.

3. *Slag gets rid of* some unwanted *impurities*.

With luck, some impurities that you don't want to have in your metal prefer to dissolve in the slag. That keeps the concentration in the metal lower than what you would get without slag.

That works for some but not for all impurities. But even so slag doesn't solve all your impurity problems, it is still better than nothing. It helps, for example, to keep rogues like phosphorous (P) and sulfur (S) in check.
Maybe, by adjusting the composition of the slag, you can get rid of a few more impurities? Get to it!

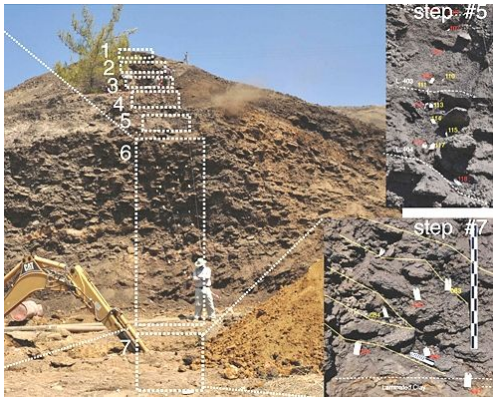
4. *Slag protects* the pool of *molten metal* at the very bottom of your furnace.

Slag can do that because it never mixes with molten metal (as, for example, water and alcohol do) but always separates (like water and oil). The key word here is "surface tension" or energy once more.
Slag is always on top because its density is smaller than that of the metals that can be smelted with carbon.

That should be enough to convince you that slag is not only nearly unavoidable but a good thing to have. So what, exactly, is slag and how can one optimize its properties? Again, I won't tell you details just a few general points.
Slag is always a rather complex mixture of several components (see above!). Since most "rocks" and thus most gangue contain silicates, you will always find silicates in there. Since "dirty silica" is just another word for glass, slag typically shows glassy behavior. It doesn't melt as it gets hot, it just become less viscous. Make it hot enough, and its fluidicy is (almost) like that of water. The temperature needed to achieve good fluidicy depends on the ingredients.

- The essential first point about optimizing slag is that you have enough (typically more than metal), and that it will be sufficiently fluid at, say, 1 100 ^{o}C (2 012^{o}F). And that's why you often add some "**flux**" to your burden, to whatever goes into your smelter. Flux is essential to obtain good fluidicy at "low" temperatures and to get enough of slag. The right flux may also improve slag properties with respect to the other points.
  Finding the right kind and amount of flux is one of the secrets of superior smelting. Here is one such secret revealed for cast-iron smelting: The flux is "Braunspat" (brown spar) and "Eisenkalk" (ferric chalk) in precise amounts - and both fluxes are in essence *siderite* or iron carbonate ($FeCO_3$). Siderite is typically a better flux than other iron ores but all iron ores "work" and were used by all and sundry throughout the millennia. Not only for iron smelting but also for copper smelting! That is the reason why ancient slags from copper smelting or from iron smelting are often quite similar in composition.
- The fact that iron ores are very good fluxes means that iron smelting can be "**self-fluxing**". Nice, but wasteful because a lot of your iron then will end up in the slag. In fact, you might produce nothing but slag in your iron smelter if you don't know exactly what you are doing.
  Rather interesting, isn't it? The chaps who by good luck have some siderite in their iron ores (like the Proto-Austrians who were sucking up to the Romans), automatically get better smelting compared to those guys who have to do without it (like the Proto-Schleswig-Holsteinians in my area, who fought the Romans).

Analyzing the composition of ancient slag, and using the knowledge gained to conclude back to the smelting technique, is a rather complex and frustrating but rewarding enterprise. It seems to come into its own right now, and it is rather certain that a lot of exciting new insights into the development of metal technologies will result in the near future.
Here, however, I will abandon the subject now before it becomes too obvious that I don't know a thing about it.



Slag heap in Cyprus from around 500 BC getting cross-sectioned

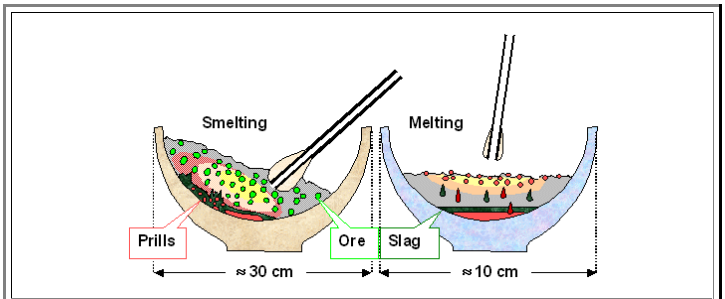
Source: Erez Ben-Yosef, Ron Shaar, Lisa Tauxe, Thomas E. Levy & Vasiliki Kassianidou: "The Cyprus Archaeomagnetic Project (CAMP): targeting the slag deposits of Cyprus and the Eastern Mediterranean", Antiquity Volume 085. Issue 330. December 2011

"Messy and Inefficient" Ancient Smelting: Crucible and Blowpipe

The first large-scale smelting produced copper. It was definitely *not* done in a smelter as large and complex as the one I used to explain the basics of smelting. A lot of people assume that it wasn't done in a smelter at all but happened accidentally in a camp fire, while making pottery, or during the burning of lime burning. Actually, I haven't read about the last one so I claim the credit. Lime burning, after all, is a technique far older than smelting or pottery, and was already quite advanced before smelting came into being.
Could that be true? Could you **smelt** something simple like tin, lead or copper *accidentially* in a **campfire** or in a kiln? The answer is: It's almost impossible - but not quite. Let's see why.

- **1.** You need to have ore in the fire. Tin ores are rather rare. It is therefore very unlikely - but not impossible - that some ends up in a campfire by accident. Same thing for lead and copper ore, even so they are not quite as rare.
  2. You need carbon monoxide for reducing the ore. Or do you? As we will see further down, you can reduce ore without carbon monoxide but that doesn't help much here. Carbon monoxide is produced if some carbon is quite hot (around 1 000 ^{o}C; 1 832 ^{o}F) and deprived of oxygen / air. That is very unlikely - but not impossible - to happen in a typical wood-fueled camp fire.
  3. If against the odds you do happen to produce a bit of metal, it would melt immediately in the case of lead and tin, getting absorbed in the ashes and coal pieces. Copper would not melt (no camp fire gets that hot) but form small flimsy pieces, prone to oxidize immediately again. In other words: if you don't look very closely at the remains of you camp fire, you would not notice that you produced some metal.
  4. So how about pottery? You adorn some pots with some colorful copper ores and then fire them. Wouldn't you smelt these ores? Well - maybe. In a proper kiln, run at high temperatures beyond, let's say, 1 000 ^{o}C; (1 832 ^{o}F) and with an *intentionally* produced reducing atmosphere (otherwise it would always be oxidizing), smelting of copper might happen - but pottery this advanced came long after smelting had already been invented! As long as pots were fired by putting them into a kind of glorified camp fire - see above!
- F. Overman, in a " A Treatise on Metallurgy (New York and London, **1852**) p. 656., wrote the following to the topic:"If a Western backwoodsman wants shot or bullets, he will kindle a fire in a hollow tree or an old stump of a tree, place some galena on the charred wood and melt it down. After cooling, he finds the metal at the bottom of the hollow."
  If that is actually true, we still need to take notice that this wasn't *accidental* smelting in a campfire but intentional smelting in a very primitive furnace.

People around the time when smelting copper came into being were obsessed with "green stones", used for making jewelry. On occasion they run into native copper (looking green since oxidized on the outside), and sometimes they recognized that as being something different an worked it into beads and awls.
Somehow, and I don't pretend to know how exactly, they must have smelted copper by accident when working with the green stuff one way or other. Most of the time nobody noticed. Sometimes somebody noticed but couldn't reproduce the "experiment" and lost interest. But eventually somebody somewhere started to make copper intentionally, and the technique caught on.
As present-day evidence strongly suggests, the very early "copper industry" was of the home-work type. You worked the stuff in your home with "imported" copper ore. No signs of copper smelting were ever found at the earliest copper ore exploits; it seems to have been done in settlements somewhere else.
First intentional copper smelting was done in the most simple smelter imaginable: a "standard" ceramic bowl, about (20 - 30) cm in diameter and (16 - 30) cm in height. We call such a bowl a **crucible** but there is no intrinsic difference to a bowl used for brewing beer, for example. As long as it was made from decent clay and well-fired (not necessarily at very high temperatures), it was fine.
Below is what it looked like schematically, real bowls are here.



Primitive smelting and melting in small crucibles

For **smelting** you pile your charcoal - ore mixture more on one side and dip your blowpipe into the charcoal bed. A few cm behind the opening of your blowpipe - a simple reed, re-enforced a the hot end with some clay - a temperature of 1200 ^{o}C (2192^{o}F) could be reached if everything was just right; enough to produce carbon monoxide (CO) somewhat further away, reducing the copper ore in the way of the blast. A bit of slag might form too, becoming liquid, and dripping down. But that only happens during the blast and in a small region. When you stop blowing because you need to breath in fresh air, everything cools down. At the next blast the temperature soars up again - but in a somewhat different area because the position of you blowpipe has changed a bit, and the way the air blasted in moves through the charcoal bed is also different, because the charcoals have settled somewhat and the geometry is different.
It is messy and inefficient, allright, but there are advantages: You can easily manipulate the contents of your "smelter": pull coals about, add fuel and ore here or there, blow on this or that spot, and so on. You can't do that in a larger blast-furnace type of smelter, at least not easily.

- Typically you will not get a pool of liquid copper covered by some liquid slag this way. Your average temperature is too low, and the spatial and temporal uniformity of the process not good enough. What you get is a messy mixture of **copper prills** embedded in a fused mess of partially liquefied slag, charcoal pieces, and ore remainders.

The early copper "industry", it appears, consisted mainly of processing the crucible contents by banging it with stone hammers to pry off the precious little pieces of copper in there. The next step would be melting (and thus also automatically refining) the copper. This was done in the same kind of crucible, just considerably smaller; here are examples.
As I have stated before, if you don't know how to smelt, you will have big problems to just melt some native copper. But if you do command a smelting technology, melting is now easy for several reasons:

1. First, the smaller crucible means you have more air "per charcoal". You can make your crucible small because you do not need produce CO, which needs more layers of charcoal.
2. Carbon monoxide production needs quite a bit of energy that is then lost for increasing the temperature.
3. Far less energy is needed to just melt some copper than to reduce the ore.

This all simply means that it is far easier to achieve and maintain high temperatures in your melting crucible.

- All you need to do is to blow directly on your bed of charcoals from above Right below the surface (the actual distance depending on how hard you blow) the temperature will be at peak values and hot enough to melt the copper in there. You also supply enough energy now to form liquid slag and you end up with a nice pool of liquid copper, protected by some slag.
  Your "**ingot**" after cooling will be a round plane-convex disc - and that's what archeologists tend to find in early copper smelting societies.

The process, however, is messy and inefficient. It is not suited for the "mass production" of copper. Moreover, while it works - not well but just so - with oxide or carbonate ores found in the surface-near gossan or a bit below of a copper ore deposit, the typical sulfides found a bit deeper would tend to produce trouble. The noxious sulfur-bearing fumes coming out of your crucible would be the first but not the only problem.

Smelting in a Crucible Heated from the Outside

Smelting in a crucible can be done in a way completely different from that above. All you need to do is to fill a crucible with a proper mixture of ore, charcoal, and flux, and to heat it from the outside. Put it inside a kiln, for example, or immerse it completely into in a charcoal fueled fire.
It is not an important method and it is no even clear if it ever was used in antiquity. However, according to some, a variant of the famous Indian crucible (or wootz) steel might have been made in this way.

- One way of doing this is to powder your ingredients. You are not blowing air through them, so you don't have to provide a lot of free space to keep air resistance small. Since the carbon in there will be very hot, and since plenty of CO_2 is around from whatever you do to make the crucible very hot, chances are that you will produce carbon monoxide inside your crucible and reduce the ore. But you do not even have to do this! Surprise:

Smelting can be done without carbon monoxide!

- You can reduce ore directly with *solid* carbon! One possible reaction (out of many) is:

$$2\ Fe_2O_3 + 5\ C \Rightarrow 4\ Fe + CO_2 + 4\ CO$$

This so-called **carbothermic reaction** is not a very efficient reaction since it can only take place where solid carbon touches solid ore, and that contact is even destroyed by the reaction! Having small particles, thoroughly mixed, will help to achieve as much contact area as possible. But then this direct reaction might produce its own carbon monoxide, as in the example above, triggering the usual reduction reaction. The long and short of all this is simple

Using the carbothermic reaction allows smelting in an oxidizing atmosphere

- Oxidizing atmospheres is what you have in regular fires or wood-fueled kilns because you always supply more oxygen than consumed by the fuel if you don't take special measures. In other words: You can employ simple and cheap wood fires.
  There is a catch, of course. Everything need to be just right because you have not much control on what is going on in your crucible as soon as you start the fire. Your crucible needs to be made of refractory materials and of very good quality to be able to withstand the heat and not become part of the slag, and so on. The crucibles used for direct blow pipe smelting, in contrast, hardly get hot on the outside, and most if the inside does not experience very high temperatures either. There are also might be a danger that the reaction "runs away" and gas is poduced so fast that the cucible explodes.

Rehder suspect that smelting in a crucible heated form the outside may have as been used extensively for all kinds of metals. Unfortunately no easily recognizable artifacts are left behind. If an ancient kiln was only used for pottery or also for crucible smelting is hard to tell from the little that remains, in particular if the process was done without producing much slag. My guess would be that crucible smelting cannot compete against a well-run bellows-blown smelter.

Can Iron be Smelted in a Copper Smelter?

That's a tricky question. It is a fact that iron was accidentally produced in antique copper smelting, causing various problems and a special new industry.

- However, if one could efficiently smelt iron in a copper smelter, just replacing copper ore by iron ore, is a different question. I will deal with that in the backbone and - indirectly - in the next module of this series.