

Theoretical and practical aspects of iron smelting in a bloomery furnace

Oliver Metz & Romain Bohr

Why experiment?

It is now over ten years since we started to experiment with bloomery smelting. Initially, our motivation stemmed merely from the desire to reproduce historical artefacts with the authentic material - bloomery iron. But the first efforts ended in failure - with only some small beads of cast iron in a sticky mass of slag. As we know now, the ores we had locally gathered, had been too lean. To avoid further frustration, we shifted to very rich limonitic iron ore for our next smelts – presumably originating from Hammersley Australia. The following successful smelts enabled us to optimize the experimental setup, allowing us to routinely draw blooms with a weight of 8-10kg out of 30-40kg of ore. Encouraged by these results we again took up the search for ores in our vicinity (both Bavaria and Luxemburg), and systematically analysed them by XRF. Thereby, we gained valuable insight into the complex interdependence between the chemical composition of the ore and the outcome of a bloomery smelt.

Results of our bloomery experiments

Our experimental setup

The requirements towards the kiln design were to build a small furnace with a reasonably low charcoal consumption, and to achieve an almost homogeneous lateral temperature distribution. In order to constrain the numerous experimental parameters, most bloomery runs were performed with an identical geometrical setup (Figure 1):

The shaft has a cylindrical to slightly conical form with an inner diameter of 25cm. Its height follows the applied airflow rate, so that the minimum top gas temperature is around 500°C. The shaft-height can be as much as 100cm (measured above the tuyère), if a high blow rate is applied. The shaft is built up of a mixture of clay, sand, and preferably a good portion of straw, which prevents cracking during the drying process. The tuyère is a simple chamotte tube (3cm inner Diameter) which protrudes roughly 3cm into the furnace, and is placed 25-30cm above the bottom of the hearth. The slagtapping arch around the tuyère, is made of a lean clay straw mixture. It



has only a thickness of about 5cm, so that it can be easily broken up to draw the bloom. In the bloomery process, several tap holes have to be drilled underneath the tuyère to lower the slag level occasionally. Immediately closing them again, prevents further loss of carbon monoxide (CO).

Right: Figure 1 - Schematic of the Bloomery setup.

The tap arch is the only part of the kiln, which must be broken up to draw the bloom. The wall of the tap arch is the only part of the furnace, which gets heavily slagged and must be restored after each run. The remaining shaft can be reused many times.

A forceful electrical blower provides the blast, but we have also successfully tested manually operated devices, like double action and single action bellows as well as Japanese style box-bellows. They all worked, as long as they provided enough airflow at a typical maximum overpressure of up to 5mbar. The airflow rate is measured with a float-type flow meter, which is connected in series with the electrical blower. Its measuring range is 10-60m³/h. If the carbon content of the charcoal (typically 80-90%) is known, the airflow can easily be calculated by the charcoal consumption rate per unit time according to equation (1). The thoroughly dried kiln is usually preheated with wood strips for a few hours, the remaining ash is cleared out and the tap arch closed. The shaft is then loaded with glowing embers and filled up with charcoal to the top. First charges consisting of mere charcoal are added in order to adjust the blow rate to the designated value. If the charcoal burning rate is constant, the charge slowly descend to the hearth, the airflow must be reduced to keep the charcoal burning rate constant.

This additional carbon consumption results from the reduction of the iron oxide. In theory, this difference in airflow rate could be used to calculate the degree of reduction of the ore, but in practice the measurement error in charcoal rate, due to non-uniform sagging of the coal/ore- column is too high, and the calculated value no more than a rough estimation. For an exact calculation, the top gas composition has to be known: at the prevailing lower temperatures in the upper part of the shaft, the CO_2 is no longer fully regenerated to CO, which means lower carbon consumption.

Temperatures inside the furnace are measured by S-type thermocouples, protected by an alumina tube, with a maximum operating temperature of 1550°C. The temperature sensor is inserted through several horizontal boreholes in the furnace wall, so that the tip protrudes to the centerline of the shaft. The boreholes are vertically aligned with a distance of 10-15cm between one another.

Relevant Experimental Parameters

Several important parameters influencing the result of a bloomery experiment have to be minuted:

- The chemical composition of the ore
- Diameter and height of the furnace
- Blow rate, or charcoal mass per time unit
- Ratio of charcoal to ore
- Weight and quality of the bloom

Conditions for a successful smelt

The bloomery process is only successful with high quality ores. A reasonable yield is achieved, if the iron content of the ore is not below 50% (equal to 70% Fe_2O_3). There are some exceptions e.g. calcium and manganese rich ores.

Blow rates in the range of 190-720l/min, which corresponds to a charcoal (85% carbon) consumption rate of 3-12kg/h will work fine for ore #1 and #2 (Table 1). Even at 720l/min, which means an extraordinary high flow rate of 1.5l/min per cm² of hearth area at tuyère level, no cast iron was formed (fuel-to-ore ratio of 1:1). This is in accordance with the results of L. Sauders¹, who is experimenting with high blow rates in similar sized furnaces.

However, contrary to L. Sauders¹, size and compactness of our blooms do not depend on blow rate. Furthermore, carbon content and yield do not show any dependence on blow rate - albeit obvious difficulties to get exact figures, because of inhomogeneous carbondistribution and slag inclusions in the bloom. We want to emphasize, that these findings may only be valid for furnaces with small cross sections, where the reduction zone reaches to the furnace wall (as discussed below). Larger kilns or kilns operated at very low blow rate have a pronounced uneven temperature distribution. Therefore, the sinking burden laterally has a non-uniform history; the process is far more complex.

			CaO	MgO	Na2O	K2O	Fe2O3	MnO	TiO2	ZrO2	AI2O3	Sum	Fe Content	Smelts
nersley Australia	3,9	0,2	0,1	0,8	0,0	0,0	91,2	0,5	0,1	0,0	3,3	100,0	63,8	20
ch Luxembourg	15,7	0,4	0,1	0,0	0,0	0,2	78,1	0,1	0,2	0,0	5,2	100,0	54,7	15
ig, Germany	15,2	0,3	0,4	0,3	0,0	0,1	66,0	0,1	0,9	0,0	16,7	100,0	46,2	no
et, Germany	11,2	0,4	0,4	0,7	0,0	0,7	73,8	6,5	0,2	0,0	6,0	100,0	51,7	Not tried
														1
	g, Germany	g, Germany 15,2 et, Germany 11,2	g, Germany 15,2 0,3 et, Germany 11,2 0,4	g, Germany 15,2 0,3 0,4 et, Germany 11,2 0,4 0,4	g, Germany 15,2 0,3 0,4 0,3 et, Germany 11,2 0,4 0,4 0,7	g, Germany 15,2 0,3 0,4 0,3 0,0 et, Germany 11,2 0,4 0,4 0,7 0,0	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 et, Germany 11,2 0,4 0,4 0,7 0,0 0,7	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 at, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 et, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8 6,5	ist ist <td>g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 et, Germany 11,2 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0</td> <td>g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 16,7 at, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0</td> <td>g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 16,7 100,0 et, Germany 11,2 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0 100,0</td> <td>g, Germany 15,2 0,3 0,4 0,7 0,0 0,1 66,0 0,1 0,9 0,0 16,7 100,0 46,2 et, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0 100,0 51,7</td>	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 et, Germany 11,2 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 16,7 at, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0	g, Germany 15,2 0,3 0,4 0,3 0,0 0,1 66,0 0,1 0,9 0,0 16,7 100,0 et, Germany 11,2 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0 100,0	g, Germany 15,2 0,3 0,4 0,7 0,0 0,1 66,0 0,1 0,9 0,0 16,7 100,0 46,2 et, Germany 11,2 0,4 0,4 0,7 0,0 0,7 73,8 6,5 0,2 0,0 6,0 100,0 51,7

tion of some ores measured by XRD, concentration in %.

Table 1 - Chemical composi- The charcoal is broken to a calibre of below 5cm, and most of the fines are sifted out, as they tend to block the shaft. The roasted ore is crushed down to a size smaller than 8mm (fines included), and is charged together with charcoal in small portions every 5-10 minutes. The intervals should be chosen in a way, that the top level of the stack is not falling below a height, where the temperature is higher than 500°C, in order not to waste any carbon monoxide, and to advantageously use the heat in the upper stack to preheat, and to dry the charges. In order to receive a reproducible test result nothing else but mere ore and charcoal is charged - no residues from previous smelts such as slag and iron residues, no hammer scale etc. The inner diameter of the tuyère is not of major concern, but it should be selected according to the blast rate. At low blast 1-2cm will work, whereas at high air rates a cylindrical tubing with 5cm inner diameter is performing well. The inclination angle of the tuyère determines the position of the bloom, but has no major influence on the experimental outcome. Everything between near horizontal and 45° down is working. At very steep angles, the rising slag level can very abruptly block the tuyère, which demands an immediate tapping of the slag. It is not always necessary to have a tuyère protruding into the furnace. A sharp air jet will suffice, if it is blown through a relatively big hole in the furnace wall. The nozzle providing the air can be made simply of copper or even wood.² Typically, in this type of furnaces it is possible to smelt 30-40kg of ore. The yield of the bloom depends on the quality of the ore. As an example, 30kg of an ore with 80% Fe₂O₃ content should deliver 8-10kg of iron.

The Theory

Chemical description of the bloomery process

The bloomery furnace is a countercurrent chemical reactor, where the descending cold burden is in contact with ascending hot gases. As a result of the gasification of charcoal in front of the tuyère, the volume in this part of the shaft is continuously decreasing, and being replaced by the descending column of charcoal and ore above. The chemical reactions, which are delivering the heat to reach the necessary process temperature, are (1) and (2).

¹ Sauders L. & S.Williams, A practical treatise of smelting and smithing of bloomery iron in: <u>Historical Metallurgy</u> 36(2) (2002) 122-133.

² Wrona, A., The Production of High Carbon Steel Directly in Bloomery Process: Theoretical Bases and Metallographic Analyses of the Experiments Results in: EXARC JOURNAL 2 (2013).

The latter reaction is producing a tremendous amount of heat in the oxidizing zone directly in front of the tuyère. The created thermal energy and the spatial extent of the oxidizing region is determined by the blow rate.

At a sufficiently high air rate, it is easily possible to melt iron (m.p. 1535° C) in this zone. When the ascending hot CO₂ comes into contact with the excess carbon in the charcoal bed, the endothermic back reaction of the Boudouard equilibration (3) predominates at temperatures above 1000°C.

Carbon monoxide is the main reducing agent in a process called "indirect reduction", in which iron oxide is not reduced directly by carbon, but indirectly via CO. Equations (5)-(8) describe the chemical reactions involved, when a limonite (FeOOH) ore descends through a bloomery furnace. The major part of the first step of equation (5) happens during the roasting of the ore in a preparative step before the proper bloomery run – the emerging water vapour creates a network of cracks in the structure of the ore, facilitating the crushing of the ore before it is charged into the furnace. While the reduction to magnetite (Fe₃O₄) and wustite (FeO) (6) and (7) is proceeding at moderate temperatures and reducing atmospheres, the reduction of wustite to metallic iron (8) requires a minimum temperature of 720°C, and at least 60% CO in a mixture of CO and CO₂ (expressed in η , (4)) as the thermodynamic prerequisites. This reaction runs only at a reasonable speed, if the temperature exceeds 900°C. The overall enthalpy of step (6)-(8) amounts to only -12.3kJ per mol iron and is therefore negligible in the heat balance of the entire process.

$$C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H_f^0 = -111 \text{ in kJ/mol}$$
 (1)

$$C + O_2 \rightarrow CO_2 \quad \Delta H_f^0 \text{ in } = -394 \text{ kJ/mol}$$
 (2)

$$CO_2 + C \rightarrow 2 CO \Delta H_f^0 \text{ in } = 283 \text{ kJ/mol}$$
 (3)

$$\eta = c(CO) / (c(CO_2) + c(CO)) * 100$$
(4)

c(CO): concentration of CO in vol.%; c(CO₂): concentration of CO₂ in vol.%

FeOOH ->
$$\frac{1}{2}$$
 Fe₂O₃ + $\frac{1}{2}$ H₂O T > 200°C (5)

$$\frac{1}{2} \operatorname{Fe}_2 O_3 + \frac{1}{6} \operatorname{CO} -> \frac{1}{3} \operatorname{Fe}_3 O_4 + \frac{1}{6} \operatorname{CO}_2 \quad \Delta H_f^{\circ} \operatorname{in} = -7.8 \text{ kJ/mol}$$
 (6)

$$\frac{1}{3} \text{ Fe}_3 \text{O}_4 + \frac{1}{3} \text{ CO} \rightarrow \text{FeO} + \frac{1}{3} \text{ CO}_2 \quad \Delta H_f^0 \text{ in = 11.2 kJ/mol}$$
 (7)

$$FeO + CO \rightarrow Fe + CO_2 \quad \Delta H_f^0 \text{ in } = -15.7 \text{ kJ/mol}$$
(8)

The Thermodynamic Prerequisites for Carbothermal Reduction

Equilibrium conditions of equation (8) can be taken from an "Ellingham Diagram" (Figure 2)³, in which the standard free energy of reaction (ΔG_R^0) is plotted against the temperature. Due to entropic reasons, the only line with declining slope is the black line, which marks the standard Gibbs energy of the Boudouard-equilibrium (3), which is shifted to the right side if temperature is increased. The red FeO (wustite) line, which marks the equilibrium of (8), crosses the black line at 720°C. This means that only above this temperature iron will be reduced from wustite. This diagram also indicates which elemental oxides will be reduced above a certain temperature level: Only oxides, whose ΔG_R^0 -lines are situated above the black line at the corresponding temperature will be reduced into the bloom. The intersections with the pink dashed line are marking the sequence, and the ease these relevant oxides are reduced at 1000°C. These are CuO, As₄O₆, NiO, SO₂, P₄O₁₀ and FeO. On the contrary, the reduction of MnO demands temperatures exceeding 1400°C, and SiO₂ exceeding 1600°C – conditions only met in a blast furnace. Al₂O₃ is not even reducible in a blast furnace – it will always stay unreduced and dissolves in the molten slag.

It has to be mentioned, that the predictions of the Ellingham Diagram are only valid under the idealized assumption of thermodynamic equilibrium, which is not fulfilled in a bloomery furnace. Therefore, it can deliver only tendencies and not a full description of real world iron smelting, which also involves the kinetics of chemical reactions among other parameters. Furthermore, the diagram is only valid for the pure oxides. If chemical compounds, like fayalite (Fe₂SiO₄), are formed, the ΔG_R^{0} -lines will be shifted downwards, which is shown in Figure 2 (dark blue line). Therefore, the minimum temperature to reduce fayalite is 800°C, which is considerably higher than the 720°C needed for the wustite.

In a more sophisticated version of the Ellingham Diagram, it is possible to read out the minimum partial pressure ratio (p_{co}/p_{co2}) for (6)-(8) to proceed to the right side. As p_{co}/p_{co2} can be converted to the already mentioned η , every reaction can be allocated to a certain minimum η , which must be surpassed to receive the correlated product.

³ Thermodynamic data from: FREED- Thermodynamic Database, Thermart Software, 12102 Calle de Maria, San Diego, Calif. 92128.



What are the key factors in bloomery

Bloomery smelting is a complex interplay of many factors e.g. slag viscosity, slag volume, slag melting point, reducibility and retention time – most of them are tightly connected to the chemical composition of the ore. This will be illustrated for five different ores we have used (among other ores) for our smelting experiments. Ore #4 is only displayed, because it is a local ore in Bavaria, found near Aichach (D), the venue of the 10th IES Symposium. However, up to know, we were not able to collect a sufficient quantity to carry out an experimental bloomery run. Table 1 shows the chemical composition of these ores. Ore #1 and #2 give excellent results while ore #3 and #5 are hardly smeltable in the applied high shaft furnaces with a charcoal to ore ratio of 1:1.

Slag viscosity

In bloomery smelting as well as in a blast furnace, the success of the process is highly dependent on the separation of slag and iron. This can only happen if one or both of them form a liquid of sufficiently low viscosity. In a blast furnace, both portions are permanently molten below the tuyère level, so that the two low-viscosity liquids can easily separate by gravity due to their major difference in density. In bloomery only

Figure 2 - Std. Free Energies of Reaction as a function of temperature. the slag is permanently in the liquid state, so that the effectiveness of this separation is tied to the viscosity of the slag. Only low-viscosity slag allows the small native iron particles (seen in Figure 5d) to agglomerate to a coherent bloom. The viscosity of a fully molten slag can be calculated with acceptable accuracy by a mechanism developed by Urbain^{4,5}, which is based on a quasi-chemical model. Due to their different chemical behavior, some oxides decrease slag viscosity (e.g. K₂O, CaO, MgO, MnO and FeO), while others (e.g. SiO₂, Al₂O₃) have an increasing effect. As an ore descends through the shaft, it is being reduced and its chemical composition changes with respect to FeO-content. The model predicts a dramatic increase in slag viscosity with decreasing FeO concentration as shown in Figure 3.

The Urbain model has a built-in Arrhenius type temperature dependence, meaning that slag viscosity is inverse exponentially decreasing with increasing temperature. The temperature of the slag bath will certainly not much exceed 1200°C, although temperatures in the oxidizing zone are much higher. The borderline for a successful bloomery process is to be set somewhere below 5000mPas (at 1200°C) which corresponds to the viscosity of honey (5000-10000mPas). Transfering these model predictions to the ores in discussion can also reveal the amount of iron, which can be reduced from the smelt: The curve of ore #3 is crossing 5000mPas at 57% FeO. As its initial composition includes 63% FeO (66%Fe₂O₃), only about 6% FeO would be available for iron production, until the slag is getting too viscous to allow for an aggregation of iron particles. 6% is far too little for a successful smelt⁶— at reasonable fuel (charcoal) to ore ratios one will always end up in the high viscosity region of the diagram. The fuel-to-ore ratio and the shaft height are the only means to influence the degree of reduction⁷.

If one of these parameters is decreased, the degree of reduction will decrease accordingly. All other ores are crossing the 5000mPas line at around 50% FeO, so they should be smeltable down to this iron content. As most acidic ores show a similar viscosity profile, a succesfull bloomery process is unlikely to reach wustite contents of less than 50%. At least this applies if no basic oxides like CaO or MgO are present in the slag. Experiments confirm this behavior, and there is a parallel to archeological findings, where the FeO-contents in the tapped slag from early bloomery process are nearly always above 50%⁸.

The low iron content of ore #5 and its high reducibility allows a reduction below the 50% FeO region. In the process, the decreasing FeO-content of the slag then again results in a high viscosity slag (at the assigned fuel-to-ore ratio of 1:1). With a modified setup, this ore is nevertheless smeltable: in a very low shaft furnace where the reducing

conditions are insufficient to reach such low FeO concentrations, a solid bloom can be smelted. It should also be possible to use a reduced fuel-to-ore rate for this ore, but this remains to be tested.

By increasing the charcoal-to-ore ratio⁷ a more reducing atmosphere is reached, i.e. higher η , which results in a higher degree of reduction: it is thereby easy to reach FeO contents lower than 50% for any other ore. For example, ore #2 was smelted with a charcoal to ore ratio of 1.5:1 and 2:1. Both experiments (Table 3, BXP14/15) ended up with a very sticky, green slag, which blocked the furnace after charging 10kg of ore.

Only 1-2kg of carburized iron in the form of small lumps could be drawn from both furnaces.

⁴ Mills, K., <u>Slag Atlas</u>, 2nd Edition (1995) 349-354.

⁵ Urbain, G. et al., <u>Trans. Brit. Ceram. Soc.</u> (1981) 80, 139.

⁶ The term "successful smelt" is not exactly defined, but rather a personal, subjective expression. In our view, a successful smelt is achieved, if a coherent bloom of several kg could be drawn (typically 4-5kg out of 20-25kg of ore). The slag should be of low viscosity and if necessary tapable. The process should run smoothly, without any blockage of the tuyère and without major damages of the furnace.

⁷ Tylecote, R.F. et al. 1971. Mechanism of the bloomery process in shaft furnaces in: Journal of The Iron and Steel Institute, Mai 1971, p342-362.

⁸ Gasssmann, G. et.al., <u>Forschungen zur keltischen Eisenverhüttung in Südwestdeutschland</u> (2005) 108.

Table 3 - Outcome of some bloomery experiments.

Experiment #	Ore	Shaft Height /cm	Shaft Diameter /cm	Tuyère Angle /°	Slag Viscosity/mPas	Air Rate /I min ^{.1} cm ^{.2}	Ore used /kg	Fuel Ratio	Bloom /kg	Iron Yield /%	Carbon Content approx.	Comment
BXP8	Ore #1	120	25	30	2000	0,4	20	1	4	29	0,5	
BXP9	Ore #1	120	25	30	2000	1,6	33,5	1	8,8	38	0,5	
BXP11	Ore #2	100	25	10	2000	1,1	35	1	10	49	0	
BXP12	Ore #2	100	25	20	1000	1,4	40	1	10	43	0	
BXP13	Ore #2	100	25	45	2000	1,1	30	1	9	52	0	
BXP14	Ore #2	100	29	20	12000	1,2	11	1,5	1	16	high	slag viscosity too high
BXP15	Ore #2	100	25	20	8000	1,2	24	2	2	14	high	slag viscosity too high
BXP16	Ore #2	100	25	20	1000	0,5	32,2	1	9,1	49	0	

In Figure 3 only the viscosities of the pure ores are shown; the intake of the charcoal ash has not been taken into account, because its chemical composition varies widely, and otherwise the diagram would have to be linked to a certain fuel-to-ore ratio. For common types of charcoal K_2O and CaO are the predominant oxides in the ash, and they always shift the curves towards lower viscosities. Especially at high fuel rates, this effect is noticeable.

The Urbain viscosity-model only covers fully molten slag, that is slag without any solids. At the zone of slag liquefaction, the former ore body is full of solid iron. These small iron particles in the molten ore are causing friction, which increases the effective viscosity. Concentration, size and morphology of these small iron beads significantly influence the overall viscosity. The initial iron content in the ore, as well as the degree of reduction is in turn biasing their concentration.



Figure 3 - Slag viscosities vs. FeO content of different ores.

Slag Volume

As the wustite is being reduced, the iron crystals are emerging from a nucleation and growth mechanism, and after a prolonged period, they appear in form of small irregular shaped particles. The micrographs in Figure 4 shows the situation after an isothermal reduction of ore #1 and ore #3 at 1000°C. For this purpose, we placed small chunks of ore in a bed of small-grained charcoal within a closed alumina crucible in an electrical kiln for 1 hour. The degree of reduction can be calculated from the mass loss of both ores, which is around 80%. Such a partially reduced chunk of ore is composed of a certain volume of solid iron and slag. If we assume a slag density of 4g/cm³ for a slag with 50% FeO, we can calculate the two volumes for each of the ores. The results are shown in Table 2. Due to its high iron content, ore #1 has a very high iron volume of 62%. For a rough simplification we can assume that these iron volume exclusively consists of monodisperse spheres with a diameter of 10µm - albeit the diameter is not relevant for this model. The theoretical density limit (volume fraction) for these spheres in random close packing is 63%.⁹ This means for ore #1, that the iron spheres are in close contact, and the slag is distributed entirely in the void volume. At the prevailing high temperature, the iron beads will sinter together at their contact points and form a rigid scaffold. This structure will not drip down at the flowing temperature of the slag - it will stay in the stack until the melting point of the iron is reached. The melting point will indeed very probably be reached, because the naked iron at the surface of this structure undergoes carburisation due to direct contact with the charcoal, shown in (9). The $[C]_{Fe}$ indicates that the carbon is dissolved in the iron.

Name	Provenance	Slag Volume /%	Iron Volume /%		
Ore 1	Hammersley Australia	38,0	62,0		
Ore 2	Garnich Luxembourg	69,6	30,4		
Ore 3	Daiting, Germany	81,5	18,5		
Ore 4	Grubet, Germany	73,5	26,5		
Ore 5	Mersch Luxembourg	80,5	19,5		

Table 2 - Slag and iron volume fraction of different ores at 50% FeO in slag.

This dissolution of carbon into the iron lowers the melting point of iron, which reaches a minimum temperature of 1154°C at the eutectic point (4.4% carbon) in the iron-carbon phase diagram.

⁹ Song, C., Wang, P. & Makse, H.A., *A phase diagram for jammed matter* in: <u>Nature</u> 453 (7195) (2008) 629-632.

Figure 4 - Isothermal reduction @1000°C, a, b: ore#1; d, c: ore#3.



In principal, there is another route for carburization (10), which is the reverse Boudouard reaction. However, the right side of the equation is only favored at low temperatures (<1000°C), so its contribution to the carbon uptake is therefore of minor importance. Equation (10) can also be precluded for carbon uptake at low temperatures i.e. temperatures below the slag softening point, because here the porous FeO controls the CO concentration through (8), at a level too low for (10) to proceed. Therefore, the only way for the iron to dissolve carbon is over close contact with charcoal, whereby the slag must be in the molten state, and must not cover the iron.

A simple reduction experiment shows the different behaviour of ore #1 and #2. Both ores are placed in a bed of granulated charcoal, with a particle size of ca. 4mm, inside a lid-covered crucible. The two pieces of ore are placed above a thin alumina sheet in a way that they are kept separated by one layer of charcoal. The purpose of the alumina sheet is to catch liquid drops leaving the ore, which would otherwise drip down without being recognized. The crucible is placed in an electric kiln, and heated to 1350°C with a rate of 10°C/min, in order to simulate the rising temperature in the decent through a furnace shaft , blown with ca. 11/min/cm².

Figure 5 shows the results, after the crucibles were allowed to cool down, and the circumventing charcoal has been removed. Ore #2 on the left, which obviously melted, has a drop-like appearance, and is connected over a thin neck to a puddle of slag, which is partially sucked up by the porous alumina sheet. A section through its body (Figure 5b, right part) reveals that it is a hollow sphere, stabilized by a thin membrane of iron, with most of its interior mass drained out. Figure 5d displays the residual iron shell, which shows only minor carburization in the outmost parts, which are not covered with slag.



Several experiments with ore #2 under same conditions always reproducibly end up with these hollow spheres, whereas ore #1 always ends up with a solid structure of spongy iron, depicted in Figure 5a (right side). Interestingly there are two pieces of cast iron (c1, c2) sitting below ore #1, which have obviously detached from the highly carburized outer layer of the ore. Figure 5c shows c2 and Figure 5e c1, which is still attached to the main part of ore #1. If these experiments are conducted without direct coal contact by shielding the ores with a small hood made of a very small, porous alumina crucible, no carburization was observed for both ores. This proves that indirect carburization via (10) does not occur.

Besides the obvious linkage between iron content in the ore and iron yield, bloomery experiments with both ores show a pronounced different behavior. Irrespective of the blast rate (0.5-1.4l/min/cm²) ore #1 is always producing steel with a carbon content of around 0.5%, while the bloom of ore #2 has always a very low carbon concentration. All these experiments are performed at a charcoal to ore ratio of 1:1. This is a clear indication, that the above-mentioned mechanism is accountable for the carbon uptake of bloomery iron. Therefore, the final bloom is always a product of iron fractions with strongly differing carbon contents. The fractions are ferrite floating in liquid slag, spongy iron with a carburized shell, and liquid cast iron detaching from it. The ratio between these fractions is strongly influenced by the chemical composition of the ore.

Figure 5 - a: Reduction in coal bed, 1350°C (10°C/min); b: Polished section of ore #1, ore #2, c1, c2, etched with Nital (4%); c: Cast iron c2 with extracted graphite lamellas; d: Shell of ore #2, ferrite with no carburization; e: Highly carburized outer region of ore #1 (left) and cast iron (c1, right).

Airflow, Temperature and Retention Time

A central key to understand the behavior of small diameter shaft furnaces is the dependence of blast rate, vertical temperature distribution and retention time. Figure 6 shows the measured temperatures in the center of a 25cm shaft furnace at different positions above tuyère level. The measurements are taken during full operation, while the shaft was filled up with a 1:1 mixture of charcoal and ore. Besides the blue line measured by P.Crew¹⁰, which was received at a very low airflow rate of 0.3I min⁻¹ cm⁻¹, the lines show surprisingly nearly the same slope. An increase in blow rate causes only an axially parallel shift of the temperature line upwards. Same slope means that the height of the wustite reduction zone (900-1100°C) in the centre is always 20cm wide, independent of the blow rate.



Figure 6 shows, that the temperature 25cm above tuyère (for 0.6 l/min/cm²) is 1100°C. As slag is not a pure compound, it has no sharp melting point, and starts to soften fairly below this temperature. This softening is accompanied by a gradual loss of porosity. It is common to describe the gradual softening of iron ore in several stages, i.e. initial deformation temperature, softening temperature, spherical temperature, and flow temperature.¹¹ The zone below the dripping zone (in figure 6), where the softening starts is called the cohesive zone. As reduction, according to (8), is bound to the solid-gas interface, it starts to get sluggish in this zone, and nearly stops at the dripping zone, where the spherical temperature is reached. The position of the ore. The higher the initial deformation temperature is, the higher the degree of reduction will be. R.F.Tylecote¹² shows more detailed temperature measurements, which were taken at the centre plane perpendicular to the tuyère, at several heights of a shaft furnace with diameter of 30cm, in a way, that the isotherms could be mapped for the entire cross section (Figure 7a).

¹¹ German Industrial Standard 51730.

Figure 6 - Temperature in the centre of a shaft furnace with an inner diameter of 25cm, measured with thermocouples type S. Blue line from P.Crew¹⁰. Black dashed line from R.F.Tylecote¹² (Fig.11, p349); the temperature values are received from a 30cm diameter shaft furnace without iron ore loading.

¹⁰ Crew, P., Twenty-five years of bloomery experiments perspectives and prospects in: <u>HMS Occasional Publication</u> 7 (2013) 25-50.

¹² Tylecote, R.F. et al., Mechanism of the bloomery process in shaft furnaces in: Journal of The Iron and Steel Institute (May 1971) 342-362.



In contradiction to our measurements, the isotherms are not crossing the vertical centreline at regular distances (black dashed curve in Figure 6). In contrast to our experiment, Tylecote has measured the temperature distribution of a pure charcoal column without any ore charges. Obviously the heat capacity of the descending cold ore is responsible for a downward shift of the isotherms to a linear temperature distribution in the centre – albeit it is not to be expected that the lateral temperature distribution is influenced by the charging of ore. Figure 7b shows a simplified version of Figure 7a – the temperature zone >900°C is sketched by the red, oval shaped area. As mentioned, the wustite reduction can only proceed in the red area, and stops at the border of the orange area where the ore reaches the dripping zone – indicated by the green droplets. The portion of the sinking burden, which bypasses the reducing zone (ca. 35%), ends up in the slag, without any contribution to the iron yield.

Apparently the air rate of 300l/min in a 30cm shaft furnace is producing a very inhomogeneous situation – a situation that should change for higher air rates or lower diameters. Figure 7c shows the fictive situation at a doubled air rate (600l/min), which is not based on measurements, but on the assumption, that the reducing zone must expand horizontally as well as vertically. Here the part of the ore, which is untouched by reduction, will be significantly smaller. In the second case, the red area, which is actually a volume, has largely increased, which at first sight should lead to a rising iron yield. This assumption has to be tested for a 30cm furnace, but for the 25cm shaft furnace this rise does not occur.

Experiment BXP8 was conducted with low air rate and produced a bloom, which was almost evenly distributed over the entire cross section of the shaft below tuyère level. This implies that no portion of the ore bypassed reduction and that the degree of reduction is uniform all over the cross section. Surprisingly, nothing changes at a doubled air rate. As mentioned above, our temperature readings are taken at the vertical centreline of the shaft. This does not mean that the isotherms are flat – they must be curved downwards at the edge of the shaft, as in figure 7a, with the difference that the red zone is touching the furnace wall. This is inevitably resulted by the thermal loss through the furnace wall. Although higher blow rates do not change the vertical extent of the reducing zone at the centreline, the red zone at the edges will enlarge. Doubling the air rate causes also the descending speed of the ore (v_{ore}) to double, which in turn causes a halving of the retention time in this zone.

Figure 7 - a: Lateral temperature distribution in a charcoal column at a blow rate of 300l/min, measured by Tylecote¹². b: Simplified outline of the different zones at 300l/min. Reduction zone (red), Dripping zone (green droplets). c: Potential situation at 600l/min. This qualitative picture suggests that these two opposing effects somehow cancel out, and indeed this is greatly confirmed by our experiments (BXP8/9, BXP11/12/13/16), which show that yield and carbon content of the bloom are not affected by blast rate. At least for our small diameter shaft furnaces and for the chosen air rates, it is a common misunderstanding that high blast rates always produce high carbon blooms or even cast iron.

At fuel-to-ore rates higher than 1, the above mentioned downward shift of the isotherms is less pronounced, which in turn causes the reducing area to grow, and this ultimately leads to higher slag viscosity (BXP14/15). It should be emphasized, that the charcoal-to-ore ratio does not influence the retention time, if the volume contribution, and the carbon consumption of the ore are neglected. The first can be done with good approximation, because the ore is mostly placed in the void volume of the charcoal, the sinking speed of the burden can only be affected by charcoal burning rate. The latter can be neglected because the charcoal is used in great excess, and variations, at least to higher fuel rates, do not change much.

Conclusions

Despite the high complexity of the bloomery process there are very few parameters, which influence the experimental outcome with respect to yield and carbon content of the bloom. For the chosen experimental setup, the chemical composition of the ore and the fuel-to-ore ratio are the major governing factors. The fuel-to-ore ratio does only leave a small experimental window, which allows to control the degree of carburization. As there is so far no historical evidence for the addition of lime in early iron age bloomery, only rich ores with a correspondingly low slag volume come into question as a source of carburized iron. – Further experiments with wider shafts are necessary and already in preparation, as our findings may only hold true for small diameter furnaces as applied in our experiments so far.

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