

CHARACTERIZATION OF BLOOMERY SLAGS

Morphology, composition and furnace operation

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ABSTRACT

Nobody has been able to reproduce the successful ironmaking, in the way it was achieved during the Roman iron age and the Middle ages. On the basis of mainly the morphology of bloomery slags from the rich finds from about year 200 BC to 1800AD in Mid-Norway, combined with metallurgical reasoning and written documents from the 18th century, certain alternative models for the operation of the furnaces are presented. These agree well with the view presented by Dr L. Beck in 1891 on early ironmaking among the Germanic people.

Introduction

Slag is a waste product with little aesthetic value. It has no direct connection with subjects like the history of art or religion. It is thus frequently disregarded or misinterpreted when found during archaeological excavations. However, it can provide important information about the *smelting process*, above all in bloomery ironmaking. A characteristic X-ray pattern of solid slag with free FeO and Fe₂SiO₄ is shown in figure 1.

In the bloomery process, iron is made in shaft or hearth furnaces. Reduction at a high temperature is achieved while the necessary heat is generated by a combustion process in the same reactor. The metal must be acceptable for the blacksmith. This requires a minimum size of each piece of metal, the correct analysis in terms of % C, little impurities such as S and P, and no harmful slag inclusions. Let us thus consider a shaft furnace, where solid ore and the reducing agent are added from the top while air is blown into the furnace near the bottom. Evidently a countercurrent motion with heat exchange takes place. Liquid slag is tapped while the metal is removed as a solid lump, a bloom.

The slag from this process can be compared with two other types: *blast furnace slags* and *steelmaking slags*, whose origin and function are better known:

The blast furnace slag is composed mainly of gangue material with certain additions, in order to enhance reducibility at moderate temperatures and fluidity at the conditions, which are characteristic for the hearth. Steelmaking slags are composed mainly of material added to the furnace, together with certain elements from the metal, transformed into oxides during refining. Some essential features are shown in table 1.

Table 1. Typical features of modern slags.

	Blast furnace slag	Steelmaking slag
Range of oxygen pressure	10 ⁻²⁰	10 ⁻³ - 10 ⁻¹⁰
Main function:	removal of gangue in liquid state	controlled oxidation, dissolution of impurities
% FeO "Rôle"	< 1% "passive"	~ 10% "active"

Based upon the metallurgy of the process, I claim that a normal bloomery slag is an active slag, while it also is a medium for the removal of gangue in the ore.

The standard approach in extractive metallurgy is 1) to evaluate equilibria at an estimated temperature, representative for the hearth of the furnace 2) to make a corresponding heat balance, in order to evaluate the true process temperature 3) to find out

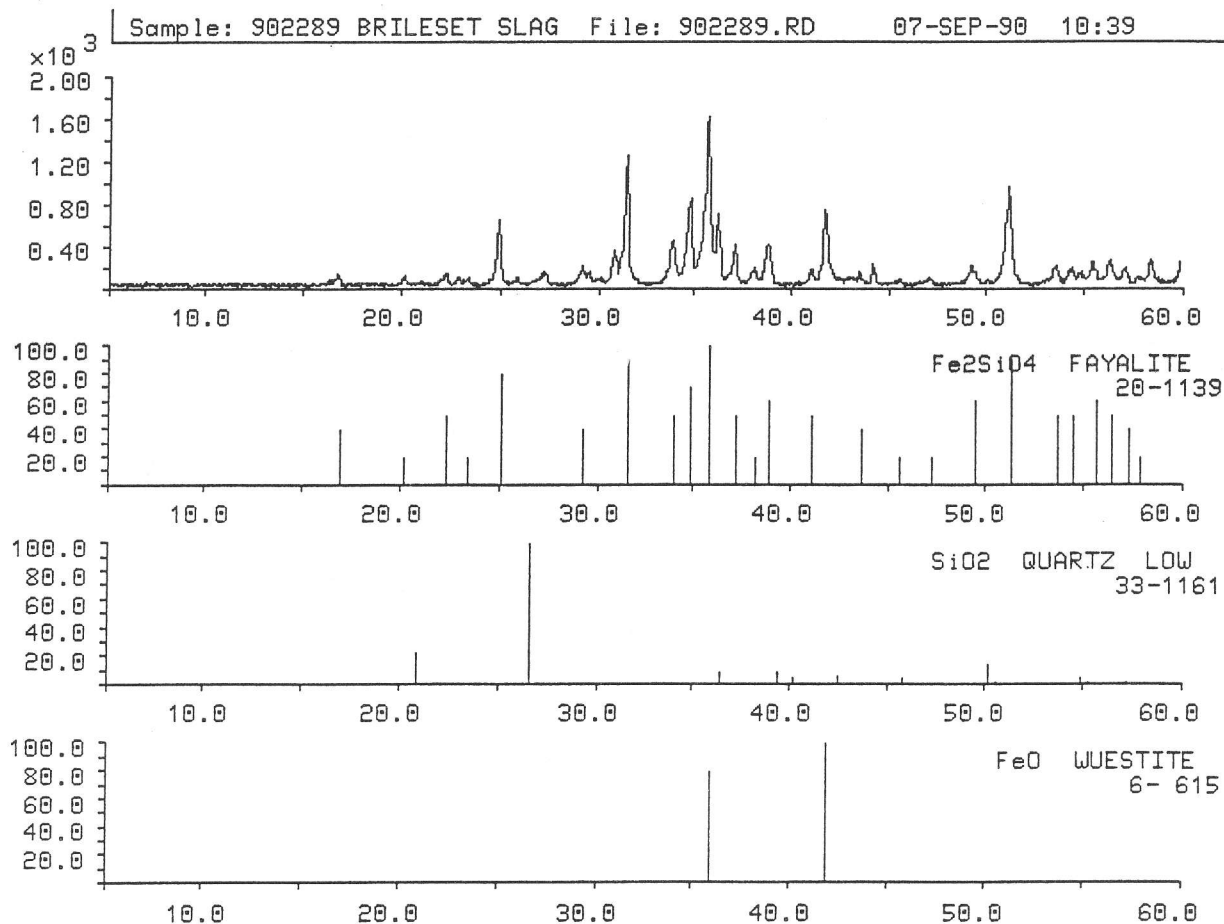


Fig 1. X-ray patterns.

about the prior history and thus the composition of the phases entering the reaction zone. The full calculation is "iterative".

The equilibria

The product of the bloomery process is iron with a carbon content near 0 %. There are four phases present in the bottom of the furnace: solid metal, liquid slag, carbon and gas.

In figure 2 a-c the four phases present in the bottom of a blast furnace and in two situations in bloomery furnaces with their corresponding analyses are shown. The blast furnace is operating near equilibrium in the hearth: The slag contains less than 1% FeO while the metal is near carbon-saturation at about 4% C. In the bloomery process, however, the low carbon content of the metallic phase can only be obtained by an equilibrium at temperatures below 900°C, rendering α - iron, (fig 3). There is an invariant point near 700°C with FeO at unit activity, a gas mixture of CO and CO₂ near 1:1, pure carbon and a

metal with practically no carbon dissolved present.

However, temperatures in the range 700 - 900°C are much too low for proper sintering of metal particles to a bloom and the decantation of slag. If the temperature is increased to the normal melting point of a bloomery slag, say 1150°C, the metal will dissolve an excessive amount of carbon¹.

At such temperatures, the low carbon content can only be obtained if it is controlled by a relatively oxidizing gas or a FeO-rich slag, requiring a non-equilibrium situation carbon - slag and/or carbon - gas. A gas will vary in composition and have a very low buffer capacity, giving a scatter in metal analyses. However, a sufficient quantity of slag containing "free" FeO can result in a reliable metal analysis².

The only bloomery process, for which we have written information from the 18th century, clearly tells that a certain amount of FeO-rich slag had to be present (Evenstad 1782, Rinman 1794). As will be shown later, this is supported by archaeological finds

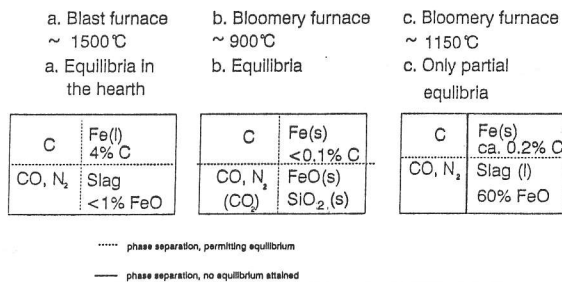


Fig 2. The four phases in ironmaking. a) the hearth of the blast furnace. b) possible equilibria in the bloomy furnace below 900°C. c) partial equilibria near 1150°C.

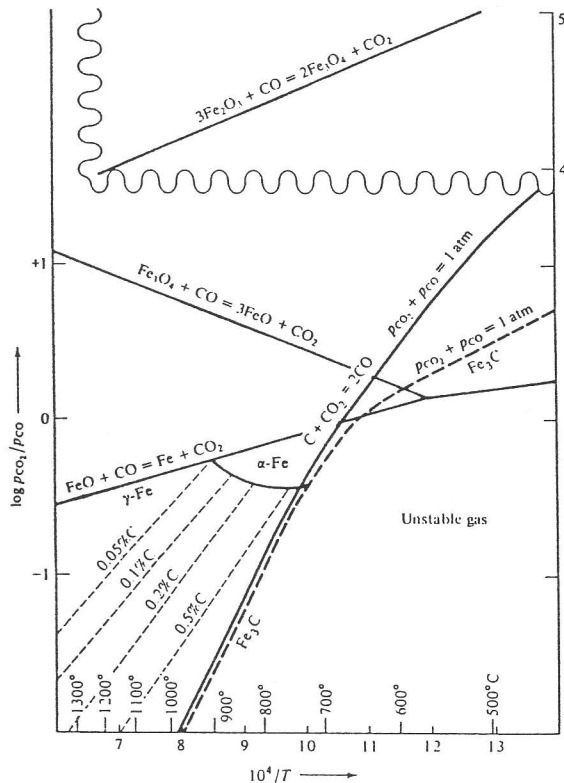


Fig 3. Equilibria in the system Fe-C-O as a function of 1/T (Rosenqvist 1974).

and experimental work. There is a certain similarity with the Catalan process (Åkerman 1844).

The heat balance

The adiabatic temperature is highly influenced by the CO₂/CO ratio created by the combustion of carbon. If equilibrium is prevailing when excess carbon burns in air, a gas mixture containing CO and N₂ is created, giving a temperature of 1200°C. - If carbon(charcoal) is preheated in a shaft by hot gas, the adiabatic temperature may increase to about 1350°C. Higher temperatures reported can only be due to CO₂-generation or other measures, such as preheating of the air³.

Reactions in the shaft

A successful extraction and separation of slag from the metal in the bloomy process is dependent on a gradual reduction of Fe₂O₃ to lower oxides and metal in the shaft. This reduction is taking place as long as the ore has maintained its great surface area, characteristic for a precipitated oxide. This is the principle of "reduction before melting". If the opposite takes place, ie sintering or fusion of the ore at a low temperature, prior to reduction, the reactivity is greatly reduced. Little or no metal is achieved. This in turn may lead to a high liquidus temperature for the slag. Even at 1200°C the slag will contain also solid Fe₃O₄, and no proper separation occurs.

The actual finds

In Mid-Norway, a large number of bloomeries have been reported during the last 10 years. They are situated near the tree line and are mostly in a well preserved condition. ¹⁴C analysis has placed the three methods between 200 BC - 600 AD (I), 700 - 1300 AD (II) and 1400 - 1850 AD (III) (Espelund 1988). The furnaces are outlined in figure 4.

Without doubt, the technology of period I is the most striking. At a normal site from eg 200 AD four furnaces are placed in a regular pattern next to each other along a terrace facing a river. The slag heap in front of every furnace contains about 10 tons of slag. Some hundred sites have been registered, with a possible total of at least 5000 tons of slag. It is likely that a total amount of 20 000 tons of slag and 10 000 tons of metal was produced during this period. A characteristic site is shown in figure 5.

The sites from the next periods are less spectacular, with individual furnaces, slag heaps in the range 1 - 10 tons and no striking topographical feature. As reported finds they are definitely underrepresented.

The slag from period I will be discussed in detail:

Slag pieces are found in all sizes with one dimension not exceeding about 40 cm. Visual examination of the surface shows a large number of cavities with the grain structure of wood, at other sites the cavities have a less evident surface character. The slag also has a flow pattern, some times with a reddish colour. Certain parts have a smooth surface, like candle wax, that has solidified on a cold surface. In situ slag in each furnace is of the same kind. A characteristic piece of slag is shown in figure 6.

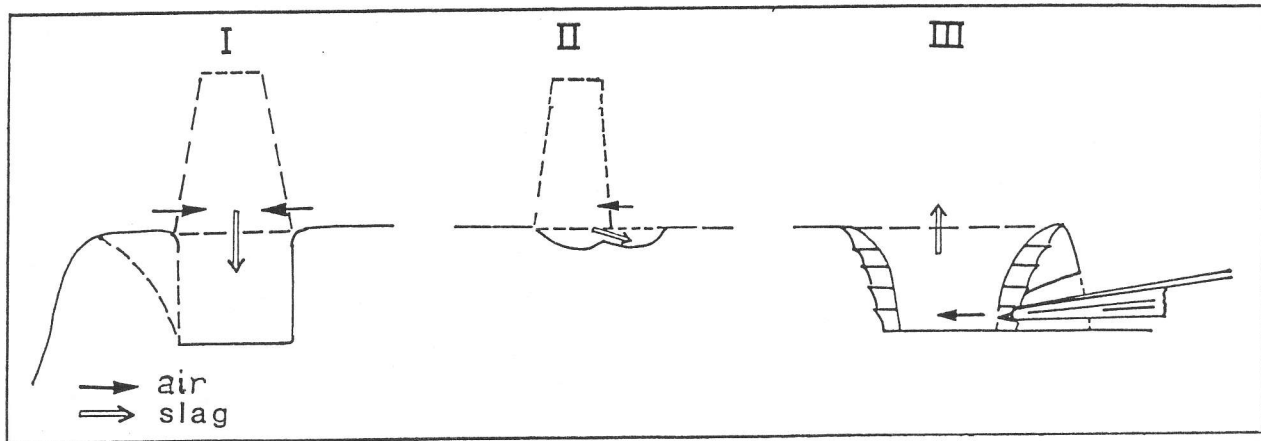


Fig 4. The three furnace types in Mid - Norway (schematic). I. The "Heglesvollen" furnace (200 BC - 600 AD) II. The Medieval furnace (700 - 1300 AD) III. The "Evenstad" furnace (1400 - 1830).

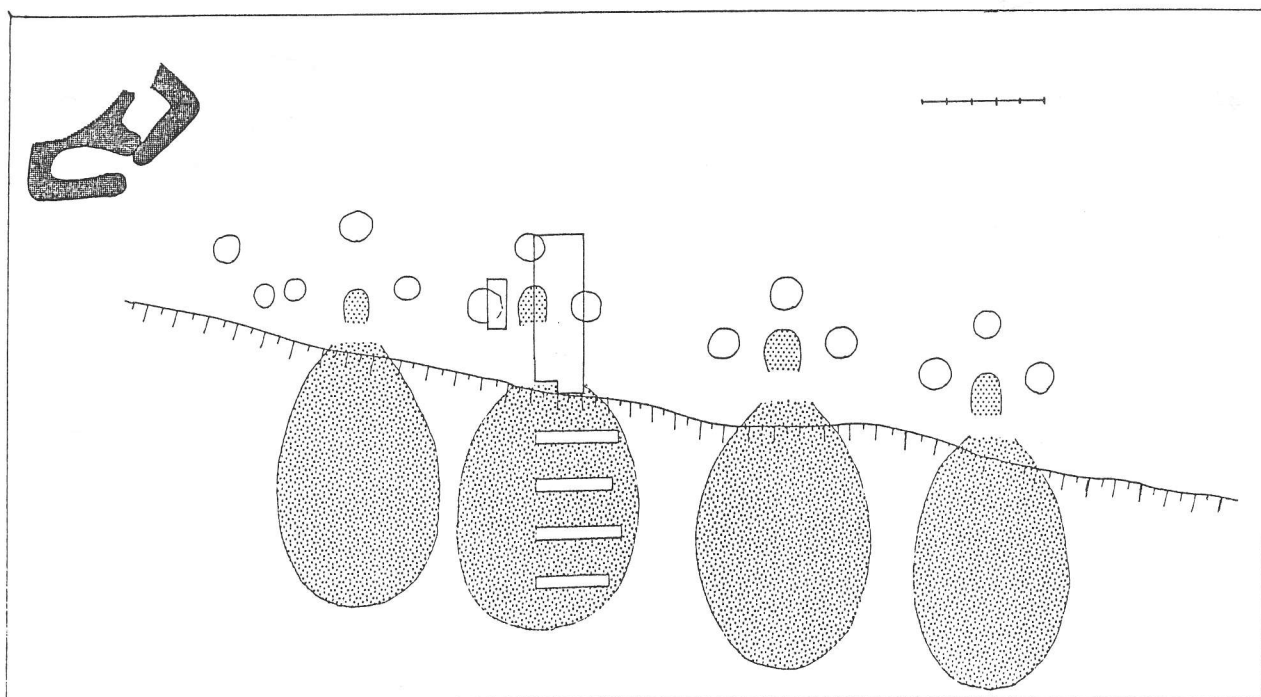


Fig 5. The characteristic layout of a smelting site from the Roman iron age in Mid-Norway (Vårhussetra, Hessdalen). Drawing: L.F. Stenvik.

Evidently the grain structure can stem from charcoal or from wood. In principle such pieces can have disappeared in two different ways: 1) charcoal by combustion 2) wood by dry calcination and combustion or 3) wood by decay.

Several features prove that pieces of *wood*, made with an axe or broken by hand were suddenly submerged by liquid slag, which immediately solidified (Espelund 1989b). The combination dry wood - liquid slag tells that the slag was created in an upper part of the furnace while the wood was present in a lower and cold part, not affected by the combustion and reduction processes higher up.

The excavation of the furnace itself and the slag heaps tells that the horseshoe-like, well preserved stone-lined "furnace" thus acted as a recipient for liquid slag. This pit was filled initially with pieces of wood, placed in a criss-cross manner, which had three purposes: 1) to form a "platform" for the charge in the shaft and 2) to provide space for liquid slag, 3) to make it possible to break the slag in the pit into pieces that could be removed through the vertical slot, so that the pit could be used anew. The pieces of wood remaining in the solid slag later disappeared by decay.

Among the debris are found broken pieces of burnt

clay, also affected by liquid slag. These stem from the shaft, which was placed above ground.

There is one important consequence of this investigation, which is based upon visual examination of the slag: *The drainage of a considerable amount of slag (up to 150 kg) can only be conceived of as the final part of a step-wise process.* Slag from a continuous operation would be created as droplets. In the present case the slag entered the pit in "integral" amounts.

The idea of a step-wise process is supported by the fact that normally four furnaces are grouped together. One can imagine a group of people, say 10 persons, working at the site. The four furnaces will be in different situations (like the pistons in an engine). In furnace no 1 charcoal may be made while in furnace no 2 reduction takes place at a moderate temperature. In furnace no 3 decantation of slag by some kind of superheating is achieved while furnace no 4 is being repaired after removal of the bloom and the slag.

Turning our attention to technology no III, it is well described in Scandinavian literature from the 18th century by both laymen and metallurgists (eg Evenstad 1790, Rinman 1794). A large number of well-preserved furnaces in West Sweden and East Norway prove that the descriptions are in accordance with real practice. Since 1982 successful smelting has been made in this furnace, using the description from 1782 by Ole Evenstad (Berre 1987).

The furnaces were built from stone and have the shape of a truncated cone. Only the front is free, with access for the air from bellows through a conical tube. The three other sides are recovered with sand and earth.

The normal practice consists of 1: partial combustion of wood, leaving the furnace full of hot charcoal. 2: three additions of ore at intervals in the relative amounts 3:2:1 while the use of bellows is gradually increased 3: removal of slag and metal with a shovel. The metal is consolidated while hot on an anvil. The process is evidently *step-wise*.

It is reasonable to point out that the ore initially is kept at a moderate temperature and that the last amount of ore is added when only little charcoal is left. This tells that *a high FeO-activity is aimed at*, in accordance with the theory presented above.

The slag from this process is varying in size, appear

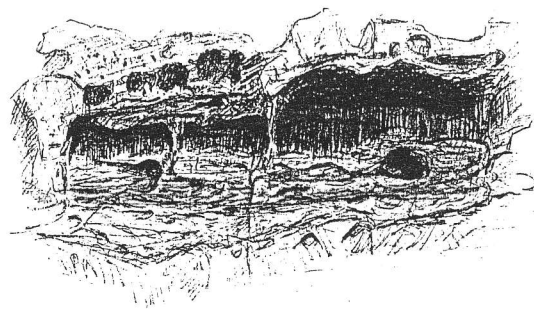


Fig 6. A characteristic piece of slag from period I with impressions of wood.

ance and composition. Some metal is often imbedded in the slag. In contrast to process I, the slag is hardly "digested". Accordingly, each piece of slag shows great porosity, as if the reduction process was interrupted. The carbon content of the metal varies between about 0.1 and 1%. One trouble with this process is the poor separation of metal and slag.

An archaeological excavation of the furnace remains and the slag could not result in the information given in the literature.

The slag from process II is invariably as flat cakes, with a worm-like pattern on one side and impressions of sand and gravel on the other. The slag stems from a shaft furnace, placed on the ground, provided with a little "pond" in front. Together with the slag are found also concave-convex slag cakes. They evidently represent accretions on the inside of the furnace.

The process has one feature in common with the first: the slag is "digested" and it has played an active rôle for the control of the carbon content.

The author has claimed that some step-wise treatment also characterises this process (Espelund 1989). Recent experiments seem to indicate that this furnace can be operated almost continuously (Jakobsen 1990). It appears that this requires an extremely high reducibility of the ore, so that "reduction before melting" is achieved during the passage of the solid charge through the furnace.

So far only the external character has been examined. It is highly advisable as a next step to make a plane cut of the slag. Such a cut is representative, and will reveal the true character of the cavities as well as any imbedded metal. Such cuts has led to the identification of a different process during the Ro-

man iron age in the region around Lillehammer, possibly extending from the Baltic Sea to Hardangervidda.

Furnace operation - an archaeo-metallurgical integration

In his book from 1891, Ludwig Beck states that "die alten Germanen" had two types of furnaces: the shaft furnace and the "Rennherd". Out of the first the "Stuckofen" and the iron blast furnace developed, while the latter may be said to be a forerunner of the hearth furnace for steelmaking.

Now returning to figure 2. Evidently two paths to malleable iron are conceivable:

a) a low-temperature reduction to carbon-free iron as a first step (fig 2b), followed by heating to temperatures, which warrant sintering of metallic particles and liquation of the slag. Carburization of the metal in the second part is avoided by means of a sufficient amount of FeO-rich slag present. The process is run as a batch process with *temperature-slag control*.

As a border case, it is conceivable to run this process continuously in a shaft furnace, provided the temperature-time pattern permits reduction before melting.

b) the direct use of the principle outlined in fig. 1 c. A slag with a high content of FeO must be present during the process, while no temperature control is aimed at. The process is run by means of *slag control*. To warrant a high FeO-content, low furnaces are used, so that ore added to the furnace immediately reacts with the slag.

The finds in Norway represent these two types of processes. The process No I (the Heglesvollen furnace) represents the first type while No III (the Evenstad furnace) represents the latter.

Other questions

- 1) How efficient was the extraction of iron from the ore?
- 2) How can we calculate the corresponding amount of iron?

The bloomery process in Norway was based upon bog iron ore, a precipitated substance (Espelund 1990). For our conditions, only Fe and sometimes Mn, having several valency states and a tendency for

complex formation, represent metals and take part in this process. Normally bog iron ore is contaminated by sand particles, causing a certain content of SiO₂ (from quartz and feldspar) and (less) Al₂O₃ (from feldspar) while CaO, MgO and alkali usually are below 1%. During roasting, crystal water and harmful sulfide is eliminated. As shown below, an acceptable upper limit for SiO₂ in the roasted ore with Fe₂O₃ lies around 20%. 10% is more favourable for a reasonable output of metallic iron.

Because of their stability, no reduction of SiO₂, MnO and Al₂O₃ takes place in the bloomery process. Thus the ratio between these three elements is maintained. (The effect of dissolved shaft material and ash from the charcoal is disregarded here).

The main constituents in the solid slag are fayalite Fe₂SiO₄, wustite FeO and glass or hercynite FeO•Al₂O₃. In the hearth of the bloomery furnace it was a homogenous liquid with mainly Fe²⁺- and SiO₄⁴⁻ ions, and with a high FeO-activity for control of the C-content of the metal. No exact calculation of the FeO-activity other than the molar ratio FeO:SiO₂ can be found. If near 2, it is likely that the slag in question is a bloomery slag. Alternatively it is a bloomery slag squeezed out of the bloom during primary smelting. The latter was evident at the medieval metalworks at Mellageret in Trondheim (Espelund 1989).

This implies that a comparison between different slags in terms of FeO-content has little value. The crucial value is *the ratio FeO:SiO₂*, with minor corrections for MnO and alkali, while the amphoteric Al₂O₃ can be disregarded. The author has presented this view as a diagram (Espelund 1987). Slags with a high content of Al₂O₃ and a low ratio FeO/SiO₂ can hardly be bloomery slags (Espelund 1989).

The final question about the amount of iron produced can be solved by making two equations, one for Fe and one for SiO₂ in the slag and in the roasted ore. The trouble is the ore: how to ascertain that the ore represents the slag in question?

Beside evidence from the excavation at the site, similar equations for Fe+MnO and Fe+Al₂O₃ should give an identical result to the one obtained for Fe+SiO₂. If not, we know that the ore was not used for the slag in question.

Summary

The bloomery process was complex. Nobody can

understand it on the basis of the furnace remains alone. In the present paper the great potential of the slag is presented, together with metallurgical theory, written documents, and, with due concern for the results from excavations.

The finds in Norway correspond to the two processes mentioned by an authority on the subject from the last century (Beck 1891). This is supported by thermodynamic reasoning, phase analysis and written documents.

This paper also emphasizes that the blast furnace represented no great innovation, other than in size.

It required a much greater *infrastructure* than the bloomery process, hardly a greater knowledge.

¹ A bloomery slag is represented by the "fayalite area" of the system FeO - Fe₂O₃ - SiO₂, presented in eg Muan & Osborn: Phase Equilibria among Oxides in Steelmaking. 1965.

² The high and constant value for the molar ratio FeO/SiO₂ in most types of bloomery slags proves that the composition is far from equilibrium with carbon, and that a slag control of the carbon content in the metal is prevailing.

³ This calculation is like normal accounting, with enthalpies of combustion and possible preheating on the "credit" side and enthalpies in the combustion products on the "debit" side.

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