Understanding the Walloon method of iron refining: archaeological and archaeometric experiments, phase 1

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ABSTRACT: The Walloon method of refining pig (cast) iron is one of the first extensions of the blast furnace process, which appears between the 14th and 16th centuries in northern Europe. This study investigates the production capacity of Walloon refining and in particular its handling of high-phosphorus pig iron through a series of experiments. A Walloon hearth was built to refine high-phosphorus pig iron, using data on the refining process found in archaeological sources and historical documents from the 18th century onwards. The chemical composition and the structure of the metals and slag produced during refining have been determined. A similar yield to those mentioned in historical sources has been obtained. These experiments suggest specific techniques enabling high-phosphorus pig iron to be refined efficiently. Finally, the results point out the importance of the metal-slag reaction phase in obtaining a carbon-free and phosphorus-free material.

Introduction

Between the 14th and 16th centuries, the blast furnace process, also referred to as indirect reduction, appeared and spread in northern Europe, gradually supplanting the earlier bloomery. In contrast with the latter, indirect reduction is a two-step process. Iron ore is first reduced in a blast furnace, producing molten pig iron, an iron alloy containing several percent carbon, silicon and phosphorus. The pig iron is then refined in a finery forge, transformed through the oxidation of carbon and silicon into either iron or steel. The bloom thus obtained is then compacted using a water-powered hammer. One of the first variants of this operation is the Walloon method. Emerging in Wallonia early in the 14th century (Awty 2006; 2007), it spread southward to the French regions of Champagne and Nivernais (Belhoste and Leon 1996) late in the 14th century and into numerous parts of Normandy from 1450 onwards (Belhoste 2001), before crossing the Channel into southern England (Belhoste *et al* 1991).

The aim of the present paper, however, is not to revisit in detail either the history or the chronology of indirect reduction and refining, but to examine what will henceforth be referred to as the 'stabilized' Walloon method: a blast furnace, two hearths – the finery and the chafery – and a water-powered hammer. A number of researchers have published articles presenting interesting data on the construction and the spatial organization of the work areas associated with the early blast furnace. Excavations of blast furnaces and a finery forge were conducted in the Weald, in England, by Crossley and Bedwin (Crossley 1972; 1975a; Bedwin 1978; 1980); a Welsh blast furnace, dating from the 16th century was uncovered by Peter Crew (Crew and Williams 1985) and the Marsolle blast furnace in Belgium has been the subject of a number of studies (Weber 1997). Yet in spite of this work, concrete information on the operation of the finery forge remains scanty.

Over the past 15 years, Danielle Arribet-Deroin has conducted excavations at the Glinet blast furnace and finery, located in Normandy and active during the 15th and 16th centuries (Arribet-Deroin 2001; 2010; Dillmann *et al* 2007). Within the site the finery, the water-powered hammer, the anvil block and a likely chafery hearth have been located. While the finery hearth has yet to be entirely excavated, numerous refining-furnace-bottom cakes clearly linked to the refining process have been found. As part of this programme a multidisciplinary approach was used to understand the course of the refining process, beyond the site's spatial and technical organization. Two goals were pursued: determining, on the one hand, the chemical composition and the structure of the metals and slag produced during refining and on the other hand understanding the steps and techniques used during refining. Indeed, few historical documents for the period have been found. Metallographic analyses of pig iron and refined metal found at Glinet (Dillmann *et al* 2007) have established that high-phosphorus pig iron, whose composition closely matches that of the iron ore, was produced in the Glinet furnace. They also show that a high-phosphorus iron, virtually free of carbon (< 0.02wt% C), was obtained through refining. Yet while numerous materials and refined products have been analyzed at Glinet, many questions remain regarding the refining operations and the details of treating high-phosphorus pig iron (Lechevallier *et al* 2000).

A limited number of descriptions of refining, which complement the archeological data, can be found in historical sources. The Walloon method of refining, and other related methods, are described by Buchwald (2008), Den Ouden (1981), Le Coze (2008), Mackenzie and Whiteman (2006) and Tylecote (1992). They show that fining takes place in an open hearth in which controlled high-temperature oxidation (at 1100–1300°C) enables carbon as well as silicon and phosphorus to be eliminated from the pig iron. Part of the oxidation reaction occurs in the tuyère's blast, which also serves to feed air for charcoal combustion into the hearth. As the operation proceeds, the slag that accumulates in the finery hearth also seems to play an important role in the oxidation of certain elements found in the pig iron, thus affecting refining yields. Thermodynamic data indicates that silicon is the first of the elements in pig iron to oxidize (Philibert *et al* 1998). Carbon, phosphorus and iron come next, their order depending for the most part on local thermodynamic conditions (temperatures and partial pressure) as well as slag composition. We know, for example, that certain iron phosphates form at high temperatures through phosphorus oxidation, but can be reduced through a reaction with carbon. To understand completely the impact of the appearance of the indirect process on late medieval and modern economies, it is essential to understand the production potential of the Walloon process and in particular how it handled high-phosphorus pig iron. To do so, it is necessary to study all the above parameters as well as the methods and techniques of iron-workers of the late Middle Ages and the modern era.

Another important point to be considered here is the production capacity of the Walloon refining process when first introduced. Crossley (1975b, 187), gives an indication of pig iron/iron refining yields during the second half of the 16th century. In 1563, for example, one document mentions a yield of three tons of sows [the term used for large pigs of cast iron that we will continue using throughout the rest of the paper] for two tons of iron. Other sources give us more accurate data for later periods, especially for the 18th century, at which time blast furnace yields were clearly superior to those of the bloomery, all other things being equal. In particular, several yields were recorded by Le Coze (2008). Diderot (1751) mentions that 'de vingt-six livres de fer crud, on n'en retire que treize d'acier' [26 pounds of crude iron yields only 13 pounds of steel], whereas Bouchu (Bouchu and Courtivon 1774) says that 'Le déchet ordinaire de la fonte réduite en fer, est au moins d'un tiers, quinze cent de fonte pour un mille de fer' [The ordinary waste of pig iron reduced to iron is at least one third, 1500 parts pig iron to 1000 parts iron]. Buchwald (2008, 278), quoting Angerstein, indicates that 1600 pounds of pig iron are needed to obtain 1000 pounds of soft iron. Dumas (1833) gives a yield of 71% for the early 19th century. Note that the above yields appear to have been given after fining and compacting with a water-powered hammer, which also cause some metal loss. For the 15th and early 16th centuries no precise data is available. Regarding production volumes, historical sources for bloomery furnaces in the Pyrenees in the 16th century (Cantelaube and Verna 2000) indicate a surprisingly high production capacity, one that could even have competed with early blast furnaces. Considering the competition between the two methods at the time, as well as the continuing use of the direct method in certain regions, these points are significant. Indeed, the great irregularity of the (early) blast furnace's performance combined with the bottleneck in refining, could have initially led to similar production capacities between the direct and the indirect methods, at least prior to the emergence of the double-hearthed Walloon forge.

To complete such archaeological and historical data through a series of experiments and to address some of these questions such as yields, we set out to build a Walloon hearth and to conduct a series of refining operations using high-phosphorus pig iron. To do so, we used archaeological data on the refining process from sites such as Glinet (the dimensions of the refining cakes, in particular, providing indications as to hearth size), and historical documents from the 18th century onward. Thus after an initial calibration campaign in 2006 when the most effective refining techniques were identified, three more experiments were carried out in 2007 within the 'Paleo-Metallurgy' experimental programme at Melle, directed by Florian Téreygeol. After a brief presentation of the post-15th century historical data which has helped us to understand the practices and principles of Walloon refining, the present paper will introduce the key results of one of our Walloon method re-enactments.

Historical data

There is virtually no historical data contemporary with the site at Glinet providing accurate information on the refining process. Such a site is not mentioned in Agricola's *De Re Metallica* (1556). Some authors (Williams 2003) believe that Vannocio Biringuccio is referring to refining when he explains, in a passage from *La Pirotechnia* (1540), how to obtain steel by a simultaneous treatment and stirring of pig-iron and iron. Biringuccio's text however is complex and its interpretation is still open to debate (Dillmann *et al* 2010). In Nicolas Bourbon's poem *Paternae ferrariae tumultuaria descriptio* (Bourbon 1529, fol LIII v) refining is succinctly described as a process in which pig iron, which is not 'actual iron' (*germanum ferrum*), is improved: 'to do so it must be transformed, improved a second time in a large furnace to turn it into malleable iron (*ferrum plicatile*). When it is gathered into a ball (*in globulos*), energetic men take it up, flatten it and smooth it'. Certain paintings by Henri Blès (*c*1490-*c*1550) also depict this process (Fig 1). But although they do shed valuable light on our understanding of the layout of the work area (for example, the fact that the hearth is located approximately 80cm from the ground), such iconographic sources do not clarify the technical aspects of the process.

The first detailed documents describing refining date from the 18th century. The notebooks of chemist Jean Hellot (1685-1766) (Birembaut and Tuillier 1966) describe in detail refining experiments that he had conducted according to the works of Réaumur. The finery hearth for producing iron is described as being made of five iron plates forming a rectangle about 70-75cm on each side. The tuyère is placed on one of the long sides, the iron plate on the side in question being slightly elevated. On the opposite side, a tap hole at the base of the hearth allows a portion of the slag to be drawn off. The author gives us a good description of the process:

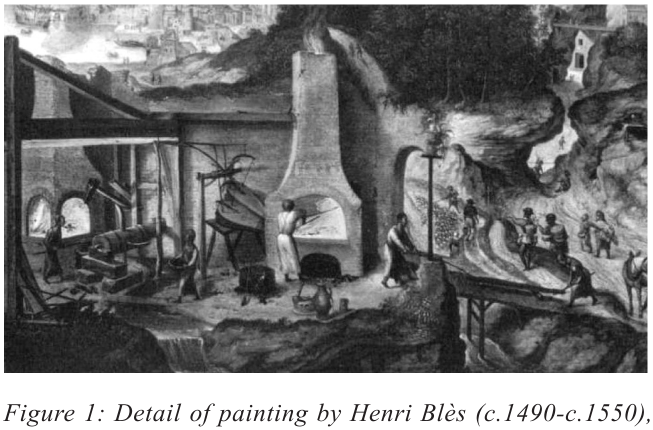


Figure 1: Detail of painting by Henri Blès (c.1490-c.1550), 'Landscape with Forge', Vaduz, collection Prince of Liechtenstein. The two men on the right are moving a sow to the finery.

> 'La gueuse, échauffée jusqu'à un certain point, se ramollit mais elle ne fond pas parfaitement. Elle laisse de temps en temps tomber de grosses gouttes dans le fond de l'ouvrage comme on laisserait tomber un morceau de cire d'Espagne qu'on tiendrait sur une bougie. Les gouttes qui forment la loupe sont pourtant moins fluides, elles ont la consistance d'une pâte molle. Ce sont ces gouttes qui exercent l'affineur. Il est debout devant l'affinerie et muni d'un long ringard dont il a fait entrer un bout dans l'ouvrage par-dessus ses bords. A mesure que les gouttes tombent, il les remue, il les agite, il les rassemble, il les pétrit pour ainsi dire. Tantôt il pousse son ringard vers l'un des côtés de l'ouvrage tantôt vers l'autre. Plus souvent il élève le bout qui est dans l'ouvrage pour soulever la fonte en fusion. Alors, avec ses deux mains, il s'appuie sur le bout qui est en dehors. Quelquefois même il s'assied dessus. Il a besoin de faire usage de ses forces car de toutes ces gouttes, il ne forme qu'une seule masse appelée loupe dans les affineries. [The sow, heated to a certain point, softens but does not completely melt. Every now and then large droplets fall to the bottom of the hearth, the way bits of Spanish wax would fall from a candle. The droplets, which make up the bloom, however, are not as fluid, having the consistency of soft dough. The finer, standing in front of the finery hearth holding a long rod that he inserts over the side and into the hearth, works the drops. As the droplets fall, he opens them and turns them, gathering them and kneading them, so to speak, into a lump. At times he pushes the rabble to one side of the works, at times to the other. He frequently picks up the molten pig iron by raising the end inside the works. Then with both hands, he presses down on the end not in the works. Sometimes he even sits on it. He needs to use all of his strength because a single mass has now been formed, called a bloom in fineries, made out of all the droplets].

In a memoir on the forges and furnaces of the Berry and the Nivernais (d'Angenoust and de Wendel 1769) the process is vividly described:

> 'La gueuse fond, et à mesure que tombant dans le creuset elle s'amoncèle en petits pelotons, le valet

> d'affinerie les jette vers le contre-vent ; lorsqu'il juge qu'il y a assès [sic] de matière pour former une Loupe, il livre l'ouvrage au maître affineur. Celui-ci reprend tous les morceaux que le valet avait jetés au contre-vent et les porte sur le charbon au dessus du vent des soufflets, ils descendent lentement en consistance pâteuse et sans se liquéfier sur la taque du fond ; le maître va les y chercher avec un ringard et les rapporte une seconde fois sur le vent, pour lors à mesure qu'ils descendent, il cherche à les rassembler au fond du creuset en une seule masse, et c'est ce qu'on appelle ravaler' [The sow melts, and as it falls into the crucible it piles up and forms little balls, the finer's assistant tosses them against the air blast; when he determines that there is enough matter to make a bloom, he gives the work to the master finer. This latter gathers all of the lumps that the assistant had tossed into the wind and places them in the coal above the bellows blast, they slowly sink to the bottom of the hearth, in a doughy consistency and without liquefying; the master picks them up with a rabble and places them in the blast a second time as they flow downward, he tries to gather them up into a single mass in the bottom of the hearth …].

Svedenborg, in his 1735 *Treatise on Iron* included in a work by Bouchu and Courtivon (1774), indicates that the temperature of the finery hearth must not be too high:

> 'The iron must also be worked in discontinuation for fear of its becoming too thin, that, in such a state, it be overly burnt or annealed... Care is taken that the liquation be not too thin. So as not to lose a part of the iron in the bloom, nor to turn it into slag or dross, the finer is careful to temper the fire when too strong'.

Here we find the above-mentioned competition between the oxidation of iron and that of the other components of pig iron. Svedenborg also discusses the role of slag:

> 'The melting of the slag helps the iron to melt... thanks to the slag, the iron is not only properly liquefied, it is stripped and separated from harmful elements, becoming molten, malleable and purified... Forgemen, moreover, with the help of slag, are in the habit of rendering the worst and rawest iron not only molten, but malleable and ductile'.

The role of slag in the refining process is clearly understood here, suggesting furthermore the idea of controlling its composition and using additives to improve the refining process. These additives are clearly mentioned by Hellot (Birembaut and Tuillier 1966):

> 'Il y a cependant des circonstances où l'on emploie d'autres laitiers, on jette du sable fondant, ou même des cailloux dans l'affinerie' [There are nonetheless situations in which other forms of slag are used, whence melted sand or even pebbles are thrown into the finery].

Grignon, in 1755, gives unmistakable evidence of limestone being added to the finery hearth to facilitate the working of the iron and to improve its quality:

> 'l'on jette dans les affineries des graviers de rivière pour adoucir le fer. Cette substance calcaire fait les mêmes fonctions que dans les fourneaux de fonderie; elle absorbe les soufres et les sels surabondants, et entame les métaux, facilite le travail du fer nerveux et plus consistant' [River gravel is thrown into the finery hearths to soften the iron. This calcareous substance serves the same purpose as it does in the foundry furnace; it absorbs excess sulphur and salt and eats into the metals, facilitating the working of a more vigorous and solid iron].

Similar details on refining methods are found in Diderot and d'Alembert's encyclopedia (1751).

Lastly, interesting descriptions of the Walloon method can be found in chemical treatises of the first half of the 19th century. At that time, puddling, which takes place in a reverberatory furnace, was a new refining method. Numerous forges, however, particularly in France, still refined cast iron using the Walloon method. Chemist Jean-Baptiste Dumas in his 1833 treatise states that hearth dimensions are 84 by 64cm per side and 18 to 23cm deep. The tuyère is placed in the hearth at a depth of 10cm; its cross section measures 52 by 33mm. Dumas also notes that slag from previous operations is placed in the hearth and is melted at the same time as the pig iron. Following the fusion phase, the actual refining begins. The metallic mass is raised to the top several times, divided into various portions, placed under an air blast and re-melted. These descriptions indicate that the metal must be worked and mixed several times before the complete decarburizing of the material.

We have referred to such historical data, as it gives an idea of both the techniques used by the forgemen as well as the positioning of the tuyère and the use of slag, information used during our experimental reconstruction whenever archaeological data was lacking.

Reconstructing the finery hearth

A hearth measuring 65 by 85 by 30cm was built with five plates of XC38 carbon steel. Its dimensions were deduced from the size of refining cakes found at the Glinet site (Dillmann *et al* 2007). An opening was made at the base of the hearth in the side opposite the tuyère

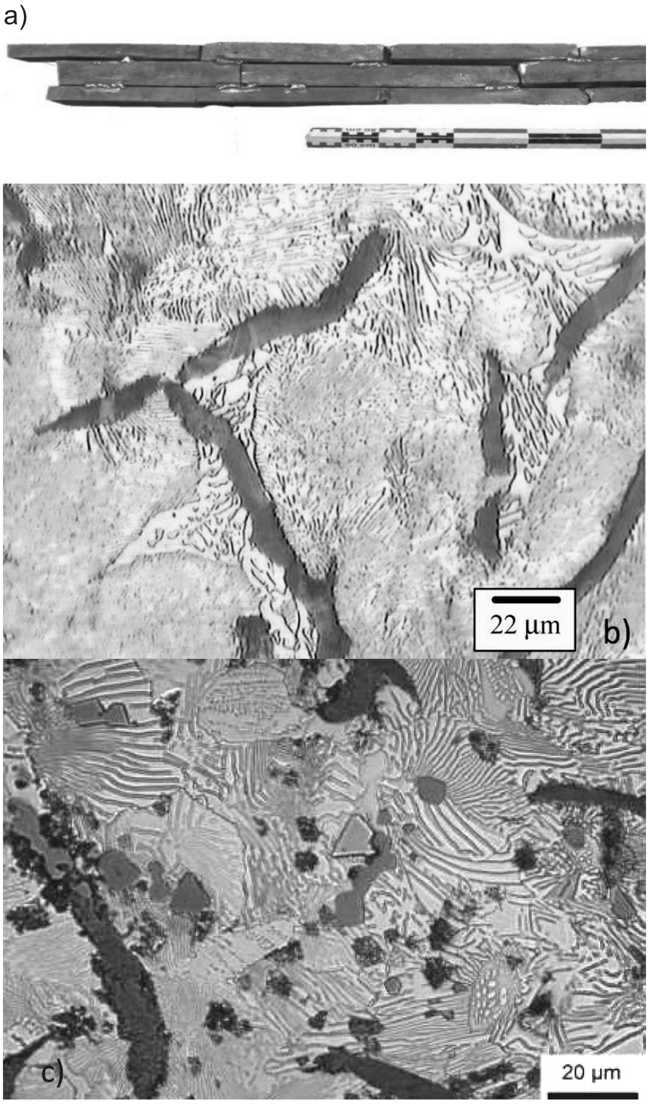


Figure 2: a) reconstituted sow, b) microstructure of an archeological iron sample from Glinet (Dillmann et al 2007), c) microstructure of the reconstituted sow used in the experimental refining.

to tap out slag. The hearth was placed about 90cm from the ground, on a support made of cinder blocks. A 15-20cm long segment of a steel tuyère was inserted into the hearth at an angle of about 30° to the horizontal; it was connected to a mechanical bellows whose speed could be altered. The strength of the tuyère blast was measured with an anemometer at varying bellows speeds.

Nature of the pig iron

As we were not able to cast a pig iron sow into a single bar one metre long, we made one out of rectilinear pieces of discarded cast iron gates (Fig 2a), of 5 by 5cm section, with a pig iron welding rod (4wt% C, 4wt% Si, elements other than Fe <0.5wt%). Prior to this, we had verified the modern iron's compositional and structural compatibility with archaeological iron samples found at the Glinet site. The reconstituted sow used in the refining weighed 42kg.

Metallographic analysis of the material showed that it was grey cast iron with lamellar graphite and a pearlitic matrix containing phosphorous eutectics, the structure and composition of which were very similar to the pig iron produced in the blast furnace at Glinet (Figs 2b and 2c). Carbon content was determined by quantitative metallography. Iron, silicon, sulphur and phosphorus levels were determined by EDS spectrometry in a scanning electron microscope (SEM) run at 15kV, averaged over the entire surface of the section, and normalized by taking into account the carbon content. No other major element was detected using these techniques. Small angular precipitates of manganese sulphides, up to a dozen microns in size, were detected in the modern

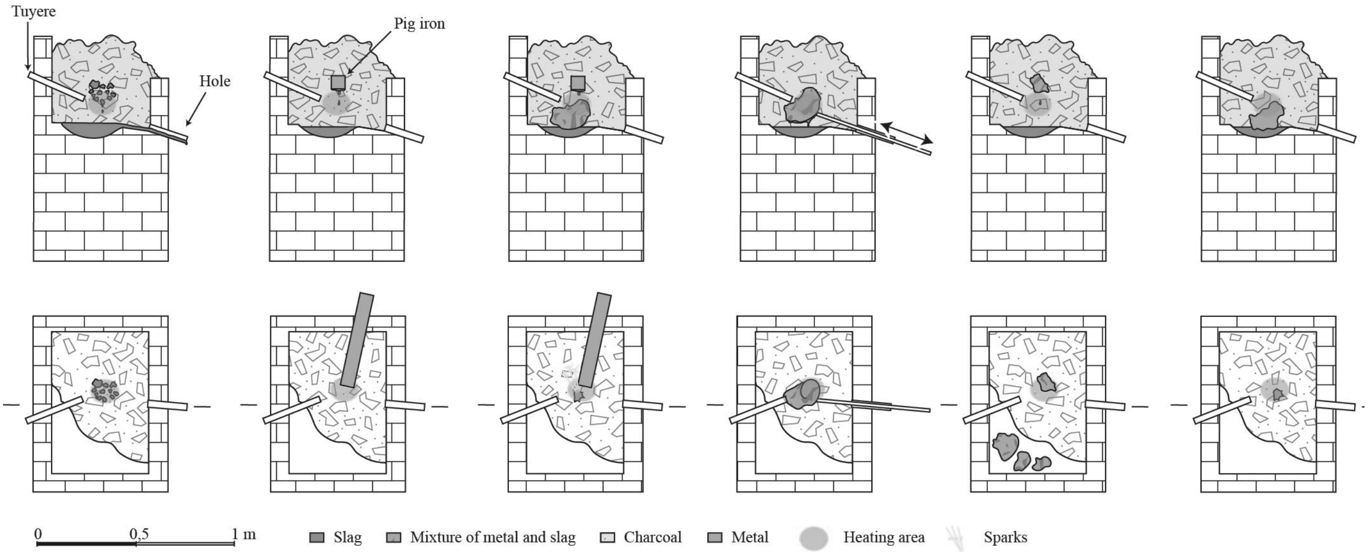


Figure 3: Sequencing of refining operations in section and in plan (drawing S. Bauvais)

Figure 4 : Different experimental phases, a) position of the sow and the tuyère, b) progression of the sow as it melts, c) and d) stirring and working phase, e) and f) refining bloom sampling.

cast iron as well as precipitates (at the centre of Fig 2c) containing titanium, vanadium and chromium, presumably carbides or carbonitrides (Dillmann *et al* 2002). Neither manganese, vanadium nor titanium, however, were detected during the macroscopic analyses of the cast iron by EDS spectrometry, the detection limit in this matrix being around 0.5wt%.

Experiments and sampling

The three experiments conducted in 2007 followed the refining process steps often described in historical sources. Namely, iron ore is smelted and then stirred, chiefly to raise the mass of metal to the level of the tuyère (Fig 3). The main difference between the first experiment and the two that followed is that during the last two, the bed of slag formed during the previous run was kept in the hearth and used for refining, a practice inferred from historical sources. Obviously, we were not able to do this during the first run, which was carried out without the use of a slag bed. Except for slag, no further additives were used during the refining process. We only re-enacted the refining stage, forgoing the fining and hammering stage that normally would have followed to consolidate the bloom obtained during refining. Lastly, the results presented in the rest of this paper relate only to the second experiment, as it was the only one that was subject to sampling throughout the entire process.

At the start of the experiment the sow (sample MEL07-08) is placed in the hearth filled with charcoal, its end within a few centimetres of the tuyère (Fig 4a), the hottest area in the hearth. The sow is covered with charcoal and the hearth is fired (Fig 4b). After an hour or so, the sow begins to melt. As the melting progresses the sow is moved forward into the hearth. The operation lasts about three hours; sample MEL07-09 was taken from the mass that melted in the bottom of the hearth during this phase. The fusion of the sow is stopped after 27kg of pig iron has been consumed; the rest is removed from the hearth. Next begins the actual stirring and working phase (Fig 4c). The mass of melted metal is divided into several parts and raised repeatedly to the level of the tuyère, an operation that lasts about two hours. Sample MEL07-10 was taken after the metal had passed in front of the tuyère a second time, whereas sample MEL07-13 came from the metallic mass at the end of the operation (Fig 5). Note that during the stirring phase, a bubbling was seen, typical of what was most likely an exothermic reaction with the slag at the bottom of the hearth. Sample MEL07-10 was taken before the bubbling began. At the end of the experiment, despite no refining cake being found, several centimetre-sized slag pieces were found mixed with the charcoal in the hearth.

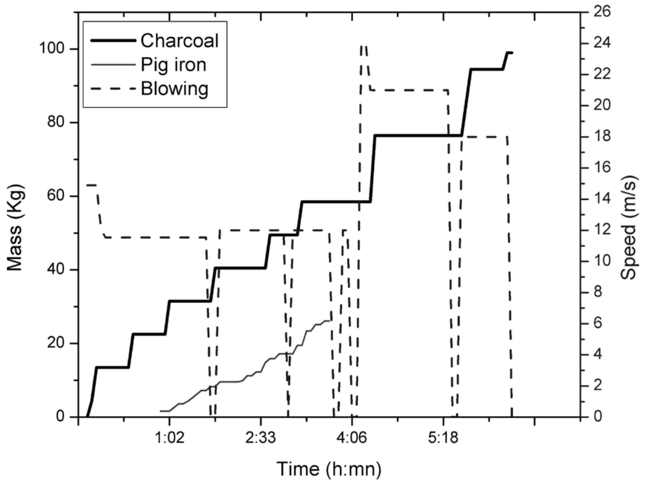


Figure 5: Quantities of sow and charcoal placed in the hearth and air flow for the duration of experiment No 2. The time at which samples were taken is shown.

The total weight of refined metal when finished was 16.2kg. 27kg of pig iron had initially been placed in the furnace. The loss material was dispersed in the slag mix with the charcoal that could not be weighed. Considering that all the pig iron placed in the hearth was decarburized (see below), the yield of the operation is 60%, similar to those mentioned by Diderot (50%) and Bouchu (66%) in the 18th century and slightly inferior to that mentioned by Dumas (71%) in the 19th century. However, the values given by these authors took into account the consolidating and fining operations, which in our case, could not be evaluated, given the wide dispersion of centimetre-sized pieces and of the presence of slag in the hearth from previous operations.

Metallographic and chemical analysis

Samples taken during each of the refining phases show various structures, with carbon levels decreasing as refining time increased. Thus sample MEL07-09, taken after a single passage before the tuyère, still shows a structure of grey cast iron with a few zones of white cast iron (Fig 6) which in this context can be associated with decarburization. Indeed, a variation in carbon

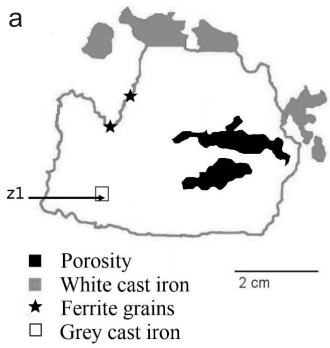
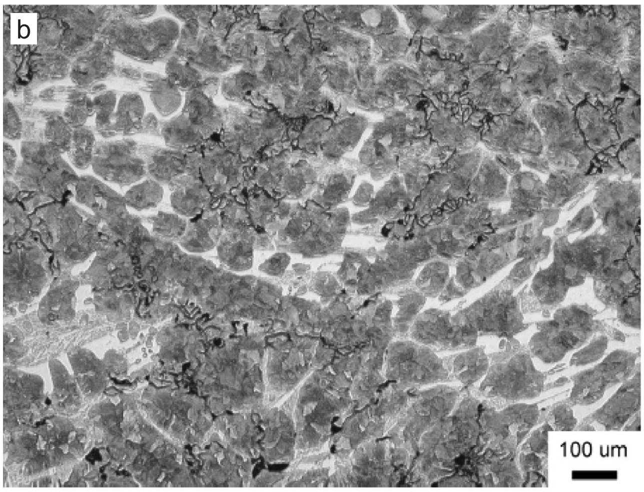


Figure 6:
(a) Metallographic section and structural distribution of the sample MEL07-09;

(b) optical micrograph of zone 1 of sample MEL07-09 after nital etching.



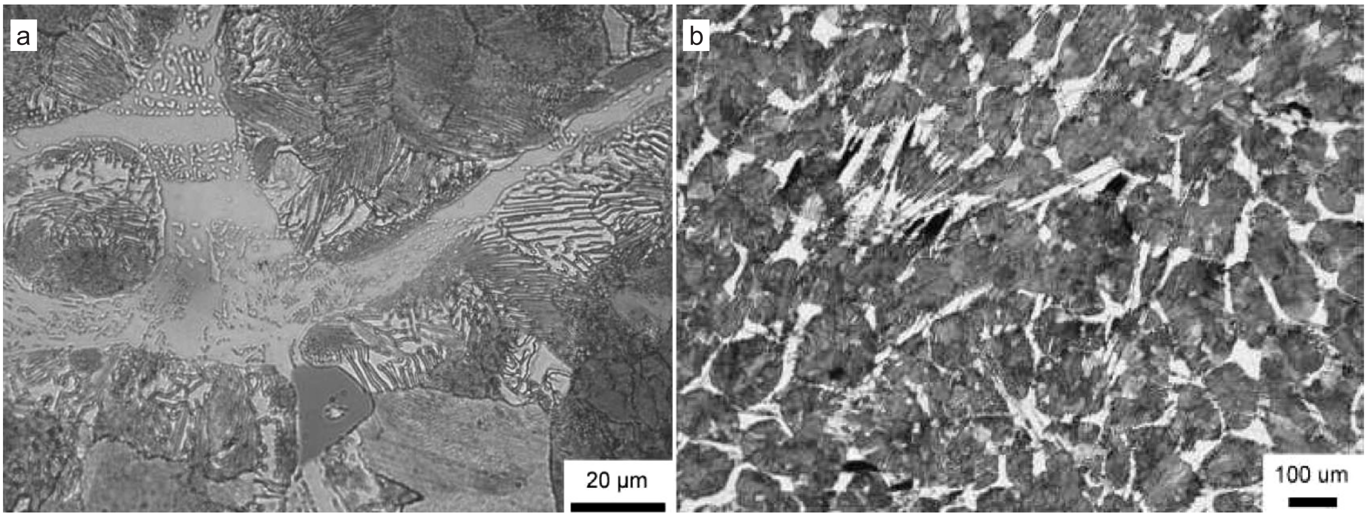


Figure 7: Optical micrographs after nital etching of, a) MEL07-09 showing pearlite, phosphorous eutectic and manganese sulphide, b) MEL07-10 showing hypereutectoid steel.

content is known to promote the formation of white cast iron (Durand-Charre 2003). In both types of cast iron the pearlite has a relatively thin structure (Fig 7a). Analysis by quantitative metallography determines a carbon content of 3.5wt% for the entire surface observed. Phosphorus eutectics, manganese sulphides, and phases containing titanium, chromium and vanadium can also be seen in this sample. EDS analysis of levels of Si, P and S indicates a slight decrease in each of the elements, for the entire surface, when compared with the original pig iron. Excepting a centimetre-sized hole at its centre, the sample shows little porosity and seems fairly homogenous in terms of structure and composition.

An even greater decrease in C, Si, P and S levels is seen after the melting is complete and the metal has passed before the tuyère once. This can be seen in sample MEL07-10, which, although still highly carburized, has the structure and composition of hypereutectoid steel (Fig 7b) with phosphorus eutectics and manganese sulphides. Quantitative metallography gives a carbon content of about 1.8wt% (Table 1) which, while remaining high, indicates a significant decline compared with the previous sample. Levels of Si, P and S are, again, significantly lower than those measured in the previous sample. Lastly, we note the low porosity and great homogeneity of the sample.

Both the metallographic structure and the composition of the metal obtained at the end of the process, after considerable reaction with the slag (MEL07-13), differ significantly from previous samples. The metallographic

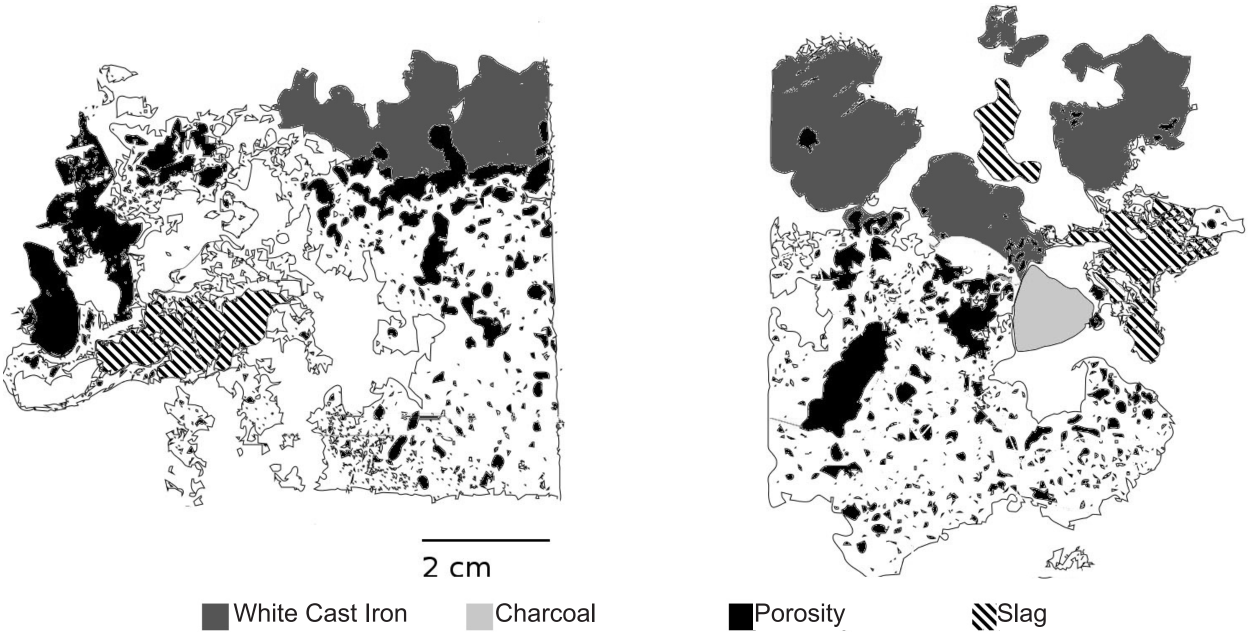


Figure 8: Metallographic section of sample MEL07-13. The white areas are hypereutectoid steel.

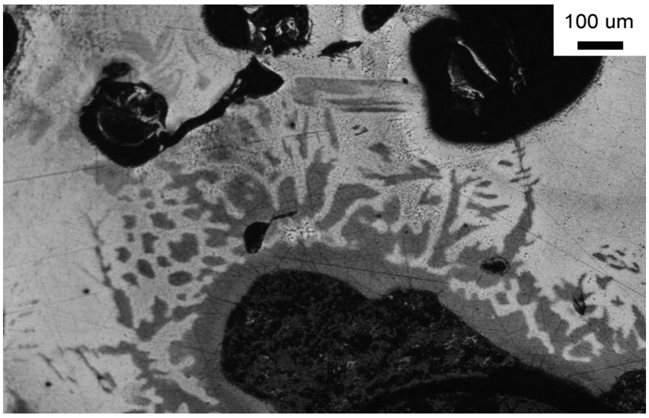


Figure 9: Optical micrograph of MEL07-13 after Oberhoffer's etching.

section presented in Figure 8 shows a very porous lower portion with slag inclusions, and a more homogenous and non-porous upper area devoid of slag inclusions. This latter area is composed of hypereutectoid steel and white cast iron, similar in structure and composition to the two previous samples. The lower microstructure of the metal block, however, is comprised solely of hypereutectoid steel, inextricably mixed, at times, with the slag (Fig 8). Average element contents in the upper half are lower than those in previous samples, namely in terms of carbon (1.2wt%) and silicon, which is no longer detectable by SEM-EDS analysis.

The lower area clearly shows a material comparable with those produced in old refining hearths. The levels of carbon are lower than the eutectoid, the iron showing levels of sulphur and silicon at less than 0.5wt%. Phosphorus content was significantly lower than that of the pig iron but remains high (0.8wt%). It should be noted, however, that it is perfectly comparable with that of ancient iron produced by direct reduction (Piaskowsky 1989). An etching with Oberhoffer's reagent was performed on this sample; the typical 'ghost' structures of phosphorous iron (Stewart *et al* 2001; Vega *et al* 2002) can be seen. We also note a characteristic phosphorus depletion in the slag interphase zones (Fig 9), revealing its dephosphorizing effect.

Table 1: Composition of cast iron from Glinet (Dillmann et al 2007) and experimental samples, in wt%. The balance is iron.

	C	Si	P	S
Glinet cast iron	2 – 4.3	1	1.7 – 2	< 0.5
MEL07-08	5 ± 1	2 ± 0.5	2 ± 0.5	0.8 ± 0.1
MEL07-09	3.5 ± 0.5	1.5 ± 0.2	1.5 ± 0.2	0.6 ± 0.1
MEL07-10	1.8 ± 0.2	0.8 ±0.1	1.5 ± 0.2	< 0.5
MEL07-13 top	1.2 ± 0.1	< 0.5	0.8 ± 0.1	< 0.5
MEL07-13 bottom	0.2 ± 0.01	< 0.5	0.8 ± 0.1	< 0.5

The metal mass obtained at the end of the process also contains a large amount of slag. The slag comprises wüstite (FeO), fayalite (Fe_2SiO_4) and a vitreous phase between the fayalite crystals. Oxide phases containing titanium, vanadium and chromium were also identified in the slag (Fig 10). Their specific forms look like smoothed remains of formerly angular shapes. This suggests that these phases are the result of the solid state oxidation of the carbides initially observed in the pig iron, due to the high melting point of the phases considered (see for example Ti-Cr-C ternary diagram (Booker *et al* 1997)). This kind of solid state oxidation in air at the same range of temperatures is mentioned in literature, *eg* for Ti-carbides in super alloys (Litz *et al* 1988). This observation is in good agreement with the hypotheses reached at the conclusion of previous studies (Dillmann *et al* 2002; Lechevallier *et al* 2000).

The chemical analyses (median value calculated from the surfaces of each analyzed zone and based on approximately 100 analyses (Dillmann and L'Héritier 2007)) of slag trapped in sample MEL07-13, shown in Table 2 (SEM-EDS measurements), indicates that part of the pig iron phosphorus and nearly all of the silicon and sulphur have been transferred into the slag. It is to be noted, however, that the phosphorus levels in the slag are relatively low compared with the expected levels when refining phosphoric pig iron, indicating that a significant proportion of the element remained in the metal. The slag inclusions, for example, found in arche-

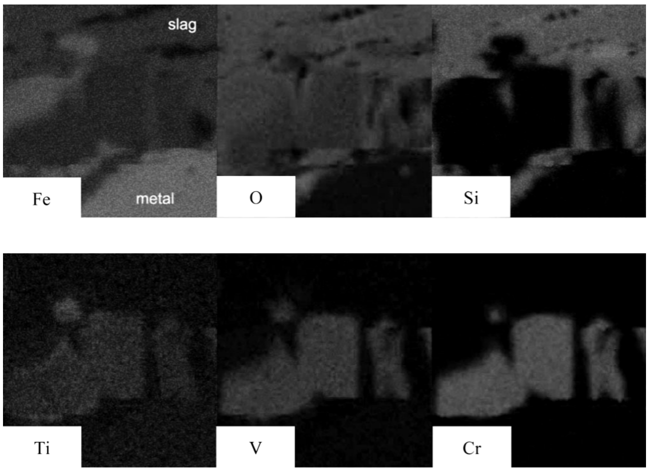


Figure 10: MEL07-13, EDS mapping of slag zones containing angular phases rich in chromium, titanium and vanadium. Image width: 50 µm, X-ray K_α lines.

*Table 2: Composition of slag in sample MEL07-13. The asterisk * indicates a weighted content taking into account the surface of the different analyzed zones.*

oxide	wt%
MgO*	0.60
Al_2O_3*	0.78
SiO_2*	12.05
P_2O_5*	2.72
SO_2*	0.16
K_2O*	0.38
CaO*	1.15
MnO*	0.60
FeO*	81.50

ological metals refined at Glinet have a P_2O_5 content of about 15wt% (Dillmann *et al* 2007). The presence of large amounts of calcium oxide also raises questions. Considering that the hearth is made out of steel, this contamination cannot be attributed to the sides of the hearth. The only other potential source is the charcoal. This point will be clarified later.

Discussion

The composition of samples obtained during refining, as seen in iron-carbon-silicon diagrams, clearly shows the change of melting temperatures. Upon further examination, and considering only the elements iron, silicon and carbon, we see that the melting point of the initial pig iron is between 1150 and 1200°C (Fig 11), a temperature easily reached in an open hearth. After an initial passage through the tuyère, and a drop in carbon and silicon content, the melting point remains around 1200°C. Given the lower content of these two elements, the material corresponding with sample MEL07-10 (lower portion) has a higher melting point, between 1350 and 1400°C. Because of the low carbon content of the mass of refined metal, its melting point approaches that of pure iron, around 1500°C. This decarburization leads the mass of refined metal to gradually solidify, which helped the refiner to assess the progress of work.

Figure 12 shows the change over time of the levels of C, P and Si compared with their initial content in the pig iron in given samples. The oxidation of carbon and silicon appears to occur at a relatively even rate. Phosphorus content, however, appears to level off after an initial decrease, reflecting the difficulty of eliminating the element from the metal. A drop in phosphorus content is nevertheless seen in the metal sample taken during the last phase. Given various observations (including the decrease of phosphorus in the vicinity of the slag and the characteristic bubbling observed at the end of refining), it is likely that the dephosphorization occurs through an exothermic interaction with the slag. Studies conducted by Im *et al* (1996) show that slag at a relatively low temperature (around 1300°C) and even with little CaO, can have a significant dephosphorizing effect. Buchwald (2008, 278) notes that the dephosphorizing effect of slag is cancelled out at higher temperatures, indicating that dephosphorization occurs in the early stages of refining in a highly oxidizing atmosphere. The two arguments are not in fact contradictory: dephosphorization is possible at the start of the refining process, at high temperatures and in the tuyère's oxidizing atmosphere; it is also possible later on, at lower temperatures and in contact with the slag.

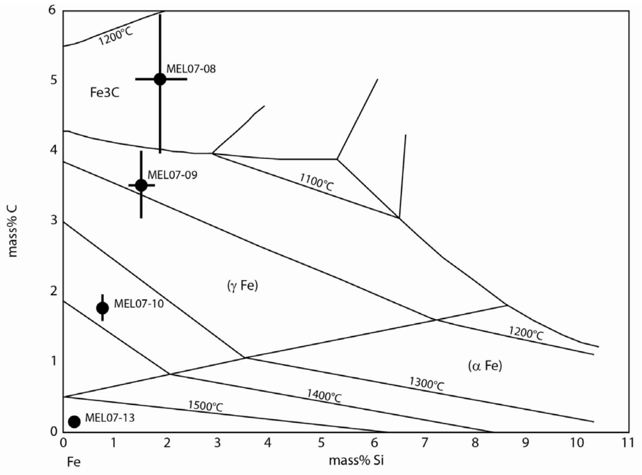


Figure 11: Composition of samples MEL07-08, MEL07-09 and MEL07-10 and MEL07-13 on a section of an iron-carbon-silicon diagram.

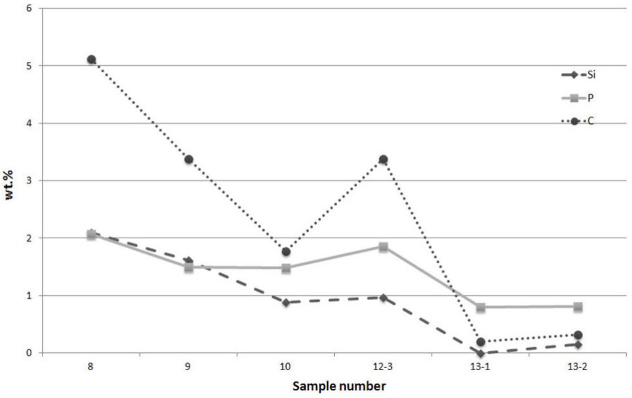


Figure 12: The levels of carbon, phosphorus and silicon in the analysed iron samples show changes when compared with their initial content.

The final product obtained from this refining experiment is a hypoeutectoid steel with significant quantities of phosphorous (0.8wt%) but entirely compatible with levels observed in materials from blast furnaces and finery forges in which phosphorous pig iron was treated. Such phosphorus levels correspond, furthermore, with that of steels and irons uncovered at the Glinet site.

Conclusion

In spite of relatively low yields (60% before bloom consolidation), this series of experiments allowed us to determine specific refining techniques enabling even phosphorous-loaded pig iron to be refined in a more efficient manner. The experiments, furthermore, clearly demonstrate the importance of the metal-slag reaction phase in obtaining a carbon-free and phosphorous-free material, pointing to the necessity of either leaving slag from previous operations in the hearth during the refining process or of adding it at the start of a new operation. It is interesting to note the absence of large refining cakes at the end of the operation, the slag being divided and scattered throughout the hearth, most likely during the stirring phase. This raises questions about the presence of the massive cakes found during the Glinet archeological excavations. Did they result from the sheer number of refining operations that were conducted in the furnaces in former times? Or did the stirring techniques and conditions of our experiments sufficiently differ from those of the Middle Ages to stop cakes from forming? This question will be clarified over the course of future experiments. Another question remains as to the presence of calcium oxide in the slag. With our experiments, the presence of this element cannot be solely traced to the charcoal used during refining. It will be necessary, therefore, in a later campaign, to evaluate the extent of the potential pollution due to charcoal impurities. Finally, the addition of calcium in the form of lime when refining phosphorous pig irons may play an important part in dephosphorization. Evidence of such additives can be found at Glinet. Our next round of experiments will test this point.

Despite these concerns, our experiments and analyses shed important light on both refining techniques and conditions. Future studies should further consider both the forming of slag and the influence of charcoal on its composition, crucial points which will need to be compared to observations made on slag inclusions in objects (for example nails) found in both bloomery and blast furnaces. Slag formation and the impact of charcoal, furthermore, will need to be considered in light of various hypotheses which will allow us to classify slags according to their composition. The next phase of this study may also require us to further pursue the thermodynamic modeling of predominance areas of the phases at play during the refining operation.

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