The performance of Abraham Darby I's coke furnace revisited, part 1: temperature of operation

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ABSTRACT: Abraham Darby I's coke-fired furnace produced a higher-silicon iron than prior charcoal ones, which was critical for the casting of thin pots in sand. This silicon content has hitherto been attributed to an enforced higher temperature of operation with coke. This paper sets out to show that there were other reasons why coke iron had a higher silicon content than charcoal iron, and that the temperature in his hearth was probably no higher than that in a charcoal furnace. The causes of high silicon content in coke iron were the higher density of coke, leading to a longer dwell time, and the now-appreciated effect of reactive silica in the coke, not present in charcoal. The paper suggests that the breakthrough by Abraham Darby II that led to coke iron being fit for the forges was the removal of sulphur by using higher temperatures in bigger furnaces.

Introduction

Williams (2013) reviewed the very significant differences between the two types of iron, one grey, one white, which could come from an 18th-century blast furnace. Each type had different applications, and Williams noted that it was very specifically a grey iron that was needed to make the vast majority of castings. He sought to show that Abraham Darby I's sand moulding patent, written two years before he first smelted iron with coke, was entirely predicated on the use of coke and that a charcoal blast furnace could not commercially have produced an iron that would cast grey a thin-walled cooking pot in his cold, greensand moulds. Before coke iron, charcoal iron masters heated their moulds to make their pots and this demanded that they used the expensive loam moulding process. As a result of his innovations in fuel and moulds, Darby's pots were much cheaper to make and he used the manufacture of pots as the economic base to develop the first dedicated general iron foundry in Britain. However, there were iron foundries on the Continent, using charcoal, long before, even in the 16th century (Evrard and Descy 1948, 207). Furthermore, there were still many operating there well into the 19th century, (Scheerer 1853, 110–121), despite the clear economic benefits that coke had been demonstrating for over 100 years.

It was actually first reported by Dud Dudley in the 1660s that iron coming from a coke blast furnace was greyer than that coming from a charcoal one (Dudley 1665, 24) and by the end of the 18th century French and German metallurgists appreciated that this greyness was down to a higher silicon content. Metallurgists writing of the historical context, such as Rehder (1987, 39) and Mott (1957/60, 78; Hiles and Mott 1944, 154), have satisfied themselves that higher silicon contents were due to coke furnaces being obliged to run at higher temperatures than charcoal ones because of the different combustion characteristics of coke. It was less reactive, they argued, so required more air to burn it and the result was a higher temperature, which facilitated the production of silicon, the reduction to which could only take place at high temperature. Tylecote was another metallurgist to write on the subject. Without detailing why, he too said that Darby would have produced a very hot iron (Tylecote 1991, 214).

This paper sets out to demonstrate that the conditions required to produce a high-silicon iron were considerably more complex than just a function of temperature and that indeed Darby's coke furnace needed to have run at no higher a hearth temperature than a charcoal one to produce the all important grey iron. It starts by considering the theoretical chemistry of silica reduction, then details how charcoal iron masters managed to get compositions that would give them grey iron in the majority of their castings, if not in thin pots. Of necessity, this requires the use of texts written chiefly in the 19th century with their increasing knowledge of the science behind the processes, while charcoal furnaces continued to be used on the Continent and in America. (Charcoal furnaces had been improved in the 100 or so years since Darby moved to coke, but only in matters of efficiency and detail. Tylecote (1991, 218) noted that outside of Russia, European furnaces stayed at much the same height that it has been assumed Abraham I's furnace had had in 1709, often considerably less than 26 feet (8m), and there is little reason to believe that they behaved in any significantly different way from their earlier predecessors.) The paper then examines the implication that such knowledge presents for a better understanding of the differences in operation between charcoal blast furnaces and Abraham Darby's first coke one.

The relationship between iron greyness and silicon content

Williams (2013) showed that the so called Carbon Equivalent (CE)

CE% = Carbon% + Phosphorus%/3 + Silicon%/3

was a valid measure of the *tendency* of an iron to cast grey. Whether it did or not then depended on the rate of cooling from the liquid state. In a mould, the cooling rate depended on the thickness of the casting wall, so to make a thin pot required a certain minimum Carbon Equivalent. Thus to make a white iron for use in the forge, a CE of 3% sufficed, to cast a heavy section cannon required a CE of about 3.5%, whilst a thin-walled pot required a CE of over 5.0% if it were to be cast into a cold mould. In fact, to obtain optimum tensile strength in a casting, the carbon equivalent needed to be specifically tailored to its section size (Walton 1958, 127).

The mechanism by which iron picked up each relevant alloying element in the blast furnace was different. The carbon was provided by the fuel and in its passage through the blast furnace, given enough time at temperature, the iron's carbon content may have reached saturation, but carbon solubility very much depended on the presence of other alloying elements, particularly, as it happens, silicon and phosphorus. Phosphorus arrived in the blast furnace via the ore (there is very little in charcoal or most coke) and whatever was in the ore found its way into the iron. In casting, it gave a very useful extra fluidity, but beyond a content of about 0.75%, it resulted in a deterioration of mechanical properties and was rarely present in concentrations much higher than 1%. It could be added from other sources and appears to have been so in the earliest centuries of cast iron. A border post, one of the oldest European iron castings (1364?) contained 6.2% of phosphorus (Niezoli 1942, 137), a level which it is difficult to see could have stemmed from the ore from which the iron was made. However, adding phosphorus to iron made from low-phosphorus ores in order to make castings was not common, because an ore low in phosphorus was of so much greater value in making high quality bar iron in the forge, a point which will be illustrated later.

Thus it fell to silicon to make the greatest difference in the question of grey tendency. To understand how silicon is picked up by the iron, it is necessary to understand a little of the thermodynamics of silica reduction.

The theoretical chemistry of silica reduction

An Ellingham diagram (Fig 1) is an elegant way of demonstrating under what circumstances solid elemental carbon can reduce silica, silicon dioxide (SiO_2), to silicon. In general, an Ellingham diagram can demonstrate how the free energy of formation of oxides varies with temperature. The free energy of oxidation is a measure of how strongly oxygen bonds to an element and the stronger that bond is, the more negative is the free energy change when the oxide forms. Elements which bond strongly with oxygen will 'steal' oxygen from oxides of elements which bond with it less strongly. Thus an element with an oxide more negative in its free energy of formation will reduce an oxide which is higher up the scale. In the case of an Ellingham diagram, at any temperature, an element with an oxide below another oxide is capable of reducing it.

In Figure 1 it can be seen that the lines for the reactions

$2C + O_2 <> 2CO$ (1)

and

$Si + O_2 <> SiO_2$ (2; the solid line)

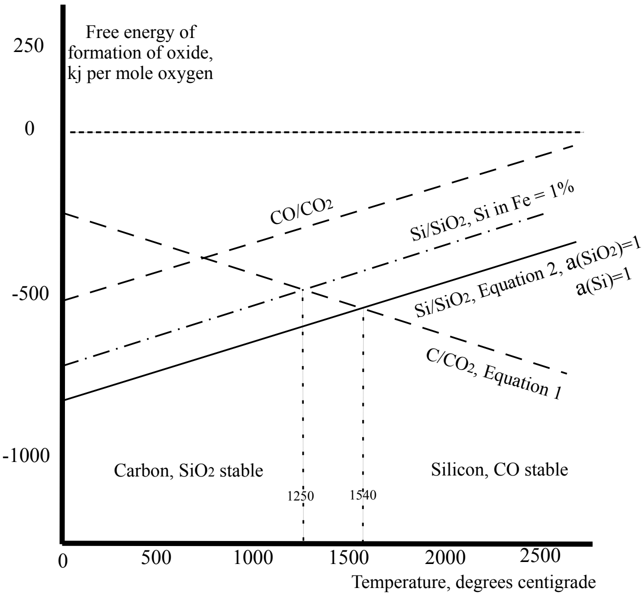

Figure 1: Ellingham diagram illustrating the circumstances under which solid carbon can reduce silica to silicon (see text for details).

slope in opposite directions, resulting in them crossing over at approximately 1500°C. This suggests that only above that temperature can carbon reduce silica to silicon. Actually this is not the case as free energies used in almost all Ellingham diagrams are *standard* free energies, that is, the free energies when the reactants are pure and un-dissolved in any other material. In a blast furnace, the states of neither silica, nor silicon are 'standard'. In the case of a substance in solution, solid or liquid, the so-called *chemical activity*, 'a' is reduced, to an extent depending on its concentration and upon the chemical affinity for it of the material in which it is dissolved. Most convention has it that activity in the pure state is unity and dissolved substances have activities which are less than one, down to zero when none is present at all. When activities are less than 1, the free energy of reaction 2 is modified according to the equation

$$\Delta G = -RT\ \mathrm{Ln}(a[SiO_2])/a[Si])$$

where G is the Gibbs Free Energy of the reaction, R is the standard gas constant, T is the Kelvin temperature and $a[SiO_2]$ and $a[Si]$ represent the activities of silica and silicon respectively.

If either constituent has its activity reduced to say 0.1, then the free energy of the reaction is changed by some 35 kjoules. All else being equal, 35 kjoules of energy change is equivalent to a reduction or elevation in the reaction temperature of about 100°C. If the silica is chemically mixed with something with which it has an affinity, lime for example, to an activity of 0.1, then the temperature at which it can be reduced is raised, whilst if the silicon is only wanted as a dilute solution in iron, the temperature at which it may be reduced is lowered by a similar amount. Bodsworth (1963, 155 fig 2) illustrated that the temperature needed to produce a 1% solution of silicon in iron is actually 250°C less than the standard state reaction, *ie* about 1250°C, considerably less than the 1500°C that might be imagined if an Ellingham diagram were taken at its face value. He also reproduced (1963, 343) a diagram in which the silica activity is superimposed onto the silica-lime-alumina ternary equilibrium diagram (Fig 2). It can be seen that silica activities approach unity as the lime content falls below 10%, but at 50% lime, the activity is reduced to 0.1. So the theory predicts that temperature is not as important as might be thought, but that the silica in the furnace should not be associated with much lime or magnesia.

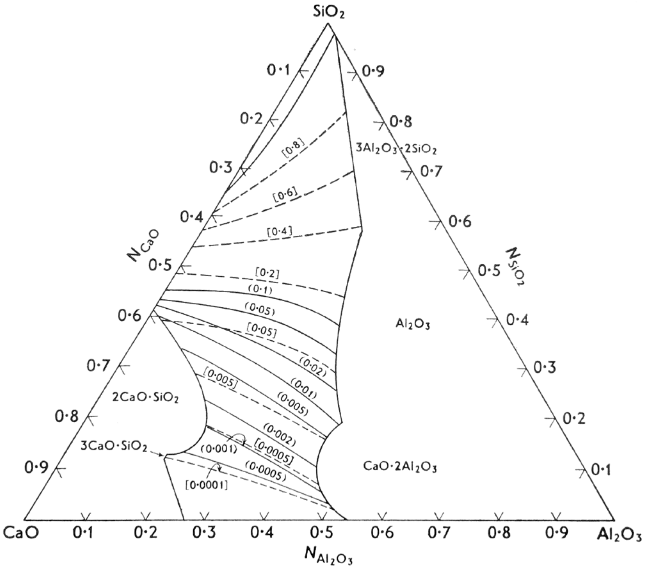

Figure 2: Ternary $CaO–SiO_2–Al_2O_3$ equilibrium diagram at 1600°C with silica activities (the figures in parentheses) superimposed upon it, demonstrating that silica in a slag or ore with a basicity of 1.0 is held at an activity approaching 0.1. (after Bodsworth 1963, 343). NCaO (molecular fraction CaO) = 0.5 represents 48% by weight, a basicity of 0.93.

The supposition amongst early metallurgists (*eg* Percy 1864, 538) always seems to have been that the reduction of silica must take place in the molten slag. This may have been due to the logic that a solid-solid reaction would be slow and therefore a liquid had to be involved, and this would only be found in the slag. However, actually, the reaction must have taken place before the slag proper, the secondary slag, had formed. The solution reaction, that deposits solid carbon in very fine form on the ore surface and which is responsible for the significant direct reduction of the solid ore by solid carbon (as opposed to the reduction by carbon monoxide), equally

Table 1: Basicities of slags from charcoal and coke furnaces cited by Pavlov (1924, 35–37).

Charcoal furnaces	Basicity	Coke furnaces	Basicity
1	0.52	**17**	**1.46**
2	0.81	**18**	**1.44**
3	0.68	**19**	**1.45**
4	0.56	**20**	**1.87**
5	0.72	**21**	**2.23**
6	0.58	22	1.24
7	**0.70**	**23**	**1.54**
8	0.93	**24**	**1.54**
9	0.66	**25**	**1.59**
10	0.60	**26**	**1.45**
11	0.73	**27**	**1.54**
12	0.61	**28**	**1.54**
13	0.44	29	1.45
14	0.45	30	1.33
15	0.69	31	1.34
16	0.81	32	1.28
Average	0.66		1.52

Notes: The figures highlighted in bold are of the higher-silicon foundry or Bessemer irons. Comparison with Tylecote (1991, 219) shows that basicities of slags from charcoal furnaces changed very little over 300 years.

provides the circumstances under which solid carbon can reduce solid silica. Had the silicon content of an iron been down to the composition of the slag, and the activity of silica in it, the very similar basicity (defined as (lime plus magnesia)/silica) of slags produced by charcoal furnaces might have been expected to have resulted in a very similar silicon content in all irons.

However, the historical record with coke furnaces seem to show that there was even a positive relationship (as opposed to inverse, as would be expected from the discussion above) between slag basicity and the silicon content of the iron. Table 1 shows which of the coke slags quoted by Pavlov (1924, 35–37) accompanied the production of foundry and Bessemer irons. (Bessemer iron, like foundry, was necessarily high in silicon. Its presence helped to provide the extra heat needed to keep the iron molten during the Bessemer process.) It is evident that high basicity slags accompanied the production of high silicon irons, not at all to be expected if the silica had been reduced in the slag. Bodsworth (1963, 156, 169) noted that in 1960s blast furnaces, silicon was reduced and dissolved into the iron above the level of the slag, and then did not achieve any sort of equilibrium in the slag as that iron passed through it on its way to the crucible.

How charcoal iron masters managed to get grey iron

Many 19th-century writers noted that whether a *charcoal* iron turned out white or grey, *ie* had a higher or a lower silicon content, depended primarily on the nature of the ore and one can perceive from much of what has been written that it was the basicity *of the ore* (and therefore the silica activity in it) which influenced how much silicon was picked up, not that of the slag. Percy (1864, 199), for example, mentioned that even with mid-19th-century hot blast coke furnaces, some ores gave a greyer iron than others. He noted that ores with uncombined quartz, *ie* pure silica, always resulted in a high silicon iron.

For charcoal furnace masters, the *fusibility* of their ores was extremely important in influencing whether an iron turned out grey or white. What sort of ore gave a grey iron was discussed by both Rinman (trans Karsten 1812, 694–7) and Karsten (1841, 190–300), who clearly stated that certain difficult ores inevitably resulted in grey metal, but de Saint Ange (1835–38, 24, 61) gave the most complete picture (Table 2). He placed magnetite, haematite and certain silicates as ores difficult to process.

Table 2: The fusibility of different ore types, proposed by de Saint Ange (1835–1838, 24).

Ore type	Sub-type	Fusibility
Magnetite		Difficult
Specular haematite	Massive	Difficult
	Sandy	Difficult
Haematite		Difficult
	Dense	Difficult
	Ochre	Moderate
Hydrated Ores	Brown	Difficult
	Dense	Moderate
	Oolitic	Moderate
	Pisolitic	Moderate
	Bog ore	Easy
Carbonate	Spathic white	Easy
	Spathic Brown	Easy
	Stone	Easy
Siliceous	Magnetite	Easy
	Haematite	Easy

Notes: The more easily fusible ores are in essence self-fluxing, containing quantities of lime alongside the silica.
Fusibility is often confused with reducibility. Rich ores tended to be both difficult to fuse and to reduce.

However, hydrated and carbonated ores were easier. He demonstrated that charcoal consumption was not a simple matter (Table 3), because ores with difficult fusibility required more charcoal to smelt a ton of iron.

More charcoal in the charge always led to a greyer iron, whether it was done as an obligation when the ores were difficult to fuse or through choice. Thus Fournel (1842, 3–8), reporting on two very similar blast furnaces in the Haute Marne using the same ores, noted that the one which concentrated on foundry work used 43% more charcoal than the one making pig to be turned into bar. When Rinman (trans Karsten 1812, 694–97) discussed the factors that decided whether an iron was going to come out of a Swedish furnace grey or white, he did so in terms of the various stages involved in starting up at the beginning of a campaign. The fire was started with charcoal only, but over a period of weeks, increasing amounts of ore and lime were added. The iron started very grey, but became less so as the burden was built up. The temptation is to assume that the extra charcoal was burned to make the furnace much hotter, because of the assumption mentioned above that it was temperature that was responsible for the higher silicon content.

However Scheerer's reports (1853, 97–121), on the operations of a large number of charcoal blast furnaces in Germany and elsewhere, show that this was not the case. Thus the Ilsenburg furnace, in the Harz (Scheerer 1853, 107) normally made grey iron for foundry use, operating on a dwell time of 16 to 17 hours. If it blew in more air, the iron actually came out white and was then only of use in the forges. Karsten made the same point (1841, 190) and noted in several places that grey iron tended to come from a furnace running cooler. Writing in the early 20th century, Johnson (1918, 40) made a definitive statement about the 'collapse of the old notion that gray iron is always made in a hot furnace and white in a cold one' and other writers in the coke era were equally definitive, white iron production demanded the blowing of air at a greater rate and was therefore accompanied by the generating of a greater quantity of heat (Greenwood 1902, 171; Fairburn 1861, 51). In Scheerer's reports (1853, 97–121) on the furnaces that sometimes made grey iron for foundry use and sometimes white iron for the forges, all used more charcoal and accepted a lower production rate when doing the former.

Ore *fusibility* and *reducibility* are nominally two different factors, but they do seem to have been lumped together or confused by some commentators. However, the easily fusible ores (Table 3) were for the most part also easily reducible. The right lime:silica ratio gave them the former property, whereas the roasting of hydrated and carbonated ores, in opening up the pore structure gave them the latter. The two effects usually acted in unison, but not always. Frequently even magnetite and haematite ores, especially in Sweden, were roasted prior to use, just to open up the pore structure. At one point, Karsten (1841, 289) noted that Swedes often deliberately made their iron greyer by refraining from roasting the ores and thus making them more difficult to reduce. That De Saint Ange (1835–1838, 24, 61) noted that higher grade ores also took more charcoal, would perhaps have stemmed from his experience with French ores, when the haematites and magnetites were not roasted and therefore hard to reduce as well as hard to fuse.

Table 3: The fuel demands of ores of different types and richness as proposed by de Saint Ange (1835–1838, 61).

Ore type	**Ore richness (% iron)**	**Charcoal used per ton of iron**
Easily fusible	27	0.80
	37	1.25
Moderately fusible	35	1.25
	55	1.95
Difficult to fuse	45	2.30
	55	2.75
Forge use at Tempillon		1.29
Foundry use at Brousseval		1.85

Note: Included for comparison are the charcoal use figures for two furnaces in the Haute Marne of identical sizes, using the same ores, but manufacturing iron for different purposes (data from Fournel 1842, 3–8).

The conclusion has to be, that above all else, it was not temperature as such, but the time at temperature available for the reaction to take place above the slag, *ie* the *dwell time*, that was the all important factor in dictating whether an iron came out grey or white, *provided that the silica in the charge was in a reasonably concentrated, 'pure', state*. The dwell time in a furnace of any given volume can be calculated theoretically by the combustion rate of the carbon it contained. It will be appreciated that the speed of descent of the charge was decided by the *weight* of carbon that there was in a fixed *volume* of that charge and its combustion rate. Thus, increasing the amount of carbon, *ie* the ratio of fuel to burden, inevitably slowed the descent and increased the dwell time. With a knowledge of the various bulk densities, it is easy to calculate at least the theoretical dwell times under any circumstance. Rehder (1987, 39) did so in his comparison of coke and charcoal and for a furnace volume of 9.1 cubic metres, he calculated for charcoal

Table 4: Calculated dwell times for various fuel loadings using both charcoal and coke.

Condition	Charge	Weight per ton of iron	Tons of iron per week	Dwell time (h)
Base charcoal [1]	Charcoal	1.6	15	12
	Ore	2.4		
	Limestone	0.6		
Base + 50% charcoal [2]	Charcoal	2.4	10	13
	Ore	2.4		
	Limestone	0.6		
Base + 100% charcoal	Charcoal	3.2	7	14
	Ore	2.4		
	Limestone	0.6		
Pure charcoal	Charcoal	100	-	15
	Ore			
	Limestone			
Supposed 1720 coke [3]	Coke	3.91*	9	23
	Ore	3.52†		
	Limestone	1		
Pure coke	Coke	100	-	30
	Ore			
	Limestone			

Notes: 1: Rehder (1987, 38) assumed Darby's furnace to have a capacity of $9.1m^3$, a height of 6.7m, and an equal combustion of 0.41 tons of charcoal per day. He used bulk density values of charcoal = 0.24, coke = 0.48, ore = 1.60 and limestone = 1.28.
2: Extra charcoal by choice or necessity.
3: Mott (1957) plus this paper. * Three tons of coal produce one ton of coke. † 30% loss on calcining.

a dwell time of 12 hours for the smelting of 15 tons of iron per week. In Table 4 this calculation of Rehder's is reproduced and compared with dwell times computed under various other conditions. Rehder's figures for bulk densities are used to allow ready comparison. Although some of his figures do seem a bit low, bulk densities did vary enormously. The calculations show that varying the charcoal:burden ratio influenced the dwell time, but the really big difference was made by switching to a denser fuel, which in the calculations of the author and Rehder (1987, 39) and the observations of Scheerer (1853, 107) and Birkinbine (1880, 175), all resulted in a near doubling of the residence time (Table 4). Whatever the dwell time, the ore was still an important factor and without easy transport for their ores, blast furnaces in certain areas would tend to concentrate their efforts on producing either castings or iron for the forges, depending on what ores were locally available to them. In Germany for instance, parts of the Harz region and Silesia seem to have been serious foundry areas and in Sweden, it was the region where the Southern bog ores were found that developed the casting industry (Percy 1864, 788).

The area of Franche Comté next to the Jura is a particularly interesting area to study in this respect, because with its particular ores it produced a grey iron as its default product. Nevertheless, it did not come to develop a concentrated foundry industry. Instead, it developed an extremely important fining process specifically to turn this grey pig iron into bar, despite that this cost more than starting with white or mottled iron (as was the situation in its neighbouring areas such as Bourgignon and Champagne (Percy,1864, 609, after Thirria 1840, 215–92)). The principal ore used in Franche Comté was *pisolitic*, or *mine en grains*, *ie* it was a hydrated oxide that had been deposited out of fresh water in the form of small round peas or bigger (the German *Bohnerz*, bean ore). Despite that it was a hydrated ore, it seems to have been of moderate rather than of easy fusibility, demanding, by the beginning of the 19th century, about a ton and a half of charcoal to produce a ton of iron (de Vollefosse 1826, 56). The principal features of its (various) chemical compositions (Table 5) were that it was low in lime and rich in silica, leading to the quite high fusibility temperature and the relatively high silica activity. However, it was also very low in phosphorus and it was this that made it prized for the production of high quality malleable (wrought) iron. Clearly the economics made it more valuable in this application than for castings, because castings in the Franche Comté region were mostly made from the inferior oolitic ores, which did contain phosphorus. The work of Thirria, as reported by Flachat *et al* (1842, 259) in providing the analyses of cold-blast charcoal operations, emphasized the point of silica purity extremely well. Iron made in the blast furnace at Montureax in the Haute Saone, part of Franche Comté, using pisolitic ores (cf Table 5) contained 1.3% silicon, whereas iron from the Cirey furnace,

Table 5: Composition (wt%) of pisolitic ores in the Franche Comté region (Thirria 1869, 200–202).

Location of ore	Equelle et Vars, red	Equelle et Vars, grey	Equillotte, Auvet	Renaucourt
Iron oxide	44.6	54.4	56.4	56
of which iron	30	37	39	39
Silica	31.2	19.9	14.8	23.4
Lime	3.2	5.8	3.6	1.8
Basicity	0.1	0.29	0.24	0.08

made with oolitic hydroxide ores from the neighbouring Haute Marne contained only 0.38% silicon.

The iron industry in Sweden had developed in much the same manner as that in Franche Comté. Sweden had very high quality, low lime and low phosphorus iron sources in many of its magnetite and haematite Bergland ores. When these ores were acid (often with visible streaks of quartz), they inevitably produced a high silicon grey iron, but the highest value was again obtained by turning them into malleable bar, a very high proportion of it for export. Sweden was one of the areas to which the Franche Comté process emigrated in the early years of the 19th century to compete with the Lancashire hearth.

The foregoing demonstrates that charcoal furnaces did frequently produce a grey iron, but how grey? When authors such as Rinman or Karsten talked about a blast furnace producing grey iron, they were perhaps mostly thinking of the pig or other ingot into which the product of the blast furnace was converted on the shop floor, *ie* by being poured into an open topped green sand mould with a triangular or square section of perhaps 100mm dimension. This would probably have resulted in a grey iron if the metal had had a carbon equivalent around 4.0%. In many parts of Europe by the end of the 18th century the practice became to cast it into iron moulds, one advantage of which was to make sure that the iron came out as white as possible as a result of it chilling quickly (Percy 1864, 494). As the data of Evrard and Descy (1948, 202) showed (Table 6), charcoal furnaces had no difficulty, other than the expenditure of more charcoal, in producing an iron with a Carbon Equivalent (CE) of 4.5%. It was achieving the 5.0% necessary to make a thin-walled cooking pot in a cold mould that was the difficulty.

Table 6: Analyses of Continental charcoal iron castings from the 16th, 17th and 18th centuries made in the 1940s (wt%, data summarised from Evrard and Descy 1948, 203, 234, 252).

	Carbon	Silicon	Phosphorus	CE	CE for grey iron
Thin section <5mm	3.89	0.91	0.86	4.47	>4.78
Medium section 10–20mm	3.67	0.85	0.93	4.26	4.23
Heavy section >25mm	3.51	0.6	1.06	4.09	<3.97

Note: Evrard and Descy found all the microstructures were grey, but admitted that the thin section castings should not have been. Williams (2013, 130) calculated that the castings would have needed a carbon equivalent approaching 5.0 to be made in cold moulds and therefore had to be cast into heated ones.

Implications of this knowledge

The information presented above allows a better understanding of the differences between charcoal and coke furnaces. For the reduction of silica, a high temperature was helpful, but when that silica was unreacted with lime and it descended slowly in the shaft, this temperature need not be much higher than the melting point of iron. Yet the statement has been repeated frequently that a coke-fired furnace achieved its greyness because it was hotter than a charcoal one. Later coke furnaces certainly were hotter, for example Johnson (1918, 50) quoted a slag temperature with coke of 1482°C versus charcoal 1260°C, but the present argument is that the 1709 furnace did not have to be. Both Mott and Rehder's convictions stemmed from the consideration of the different modes of combustion of the two fuels (Rehder 1987, 39; Mott 1957/60, 78; Hiles and Mott 1944, 154). They argued that the physical properties of coke meant that it had to burn hotter than charcoal. However, that argument misses the point. With both fuels the heat generated *in the hearth,* which dictated the temperatures of the metal and the slag, was set by the amount of air that was blown in. *The men in charge set the hearth temperature they wanted according to the demands of the chosen input and the desired output*. It was what happened further up the shaft that was dictated by the characteristics of the fuel, as well as by the loading and the size and shape of the furnace.

In fact, as Lowthian Bell reported (Bell 1884, 295) the effect of burning the less reactive fuel was to decrease the temperature gradient within the stack. This was the principal source of the inefficiency of the early coke furnaces; the gasses left the furnace at a much higher temperature than they did with charcoal ones. Raising the height of the furnace to capture this lost heat was the answer, a solution which was pursued throughout the 18th and 19th centuries, whilst charcoal furnaces remained much shorter. Thus the average temperature in a coke furnace was higher, but not necessarily the hearth temperature. The temperature at which an operator ran his furnace was almost always set by the 'melting point' of the slag required (Bodsworth 1963, 127; Johnson 1918, 41). This was above the melting point of the pig iron and well above the temperatures at which all other reactions in the blast furnace happened.

There are two possible reasons for Darby wanting to run his furnaces above the fluidity point of a charcoal slag. One would be to increase the fluidity of the iron if he was making his thin castings straight from the blast furnace, but he tended to make his pots in a separate foundry, using an air furnace to re-melt the pig iron. Pouring small castings directly from the blast furnace required the furnace to be on hold for a long period of time and only large castings were regularly made in this way. The other is if he wanted to remove the sulphur that arrived in the iron from the coke.

The purpose of the slag and the problem of sulphur

Three primary tasks are required of a slag.

- The first is to maintain the unwanted gangue impurities in a liquid state so that they can be readily removed from the furnace.
- The second is to ensure that as little iron as possible dissolves in it.
- The third is to remove sulphur from the charge when too much is present.

It is the lime in the slag that performs both the second and third tasks. To keep iron out of the slag requires an effective lime content of perhaps 40%. To remove sulphur requires an effective lime content of well over 50%. 'Effective' because silicon counterbalances lime and because in particular magnesia (magnesium oxide) behaves in much the same way as lime does. 'Effective' lime contents are described by the *slag basicity*, which is in its simplest form the weight ratio of basic oxides (those of calcium plus magnesium) to acid oxide (silicon).

Ward (1965, 42) gives a very good summary of basicity chemistry. A low basicity slag was applicable to most charcoal blast furnaces, but when the issue of sulphur arose, as it did when coke appeared or when charcoal furnaces were obliged to use sulphurous ores, higher basicities were needed. The relative amounts of silica, lime, and magnesia determine the melting point of a slag. The pure constituents have very high melting points, but they are lowered when they are mixed with each other. The temperature at which a slag becomes suitably fluid thus comes down to its basicity. It has been said that in early blast furnaces, with only low temperatures achieved, excess gangue needed to be fluxed with iron oxide (Morton 1966, 54), which involved a loss of valuable metal. However, thermodynamic considerations make it unlikely that this was ever significantly so, although it was clearly true of lower temperature bloomery slags. The maximum iron oxide found in blast furnace slags seems to be rarely more than 5% and it is generally much lower. Wagner (2008, 237) reported slag from a 15 foot (4.5m) high blast furnace in 1st-century BC China having an FeO content of 3% and a basicity of 0.53.

By Abraham Darby I's time the artificial addition of limestone was understood and used extensively. His accounts show that from the start he used it, separately added in his furnace and almost certainly in larger amounts than would have been used with the same ores when charcoal was employed. He would have found this out by simple trial and error, although it had probably already been established by earlier workers such as Dud Dudley, Shadrach Fox or Thomas Addison (King 2002, 40). The fluidity of a lime-silica slag reaches a maximum around 40% lime, depending on the alumina content, but decreases either side of this percentage (Morton 1966, 52). Tylecote (1991, 225) noted that charcoal furnaces employed a slag basicity of less than 0.7, whereas coke furnaces (or at least coke ones later than 1750) used basicities in excess of 1.0, a point amply confirmed by other writers, for example Pavlov (1924, 29–37; Table 1).

There has been some considerable debate over the years over why it was that early coke iron did not find more application in the forges to make malleable bar, but was essentially confined to the foundry trade until the 1740/50s, most significantly when Abraham Darby II then started to sell significant quantities of pigs from the Horsehay furnace into the Stour forges. Hyde (1977, 67) argued that there was an economic reason as it was, at least in part, its higher price that initially prevented coke iron being used to make bar before then. King (2011, 143) disputed this and showed that coke iron prices were very similar to charcoal ones by 1720. Both agreed that it was more expensive to convert coke iron to bar in the very earliest days. Alternative suggestions were that the reason was technical, this was down to silicon (Rehder 1987, 40), but quite high silicon irons made in charcoal blast furnaces were turned into excellent bar in both Sweden and Franche Comté, although it did cost slightly more to do it (Percy,1864, 610). Trinder, (1973, 30) suggested that it was phosphorus that caused the problem, but the phosphorus content was a property of the ore, not of the coke. The only contemporary reports that we have on this subject, those by iron experts from Sweden who had visited England in the 17th and 18th centuries, are most convincingly summarized in a seemingly unlikely source, Donald Wagner's book on Chinese iron (Wagner 2008, 314–317). They were agreed that the problem was down to sulphur. Swedenborg's detailed views in 1734 may be read in one of the 18th-century French encyclopedias, *Descriptions des Arts et Mètiers*, (Swedenborg, trans Bouchu 1780, 404).

Sulphur in forge iron made it very difficult to work at the red heat that forge operations needed, when it was very brittle, or 'hot short'. Depending on just how much sulphur was present, it could be done but took a lot more time, fuel and work and the result was probably never a very satisfactory iron. In castings, sulphur was not nearly so much of a problem, although its presence had little to recommend it as such. It could result in some extra strength in small quantities, chiefly because it opposed the action of silicon and phosphorus which made the iron greyer. Iron became very brittle if too much was present, but Moldenke (1917, 48), for example, said that in high silicon irons, sulphur was not an issue and he had made perfectly good castings containing 0.22% of sulphur. Forges needed the sulphur level to be below 0.1% (roughly) as a reading of Percy's chapter (1864, 532–552) on pig iron compositions will reveal. He reports though that up to 0.7% of sulphur was present in irons containing above 2% of silicon, clearly intended for foundry use (Percy 1864, 540).

It must be said that Rehder (1987, 42) whilst principally blaming silicon for the difficulty of fining coke pig, did raise the possibility that sulphur might have something to do with the issue, without noting the comments of the Swedish observers (see above). Tylecote too wrote that the issue of sulphur must have been solved by the time Wilkinson was running his Bradley furnace after 1770 (Tylecote 1991, 226), but did not connect this solution specifically with the Abraham Darby II development, because, based on a questionable calculation, he thought that Abraham Darby I might have achieved slags high enough in lime in 1709. The author has attempted a similar calculation.

Can we calculate the 1709 slag basicity?

Mott (1957, 69) provides information from the Coalbrookdale accounts on the purchases that Abraham Darby I made to run his furnaces for a number of years between 1709 and 1737. It is therefore possible, to deduce his slag basicities for the ores of the Shropshire coalfield for which we have analyses (Table 7). Taking all these at face value, we get high basicities, but several questions are posed by the exercise, which must cast doubt on the meaningfulness of the results. The first is that Mott implies that a much lower grade of ore than any of the ores quoted was charged into the furnaces. He said that 5 tons of ore was needed to make a ton of iron. It is difficult to reconcile this figure with the analyses given in Table 7 and technical considerations. Raistrick noted that in 1709 Abraham Darby I purchased approximately equal quantities of flatstone and ballstone (Raistrick 1970, 35). Ballstone is a bit of a mystery. It does not appear in any analysis known to this author, and certainly not in the Geological Survey of Shropshire. Mushet (1840, 58) says that ballstone was a general description of 'stone' ores with spheroidal shape, but it certainly was a specific type in the Coalbrookdale area, being listed in the strata (Kendall 1893, 159). Modern observations note waste remains from it that are much more saline than from other ores (Brown 1990, 8). There is reason to believe that it contained little lime and more silica (see later). Furthermore the ore analyses quoted would, one hopes, have been of clean samples. In furnace practice the materials would be contaminated with a gangue, which would have been significantly siliceous.

The clod coal that Darby used to make his coke had to be chosen in large lumps, it was not a caking coal; sizewise, what he put in was what he got out, and it would have therefore been quite cleanly selected. The same was true of the ores to an extent. The 'flats' and 'stones' of the ores were discrete pieces of quite pure ore disseminated in a shale matrix. They were sorted by hand in many cases, but it is worth making the point that the charge would have needed to contain only 2.5% extraneous silica for the basicity calculated in Table 7 to have turned from 1.2 to 0.7. Tylecote (1991, 226) also attempted to calculate the Coalbrookdale basicity from a different knowledge of the charge and suggested a figure just over 1 but that calculation too would be subject to the same error.

Table 7: Slag basicities when using Shropshire ores calculated using Mott's (1957, 69) furnace charges for the year 1720 (ore analyses from Kendall, 1893, 161).

Ore	Iron %	CaO%	MgO%	SiO_2%	Ore basicity	Slag basicity Charge 1	Slag basicity Charge 2
Black stone	37.9	2.3	1.8	7.4	0.6	1.3	0.7
Blue flats	36.5	2.3	2.1	8.2	0.5	1.2	0.7
White flats	35.6	3	2	9.9	0.5	1.1	0.6
Pennystone	35.6	3.1	4.2	6.2	1.2	1.7	0.9
Crawstone	40.3	2.1	0.4	6.9	0.4	1.2	0.6

Notes: Mott charged 5.0 tons ore, 11.6 tons coal (with 2% silica) and 1.0 tons of limestone (50% lime) per ton of iron produced for Charge 1. As calculated, the basicities are similar to later coke slags, but it would take only 2.5% overall of extra silica trash (Charge 2) alongside the ore, fuel and limestone for a basicity more akin to a charcoal slag to be formed. Yields calculated from Mott's charges imply a far greater input of gangue than that.

Charcoal furnaces could actually be made to run hotter than coke ones

If the 1709 coke furnace was not run hot enough to give a sulphur-reducing regime, a charcoal one could certainly be made so. Karsten (1841, 201) noted that when charcoal furnaces were smelting sulphurous ores, a higher lime addition and higher temperature were required. Karsten's fourth edition was written after the advent of hot blast, but the statement can be found in pre-hot blast editions, *eg* Culmann's (1830, 259) translation of Karsten. Hassenfratz, who wrote in 1812, (by which time the Le Creusot furnaces had been in operation in France for some 30 years) said that it was the opinion of most of his colleagues that the greatest practical temperature in a blast furnace was reached with hardwood charcoal as the fuel (Hassenfratz 1812, 35). Pelouze (1827/8, 128), basing his argument on the balance of combustibility and density, agreed. The temperatures cited by Johnson (1918, 50) illustrate this point. To run a basic slag that would remove sulphur required a temperature of nearly 1500°C, whilst a charcoal furnace merely intent on keeping iron out of the slag and removing the unwanted gangue materials, did it with a slag temperature of 1250°C (the melting point of a foundry iron with silicon and phosphorus in it would have been about 1140°C). The contention is that Darby's 1709 furnace ran at nearer this lower temperature than the higher one, because he did not need to run it any higher for his casting production and quite possibly because of the lack of height, he could not do so.

If Darby did not use a higher temperature in his hearth and thus made no attempt to remove sulphur, it is easier to understand what was the most likely technical breakthrough when, at some time before 1740, the company first started to sell iron into the forges, culminating in the building of the Horsehay furnace in 1754. Then, the use of a more assured blast due to a steam engine recirculating the water for the bellows, together with a consequently-enabled larger furnace, did make it easy to raise the temperature of the hearth and the slag, thus permitting the use of a significantly higher slag basicity and the removal of the excess sulphur, the practice which became regularly applied from then on. So Abraham Darby's first furnace was no hotter than a charcoal furnace *could be made to be* and probably no hotter than a charcoal one normally worked at. Yet a charcoal furnace could not make iron grey enough to make a cooking pot in a cold mould with the same facility that a coke one could. From the starting up of his new furnace, Abraham Darby I could do it easily.

High silicon in Abraham Darby I's furnace

If it was not down to temperature, why was it that Abraham Darby I's default production was of a much greyer iron than a charcoal furnace could make, without 'exceptional' and costly extra charcoal consumption?

Clearly the dwell time played a major part, although the dwell might not have been as great with Darby's coke as calculated in Table 4. Several observers have noted that his coke was very light. Charles Wood wrote in 1754 that it was 'near as light as wood coal' (Gross 2001, 223). Morton (1966, 50), quoting Beaver (1951, 133), noted the same thing. Almost certainly Darby was attracted to the Clod type of coal because the combustion properties of the coke made from it were the most akin to those of charcoal. The relatively low sulphur cited by Mott was certainly very useful, but the other principal coals in the locality had equally low sulphur contents, whilst it is plain that the Coalbrookdale Company throughout the first half of the 18th century not only insisted on using the Clod coal seam, but that it had to be a particularly soft form of that seam. Giving evidence in 1754 in a case at the Court of Exchequer, one Henry Cartwright, an employee of the Coalbrookdale Company, reported that he had accompanied Abraham Darby II to the Dingle Pit to view clod coals and had told him 'that they were too hard and not fit for the ironworks at Coalbrookdale'. He added that the company 'used a soft and mellow clod coal and no other sort' (Thomas 2001, 58).

There is another important factor which has apparently not been observed yet by historical metallurgists. Work on modern steelworks in the last 60 or so years has come to appreciate that one of the most significant sources of silicon in iron is actually the coke itself (Williams 1983, 44; Geerdes *et al* 2015, 134). The ash from the coking of coal which becomes concentrated in coke, is high in silica, and cokes can contain above 5% of it, mixed with alumina but very rarely compromised with lime. It is intimately mixed with the carbon in the form of fine particles and therefore quite capable of the solid-solid reaction required higher up in the furnace, quite apart from any fine carbon deposition from the solution reaction. Percy (1864, 537) may have been confronted by the phenomenon when he questioned the result of a chemical analysis because there did not seem to have been enough silica in the ore to explain the silicon content of the high-ash coke-made iron.

There is the question of Darby's ores (which came from the Coal Measures) and those we know about (Table 8)

Table 8: Analyses of Shropshire ores (data from Kendal 1893,160 and 168).

Ore	FeO	Fe_2O_3	MnO	Al_2O_3	CaO	MgO	P_2O_5	SiO_2	CO_2	*Fe*tot	*P/Fe %*	*Basicity*
Blackstone	48.3	0.5	0.8	4.2	2.3	1.8	0.3	7.4	34.5	*37.9*	*0.3*	*0.6*
Blue flats	46.3	0.7	0.8	4.3	2.3	2.1	0.5	8.2	33.4	*36.5*	*0.6*	*0.5*
White flats	44.3	1.6	1.0	4.5	3.0	2.0	0.7	9.9	32.6	*35.6*	*0.9*	*0.5*
Pennystone	45.1	0.8	1.7	2.4	3.1	4.2	0.5	6.2	35.3	*35.6*	*0.6*	*1.2*
Crawstone	51.5	0.4	0.5	2.9	2.1	0.4	0.2	6.9	35.2	*40.3*	*0.3*	*0.4*
Staffordshire gubbins	46.3	0.1	1.4	4.8	0.8	0.9	0.7	10.3	33.0	*36.1*	*0.9*	*0.2*

Note: The basicities are relatively high in comparison with the Franche Comté ores (Table 5). The Shropshire ores would not naturally have produced a grey iron in a charcoal furnace. The Staffordshire gubbins was an excellent foundry ore and might well have done. The P/Fe ratio represents the phosphorus % that would be expected in the iron from each ore.

contained considerable lime in with the silica. Whatever the dwell time, the furnace would have required its silica to be at a high activity, which it was clearly not in most of the local ores, where basicities were of the order of 0.6. However, there is the mysterious ballstone which formed 50% of his ore charge. In a document recently found at Chatsworth House (Devonshire mss, Chatsworth L114/38) penned by Charles Hornblower, a known middle manager in the Coalbrookdale company, around 1783, ballstone is particularly described as a foundry ore, whereas pennystone and flatstone are designated as ores for iron for the forges. It would fit the foundry bill if ballstone turned out to have less lime alongside the silica and rather more phosphorus, like for example, the gubbins of South Staffordshire (shown for comparison in Table 8). This would provide another reason for calculated slag basicities to be too high.

Summary and Conclusion

Whereas a high temperature was conducive to obtaining a high silicon iron, it was possible to get high levels of silicon in the products of 18th-century coke-fired blast furnaces without needing to raise temperatures higher than necessary to produce a relatively low basicity slag. Four other factors were important:

- the absence of lime or magnesia in the ore;
- the length of time that the charge was in the furnace;
- the average temperature in the stack, facilitated by a low temperature gradient;
- the high silica content of the fuel.

The use of coke enhanced all of the last three of these conditions, which made the production of an iron that could make a thin walled pot in a cold mould relatively easy.

Abraham Darby recognized this before 1707. The use of coke before, for example by Dud Dudley (Mott 1934/5, 17–31), had failed because of the presence of sulphur in it as the desire of the iron masters was principally to use their pig iron to make bar in the forges. Darby accepted the limitation of this higher sulphur content and concentrated his business on a foundry activity, where sulphur was not a problem, and thus developed the first dedicated general iron foundry in Britain. In accepting levels of sulphur in his iron, he did not need to run his furnace at a temperature any higher than charcoal furnace operators ran theirs because he did not need to use a highly basic slag.

A logical conclusion from this is that the success of Abraham Darby II before 1755 in selling significant quantities of coke iron into the forges for the first time was due to the fact that he did run his bigger furnaces at a higher temperature and with a more basic slag and thereby allowed the manufacture of a malleable iron which was no longer hot short as a result of its sulphur content.

A companion paper (Williams forthcoming) will consider the questions of output and efficiency that faced Abraham Darby I with his first furnace and how and why these differed from those of charcoal furnaces. It will attempt to demonstrate that his output was not fundamentally as low as other writers have calculated, nor his coke usage as high. There were technical reasons why his coke usage was less efficient than that of charcoal, but the manner in which Darby was obliged to manage his furnace whilst using it to make castings, rather than large pigs, greatly exaggerated the difference.

Acknowledgements

I must acknowledge the contribution of Peter King, for his helpful support, discussion and criticism. The inevitable kindness of Joanne Smith at the library of the Ironbridge Gorge Museum has also been greatly appreciated.

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