Iron smelting in Argyll, and the chemistry of the process

by Julian Overnell, Kilmore.

The history of local iron making, particularly the history of the Bonawe Furnace, is well described in the Historic Scotland publication of Tabraham (2008), and references therein. However, the chemistry of the processes used is not well described, and I hope to redress this here.

The iron age started near the beginning of the first millennium BC, and by the end of the first millennium BC sufficient iron was being produced to equip thousands of troops in the Roman army with swords, spears, shovels etc. By then, local iron making was widely distributed around the globe; both local wood for making charcoal, and (in contrast to bronze making) local sources of ore were widely available.

The most widely distributed ore was “bog iron ore”. This ore was, and still is, being produced in the following way: Vegetation in stagnant water starts to rot and soon uses up all the available oxygen, and so produces a water at the bottom with no oxygen (anaerobic) which also contains dissolved organic compounds. This solution is capable of slowly leaching iron from the soils beneath to produce a weak solution of dissolved iron (iron in the reduced, ferrous form). Under favourable conditions this solution percolates down until it meets some oxygen (or oxygenated water) at which point the iron precipitates (as the oxidized ferric form). This is bog iron ore and comprises a somewhat ill-defined brown compound called limonite (FeOOH.nH₂O), often still associated with particles of sand etc. from where it was formed. This mode of formation has the potential also for concentration of any available phosphate, which binds to the limonite and can lead to a poorer quality iron.

Where were the sources of bog iron ore available to the Argyll iron makers? The only historical reference that I have seen is: Murray (1740, quoted in Lewis 1984) who says: “... and bog ore from Jura and Islay were brought by sea and up Loch Etive to the pier at Ardmaddy.” I know of no old bog iron ore mines, on Jura or Islay (or anywhere else). Two local occurrences of bog iron ore are recorded in the Huntarian Museum catalogue, on Mull and on Skye, see Appendix 1. MacGregor (1920) makes only a passing reference to locations of bog iron ore, and only in connection with the Loch Maree furnaces: “The only deposits known,
however, consist of comparatively small pans of bog iron ore. A good example of these pans formerly existed at South Erradale (1-inch sheet 91), where a field wall was constructed of blocks taken from it.” A plausible explanation for this apparent lack of bog ore mines is that production of bog iron ore may have been a by-product of peat digging (R. Anderton, personal communication).

For about two thousand years, until about the end of the first millennium AD, the iron was produced in small local hearths by the “bloomery” process. In this process a hearth was constructed and in it was placed multiple layers of charcoal and iron ore until a mound was produced. Round this was built a casing of clay and brick leaving a hole at the top for the exhaust gases and a hole at the bottom for a blast of air produced by operating bellows. [The size of these structures is not given in archaeological investigations (presumably because they were usually destroyed after use). A modern reconstruction of a bloomery furnace had internal dimensions of 30cm dia. x 100cm high (Wealden, 2009).] The charcoal was then lit and the bellows operated until the charcoal was exhausted. The casing was then broken open, and if all had gone well there would have been a pile of spongy iron and a puddle of slag. The spongy iron was beaten (hot) in a forge to produce an iron billet or iron products. The reactions taking place in the smelting are summarized in Fig. 1. The charcoal fire produces carbon monoxide (reaction 1) and the heat drives off water from the bog ore to produce hematite (2). The carbon monoxide reduces the hematite to ferrous oxide, wüstite (3). (This otherwise rare mineral has often been found in bloomery slags.) The carbon monoxide then reduces the wüstite to elemental iron (4). The reaction does not go all the way; it proceeds to an equilibrium position and so the resulting gas is a mixture of carbon monoxide and carbon dioxide. However, wüstite can also react with any sand to produce iron olivine, (fayalite) (5), which is the major component of the slag produced. This fayalite is a dead end as far as the smelting process is concerned because it cannot be reduced to elemental iron under the furnace conditions (6). The iron produced has a melting point of approx. 1,540°C, whereas the slag melts at ~ 1,100°C. The temperatures reached were high enough to melt the slag, but not high enough to melt the iron. The process worked well enough, although the remaining slag still contained much iron, often up to and over 60% FeO (MacAdam 1887, Selskine 2007, Wealden 2008).
These early bloomery sites in Scotland were recorded by McAdam (1887), and the largest in Argyll appears to have been on the south east shore of Loch Fyne: “Esmore, Stralachan, is one of the largest bloomeries I have met with. The site, which is at the mouth of the Stucreach burn, about 2½ miles south-west of Strachur, covers some acres, and includes hearths for charcoal burning of large extent.” Macadam goes on to say: “The slag is of two varieties, being partly of the open porous nature of bog-ore scoriae, and partly compact, hard, and very infusible, as obtained from red iron ore. These works must have done an extensive business for a long period.” I have found some magnificent pieces of bloomery slag at the top of the foreshore at Strachur. These are black and heavy (specific gravity 3.37-3.78 and are packed with large skeletal fayalite crystals. I suspect that these pieces of slag were out of context and were probably the result of using the Stralachan slag heap for road making. I do not have any information on the possible age of this bloomery site, nor where the ore came from. More recent excavations have been reported by Photos-Jones et al. (1998).

Eventually, the iron makers wanting to scale up the process, started to build large permanent blast furnaces. The earliest reference to this in Europe that I have found was at Lapphyttan in Sweden, sometime between 1150 and 1350 (Anon 2008). When the process was scaled up there was a fundamental change in the process, which must have amazed the first operators. They found that molten iron sank to the bottom of their furnace. This was a huge bonus because it meant that the furnace could run continuously and did not need to be cooled and opened up after each firing; the molten iron and slag could be tapped off periodically. So what had changed? The temperature had not exceeded the 1,540°C needed to melt elemental iron. What had changed was that the somewhat higher temperature had caused reaction (7), Fig. 1 to occur. This is a disproportionation reaction in which carbon monoxide breaks down to carbon and carbon dioxide, catalyzed on the freshly-reduced iron. The carbon then dissolved in the iron to form a mixture of iron carbide, Fe₃C (cementite) and iron with dissolved carbon (austenite). This mixture has a melting point of only 1,130°, and hence was able to flow from the furnace with the slag when the furnace was tapped. This iron was suitable for making castings, but needed to have some carbon removed in order to make wrought iron and steel. This removal may have been carried out in Argyll at Furnace (Lewis 1984).
\[
2C + O_2 \rightarrow 2CO \quad \text{Charcoal} + \text{Oxygen} \rightarrow \text{Carbon monoxide} \quad 1
\]

\[
2(\text{FeOOH.nH}_2\text{O}) \rightarrow \text{Fe}_2\text{O}_3 + (2n+1)\text{H}_2\text{O} \quad \text{Limonite} \rightarrow \text{Hematite} \quad 2
\]

\[
\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2 \quad \text{Hematite} + \text{Carbon monoxide} \rightarrow \text{Ferrous oxide, Carbon dioxide, wüstite} \quad 3
\]

\[
\text{FeO} + \text{CO} \leftrightarrow \text{Fe} + \text{CO}_2 \quad \text{Iron} \rightarrow \text{Iron} \quad 4
\]

\[
2\text{FeO} + \text{SiO}_2 \rightarrow \text{Fe}_2\text{SiO}_4 \quad \text{Silica (sand)} \rightarrow \text{Iron olivine, fayalite} \quad 5
\]

\[
\text{Fe}_2\text{SiO}_4 + \text{CO} \rightarrow \text{Fe, C dissolved} + \text{Fe}_3\text{C} \quad \text{Fe catalyst} \quad 6
\]

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad \text{Fe kg catalyst} \rightarrow \text{Carbon} \quad 7
\]

\[
\text{Fe} + \text{C} \rightarrow \text{Fe, C dissolved} + \text{Fe}_3\text{C} \quad \text{Iron} + \text{Carbon} \rightarrow \text{Iron carbide} \quad 8
\]

The Importance of “Flux”

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \quad \text{Calcium carbonate} \leftrightarrow \text{Calcium oxide} + \text{Carbon dioxide} \quad 9
\]

\[
\text{Fe}_2\text{SiO}_4 + 2\text{CaO} \leftrightarrow 2\text{FeO} + \text{Ca}_2\text{SiO}_4 \quad \text{Iron olivine} \leftrightarrow \text{wüstite} + \text{Lime olivine} \quad 10
\]

\[
\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \quad \text{Calcium silicate} \rightarrow \text{(Glassy slag)} \quad 11
\]

\[
2\text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Ca}_2\text{Al}_2\text{SiO}_7 \quad \text{Melilite} \quad 12
\]

Fig. 1. The chemical reactions involved in iron smelting
The next great innovation in the iron making process was the addition of limestone to the charge. In 1619, Jan Andries Moerbeck, a Dutch ironmaster, introduced the use of limestone in the charge of the blast furnace as a “flux” (Anon 2008). In this process limestone becomes one of the reactants in the mixture. The heat of the furnace decomposes the limestone to quick lime (reaction 9), and this, when in excess, can liberate the iron from iron olivine to return it to hematite (reaction 10), to yield a slag of a different composition (reaction 11). The important result of this innovation is that all the iron in the ore is converted to metallic iron. After this was introduced ironmasters reworked some of the old iron-rich slags to produce more iron. (The use of limestone also enabled iron silicate ores, such as the chamosite ores of Raasay, to be used, but not in Argyll). One downside to the use of limestone was that the slag was a bit viscous. This could be overcome by including some alumina in the charge to yield calcium aluminium silicate (reaction 12) in addition to the calcium silicate. A convenient source of the alumina is clay, or towards the end of the 19th century, the lateritic iron ore, lithomarge, from Antrim, which is high in alumina.

The final innovation that I will mention was that introduced by Abraham Darby in 1709 at Coalbrookdale. He started smelting iron using coke instead of charcoal (because there were insufficient trees to make enough charcoal in the vicinity).

In the 18th Century three blast furnaces were established in Argyll: Glen Kinglass 1725 to 1738, Bonawe 1753 to 1876, and at Inverlacken (later renamed Furnace), 1755 to 1813. They all used charcoal made locally, and imported iron ore. What was the reason for this when coke would have been cheaper as fuel and available nearer the industrial centres? The reason was, most probably, that the charcoal furnaces produced a better product. Coke introduced sulphur and possibly phosphorus (and hence a poorer quality iron) and was difficult to remove with the technology existing then.
Fig. 2. Sketch, not to scale, of a cross section through a 18th century blast furnace, roughly modeled on the Argyll furnaces, Glenkinglass furnace on the left hand side and Bonawe on the right.

In Fig. 2 The salient features of the blast furnace are: An opening at the top for adding fresh charge, a chamber in the middle for the reactions to take place, and a tapered lower part with crucible at the bottom to collect the iron and slag. In the crucible were two openings the one to permit a blast of air and the other to allow periodic tapping of the molten iron and slag. (The Argyll furnaces had two access arches at 90° to each other; the 180° arrangement in Fig. 2 is for ease of illustration.) The air blast in the 18th C was produced by bellows operated by a water wheel, and led into the
bottom the furnace through cast iron nozzles called tuyeres. All three Argyll furnaces were square buildings in plan with two arches.

The Inverlacken furnace is still complete but the blowing arch and tapping arches are plugged so it is impossible to see inside. The blowing engine and tuyeres are absent. I could see no sign of the slag heap, so very little information can now be gleaned of the process used. Lewis (1984) states: “...Craleckan had a forge and although its precise location is not known ...” Presumably this was for making steel and wrought iron.

The Bonawe furnace (NN 009,318) is now under the care of Historic Scotland. With a brick lining and tapered upper section, the design corresponds to the right hand part of the sketch in Fig. 2. The lower part of the furnace has been opened up some time in the past and the tapered lower section removed so that only vestiges of the crucible can now be seen in the ground. Above the half way mark the original circular brick furnace lining can still be seen. The tuyeres are absent and so is the blowing engine. Originally bellows were used for producing the blast. These were subsequently replaced and the present foundations probably supported a blowing engine with upright iron cylinder(s) and piston(s) (McAdam 1887). The furnace was in operation for 123 years and the amount of slag produced in that time must have been large. The margins of the slag heap, which still contain much slag, are still present, but the bulk seems to have been removed to create a car park. The samples of hematite ore and limestone displayed in the exhibition at Bonawe were found on site, but the bog iron and clayband ore were brought in to the exhibition from elsewhere (P. Yeoman, personal communication). The hematite ore was imported by boat from Ulverston (McAdam 1887), and the charcoal was made locally. Hematite was also brought from the mines near the Pennel Burn, Muirkirk (after smelting there ceased for want of charcoal); the ore was taken by pack horse to Ayr and ship to Bonawe. The iron was then returned to Muirkirk for forging. Lewis (1984) reports: “Local trade at Bonawe was overwhelmed by the import of haematite from Cumbria and clayband from central Scotland and the export of pig iron ...” (Clayband ore is an iron ore).
Fig. 3. Glassy green slag from Bonawe furnace with ropey surface; size of coin, 2cm.

There has not been an archaeological investigation of the slag heap, nor to my knowledge, mineralogical or chemical examination of slag samples. The slag at the car park is greenish or bluish in colour and of much lower specific gravity than the bloomery slag (two samples were 2.6 and 2.7). Fig. 3 is a photograph of sample of glassy slag from the Bonawe slag heap. This slag has a “ropey” surface similar to the surface of basalt lava flows, and beneath the surface it is a green colour.

Glenkinglass furnace is located on the SE side of the river Kinglass at NN 082,371, almost opposite the old settlement of Inverkinglass. The casting house and furnace were excavated during work which commenced in 1979 (Lewis 1984) but river action had by then taken away the blowing house. Figs. 4 and 5 are photographs of the remains of the furnace, taken in January 2008, looking east from the wide bed of the River Kinglass. The (walking) stick in the middle is ~ 1.4m long. In Fig. 4 the furnace remains are at the foot of a slope seen above and to the right of the remains. This
slope is the eroded edge of a sand and gravel terrace, eroded by action of the river Kinglass. The charcoal and ore stores were on the top of the terrace and the furnace charge was presumably barrowed across a bridge to the top of the furnace. The river has now further eroded the terrace and pieces of charcoal, hematite and bog iron ore can be seen on the slope. I did not notice any pieces of limestone on the slope, so perhaps the limestone store was further from the river.

Fig. 4 The remains of the Glenkinglass furnace

When the site was excavated (Lewis 1984) the outline of the furnace at the base, the casting house area and the slag heap were all still complete, but since that date the river Kinglass has taken away the casting house area and slag heap, and presumably at the same time, distributed some slag over a wide area downstream above the present river bank. The river has also taken away half the basal area of the blast furnace and left us with a rather interesting cross section through it, including a cross section through the furnace crucible, which can be seen in Fig. 5 with the stick in it. The tapping hole was to the left and the blowing hole facing the camera. The
crucible appeared to be made of blocks of sandstone, with an undulating glassy surface on the inside. There appeared to be a margin on the inside 1-2 cm thick, which may represent an original lining of sand and clay, a mixture called ganister which was widely used for lining furnaces. The crucible is now standing free, with a gap between it and the blockwork of the furnace structure. When Lewis (1984) excavated the site he found: “Between the outer casing and the inner core of the furnace, around the whole circumference of the inner structure, was a 200 mm gap filled with coarse red sand.”. This sand was probably put there for thermal insulation, but it has now all been washed away.

Fig. 5 The crucible area of the Glenkinglass furnace.

The furnace used locally-produced charcoal and imported ore. Murray (1740, quoted in Lewis 1984) stated: “Haematite from Cumbria and bog ore from Jura and Islay were brought by sea and up Loch Etive to the pier at Ardmaddy. The iron produced was taken by sea back to Cumbria.” The only analysis of iron from the furnaces of which I am aware is that of Lewis (1984) who analyzed a sample of cast iron found at the Glenkinglass
site: “A sample of pig iron, when analyzed, produced the following percentages of trace elements:

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.59</td>
<td>0.05</td>
<td>0.003</td>
<td>0.26</td>
<td>3.60</td>
</tr>
</tbody>
</table>

The sample taken was of a remarkably good iron, being quite low in silicon and very low in phosphorus and sulphur. There is very little iron produced today with a phosphorus content as low as 0.05% or a sulphur content less than 0.04%.”

The Glenkinglass slag is mostly light in weight, green and glassy, indicating that limestone must have been in the charge. The specific gravity of two samples was 2.5 and 2.7. However a number of pieces are dark and rusty suggesting that separation of slag from iron was often incomplete. This might have been because the composition of the charge did not produce a slag that was sufficiently fluid. As the furnace only operated for a short period the remains represent a snapshot in time of blast furnace practice in the 1740s. It would be revealing to be able to analyze the chemical composition of some slag and ore samples to try to define the furnace charge. It could be even more interesting to be able to follow the changes in practice at Bonawe during its 120 years in operation but this would require obtaining slag samples from representative periods.

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References


Selskiene A. 2007. Examination of smelting and smithing slags formed in bloomery iron-making process. Chemija. 18. 22-28

Appendix 1

Hunterian Museum and Art Gallery catalogue entries, reproduced by permission.

"bog iron ore"; entire thickness of ore layer, showing included clasts from underlying moraine on base.
Locality: Creich, Fionnphort, Mull, Argyll and Bute, Strathclyde, Scotland
Geology: *in situ*, at junction of peat and underlying moraine, Pleistocene
Catalogue number: 106355

"bog iron ore"
Locality: Creich, Fionnphort, Mull, Argyll and Bute, Strathclyde, Scotland
Geology: *in situ*, at junction of peat and underlying moraine, Pleistocene
Catalogue number: 106356

"bog iron ore"
Locality: Rubha nan Clach, (north of Talisker), Skye, Highland, Scotland
Geology: from boggy seep containing numerous blocks of bog iron ore, Pleistocene
Catalogue number: 134107

(The Creich deposit on Mull is not believed to have been worked (J. Faithfull, personal communication).)
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